

# **Handbook of Adhesion**

## **Second Edition**

# **Handbook of Adhesion**

## **Second Edition**

**D. E. Packham**

*University of Bath, Bath, UK*



John Wiley & Sons, Ltd

Copyright © 2005

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester,  
West Sussex PO19 8SQ, England

Telephone (+44) 1243 779777

Email (for orders and customer service enquiries): [cs-books@wiley.co.uk](mailto:cs-books@wiley.co.uk)

Visit our Home Page on [www.wiley.com](http://www.wiley.com)

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except under the terms of the Copyright, Designs and Patents Act 1988 or under the terms of a licence issued by the Copyright Licensing Agency Ltd, 90 Tottenham Court Road, London W1T 4LP, UK, without the permission in writing of the Publisher. Requests to the Publisher should be addressed to the Permissions Department, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, or emailed to [permreq@wiley.co.uk](mailto:permreq@wiley.co.uk), or faxed to (+44) 1243 770620.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The Publisher is not associated with any product or vendor mentioned in this book.

This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the Publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

### ***Other Wiley Editorial Offices***

John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 33 Park Road, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada M9W 1L1

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

### ***Library of Congress Cataloging-in-Publication Data:***

Handbook of adhesion /[edited by] D. E. Packham. – 2nd ed.  
p. cm.

Includes bibliographical references and index.

ISBN-13 978-0-471-80874-9 (cloth: alk. paper)

ISBN-10 0-471-80874-1 (cloth: alk. paper)

1. Adhesives – Handbooks, manuals, etc. 2. Adhesion – Handbooks, manuals,  
etc. I. Packham, D. E. (David Ernest), 1939-

TP968.H34 2006

668'.3 – dc22

2004023727

### ***British Library Cataloguing in Publication Data***

A catalogue record for this book is available from the British Library

ISBN-13 978-0-471-80874-9 (HB)

ISBN-10 0-471-80874-1 (HB)

Typeset in 10/12pt Times by Laserwords Private Limited, Chennai, India

Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire

This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

# Contents

---

<b>Preface to the second edition</b>	<b>vii–viii</b>
<b>Preface to the first edition</b>	<b>ix–x</b>
<b>Introduction</b>	<b>xi–xii</b>
<b>List of articles – alphabetical</b>	<b>xiii–xxvi</b>
<b>List of articles – classified</b>	<b>xxvii–xlvi</b>
<b>List of contributors</b>	<b>xlix–liv</b>
<b>Handbook entries</b>	<b>1–622</b>
<b>Appendix</b>	<b>623–628</b>
<b>Index</b>	<b>629–638</b>

# Preface to the second edition

---

The original edition of the *Handbook of Adhesion* was published in 1992. It was intended to fill a gap between the necessarily simplified treatment of the student textbook and the full and thorough treatment of the research monograph and review article. It provided concise and authoritative articles covering many aspects of the science and technology associated with adhesion and adhesives. The articles were structured in such a way, with internal cross-references and external literature references, that the reader could build up a broader and deeper understanding, as the particular need required.

Since the first edition went out of print, there has been a continuing demand for the book, and Wiley agreed to publish a second edition, again under my editorship. The short article format of the first edition has been retained. Some of the articles are derived from the earlier edition and have been revised and updated where needed. There are many new articles covering developments that have risen in prominence in the intervening years.

An increasing environmental awareness is one of the developments throughout this period: time and again authors draw attention to the environmental impact of adhesive technologies. It is interesting to note that, in the period 1992–2004, sales of adhesives and sealants in the United States has increased by around 5% per annum. Sales in other industrialized countries are likely to be similar. These are the sorts of figures for growth about which business corporations boast in their annual reports. Yet, in the same period, many indicators of environmental well-being continued to deteriorate. Atmospheric carbon dioxide concentrations increased by 5% and “extreme” weather events became more frequent. In both the United States and Europe, the incidence of asthma doubled.

This raises some disconcerting issues. Are our endeavours to reduce organic vapour emissions, to eliminate chromates, and so forth (repeated, *mutatis mutandis*, throughout industry), really sufficient to prevent an environmental crisis? Perhaps serious questions of sustainability and of limits to growth now have to be faced seriously.

The task of assembling nearly 250 articles from well over 60 authors has been formidable and I am grateful to the publishers and, in particular, to Jenny Cossham and Lynette James for their patience and to the authors for their cooperation. An increasingly dirigiste management culture has spread from industry into the quasi-privatized civil service and now into universities. This brings with it a narrow perception of the role and purpose of science and of research, which makes the production of material for a book such as this increasingly difficult. Its achievement is a credit to the dedication of authors involved.

In an attempt to keep the style of the book uniform throughout, all the articles have been subject to editorial modification, so the final form of the text, including errors, is the Editor's responsibility. There are a few first edition articles that, for a variety of reasons, the original authors were not able to update. I have revised these myself and indicated this by placing an asterisk (\*) after the original authors' names.

D. E. PACKHAM  
*University of Bath*  
*August, 2004*

# Preface to the first edition

---

There is a long and valuable tradition of members of academic staff of universities acting as authors and editors of reference works written for the benefit of the general public as a whole or of sections of it with specialized interests. This is one way in which a university repays its debt to the society that sustains it. Thus, when asked by the series editors if I would act as editor for the *Handbook of Adhesion*, I agreed to do so. It was not without misgivings that I gave my agreement. I was somewhat overawed at the prospect of commissioning some 200 articles from over 50 authors in industry and higher education and then relating the articles to one another in a single book with consistent style. In practice, the job was lightened by the enormous support given to me by the publishers' staff, particularly Dr Michael Rogers and Dr Paula Turner, and also by the series editors, Professor David Briggs and Dr Derek Brewis. I would also like to thank the individual authors for their patience with my editorial idiosyncrasies. In an attempt to keep the style of the book consistent, it has sometimes been necessary to modify articles in a way that individual authors would not have chosen. I must emphasize that the responsibility for the final form of the text, including the errors, is mine.

This book, then, represents the fruits of fifty to sixty authors drawn from universities and industry. Such an authorship is unexceptional: there are hundreds of books resulting from collaboration like this in many areas of pure science, applied science and engineering.

In the past decade, in the United Kingdom, there has been an enormous emphasis on the importance of universities collaborating with industry and serving its needs. This emphasis has been backed up by Government financial policies designed to make universities change their ways. Many of the practices of industry have been introduced into universities, with the result that increasingly the performance of academics is being judged in terms of *cash* they can bring in from research contracts and the income they can raise by selling their services in the marketplace. It is ironical that the hard canons of market forces being imposed on universities will mean that collaborative ventures, such as this book, will become things of the past: they are bound to fail the market criterion of cost effectiveness.

The changes being urged on universities represent much more than a trimming of the sails to the winds of political change. They represent a determined effort to change their fundamental values radically, or, in the more percussive language used recently by the leader of a powerful pressure group, "to break the academic mould". If this happens, books of this sort will be among the lesser casualties of the breaking of the academic mould.

D. E. PACKHAM

# Introduction

---

## *Scope of the Handbook*

The *Handbook of Adhesion* is intended as a book of reference in the field of adhesion. Adhesion is a phenomenon of interest in diverse scientific disciplines and of importance in a wide range of technologies. Therefore, the scope of this handbook includes the background science (physics, chemistry and materials science) and engineering and aspects of adhesion relevant to the use of adhesives, sealants and mastics, paints and coatings, printing and composite materials.

## *Intended readership*

The book will be of value to professional people of many different backgrounds who need to have an understanding of various facets of adhesion. These will include those working in research, development or design, as well as others involved with marketing or technical service. The first edition proved to be a valuable resource for both undergraduate and research students. This book is intended as a reference work for all those needing a quick, but authoritative, discussion of topics in the field of adhesion, broadly interpreted. It is intended for scientists and engineers qualified at national certificate or degree level. The aim has been to write it so that a detailed knowledge of individual science and engineering disciplines is not required.

## *Length of articles*

The *Handbook* has been designed so that it is easy to retrieve the information required, whether this is confined to a single point or it is more extensive. Thus, articles are arranged alphabetically and it has been the editorial policy for each article to be, as far as possible, intelligible on its own, and to limit its length to around three pages, which can be quickly assimilated. Many enquirers will want more extensive information than a single article can provide. For this reason, there is copious cross-referencing to related articles elsewhere in the *Handbook*, and a comprehensive index. **Cross-references** are shown by giving titles of articles in **bold**.



*Literature references*

The literature references at the end of the articles are intended to give further information to the *general* enquirer, so where possible, they list authoritative reviews, monographs or textbooks, rather than original research papers. Those who need access to original papers should easily find the reference through these secondary sources. The **Appendix** gives concise guidance on literature and information sources.

*Broader study*

As well as providing an answer to a specific query, the *Handbook* can be used for a broader study of topics in adhesion. For this reason a **Classified list of articles** is provided (p. xxvii) where articles on related topics are grouped together and arranged in a logical sequence for reading.

*How to use the Handbook*

Detailed instructions on use of the *Handbook* are given inside the front cover. **Cross-references** are shown by giving titles to articles in **bold**.

# List of articles – alphabetical

---

- Abrasion treatment* J F WATTS Removal of loose layers, roughening, improved adhesion
- Accelerated ageing* G W CRITCHLOW Shear and wedge tests, humidity, corrosive environments
- Acid–base interactions: introduction* D E PACKHAM Relation to work of adhesion, Drago equation
- Acid–base surface energy parameters* D E PACKHAM Surface energy components
- Acids* D E PACKHAM Concept of acid – Brønsted–Lewis, conjugate bases-electron donor/acceptor
- Acrylic adhesives* B KNEAFSEY Basic material, setting mechanism, applications, advantages, disadvantages
- Adhesion* D E PACKHAM Etymology, usage – qualitative, quantitative, practical, theoretical, bonds at interface
- Adhesion – fundamental and practical* D E PACKHAM Relationship between joint strength and interfacial forces
- Adhesion in dentistry: orthodontics and prosthodontics* M SHERRIFF Dental applications
- Adhesion in dentistry: restorative materials* M SHERRIFF Polymers as filling materials
- Adhesion in medicine* M E R SHANAHAN Macroscopic level (e.g. prostheses) and cellular level
- Adhesive classification* B C COPE Classified by setting mode and chemical nature

- Adhesives – historical perspective* M W PASCOE Adhesives before the industrial age
- Adhesives for textile fibre bonding* A J G SAGAR Non-woven materials, flocking, tyres, belts and hose
- Adhesives in textile coating laminating and printing* A J G SAGAR Types of adhesive for coated fabrics, lamination, seaming, carpets and pigment printing
- Adhesives in the textile industry* A J G SAGAR Applications and adhesive types
- Adsorption theory of adhesion* K W ALLEN Adsorption via primary or secondary bonds
- Aerospace applications* D G DIXON Adhesives used: structures bonded
- Alkyl-2 cyanoacrylates* J GUTHRIE Monomer synthesis; polymerization
- Anaerobic adhesives* D P MELODY Chemical constitution, applications
- Animal glues and technical gelatins* C A FINCH Origin and uses
- Anodizing* D E PACKHAM As a pre-treatment: different electrolytes and uses
- Atomic force microscopy* G J LEGGETT Basis, scope limitations
- Auger electron spectroscopy* J F WATTS Basis of technique, application to adhesion problems
- Automotive applications* A MADDISON Types of adhesive used, advantages
- Autophoretic primers* N WHITEHOUSE Aqueous dispersions containing acids that deposit corrosion-resistant films
- Blister test* D E PACKHAM Use, theory, variations
- Bonds between atoms and molecules* D E PACKHAM Classification of primary and secondary bonds
- Cathodic disbondment* J F WATTS Failure of bonds to ferrous alloys in an aqueous environment
- Chain polymerization* J COMYN Initiation, propagation termination; application to adhesives
- Climbing drum peel test* K B ARMSTRONG Peeling of metal sheet, for example, skin from honeycomb
- Coextrusion* R J ASHLEY Production of a laminate in a single process

- 
- Compatibility* J COMYN Free energy of mixing; solubility parameter; diffusion; weak boundary layers
- Composite materials* D E PACKHAM General introduction – emphasis of crucial role of interfacial adhesion
- Contact adhesives* J M MARTÍN MARTÍNEZ Plasticized CR or NR adhesives
- Contact angle* J F PADDAY Young's equation; nature of the contact angle; roughness
- Contact angle measurement* J F PADDAY Techniques – where applicable; precautions needed to get reproducibility
- Contact angles and interfacial tension* D E PACKHAM Young's equation; work of adhesion, interfacial tension and surface energy
- Conversion coating* G W CRITCHLOW Phosphate, chromate and alkali oxide treatments
- Corona discharge treatment* D BRIGGS Form of plasma treatment applied, especially to polyolefins
- Creep* A D CROCOMBE Occurrence; protection against creep failure
- Critical surface tension* D E PACKHAM Measurement; typical values; relationship to surface energy
- Cyanoacrylate adhesives* J GUTHRIE Anionic polymerization, additives, applications, advantages and disadvantages
- Degreasing* J F WATTS Solvent, alkali and emulsion cleaners; efficiency
- Diffusion theory of adhesion* K W ALLEN Polymer/polymer autohesion, molecular weight dependence
- Dispensing of adhesives* C WATSON Techniques used industrially for the application of adhesives to surfaces to be bonded
- Dispersion forces* K W ALLEN Nature of dispersion forces, ubiquity, energy–distance relationships; Lennard–Jones potential
- Displacement mechanisms* D M BREWIS Displacement of organic contaminants from high-energy surfaces by adhesives
- Durability: creep rupture* D A DILLARD Creep under sustained stress
- Durability: fatigue* D A DILLARD Effect of cyclic loads

*Durability: fundamentals* G W CRITCHLOW Modes of failure; water ingress; pre-treatments

*Durability: sub-critical debonding* D A DILLARD Deleterious effects water may have on adhesion

*Electrical adhesion* K KENDALL Adhesion in a strong electrical field; applications

*Electrochemical pre-treatment of polymers* R H DAHM Recently developed surface treatment methods

*Electron microscopy* D E PACKHAM TEM and STEM applied to adhesion studies

*Electron probe microanalysis* B C COPE Basis of technique; examples in adhesion science

*Electrostatic theory of adhesion* K W ALLEN Outline of theory; discussions of applicability

*Ellipsometry* R GREEF Theory, application to adhesion problems

*Emulsion and dispersion adhesives* G C PARKER Polyvinyl acetate and copolymers, setting, advantages and disadvantages

*Engineering design with adhesives* C WATSON Advantages of use of adhesives: specific examples of improved design

*Engineering surfaces of metals* J F WATTS Practical metallic surfaces are oxidized, contaminated and rough: pre-treatments; adhesion

*Environment and the impact of adhesive technology* D E PACKHAM Resources, energy, pollution

*Environment: sustainability* D E PACKHAM Considers depletion of resources, limits to growth

*Epoxide adhesives* J A BISHOPP Basic resin types, applications

*Epoxide adhesives: curatives* J A BISHOPP Cross-linking agents

*Etch primers* N WHITEHOUSE Chemical action; application to aluminium and steel

*Ethylene–vinyl acetate copolymers* D E PACKHAM Copolymer composition and properties; hot melt and emulsion adhesives

*Extrusion coating* R J ASHLEY Techniques and materials used

---

*Fibre composites – introduction* B C COPE Fibre orientation, fibre–matrix interface; surface treatment

*Fibre composites – joining* K B ARMSTRONG Thermoset matrices, peel-ply, abrasion; thermoplastic matrices, corona discharge

*Fibre composites – matrices and fibres* B C COPE Scope of different fibre and matrix materials

*Fibre composites – processing techniques* B C COPE Comparison of processing methods

*Fibre–matrix adhesion – assessment techniques* F R JONES Direct and indirect test methods

*Fibre–matrix adhesion – carbon fibres* F R JONES Structure of carbon fibre; effect of surface treatment

*Fibre–matrix adhesion – glass fibres* F R JONES Types of fibre: surface treatment

*Filler–matrix adhesion* V KOVAČEVIĆ, S LUČIĆ BLAGOJEVIĆ and M LESKOVAC Surface treatment of fillers and composite properties

*Finite-element analysis* A D CROCOMBE Principles and application to adhesive joints

*Finite-element analysis: rubber* M A WAHAB Application to highly elastic materials

*Flame treatment* D BRIGGS Pre-treatment of polymers, scope

*FPL etch* D E PACKHAM Sulphochromate treatment for Al; ductility; topography

*Fractals* D E PACKHAM Concept of fractal lines and surfaces

*Fractals and fractal dimension* D E PACKHAM Concept of fractal dimension

*Fractals and surface roughness* D E PACKHAM Measurement of fractal dimension, relation to roughness factor

*Fracture mechanics* A J KINLOCH Basis: energy balance and stress-intensity factor approaches

*Fracture-mechanics test specimens* A J KINLOCH Test methods for flexible and rigid joints

*Friction – adhesion aspects* A D ROBERTS Influence of adhesion on friction; Schallamach waves

*Glass transition temperature* D A TOD Property changes at  $T_g$ ; measurement; effect of molecular structure and moisture

*Good–Girifalco interaction parameter* D E PACKHAM Definition of  $\phi$ ; evaluation for “dispersion force” interface; interfacial tension; solid surface energies

*Health and safety* M FAKLEY Hazards associated with adhesives: sources of information

*High-temperature adhesives* S J SHAW Comparison of different types; recent developments

*High-temperature stability principles* D E PACKHAM Molecular structure and thermal stability

*Hot melt adhesives* D M BREWIS Basic composition, advantages and disadvantages, uses

*Humidity* J COMYN Relative humidity, laboratory control of humidity

*Hydrogen bonding* D BRIGGS Nature and occurrence of hydrogen bonding, work of adhesion, examples where important

*Impact resistance* A MADDISON Impact behaviour of different adhesives; effects of pre-treatment

*Industrial applications of adhesives* C WATSON Scope of adhesives; bonding cylindrical components

*Inelastic electron tunnelling spectroscopy* R R MALLIK Basis of technique – its potential in the study of adhesion

*Infrared spectroscopy* F J BOERIO IR and adhesion

*Infrared spectroscopy: attenuated total reflection* F J BOERIO ATR of surface region

*Infrared spectroscopy: RAIR* F J BOERIO Reflection–adsorption IR of surfaces

*Internal stress* K KENDALL Origin; effect on adhesion measurement; reduction of internal stresses

*Inverse gas chromatography* M-L ABEL and J E WATTS Basis of technique

*Inverse gas chromatography and acid–base interactions* M-L ABEL and J E WATTS Use for assessing acid–base interactions

*JKR theory* K KENDALL Basic equation of contact mechanics relating area of contact to surface forces

- 
- Joint design – cylindrical joints* C WATSON Factors affecting joint performance; specimen calculation
- Joint design – general* C WATSON Flat and cylindrical joints; good and bad practice
- Joint design: strength and fracture perspectives* D A DILLARD Two approaches to design of joints
- Laminating* R J ASHLEY Use of aqueous-based, solvent-based and hot melt adhesives
- Lifshitz-van der Waals forces* D E PACKHAM Basis of Lifshitz' treatment of secondary bonds
- Mechanical theory of adhesion* K W ALLEN Macro- and micro-interlocking; influence on adhesion
- Metallizing plastics* R H DAHM Vapour and solution methods
- Microfibrous surfaces* D E PACKHAM Examples of preparation Fe, Cu, Zn. Use as substrates in adhesion-energy dissipation
- Microstructure of joints* D E PACKHAM Microstructural features of adhesive and substrate and their effect on adhesion
- Moisture cure of adhesives* J COMYN Cyanoacrylates and isocyanates
- Mould adhesion – measurement* D E PACKHAM Peel, blister, etc., for low adhesion
- Mould adhesion and fouling* D E PACKHAM Relevant factors such as surface layers
- Napkin ring test* D E PACKHAM Calculation of shear stress: refinements
- Natural rubber-based adhesives* J M MARTÍN MARTÍNEZ Nature and properties
- Nitrile rubber adhesives* J M MARTÍN MARTÍNEZ Nature and properties
- Non-destructive testing of adhesively-bonded structures* G J CURTIS Acoustic wave techniques, resonance and pulse-echo testers
- Optical microscopy* B C COPE Resolution; phase contrast; Nomanski differential inference contrast
- Packaging industry* R J ASHLEY Adhesives used, service requirements
- Paint constitution and adhesion* N WHITEHOUSE Binder, pigment, adhesion mechanism



- Paint primers* N WHITEHOUSE Function; make-up
- Paint service properties and adhesion* N WHITEHOUSE Internal stress; testing; weathering
- Peel tests* D E PACKHAM Peel force and peel energy; factors affecting peel energy; angle variation
- Phenolic adhesives: single-stage resoles* J A BISHOPP Resoles; structure modifications; uses
- Phenolic adhesives: two-stage novolacs* J A BISHOPP Novolacs; structure modifications; uses
- Plasma-polymerized coatings* W J VAN OOIJ Production of polymer coatings from range of organic precursors
- Plasma pre-treatment* D BRIGGS Plasmas from noble gases, reactive gases; plasma polymerization
- Polar forces* K W ALLEN Nature of Keesom and Debye forces, attraction constants; Lennard–Jones potential
- Polybenzimidazoles* S J SHAW Structure: use as high-temperature adhesive
- Polychloroprene rubber adhesives: applications and properties* J M MARTÍN MARTÍNEZ Adhesion characteristics and applications
- Polychloroprene rubber adhesives: modifiers and additives* J M MARTÍN MARTÍNEZ Resin, tackifier, cross-linking agent addition
- Polyether ether ketone* D A TOD High-temperature stability; use as matrix for fibre composites
- Polyimide adhesives* S J SHAW Condensation and thermoplastic polyimides, imide prepolymers; high-temperature stability
- Polymer diffusion: reptation and interdigitation* R P WOOL Mechanisms for polymer chain diffusion
- Polymer–polymer adhesion: incompatible interfaces* R P WOOL Interdiffusion, compatibilizers
- Polymer–polymer adhesion: models* R P WOOL “Nail” and vector percolation models
- Polymer–polymer adhesion: molecular weight dependence* R P WOOL Fracture energy and molecular weight

- 
- Polymer–polymer adhesion: weld strength* R P WOOL Implications for moulding technology
- Polyphenylquinoxalines* S J SHAW Chemical constitution: use as high-temperature adhesive
- Polyurethane* G C PARKER Solvent-free and solvent-based systems, toxicology
- Polyvinyl alcohol in adhesives* C A FINCH Production and uses
- Powder adhesion* K KENDALL Adhesion between fine powder particles: practical consequences
- Pressure-sensitive adhesives* D W AUBREY Nature of pressure-sensitive adhesion, materials used
- Pressure-sensitive adhesives – adhesion properties* D W AUBREY Shear and peel strengths; tack tests
- Pre-treatment of aluminium* G W CRITCHLOW Chronic acid etch, chronic acid anodizing, phosphoric acid anodizing; relative bond durability
- Pre-treatment of copper* D E PACKHAM Conventional and microfibrinous surfaces
- Pre-treatment of fluorocarbon polymers* D M BREWIS Problems of these materials, chemical and plasma treatment
- Pre-treatment of metals prior to bonding* G W CRITCHLOW Survey of mechanical and chemical treatments
- Pre-treatment of metals prior to painting* N WHITEHOUSE Need for pre-treatment; survey of common methods
- Pre-treatment of steel* J F WATTS Abrasion, pickling and conversion coatings
- Pre-treatment of titanium* G W CRITCHLOW Survey of important types of pre-treatment and comparisons of bond durability
- Pre-treatments of polymers* D M BREWIS Effects of solvent, mechanical, oxidative and plasma treatment
- Pre-treatments of polyolefins* D M BREWIS Polyolefins, scope and effects of different treatment types
- Primary bonding at the interface* J F WATTS Examples in organic coatings, metallized plastics and adhesion promoters

*Primers for adhesive bonding* J A BISHOPP Types of primers for metals and polymers

*Primers for sealants* G B LOWE Types for porous and non-porous surfaces

*Radiation-cured adhesives* M FAKLEY Electron beam and UV curing systems: advantages, disadvantages, uses

*Reaction-setting adhesives* D M BREWIS One- and two-part adhesives; applications

*Release* J S TONGE Examples where low adhesion needed – internal and external release agents

*Renewable sources of adhesives* C A FINCH Non-fossil fuel sources, biotechnology

*Repair methods* K B ARMSTRONG Methods for composites and honeycomb panels on large structures such as aircraft

*Rheological theory* D E PACKHAM Rheology and joint strength: the possibility of adhesive failure

*Roughness and adhesion* D E PACKHAM How roughness affects adhesion

*Roughness of surfaces* D E PACKHAM Characterization of roughness, effect on adhesion

*Rubber fillers* J A LINDSAY Role of fillers, non-reinforcing and reinforcing fillers, adhesion aspects

*Rubber to metal bonding – applications* G LAKE Tyres; bearings; durability

*Rubber to metal bonding – basic techniques* P LEWIS In- and post-vulcanization bonding

*Rubber to metal bonding – pre-treatments* P LEWIS Degreasing, mechanical cleaning, chemical cleaning

*Rubber to metal bonding – testing* J A LINDSAY Peel tests, tests in tension

*Rubber to metal bonding: processing effects* J A LINDSAY Importance of good mould design

*Rubber: tyre cord adhesion* W J VAN OOIJ Adhesion to brass-coated steel

*Rubber-based adhesives* J M MARTÍN MARTÍNEZ General introduction

*Rubber-based adhesives: compounding* J M MARTÍN MARTÍNEZ Formulations, etc.

- 
- Rubber-based adhesives: typical characteristics* J M MARTÍN MARTÍNEZ  
Advantages
- Scanning electron microscopy* B C COPE Mode of operation, examples of use
- Scanning probe microscopy* G J LEGGETT Basis and use
- Scratch test* D E PACKHAM Assessment of thin film adhesion
- Sealant joint design* J C BEECH Design of butt and lap joints
- Sealants* G B LOWE Chemical composition, use
- Sealants in double glazing* G B LOWE Types of materials, durability
- Secondary ion mass spectrometry* D BRIGGS Static, dynamic and imaging SIMS
- Selection of adhesives* D M BREWIS Setting time, initial performance, durability, cost
- Selection of joint sealants* J C BEECH Comparison and criteria for selection
- Shear tests* A D CROCOMBE Tests in tension and torsion
- Silanes as metal pre-treatments* W J VAN OOIJ Silanes, structure and effectiveness
- Silane adhesion promoters* D G DIXON Silanes, coupling agents, surface films
- Silicone adhesion* B PARBHOO Wide range of bond strength and applications
- Silicone adhesives: addition cure* B PARBHOO Cross-linking by addition reactions
- Silicone adhesives: condensation cure* B PARBHOO Cross-linking by step reactions
- Silicones: properties* B PARBHOO Range of properties
- Silicones: structures* B PARBHOO Chemical structure
- Solvent welding* M WARWICK Scope, advantages and disadvantages
- Solvent-based adhesives* J PRITCHARD Aqueous- and organic solvent-based adhesives; uses; advantages and disadvantages
- Standards for adhesives and adhesion* S MILLINGTON Discussion of scope and background to national standards
- Statistics* C CHATFIELD Data collection and analysis; quality control; reliability

*Step polymerization* J COMYN Application to adhesives

*Stress distribution: beam on elastic foundation* D A DILLARD Stresses in shear joints

*Stress distribution: bond thickness* D A DILLARD Adhesive thickness and fracture energy

*Stress distribution: mode of failure* D A DILLARD Locus of failure depends on energy and stress distribution

*Stress distribution: Poisson's ratio* D A DILLARD Poisson contraction and stress distribution

*Stress distribution: shear lag solution* D A DILLARD Stresses in shear joints

*Stress distribution: stress singularities* D A DILLARD Stress concentration – sharp cracks

*Structural adhesives* B KNEAFSEY Properties required, adhesive types; applications

*Surface analysis* D BRIGGS Comparison of XPS, AES, SIMS and ion scattering spectroscopy

*Surface characterization by contact angles – metals* M E R SHANAHAN Use of “one-liquid” and “two-liquids” methods

*Surface characterization by contact angles – polymers* M E R SHANAHAN Critical surface tension, “one-liquid” and “two-liquids” methods

*Surface energy* D E PACKHAM Thermodynamic definitions of surface tension and surface energy: connection with bond type

*Surface energy components* D E PACKHAM Dispersion and polar components; geometric mean relationships; solid surface energies

*Surface forces apparatus* A V POCIUS Adhesion measured via contact mechanics

*Surface nature of polymers* D BRIGGS Migration of additives and low molecular weight fraction to the surface

*Tack* D W AUBREY Definition; cohesive, adhesive and autohesive tack; tackifier resins

*Tensile tests* D E PACKHAM Description, uneven stress distribution

*Testing of adhesives* D A TOD Survey of tests including mechanical, rheological and thermal

- 
- Tests of adhesion* D A TOD Basic principles, effects of test parameters, peel, shear, tensile, wedge test
- Theories of adhesion* K W ALLEN General introduction to mechanical, adsorption, diffusion and electrostatic theories
- Thermal analysis* D E PACKHAM Differential scanning calorimetry – crystallinity, heat of reaction, glass transition temperatures
- Thermal spray coatings used for adhesion* G D DAVIS and R A ZATORSKI As a surface treatment
- Thermal spray processes* G D DAVIS and R A ZATORSKI Technique and equipment
- Tie layers* R J ASHLEY Uses in coextrusion to aid adhesion
- Toughened acrylic adhesives* B KNEAFSEY Setting mechanism; applications; advantages and disadvantages
- Toughened adhesives* J GUTHRIE Mechanism of toughening; advantages and disadvantages
- Toughened epoxide adhesives* J A BISHOPP Basis of toughening
- Toughened epoxide adhesives: blend synergy* J A BISHOPP Effects of two types of particles
- Toughened epoxide adhesives: particle formation prior to cure* J A BISHOPP A toughening technology
- Toughened epoxide adhesives: precipitation during cure* J A BISHOPP The most widely used method
- Tyre cord adhesion* W J VAN OOIJ Adhesion to brass-coated steel
- Underwater adhesives* J M LANE Wetting problems; pre-treatments; durability
- Viscoelasticity* D W AUBREY Transient and dynamic viscoelastic functions; Boltzmann superposition principle
- Viscoelasticity – time–temperature superposition* D W AUBREY Shift factor, WLF equation
- Weathering of adhesive joints* J SARGENT Exposure in temperate and tropical sites
- Weathering tests* S T TREDWELL Long-term exposure
- Wedge test* D G DIXON Use of test for comparing joint durability

*Welding plastics – electromagnetic radiation* A BUXTON IR microwave, high frequency, etc.

*Welding plastics – external heat source* A BUXTON Hot plate, impulse welding, etc.

*Welding plastics – mechanical movement* A BUXTON Frictional heating

*Wetting and spreading* M E R SHANAHAN Young's equation, work of adhesion and cohesion, spreading coefficient

*Wetting and work of adhesion* J F PADDAY Thermodynamic works of adhesion, wetting, spreading and cohesion; Young's equation

*Wetting kinetics* M E R SHANAHAN Spreading on a solid surface; capillary rise

*Wood adhesives – aminoplastics* A PIZZI UF, MF and related adhesives

*Wood adhesives – basics* A PIZZI General introduction

*Wood adhesives – hot melts* A PIZZI EVA and polyamide

*Wood adhesives – isocyanates/urethanes* A PIZZI Bonding to damp wood

*Wood adhesives – phenolics* A PIZZI Types and applications

*Wood bonding by vibration welding* A PIZZI Innovative technique for wood

*Wood composites – adhesives* B H PAXTON Scope for different adhesive types

*X-ray photoelectron spectroscopy* D BRIGGS Basis of technique, application to adhesion problems

*Appendix: Literature and test methods* D E PACKHAM Literature and information sources, test methods

# List of articles – classified

---

## General

*Adhesion* D E PACKHAM Etymology, usage – qualitative, quantitative, practical, theoretical, bonds at interface

*Adhesion – fundamental and practical* D E PACKHAM Relationship between joint strength and interfacial forces

*Adhesives – historical perspective* M W PASCOE Adhesives before the industrial age

*Environment and the impact of adhesive technology* D E PACKHAM Resources, energy, pollution

*Environment: sustainability* D E PACKHAM Considers depletion of resources, limits to growth

*Renewable sources of adhesives* C A FINCH Non-fossil fuel sources, biotechnology

*Health and safety* M FAKLEY Hazards associated with adhesives: sources of information

*Statistics* C CHATFIELD Data collection and analysis; quality control; reliability

*Fractals* D E PACKHAM Concept of fractal lines and surfaces

*Fractals and fractal dimension* D E PACKHAM Concept of fractal dimension

*Friction – adhesion aspects* A D ROBERTS Influence of adhesion on friction; Schallamach waves

*Mould adhesion and fouling* D E PACKHAM Relevant factors such as surface layers

*Acids* D E PACKHAM Concept of acid – Brønsted–Lewis, conjugate bases-electron donor/acceptor



**Background materials science****Secondary bonds, surface energy, interfacial tension**

*Bonds between atoms and molecules* D E PACKHAM Classification of primary and secondary bonds

*Dispersion forces* K W ALLEN Nature of dispersion forces, ubiquity, energy–distance relationships; Lennard–Jones potential

*Polar forces* K W ALLEN Nature of Keesom and Debye forces, attraction constants; Lennard–Jones potential

*Lifshitz–van der Waals forces* D E PACKHAM Basis of Lifshitz’ treatment of secondary bonds

*Acid–base interactions introduction* D E PACKHAM Relation to work of adhesion, Drago equation

*Hydrogen bonding* D BRIGGS Nature and occurrence of hydrogen bonding, work of adhesion, examples where important

*JKR theory* K KENDALL Basic equation of contact mechanics relating area of contact to surface forces

*Surface energy* D E PACKHAM Thermodynamic definitions of surface tension and surface energy: connection with bond type

*Good–Girifalco interaction parameter* D E PACKHAM Definition of  $\phi$ ; evaluation for “dispersion force” interface; interfacial tension; solid surface energies

*Surface energy components* D E PACKHAM Dispersion and polar components; geometric mean relationships; solid surface energies

*Acid–base surface energy parameters* D E PACKHAM Surface energy components

*Contact angle* J F PADDAY Young’s equation; nature of the contact angle; roughness

*Contact angle measurement* J F PADDAY Techniques – where applicable; precautions needed to get reproducibility

*Contact angles and interfacial tension* D E PACKHAM Young’s equation; work of adhesion, interfacial tension and surface energy

*Surface characterization by contact angles – metals* M E R SHANAHAN Use of “one-liquid” and “two-liquids” methods

*Surface characterization by contact angles – polymers* M E R SHANAHAN Critical surface tension, “one-liquid” and “two-liquids” methods

*Wetting and spreading* M E R SHANAHAN Young's equation, work of adhesion and cohesion, spreading coefficient

*Wetting and work of adhesion* J F PADDAY Thermodynamic works of adhesion, wetting, spreading and cohesion; Young's equation

*Wetting kinetics* M E R SHANAHAN Spreading on a solid surface; capillary rise

*Roughness of surfaces* D E PACKHAM Characterization of roughness, effect on adhesion

*Fractals and fractal dimension* D E PACKHAM Concept of fractal dimension

*Fractals and surface roughness* D E PACKHAM Measurement of fractal dimension, relation to roughness factor

### **Polymer Science**

*Chain polymerization* J COMYN Initiation, propagation termination; application to adhesives

*Step polymerization* J COMYN Application to adhesives

*Plasma-polymerized coatings* W J VAN OOIJ Production of polymer coatings from range of organic precursors

*Silicone adhesives: addition cure* B PARBHOO Cross-linking by addition reactions

*Silicone adhesives: condensation cure* B PARBHOO Cross-linking by step reactions

*Silicones: structures* B PARBHOO Chemical structure

*Polymer diffusion: reptation and interdigitation* R P WOOL Mechanisms for polymer chain diffusion

*Glass transition temperature* D A TOD Property changes at  $T_g$ ; measurement; effect of molecular structure and moisture

*Viscoelasticity* D W AUBREY Transient and dynamic viscoelastic functions; Boltzmann superposition principle

*Viscoelasticity – time–temperature superposition* D W AUBREY Shift factor, WLF equation

*Compatibility* J COMYN Free energy of mixing; solubility parameter; diffusion; weak boundary layers

*Polymer–polymer adhesion: incompatible interfaces* R P WOOL Interdiffusion, compatibilizers

*Thermal analysis* D E PACKHAM Differential scanning calorimetry – crystallinity, heat of reaction, glass transition temperatures

### **Mechanics**

*Fracture mechanics* A J KINLOCH Basis: energy balance and stress-intensity factor approaches

*Fracture-mechanics test specimens* A J KINLOCH Test methods for flexible and rigid joints

*Finite-element analysis* A D CROCOMBE Principles and application to adhesive joints

*Finite-element analysis: rubber* M A WAHAB Application to highly elastic materials

*Internal stress* K KENDALL Origin; effect on adhesion measurement; reduction of internal stresses

*Stress distribution: mode of failure* D A DILLARD Locus of failure depends on energy and stress distribution

*Stress distribution: bond thickness* D A DILLARD Adhesive thickness and fracture energy

*Stress distribution: stress singularities* D A DILLARD Stress concentration – sharp cracks

*Stress distribution: Poisson's ratio* D A DILLARD Poisson contraction and stress distribution

*Stress distribution: beam on elastic foundation* D A DILLARD Stresses in shear joints

*Stress distribution: shear lag solution* D A DILLARD Stresses in shear joints

*Creep* A D CROCOMBE Occurrence; protection against creep failure

*Durability: creep rupture* D A DILLARD Creep under sustained stress

*Durability: fatigue* D A DILLARD Effect of cyclic loads

**Others**

*Acids* D E PACKHAM Concept of acid-Brønsted–Lewis, conjugate bases-electron donor/acceptor

*Humidity* J COMYN Relative humidity, laboratory control of humidity

*Statistics* C CHATFIELD Data collection and analysis; quality control; reliability

**Theories of adhesion**

*Theories of adhesion* K W ALLEN General introduction to mechanical, adsorption, diffusion and electrostatic theories

*Mechanical theory of adhesion* K W ALLEN Macro- and micro-interlocking; influence on adhesion

*Roughness and adhesion* D E PACKHAM How roughness affects adhesion

*Adsorption theory of adhesion* K W ALLEN Adsorption via primary or secondary bonds

*Wetting and work of adhesion* J F PADDAY Thermodynamic works of adhesion, wetting, spreading and cohesion; Young's equation

*Primary bonding at the interface* J F WATTS Examples in organic coatings, metallized plastics and adhesion promoters

*Diffusion theory of adhesion* K W ALLEN Polymer/polymer autohesion, molecular weight dependence

*Polymer–polymer adhesion: models* R P WOOL “Nail” and vector percolation models

*Electrostatic theory of adhesion* K W ALLEN Outline of theory; discussions of applicability

*Electrical adhesion* K KENDALL Adhesion in a strong electrical field; applications

*Powder adhesion* K KENDALL Adhesion between fine powder particles: practical consequences

*Adhesion fundamental and practical* D E PACKHAM Relationship between joint strength and interfacial forces

*Rheological theory* D E PACKHAM Rheology and joint strength: the possibility of adhesive failure

*Peel tests* D E PACKHAM Peel force and peel energy; factors affecting peel energy; angle variation

*Stress distribution: mode of failure* D A DILLARD Locus of failure depends on energy and stress distribution

*Fracture mechanics* A J KINLOCH Basis: energy balance and stress-intensity factor approaches

### **Adhesive–substrate interface**

*Adhesion fundamental and practical* D E PACKHAM Relationship between joint strength and interfacial forces

*Rheological theory* D E PACKHAM Rheology and joint strength: the possibility of adhesive failure

*Stress distribution: mode of failure* D A DILLARD Locus of failure depends on energy and stress distribution

*Microstructure of joints* D E PACKHAM Microstructural features of adhesive and substrate and their effect on adhesion

*Wetting and work of adhesion* J F PADDAY Thermodynamic works of adhesion, wetting, spreading and cohesion; Young's equation

*Primary bonding at the interface* J F WATTS Examples in organic coatings, metallized plastics and adhesion promoters

### **Surface characterization**

*Surface analysis* D BRIGGS Comparison of XPS, AES, SIMS and ion scattering spectroscopy

*X-ray photoelectron spectroscopy* D BRIGGS Basis of technique, application to adhesion problems

*Auger electron spectroscopy* J F WATTS Basis of technique, application to adhesion problems

*Secondary ion mass spectrometry* D BRIGGS Static, dynamic and imaging SIMS

*Electron probe microanalysis* B C COPE Basis of technique; examples in adhesion science

*Infrared spectroscopy* F J BOERIO IR and adhesion

- Infrared spectroscopy: attenuated total reflection* F J BOERIO ATR of surface regions
- Infrared spectroscopy: RAIR* F J BOERIO Reflection–adsorption IR of surfaces
- Inelastic electron tunnelling spectroscopy* R R MALLIK Basis of technique – its potential in the study of adhesion
- Ellipsometry* R GREEF Theory, application to adhesion problems
- Optical microscopy* B C COPE Resolution; phase contrast; Nomanski differential inference contrast
- Electron microscopy* D E PACKHAM TEM and STEM applied to adhesion studies
- Scanning electron microscopy* B C COPE Mode of operation, examples of use
- Atomic force microscopy* G J LEGGETT Basis, scope limitations
- Scanning probe microscopy* G J LEGGETT Basis and use
- Good–Girifalco interaction parameter* D E PACKHAM Definition of  $\phi$ ; evaluation for “dispersion force” interface; interfacial tension; solid surface energies
- Surface energy components* D E PACKHAM Dispersion and polar components; geometric mean relationships; solid surface energies
- Acid–base surface energy parameters* D E PACKHAM Surface energy components
- Inverse gas chromatography* M-L ABEL and J F WATTS Basis of technique
- Inverse gas chromatography and acid–base interactions* M-L ABEL and J F WATTS Use for assessing acid–base interactions
- Surface characterization by contact angles – metals* M E R SHANAHAN Use of “one-liquid” and “two-liquids” methods
- Surface characterization by contact angles – polymers* M E R SHANAHAN Critical surface tension, “one-liquid” and “two-liquids” methods
- Critical surface tension* D E PACKHAM Measurement; typical values relationship to surface energy

## Adhesive types

### Classification

- Adhesive classification* B C COPE Classified by setting mode and chemical nature

*Selection of adhesives* D M BREWIS Setting time, initial performance, durability, cost

*Selection of joint sealants* J C BEECH Comparison and criteria for selection

### **Broad categories**

*Selection of adhesives* D M BREWIS Setting time, initial performance, durability, cost

*Anaerobic adhesives* D P MELODY Chemical constitution, applications

*Animal glues and technical gelatins* C A FINCH Origin and uses

*Contact Adhesives* J M MARTÍN MARTÍNEZ Plasticized CR or NR adhesives

*Emulsion and dispersion adhesives* G C PARKER Polyvinyl acetate and copolymers, setting, advantages and disadvantages

*Hot melt adhesives* D M BREWIS Basic composition, advantages and disadvantages, uses

*Pressure-sensitive adhesives* D W AUBREY Nature of pressure-sensitive adhesion, materials used

*Pressure-sensitive adhesives – adhesion properties* D W AUBREY Shear and peel strengths; tack tests

*Radiation-cured adhesives* M FAKLEY Electron beam and UV curing systems: advantages, disadvantages, uses

*Reaction-setting adhesives* D M BREWIS One- and two-part adhesives; applications

*Rubber-based adhesives* J M MARTÍN MARTÍNEZ General introduction

*Rubber-based adhesives: compounding* J M MARTÍN MARTÍNEZ Formulations, etc.

*Rubber-based adhesives: typical characteristics* J M MARTÍN MARTÍNEZ  
Advantages

*Solvent welding* M WARWICK Scope, advantages and disadvantages

*Solvent-based adhesives* J PRITCHARD Aqueous- and organic solvent-based adhesives; uses; advantages and disadvantages

*Wood adhesives – basics* A PIZZI General introduction

- Wood adhesives – hot melts* A PIZZI EVA and polyamide
- Wood composites – adhesives* B H PAXTON Scope for different adhesive types
- High-temperature adhesives* S J SHAW Comparison of different types; recent developments
- High-temperature stability principles* D E PACKHAM Molecular structure and thermal stability
- Renewable sources of adhesives* C A FINCH Non-fossil fuel sources, biotechnology
- Structural adhesives* B KNEAFSEY Properties required, adhesive types; applications
- Toughened adhesives* J GUTHRIE Mechanism of toughening; advantages and disadvantages
- Tyre cord adhesion* W J VAN OOIJ Adhesion to brass-coated steel
- Underwater adhesives* J M LANE Wetting problems; pre-treatments; durability

### Specific chemical types

- Acrylic adhesives* B KNEAFSEY Basic material, setting mechanism, applications, advantages, disadvantages
- Toughened acrylic adhesives* B KNEAFSEY Setting mechanism; applications; advantages and disadvantages
- Alkyl-2 cyanoacrylates* J GUTHRIE Monomer synthesis; polymerization
- Cyanoacrylate adhesives* J GUTHRIE Anionic polymerization, additives, applications, advantages and disadvantages
- Epoxy adhesives* J A BISHOPP Basic resin types, applications
- Epoxy adhesives: curatives* J A BISHOPP Cross-linking agents
- Toughened epoxy adhesives* J A BISHOPP Basis of toughening
- Toughened epoxy adhesives: blend synergy* J A BISHOPP Effects of two types of particles
- Toughened epoxy adhesives: particle formation prior to cure* J A BISHOPP A toughening technology
- Toughened epoxy adhesives: precipitation during cure* J A BISHOPP The most widely used method



- Phenolic adhesives: single-stage resoles* J A BISHOPP Resoles; structure modifications; uses
- Phenolic adhesives: two-stage novolacs* J A BISHOPP Novolacs; structure modifications; uses
- Wood adhesives – phenolics* A PIZZI Types and applications
- Wood adhesives – aminoplastics* A PIZZI UF, MF and related adhesives
- Polybenzimidazoles* S J SHAW Structure: use as high-temperature adhesive
- Polyphenylquinoxalines* S J SHAW Chemical constitution: use as high-temperature adhesive
- Polyether ether ketone* D A TOD High-temperature stability; use as matrix for fibre composites
- Polyimide adhesives* S J SHAW Condensation and thermoplastic polyimides, imide prepolymers; high temperature stability
- Polyurethane* G C PARKER Solvent-free and solvent-based systems, toxicology
- Wood adhesives – isocyanates/urethanes* A PIZZI Bonding to damp wood
- Natural rubber-based adhesives* J M MARTÍN MARTÍNEZ Nature and properties
- Nitrile rubber adhesives* J M MARTÍN MARTÍNEZ Nature and properties
- Polychloroprene rubber adhesives: applications and properties* J M MARTÍN MARTÍNEZ Adhesion characteristics and applications
- Polychloroprene rubber adhesives: modifiers and additives* J M MARTÍN MARTÍNEZ Resin, tackifier, cross-linking agent addition
- Ethylene–vinyl acetate copolymers* D E PACKHAM Copolymer composition and properties; hot melt and emulsion adhesives
- Polyvinyl alcohol in adhesives* C A FINCH Production and uses
- Silicone adhesion* B PARBHOO Wide range of bond strength and applications
- Silicone adhesives: addition cure* B PARBHOO Cross-linking by addition reactions
- Silicone adhesives: condensation cure* B PARBHOO Cross-linking by step reactions

*Silicones: properties* B PARBHOO Range of properties

*Silicones: structures* B PARBHOO Chemical structure

### Testing

*Testing of adhesives* D A TOD Survey of tests including mechanical, rheological and thermal

*Tests of adhesion* D A TOD Basic principles, effects of test parameters, peel, shear, tensile, wedge test

*Standards for adhesives and adhesion* S MILLINGTON Discussion of scope and background to national standards

*Appendix: literature and test methods* D E PACKHAM Literature and information sources, test methods

*Non-destructive testing of adhesively-bonded structures* G J CURTIS Acoustic wave techniques, resonance and pulse-echo testers

*Tensile tests* D E PACKHAM Description, uneven stress distribution

*Peel tests* D E PACKHAM Peel force and peel energy; factors affecting peel energy; angle variation

*Climbing drum peel test* K B ARMSTRONG Peeling of metal sheet, for example, skin from honeycomb

*Shear tests* A D CROCOMBE Tests in tension and torsion

*Napkin ring test* D E PACKHAM Calculation of shear stress: refinements

*Fracture mechanics* A J KINLOCH Basis: energy balance and stress-intensity factor approaches

*Fracture-mechanics test specimens* A J KINLOCH Test methods for flexible and rigid joints

*Blister test* D E PACKHAM Use, theory, variations

*Scratch test* D E PACKHAM Assessment of thin film adhesion

*Fibre-matrix adhesion – assessment techniques* F R JONES Direct and indirect test methods

*Rubber to metal bonding – testing* J A LINDSAY Peel tests, tests in tension

*Mould adhesion – measurement* D E PACKHAM Peel, blister, etc., for low adhesion

*Paint service properties and adhesion* N WHITEHOUSE Internal stress; testing; weathering

*Weathering of adhesive joints* J SARGENT Exposure in temperate and tropical sites

*Weathering tests* S T TREDWELL Long-term exposure

*Accelerated ageing* G W CRITCHLOW Shear and wedge tests, humidity, corrosive environments

*Wedge test* D G DIXON Use of test for comparing joint durability

### **Pre-treatment of surfaces**

#### **Metals**

*Engineering surfaces of metals* J F WATTS Practical metallic surfaces are oxidized, contaminated and rough: pre-treatments; adhesion

*Pre-treatment of metals prior to bonding* G W CRITCHLOW Survey of mechanical and chemical treatments

*Pre-treatment of metals prior to painting* N WHITEHOUSE Need for pre-treatment; survey of common methods

*Rubber to metal bonding – pre-treatments* P LEWIS Degreasing, mechanical cleaning, chemical cleaning

*Degreasing* J F WATTS Solvent, alkali and emulsion cleaners; efficiency

*Abrasion treatment* J F WATTS Removal of loose layers, roughening, improved adhesion

*Conversion coating* G W CRITCHLOW Phosphate, chromate and alkali oxide treatments

*Silane adhesion promoters* D G DIXON Silanes, coupling agents, surface films

*Silane as metal pre-treatments* W J VAN OOIJ Silanes, structure and effectiveness

*Thermal spray processes* G D DAVIS and R A ZATORSKI Technique and equipment

*Thermal spray coatings used for adhesion* G D DAVIS and R A ZATORSKI As a surface treatment

*Primers for adhesive bonding* J A BISHOPP Types of primers for metals and polymers

*Primers for sealants* G B LOWE Types for porous and non-porous surfaces

*Microfibrous surfaces* D E PACKHAM Examples of preparation of Fe, Cu, Zn. Use as substrates in adhesion-energy dissipation

*Pre-treatment of aluminium* G W CRITCHLOW Chronic acid etch, chronic acid anodizing, phosphoric acid anodizing; relative bond durability

*FPL etch* D E PACKHAM Sulphochromate treatment for Al; ductility; topography

*Anodizing* D E PACKHAM As a pre-treatment: different electrolytes and uses

*Pre-treatment of copper* D E PACKHAM Conventional and microfibrous surfaces

*Pre-treatment of steel* J F WATTS Abrasion, pickling and conversion coatings

*Pre-treatment of titanium* G W CRITCHLOW Survey of important types of pre-treatment and comparisons of bond durability

## **Polymers**

*Surface nature of polymers* D BRIGGS Migration of additives and low molecular weight fraction to the surface

*Pre-treatments of polymers* D M BREWIS Effects of solvent, mechanical, oxidative and plasma treatment

*Pre-treatments of polyolefins* D M BREWIS Polyolefins, scope and effects of different treatment types

*Flame treatment* D BRIGGS Pre-treatment of polymers, scope

*Corona discharge treatment* D BRIGGS Form of plasma treatment applied especially to polyolefins

*Plasma pre-treatment* D BRIGGS Plasmas from noble gases, reactive gases; plasma polymerization

*Electrochemical pre-treatment of polymers* R H DAHM Recently developed surface treatment methods

*Pre-treatment of fluorocarbon polymers* D M BREWIS Problems of these materials, chemical and plasma treatment

**Primers**

*Primers for adhesive bonding* J A BISHOPP Types of primers for metals and polymers

*Primers for sealants* G B LOWE Types for porous and non-porous surfaces

*Paint primers* N WHITEHOUSE Function; make-up

*Autophoretic primers* N WHITEHOUSE Aqueous dispersions containing acids that deposit corrosion-resistant films

*Etch primers* N WHITEHOUSE Chemical action; application to aluminium and steel

*Silane adhesion promoters* D G DIXON Silanes, coupling agents, surface films

*Silane as metal pre-treatments* W J VAN OOIJ Silanes, structure and effectiveness

**Durability – hostile environments**

*Durability: fundamentals* G W CRITCHLOW Modes of failure; water ingress; pre-treatments

*Weathering of adhesive joints* J SARGENT Exposure in temperate and tropical sites

*Displacement mechanisms* D M BREWIS Displacement of organic contaminants from high-energy surfaces by adhesives

*Cathodic disbondment* J F WATTS Failure of bonds to ferrous alloys in an aqueous environment

*Creep* A D CROCOMBE Occurrence; protection against creep failure

*Durability: sub-critical debonding* D A DILLARD Deleterious effects water may have on adhesion

*Accelerated ageing* G W CRITCHLOW Shear and wedge tests, humidity, corrosive environments

*Weathering tests* S T TREDWELL Long-term exposure

*Wedge test* D G DIXON Use of test for comparing joint durability

**Engineering design**

*Environment: sustainability* D E PACKHAM Considers depletion of resources, limits to growth

- 
- Environment and the impact of adhesive technology* D E PACKHAM Resources, energy, pollution
- Health and safety* M FAKLEY Hazards associated with adhesives: sources of information
- Engineering design with adhesives* C WATSON Advantages of use of adhesives: specific examples of improved design
- Industrial applications of adhesives* C WATSON Scope of adhesives; bonding cylindrical components
- Joint design – general* C WATSON Flat and cylindrical joints; good and bad practice
- Joint design – cylindrical joints* C WATSON Factors affecting joint performance; specimen calculation
- Dispensing of adhesives* C WATSON Techniques used industrially for the application of adhesives to surfaces to be bonded
- Joint design: strength and fracture perspectives* D A DILLARD Two approaches to design of joints
- Stress distribution: beam on elastic foundation* D A DILLARD Stresses in shear joints
- Stress distribution: shear lag solution* D A DILLARD Stresses in shear joints
- Stress distribution: Poisson's ratio* D A DILLARD Poisson contraction and stress distribution
- Stress distribution: stress singularities* D A DILLARD Stress concentration – sharp cracks
- Durability: creep rupture* D A DILLARD Creep under sustained stress
- Durability: fatigue* D A DILLARD Effect of cyclic loads
- Impact resistance* A MADDISON Impact behaviour of different adhesives; effects of pre-treatment
- Repair methods* K B ARMSTRONG Methods for composites and honeycomb panels on large structures such as aircraft
- Sealant joint design* J C BEECH Design of butt and lap joints

**Processing and assembly**

*Coextrusion* R J ASHLEY Production of a laminate in a single process

*Extrusion coating* R J ASHLEY Techniques and materials used

*Tie layers* R J ASHLEY Uses in coextrusion to aid adhesion

*Laminating* R J ASHLEY Use of aqueous-based, solvent-based and hot melt adhesives

*Rubber to metal bonding – basic techniques* P LEWIS In- and post-vulcanization bonding

*Rubber to metal bonding: processing effects* J A LINDSAY Importance of good mould design

*Rubber-based adhesives: compounding* J M MARTÍN MARTÍNEZ Formulations, etc.

*Thermal spray processes* G D DAVIS and R A ZATORSKI Technique and equipment

*Plasma-polymerization* W J VAN OOIJ Deposition of polymers from non-conventional precursors

*Fibre composites – introduction* B C COPE Fibre orientation, fibre–matrix interface; surface treatment

*Fibre composites – joining* K B ARMSTRONG Thermoset matrices, peel-ply, abrasion; thermoplastic matrices, corona discharge

*Fibre composites – processing techniques* B C COPE Comparison of processing methods

*Repair methods* K B ARMSTRONG Methods for composites and honeycomb panels on large structures such as aircraft

**Welding and autohesion**

*Diffusion theory of adhesion* K W ALLEN Polymer/polymer autohesion, molecular weight dependence

*Polymer–polymer adhesion: molecular weight dependence* R P WOOL Fracture energy and molecular weight

*Polymer–polymer adhesion: weld strength* R P WOOL Implications for moulding technology

*Polymer–polymer adhesion: incompatible interfaces* R P WOOL Interdiffusion, compatibilizers

*Welding plastics – electromagnetic radiation* A BUXTON IR microwave, high frequency, etc.

*Welding plastics – external heat source* A BUXTON Hot plate, impulse welding, etc.

*Welding plastics – mechanical movement* A BUXTON Frictional heating

*Solvent welding* M WARWICK Scope, advantages and disadvantages

*Wood bonding by vibration welding* A PIZZI Innovative technique for wood

### **Applications of adhesives**

*Industrial applications of adhesives* C WATSON Scope of adhesives; bonding cylindrical components

*Engineering design with adhesives* C WATSON Advantages of use of adhesives: specific examples of improved design

*Dispensing of adhesives* C WATSON Techniques used industrially for the application of adhesives to surfaces to be bonded

*Paint constitution and adhesion* N WHITEHOUSE Binder, pigment, adhesion mechanism

*Sealants* G B LOWE Chemical composition, use

*Sealants in double glazing* G B LOWE Types of materials, durability

*Silicones: properties* B PARBHOO Range of properties

*Metallizing plastics* R H DAHM Vapour and solution methods

*Aerospace applications* D G DIXON Adhesives used: structures bonded

*Automotive applications* A MADDISON Types of adhesive used, advantages

*Adhesion in dentistry: restorative materials* M SHERRIFF Polymers as filling materials

*Adhesion in dentistry: orthodontics and prosthodontics* M SHERRIFF Dental applications

*Adhesion in medicine* M E R SHANAHAN Macroscopic level (e.g. prostheses) and cellular level



*Packaging industry* R J ASHLEY Adhesives used, service requirements

*Pressure-sensitive adhesives* D W AUBREY Nature of pressure-sensitive adhesion, materials used

*Rubber to metal bonding – applications* G LAKE Tyres; bearings; durability

*Rubber: tyre cord adhesion* W J VAN OOIJ Adhesion to brass-coated steel

*Adhesives in the textile industry* A J G SAGAR Applications and adhesive types

*Adhesives for textile fibre bonding* A J G SAGAR Non-woven materials, flocking, tyres, belts and hose

*Adhesives in textile coating laminating and printing* A J G SAGAR Types of adhesive for coated fabrics, lamination, seaming, carpets and pigment printing

*Underwater adhesives* J M LANE Wetting problems; pre-treatments; durability

*Wood adhesives – basics* A PIZZI General introduction

### **Composite materials**

*Composite materials* D E PACKHAM General introduction – emphasis of crucial role of interfacial adhesion

*Fibre composites – introduction* B C COPE Fibre orientation, fibre–matrix interface; surface treatment

*Fibre composites – matrices and fibres* B C COPE Scope of different fibre and matrix materials

*Fibre–matrix adhesion – glass fibres* F R JONES Types of fibre: surface treatment

*Fibre–matrix adhesion – carbon fibres* F R JONES Structure of carbon fibre; effect of surface treatment

*Fibre composites – processing techniques* B C COPE Comparison of processing methods

*Fibre composites – joining* K B ARMSTRONG Thermoset matrices, peel-ply, abrasion; thermoplastic matrices, corona discharge

*Repair methods* K B ARMSTRONG Methods for composites and honeycomb panels on large structures such as aircraft

---

*Filler–matrix adhesion* V KOVAČEVIĆ, S LUČIĆ BLAGOJEVIĆ and  
M LESKOVAC Surface treatment of fillers and composite properties

*Rubber fillers* J A LINDSAY Role of fillers, non-reinforcing and reinforcing fillers,  
adhesion aspects

*Wood composites – adhesives* B H PAXTON Scope for different adhesive types

*Toughened adhesives* J GUTHRIE Mechanism of toughening; advantages and  
disadvantages

*Toughened acrylic adhesives* B KNEAFSEY Setting mechanism; applications;  
advantages and disadvantages

*Toughened epoxide adhesives* J A BISHOPP Basis of toughening

*Toughened epoxide adhesives: particle formation prior to cure* J A BISHOPP A  
toughening technology

*Toughened epoxide adhesives: precipitation during cure* J A BISHOPP The most  
widely used method

*Toughened epoxide adhesives: blend synergy* J A BISHOPP Effects of two types of  
particles

### **Paint**

*Paint constitution and adhesion* N WHITEHOUSE Binder, pigment, adhesion  
mechanism

*Pre-treatment of metals prior to painting* N WHITEHOUSE Need for pre-treatment;  
survey of common methods

*Paint primers* N WHITEHOUSE Function; make-up

*Paint service properties and adhesion* N WHITEHOUSE Internal stress; testing;  
weathering

### **Rubber**

*Rubber to metal bonding – applications* G LAKE Tyres; bearings; durability

*Rubber: tyre cord adhesion* W J VAN OOIJ Adhesion to brass-coated steel

*Rubber to metal bonding – basic techniques* P LEWIS In- and post-vulcanization  
bonding

*Rubber to metal bonding – pre-treatments* P LEWIS Degreasing, mechanical cleaning, chemical cleaning

*Rubber to metal bonding – testing* J A LINDSAY Peel tests, tests in tension

*Rubber to metal bonding: processing effects* J A LINDSAY Importance of good mould design

*Release* J S TONGE Examples where low adhesion needed – internal and external release agents

*Mould adhesion – measurement* D E PACKHAM Peel, blister, etc., for low adhesion

*Mould adhesion and fouling* D E PACKHAM Relevant factors such as surface layers

*Rubber fillers* J A LINDSAY Role of fillers, non-reinforcing and reinforcing fillers, adhesion aspects

*Tack* D W AUBREY Definition; cohesive, adhesive and autohesive tack; tackifier resins

*Rubber-based adhesives* J M MARTÍN MARTÍNEZ General introduction

*Rubber-based adhesives: compounding* J M MARTÍN MARTÍNEZ Formulations, etc.

*Rubber-based adhesives: typical characteristics* J M MARTÍN MARTÍNEZ Advantages

*Natural rubber-based adhesives* J M MARTÍN MARTÍNEZ Nature and properties

*Nitrile rubber adhesives* J M MARTÍN MARTÍNEZ Nature and properties

*Polychloroprene rubber adhesives: applications and properties* J M MARTÍN MARTÍNEZ Adhesion characteristics and applications

*Polychloroprene rubber adhesives: modifiers and additives* J M MARTÍN MARTÍNEZ Resin, tackifier, cross-linking agent addition

*Contact adhesives* J M MARTÍN MARTÍNEZ Plasticized CR or NR adhesives

### **Sealants and mastics**

*Sealants* G B LOWE Chemical composition, use

*Selection of joint sealants* J C BEECH Comparison and criteria for selection

*Primers for sealants* G B LOWE Types for porous and non-porous surfaces

---

*Sealant joint design* J C BEECH Design of butt and lap joints

*Sealants in double glazing* G B LOWE Types of materials, durability

*Silicones: properties* B PARBHOO Range of properties

### **Wood**

*Wood adhesives – basics* A PIZZI General introduction

*Wood composites–adhesives* B H PAXTON Scope for different adhesive types

*Wood adhesives – hot melts* A PIZZI EVA and polyamide

*Wood adhesives – aminoplastics* A PIZZI UF, MF and related adhesives

*Wood adhesives – phenolics* A PIZZI Types and applications

*Wood adhesives – isocyanates/urethanes* A PIZZI Bonding to damp wood

*Wood bonding by vibration welding* A PIZZI Innovative technique for wood

*Appendix: literature and test methods* D E PACKHAM Literature and information sources, test methods

# List of contributors

---

**Dr M L Abel**

University of Surrey, Guildford, UK.

**Dr K W Allen**

Oxford Brookes University, Oxford, UK.

**Dr K B Armstrong**

Consultant

**Mr R J Ashley**

BA Consultants, Cumbria, UK.

**Dr D W Aubrey**

London, UK

**Mr J C Beech**

Building Research Establishment, Garston, UK

**Dr J A Bishopp**

Star Adhesion Ltd, Cambridge, UK.

**Professor F J Boerio**

University of Cincinnati, Ohio, USA.

**Dr D M Brewis**

Loughborough University, Loughborough, UK.

**Professor D Briggs**

Siacon Consultants, Malvern, UK.

**Dr A Buxton**

TWI Ltd, Cambridge, UK.

**Dr C Chatfield**

University of Bath, Bath, UK.

**Professor J Comyn**

Loughborough University, Leicestershire, UK.

**Dr B C Cope**

Formerly of De Montfort University, Leicestershire, UK.

**Dr G W Critchlow**

Loughborough University, Leicestershire, UK.

**Dr A D Crocombe**

University of Guildford, Surrey, UK.

**Dr G J Curtis**

AEA Horwell, Didcot, UK

**Dr R H Dahm**

Loughborough University, Leicestershire, UK.

**Dr G D Davis**

DACCO SCI inc, Columbia, USA.

**Professor D Dillard**

Virginia Polytechnic, Virginia, USA.

**Dr D G Dixon**

BAE Systems, Bristol, UK.

**Dr M Fakley**

PermaBond, Southampton, UK.

**Dr C A Finch**

Pentafin Associates, Aylesbury, Bucks, UK. – deceased

**Dr R Greef**

Southampton University, Southampton, UK.

**Dr J Guthrie**

Henkel-Loctite Ltd, Dublin, Ireland.

**Professor F R Jones**

University of Sheffield, Sheffield, UK.

**Professor K Kendall**

University of Birmingham, Edgbaston, UK.

**Professor A J Kinloch**

Imperial College London, London, UK.

**Dr B Kneafsey**

Henkel-Loctite Ltd, Dublin, Ireland.

**Professor V Kovacevic**

University of Zagreb, Croatia.

**Dr G Lake**

Abbot's Langley, Herts, UK

**Dr J M Lane**

Wessex Resins & Adhesives Ltd, Hampshire, UK.

**Professor G J Leggett**

The University of Sheffield, Sheffield, UK.

**Dr M Leskovac**

University of Zagreb, Croatia.

**Mr P Lewis**

T.A.R.R.C. Brickendonbury, Hertford, UK.

**Mr J A Lindsay**

Trowbridge, Wilts, UK

**Dr G B Lowe**

GBL Consultants, Leicester, UK.

**Dr S Lucic Blagojevic**

University of Zagreb, Croatia.

**Dr A Maddison**

Stoke Golding Applied Research, Leicester, UK.

**Professor R R Mallik**

The University of Akron, Ohio, USA.

**Dr J M Martín Martínez**

University of Alicante, Spain.

**Dr D P Melody**

Formerly of Henkel-Loctite Ltd, Dublin, Ireland.

**Mr S Millington**

QinetiQ Ltd, Farnborough, UK.

**Dr D E Packham**

University of Bath, Bath, UK.

**Dr J F Padday**

Formerly Kodak – deceased.

**Dr B Parbhoo**

Dow Corning Ltd., Glamorgan, UK.

**Mr G C Parker**

Swift Adhesives, Chatteris, Cambridgeshire, UK.

**Dr M W Pascoe**

Formerly Keeper of Conservation & Technical Services, The British Museum and Head of Science for Conservation, University of the Arts, Camberwell College.

**Mr B H Paxton**

Formerly of the Building Research Establishment, Watford, UK.

**Professor A Pizzi**

ENSTIB, University of Nancy 1, Epinal, France.

**Dr A V Pocius**

3M Corporate Research Materials Laboratory, MN, USA.

**Mr J Pritchard**

Birmingham, UK

**Dr A D Roberts**

Tun Abdul Razak Research Centre, Hertford, UK.

**Dr A J G Sagar**

Shirley Technologies Ltd, Manchester, UK.

**Dr J Sargent**

BAE Systems, Bristol, UK.

**Dr M E R Shanahan**

Centre des Matériaux, (CMGD), Evry, France.

**Professor S J Shaw**

Defence Science & Technology Laboratory, Wiltshire, UK.

**Dr M Sheriff**

Kings College, London, UK.

**Dr D A Todd**

QinetiQ Ltd, Sevenoaks, UK.

**Dr J S Tonge**

Dow Corning Corporation, MI, USA.

**Dr S T Tredwell**

BP Chemicals, Sully, UK

**Professor W J Van Ooij**

University of Cincinnati, Ohio, USA.

**Dr M A Wahab**

University of Surrey, Guildford, UK.

**Dr M Warwick**

TWI Ltd Cambridge, UK.



**Mr C Watson**

Formerly of Loctite UK, Welwyn Garden City, UK.

**Professor J F Watts**

University of Surrey, Guildford, UK.

**Dr N R Whitehouse**

PRA Coatings Technology Centre, Middlesex, UK.

**Professor R P Wool**

University of Delaware, Newark, USA.

**Mr R A Zatorski**

VP Engineering, ZCC Inc, CT, USA.

# A

---

## *Abrasion treatment*

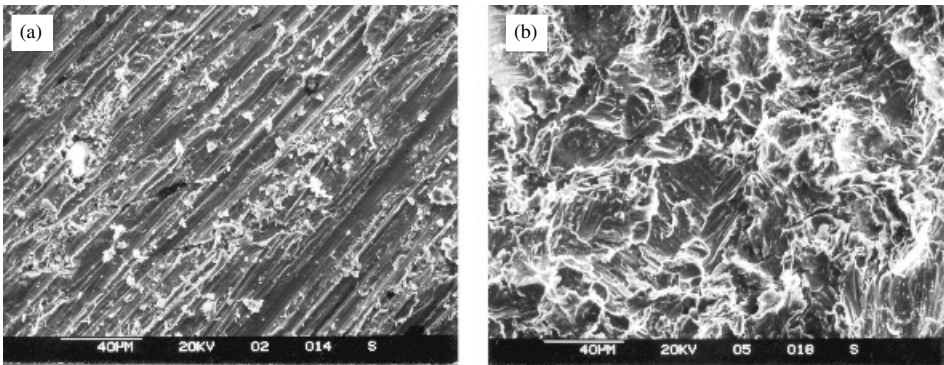
---

JOHN F WATTS

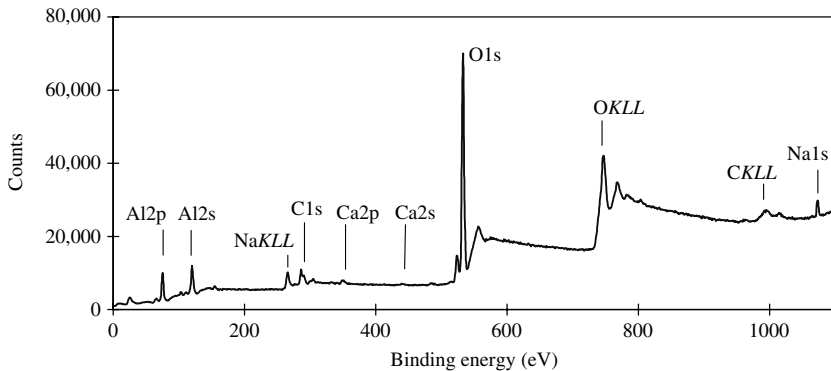
If **Engineering surfaces of metals** possess large quantities of extraneous material requiring removal as a preliminary to **Pre-treatment of metals prior to bonding** or **Pre-treatment of metals prior to painting**, it is often appropriate to consider some form of abrasive treatment. In general, such treatments can only be employed successfully to remove brittle materials such as native oxides (e.g. mill scale), and attempts to remove large quantities of energy-absorbing material such as previous coats of paint are not successful. Although abrasion cleaning includes all processes that involve the passage of an abrasive medium over the surface to be cleaned, the most widely employed, particularly where consistency of finish and high throughput are required, is abrasive blast cleaning. Other methods, either carried out by hand or machine, include wire brushing and sanding, buffing and so on.

Any abrasive treatment has a twofold purpose: to remove rust, mill scale and other surface detritus and also to provide an appropriate surface profile to which the organic phase can be applied. Whether blast cleaning or some other abrasive method is used, the cleanliness of the abrasive medium is of prime importance. That is to say, if the wire brush, or the abrasive in the blast cleaning process, has been used to clean an oily substrate, it will exhibit a memory effect and the oil will contaminate the abrasive and transfer the organic material to the next surface to be cleaned. As far as the efficacy of abrasion treatment is concerned, it is one of the most effective ways of producing a chemically clean surface<sup>1</sup> in terms of the residual level of hydrocarbons and associated material. The reuse of abrasive media should be viewed with caution, and where grit blasting is used as part of a pre-treatment process in structural adhesive bonding research, it is standard practice to discard the grit after a single use. This is a rather wasteful process but ensures the elimination of the memory effects described above.

Any form of abrasion treatment necessarily involves the removal of material and the exposure of new surface to the atmosphere. The geometry and size of the abrasive medium will affect the surface profile, as illustrated by the examples of Fig. 1, which compares the surface topography of cold rolled steel obtained by emery abrasion (120 grit) with that generated by blasting with chilled iron grit (G12). In the case of blast cleaning, the particles may either be inorganic (silica, alumina or mineral slags) or metallic, invariably iron, although zinc is used to confer temporary corrosion resistance in marine environments. The use of zinc grit is successful, as a thin film of zinc is transferred to the substrate and in the case of a steel structure becomes the sacrificial anode in a short-lived cathodic protection system. In other instances, the transfer of the abrasive media to the substrate shows no discernible advantages, although there may be some deleterious side effects. The surface analysis, by **X-ray photoelectron spectroscopy**, of an aluminium substrate blasted by fresh alumina grit is shown in Fig. 2. The Na1s, NaKLL, Ca2p and 2s features in the spectrum are a result of transfer of minor constituents of the grit (CaO and NaO) to the metal surface during the blasting process. In general, the use of fresh, rather than recycled, grit is recommended when grit blasting is used as a **Pre-treatment of metals prior to bonding**.



**Fig. 1.** Surface morphology produced by (a) emery abrasion and (b) grit blasting, of a mild steel substrate



**Fig. 2.** XPS survey spectrum of aluminium sheet blast cleaned with alumina grit (by courtesy of Acharawan Rattana, University of Surrey)

The shape of the blasting media varies widely from spherical to particular size fractions of the crushed source material.<sup>2</sup> In the case of spherical abrasive particles, a peening action at the surface is achieved, and although this produces some surface cleaning, the overriding effect is to produce compressive stresses in the surface region. This is particularly important if the article is to be subjected to mechanical constraints, as it is known to improve fatigue resistance, in addition to the important criterion of paint adhesion.

The increase in adhesion of an organic system to an inorganic surface cleaned by an abrasion method can be a result of the increased surface area, and therefore of the increased interfacial contact, that is generated by these methods<sup>3</sup> (see **Roughness of surfaces** and **Roughness and adhesion**).

Although blast cleaning is the most effective method, the performance of the coated substrate depends on the type of abrasive employed. Sand and other non-metallic abrasives are somewhat better than metallic shot or grit, and metallic grit appears to give better adhesion than a shot-peened surface.<sup>4</sup> Although this subject has yet to be exhaustively investigated, it seems that abrasive shape and fracture characteristics are the important factors in obtaining a well-cleaned substrate that will yield good durability when the organic system is applied.

### References

1. J. E. Castle and J. F. Watts, in *Corrosion Control by Organic Coatings*, H. Leidheiser, Ed., NACE, Houston, 1981, pp. 78–87.
2. C. G. Munger, *Corrosion Prevention by Organic Coatings*, NACE, Houston, 1984, pp. 229–233.
3. J. F. Watts and J. E. Castle, *J. Mater. Sci.*, **19**, 2259–2272 (1984).
4. L. K. Schwab, R. W. Drisko, in *Corrosion Control by Organic Coatings*, H. Leidheiser, Ed., NACE, Houston, 1981, pp. 222–226.

---

### Accelerated ageing

---

G W CRITCHLOW

An understanding of the long-term performance of adhesively bonded structures (see **Durability – fundamentals**) is a fundamental requirement for bonding technology to be fully utilized in manufacturing situations.<sup>1,2</sup> Items such as airframes could have a design life of fifty years or more. While initial levels of adhesion are relatively straightforward to measure as a function of different test geometry, manufacturers are not willing, or able, to wait for such prolonged time periods for in-service type testing. In such situations, some degree of accelerated ageing is required to help identify long-term performance or durability from short-term tests. These tests are invariably laboratory based although outdoor exposure in extreme conditions can be used to accelerate failure of bonds, which would normally be exposed to more benign conditions.

The purpose of accelerated ageing is clearly to cause deterioration to the bonding system under investigation, that is, the adhesive-primer-pre-treatment-substrate combination. It is of critical importance that the ageing conditions should be selected to recreate the same failure mechanisms as would be seen in service conditions.

In service conditions, moisture ingress is thought to be responsible for many examples of premature joint failure. Accelerated ageing tests are, therefore, commonly carried out by exposing joints or structures to either water immersion or to water vapour. Deionized water is often used to give a degree of control to such tests. Variable relative humidity (RH) conditions are usually controlled either by a hygrometer or by saturated salt solutions up to values close to 100% RH. Moisture ingress in joints can occur either by bulk diffusion through permeable substrates or the adhesive or by wicking across an interface or through cracks or voids in the adhesive. Once present, water molecules can cause a modification in the adhesive mechanical properties, for example by plasticization or by a reduction in the glass transition temperature. Alternatively, it is proposed that interfacial bonds can be disrupted or modification of the adherend surface can result, for example, by hydration of a metal.

The rate of water ingress by diffusion through the adhesive is principally determined by its diffusion coefficient. An increase in temperature will rapidly increase the rate of water uptake in line with Fickian diffusion models as the diffusion coefficient will increase significantly with temperature. Such a hot-wet environment is generally regarded as a very aggressive form of accelerated ageing. Other test media can include saline solution or salt spray exposure to mimic a seacoast environment or aviation fluids, for example, oils, cleaning solutions or fuel to represent spillage or other contamination conditions. To further accelerate moisture ingress, perforated test coupons can be used to drastically reduce diffusion path lengths.<sup>3</sup>

Harsh environmental exposure conditions can also be combined with externally applied loads. These loads can be static, quasi-static or cyclic; cyclic loads are usually sinusoidal although other waveforms, for example square, have also been used.

For example, single-lap shear joints can have a known static load applied, then inserted into a specified environment, and the time-to-failure of joints noted as a function of variables such as adhesive type, pre-treatment and stress (see **Shear tests**). Static loads can also be applied to other joint configurations. Many studies have shown that such tests exhibit good discrimination between different surface pre-treatments. The creep performance of adhesives can also be measured by means of static load testing (see **Durability: creep rupture** and **Durability: sub-critical debonding**).

The standard **Wedge test** was developed by Boeing Aerospace Corp. to provide a rapid quality control check for bonding systems. The results from this are reported to correlate well with observed in-service performance. The standard wedge test can be thought of as essentially applying a quasi-static load by the bending of the two beams following wedge insertion". Allied to this is monotonic or constant displacement rate testing, which can be carried out under various ageing conditions to determine elastic energy release rates for joints.<sup>4</sup>

Fatigue test data are widely reported, for example, the TDCB configuration (see **Fracture mechanics test specimens** and **Durability: fatigue**) is used with a sinusoidal load applied and the environment varied with the most demanding tests incorporating hot-wet exposure conditions. In this case, the test frequency is typically a few hertz. From these tests, a relationship is determined between the rate of crack growth per cycle and the maximum strain energy release rate  $G_{\max}$ . These data can be used to determine threshold values for the strain energy release rate below which joint failure would not be expected to occur. Such an approach can also be applied to single-lap shear joints under cyclic fatigue loading. This approach can therefore be regarded as accelerated ageing in that the

results of long-term exposure are predicted from short-term tests, which may be carried out in harsh environmental exposure conditions.<sup>4,5</sup> In contrast, the use of variable loading conditions in joints or structures to mimic real-life situations has not been widely reported.

The above-mentioned TDCB test is unusual in that it provides fundamental design data useful to engineers or designers. The majority of reported studies on joints or structures that have undergone environmental ageing provide a simple ranking of adhesion performance; usually, these are relative to an established datum. A simple relationship or “acceleration factor” between the time spent on an ageing test and the expected service life is not generally available. Levi<sup>6</sup> has applied the “reaction rate model” to this subject but his approach has not generally been adopted.

There are a number of **Standards for adhesives and adhesion** that relate to environmental exposure and test conditions. These exist within industry sectors and are also, in some instances, the subject of both nationally and internationally agreed standards documents.<sup>1,2</sup>

### References

1. A. J. Kinloch, *Adhesion and Adhesives: Science and Technology*, Chapman and Hall, London, 1987.
2. J. D. Minford, *Handbook of Aluminum Bonding Technology and Data*, Marcel Dekker, New York, 1993.
3. D. J. Arrowsmith and A. Maddison, *Int. J. Adhes. Adhes.*, **7**(1), 15–24 (1987).
4. D. R. Arnott and M. R. Kindermann, *J. Adhes.*, **48**, 85–100 (1995).
5. H. Hadavinia, A. J. Kinloch, M. S. G. Little and A. C. Taylor, *Int. J. Adhes. Adhes.*, **23**, 449–461 (2003).
6. D. W. Levi, *J. Appl. Polym. Sci.*, **32**, 189–199 (1977).

---

### Acid–base interactions: introduction

---

D E PACKHAM

As discussed in the article on **Surface energy components**, it is common to regard surface energy  $\gamma$ , and thus the work of adhesion  $W_A$ , as being made up of the sum of components associated with the types of bonding appropriate to the chemical nature of the materials involved. Thus, in general,

$$\gamma = \gamma^d + \gamma^p + \gamma^h + \gamma^{AB} + \dots \quad [1]$$

and

$$W_A = W_A^d + W_A^p + W_A^h + W_A^{AB} + \dots \quad [2]$$

where the superscripts refer respectively to dispersion force, polar force, hydrogen bonding and acid–base interactions. It has been increasingly argued that the forces significant in most adhesion contexts are van der Waals forces, best represented as **Lifshitz-van der**

**Waals forces** (LW), and acid–base interactions. Equations 1 and 2 are then written as

$$\gamma = \gamma^{\text{LW}} + \gamma^{\text{AB}} \quad [3]$$

and

$$W_{\text{A}} = W_{\text{A}}^{\text{LW}} + W_{\text{A}}^{\text{AB}} \quad [4]$$

The acid–base term arises as a result of interactions between Lewis acids (electrophiles) and Lewis bases (nucleophiles); see **Acids**.

The article on **Surface energy components** describes how surface energies of solids and thence the work of adhesion between adhesive and substrate could be calculated from an assumption that the surface energy is composed of the sum of a dispersion and polar component (Eqn. 9 therein). Practical measurements of surface tensions of liquids and of contact angles of liquids on solids were involved. In a similar way, solid surface energies and works of adhesion can be obtained from the assumption (Eqns. 3 and 4 above) that surface energy is made up of the sum of a Lifshitz-van der Waals and an acid–base component. The  $\gamma^{\text{LW}}$  term is obtained using non-polar liquids in exactly the same way as the dispersion components,  $\gamma^{\text{d}}$ , were obtained. This article is concerned with expressions that can be used to represent acid–base interactions and which can then be used in equations such as 3 and 4 and those derived from them.

#### *Fowkes' method of evaluation of acid–base component*

Fowkes was one of the first people to emphasize the importance of acid–base interactions in the context of adhesion. The volume of papers collected to honour his 75<sup>th</sup> birthday provides an important source of detailed information.<sup>1</sup> Fowkes<sup>2</sup> has argued that the acid–base component of the work of adhesion can be related to the molar enthalpy,  $\Delta H^{\text{AB}}$ , for the acid–base reaction by

$$W_{\text{A}}^{\text{AB}} = -f n_{\text{ab}} \Delta H^{\text{AB}} \quad [5]$$

where  $f$  is a factor converting enthalpy to free energy and  $n_{\text{ab}}$  is the number of moles per unit area of acid–base pairs at the interface. Fowkes applied the concepts of Drago to evaluate  $\Delta H^{\text{AB}}$ :

$$-\Delta H^{\text{AB}} = C^{\text{a}} C^{\text{b}} + E^{\text{a}} E^{\text{b}} \quad [6]$$

where  $C$  and  $E$  are constants related to the tendency of the acid or base to form covalent or ionic bonds respectively. Values of the Drago constants have been tabulated for a range of liquids<sup>2</sup> and may be evaluated for solid surfaces by contact angle studies of solutions of acids and bases at a range of concentrations and temperatures.<sup>2</sup>

Berg<sup>3</sup> has pointed out some limitations of this approach. Equation 6 is limited to adducts of 1:1 stoichiometry. Initially, the conversion term,  $f$  in Eqn. 5, was considered to be close to unity. It is now recognized that entropy effects that invalidate this assumption and complicate its evaluation are often present. If there is more than one type of functional group on the solid surface or both acid and basic sites are present, Eqn. 5 has to be written

as a summation, making the unambiguous deconvolution of the terms a “challenging task”.<sup>3</sup>

$$W_A^{AB} = \Sigma - fn_{ab}\Delta H^{AB} \quad [7]$$

### Other methods

Berg<sup>3</sup> has provided a wide-ranging discussion of a range of methods – many described as “tedious” – by which acid–base interaction can be obtained. In addition to the method of Fowkes, considered above, two others are described: **Inverse gas chromatography** and the contact angle method introduced by Good, Chaudhury and van Oss, which involves **Acid–base surface energy parameters**.

### References

1. K. L. Mittal and H. R. Anderson, Eds., *Acid-base Interactions: Relevance to Adhesion Science and Technology*, VSP, Utrecht, 1991.
2. F. W. Fowkes, *Acid-base Interactions: Relevance to Adhesion Science and Technology*, VSP, Utrecht, 1991, pp. 93.
3. J. C. Berg, Role of acid-base interactions in wetting and related phenomena, in *Wettability*, J. C. Berg, Ed., Marcel Dekker, New York, 1993, pp. 75.

---

## *Acid–base surface energy parameters*

---

D E PACKHAM

The significance in contemporary adhesion theory of Lewis acid–base interactions has been discussed in **Acid–base interactions: introduction**. It was argued that in many cases the surface energy ( $\gamma$ ) and the work of adhesion ( $W_A$ ) can be expressed as the sum of a component associated with **Lifshitz-van der Waals forces** (LW) and an acid–base (AB) component:

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad [1]$$

$$W_A = W_A^{LW} + W_A^{AB} \quad [2]$$

Some methods of evaluating the acid–base components have been discussed under **Acid–base interactions: introduction** and **Inverse gas chromatography**. Here, the method introduced by Good, Chaudhury and van Oss, which involves acid–base surface energy parameters, is considered.<sup>1–3</sup>

This approach introduces the concept of a Lewis acid parameter of surface energy,  $\gamma^+$  and a Lewis base parameter of surface energy,  $\gamma^-$ . This recognizes that a given solid or liquid (e.g. chloroform) may only exert acid properties, that is be monofunctional. In this case,  $\gamma^-$  is zero. For a mono-functional base (e.g. triethylamine),  $\gamma^+$  is zero. Some substances, such as water, show both electron donor and electron acceptor properties, so both  $\gamma^+$  and  $\gamma^-$  are finite. These are termed “bifunctional”. An “inert” molecule shows



no acid or base activity: both  $\gamma^+$  and  $\gamma^-$  are zero. (Good uses “monopolar” in place of “monofunctional”, and so on).

The surface energy parameters are *defined* by Eqn. 3 for the acid–base component of the work of adhesion between phases 1 and 2:

$$W_A^{AB} = 2\sqrt{(\gamma_1^+ \gamma_2^-)} + 2\sqrt{(\gamma_1^- \gamma_2^+)} \quad [3]$$

From this it follows that the acid–base contribution to the work of cohesion is

$$W_C^{AB} = 4\sqrt{(\gamma_1^+ \gamma_1^-)} \quad [4]$$

As work of cohesion is defined as twice the surface energy (**Wetting and spreading**),

$$\gamma_1^{AB} = 2\sqrt{(\gamma_1^+ \gamma_1^-)} \quad [5]$$

giving the relation between the acid–base component of surface energy,  $\gamma^{AB}$ , and Good’s parameters of surface energy. Clearly, if the material is either monofunctional ( $\gamma_1^+ = 0$  or  $\gamma_1^- = 0$ ) or inert ( $\gamma_1^+ = \gamma_1^- = 0$ ), the acid–base component of surface energy will be zero.

A more explicit form of Eqn. 2 can now be written incorporating Eqn. 11 in **Surface energy components** and Eqn. 3 above:

$$W_A = 2\sqrt{(\gamma_1^{LW} \gamma_2^{LW})} + 2\sqrt{(\gamma_1^+ \gamma_2^-)} + 2\sqrt{(\gamma_1^- \gamma_2^+)} \quad [6]$$

and, similarly, interfacial tension can be expressed as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^{LW} \gamma_2^{LW})^{1/2} - 2\sqrt{(\gamma_1^+ \gamma_2^-)} + 2\sqrt{(\gamma_1^- \gamma_2^+)} \quad [7]$$

This equation should be compared with Eqn. 10 in **Surface energy components**.

### *Evaluation of surface energies*

The evaluation of surface energies of liquids and solids using the theoretical approach of Good *et al.* is, in many respects, analogous to that used when working from the earlier “dispersion plus polar” approach described in **Surface energy components**.  $\gamma_{12}$  is eliminated between Eqn. 7 and the Young equation with the common assumption of zero spreading pressure. Taking phase 1 to be liquid (L) and phase 2 to be solid (S), this gives

$$\gamma_L(1 + \cos\theta) = 2\sqrt{(\gamma_S^{LW} \gamma_L^{LW})} + 2\sqrt{(\gamma_S^+ \gamma_L^-)} + 2\sqrt{(\gamma_S^- \gamma_L^+)} \quad [8]$$

where  $\theta$  is the contact angle of the liquid on the solid.

By measuring the contact angles of a number of different probe liquids on the same solid surface, the components for the solid surface can be evaluated. For a liquid, without acid–base activity, the total surface energy,  $\gamma_L$ , is  $\gamma_L^{LW}$  and the two last terms in Eqn. 8 are zero, enabling  $\gamma_S^{LW}$  to be calculated.

Table 1. Surface energy components and parameters in mJ m<sup>-2</sup>. Symbols are defined in text

	$\gamma$	$\gamma^{\text{LW}}$	$\gamma^{\text{AB}}$	$\gamma^+$	$\gamma^-$
<b>Liquids</b> <sup>2</sup>					
Water	72.8	21.8	51.0	25.5	25.5
Glycerol	64	34	30	3.92	57.4
Ethylene glycol	48.0	29	19.0	1.92	47.0
Formamide	58	39	19	2.28	39.6
Dimethyl sulphoxide	44	36	8	0.5	32
Chloroform	27.15	27.15	0	3.8	0
$\alpha$ -Bromonaphthalene	44.4	43.5	$\cong 0$		
Diiodomethane	50.8	50.8	0		
<b>Solids</b> <sup>1,3</sup>					
Polymethyl methacrylate	39–43	39–43	0	0	9.5–22.4
Polyvinyl chloride	43.75	43	0.75	0.04	3.5
Polyoxyethylene	45	45	0	0	66
Cellulose acetate	40.21	35	5.21	0.3	22.7
Cellulose nitrate	45	45	0	0	16
Polystyrene	42	42	0	0	1.1

Before the acid–base component of solid surface energy can be calculated, it is necessary to assume some *arbitrary* relation between the parameters of surface energy for one test liquid. Good chose to take

$$\gamma_{\text{L}}^- = \gamma_{\text{L}}^+ \quad [9]$$

for water. This enables the acid and base parameters to be evaluated for other test liquids. Then, Eqn. 8 is used to calculate  $\gamma_{\text{S}}^+$  and  $\gamma_{\text{S}}^-$  values for the solid surface from measured contact angles of the test liquids. Some results of work of this kind are given in Table 1.

### Conclusions

The use of the Good, Chaudhury and van Oss surface energy parameter concept allows values to be obtained for solid surface energies from contact angle measurement in a straightforward way. The fact that the parameters are introduced by way of a definition (Eqn. 3) and that numerical values can only be obtained by making an arbitrary assumption (Eqn. 9) does not in itself detract from their usefulness. Many concepts used in science – consider scales of pH and temperature – originate in judicious definitions and their numerical values result from arbitrary choice. What is important is the usefulness of the concepts in the sense of helping to rationalize the results of experiments and to predict results of new ones. So far, the surface energy parameter approach has had some success.

### References

1. R. J. Good, M. K. Chaudhury and C. J. van Oss, in *Fundamentals of Adhesion*, L.-H. Lee, Ed., Plenum, 1991, p. 153.
2. R. J. Good, in *Contact Angle, Wettability and Adhesion*, K. L. Mittal, Ed., VSP, Utrecht, 1993, p. 3.
3. J. C. Berg, Role of acid-base interactions in wetting and related phenomena, in *Wettability*, J. C. Berg, Ed., Marcel Dekker, New York, 1993, p. 75.

---

**Acids**

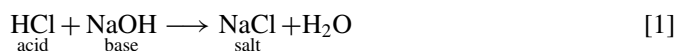

---

D E PACKHAM

Science commonly takes words from everyday language and gives them a special meaning. With the passage of time, meaning of a particular scientific term may well change: it is quite possible that several different meanings will be current at the same time, being used in different contexts.

The word “acid” is a good example. A discussion of its meaning is relevant in this book because **Acid–base interactions** play a significant role in considerations of the theory of interfacial tension and of adhesion.

The scientific concepts of acids and the complementary compounds, “bases”, have developed over several centuries with the development of chemistry.<sup>1,2</sup> Here, it is only necessary to start with the idea associated with Liebig (1838) and Arrhenius (1887), which is still familiar from introductory courses in chemistry. This defines an acid as a compound containing hydrogen that can be replaced by a metal to form a salt. In ionic terms, this amounts to defining an acid as a species that gives hydrogen ions (protons): a base is associated with hydroxyl ions. A typical acid–base reaction can be represented as



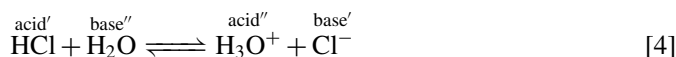
or



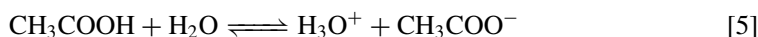
The presence of water as a solvent is implicit in these reactions; indeed, the hydrogen ion in reaction ii should be shown hydrated:

*Brønsted acids*

In 1923, Brønsted extended the concept of an acid as a species that produces hydrogen ions, to put forward a broader definition of an acid as a proton donor. A base, by analogy, was a proton acceptor (see also **Hydrogen bonding**). The reaction of a conventional acid with water becomes an acid–base reaction:



and



Two points should be noted. Water accepts a proton, so it is acting as a Brønsted base. The “first” acid (acid') gives rise to a species, for example,  $\text{Cl}^-$ , which can act as a base – a conjugate base (base'). Similarly, there is a conjugate acid,  $\text{H}_3\text{O}^+$  (acid''), associated with the base water. Here, the chloride ion and acetate ion, which would not traditionally be regarded as bases, are so regarded because they are capable of accepting protons (for

example in the reverse of reactions 4 and 5). The Brønsted definitions freed the concept of a base from being associated with the hydroxyl ion.

It is important to remember that the justification of definitions such as these in science is not a matter of “right” or “wrong”: it is a matter of whether the definitions are “useful” in the sense of aiding clear thinking and being helpful in the classification of reactions. That the Brønsted definitions have been much used for nearly 70 years suggests that they satisfy these criteria.

### Lewis acids

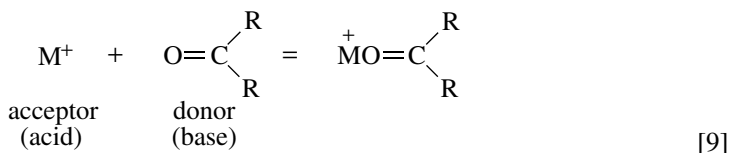
In 1923, and more prominently in 1938, Lewis extended the concept of an acid still further, defining an acid as an acceptor of electron pairs (and a base as an electron pair donor). An electron is, in a sense, the “opposite” of a proton, so these definitions can be seen as a development of Brønsted’s. Brønsted enabled the concept of “base” to be freed from exclusive attachment to the hydroxyl ion: Lewis went further in also broadening the concept of “acidity” beyond hydrogen-containing species.

In conventional neutralization of an acid in aqueous solution, the  $\text{OH}^-$  base donates a pair of non-bonding electrons, so these are still seen as acid–base reactions. The Lewis definition extends the concept to reactions with a formal similarity, which would not previously have been considered as acid–base reactions.

Consider reactions 6–9.



or



Reactions 6 and 7 are the traditional neutralizations of an acid by an hydroxyl ion: here, the donation of a non-bonding electron pair from the oxygen to the proton should be noted. Reaction 8 can be considered analogous; a non-bonding electron pair is donated from the chlorine to the silver ion.

Reaction 9 represents the reaction between a carbonyl compound, perhaps part of a polymer chain, and a cation on a substrate surface; this is the kind of reaction that might occur at some interfaces in adhesive bonds. The oxygen atom of the carbonyl group donates a non-bonding electron pair, this time into a vacant orbital in the metal ion, so, again it is a Lewis acid–base reaction. Lewis acids are also known as *electrophiles*, Lewis bases as *nucleophiles*.

### Conclusions

Acid–base reactions, especially donor–acceptor interactions, occur widely and some knowledge of them is necessary to follow contemporary debates on theories of surface

interactions relevant to adhesion. Jensen<sup>1</sup> gives a good historical survey of the development of the acid–base concept and detailed critiques of the Brønsted and Lewis theories. Many recent accounts of Lewis acid–base theory are available.<sup>2–4</sup>

### References

1. W. B. Jensen, *The Lewis Acid-Base Concepts*, Wiley-Interscience, New York, 1980.
2. M. Munowitz, *Principles of Chemistry*, Norton, New York; London, 2000.
3. M. R. Leach *The Lewis Acid/Base Reaction Chemistry Package* (Book + Poster + CD-ROM) ISBN 0-9536960-0-6 Meta-synthesis.com, 56 Downland Road, Brighton BN2 6DJ, UK, 1999.
4. *Introduction to Lewis acid-base chemistry*, University of Texas at Dallas, [http://www.utdallas.edu/~scortes/ochem/lewis\\_acidbase\\_chem.pdf](http://www.utdallas.edu/~scortes/ochem/lewis_acidbase_chem.pdf) (3.7.03).

## Acrylic adhesives

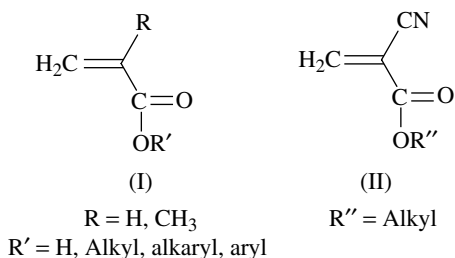
B KNEAFSEY

### Introduction

Acrylic adhesives are a versatile class of reactive adhesives that have in recent years gained wide acceptance in industry as bonding agents in the assembly of components. They are also to be found in the consumer market, where the industrially important benefits of rapid bonding, strength and “ease of use” can also be appreciated.

### Chemistry and properties

Acrylic adhesives are based on the esters of acrylic and substituted acrylic acids and can be categorized into two main groups; the acrylates and methacrylates (I), which cure by free radical–catalysed addition polymerization, and the cyanoacrylates (II), which cure by anion-catalysed addition polymerization. The term acrylic adhesives is normally restricted to include the former, while the latter is usually considered separately (see **Cyanoacrylate adhesives**); this categorization is adhered to here.



Acrylic adhesives are applied to the substrates to be bonded as a liquid mixture of unreacted methacrylate (or acrylate) monomers, polymers to thicken or toughen, reactive resins for strength, adhesion promoters and polymerization agents. Polymerization or curing is

started by the formation, by various methods, of free radicals; the polymerization then proceeds very rapidly by sequential addition to form the solid adhesive in the bond line (see **Chain polymerization**).

The versatility of acrylic adhesives comes from the large number of different monomers and resins available, which give flexible and tough or hard and rigid adhesives when cured, depending on the potential **Glass transition temperature** or on the functionality of the monomers (see **Toughened acrylic adhesives**).

Curing or setting of the adhesive can be achieved by irradiation by ultraviolet (UV) light (through glass) (see **Radiation-cured adhesives**), by the use of an activator on one or both substrates, by reaction with impurities or contamination on the substrates (see **Anaerobic adhesives**), by mixing two components either before applying the adhesive to the bond area or by mixing within the bond line as the components are assembled, or by heat or air. In each case, free radicals are formed by the reaction of an initiator in the adhesive with a second agent, such as UV light, heat, oxygen or a chemical activator. The polymerization is rapid, with strong bonds being formed in as little as 10 s. More information on the chemistry and variety of acrylic adhesive systems is given in Ref.<sup>1-3</sup> Some performance data are shown in Table 1, which highlights the strength and speed of bonding obtainable.

### Applications

Acrylic adhesives can be formulated to have low, controllable viscosity, which makes possible rapid, precise dispensing to parts to be bonded. In addition, rapid curing or setting, without long periods in ovens, makes these adhesives particularly useful for the assembly of various components in automatic or semi-automatic production lines (see **Engineering design with adhesives**).

Examples of these are the bonding of decorative glass figures, jewellery, sporting equipment, toys, loudspeakers (both ferrite/metal and paper and plastic cones) and small motors. Because the acrylic adhesives bond a wide range of substrates (metals, plastics, wood, glass), they can be used to bond different components and have found wide use in many industries.

Table 2 compares acrylic adhesives to two other important classes of adhesives used widely in industrial assembly operations: **Epoxide adhesives** and **Cyanoacrylate adhesives**. The speed of bonding and ease of use of cyanoacrylates makes them ideal where

Table 1. Performance<sup>a</sup> of acrylic adhesives

	Fast adhesive	Tough adhesive
Viscosity	10–20,000 mPa	20–80,000 mPa
Speed (time to fixture)	30–60 s	60–120 s
<i>Strength</i>		
Tensile shear (ASTM D1002-64) GB steel	20 N mm <sup>-2</sup>	15–25 N mm <sup>-2</sup>
<i>Toughness</i>		
T-peel (ASTM D 1876-69T) GB aluminium	2 N mm <sup>-1</sup>	3–4 N mm <sup>-1</sup>
Recommended substrates	Metals ferrites	Metals, ferrites glass, plastics, wood

<sup>a</sup> Data are taken from technical literature and are believed to be typical.

Table 2. Comparative benefits of industrial adhesives (epoxies, cyanoacrylates, acrylics)

	Epoxies		Cyanoacrylates	Acrylics
	2-part mixed	1-part heat cured		
<i>Bond strength</i>				
Metals, ferrites	+	++	+	++
Plastics	0	-	++	0
Toughness	-	++	0	++
Temperature/humidity	+	++	0	+
Speed of bonding	0	-	++	+
Ease of bonding				
Automatic application	-	-	++	++

Note: ++ great benefit, + significant benefit, 0 no benefit, - significant disadvantage.

toughness and high-temperature resistance are not critical. Epoxies provide good bond strengths to many substrates, but are slow curing and require either precise mixing or a heat cure. Acrylic adhesives can be seen to complement epoxies and cyanoacrylates, providing better temperature resistance and toughness than cyanoacrylates and better speed and ease of use than epoxies while giving good bonding performance.

Other articles of relevance are **Cyanoacrylate adhesives**, **Epoxide adhesives** and **Anaerobic adhesives**.

### References

1. R. Martin, Acrylic adhesives, in *Structural Adhesive – Developments in Resin and Primers*, A. J. Kinloch, Ed., Applied Science Publishers, Barking, 1986, Chap. 2.
2. Alphonsus. V. Pocius, *Adhesion and Adhesion Technology, An Introduction*, 2nd edn, Hanser Gardner Publications, 2002.
3. C. W. Boeder, Anaerobic and structural acrylic adhesives, in *Structural Adhesives – Chemistry and Technology*, S. R. Hartshorn, Ed., Plenum Press, New York, 1985, Chap. 5.

---

## Adhesion

---

D E PACKHAM

The chief aim of this entry is to show the various ways in which the term “adhesion” is employed in a technical sense, drawing attention to confusion that can occur because of its use in different contexts.

### Etymology

“Adhesion” seems to have come into the English language in the seventeenth century. It is interesting that one of the earliest examples (1661) quoted by the *Oxford Dictionary* is its use in a scientific context by Robert Boyle.<sup>1</sup>

The word “adhesion” comes from the Latin *adhaerere*, which means to stick to.<sup>2</sup> Its use by Lucretius in the context of iron sticking to a magnet anticipates the present technological application of the word. *Adhaerere* itself is a compound of *ad* (to) + *haerere*, where *haerere* also means to stick. Cicero uses the expression *haerere in equo* literally “to stick to a horse” to refer to keeping a firm seat.<sup>3</sup> (It follows from this that the word “abhesion” sometimes encountered, supposedly meaning “no adhesion” or “release”, is etymological nonsense and should be abandoned.)

### *Adhesion as a phenomenon*

The use of “adhesion” to describe the commonplace phenomenon or state where two bodies are stuck together is relatively straightforward. It is unlikely to lead to any serious confusion in a practical context, despite worries that have been expressed about the circularity of such a definition.<sup>4</sup>

It is perhaps worth pointing out that some are not content with so simple a concept but insist on building theoretical models into a definition of adhesion. Were we to accept the ASTM D 907 definition of “adhesion” as “the state in which two surfaces are held together by interfacial forces, which may consist of valence forces or interlocking forces or both”, we would have a serious problem. We would have to have a detailed insight into the dispositions of electrons at the interface before we could decide whether we had an example of the phenomenon of adhesion. The definition subjugates the readily observed phenomenon to a particular scientific theory, and scientific theories of their nature are subject to revision.

### *The magnitude of adhesion*

When we ask how large the adhesion is, we enter a realm where the term is used in a number of quite different ways.

*“Fundamental” adhesion* In one use, adhesion refers to the forces between atoms at the interface. This is sometimes called *true adhesion* or *fundamental adhesion*. Here, of course, the concept is necessarily tied to one of the **Theories of adhesion** and to a particular model for the interface concerned.

Many different measures may be used to specify this “fundamental” adhesion. It may be expressed in terms of forces or in terms of energies. Again, depending on the context, these may be forces or energies of attachment or else of detachment. Sometimes values of fundamental adhesion can be calculated from a theoretical model (see **Electrostatic theory of adhesion, Good–Girifalco interaction parameter**); occasionally, they may be deduced from experimental measurement (see **Adhesion–fundamental and practical**); for many practical adhesive bonds, they are not available by either route.

The work of adhesion (see **Wetting and work of adhesion, Contact angles and interfacial tension**) is a simple example of a concept that could be regarded as a “fundamental” measure of adhesion between two surfaces.

*Practical adhesion* Destructive **Tests of adhesion** are also said to measure the adhesion of a joint or coating. “Adhesion” here refers to the number that results from **Shear test**,



**Tensile tests** and so on. It can be a peel strength or a **Fracture mechanics** parameter. These measures are sometimes referred to as the *practical adhesion* of a particular joint: they more or less satisfactorily answer the question, “How strong is the joint?”

As explained in specialized articles on testing, the numerical result obtained in a particular type of test usually depends on the operational variables—dimensions of the test piece, rate of loading and so forth. Thus, there is not one, but many, values of practical adhesion for a particular joint.

The adhesion recorded reflects not only the “fundamental” adhesion at the interface but also the mechanical response of the adhesive, substrate and interfacial region (see **Rheological theory**). Equation 7 in the article on **Peel tests** shows how the “practical” adhesion (peel strength) may be related to the “fundamental adhesion” (work of adhesion) for that type of test.

The mode of failure in a test may be adhesive, cohesive or mixed (see **Stress distribution: mode of failure**). Sometimes authors talk as if a test only measured “adhesion” in the first of these cases. Such a distinction does not seem helpful as none directly measures “fundamental” adhesion and all give a number that reflects indirectly the interfacial forces.

### *Conclusion*

Good<sup>4</sup> has lamented the lack of unanimity on the meaning of the term “adhesion” and has suggested definitions, which would reduce the ambiguity when it is used in a scientific context. This article has been concerned with the situation as it is rather than as, perhaps, it should be. It has tried to indicate the depth of meaning of the term as it is actually used in the technical literature.

### *References*

1. J. A. Simpson and E. S. C. Weiner, *Oxford English Dictionary*, 2nd edn, Clarendon Press, Oxford, 1989.
2. C. T. Onions, *The Oxford Dictionary on English Etymology*, Clarendon Press, Oxford, 1966.
3. C. T. Lewis and C. Short, *A Latin Dictionary*, Clarendon Press, Oxford, 1879.
4. R. J. Good, in *Treatise on Adhesion and Adhesives*, Vol. 5, R. L. Patrick, Ed., Marcel Dekker, New York, 1981, p. 293.

---

## *Adhesion – fundamental and practical*

D E PACKHAM

As discussed in the article **Adhesion**, the term is used both for the fundamental atomic and molecular forces responsible for holding the two phases together and for the quantities such as peel strengths that come from destructive **Tests of adhesion**. Over the past decades, general understanding of the relation between “fundamental” and “practical” adhesion has developed considerably.

At one time many thought, or wrote as if they thought, that adhesion tests more or less gave a direct indication of the fundamental forces at the interface. This led to a

reaction where it was argued that “those . . . interested in the fundamental interfacial forces responsible for adhesion can get little, if any, information from destructive tests”.<sup>1</sup> The reaction was based on the observation that the results of tests of adhesion depend on the test parameters, for instance the values obtained with most adhesives depend upon the test rate because of the influence of the **Viscoelasticity** of the adhesive on the test result. Thus, destructive tests were considered simply to reflect the overall rheology of the joint. Bikerman was a forceful advocate of this position – see **Rheological theory**.

We have now come to a position where most recognize that both joint rheology and fundamental interfacial forces contribute to the measures given by destructive tests, and both determine the loads under which the joint will fail in service. The relation between the three – fundamental forces, rheology and test results – is understood in broad principle, and in a few cases has been elucidated in quantitative detail. This will now be discussed.

A relatively simple way to an understanding is via an energy-balance approach to the theory of peel adhesion, which is essentially an application of the first law of thermodynamics. This is developed in the article on **Peel tests**. For ease of illustration, consider the 90° peel of an inextensible strip. Equation 7 in the article cited gives peel energy  $P$  as

$$P = F/b = W_A[\text{or } W_C] + \psi_{\text{plast}} + \psi_{\text{v/e}} + \psi_{\text{bend}} + \dots \quad [1]$$

This relates the test result (the measured peel load  $F$ ) to a measure of intermolecular forces (the work of adhesion  $W_A$  or of cohesion  $W_C$ , see **Wetting and spreading**) and to the rheology via various terms such as energy dissipated in plastic deformation  $\psi_{\text{plast}}$ , in viscoelastic loss  $\psi_{\text{v/e}}$ , in bending  $\psi_{\text{bend}}$ , and so on. Here,  $b$  is the width of the peeled strip.

A similar approach is possible for other tests that measure, in some form, an energy of fracture. Tests based on the principles of **Fracture mechanics** can give a measure of  $G_C$ , the critical energy release rate, which is essentially an energy of fracture under precisely defined conditions. Here,  $G_C$  can be expressed as a sum of interfacial energy terms and other terms for bulk energy dissipation in a way analogous to peel energy  $P$  in Eqn. 1. (The energy-balance approach is essentially one of fracture mechanics.)

Many tests, for example **Tensile tests** and **Shear tests**, measure a critical stress rather than an energy of fracture. Good has pointed out that this critical stress will also depend on the fracture energy.<sup>2</sup> He adapted the Griffith – Irwin theory of fracture for application in adhesive bonds. According to this theory,<sup>2</sup> the fracture stress  $\sigma_f$  of material of modulus  $E$  will be given by

$$\sigma_f = k\sqrt{(EG/l)} \quad [2]$$

where  $k$  is a constant,  $l$  is the length of the critical crack and  $G$  is the work of fracture per unit area. Like peel energy  $P$  in Eqn. 1,  $G$  can be expressed as the sum of the various energy-dissipation terms involved in the fracture. (The first law of thermodynamics again.) So,  $G$  may be written as

$$G = W_A[\text{or } W_C] + \psi \quad [3]$$

Depending on the locus of failure (see **Stress distribution: mode of failure**), either the work of adhesion  $W_A$  or the work of cohesion  $W_C$  will be appropriate:  $\psi$  represents all the other energy-dissipation terms.

Good argues that  $G$  and  $E$  will be semi-local properties, which will vary as one passes from one phase bonded through the interface to the second phase. The way in which

the product  $EG$  varies throughout the bond (and the lengths and positions of potentially critical flaws<sup>2</sup>) will determine the mode of failure, interfacial or cohesive within the bulk or close to the interface. Failure will occur where the term  $(EG/l)$  is at a minimum, at the stress given by Eqn. 2.

In some uncomplicated examples, it has been possible to analyse the results of adhesion tests to obtain numerical values associated with interfacial forces. An example of this was the work of E. H. Andrews and A. J. Kinloch,<sup>3</sup> who measured the adhesion of SBR (styrene – butadiene rubber) to different polymeric substrates over a range of temperatures and test rates. Three types of tests including a 90° peel test were used. The results were analysed to evaluate the fracture energy per unit area  $G$ . (For the peel test,  $G$  was  $P$ , the peel energy.)

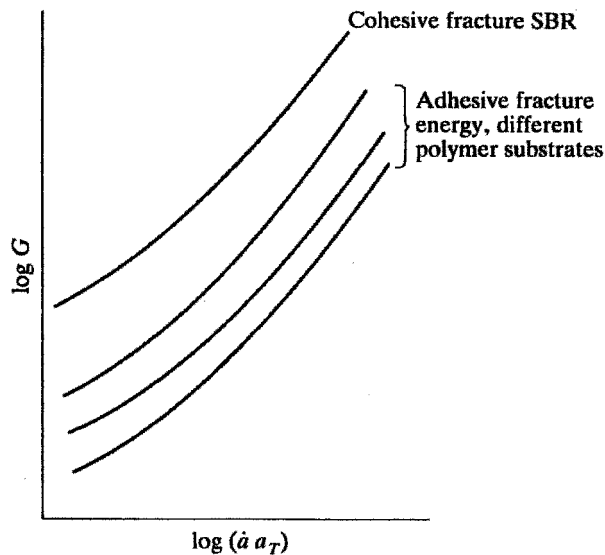
The polymer SBR is mechanically simple, and it was found that the results for  $G$  for a given substrate could be superimposed using the Williams, Landel and Ferry (WLF) technique (see **Viscoelasticity – time–temperature superposition**). The master curves for each substrate were close to being parallel to each other and to a similar curve for cohesive fracture of the SBR (Fig. 1).

The parallel log/log curves imply some mathematical relationship of the form

$$G = G_0\phi(\dot{a}, T) \quad [4]$$

where  $\phi(\dot{a}, T)$  is a rate ( $\dot{a}$ ) and temperature-dependent viscoelastic factor, and  $G_0$  is some intrinsic failure energy characteristic of the substrate and independent of rate and temperature. As a value of  $G_0$  could be obtained for cohesive tearing of the SBR itself, values of  $G_0$  could be deduced from the adhesion measurements for each substrate.

The work of adhesion for the various SBR/substrate combinations were evaluated from contact angle measurements (see **Surface energy components**) and were compared with



**Fig. 1.** Master curve of fracture energy  $G$  against reduced test rate  $(\dot{a}a_T)$  for SBR and for adhesion bonds between SBR and various polymer substrates. After Andrews and Kinloch<sup>3</sup>

the values of  $G_0$ . For bonds where adhesive failure occurred, there was a good agreement between  $W_A$  and  $G_0$ . Where the locus of failure was cohesive,  $G_0$  could be related to the cohesive failure energy of the materials concerned.

This work shows how the type and magnitude of interfacial forces can be deduced from the results of adhesion tests. For this simple polymer, the adhesive fracture energy is made up of an intrinsic term  $G_0$  related to the interfacial forces, and a term related to the viscoelastic energy losses during testing. The viscoelastic loss can be expressed as an additive term (see Eqns. 1 and 3) or, for this system, as a multiplicative factor, Eqn. 4. Although for SBR at all normal rates and temperatures of test the viscoelastic term  $\psi$  is much greater than the interfacial term  $W$ ,  $W$  exerts a profound influence on the measured adhesion because of the multiplicative relationship.

In summary, the relationship between fundamental and practical adhesion is now understood in broad terms. Information about fundamental interfacial forces can be obtained from destructive tests (*pace de Bruyne*).

### References

1. N. A. de Bruyne, in *Adhesion and Cohesion*, P. Weiss, Ed., Elsevier, Amsterdam, 1962, p. 46.
2. R. J. Good, *J. Adhes.*, **4**, 133 (1972).
3. A. J. Kinloch, *Adhesion and Adhesives: Science and Technology*, Chapman and Hall, London, 1987, p. 314.

---

## *Adhesion in dentistry: orthodontics and prosthodontics*

---

M SHERRIFF

Orthodontics is concerned with facial growth, the development of occlusion and the prevention and correction of occlusal anomalies. There are currently two main theories for the application of force for effective orthodontic tooth movement: (1) light intermittent forces to enable the tooth to move followed by a period of tissue remodelling and recovery and (2) light continuous forces to enable the tooth to move continuously without recovery.

The forces are transmitted to the tooth by a wire that is coupled to a bracket bonded to the tooth surface. The most common brackets are made of stainless steel and have either a groove cast into the base or a metal mesh brazed onto the bracket base to increase the available surface area for bonding. The challenge of orthodontic bonding is that the bracket/enamel bond must be sufficient to withstand the forces applied by the wire and the fatigue conditions produced by thermal and occlusal load cycling in the mouth, yet must be easily debonded without damaging the enamel surface at the end of treatment (typically two years).

The predominant bonding mechanism is mechanical retention and the most common bonding systems are either a composite, generally light-cured, or polyalkenoate cements similar to those used in restorative dentistry (see **Adhesion in dentistry: restorative materials**). In a recent development to minimize operator errors, the bracket base is pre-coated with the adhesive so that there is no mixing, no contamination and there is a controlled amount of adhesive. The adhesive is typically a lightly filled combination of bisphenol A diglycidyl dimethacrylate and bisphenol A bis(2-hydroxyethyl ether)

dimethacrylate (see **Chain polymerization**). The enamel is prepared using a “self etching primer” that consists of a methacrylated phosphoric acid ester to minimize the number of clinical bonding steps. The phosphate groups act in a similar manner to a conventional acid etch; however, rather than being rinsed away, the calcium forms a complex with the phosphate groups and becomes incorporated into the network when the primer is polymerized. Bands on molar teeth are usually retained with a glass-ionomer cement. Ideally, orthodontic bonding systems will leach fluoride to prevent white spot lesions and caries.

Ceramic brackets are used for aesthetic reasons, and they are commonly treated with **Silane adhesion promoters**, either a vinyl silane, typically methacryloxypropyltrimethoxysilane, coupling agent or a micro-crystalline roughened base to enhance mechanical retention.

### *Prosthodontics*

The development of adhesive systems for metal–polymer bonding has led to many advances in prosthodontics, such as<sup>1</sup> bridges retained by resin on the teeth, which have undergone a minimal amount of preparation and the resin bonding of crowns.

Again, mechanical retention, either macro or micro, is the predominant mechanism. The metal structure can be perforated and the bonding system, a structural adhesive, flows through the holes to provide the retention, for example Rochette Bridge. The metal can be etched either chemically or electrochemically to produce a surface suitable for micro-mechanical retention.

Adhesive systems for bonding to Ni–Cr base metal systems have been developed, and they typically involve 4-META (4-methacryloxyethyl trimellitate anhydride) and MDP (10-methacryloyloxy-decyl dihydrogen phosphate). The metal bonding is facilitated through the affinity of the phosphate or carboxylate group to the oxide layer on the base metal alloy, and bonding to the composite via vinyl groups. A clinical disadvantage of the MDP system is that the polymerization is strongly inhibited by oxygen; thus, it is necessary to exclude oxygen as much as possible and seal the edges of the restoration with a polyethyleneglycol gel to achieve a satisfactory bond.

This technique is not successful with gold and other precious metal alloys because of the lack of a surface oxide layer. Attempts to overcome this involve preparing the surface by sandblasting and then depositing tin onto the surface either thermally or by electroplating. The tin oxidizes and facilitates bonding by providing both a micro-rough surface for mechanical retention and an oxide layer to react with the 4-META. Adhesives based on biphenyl dimethacrylate (BPDm) are being developed as they bond to both precious and non-precious surfaces without the need for tin plating.

Intermediate layers of metals or ceramics have been used to enhance resin bonding for veneers and pontics by a combination of micro-mechanical and mechanical bonding. In one commercial system, the metal surface is cleaned by sandblasting and then a thin layer of silica is pyrolytically deposited on the surface. This bonds to the metal and the layer is then coated with a vinyl silane to enable bonding to the resin. As an alternative, the metal surface is blasted with a combination of alumina and silica, which bonds and fuses to the surface under the kinetic energy of impact. The impacted material layer becomes coloured to allow accurate control. Again this is coated with a vinyl silane.

Despite concerns about mercury toxicity, amalgam is still the most-common posterior restorative material. As it is non-adhesive, it is retained in the cavity mechanically by

using a cavity design with undercuts to provide mechanical retention. This involves cutting away sound enamel. There have been attempts to bond amalgam to tooth substance using systems based on 4-META, MDP and BPDM as described above.<sup>2</sup>

### References

1. H. F. Albers (editor) *Adept Report Metal-Resin Bonding*, Adept Institute, Santa Rosa, USA, 1991.
2. J. C. Setcos, M. Staninec and N. H. F. Wilson, *Br. Dent. J.*, **186**, 328 (1999).

---

## Adhesion in dentistry: restorative materials

---

M SHERRIFF

The main problems associated in getting the filling and other restorative materials to bond to teeth are that tooth substance is living tissue, dentine is hydrophilic and most restorative systems are hydrophobic and adhesive system must be non-toxic and easy to use.

The predominant bonding mechanism is mechanical, involving thin films of luting agents (gap-filling cements that join two solid objects together) such as zinc phosphate cement for the retention of crowns or creating undercut areas of a dental cavity for the retention of dental amalgam. The ideal system would be “adhesive”, resulting in minimal cavity preparation and loss of sound enamel and dentine.

### The substrate

The outer layer of a tooth is composed of calcified tissue, enamel, the hardest substance in the body. Enamel consists of ~92%, by volume, hydroxyapatite laid down as a series of interlocking prisms aligned perpendicular to the tooth surface. The remaining constituents are 6% water and 2% organic material (mainly collagen). The bulk of the inside of the tooth consists of dentine, which is a vital tissue perforated throughout by tubules. These tubules are continuous from the pulp of the tooth to the outer surface and allow liquid flow. The approximate composition of dentine is 48% hydroxyapatite, 29% collagen and 23% water.

### Restorative dentistry

The most common restoratives comprise a mineral filler mixed with a vinyl monomer (often called a resin), which undergo photoinitiated free radical **Chain polymerization**. Typical components include the adduct of bis-phenol A and glycidyl methacrylate (bis-GMA) or urethane dimethacrylate (UDMA), camphorquinone initiator (activated by a visible blue light source of ~480 nm) and a filler such as zirconia or borosilicate glass, which can comprise ~70% by mass of the system and provides the “strength”. The whole is referred to as a “composite”.

### Bonding to enamel

The enamel is etched with 37% ortho-phosphoric acid (often in the form of a gel) to produce a rough surface. The composite flows into this etch pattern and can be retained

by micro-mechanical retention (see **Mechanical theory of adhesion**). Additionally, the acid removes organic surface contaminants such as pellicle and plaque and increases the surface energy to assist **Wetting and spreading**.

*Bonding to dentine – the smear layer*

The smear layer is formed during the cavity cutting process and can consist of cutting debris, smeared odontoblasts (one of a layer of connective tissue cells lining the pulp cavity, which takes place in the formation of dentine) and micro-organisms. It cannot be formed in a reproducible manner. There are three main approaches to dealing with the smear layer.

*Preservation* Such systems involved phosphonated esters of bis-GMA such that the phosphate group can bond to the calcium in the hydroxyapatite, or polyurethanes where the isocyanate group could bond to carboxyl, hydroxyl and amino groups in the dentine.

*Modification* This was the first really clinically successful system. The enamel margins are etched with phosphoric acid, and a “self-etching primer” (SEP), such as maleic acid, is used to dissolve the smear layer. This also results in superficial demineralization of the underlying dentine. An amphiphilic primer such as hydroxyethyl methacrylate, HEMA is used to impregnate the collagen fibres. Hydroxyapatite and inorganic phosphates are detached from the superficial dentine layers. The bonding monomer is then applied and it flows into the resultant network structure of the collagen. This region of resin-infiltrated demineralized dentine, effectively a transition zone between the dentine and restorative, is known as the “hybrid zone” and is thought to be crucial to a successful dentine bonding agent (DBA).<sup>1</sup> The predominant bonding mechanism in this system is mechanical.

*Removal* This is the basis of most modern DBAs, often known as a “total etch”.

The smear layer is often removed with phosphoric acid, which again demineralizes the superficial dentine and exposes collagen. The amphiphilic monomer creates the hybrid layer and diffuses into the dentinal tubules where it forms “tags” and provides additional micro-mechanical retention. If the collagen layer becomes desiccated, then it collapses, monomer infiltration is inhibited and the hybrid zone is not successfully formed.

DBAs are now classified according to the number of clinical steps involved in treatment of the smear layer:<sup>2</sup>

Type 1: Remove smear layer: 3 clinical steps: etch, prime, bond.

Type 2: Remove smear layer: 2 clinical steps: etch, prime and bond combined.

Type 3: Dissolve smear layer: 2 clinical steps: etch and prime combined, bond.

Type 4: Dissolve smear layer: 1 clinical step: etch, prime and bond combined.

The fewer clinical steps, the less chance of error.

In a typical Type 1 system, the smear layer is removed using 10% maleic or 35% phosphoric acid. The dentine is then primed with an aqueous solution of HEMA, and the adhesive is a combination of bis-GMA and HEMA together with an amine that can be used to initiate a light-cured reaction. In the type 4 systems, all steps are combined to ensure no desiccation and the successful formation of the hybrid zone. A typical type

4 DBA is an aqueous system of methacrylated phosphoric esters and HEMA with a camphorquinone initiator. The phosphoric esters etch the enamel and dentine in a similar manner to phosphoric acid. A hybrid zone and dentinal tags are formed, the monomers that cause etching also being responsible for bonding. There is also the possibility of the mechanical bond being enhanced by a chemical bond between the phosphoric ester and the hydroxyapatite. Bonding to the restorative composite is via a free radical reaction between the terminal vinyl groups of the DBA and composite.

In addition to providing a bridge between the hydrophilic dentine and hydrophobic composite, the DBA also has to accommodate the stresses resulting from polymerization contraction of the monomer.

#### *Polyalkenoate (glass ionomer) systems*

These are the only inherently adhesive restorative materials currently available. These are simple aqueous systems consisting of an ion-leachable fluoro/alumino/silicate glass (FAS) and a polyalkenoate acid such as poly(acrylic acid) or poly(maleic acid) and their copolymers. When the components are mixed, a simple acid:base reaction occurs.  $H^+$  ions diffuse into the FAS and  $Ca^{2+}$  and  $Al^{3+}$  diffuse out of the FAS and cause cross-linking of the dissociated polyacid. The exact mechanism of adhesion to enamel and dentine is uncertain but is thought to involve **Hydrogen bonding** to the bound water layer and amino groups in dentine, and ionic bonding to the  $Ca^{2+}$  in hydroxyapatite.<sup>3</sup>

Related articles include **Adhesion in dentistry: orthodontics and prosthodontics** and **Adhesion in medicine**.

#### *References*

1. N. Nakabayashi, K. Kojima and E. Masuhara, *J. Biomed. Mater. Res.*, **16**, 265 (1992).
2. *Adhesive Technology*, Theoretical and Practical Guidelines, 3M ESPE AG. ISBN 3-00-008488-6 (2001).
3. J. W. Nicholson, *Int. J. Adhes. Adhes.*, **20**, 11 (2000).

---

### *Adhesion in medicine*

---

M E R SHANAHAN

Although adhesion intervenes in many phenomena occurring in the industrial world, sight must not be lost of its importance in the natural, biological context and, in particular, the role it plays in medical applications. It would seem that the vast range of natural phenomena in which adhesion is fundamental has only fairly recently been appreciated. As far as medicine is concerned, research is being actively pursued even if understanding is still at a fairly rudimentary level in many domains. Clearly, enormous problems exist because of the sheer complexity of the systems to be examined. In addition, since virtually all the cases of interest are in an essentially aqueous environment, there are considerable difficulties in direct observation and modelling is not easy. **Polar forces** and **Hydrogen bonding** will be predominant. Nature nevertheless uses adhesion and polymer science to great benefit! The coagulation of blood at a wound, although a complex process,



is a perfect example. Platelets in the blood are attracted to the site of the wound and an enzyme called *thrombin* is produced from prothrombin. Thrombin acts as a catalyst by converting the protein fibrinogen (from the blood plasma) into fibrin, an insoluble, polymerized protein. This fibrous material constitutes one of the essential materials of the clotting process. The conversion from fibrinogen into fibrin is therefore a reaction of natural polymerization with thrombin as the “curing” agent and as such the system can be compared not unreasonably to a two-component adhesive!

Although the areas of medicine in which adhesion is important must be very extensive, there are basically two scales to be considered.

Firstly, there is the macroscopic aspect, which concerns essentially the manufacture of prostheses in their various forms (joints, “pace-makers”, dentures, and so on; see **Adhesion in dentistry: orthodontics and prosthodontics**). Problems to be overcome here involve the creation of suitable and resistant bonds to organic elements existing in the body, such as bone or muscle, and the need for the synthetic components to be biocompatible. Not only must adhesive bonds be established in an aqueous environment, conditions which are plainly avoided when possible in an industrial context where the choice usually exists, but also body fluids are potentially capable of reducing adhesion over a long period both on simple thermodynamic grounds and for reasons of degradation (comparable to environmental stress cracking and stress corrosion). The thermodynamic argument is simple and based on Dupré’s equation (**Wetting and work of adhesion**). If substance A (say the naturally occurring material) adheres to substance B (the prosthesis), their thermodynamic work of adhesion (in air) is given by

$$W = \gamma_A + \gamma_B - \gamma_{AB} \quad [1]$$

where  $\gamma_A$  and  $\gamma_B$  represent the surface free energies of A and B and  $\gamma_{AB}$  is their mutual interfacial free energy. However, if separation is apt to occur in a liquid (body fluid) L, the work of adhesion is modified to  $W_L$ :

$$W_L = \gamma_{AL} + \gamma_{BL} - \gamma_{AB} \quad [2]$$

where  $\gamma_{AL}$  and  $\gamma_{BL}$  are the interfacial free energies of A and B with L. If  $\gamma_{AL} + \gamma_{BL} < \gamma_A + \gamma_B$  the presence of L will reduce the propensity for adhesion of the system (see **Durability: fundamentals**). Although this thermodynamic aspect may present us with considerable problems, nature would seem to have overcome them, at least in certain cases. For example, mussels (*Mytilus galloprovincialis*) adhere strongly to rocks and other solids despite the presence of water.<sup>1</sup> The water-resistant adhesive is based on a protein secreted by the mollusc, which reacts with a specific enzyme.

The second main aspect of adhesion in medicine corresponds to the cellular level. A few examples will be given. In the development of a cancer, one major problem is that the patient is often only aware of the primary tumour when it has evolved sufficiently for metastases to have been released. These malignant cells are free to migrate within the body, often in the blood circulation, and create secondary tumours elsewhere in the body leading to a generalized illness.<sup>2</sup> Were we able to increase the adhesion of metastases to their source, many treatments of cancer could be limited to a specific area of the body. By contrast, consider a case where adhesion is undesirable. Heart disease is often related to the blocking of arteries by matter, in particular thrombi, or locally produced blood clots,

adhering to the walls of the blood vessels. Reduction of this restriction to the circulation would clearly be beneficial since the essential flow of blood to the heart muscle would then be less impeded. An important step during the ingestion of foreign particles by phagocytes<sup>3</sup> is the establishment of bonds between the immunological effector and its target. The engulfment of bacteria by macrophages is almost certainly related to surface free energy and, thus, adhesion-controlled processes.<sup>4</sup>

For these, and other reasons, various researchers have looked at the complexities of cell adhesion.<sup>5,6</sup> The reader is referred to the review by Bongrand and Bell<sup>6</sup> and the references therein for a more complete appraisal of this complex field.

### References

1. P. Marks, *New Scientist*, 23rd October 1999, p. 12.
2. M. McCutcheon, D. R. Coman and F. B. Moor, *Cancer*, **1**, 460 (1948).
3. C. Capo, P. Bongrand, A. M. Benoliel and R. Depieds, *Immunology*, **35**, 177 (1978).
4. A. W. Neumann, *Adv. Colloid Interface Sci.*, **4**, 105 (1974).
5. C. J. van Oss, *Interfacial Forces in Aqueous Media*, Marcel Dekker, New York, 1994.
6. P. Bongrand and G. I. Bell, in *Cell Surface Dynamics: Concepts and Models*, A. S. Perelson, C. Delisi and F. W. Wiegel, Eds., Marcel Dekker, New York, 1984, Chap. 14.

### Adhesive classification

B C COPE

The primary purpose of an adhesive may be said to be **Wetting and spreading** on the surfaces of the substrates, to fill the gap between them, and subsequently to form a relatively permanent, coherent bond.

The wetting and spreading action necessarily demands that the adhesive is applied in the liquid phase, whereas the final bond depends on the adhesive being a solid with appropriate mechanical characteristics. The two most widely used and useful taxonomic schemes for adhesives address either the way in which this phase change takes place or the chemical nature of the adhesive itself, although other schemes such as a classification by suitability for a particular type of adherend or end-use industry are also current and sometimes more applicable.

The final bond produced by the vast majority of adhesives consists largely of a solid organic polymer. The fluidity necessary at the time of application and the subsequent means of transition to solidity thus form the basis of the most frequently used system of classification.

In the case of **Solvent-based adhesives**, the polymer or blend of polymers that will eventually form the bond is dissolved in a carrier solvent. Sometimes, as in many materials for packaging applications, the solvent is water, but since the bonds thus produced will be moisture-susceptible, the use of organic solvents is more usual. An added advantage of the use of organic solvents over water is that their lower latent heat of evaporation ensures faster drying. Against this, such solvents are more expensive than water, are usually inflammable and are sometimes irritant or toxic. Growing concern about

the release of solvents to the atmosphere (see **Environment and the impact of adhesive technology**) has combined with **Health and safety** considerations and ever-rising fire insurance premiums to accelerate a movement away from organic solvent-based systems.

Whatever the solvent system is, polymers produce highly viscous solutions at quite low concentrations, thus limiting the weight of adhesive coating that may economically be applied in a single operation and increasing the bulk and cost of an adhesive system containing a given quantity of solid adhesive. High shrinkage can also be a problem.

When a solvent-based system is applied to a porous or permeable substrate, the solvent may pass out of the bond through the adherends. When the adherends are relatively impermeable, a common practice is to coat both mating surfaces and allow them to become substantially dry before bringing them into contact while the adhesive still retains some degree of **Tack**. This technique is familiar to many through its application to the repair of punctures in bicycle tyres or the lamination of decorative (“melamine”) laminates to various substrates.

Polymer dispersions (in non-solvent liquids, usually water) have much lower viscosities than solutions with the same polymer content. So great is the disparity in viscosities that a 50% solids dispersion may have a considerably lower viscosity than a 10% solution. Such dispersion or suspension adhesives, often called emulsion adhesives or even more loosely “water-based adhesives”, combine the advantages of a high solids content with low inflammability and toxicity hazard, but suffer from long drying times (see **Emulsion and dispersion adhesives**). Their use on non-porous substrates is restricted in a similar way to that of solution adhesives.

There exist two obvious ways of increasing the active solids content of an adhesive effectively to 100%: use of **Hot melt adhesives** and **Reaction setting adhesives**. The main constituent of hot melts is a thermoplastic polymer that may be blended with thermoplastic modifiers and extenders and inert fillers to create a system that is a load-bearing solid at the service temperature but a mobile liquid at the (higher) application temperature. Polyolefins, ionomers, polyesters and polyamides are among the polymer types that have been used as bases for **Hot melt adhesives**.

The **Animal glues and technical gelatins**, applied hot and previously popular for wood bonding and book binding, are very concentrated aqueous solutions of gelatin. Their hardening is a combination of solution and hot melt mechanism in that solidification on chilling is augmented by diffusion of moisture into the porous substrate.

The second means of transforming a liquid adhesive entirely into a solid without the loss of a solvent or dispersion medium is to produce solidification by a chemical change rather than a physical one. Such reactive adhesives may be single-part materials that generally require heating or exposure to electron beam or UV or visible radiation (see **Radiation-cured adhesives**) to perform the reaction, and which may be solids (that must be melted before application), liquids or pastes. The alternative two-part systems require the reactants to be stored separately and mixed only shortly before application. The former class is exemplified by the fusible, but ultimately reactive, epoxide film adhesives and the latter by the two-pack **Epoxide adhesives** and **Polyurethane** adhesives and by the **Toughened acrylic adhesives** that cure by a free-radical **Chain polymerization** mechanism.

Two types that may be considered to be special cases of single-component reactive systems are the **Anaerobic adhesives** and **Cyanoacrylate adhesives**. These are similar

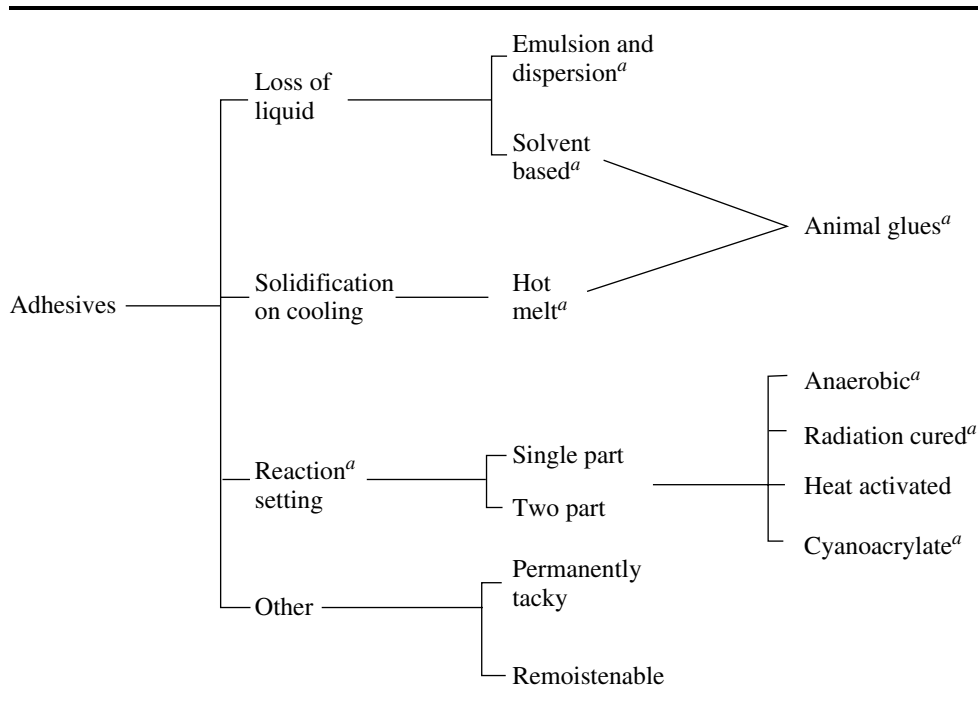
in that they are single-pack liquids or blends of liquids that are stable on storage, but which polymerize and solidify at ambient temperature when spread as a thin film between adherends. The cure mechanisms differ in that the anaerobics depend on the fact that oxygen inhibits their otherwise rapid polymerization, and so exclusion of oxygen, as in a joint, permits polymerization that may be catalysed by species on the adherent surfaces, whereas the cyanoacrylates depend on catalysis by hydroxy groups on the adherends.

Permanently tacky or **Pressure-sensitive adhesives** are those that may be applied as dispersions, solutions or hot melts and that convert to a rubbery, tacky film of relatively low adhesive strength and rather higher cohesive strength. They may be used to produce bonds that are permanent, but not creep resistant, and also temporary or serial temporary bonds. Such materials are often used supported on flexible tapes.

Remoistenable adhesives are water-based compositions that dry to a non-tacky film that may have its adhesive power regenerated by the absorption of water. Envelope gums are a familiar example.

The classification of adhesives by hardening mechanism (Table 1) is probably the most informative, but a classification based on the chemical nature of the main polymer present is often used. Such systems require little explanation and might typically order materials first by the class of polymer, thermoset, thermoplastic or (thermoset) elastomeric, often with a separate class for natural polymers, and then subdivide these classes according to the chemical structure. Table 2 shows how this might be accomplished.

Table 1. Classification of adhesives by setting mode



<sup>a</sup> There are specialized entries with these titles.

Table 2. Classification of adhesives by chemical nature

Thermosets (a)	Elastomers (b)
Urea formaldehydes <sup>b</sup>	Nitrile rubber
Phenol formaldehydes <sup>ab</sup>	Butyl rubber
Melamine formaldehydes	Polychloroprene
Furane resins	Polyisobutene
Polyurethanes <sup>a</sup>	Styrene -butadiene rubber
Epoxides <sup>a</sup>	Silicone rubber
Polybenzimidazoles <sup>a</sup>	Reclaimed rubber
Polyesters	Natural rubber
Anaerobic diacrylate	Cyclized natural rubber
Polyimide <sup>a</sup>	Chlorinated natural rubber
Others	Others
Thermoplastics (c)	Natural products and modified natural polymers
Acrylics <sup>a</sup>	Animal glue <sup>a</sup>
Cyanoacrylates <sup>a</sup>	Fish glue
Ethylene vinyl acetate <sup>a</sup>	Casein
Polythene	Bitumen
Polyesters	Dextrins
Polyamides	Starches
Polyvinyl acetate	Gums
Polyvinyl alcohol <sup>a</sup>	Cellulose esters
Polyvinyl chloride	Cellulose ethers
Polyvinyl butyral	Others
Polyvinyl ethers	
Polyether etherketone <sup>a</sup>	
Polyimide <sup>a</sup>	
Polyphenylquinoxaline <sup>a</sup>	
Others	

<sup>a</sup> There are specialized articles with these titles. See also (a) **Reaction setting adhesives** (b) **Rubber based adhesives** (c) **Hot melt adhesives** and

<sup>b</sup> **Wood adhesives.**

### Select References

- A. V. Pocius, *Adhesion and Adhesives Technology-an Introduction*, Hanser, Cincinnati, 1997.  
 I. Skeist, *Handbook of Adhesives*, 3rd edn, Van Nostrand-Reinhold, New York, 1997.  
 W. C. Wake, *Synthetic Adhesives and Sealants*, Wiley, Chichester, 1987.  
 S. C. Termin, Adhesive compositions, in *Encyclopedia of Polymer Science and Engineering*, Vol. 1, Wiley Interscience, 1985, pp. 547–77.  
 J. Shields, *Adhesives Handbook*, 3rd edn, Butterworths, London, 1984.  
 W. C. Wake, *Adhesion and the Formulation of Adhesives*, 2nd edn, Applied Science Publishers, London, 1982.

### Adhesives – historical perspective

M W PASCOE

The sensation of the stickiness is among the commonplace experiences of humanity. Resin oozing from a pine branch and the sap from a dandelion stem are among a multitude of

natural examples from which it can be asserted with confidence that humans have “always” been aware of the phenomenon of adhesion. Indeed for millennia, as a species, we have made use of viscous liquids capable of setting to solids. In the upper palaeolithic era (between 40,000 and 10,000 years ago), stone and bone points were glued with resin to wooden shafts to produce spears. Thirty-one thousand years ago, coloured pigments were being glued to the walls of the Chauvet cave in Vallon-Pont-d’Arc in the Ardèche to create the earliest known cave paintings. By the first dynasty of ancient Egypt (ca. 3000 B.C.), natural adhesives were used to attach inlays to furniture.

Apart from soft metals and sulphur, ancient adhesives are organic polymers, some of which are natural products and many of which required some sort of processing such as heating. Hydrocarbons, proteins and carbohydrates form the main classes, and while they are of biological origin, they may be transformed by ageing, oxidation, enzymes, fossilization and hydrolysis, as for example, in cooking by boiling in water. Besides wetting the surfaces to be joined, adhesives must be transformed in a convenient time to a solid of sufficient strength. Various mechanisms for the transformation of liquids into solids have been used – such as freezing, coagulation of dispersions, solvent or carrier evaporation and ionic crosslinking.

The adhesion to surfaces of natural materials, such as wood, textiles or skin products is often determined by the **Hydrogen bonding** forces, as is the cohesion of the adhesive itself. The uses of natural polymers are numerous, as exemplified by their occurrence in varnishes, paint binders, inks and sealants. There are many similarities between these materials and adhesives. Mixtures are not uncommon, and therefore inconsistent performance may be expected. The adhesives are then better described principally in relation to their use and not exclusively on their chemical, geographical or historic attributes.

### *Hot melt adhesives*

Waxes, such as beeswax, plant waxes and mineral waxes, though not strong, were readily available in the ancient world, as were tars, bitumens and pitches. More complex resinous substances such as gums exuded from trees, or from insects (shellac) and amber, a fossilized resin, have also found uses. Manipulation of **Hot melt adhesives** is not easy; consequently, their uses were limited. Wax binders for pigments were used in encaustic painting, giving images of long durability, but artists preferred more manageable materials.

### *Solution-based adhesives*

Non-aqueous solvents made many adhesives spread much more easily, but they require technical skills and distillation equipment to produce the solvents (see **Solvent-based adhesives**). Alcohol from fermentation has been widely available, but hydrocarbons solvents from the destructive distillation of tree resins and so on, could produce some powerful hydrocarbon solvents such as turpentine. Water, however, is the most attractive solvent for sugars, gums and proteins of various origins, some of which have undergone processing, usually through prolonged boiling, which hydrolyses and breaks up the large insoluble large polymer molecules into smaller soluble entities. Thus, gelatine glues are made from bone collagen, skin, including used parchment fragments, fins and other parts of fishes, notably the sturgeon. These solution glues have high viscosities and relatively

low solid content; consequently, they are not very effective in filling gaps. Moreover, the water has to escape generally by absorption into the substrates, which must therefore be porous and hydrophilic. Wood, papers and skins have these properties and share the common feature of extensive hydrogen bonding, involving –OH or –NH groups in the glues and in the substrates. Because they are hydrophilic and often predigested, they are liable to breakdown when damp through enzymatic and other biological agencies including fungi. Moisture makes joints an attractive nutrient for insects and small animals.

### *Aqueous dispersion adhesives*

When the adhesive substances are not broken down by water to form a complete solution, they form adhesives with relatively low viscosities and quite high solid contents. They are therefore more useful for gap filling, though the water still has to be removed by absorption. Pastes and emulsions (latices) form this class (see **Emulsion and dispersion adhesives**). There are many paste formulations derived from starch, a branched polymer of glucose, which is broken down into shorter chains of glucose units often by boiling in water as in cooking. Alternatively, the starch may be left for a decade in cold water to bring it to a workable condition. Such pastes have traditionally been used in the mounting of Japanese scroll paintings. As starch from cereals is so cheap, it has undergone many chemical and physical variations; this aspect is outside our present scope. Starch paste joints suffer from aqueous and biochemical breakdown. Like the water-soluble adhesives, they are effective only on hydrophilic surfaces such as papers, wood and skins.

In nature, several plants and trees produce a latex of very small rubber particles suspended in aqueous medium, which consequently has a very low viscosity and a high solid content. Although such latices were worked up by coagulation to make several types of rubber objects, it is not certainly known that they were used as adhesives, even though they are common today. Both the latices themselves and the rubber objects are not very stable. The latex coagulates unless stabilized by chemicals, and the rubbers themselves have potential chemical activity because of the extensive carbon–carbon double bonds along the molecular chains.

### *Chemically formed adhesive joints*

Solidification of adhesives within a joint can be engineered by a reaction contrived within the joint at an appropriate speed. An example is the coagulation of milk protein (casein), which is mainly soluble in water but which coagulates in the presence of lime (calcium hydroxide). The protein solidifies through the action of alkalinity and remains so because the doubly charged calcium ions form bridges (crosslinks) between the protein molecules. Such adhesives are stable for millennia.

### *Analysis, conservation and history*

Recent significant advances in analytical techniques have made investigations into the nature of the highly complex organic substances much more precise (see **Surface analysis**), but most of the literature derives from times when techniques were less reliable. Even so, the full identification remains a difficult matter, and written accounts may well be

open to question. They are mostly easily found in archaeology and conservation texts and journals. There are substantial texts covering Middle Eastern and Egyptian technologies. The conservation literature, particularly those parts concerned with bookbinding, picture and painting conservation is abundant. Oriental works are well documented in respect of adhesives in Chinese and Japanese paintings and scrolls.

Analyses of the adhesives on ancient objects are confused by their deterioration, which superficially generally causes colour changes and embrittlement. In many conservation treatments, degraded adhesives have to be removed and replaced, usually by simple means such as dissolution. Aged adhesives are often insoluble and intractable, though there are some ingenious treatments to soften and remove materials such as shellac, where very polar solvents such as pyridine are effective, or with aged starch, *N*-methyl pyrrolidine has saved old master drawings by separating them from harmful acidic backing boards. Other techniques for softening protein animal glues on papyri require the use of protolytic enzymes, and with some other pastes, amylase preparations are effective.

The brittleness, however, may be an advantage insofar as joints in woodwork may be broken by a sudden impact and the residues are more easily scraped off. Intractable adhesive residues may also be removed by argon–oxygen plasmas, which slowly oxidize all organic materials into volatile gases.

In ancient craftwork, the choice of materials and techniques depended on the skills and the availability of materials, which inevitably had to be of botanical, mineral, animal or piscine origin. The variety of sources is remarkably wide. Great strength was not expected in most applications, especially when the areas were large, in lamination, for instance, or when items such as precious stones were being sealed into a mounting. Gluing materials for significant structural strength was not practical until synthetic adhesives were developed alongside more reliable techniques for surface preparation before gluing. Such arts have only a few decades of history.

Some adhesives were obviously useful because they were naturally tacky – tree gums and rubbers are typical examples. Others depended on the skilful control of fire so that melting and cooking by boiling could be carefully controlled. Mixtures such as sealing wax (beeswax and rosin – mainly abietic acid) would require careful dispensing, stirring and control. Such skills were also developed by medieval ink makers, who like varnish makers, cooked mixtures of drying oils, such as linseed oil, with rosin in large cauldrons. Such processes were very difficult to control. Craft reticence would have hindered the transfer of skills to other specialists, but evaluation and standardization would not have taken place until industrialization forced suppliers to maintain quality standards.

### *Literature*

Specialized sources dealing with archaeology or conservation are generally needed to find information about adhesive use in an historical context. There are specialized abstracting journals<sup>1</sup> and computer databases.<sup>2</sup> Some relevant journals are listed under reference<sup>3</sup>; useful texts concerning particular industries and technologies are given in reference<sup>4</sup>.

### *References*

1. Art and Archaeology Technical Abstracts (AATA), Getty Conservation Institute, Los Angeles, CA 90049-1684 on line <http://aata.getty.edu/NPS/>



2. Conservation Information Network (BCIN), <http://daryl.chin.gc.ca>
3. Adhesives and Considants, Preprints of the Contribution to the Paris Congress 2–9 September 1984 Bromelle N S *et al.* IIC (International Institute for Conservation of Historic & Artistic Works, London 1984 – Studies in Conservation, IIC v.i.) *The Conservator; The Paper Conservator; J. Am. Inst. Conserv.; Restaurator.*
4. R. J. Gettens and G. L. Stout, *Painting Materials*, Van Nostrand, New York, 1942; A. P. Laurie, in *The Painter's Methods and Materials*, Dover publications, New York, 1967; P. Nicholson and I. Shaw, Ed., *Ancient Egyptian Materials & Technology*, Cambridge University Press, 1999; L. Masschelein-Kleiner, *Ancient Binding Media, Varnishes and Adhesives*, ICCROM, Rome, 1985; R. H. Bogue, *The Chemistry & Technology of Gelatin and Glue*, McGraw Hill, New York, 1922; J. S. Mills and R. White, *The Organic Chemistry of Museum Objects*, Butterworth Heineman, London, 1994; R. J. Forbes, *Studies in Ancient Technology*, EJ Brill, Leiden, 1964.

### *Adhesives for textile fibre bonding*

---

A J G SAGAR

A general discussion of **Adhesives in the textile industry** is given in an article of that title.

#### *Non-woven materials*

These are produced by converting a loose web or fleece of fibres into an integral structure. To stabilize the construction of most non-wovens, an adhesive is applied either as a polymer dispersion/latex (binder) or incorporated in the fleece as a thermoplastic (fusible) material.

Latex adhesives, of which there are many types (**Nitrile rubber adhesives** (NBR), SBR, **Ethylene–vinyl acetate copolymers**, acrylics, polyvinylidene chloride, etc.), should ideally be cross-linkable (for wash and dry-clean resistance), preferably with a low cure (reaction) temperature (see **Reaction setting adhesives**), as some fibres, such as polypropylene, may be damaged by high temperatures. The binder (adhesive) type can markedly affect physical properties and performance; the amount of hard and soft polymer in the binder controls the softness of the finished product. Most binders impart adequate dry-state adhesion and so the choice of adhesive is usually governed by secondary requirements such as the method and conditions of application and costs.

Synthetic rubbers (SBR, NBR) are used extensively where soft fabrics having some degree of stretch are required, whereas acrylic copolymers are widely used for less extensible fabrics. Acrylics are the best all-round binders, having good lightfastness in particular, and good wet strength. Nitrile rubbers (NBR) impart resistance to dry-cleaning solvents and to oils.

Thermoplastic fusible adhesives (see **Hot melt adhesives**) may be used in the production of adhesive-bonded non-wovens, as powders, fibres or sheet films. The formation of strong bonds between the fibres occurs as the softened thermoplastic adhesive material resolidifies on cooling. The amount of adhesive incorporated in the web governs the strength of the fabric.

The use of bicomponent fibres, in which each individual fibre is made up of two types of polymer, lying either side by side or in a sheath-core formation, may be regarded as

a special case of adhesive bonding with a thermoplastic material. One polymer, with a lower melting point than the other, melts and forms the bond while the second remains solid and maintains the fibrous network.

### *Flocking*

This is a means of attaching a fibre pile to a base fabric or paper; the flock is attached using an adhesive. The adhesives may be water-based (synthetic latices), **Solvent-based adhesives** or solvent-free (see **Adhesive classification**); the preferred ones are acrylic latices, polyurethanes and PVC plastisols. On curing, to form a cohesive solid, acrylic and polyurethane adhesives yield bonds that are resistant to dry-cleaning and laundering; PVC adhesives are only resistant to water-based cleaning agents as solvents extract plasticizer from PVC. The high gel temperature required for PVC (170–180 °C) may restrict the choice of base material.

### *Sizing*

Size, which is used to treat warp yarns prior to weaving, commonly consists of an adhesive and an emulsified lubricant. The function of the adhesive is to bind together the fibres or filaments of a yarn, thus supplementing the cohesive effect of twist, and to form a film on the surface of the threads as protection against the abrasive action of the loom. The requirements of the adhesive are that it must be water dispersible or soluble, form a film, have good adhesion, allow separation of each warp yarn, be flexible and, finally, must be easily removed from the woven material during desizing.

Adhesives used in size formulations include starches (natural such as potato, maize or sago, or chemically modified, e.g. starch ethers), natural gums (guar, carob or locust bean flour), gelatin, **Polyvinyl alcohol**, polyacrylic acid, vinyl and acrylic resins and sodium carboxymethyl cellulose (SCMC).

### *Tyres, belts and hose*

Rubber products such as tyres, belts and hose rely on reinforcement by textiles to achieve the required physical properties. To effect reinforcement, textile and rubber must be adequately bonded together, and to promote adhesion, there is a range of treatments to suit most fibre–rubber systems. The adhesion-promoting material (dip) is usually a terpolymer latex of butadiene–styrene–vinyl pyridine (or a blend of SBR and vinyl pyridine), which bonds well to the fibres, together with a resorcinol formaldehyde precondensate, which, on curing, bonds well to rubber; a three-dimensional resin network is formed.

**Adhesives in textile coating, laminating and printing** are discussed in a separate article.

### *Select References*

- W. C. Wake and D. B. Wooton, Eds., *Textile Reinforcement of Elastomers*, Applied Science Publishers, London, 1982.
- D. B. Wooton, in *Developments in Adhesives*, Vol. 1, W. C. Wake, Ed., Applied Science Publishers, London, 1977.
- J. A. Radley, Ed., *Industrial Uses of Starch and its Derivatives*, Applied Science Publishers, London, 1976.

---

***Adhesives in textile coating, laminating and printing***

---

A J G SAGAR

**Adhesives for textile fibre bonding** are discussed elsewhere; a more general article considers **Adhesives in the textile industry**.

*Coated fabrics*

Adhesives in relation to coated fabrics can be thought of as either the tie-coat to bond the surface coating to the fabric, or the surface coating itself, directly bonded to the fabric. The types of polymers used in coating fabrics are rubbers, PVC, polyurethane, acrylics and silicones; the coatings are usually cross-linked to increase durability but some topcoats can be thermoplastic, for example polyurethanes, to facilitate thermal bonding of seams in production of garments or other articles.

*Lamination*

Lamination (sticking together of layers) of fabric, foam and film, in various combinations, can be performed using latex- and solvent-based or fusible adhesives (see **Adhesive classification**). In addition, adhesives are sometimes applied from solution or latex for subsequent reactivation by heat during lamination. Acrylic dispersions are the main type of latex-based adhesives used in the laminating industry; butadiene rubbers and polyurethanes are also utilized in smaller quantities. The latex-based adhesives are used for aesthetic reasons and also on heat-sensitive or open-structured fabrics. The solvent-based adhesives, for example rubbers and polyurethanes, are used in applications similar to those for latex adhesives.

Thermal bonding using fusible adhesives (see **Hot melt adhesives**) can be achieved in three ways. Where one of the layers is a thermoplastic material or can be softened and tackified by heat, the use of a separate adhesive is not necessary. A special type of this sort of fusing is flame lamination using polyurethane foam. Besides mechanical bonding of the softened foam to the second substrate, some chemical bonding may be possible because of decomposition of the foam to give reactive chemical groups. Flame lamination is not a suitable method for use on heat-sensitive or open fabrics, but on other fabrics, it is a simple and cheap method of laminating; another plus is there are no solvents or water to remove, but this must be set against the production of toxic fumes during the flaming process.

The second method of thermal bonding utilizes nets and webs of thermoplastic material; this is now challenging flame lamination. Co-extruded nets, where one polymer acts as a cheap carrier for a lower-melting, more expensive polymer, are also available.

The third thermal bonding method involves the application of powders to one substrate in a separate application. The powders can be applied as a compounded paste by rotary screen-printing, as powders from hot engraved rolls (powder point process), or by scatter coating followed by sintering (heating below the polymer's melting point with application of light pressure). The scatter-coating method is probably the most versatile and widely used.

Whichever method is used to get adhesive on to a fabric, the distribution of adhesive usually has to be discontinuous to retain the flexibility, handle and other aesthetics of the bonded assembly.

A special example of lamination, and probably the most important use of adhesives in the assembly of garments, is fusible interlinings. These are used in garment production for collars, cuffs, jacket fronts and so on, so they retain their shape after repeated laundering or dry-cleaning. The performance of interlining-stabilized fabrics very much depends on the properties of the adhesive; the desirable properties are low cost, strong bond at low add-on (weight of adhesive used), minimum strike-back or strike-through and stability to dry-cleaning and or laundering.

The adhesive coating materials, applied to the base cloth to form the fusible interlining, are thermoplastic materials, which melt and flow in the fusing press and so form the bond between interlining and face fabric. The materials most commonly used as adhesives have already been described (under **Hot melt adhesives**), that is polyethylene, copolyamide, copolyester, plasticized PVC, cellulose acetate and polyvinyl acetate.

### *Seaming*

In the seaming of articles, use of hot melts is limited to relatively simple operations such as joining of straight edges. The thermoplastic material can be incorporated into the fabric or there is a wide range of films, tapes, nets and even coated threads that can be sandwiched between layers of non-thermoplastic material.

Use of **Solvent-based adhesives** in seaming stems from the pioneering work of Charles Macintosh in the last century; seam bonding with rubber solutions was a method used in the original waterproof coats carrying his name. Developments of the rubber-bonded seams are used in the manufacture of items such as life jackets and life rafts. The following (in cross-linked form) are commonly used: **Natural rubber-based adhesives**, **Polychloroprene rubber adhesives**, **Polyurethane** and butyl rubber.

### *Carpets*

Adhesives are used in tufted carpets to anchor and stabilize the yarns; they can also be used to attach a foam backing or a laminated secondary backing. Latices predominate with SBR (cross-linked) being the most widely used; EVA latex (see **Ethylene–vinyl acetate copolymers**) is cheaper but has lower bond strength and is water sensitive. Other adhesives used are PVC plastisols in carpet tiles and hot melts and two-component polyurethanes in top-quality products (because hot melts and polyurethanes are relatively expensive).

### *Pigment printing*

This technique, the surface application of insoluble colourants, has several potential advantages over dyes, which react with the fibre; their colour is fully developed at the time of application, as compared with reactive dyes, which only develop full colour after complete fixation, and the colour of the pigment is intrinsic to that pigment and will not change appreciably on different fibre substrates. The drawback is that, as the colour is

inert, it needs an adhesive to hold it in place and prevent loss through abrasion, washing or dry-cleaning.

The binder, therefore, must have the following properties: good adhesion to fibre and pigment in the dry state, and in water and solvent; a soft, non-tacky handle; elasticity; light-fastness, clarity and no colour; compatibility with, and stability towards, other ingredients in the mix. Some styrene butadiene copolymer rubbers and vinyl latices are used successfully but the most suited are the acrylics. The polymers are usually either self-cross-linking (with heat) or incorporate a cross-linkable resin such as melamine–formaldehyde.

*Select References*

L. M. Smith, *Developments in Adhesives* Vol 1, W. C. Wake, Ed., Applied Science Publishers, London, 1977.  
 G. R. Lomax, *Textiles*, **14** (1), 2–8; **14** (2), 47–56 (1985).

**Adhesives in the textile industry**

A J G SAGAR

This article gives a survey of the types of adhesive used; more specialized aspects are covered in **Adhesives for textile fibre bonding** and **Adhesives in textile coating, laminating and printing**.

Adhesives are widely used in the textile industry as shown in Table 1. If sizes and tyre cord dips are excluded, approximately 65% are used in carpet backing (mostly styrene–butadiene rubbers). Other major uses of adhesives are in non-wovens as binders (15%), in fabric backing (8%), in flocking and laminating (8%) and in fusible interlinings (2%).

Excluding warp yarn sizes for weaving, which are still dominated by starch and cellulose derivatives, most applications use synthetic polymers.

The quantities used are relatively small amounts compared with, say, the construction and the **Packaging industry**, so there is less incentive for manufacturers to develop products specifically for textiles. Nevertheless, a good variety of products are made that are well able to meet the often stringent requirements in the textile industry (Table 2).

Table 1. Applications for textile adhesives

Type of use	Textile application
Bonding layers of materials together	Lamination, fusible interlinings, seam and hem sealing, labels, bookbinding, surgical dressings
Bonding fibres together	Joining yarns, warp sizing for weaving, twistless spinning, formation of bonded-fibre fabrics (non-wovens)
Application of protective layers	Coated fabrics, carpet backing
Application of decorative finishes	Flock and pigment printing, motifs
Adhesion promotion	Tyre cord and belt fabric dips

Table 2. Classes of polymers used as textile adhesives

*Natural products*

Starches, modified starches, cellulose derivatives, natural gums, natural rubber

*Synthetic polymers*

Polyethylene, polypropylene, polyvinyl chloride, polyvinyl acetate and alcohol, **Ethylene–vinyl acetate copolymers**, polyacrylates, polyamide, polyester, **Polyurethane**, polychloroprene (neoprene), butadiene rubber, nitrile rubbers

If a polymer is to be used as an adhesive, several properties have to be considered: strength, elongation, flexibility, melt viscosity (for **Hot melt adhesives**), solubility or swelling characteristics in aqueous or dry-cleaning solvents, resistance to heat, light and hydrolysis and resistance to microbiological degradation.

These types of adhesives can be broadly classified by their physical form of application and/or the way they are activated to form a bond with the material to which they are applied, for example, as emulsion polymers, solution polymers, hot melts and reactive polymers (see **Adhesive classification**). Each of these will now be considered in turn.

*Emulsion polymers*

These products consist of a dispersion of very small particles of polymer in an aqueous medium (see **Emulsion and dispersion adhesives**). Their major advantage, apart from being based on water rather than organic solvents, is that high-molecular-weight products can be made and dispersed, to give high-solids-content emulsions (up to 65%), which have low viscosities (water-thin). Solution-based polymers of the same molecular weight and solids content would be unworkable because of their very high viscosities. The main disadvantage is that the water medium can cause swelling, and hence curl, of water-sensitive substrates such as fabrics. Emulsion adhesives include natural rubber latex and polymers and copolymers of acrylic esters and acids, vinyl and vinylidene chloride, vinyl acetate and chloroprene.

*Solution polymers*

Water can be used as the medium for a solvent-based adhesive when the polymeric material is water soluble. An example of such an adhesive would be a yarn-sizing formulation based on modified cellulose, **Polyvinyl alcohol** or polyacrylic acid. Generally, however, solvents are organic compounds, for example hydrocarbons (hexane, toluene), ketones (butan-2-one) and esters (ethyl acetate); see **Solvent-based adhesives**.

Usually, only rubbery polymers are considered for textile applications; however, for example in tyre cord and vee belt and transmission belt fabric dips, stiffer (resinous) polymers can be used.

*Hot melts*

The **Hot melt adhesives** suitable for textile use are copolyamides, copolyesters, **Polyurethanes**, acrylics, polyethylenes, polypropylene, ethylene copolymers (mainly with vinyl

acetate and vinyl alcohol), polyvinyl acetate and blends with **Phenolic resins**, plasticized vinyl acetate/PVC copolymers and plasticized cellulose acetate. They are used extensively for fusible interlinings, application of motifs and decorations, in seam and hem sealing, for fabric lamination (including wall coverings) and in carpet backing and bonding; in addition, fusible bicomponent fibres (two polymers in one fibre) in non-woven melded fabrics are, in effect, hot melt adhesives; when an assembly partially or wholly composed of these fibres is heated, the contact points of the fibres fuse together, thereby giving structural coherence to the fabric. In selecting hot melts, serviceability in use must be balanced with ease of application.

The melting point needs to be above service temperatures (NB: medical textiles are often steam-sterilizable at 130 °C for several minutes), but too high a melting point may adversely affect the dimensional stability, colour and handle of the fabric.

If the melt viscosity is too high, the polymer will not flow into the substrate and an inadequate bond results: if too low, strike through or strike back can occur, resulting in a stiff substrate and a bond starved of adhesive. Thermal stability must be adequate should the polymer be kept molten in the application for long periods. The physical form is important; for example, a discontinuous coating is preferred in some applications to give products with a soft handle, and the ability to form reticulated films is therefore a consideration.

#### *Reactive adhesive compositions*

Many of the emulsion- and solution-based adhesives, already described, can be cross-linked, and can therefore be termed **Reaction setting adhesives**.

There are other systems, where a prepolymer of low molecular weight reacts with a second component to give a three-dimensional structure and a very durable polymer. Examples include urea and melamine resins used with formaldehyde in fabric finishing, resorcinol/formaldehyde systems used in cord and fabric dips and low-molecular-weight silicones, which react on the substrate to give durable water-repellent finishes.

Further details appear in other articles, **Emulsion and dispersion adhesives, Solvent-based adhesives, Adhesive classification, Hot melt adhesives, Rubber-based adhesives**.

#### *Select References*

W. C. Wake, Ed., *Synthetic Adhesives and Sealants*, John Wiley, Chichester, 1987.

K. O. Calvert Ed., *Polymer Latexes and their Applications*, Applied Science Publishers, London, 1982.

---

### *Adsorption theory of adhesion*

K W ALLEN

The title “adsorption” theory is a reflection of the extent to which there are very close parallels between some of the ultimate forces involved in adhesion and those involved in the adsorption of gases and vapours on to solid surfaces. It has been well known for

80 years or more, the phenomena can be divided into two separate types: physical adsorption (or physisorption) and chemical adsorption (chemisorption or activated adsorption) (see **Bonds between atoms and molecules**). It is now clear that a similar distinction has to be made in discussions of adhesive bonding.

The forces that are involved are those that act between atoms and molecules in the structure of matter. They are summarized, with some of their major characteristics, in Table 1.

It is immediately obvious that all these forces and bonds have an exceedingly short range of effective action. While any may be involved in bonding, the London **Dispersion forces** are of particular importance since they are universally present and depend upon two surfaces being in sufficiently close contact. This is because they arise from and depend solely upon the presence of nuclei and electrons. The other types are only effective in situations where specific, appropriate chemical groupings are present.

Although the possibility of conventional chemical valence forces being involved in adhesive bonding has been recognized as at least a theoretical possibility, it is only relatively recently that it has been possible to demonstrate conclusively their significance. This has depended upon the development of sophisticated techniques (e.g. **X-ray photoelectron spectroscopy** and **Secondary ion mass spectroscopy**) for investigating the composition of surfaces. This has enabled the detection of fragments of chemical bonding in the surfaces exposed when bonded joints are broken (see **Primary bonding at the interface**).

These techniques were first successfully exploited in the study of silane primers, which have been used for improving the water resistance of joints. Gettings and Kinloch were able to show  $\text{-Fe-O-Si-}$  bonds from a steel substrate treated with a trimethoxy silane primer. Following this a number of workers have produced similar results in a variety of examples.

The adsorption theory of adhesion attributes adhesive strength to the action of London dispersion forces, combined in many instances with contributions from other forces (dipolar, polar or primary bonding) Calculations indicate that, in spite of their relatively low strength compared with the other types of bonding, these force can account for far greater strengths than are ever achieved experimentally. It is because all these forces are

Table 1. Primary and secondary bonds

Bond type	Bond energy $\text{kJ mol}^{-1}$	Equilibrium length nm
<i>Primary, chemical</i>		
Ionic	600–1000	0.2–0.4
Covalent	60–800	0.1–0.3
Metallic	100–350	0.2–0.6
<i>Acid-base interactions</i>		
Conventional Brønsted	<1000	
Lewis	<80	
<i>Secondary, physical</i>		
Hydrogen	~50	0.3
Van der Waals		
Dipole interactions	5–20	0.4
London, dispersion	1–40	<1



of such short range that adhesives all have to pass through a liquid stage so that they can attain the necessary close contact and interaction with the substrate surface (**Wetting and spreading**). Thus, the whole topic of the energies of interaction of liquids with the solid surfaces (surface thermodynamics) is important and has been studied extensively in this context.

An account of different theories is given under **Theories of adhesion**.

### *Select References*

- R. J. Good, in *Treatise on Adhesion and Adhesives*, Vol. 1, R. L. Patrick, Ed., Marcel Dekker, New York, 1967, Chap. 2
- M. Rigby, M. Rigby, E. B. Smith, W. A. Wakeham and G. C. Maitland, *Forces between Molecules*. Clarendon Press, Oxford, 1986, Chap 1.

---

## *Aerospace applications of adhesives*

---

D G DIXON

There are many potentially advantageous **Industrial applications of adhesives** which are relevant to aerospace structures in which the major concerns include light weight, reliability, structural efficiency and safety. These advantages are often cited as:

- The ability to join dissimilar materials.
- The ability to join thin sheet and large areas.
- A reduction in the number of fasteners and holes in the structure.
- Good fatigue resistance and vibration damping.
- The bond is continuous, providing good load transfer and a more uniform stress distribution than fasteners.
- Can offer good corrosion resistance.
- Joining and sealing can be accomplished in one operation.
- Can be cost-effective.

However, there can also be disadvantages:

- Rigorous process control is essential.
- Adhesives for high-temperature applications are often brittle and expensive.
- Bonded structures are usually difficult to dismantle for repair.
- NDT methods cannot measure the joint strength directly.
- There are no universal methods to predict long-term performance from short-term tests.

Wooden airframes have historically been bonded, originally with glues such as casein or synthetic urea-formaldehyde systems, but today most aerospace structures are made from fibre composites (glass fibre and carbon fibre, predominantly) and metals (mostly aluminium but also titanium). Adhesives are well suited for joining composite materials since the need to drill holes through the composite can be avoided and, in some cases, the

adhesive bonding can be carried out during the composite processing, forming an integral structure (see **Fibre composites – introduction** and **Fibre composites – joining**). Alternatively, cured composites can be bonded in a separate operation.

An appropriate surface treatment is essential to prepare surfaces for adhesive bonding to assure good initial strength as well as long-term performance in service (see **Pre-treatment of metals prior to bonding**). The adhesive, surface treatment and adherend material should be considered as a system and need to be proven in a wide-ranging series of test conditions before they may be used for safety-critical structures. Traditionally, test regimes will begin with laboratory characterization of the materials and processes, moving up to coupon testing and then to structural tests of large structures (see **Tests of adhesion**). Some tests will be dependent upon the exact structure and operating conditions, but it is typical to include a wide temperature range (e.g.  $-55^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ ) and to evaluate the effects of water and chemicals such as hydraulic fluids as well as mechanical tests and fatigue.

Aluminium aerospace structures are usually prepared by **Anodizing** before bonding. This electrochemical process ensures that the metal presents a surface with a finely structured oxide layer that is receptive to the adhesive and essential for durability. Phosphoric acid anodizing and chromic acid anodizing are the most common, with the latter being used more in Europe. However, chromic acid-based processes are coming under scrutiny for environmental reasons, and this has spurred a large body of research to find replacements (see **Environment and the impact of adhesive technology**).

Composite materials can be prepared for bonding in several ways. Common procedures include mechanical abrasion of the cured composite surface and the use of a peel ply. This is a removable layer that is applied prior to curing the composite and then stripped to reveal a textured surface prior to adhesive bonding; abrasion is sometimes used in addition to remove residues that may have been left by the peel ply (see **Fibre composites – joining**). There are also other surface treatments available, but all aerospace bonding and pre-treatment processes will require high standards of control.

The adhesives used in aerospace are often supplied as pre-formed films, which can be cut to shape and laid into the joint area. These are then cured at high temperature while pressure is applied in an autoclave or press. Paste adhesives, available as one-part or two-part systems, are also used; one-part adhesives, including film adhesives, are pre-mixed so they have a limited shelf life and must be stored in a freezer. Typical hot-curing **Epoxide adhesives** with a nominal maximum service temperature of  $100^{\circ}\text{C}$  would be cured at  $120^{\circ}\text{C}$  for an hour with an applied pressure of 100–350 kPa, but different formulations will require different curing regimes. Redux 775, based on phenolic-adhesives (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**) has been used for many years in metal bonding but **Toughened epoxide adhesives** are the most common type of adhesives for metals and composites. For higher temperature applications (typically above  $100^{\circ}\text{C}$ , depending on the application), there are modified epoxies or other types such as bismaleimides or cyanate ester-based adhesives. It is worth noting, however, that high-temperature adhesives are usually more difficult to process than epoxies and are often significantly more brittle; they are also likely to be more expensive.

Adhesive bonding is also useful for the repair of both metals and composites; patches can be applied as temporary or permanent repairs to reinforce damaged structures and bonded in place using special equipment to apply heat and pressure (see **Repair methods**). In these circumstances, it is not always possible to use the same pre-treatment and bonding

conditions that would be found during manufacture so specific procedures for repair have to be developed.

While there has been an extensive effort over many years to characterize the degradation of adhesive joints, there remains no universal method to predict long-term behaviour from short-term tests, and the development of improved predictive tools would be of great service to the designer and operator.

### Select References

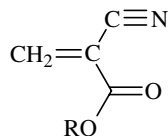
1. F. L. Matthews, Ed., *Joining Fibre-Reinforced Plastics*, Elsevier Applied Science, 1987.
2. Anon, *Adhesive Bonding Handbook for Advanced Structural Materials*, European Space Research and Technology Centre, European Space Agency, Noordwijk, The Netherlands, 1990.
3. J. D. Minford, *Handbook of Aluminum Bonding Technology and Data*, Marcel Dekker, 1993.

## Alkyl-2-cyanoacrylates

J GUTHRIE

### Basic materials

Cyanoacrylate adhesives were introduced in 1958 by Eastman Kodak. They are based on alkyl-2-cyanoacrylate monomers.

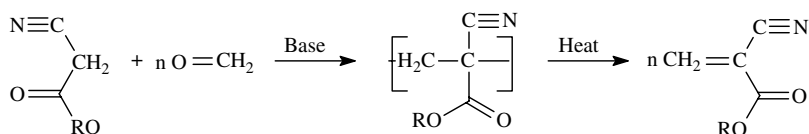


Cyanoacrylates are rapidly polymerized by nucleophilic species to give linear polymers with high molecular weights. Unlike other adhesives, cyanoacrylates consist of pure monomer in admixture with low levels of stabilizers, accelerators and modifiers. The patent literature abounds with references to many different monomers, but only a restricted group are used in commercial products. The structures of the most common monomers are shown below

$\begin{array}{c} \text{C}\equiv\text{N} \\   \\ \text{CH}_2=\text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{RO} \end{array}$	Commercially important esters	
	R	
	Methyl	CH <sub>3</sub>
	Ethyl	CH <sub>3</sub> CH <sub>2</sub>
	<i>n</i> -Butyl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>
	Allyl	CH <sub>2</sub> =CHCH <sub>2</sub>
	β-Methoxyethyl	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub>
	β-Ethoxyethyl	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub>

*Monomer synthesis*

Alkyl-2-cyanoacrylates can be prepared by several synthetic procedures. The only method of importance involves the Knoevenagel condensation of an alkylcyanoacetate with formaldehyde. As this is a base-catalysed reaction, the monomer is rapidly polymerized to give a low-molecular-weight poly(alkyl-2-cyanoacrylate). The resulting polymer is retropolymerized by heating under controlled conditions to yield monomeric cyanoacrylate (Scheme 1).

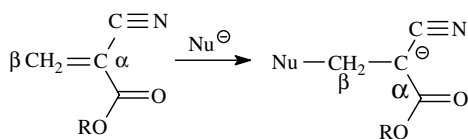


Scheme 1

Depolymerization is carried out under vacuum in the presence of an acid such as sulphur dioxide. The monomer which distils from the reaction mixture is collected in a vessel containing radical and anionic polymerization inhibitors.

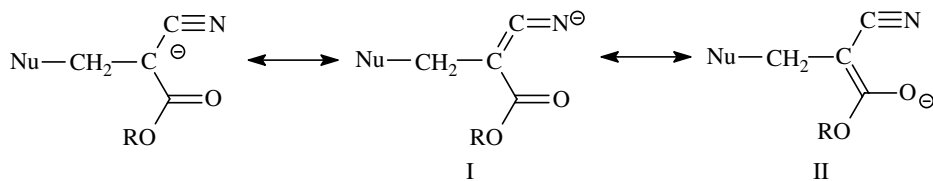
*Polymerization of alkyl-2-cyanoacrylates*

Cyanoacrylates can be polymerized by free radical and ionic initiators (see **Chain polymerization**). In adhesive applications, ionic polymerization is by far the most important mode of chain growth. It is their marked susceptibility to initiation by anions and nucleophiles that is responsible for their usefulness as adhesives. The cyanoacrylate  $\pi$ -electron system is under the influence of two strongly electron-attracting groups. This results in a reduced electron density on the  $\beta$ -carbon and enhanced susceptibility to nucleophilic attack (Scheme 2).



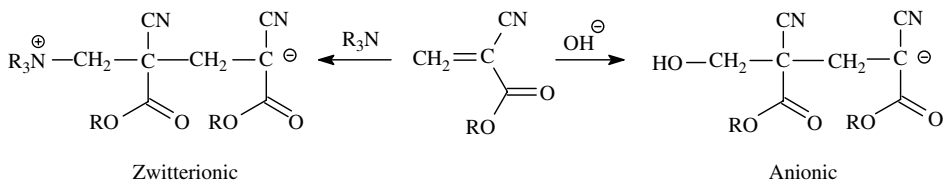
Scheme 2

The carbanion formed at the  $\beta$ -carbon is stabilized by delocalization (I and II).



The combination a high electrophilic  $\beta$ -carbon, a stable carbanion and an unhindered  $\beta$ -carbon confer on alkyl-2-cyanoacrylates their unique reactivity.

When used as adhesives, polymerization or curing is brought about by nucleophilic species present on the substrate. The nucleophile can be an ion or a neutral molecule (amine). If the initiating species is an ion, the polymerization proceeds by an anionic mechanism. If a neutral molecule is involved, the reaction is referred to as a zwitterionic polymerization (Scheme 3).



**Scheme 3**

The nature of the polymerization is presumably dependent on the substrates involved. In any case, both are extremely rapid with overall rates much greater than radical polymerizations. Ionic polymerizations are normally sensitive to termination reactions, but in the case of cyanoacrylates only strong acids are capable of terminating the growing chain. Some chain-transfer reactions are believed to occur because of the presence of carboxylic acids formed by monomer hydrolysis. A proton is transferred to the growing carbonium ion to give a “dead” polymer chain. The weak acid anion is capable of acting as an initiator and a new active centre is generated by reaction with monomer.

### Select References

- H. W. Coover, D. W. Dreifus and J. T. O'Connor, in *Handbook of Adhesives*, 3rd, I. Skeist, Ed., Van Nostrand, Reinhold, New York, 1990, p. 463.
- G. H. Millet, in *Structural Adhesives, Chemistry and Technology*, S. R. Hartshorn, Ed., Plenum Press, New York, 1986, Chap. 6.
- D. C. Pepper, *J. Polym. Sci., Polym. Symp.*, **62**, 65 (1978).
- P. Klemarczyk, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, p. 847.

## Anaerobic adhesives

D P MELODY

### *Basic chemistry and properties of the uncured adhesives*

Anaerobic adhesives and sealants are based on acrylic (usually *methacrylic*) functional monomers and cure by a redox-initiated free radical polymerization (see **Chain polymerization**). They are so named because of the characteristic of requiring a relatively air-free condition to allow curing. Hence, anaerobic adhesives are very suitable for the bonding and sealing of close-fitting metal components.

Anaerobic adhesive formulations vary substantially depending upon the properties sought in the cured and uncured composition. Typical formulations contain (meth)acrylate

monomer(s), modifiers, initiator(s), accelerator(s) of redox-initiated free radical polymerization and stabilizers/inhibitors. Methacrylate monomers are preferred to acrylate as the latter have a greater tendency to cause skin irritation (see **Health and safety**).

While dimethacrylates of polyalkoxy diols, such as triethyleneglycol dimethacrylate, are commonly employed, advanced resins carrying suitable functionality have been used in many recent anaerobic adhesives to expand the range of properties available in the cured products.

Modifiers can include dyes, thickeners, gelling agents, fillers and lubricity controllers and the like as agents that influence the properties of the uncured composition. Plasticizers, reinforcing and/or toughening agents, adhesion promoters and thermally polymerizable prepolymers may be added as “modifiers” of the cured adhesives.

The initiator is usually a hydroperoxide.

Accelerators, which interact with initiator(s), speed up the curing reaction. Many conventional free radical polymerization stabilizers and inhibitors can be used. However, such additives are minimized to give a high level of reactivity. Oxygen in air is often enlisted as a fugitive inhibitor by using partially filled, low-density polythene bottles (or tubes) as packages.

Anaerobic adhesives differ from related **Acrylic adhesives** by being very finely balanced in terms of stability and reactivity.

### *Properties of cured anaerobic adhesives*

Properties of cured anaerobic adhesives are related to the formulation chosen for a given application area. For example, anaerobic threadlocking formulations cure to very hard materials for studlocking applications and to relatively soft solids for locking precision screws. Usually, cured anaerobic products are highly cross linked and form strongly adhesive, but somewhat, brittle solids. They are resistant to water and solvents and perform well under extremes of temperature ( $-50^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ ).

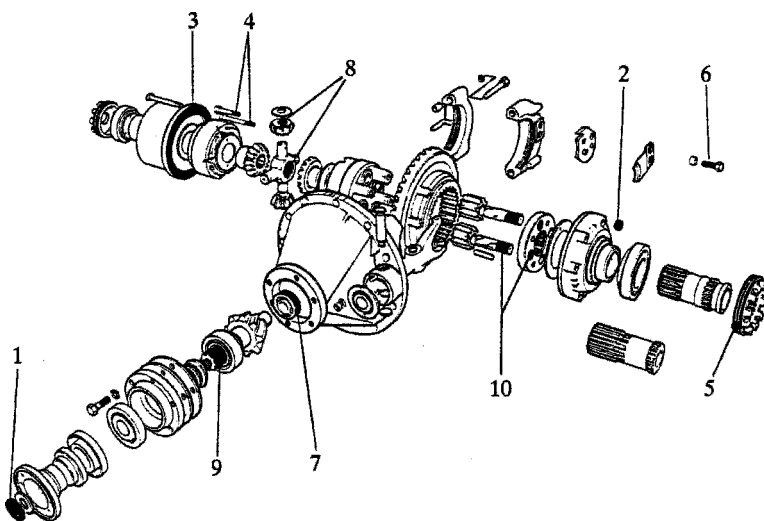
Owing to their curing properties, anaerobic adhesives remain uncured outside the joint assembly: this allows removal with solvent. Some formulations now include sensitizers, which allow drying of the excess with UV light.

### *Applications*

The major application areas for anaerobic adhesives are as follows: locking and vibration proofing threaded assemblies; sealing threaded joints and pipe fittings; sealing porous and flanged metal structures; strengthening cylindrical fits; structural bonding of rigid metal and ceramic components.

Adhesives for threadlocking provide resistance to vibration and maintain the tension achieved in threaded joints. Adhesives for thread sealing generally contain fillers to give suitable viscosity characteristics and some physical sealing in the uncured form. When cured, they give good durability (see **Durability – fundamentals**) with the ability to disassemble later. Anaerobic porosity sealants are used effectively to ensure sealing of welds and coatings.

Anaerobic sealants are particularly effective as form-in-place gaskets for rigid flange structures. The “anaerobic gasket” replaces gasket inventories, but more importantly,



**Fig. 1.** Applications for anaerobic adhesives in an automotive final drive

it eliminates gasket yielding (with loss in structural rigidity) by allowing metal–metal contact in the clamped assembly.

Traditional methods of cylindrical fitting parts such as gears, bushings and bearings have involved interference fitting. The expense and risks of defect in this methodology can now be eliminated by use of anaerobic adhesives. The combination of anaerobic adhesives and “interference fitting” can be used to give outstanding performance (see **Joint design – cylindrical joints**).

Given the surface initiation, central to the function of anaerobic structural adhesives, they work best in face-to-face bonding of small flat components. Whereas traditional anaerobic adhesives cure to rigid solids, which have high shear and tensile strengths but low cleavage and peel strengths, newer anaerobic structural adhesives offer good impact, fair peel strengths and more tolerance for surface contamination. In bonding, as in all anaerobic applications, use of a redox activator can be used to increase cure speed and to facilitate cure through larger gaps ( $\geq 0.2$  mm).

Figure 1 shows a series of uses for anaerobic adhesives in the final drive of an automobile as examples of application areas (see also **Automotive applications**).

Aspects of this subject are also dealt with in other articles, notably **Acrylic adhesives**, **Durability – fundamentals**, **Joint design: general**, **Joint design: cylindrical joints**, **Joint design: strength and fracture perspectives**. In the article on **Toughened acrylic adhesives**, some properties are compared with those of **Epoxide adhesives** and anaerobic adhesives.

Some test methods are given in the Appendix.

### Select References

- C. W. Boeder, in *Structural Adhesives, Chemistry and Technology*, S. R. Hartshorn, Ed., Plenum Press, New York, 1986.
- G. S. Haviland, *Machinery Adhesives for Locking, Retaining and Sealing*, Marcel Dekker, New York, 1986.
- B. George, Y. Grohens, F. Touyeras and J. Vebrel, *Int. J. Adhes. Adhes.*, **20**, 245–251 (2000).

---

*Animal glues and technical gelatins*

---

C A FINCH

Animal glues are probably the oldest type of adhesives: they were used to bond the wood of the coffins of Egyptian mummies (see **Adhesives – historical perspective**). Several animal proteins have been used as the raw materials for adhesives, including blood proteins, caseins (the protein of milk), albumin (from egg white) and collagen products from skin, leather and, especially, animal bone. Over the centuries animal glues have been used extensively, as concentrated aqueous solutions, to make furniture, wooden weapons (such as longbows and crossbows), to bind the inflammable heads of matches, and to coat paper, especially abrasive papers (“sandpaper” or “glasspaper”) and high-quality rag papers for banknotes and security documents. Some animal glues are still employed for these purposes, and also in craft woodworking, for making musical instruments, such as violins, which are conventionally made using a high-quality glue derived from rabbit skins.

Technical gelatin is a convenient term for gelatin and animal glues used for non-edible purposes. Chemically, it is, like pure edible gelatin, a mixture of gelling proteins obtained by partial hydrolysis, by thermal or chemical means, of waste collagen protein from animal connective tissue, skin and bone. The chief features of the amino-acid composition of animal glues are those of collagen – an unusually high content of glycine and of the imino acids, proline and hydroxyproline (which affect gelling properties due to inter-chain **Hydrogen bonding**), with very small amounts of the aromatic and sulphur-containing amino acids. There is very little difference in amino acid composition between animal glues from different types of raw material (bone or skin), or from different animals. However, non-gelling fish glues, from cold-blooded organisms, have a low hydroxyproline content. In all animal glue production, the degreased raw material is subjected to the basic reaction of the hydrolysis of collagen, a multiple helical chain protein: the rate of this hydrolysis increases with temperature and with stronger acid or alkaline conditions. Hide glues are usually made by an acid process. The production conditions are designed to break down the collagen but retain large molecules in the resulting soluble proteins. The resulting dilute protein solutions are concentrated by evaporation and then gelled by cooling. The resulting gels are chopped into small pieces and then dried by passage through a series of warm, dehumidified chambers.

Production of animal glue is considered as environmentally “friendly”, since it involves conversion of unpleasant waste into useful products, but economic operation depends on satisfactory disposal of residues: some of these are used as slow-release nitrogenous fertilizers. The mineral residue from bone glue production (“bone meal”) by thermal methods is used as a phosphate supplement in animal feed and fertilizers: it is also calcined at 1000–1200 °C to produce calcined bone, used in the manufacture of bone china to provide strength and translucency. Animal glues and technical gelatins contain added preservatives and a proportion of non-protein materials, usually mucopolysaccharides and soluble inorganic salts. These impurities differ with the source of raw material.

The physical and chemical properties of animal glues depend on the nature of the raw material and on the method of processing. The “quality” depends on the gelling point, and the viscosity, measured at standard concentration (6.67 wt% for technical gelatin; 12.5 wt% for animal glue). The “jelly strength” (or “bloom strength”) is measured using



a “gelometer” (a type of penetrometer) by determining the force (in grams) needed to depress the surface of a standard gel, conditioned at 10°, by a flat plunger 12.5 mm in diameter, to a depth of 4 mm. Viscosity is measured with a calibrated Ostwald viscometer at 60: results are normally reported in millipoise (mP), centistokes (cP), or millipascal seconds (mPa s). The test methods are detailed in well-established national and international standards, which also describe the measurement of pH, foam characteristics, grease content and melting and setting points (see Select references).

Only small amounts of technical gelatin are used in adhesives in industrialized countries, mainly in specialist applications, and to a limited extent in craft woodworking, since the concentrated technical gelatin solutions exhibit **Viscoelasticity** and have the property of **Tack**, which allows the temporary “grab” between the surfaces being joined, so that they can be adjusted to their exact position before the final joint is allowed to harden and become permanent. Animal glue bonds between suitable wood surfaces can have tensile strengths comparable to those of high-performance synthetic adhesives. Other craft operations using animal glues (as warm aqueous solutions, often formulated with polyhydroxy compounds as humectants, soluble salts (usually magnesium sulphate), gel depressants and preservatives) include bookbinding (which involves a long-life paperboard-to-book cloth or leather bond), and other paper-to-paper applications, such as remoistenable-gummed paper tape, and decorative paper box making. Significant amounts of low-quality animal glue are also manufactured in developing countries for general and domestic use.

There are several specialist uses of technical gelatin: one of the most important includes the binder component of the head composition mixture of matches. The gelatin quality controls the ignition performance of the match, by affecting the microfoam properties of the match head, and the adhesion of the head to the match splint. Technical gelatin is used (among other polymers) in coated abrasive paper (“sandpaper”) as the adhesive between the paper substrate and the abrasive component (of glass powder). The glue binder is dried by passing the paper web through a heated oven, and treated with a formaldehyde-releasing compound, which cross-links the dried film, so improving adhesion and reducing moisture sensitivity and increasing the working life of the product. Technical gelatin is also used as size coating for high-quality rag-based paper used for security documents such as banknotes. The coating provides good moisture and abrasion resistance and good adhesion to the special inks used in the banknote design.

### Select References

- E. Sauer, *Tierische Leime und Gelatine*, Springer-Verlag, Berlin, 1958. This describes the technology of skin-based and bone-based glues, and also casein adhesives.
- A. G. Ward, A. Court Eds., *Science and Technology of Gelatin*, Academic Press, London, 1977. This volume gives the definitive account of the classical nature, properties and manufacturing technology of edible and pharmaceutical gelatin, including technical gelatin, based on the many research reports of the Gelatine and Glue Research Association.
- British Standard 647, *Methods for Sampling and Testing Glues (Bones, Skin and Fish Glues)* German Standard DIN 53260: 1963 (rev.), *Pruefung von Glutinleimen* 1981. (These standards are incorporated into International Standard IS 9665: 1992, and CEN Standard 29.665: 1993.) The older standards describe several chemical test methods not included in the International Standards.
- J. Alleavitch, W. A. Turner, C. A. Finch and Gelatin, in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol A12, 5th edn, VCH Verlagsgesellschaft, Weinheim, 1989.

---

**Anodizing**

---

D E PACKHAM

Anodizing has been used as a **Pre-treatment for metals prior to bonding** both in practical processes and fundamental scientific studies where it has played a role in the development of the **Mechanical theory**. It is applied most commonly to aluminium.

The basic principle of anodizing, namely, that the component to be treated is made the anode in an electrolytic cell, may be applied using a great variety of conditions. The morphology and chemistry of these electrochemically generated surfaces is influenced by a number of factors, principally cell voltage, the solubility of the film in the electrolyte, component and electrolyte composition and the pre-treatment employed. In anodizing processes, considerable scope therefore exists for the optimization of surface properties for specific applications.<sup>1,2</sup>

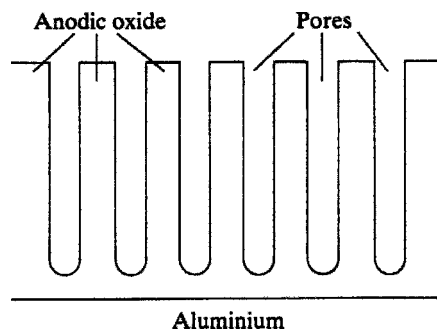
The anodic film formed on aluminium in aggressive electrolytes such as phosphoric, sulphuric and chromic acids is porous. The classical description of the film is of a regular hexagonal array of cylindrical pores penetrating normal to the surface almost to the base metal (Fig. 1). The actual structure revealed by **Electron microscopy** varies greatly with electrolyte and anodizing conditions.<sup>1,3</sup> Some details are given in **Mechanical theory of adhesion**: see also Fig. 2 in **Electron microscopy**.

Most commercial anodizing of aluminium is performed in sulphuric acid electrolytes to yield oxide films, which, of the order of tens of micrometres thick, provide good corrosion and abrasion resistance, in addition to a useful dye-absorption capability. Other anodizing processes utilize chromic, oxalic, nitric or phosphoric acids, or mixed electrolytes.

Relatively few anodic treatments find application in structural adhesive bonding where durability (see **Durability – fundamentals**) in hostile service conditions is of paramount importance.<sup>3-5</sup>

Processes practised in the aircraft industry include the long-established UK Ministry of Defence specification DEF 151 Type 2 method, which uses a dilute chromic acid solution operated at approximately 40 °C and a programmed voltage sequence peaking at 50 V dc. A dense oxide structure a few micrometres thick is formed.

Boeing Aircraft Specification BAC 5555 anodizes for 20 min at 10 V dc in a 10% solution of phosphoric acid at room temperature and generates a surface structure on aluminium alloy to which highly durable bonds may be obtained.



**Fig. 1.** Schematic representation of porous anodic oxide layer on aluminium

Typical procedures for chromic and phosphoric acid anodizing are given in **Pre-treatment of aluminium**, and the durability (see **Durability – fundamentals**) of bonds to the surfaces formed is discussed. An example of a profile of elemental composition in depth for a phosphoric acid anodized film is shown in **Auger electron spectroscopy**.

The mechanisms by which stable bonds to these anodized surfaces are achieved have been extensively studied.<sup>3,4</sup> In the BAC 5555 process, a whiskered porous oxide structure less than 1  $\mu\text{m}$  thick is developed over a thin barrier layer. The incorporation of phosphate ions in cell walls inhibits oxide hydration and contributes to greater bond durability.

For bonding applications, the performance of sulphuric acid and chromic acid anodized surfaces may be improved by controlled oxide dissolution in phosphoric acid to yield morphologies more readily penetrated by adhesives and primers.

In contrast to the above slow batch methods, A.C. anodizing processes have been developed for the treatment of aluminium at the coil stage, using either sulphuric acid or phosphoric acid electrolytes.

Anodic treatment may also be considered when bonding other metals. Examples include the anodizing of magnesium in ammonium bifluoride solution, the anodic etching of stainless steel in nitric acid and anodizing of titanium in sodium hydroxide or chromic acid<sup>6</sup> (see **Pre-treatment of titanium**). Alternative anodizing of copper can produce a **Microfibrinous surface** (see **Pre-treatment of copper**).

### References

1. S. Wernick, P. G. Sheasby and R. Pinner, *Surface Treatment and Finishing of Aluminium and its Alloys, Vols. 1 and 2*, 5th edn, Finishing Publishers, Stevenage, 1987.
2. S. Kawai, *Anodizing and Coloring of Aluminium Alloys*, Finishing Publications & Metal Finishing Information, Stevenage, 2002.
3. G. D. Davis and J. D. Venables, in *Adhesion Science and Engineering-2, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, p. 947.
4. A. Bjorgum, F. Lapique, J. Walmsley and K. Redford, *Int. J. Adhes. Adhes.*, **23**(5), 401–412 (2003).
5. G. W. Critchlow and D. M. Brewis, *Int. J. Adhes. Adhes.*, **16**, 255–275 (1996).
6. G. W. Critchlow and D. M. Brewis, *Int. J. Adhes. Adhes.*, **15**(3), 161–172 (1995).

## Atomic force microscopy

---

GRAHAM LEGGETT

In the atomic force microscope, a sharp tip attached to a flexible cantilever is rastered across a sample surface. As the interaction force between the tip and the sample changes, the deflection of the cantilever varies. The cantilever deflection is readily measured (by optical deflection in most commercial systems), and is proportional to the interaction force leading to quantification provided the spring constant of the lever is known (see **Surface forces apparatus** and **Roughness of surfaces**). Either the cantilever or the sample is mounted on a piezoelectric crystal in order to exact fine control over the relative movements of the tip. In the most commonly used mode of operation, the tip remains in

contact with the sample during imaging (*contact mode*). In *constant height mode*, the variable deflection of the cantilever is measured as the sample is scanned, while in *constant force mode*, the cantilever deflection is maintained at a preset value (the set point) by adjustment of the piezoelectric scanner so that the tip effectively traces the contours of the sample surface. It should be noted that the name of the technique (“*atomic force microscopy*”) remains a misnomer under most circumstances. The popular conception of a single atom asperity contacting a surface is false. A typical contact-mode load (a few nN) applied through a single atom would result in a pressure that exceeds the tensile strength of any known material by several orders of magnitude. In fact, contact-mode tips have rather large radii of curvature on the atomic scale (ca 50 nm) and it is instructive to attempt to draw a scale diagram of a tip of such dimensions beside a single atom. However, in *non-contact mode AFM (atomic force microscopy)*, the situation is rather different. The tip oscillates close to the surface, but not in continual contact with it, leading to interactions between a single atom at the tip apex and surface atoms and enabling the acquisition of force images with atomic resolution. Quite specific measurements may be made, including the direct measurement of forces associated with bond formation. However, the technique is usually used in ultra-high vacuum (UHV) conditions with very well defined surfaces.

### *Tapping mode*

This is one of the most useful developments for the imaging of delicate specimens. Contact-mode imaging may lead to the disruption of surface structure at elevated loads. For some materials, reduction of the load is not guaranteed to eliminate damage. In tapping mode, the cantilever oscillates at high frequency (100–200 kHz) and high amplitude, and only intermittently strikes the sample. This eliminates the frictional forces that contribute to damage, and reduces the rate of energy dissipation, rendering the topographical imaging of delicate materials much easier. However, it should be noted that even in tapping mode it is possible to damage polymeric materials. Energy dissipation still occurs, and provides access to important additional information in the form of phase images. In *phase imaging*, the lag between the driving oscillation and the cantilever response is measured. Elastic contacts lead to a small phase lag, while contacts with viscoelastic materials, which result in a higher rate of energy dissipation, lead to a larger phase angle. Much effort has been directed towards the development of a detailed theoretical understanding of phase imaging, although with limited success. However, qualitative interpretations of phase images are very valuable, often yielding details of nanoscale morphology absent from tapping mode topographical images. Phase images do not reflect the topography of homogeneous materials, but reveal local variations in mechanical properties (e.g. stiffness). In polymers, for example, crystalline and amorphous regions may exhibit different phase angles because of their different mechanical responses to the tip–sample contact.

### *Friction force microscopy (FFM)*

On commercial AFM systems, data on the lateral deflections of the cantilever are readily acquired simultaneously with topographical data in contact mode. The lateral forces

arise from both topographical and frictional effects (**Friction – adhesion aspects**). Topographical contributions are removed by subtracting images acquired with opposite scan directions. Frictional forces in AFM result from both ploughing and adhesive interactions. Differences in local stiffness, for example, may yield contrast. However, differences in surface composition also yield differential responses. For a commercial cantilever fabricated from silicon nitride, the outer surface of the tip is polar (largely silicon dioxide) and interacts more strongly with polar material than with non-polar regions of the sample, leading to higher rates of energy dissipation through shearing of attractive interactions with the polar regions. As a result, a larger friction force is measured for polar material. The process may be made more specific by depositing a molecular layer onto the tip (*chemical force microscopy*). A variety of approaches to quantification have been explored. A common one is to plot the friction force as a function of the applied load. The gradient of the friction–load plot is equal to the coefficient of friction (Amonton’s law), a useful parameter to characterize a particular tip–sample combination.

#### *Pull-off force measurement*

Force–distance experiments involve the measurement of the interaction force as the tip is lowered onto the surface, pushed into the sample a small distance and then withdrawn. Where adhesion occurs, there is hysteresis and the tip must be pulled further than the position at which it first contacted the surface in order to separate it. Eventually the tip separates, and the detachment force may be measured and used to characterize the tip–sample interaction. Quantitatively, the data may be modelled using appropriate contact mechanics (usually the Johnson–Kendall–Roberts model, see **JKR equation**, because it explicitly includes terms related to adhesion). By depositing a self-assembled monolayer of alkanethiols onto a tip coated with a thin layer of gold, it is possible to render the interaction highly specific, for example, probing hydrogen-bonding interactions by adsorbing carboxylic acid–terminated molecules to the tip.

AFM is related to other techniques of **Scanning Probe Microscopy**.

#### *Select References*

- R. W. Carpick and M. Salmeron, *Chem. Rev.*, **97**, 1163–1194 (1997).  
H. Takano, J. R. Kenseth, S.-S. Wong, J. C. O’Brien and M. D. Porter, *Chem. Rev.*, **99**, 2845–2890 (1999).  
E. Meyer, *Atomic Force Microscopy*, Springer-Verlag, Berlin, 2004.  
R. Wiesendanger, *Scanning Probe Microscopy*, Springer-Verlag, Berlin, 1998.

---

## **Auger electron spectroscopy**

JOHN F WATTS

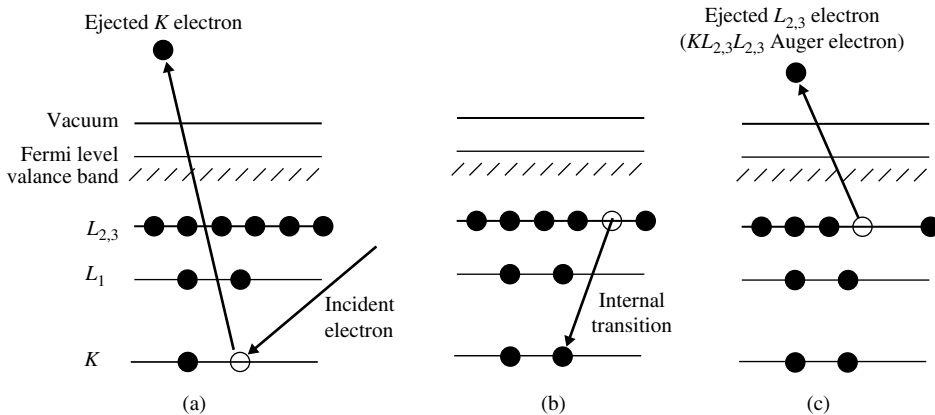
Auger electron spectroscopy (AES)<sup>1,2</sup> is one of a family of surface analytical techniques that have assumed increasing importance in materials science investigations over the last three decades. The other two are **X-ray photoelectron spectroscopy** (XPS or ESCA)<sup>1,2</sup>

and **Secondary ion mass spectrometry** (SIMS)<sup>3</sup>; indeed, AES has many features in common with the former technique and, for this reason, they are often to be found on the same analytical system.

The basis of AES is the relaxation of an excited atom or ion following the emission of a core level electron, that is, the generation of a core level vacancy. The process is illustrated in Fig. 1, which shows the three processes involved in the generation of a  $KL_{2,3}L_{2,3}$  Auger electron; the initial process is the ejection of a  $K$  electron, which will usually be achieved by electron beam irradiation although both X-ray photons or ions may also be employed, the vacancy in the  $K$  shell that results is filled by the promotion of an electron from the  $L_{2,3}$  level, and in order to conform with conservation of energy principles another electron must be ejected, in this case an  $L_{2,3}$  electron. This electron is termed the  $KL_{2,3}L_{2,3}$  Auger electron, and the kinetic energy it possesses as it leaves the atom or ion is approximately the difference of the three energy levels involved:

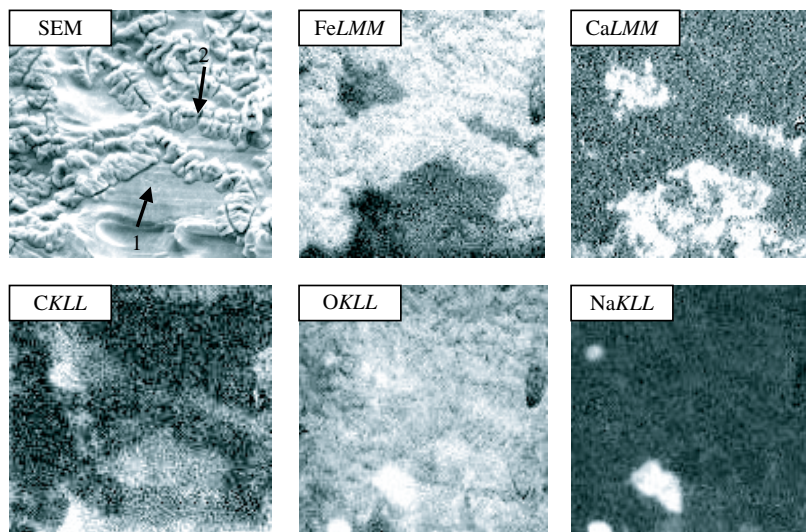
$$E_{KL_{2,3}L_{2,3}} = E_K - E_{L_{2,3}} - E_{L_{2,3}}$$

In most cases, the kinetic energy of the outgoing Auger electron is in the range 50–2000 eV and it is this relatively modest energy that gives the technique its surface specificity, as the distance an electron will travel in a solid varies as  $E^{1/2}$  (where  $E$  is the kinetic energy of the Auger electron). This gives an analysis depth of 2–5 nm depending on experimental conditions. In AES, in contrast to characteristic X-ray analysis in the SEM, it is the energy of the outgoing particles, rather than that of the primary beam, that determines the analysis depth of the technique. The spatial resolution of the method depends on the characteristics of the primary electron beam but can vary from a few micrometers down to 20 nm on current state-of-the-art scanning Auger microscopes. There are three common modes of operation in AES: point analysis, production of a chemical map by scanning Auger microscopy and sputter depth profiling.



**Fig. 1.** Production of an Auger electron. (a) Creation of the initial core vacancy in the  $K$  shell by the incident electron beam, (b) internal rearrangement in which a  $L_{2,3}$  electron fills the vacancy created in the previous step and (c) emission of an  $L_{2,3}$  electron as a  $KL_{2,3}L_{2,3}$  Auger electron

The use of AES and scanning Auger microscopy in adhesion studies can be illustrated very well by the following case study. This involves the delamination of nylon coating from an organosilane-treated steel substrate during a salt spray test. Upon removal of the coated panel from the test environment, extensive delamination of the coating was observed along with traces of rust on the steel substrate. A scanning electron micrograph (SEM) of the substrate is shown in Fig. 2(a). Two regions of distinctly different morphology can be observed: a smooth, featureless region (indicated by Point 1) and rough, undulating features typified by Point 2. These two areas represent the anodic and cathodic areas that occur during corrosion. Rusting of the substrate has taken place to yield the regions typified by Point 2 while the electrons produced by the anodic dissolution of iron are consumed at the cathodic region (leading to the production of hydroxyl ions and a localized increase in pH). More details of this phenomenon and the reasons for coatings failure are provided in the article on **Cathodic disbondment**. An AES spectrum from Point 1 is shown in Fig. 3(a), and strong Auger peaks of iron, oxygen and adventitious carbon are seen. This is as expected and is associated with a true interfacial failure. The cations Na, Ca and Mg are also detected and indicate that this surface was acting as a cathode during the corrosion process. The Si $KLL$  transition shows the organosilane has not been displaced during salt spray testing. A spectrum in this format is referred to as the direct spectrum, and the alternative mode of presentation, the differential spectrum, is illustrated in Fig. 3(b). This spectrum was obtained by digital treatment of Fig. 3(a), although in some cases, spectra of this type will be acquired by analogue detection methods. The spectrum from Point 2 is shown in direct form in Fig. 3(c); this spectrum shows the presence of iron and oxygen together with a very small amount of carbon and sodium. The very low surface concentration of adventitious carbon is typical

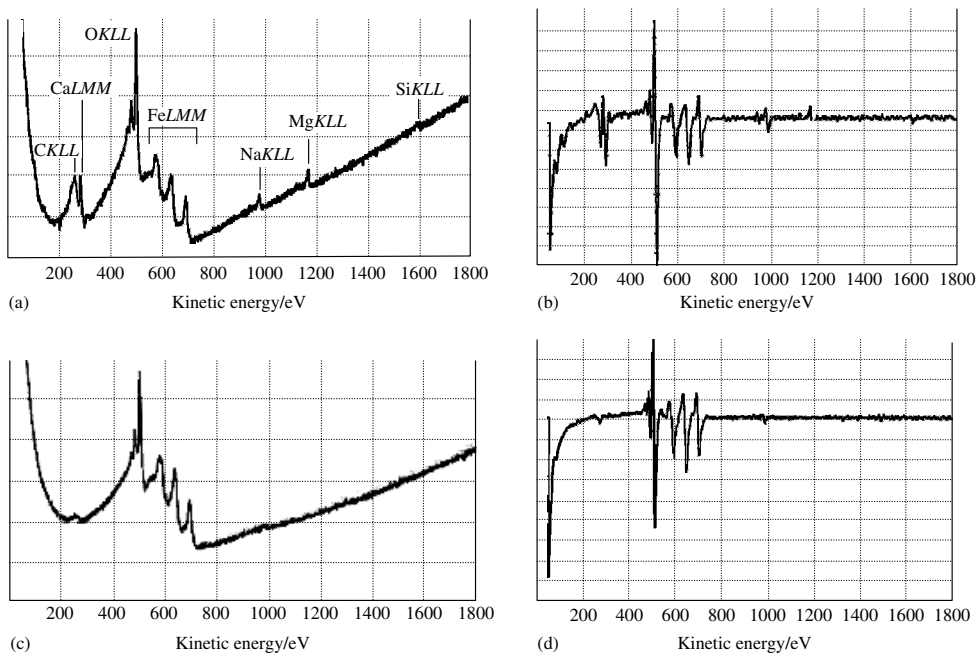


**Fig. 2.** Secondary electron image and a series of scanning Auger images taken from a steel substrate treated with an aminosilane from which the nylon coating has disbonded during a salt spray test. Width of micrographs is 85  $\mu\text{m}$ . (Courtesy of Marianne Guichenuy, University of Surrey)

of a high surface area corrosion product. The equivalent differential spectrum is shown in Fig. 3(d).

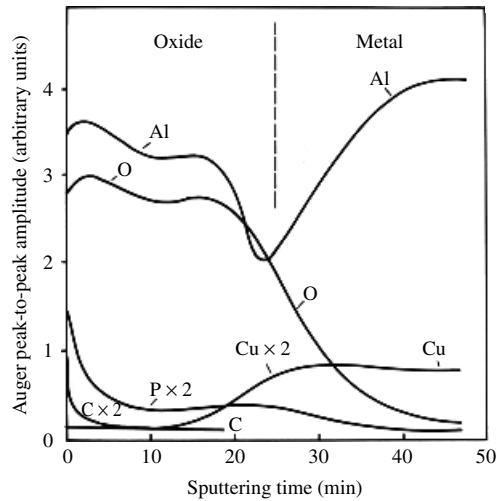
The spatial distribution of elements present in the surface analysis is readily achieved at a sub-micrometer spatial resolution using scanning Auger microscopy as shown in Fig. 2. The cathodic marker calcium maps out the smooth areas very clearly and is coincident with the increased level of carbon in these regions. The iron map is able to delineate the two regions quite readily as a result of the more intense signal from the corroded regions. This simply arises as a result of the lower carbon concentration on the corrosion product. Sodium ions will deposit from the test solution at a higher pH than  $\text{Ca}^{2+}$  and such areas are clearly seen in the  $\text{NaKLL}$  map. A slight increase in surface oxygen (attributable to increased  $\text{OH}^-$  concentration) is also associated with these areas.

Although AES is essentially a surface technique, it is possible to combine it with inert gas ion sputtering to remove material and thus produce a depth profile many nanometres into the sample. In general, the sputtering depth will not exceed  $1\ \mu\text{m}$  but the depth profile will have a depth resolution of 1–3 nm. For depths greater than  $1\ \mu\text{m}$ , some form of mechanical removal of material will be required. Such depth profiles are particularly useful in adhesion studies for the determination of segregated or impurity layers at surfaces and the estimation of the thickness of conversion coatings. Figure 4 shows such a depth profile for phosphoric acid-anodized aluminium alloy substrate.



**Fig. 3.** Auger point analyses taken from the location indicated on the SEM image of Fig. 2. Spectrum (a) is taken from Point 1, spectrum (c) from Point 2. The spectra of (b) and (d) were obtained by numerical differentiation of the direct spectra (a) and (c). (Courtesy of Marianne Guichenuy, University of Surrey)





**Fig. 4.** Auger depth profile of an anodized aluminium substrate. The oxide is approximately 300-nm thick

### References

1. D. Briggs and M. P. Seah, *Practical Surface Analysis Vol. 1 Auger and X-ray Photoelectron Spectroscopy*, John Wiley and Sons, Chichester, 1990.
2. J. F. Watts and J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES*, John Wiley & Sons, Chichester, 2003.
3. J. C. Vickerman, A. Brown and N. Reed, *Secondary Ion Mass Spectrometry: Principles and Applications*, Oxford University Press, 1989.

### Automotive applications

A MADDISON

In recent years, the range of adhesive materials used in automotive manufacture has expanded to include polyurethanes, plastisols, phenolics, hot melts, anaerobics, cyanoacrylates, toughened acrylics and epoxies (see **Structural** and **Hot melt adhesives**). Selection criteria are based principally upon the nature of the adherends, the mechanical properties required under service conditions and application and curing characteristics.

Compliant, gap-filling materials are effective in direct glazing and panel-stiffening roles in which the service stresses are low, but the evaluation of high-performance **Toughened adhesives** now challenges traditional techniques in the construction of safety-critical assemblies. In body-shell manufacture, there are a number of advantages of **Structural adhesive** bonding. Reduction of stress concentrations means that thinner-gauge materials can be used. Dissimilar materials can be joined, and seam sealants are eliminated. There are improvements in fatigue and **Impact resistance** (see **Durability: fatigue**). All of this gives new freedom in design and the scope for improved appearance of the vehicle (see **Joint design-general**).

For jiggling purposes, and to provide handling strength prior to adhesive cure, supplementary mechanical fasteners are desirable. A further consideration is the improved peel resistance and impact performance, which may be realized by strategic mechanical fastening. In this respect, spot welding remains the favoured method.

In contrast to the aerospace industry (see **Aerospace applications**), conditions prevailing in automobile manufacture dictate that pre-treatments (see **Pre-treatment of aluminium**) should have short process times and be tolerant of production variables. The surfaces produced should retain adequate bonding properties during extended storage under poorly controlled conditions. The surface may need to be sufficiently conductive to permit weld-bonding techniques. Pre-treatments applied at the coil stage must be compatible with mill oils and press lubricants, and withstand mechanical deformation in the press.

The above approach has not, to date, been extended to include steel, although considerable effort is expended in its pre-treatment prior to painting. The current practice is to weld bond oil steel using single-part epoxy adhesives curing during the first (electrocoat) paint stage.

It has been shown, however, that the **Durability fundamentals** of such bonds is questionable, particularly when stressed. Reduced dependence on mechanical fasteners will require the development of production-viable treatments for steel or the introduction of coated variants.

Further examples are given in **Anaerobic adhesives, Industrial applications of adhesives** and **Joint design – cylindrical joints**.

### *Select References*

- E. H. Cordes, Adhesives in the automobile industry, in *Handbook of Adhesive Technology*, 2nd edn., K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 999.  
J. Fenton, *Handbook of Automotive Body Construction and Design Analysis*, Professional Engineering, London, 1998.  
F. Rosselli and P. Carbutt, *SAMPE J.*, **37**(6), 7–13 (2001).

---

### *Autophoretic primers*

N R WHITEHOUSE

Other related articles discuss **Pre-treatment of metals prior to painting**, **Paint primers** in general, and **Etch primers**.

Autophoretic primers are novel, water-borne primers and are based on aqueous dispersions (3–5% volume solids) of either acrylic or polyvinylidene chloride (PVDC) polymers. They are used to coat ferrous metal components, such as automotive brake parts, in a dip coating process. The coating is acidic (pH 2.5–3.5) and contains an oxidizing agent, usually hydrogen peroxide. Firmly adherent films (7–25  $\mu\text{m}$  in thickness), with good corrosion resistance, can be achieved.

Workpieces must be scrupulously clean for the autophoretic deposition process to operate. On immersion in the coating bath, the metal articles are attacked by the acid, liberating

ferrous ions, which are then oxidized to ferric ions. The ferric ions destabilize the coating dispersion in the immediate vicinity of the article, resulting in localized coagulation and deposition of a gelatinous film. An even coating can be built up on all wetted surfaces in about 2 min, including cut edges and recesses. After rinsing, the coated articles are then stoved (heat cured).

#### *Select Reference*

N. R. Roobol, *Industrial Painting: Principles and Practice*, 2nd edn, Hanser Gardner Publications, Cincinnati, 1997, Chap. 2.

# B

---

## *Blister test*

---

D E PACKHAM

### *Introduction*

The blister test is a method for determining the adhesive fracture energy of a joint or coating. The common form of the pressurized blister test specimen basically consists of pressurizing the adhesive, or coating layer, so that it forms a blister that at a critical pressure begins to debond from a rigid substrate (see **Fracture mechanics**). A good feature of the test is that the pressurizing medium may be an inert one, such as dry nitrogen, or an active hostile environment such as water. The test has been adapted to study the effectiveness of **Release** agents. A problem with the blister test when using very rigid and brittle adhesives or coatings is that of inserting a sharp crack at the interface. A debond is often inserted using a release film or release paint, but this may not be sufficiently sharp for these materials.

### *Theoretical aspects*

To determine the value of the adhesive fracture energy, it is necessary to decide the mode of deformation of the pressurized layer. In the case of a relatively thin blister, the mode of deformation is considered to be mainly that of tensile deformation of the blister, and the blister is then modelled as an elastic membrane. Alternatively, in the case of a relatively thick blister, the pressurized layer is considered to deform mainly by bending, and this is modelled as an elastic circular plate with a built-in edge constraint. A further contribution to the stored elastic energy, which is available to assist growth of a debond, arises from an internal stress inherent in the test specimen.<sup>1,2</sup> Such stresses may be introduced during

manufacture of the specimen. In some specimens, the effects of plastic yielding must be considered.<sup>3</sup>

### *Recent developments*

Recently, there have been reported several developments of the common blister test method.<sup>4,5</sup> These include the “island-blister” test<sup>6</sup> and the “inverted-blister” test developed by Fernando and Kinloch.<sup>7</sup> Both of these test methods are designed to enable the adhesive fracture energy to be measured for a coating of thin adhered film where the coating or film has insufficient strength to resist the pressure needed for debonding if the standard blister test was employed. Wan and Mai have described a blister test in which the crack is driven by the expansion of a fixed mass of gas and stable growth ensues.<sup>8</sup>

### *References*

1. H. M. Jensen and M. D. Thouless, *Int. J. Solids Struct.*, **30**, 779–795 (1993).
2. C. Wang, *J. Appl. Polym. Sci.*, **73**, 1899–1912 (1999).
3. J. G. Williams, *Int. J. Fracture*, **87**, 265–288 (1997).
4. Y. Z. Chu and C. J. Durning, *J. Appl. Polym. Sci.*, **45**, 1151–1164 (1992).
5. R. J. Hohlfelder, J. J. Vlassak, W. D. Nix, H. C. Luo and E. D. Christopher, *Materials Research Society Symposium – Proceedings*, v 356, Thin Films: Stresses and Mechanical Properties V, 1995, pp. 585–590.
6. Y.-H. Lai and D. A. Dillard, *A study of the fracture efficiency parameter of blister tests for films and coatings in Adhesion Measurement of Films and Coatings*, K. L. Mittal, Ed., VSP, 1995.
7. M. Fernando and A. J. Kinloch, *Int. J. Adhes. Adhes.*, **10**, 69 (1990).
8. K. T. Wan and Y. W. Mai, *Acta Metall. Mater.*, **43**, 4109–4115 (1995).

---

## ***Bonds between atoms and molecules***

---

D E PACKHAM

Adhesion is a subject with many important practical applications. The practical properties of an adhesive bond are a consequence of the bonding between the atoms and molecules involved (**Adhesion fundamental and practical**). Much of the theory of adhesion that can give an insight of practical importance makes use of concepts used in chemistry when discussing bonding between atoms and molecules. The distinction is widely made between strong “primary” bonds between atoms and weak “secondary” bonds between molecules. This article gives a brief explanation of terms commonly used for both.

### *Primary bonds*

Primary bonds are considered to be covalent, ionic or metallic. A covalent bond involves the sharing of outer electrons between the two atoms making the bond. Thus, each hydrogen atom is covalently bonded to the oxygen atom in a water molecule, and the H<sub>2</sub>O unit

is thermally stable well above 1000 °C. In methane, a carbon atom forms covalent bonds to four hydrogen atoms, CH<sub>4</sub>.

An ionic bond involves the complete transfer of one or more electrons from one atom (commonly a metal) to another atom. In common salt, an electron has been transferred from the sodium atom to the chlorine atom, giving the thermally stable sodium chloride, Na<sup>+</sup>Cl<sup>-</sup>.

In metals themselves, the outer electron or electrons are delocalized from the individual atoms and are associated with the whole crystal. The characteristically high melting points of metals are a consequence of the strength of the metallic bond.

Although these three types, covalent, ionic and metallic, are sharply distinguished in elementary treatments of the subject, more advanced considerations lead to the recognition that a better description can be given of most real molecules by regarding the bonds as intermediate between the three ideal types. Thus, a carbon–chlorine bond (e.g. in PVC.) is regarded as predominantly covalent, but as having some ionic character. It thus has a dipole moment: the chlorine atom has a small negative charge and the carbon has a small positive charge (see **Polar forces**).

### Secondary bonds

Weaker “secondary” bonds act between molecules. Thus, below –182 °C, methane is a solid, the covalent molecules being held in a solid lattice by weak secondary bonds. These weak forces are associated with interactions between dipoles. Three different types of interaction have been described by London, Debye and Keesom, known respectively as dispersion, induction and orientation forces; see Table 1 and **Dispersion forces** and **Polar forces**. The three types of interaction are often referred to collectively as van der Waals forces, as indicated in Table 1. However, it is necessary to note that some authors use the term “van der Waals” to refer exclusively to dispersion forces, the other two types being referred to as “polar forces”, Table 2. (The term “dispersive” is sometimes used by francophone authors writing in English where “dispersion” would be correct.)

These terms “dispersion”, “polar” and “van der Waals” are widely used in the literature on adhesion, especially in which **Contact angles** and **Surface energy** are under discussion.

Table 1. Classification of secondary forces

		<b>Dipolar interaction:</b>
<b>van der Waals</b>	London dispersion	Transient/transient
	Debye induction	Permanent/induced
	Keesom orientation	Permanent/permanent

Table 2. Alternative classification of secondary forces

		<b>Dipolar interaction:</b>
<b>van der Waals</b>	London dispersion	Transient/transient
<b>Polar forces</b>	Debye induction	Permanent/induced
	Keesom orientation	Permanent/permanent

Lifshitz has given a treatment of weak secondary forces, which does not classify them according to the London, Debye and Keesom criteria. The term **Lifshitz-van der Waals forces** then corresponds to “van der Waals forces”, as used in Table 1.

### *Hydrogen bonds*

**Hydrogen bonding** gives rise to bonds of strength intermediate between those of primary and secondary bonds. The much higher melting point of ice, compared with that of methane, is a result of hydrogen bonds, in addition to van der Waals bonds, acting between H<sub>2</sub>O molecules.

### *Acid–base interactions*

These are now frequently referred to in discussions of adhesion. They make use of the Lewis concept of **Acids** as acceptors of electron pairs. Thus, **Acid–base interactions** are electron donor–electron acceptor interactions. Hydrogen bonding provides a particular example. The strength of acid–base interactions varies widely according to the molecular species involved.

### *Select References*

- R. L. DeKock and H. B. Gray, *Chemical Structure and Bonding*, 2nd edn, University Science Books, Mill Valley, CA, 1989.  
P. Atkins and L. Jones, *Chemical Principles the Quest for Insight*, Freeman, New York, 1999.  
P. A. Cox, *Inorganic Chemistry*, BIOS Scientific, Oxford, 2000.

# C

---

## *Cathodic disbondment*

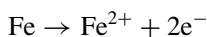
---

JOHN F WATTS

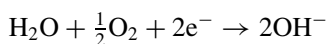
Adhesive joints and coatings not uncommonly fail in an aqueous environment (see **Durability: fundamentals, Weathering of adhesive joints** and **Wedge test**). One of the mechanisms by which this may occur on metals is by cathodic disbondment.

Cathodic disbondment (or delamination) occurs when failure of an organic coating is associated with a cathodic potential on the metal substrate, a phenomenon most widely considered with respect to iron-based alloys. Such a potential may emanate from the electrolytic cell that exists at the surface of a corroding metal or it may have been applied by way of an impressed potential to ensure the entire metal structure is cathodically protected.

In the former category, we are concerned with localized damage to a paint film, exemplified by a stone chip on the body of a motor car. The exposed metal surface, in the case of steel, undergoes the anodic reaction, which will eventually lead to a characteristic rust deposit on the surface:



The electrons produced by this reaction are consumed in the cathodic reaction, which occurs adjacent to the anodic area, and may involve both oxygen and water:



Thus, the cathodic reduction of water and oxygen leads to the production of hydroxyl ions, which in turn leads to an increase in the pH of the electrolyte in the environs of the coating/substrate interface. It is this alkalinity that is responsible for the rapid failure of coatings or adhesive joints and has given rise to the term cathodic disbondment. The case of an entire structure being polarized cathodically is frequently encountered when cathodic protection is used to prevent corrosion of massive steel structures such as ships



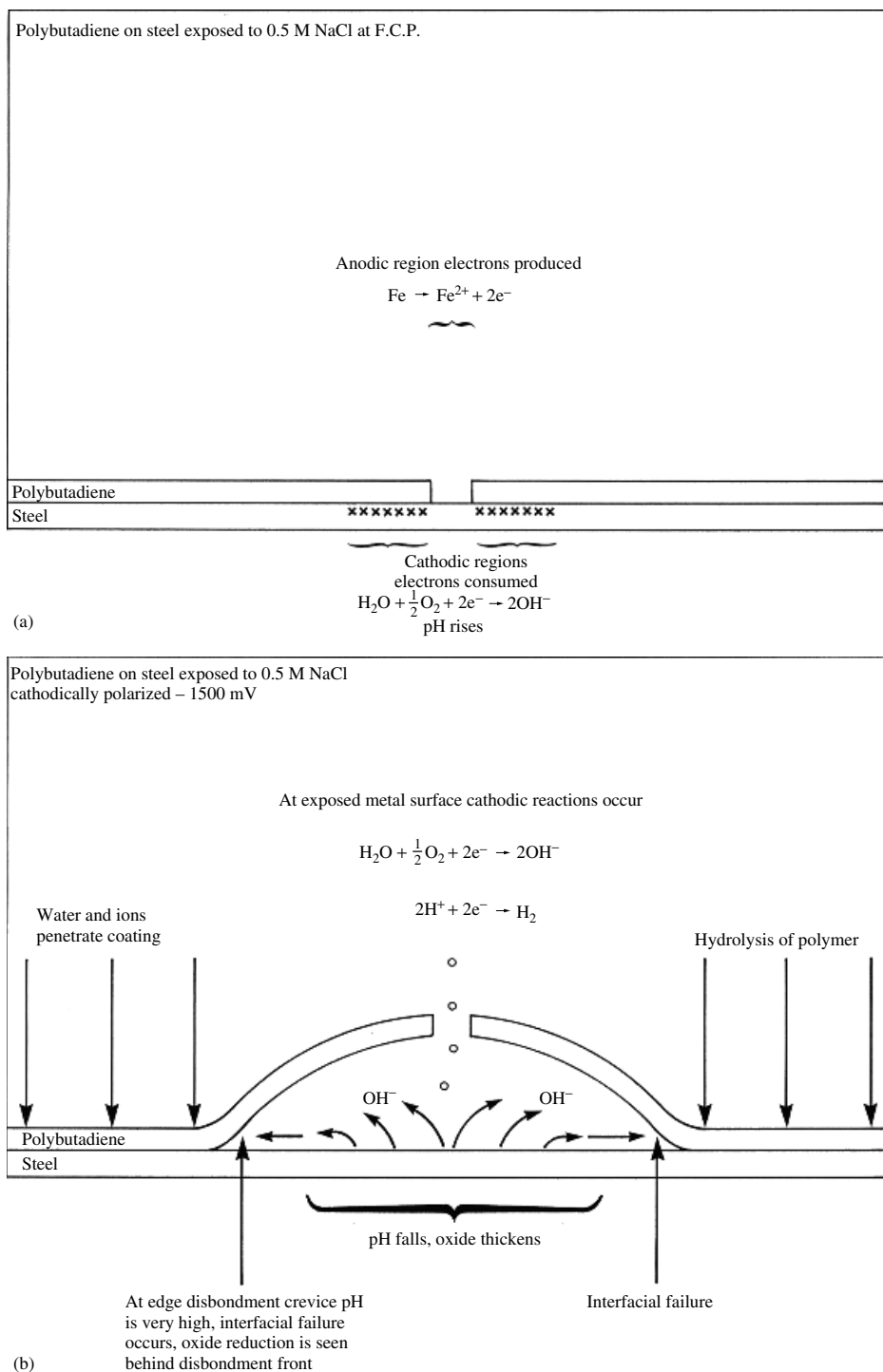
or pipelines.<sup>1</sup> The cathodic reaction will occur at any regions of exposed metal, bringing about rapid failure of the coating. The manner in which these two situations can lead to cathodic disbondment is shown schematically in Fig. 1.

There are several ways in which the susceptibility to cathodic disbondment of coatings applied to a steel surface may be assessed. The most widely used in the United Kingdom<sup>2</sup> makes use of an impressed cathodic potential of 1.5 V versus saturated calomel electrode as illustrated in Fig. 2, while the test popular in the United States couples the coated panel to a zinc electrode providing a cathodic potential of 1.0 V. In both tests, the pre-damaged panel is exposed in an aqueous solution and the results are reported as the extent of disbondment from the exposed metal as a function of time. In practice, a set of tests would be terminated at predetermined time intervals (e.g. 1, 3, 6 months) to compare candidate coatings, the system showing the least disbondment being the best.

In this type of test, it is essential, when evaluating coatings, that the substrate pre-treatment is kept constant, as changes in surface profile will alter the interfacial path length and hence the kinetics of failure if interface diffusion is the rate controlling step.<sup>3</sup>

There is no universal mechanism of cathodic disbondment, and although it is the production of hydroxyl ions that is eventually responsible for the degradation of adhesion, this may be achieved in any of three ways depending on polymer, substrate and exposure conditions.<sup>4</sup> The classical mode of failure by cathodic disbondment is that of interfacial separation, that is to say the interfacial bonding is attacked by the alkali to such an extent that interfacial failure occurs with no traces of polymer remaining on the metal surface. This type of failure is often associated with lateral diffusion of the active species from the exposed metal, although there is speculation that the rate controlling step is the diffusion of water through the coating towards the crevice tip.<sup>5</sup> If such a hypothesis is correct, the important parameter will be the activity of water molecules (solute) in the polymer host (solvent), and although there is a plethora of thermodynamic data available that treats water as the solvent, none seems to be available in the literature where water is the solute. If failure does not occur at the interface, it may occur within the interfacial region of the polymer, leaving a very thin (<5 nm) polymer residue; such a residue can only be detected by surface analysis methods such as **X-ray photoelectron spectroscopy** (XPS) or **Auger electron spectroscopy** (AES). This failure mechanism is often described as alkaline hydrolysis of the polymer and results in the cohesive failure of the polymer very close to the interface as a result of downward diffusion of active species through the thickness of the coating and is thus usually confined to thin coatings. The final possibility is the degradation of the substrate oxide, and this phenomenon will occur as a result of the combination of high underfilm pH and very noble electrode potential, the situation that is known to occur in the case of impressed current cathodic protection. However, the likelihood of such an oxide reduction mechanism being the only cause of failure is remote, and although the process may act as an initiator of disbondment<sup>3</sup> or occur in a random manner,<sup>6</sup> the kinetics of the process ensure that it will be generally overtaken by either interfacial failure or cohesive failure within the polymer.

With the advent of use of high-performance organic coatings on cathodically protected structures such as gas and oil transmission linepipe, the cathodic disbondment properties of a particular coatings system have become important material parameters and are now to be found in the manufacturer's technical data for such systems. However, the standards



**Fig. 1.** Electrochemical reactions involved in cathodic disbondment; (a) in a system at rest potential, (b) in a system that is cathodically polarized (i.e. cathodically protected by an impressed current)

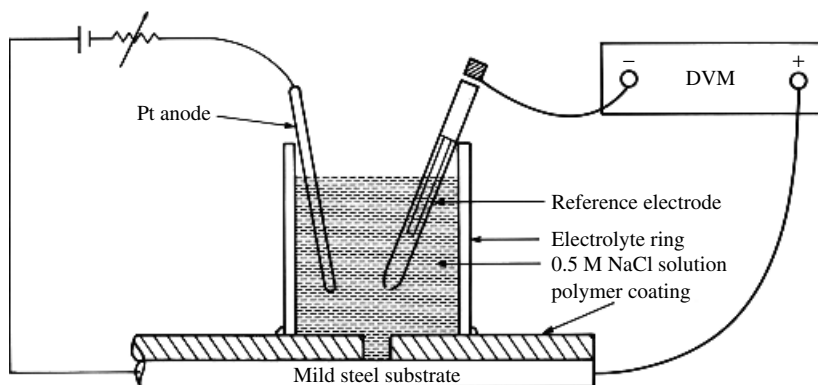


Fig. 2. The standard cathodic disbondment test used in the United Kingdom<sup>2</sup>

employed are many and varied with regard to temperature, potential and surface finish prior to application, and care must be taken in interpreting data from dissimilar tests.

Although the term was originated to describe the failure of organic coatings, it is clear that cathodic disbondment can lead to the accelerated failure of adhesive joints as well. The work of Davis and Watts<sup>7</sup> illustrates this phenomenon for steel substrates bonded with an epoxy adhesive and shows how a combination of XPS and **Secondary ion mass spectroscopy (SIMS)** are able to provide a definitive picture of the locus of failure. Such a combined approach enables a detailed mechanism of failure to be postulated.

### References

1. J. Morgan, *Cathodic Protection*, NACE Houston, 1987.
2. British Gas Specification PS/CW6, British Gas, 17, London Road, Staines, TW184AE, UK.
3. J. F. Watts and J. E. Castle, *J. Mater. Sci.*, **19**, 2259–2272 (1984).
4. J. F. Watts, *J. Adhes.*, **31**, 73–85 (1989).
5. J. E. Castle, in *Organic Coatings*, P. C. Lacaze, Ed., AIP Conference Series 354, American Institute of Physics, Woodbury, NY, 1996, pp. 432–449.
6. J. F. Watts and J. E. Castle, *J. Mater. Sci.*, **18**, 2987–3003 (1983).
7. S. J. Davis and J. F. Watts, *J. Mater. Chem.*, **6**, 479–493 (1996).

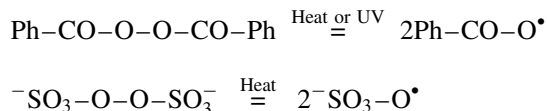
## Chain polymerization

J COMYN

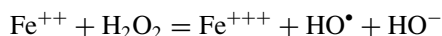
Monomers containing rings or double bonds can be polymerized by chain polymerization, which is also known as addition polymerization. (It should be contrasted with **Step polymerization**.) The chain reaction involves the sequential steps of initiation, propagation and termination. Initiation is the process by which active centres are formed; these may be free radicals, anions or cations. The *free radical* chain polymerization of a vinyl monomer is illustrated below.

*Initiation*

Free radicals can be produced by the thermal or photochemical decomposition of an azo or peroxy compound; examples given below are benzoyl peroxide and persulphate ion.

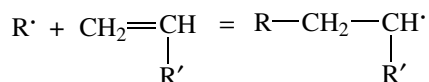


They can also be generated in a redox reaction, such as is exemplified below.

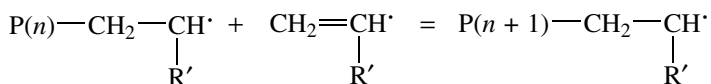


The first of these three particular reactions would be suitable for an organic medium, and the second and third would be appropriate when water is the medium. Chain polymerization can also be directly initiated using ionizing radiation, such as an electron beam.

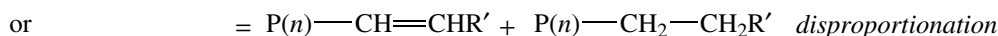
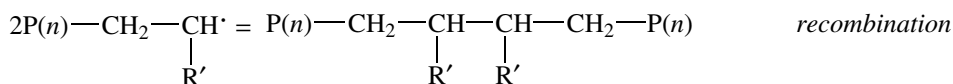
The primary radicals attack the monomer thus.

*Propagation*

Many monomer molecules are now added to the radical to produce a long-chain macroradical. Radical lifetimes are typically a few seconds, and during this time, thousands of monomer units can be added. The propagation reaction can be symbolized by a monomer molecule adding to the radical at the end of a polymer chain. Here, P(*n*) symbolizes a polymer chain with *n* monomer units.

*Termination*

In termination, two macroradicals react, either by recombination or disproportionation.



In addition to initiation, propagation and termination, further processes that can occur are chain transfer, inhibition and retardation.

High-mass macromolecules are produced from the start of chain polymerization, and the molar mass and its distribution are controlled by the rates of initiation and propagation, the mode and rate of termination and by chain-transfer reactions.

Chain polymerization can be carried out in bulk, solution or by suspension or emulsion polymerization with water as the medium.

#### *Chain polymerization in making adhesives*

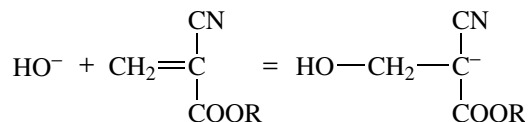
There are several polymers that form the basis of adhesives, and which are made by free radical chain polymerization. These include the carbon-chain synthetic rubbers, **Acrylic adhesives**, **Ethylene vinyl acetate copolymers** and polymer lattices.

Thermoplastic rubbers are used in pressure-sensitive adhesives, and these are synthesized by “living” anionic polymerization. Cationic polymerization is used to make butyl rubber, and some low molar mass tackifiers, which are used in **Pressure-sensitive adhesives**.

Copolymerization, that is, with two or more monomers, is a useful way of obtaining materials with specific properties, and in the case of ethylene vinyl acetate copolymers, the effects of the vinyl acetate units is to reduce the crystallinity of polyethylene, and to introduce polar groups, which improve adhesion.

#### *Chain polymerization in curing adhesives*

**Cyanoacrylate adhesives** consist mainly of alkylcyanoacrylate monomer, which undergo rapid anionic chain polymerization when the adhesive bond is closed. Hydroxide ions in absorbed water are generally thought to be the initiators, and the rapidity of anionic polymerization is due to two electron-withdrawing groups (–CN and –COOR), which stabilize the propagating anion. The initiation step is



It is a general point that a chain polymerization is more likely to occur if the active center is relatively stable.

Reactive acrylic adhesives generally consist of a solution of a toughening rubber (chlorosulphonated polyethylene) in a partly polymerized mixture of monomers; this is mainly methylmethacrylate but ethane diol dimethacrylate is added as a cross-linking agent. The remaining monomer is polymerized in a free radical chain polymerization: redox initiation involves an organic peroxide and a tertiary amine. Acrylic cements consist of a partly polymerized acrylic monomer containing an initiator. Cure is established by the thermal or UV decomposition of the initiator (see **Radiation-cured adhesives**).

When mixed with acid anhydrides or primary or secondary amines, epoxide adhesives cure by step polymerization. However, when the hardener is a tertiary amine or a Lewis acid such as  $\text{BF}_3$  (**Acids**), cure is by ring opening ionic chain polymerization.

*Select References*

- J. Comyn, *Adhesion Science*, Royal Society of Chemistry, Cambridge, 1997.  
R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*, 2nd edn, Chapman & Hall, London, 1997, Chap 5.  
G. Odian, *Principles of Polymerization*, 3rd edn, John Wiley & Sons, New York, 1991.

*Climbing drum peel test*

K B ARMSTRONG

This test is used where the bonded members are not flexible enough to be peeled in a more usual manner (see **Peel tests**). The less rigid of the two members is peeled by winding it around a rigid cylinder – the “climbing drum” (Fig. 1) – in this way a very high force can be applied to the peel front.

It is a practical test used both for assessing the quality of adhesive bonds between thin skins (usually aluminium alloy) and honeycomb or other core materials for lightweight sandwich panels.<sup>1,2</sup> and also for testing adhesives by peeling a thin sheet from a much thicker one.<sup>3</sup> In the former case, its purpose is to peel the skin away from the core and thereby to assess the bond strength/quality. This test is used mainly by the aircraft industry. In the latter case, it measures the peel performance of adhesives (see **Tests of adhesion**). The standard test method is ASTM D-1781, which describes the test and the apparatus required. The apparatus consists of a drum with each end of larger diameter than the centre section to which one skin of the honeycomb panel is connected. Flexible bands or bicycle chains are connected to the ends of the drum at one end and to the base of the testing machine at the other. The opposite end of the specimen is held in a grip, which is connected to the crosshead of the testing machine. This test is easier to demonstrate than it is to describe. During loading, the flexible bands, or chains, unwind from the drum causing it to travel up the specimen while wrapping one skin of the specimen around the centre part of the drum. It is recommended that the specimen be 308 mm (12 in.) long by 76 mm (3 in.) wide with 38 mm ( $1\frac{1}{2}$  in.) of skin and honeycomb cut away at one end and 25 mm (1 in.) at the other to leave just the skin for attachment to the climbing drum at one end and the testing machine at the other (Fig. 2).

Loading should be carried out in a screw-driven tensile testing machine with the crosshead speed set to 25 mm (1 in.)  $\text{min}^{-1}$  and at least 152 mm (6 in.) of the skin/honeycomb bond should be peeled. The machine should have a chart recorder so that the peeling

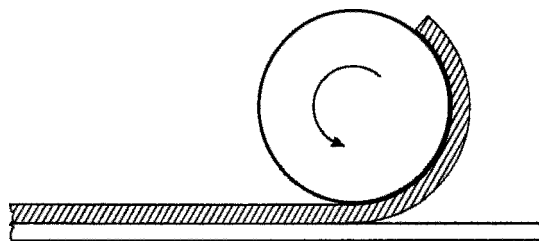
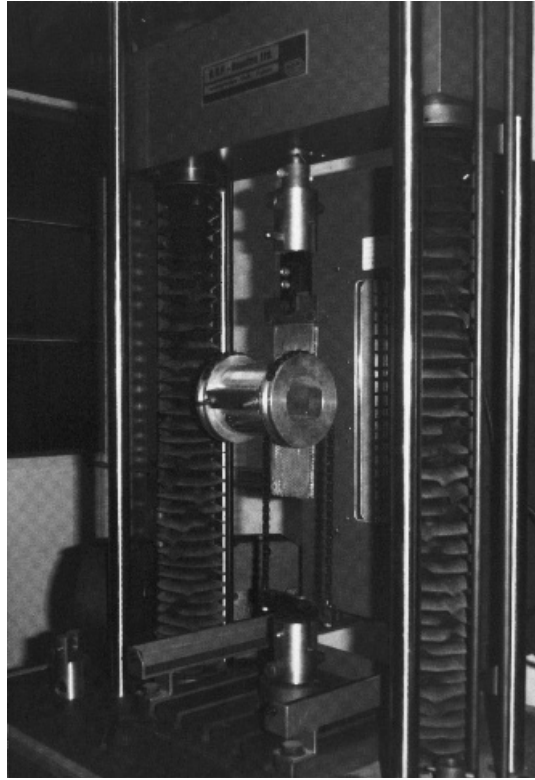


Fig. 1. Schematic representation of the climbing drum peel test



**Fig. 2.** Side view of a climbing drum peel test in which the skin of a honeycomb structure is being peeled away

force can be recorded and an average taken for calculation of the peel torque. Testing has shown that the frequency of the oscillations on the chart record can be related to the cell size of the honeycomb used. This test can result in a variety of failure modes and mixtures of them.

With care, this test can also be performed on honeycomb sandwich test pieces having thin fibreglass, Kevlar or carbon-fibre skins.

### *Failure modes*

Various modes of failure may be observed depending on the adhesive, the materials bonded and their surface pre-treatments (see **Stress distribution: mode of failure**). For metal–metal peeling, very effective surface treatment is necessary to achieve cohesive failure in the adhesive; otherwise, failure occurs at, or close to, one substrate surface.

Similarly, with aluminium honeycomb structures, failure may occur at the skin or the surface of the honeycomb itself, especially if the respective surface preparation is poor (see **Pre-treatment of aluminium**). Untreated aluminium alloy honeycomb can result in disbonding in service. The use of “anodized” aluminium alloy honeycomb is strongly recommended.

With appropriate pre-treatment, however, failure will occur either by tearing the honeycomb or cohesively in the adhesive fillet. The locus of failure will depend on the strength of the honeycomb itself: this in turn depends upon the thickness and strength of the alloy from which it is made.

“Nomex” honeycomb, made from aromatic nylon fibre in an aromatic polyamide resin, will also fail in the honeycomb if the adhesive bond is good.

### *Peel torque and peel strength*

According to ASTM D-1781, the results of the test should be expressed as the torque (per unit width) required to peel the strip. This is to be calculated from the load and dimensions of the apparatus: a formula is given in the standard. A test run using the drum alone is required to obtain the peel torque needed for the drum to climb in the absence of an adhesive. This may be carried out using a piece of strong fabric so that only the torque to climb the weight of the drum is measured, or a piece of metal skin of the same gauge and type as the test piece can be used. A significant torque can be required to bend the skin. It can be argued that, in practice, the forces required to separate the skin and honeycomb may include those required to bend the skin. In this case, the calibration torque obtained using fabric can be used.

Thus, there is a choice as to whether the peel torque calculated included the contribution needed to bend the flexible member. Circumstances will determine which is the more appropriate.

The peel torque is a satisfactory number to quote when comparing like systems, but it has no direct fundamental significance. It is straightforward to apply the energy-balance approach to the climbing drum test and to calculate a “peel strength”, that is, an energy of fracture during peeling per unit area from the peel force recorded and the dimensions of the apparatus (see **Peel tests**).

### *References*

1. G. C. Grimes, *Appl. Polym. Symp.*, No. 3, 157–190 (1966).
2. R. D. Adams and W. C. Wake, *Structural Adhesive Joints in Engineering*, Applied Science Publishers, London, 1984.
3. R. Houwink and G. Salomon, Eds., *Adhesion and Adhesives*, Vol. 1, *Adhesives*, Elsevier, Amsterdam, 1965.

---

## *Coextrusion*

R J ASHLEY

Lamination techniques allow the combination of several materials to form a multi-layer structure with properties superior to their component layers (see **Laminating**). However, adhesive lamination as a means of producing a multi-layer laminate generally involves several machine passes or expensive, large, complex multi-station laminators. In addition, these techniques generally rely on solvent-based materials, although some 100%



solids systems can be used in limited circumstances. There is often a time delay for cross-linking to occur before full bond strength is achieved. Environmental protection laws have challenged conventional techniques, and the coextrusion route to preparation of multi-layer structures has gained importance. Coextrusion allows the production of a laminate in a single process best suited to large volume outlets where a structure can be produced in continuous operation. The process is generally used for laminates composed of thermoplastic polymers, and a wide variety of structures can be made. Very thin layers of expensive polymers can be incorporated effectively. It finds application in the **Packaging industry**.

The coextrusion method can offer advantages over other lamination techniques in terms of cost because of the one-step process and ability to use expensive polymers in thin layers. As the process operates in the melt phase, wet adhesive materials and primers with drying and solvent removal can be avoided. Through selection of materials, gas or moisture barrier and superior mechanical properties can be provided. Selection of polymers with similar melting properties allows for some interfacial mixing for achieving good bond strengths, although functionally modified polymers may be required for chemical bonding.

Of particular relevance, is the ability to include a barrier polymeric layer such as poly(ethylene vinyl alcohol) [EVOH] within layers of polyethylene. Such a combination provides composites with good barriers to both moisture and oxygen while maintaining a transparent appearance.

The coextrusion operation may be applied to the standard processes used for film extrusion, that is cast or blown (tubular). In the process, two or more thermoplastic materials are extruded separately and combined either internally in the die or immediately after leaving the die in a feedblock or manifold unit and then to chill rollers. Thus, each polymer provides a distinct layer in the final complex. Two or more extruder barrels are connected to the multi-channel die and the flow rates adjusted to give plies of the film at the desired gauge. In a typical blown coextrusion line, the film is fed upwards through a circular die with air inserted into the tubular bubble to expand the structure, providing orientation in one direction. Control of the haul-off speed provides orientation in the other direction; hence, film may be referred to as biaxially oriented. In a variation of the blown process, the film is extruded downwards with the bubble cooled by water. Control of the cooling is critical to achieve desired polymer crystallization and clarity. Typical blown film coextrusion lines can provide films of up to 2 m width. Apart from clear film structures, the process may allow white pigmented or other colour layer options and variations to surface texture.

Adhesion between the plies is partially mechanical since the materials are molten when combined, but the major bond has to be chemical (see **Theories of adhesion**). Where compatible materials are used, such as low-density polyethylene or high-density polyethylene (LDPE/HDPE), strong bonds can be achieved between the layers without additional means (see **Compatibility**). However, where the wider opportunities to use coextrusion are taken and multi-layers conceived with non-compatible materials such as polyamides, polyolefins, polycarbonate and polyethylene vinyl alcohol, adequate adhesion may be difficult to achieve. In these circumstances, a specific polymeric layer may be used to act as a compatibilizing agent or **Tie layer**. A very thin layer of the extrudable adhesive has functional groups to enhance the chemical bonding at the interface.

Typical combinations may be of three or five layers such as LDPE/HDPE/LDPE or PP/tie layer/EVOH/tie layer/PP. There has been some use of coextrusion to replace monolayer films with the multi-layer complexes, often retaining the same overall thickness in order to provide laminates with higher mechanical properties. Use may also be made of some of the newer polymer grades such as linear low-density polyethylene (LLDPE) and metallocene technology as internal layers with the bulk being of cheaper polymers. This has been used for the production of high strength sacks and bags. Some of the laminates made are symmetrical in terms of materials used while others allow for non-symmetrical structures to achieve peel seal layer/barrier layer/mechanical strength. Applications include provision of slip, gloss or heat seal to a base polymer or a priming layer for addition of print coatings and metallization. One application for coextrusion is the production of multi-layer films with a total thickness of about 30–100 microns. Another application can be the assembly of multi-layer sheet with thickness of around 500–1000 microns including pigmented layers for subsequent thermoforming into trays and containers or for blow-moulded barrier plastic bottles.

The use of coextrusion in areas outside packaging has enabled very complex structures with many plies being built up at thin layers only microns thick. A typical equipment set-up will involve five extruder barrels feeding into the die unit.

One disadvantage is the ability to provide printed structures where the print layer is sandwiched as is often used with conventional adhesive lamination. A way around this is to use a combination of adhesive lamination and coextrusion coating such that the coextruded structure is assembled with a pre-printed web of film. In addition, other non-extrudable materials, such as paper and metal foils, can be combined.

Also, see **Extrusion coating**.

### Select Reference

R. J. Ashley, D. Briggs, K. S. Ford and R. S. A. Kelly, in *Industrial Adhesion Problems*, D. M. Brewis and D. Briggs, Eds., Orbital Press, Oxford, 1985, Chap 8.

---

## Compatibility

J COMYN\*

Compatibility is a measure of the ability of two substances to mix. If two compatible substances are placed in contact, then one of the following may take place.

1. The two substances completely mix to form a homogeneous mixture. An example is ethanol and water, which are miscible in all proportions.
2. One substance dissolved in the other to form a homogeneous mixture; an example is to place a sheet of rubber in benzene, when the solvent swells and mixes with the polymer.
3. Two separate phases are formed, but each phase is a mixture of two components. Under some conditions, phenol and water behave in this manner; one phase is a solution of water in phenol, and the other a solution of phenol in water.

*Conditions for compatibility*<sup>1,2</sup>

The condition for compatibility is that the Gibbs free energy for mixing is negative. The Gibbs free energy of mixing  $\Delta G_m$  is related to the enthalpy (heat) of mixing  $\Delta H_m$  and entropy of mixing  $\Delta S_m$  by the following equation, where  $T$  is the absolute temperature:

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad [1]$$

As mixing always increases disorder,  $\Delta S_m$  is positive so that the  $-T \Delta S_m$  term is always negative and therefore favours mixing. Whether mixing actually may occur, therefore, depends on the enthalpy of mixing, and of course, the most favourable situation is for this to be large and negative, in other words for a large amount of heat to be evolved on mixing.

It is, however, common where polymers are involved for the enthalpy term to be positive. The enthalpy expression for a “regular solution” of component 1 in component 2, often used in this context, is

$$\Delta H_m = V \phi_1 \phi_2 (a_1^{1/2}/b_1 - a_2^{1/2}/b_2)^2 \quad [2]$$

where  $a$  and  $b$  are constants from the van der Waals equation, the  $\phi$ 's are volume fractions and  $V$  is molar volume.

This approach to mixing is very abstract, and it is not possible to take values of the parameters from collections of data and then predict whether mixing may take place. Simpler and more practicable approaches are to compare chemical structures or to use solubility parameters. The first of these depends on the sound principle of “like generally dissolves like”, and it is successful in predicting the solubility of polyvinyl alcohol in water and of polystyrene in benzene but does not predict the insolubility of cellulose in water. The latter is an interesting case. The similarity of water and cellulose is that they contain hydroxyl groups, but cellulose is prevented from dissolving in water because it is cross-linked by hydrogen bonds. However, this does not mean that they are incompatible; indeed, cellulose in the form of cotton absorbs about a quarter of its own weight of water from saturated air.

Solubility parameter  $\delta$  is a measure of the energy required to separate the molecules of a liquid, and is given by Eqn. 3, where  $\Delta U_E$  is the change in internal energy on evaporation,  $\Delta H_E$  the enthalpy of evaporation,  $R$  the gas constant,  $T$  the absolute temperature and  $V_m$  the molar volume:

$$\delta = (\Delta U_E/V_m)^{1/2} = ([\Delta H_E - RT]/V_m)^{1/2} \quad [3]$$

Solubility parameters of liquids can be calculated from experimentally measured values of  $\Delta H_E$  and  $V_m$ . In contrast, the vapour state is inaccessible to polymers, so  $\Delta H_E$  cannot be measured; they can, however be estimated by one of the group contribution methods,<sup>3</sup> or by measuring the swelling of a polymer in a range of solvents and taking the position that the highest swelling occurs in the solvent most similar to the polymer in the value of its solubility parameter.

Equation 2 can be rewritten as

$$\Delta H_m = V \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad [4]$$

which shows the significance of solubility parameters: the closer the values for two substances, the more likely they are to be compatible. Improvements in prediction can be gained if comparisons of **Hydrogen bonding** and dipole moment are also made.<sup>2</sup>

Some values of  $\delta$  for a range of solvents are given in Table 1, and some for some common polymers appear in Table 2. In both cases, substances are listed in order of increasing solubility parameter.

### *Compatibility in the context of adhesion*

Compatibility is an issue of relevance in a number of aspects of adhesion. Perhaps, the most obvious is the selection of solvents in the making of a **Solvent-based adhesive**, or for **Solvent welding** of thermoplastics. In both cases, solubility parameters can be employed.

If an adhesive joint has to survive in the presence of a particular liquid, then the solubility parameter can be used to indicate adhesives that would not swell.

The majority of adhesives contain various components added to the base polymer, so the question of compatibility is one of major importance.

It is often obvious that the retention of additives, such as tackifiers in **Pressure-sensitive adhesives**, plasticizers in PVC and antioxidants in many polymers, is essential for making

*Table 1.* Solubility parameters of some solvents

Solvent	$\delta/(\text{MPa})^{1/2}$
Aliphatic fluorocarbons	11.3–12.7
Diethyl ether	15.1
Octane	15.6
Dioctyl phthalate	16.2
Tricresyl phosphate	17.2
Toluene	18.2
Ethyl acetate	18.6
Benzene	18.8
Trichloromethane	19.0
Tetrachloroethene	19.0
Acetone	20.3
Dimethylformamide	21.7
Ethanol	26.0
Ethane diol	29.9
Water	47.9

*Table 2.* Solubility parameters of some polymers

Polymer	$\delta/(\text{MPa})^{1/2}$
Polytetrafluoroethylene	12.7
Polyethylene	16.0–16.4
Natural rubber	16.2–17.0
Polymethylmethacrylate	18.6–19.5
Polyvinyl acetate	19.2
Polyvinyl alcohol	25.8
Cellulose	32.0

the adhesive and for successful functioning in service. Less obvious is the danger of the migration of additives to the adhesive–substrate interface, forming a weak boundary layer to the detriment of adhesion, either during application or service (see **Surface nature of polymers** and **Environment and the impact of adhesive technology**).

On the other hand, some additives are designed with an incompatibility, which causes them to migrate to the interface. **Silane adhesion promoters** in thermoset resins and internal **Release** agents are examples. A deeper issue than these, however, is compatibility between polymers at an interface. It is fundamental to the concepts which underlie the **Diffusion theory of adhesion**, which depend on the ability of polymer chains at an interface to mix by interdiffusion, and to the welding of polymers, which occurs in so many moulding processes (**Polymer–Polymer Adhesion: Weld Strength**). Where the polymers each side of the interface are identical, there will be, of course, complete mixing at thermodynamic equilibrium (see **Polymer diffusion: Reptation and interdigitation** and **Polymer–Polymer Adhesion: Models**). However, even polymers that are chemically very similar often do not mix. This is because, although the entropy of mixing is negative, enthalpies of mixing are often small and positive, making the Gibbs free energy of mixing positive.

This said, it is now recognized that despite this bulk thermodynamic incompatibility, an atomically sharp interface between two incompatible polymers will not be stable.<sup>4</sup> Some interpenetration will occur, because, although there is an enthalpy debt to be paid, there is an entropy gain (**Polymer–polymer adhesion: Incompatible interfaces**).

There are, however, a number of instances in which interfacial diffusion has been demonstrated experimentally between differing polymers; they include the following: polyvinylchloride and polycaprolactone; polyvinylchloride and polymethacrylate; polyvinylchloride and styrene–acrylonitrile copolymer; polyvinylidene fluoride and polymethylmethacrylate. Nevertheless, the thermodynamic incompatibility of so many polymers is a fundamental problem in the making of polymer blends.<sup>1,2</sup>

### References

1. Y. S. Lipatov and A. E. Nesterov, *Thermodynamics of Polymer Blends*, Technomic, 1997.
2. S. Datta and D. J. Lohse, *Polymeric Compatibilizers*, Hanser, 1996.
3. E. A. Grulke, in *Polymer Handbook*, 4th edn, J. Brandrup, E. H. Immergut and E. A. Grulke, Eds., A. Abe and D. R. Bloch, associate editors, Wiley, New York, Chichester, 1999, p. VII 675.
4. R. P. Wool, *Polymer Interfaces: Strength and Structure*, Hanser, 1995.

---

## Composite materials

D E PACKHAM

If the term “composite material” is applied loosely to encompass any material consisting of two or more phases, its scope is very wide. The vast majority of materials come into this category, both those developed technologically and those occurring naturally. Some polymers, many alloys and most ceramics comprise more than one phase, as do concrete and timber, the most widely used constructional materials.

The properties of these materials depend not only on the properties of the individual phases but also on the adhesion between them. The influence of this interfacial adhesion is multifarious. High adhesion may give rise to high mechanical strength, but lower adhesion in a similar material may give greater fracture energy. If the adhesion between phases can be modified, there is scope for developing materials with a range of properties and applications.

Many of the entries in this book dealing with the science of adhesion and **Theories of adhesion** are relevant to composition materials in general. There are a number of articles that discuss specific aspects of composite materials that come within the scope of this book. **Toughened adhesives**, particularly **Epoxide adhesives** and **Toughened acrylics**, consist of polymers with a rubbery phase dispersed as small spheres within a more glassy matrix.<sup>1,2</sup> Appropriate adhesion between the phases is crucial for effective toughening.

Dispersion of inorganic particles gives rise to filled polymers. A wide variety of properties can be achieved, depending on the filler and its adhesion to the matrix.<sup>3</sup> See **Filler-matrix adhesion**. The scope of application of rubbers is enormously extended by use of fillers that can give increased strength, stiffness and abrasion resistance to the material (see **Rubber fillers**).

Fibre compositions represent a class of composite material that combines low weight with good mechanical properties.<sup>4,5</sup> Usually, a strong and stiff fibre, such as glass or carbon, is incorporated in a polymer matrix.

Several articles are included on different aspects of **Fibre-matrix adhesion** in these materials. Special techniques are required for **Fibre composite joining**.

The application of coupling agents to an inorganic surface provides a powerful way of affecting the bonding properties of the surface. This plays an important part both in filled polymers and (see **Fibre composites – introduction**).

Attention is also drawn to articles on textiles and wood, both of which may be regarded as composite materials.

## References

1. B. S. Munteanu, M. Brebu and C. Vasile, in *Handbook of Polymer Blends and Composites*, Vol. 4A, A. K. Kulshreshtha and C. Vasile, Eds., RAPRA Technology, 2003, p. 121.
2. B. Kothandaraman and A. K. Kulshreshtha, in *Handbook of Polymer Blends and Composites*, Vol. 4B, A. K. Kulshreshtha and C. Vasile, Eds., RAPRA Technology, 2003, p. 411.
3. C. Vasile, A. Grigoriu and V. Blascu, in *Handbook of Polymer Blends and Composites*, Vol. 1, A. K. Kulshreshtha and C. Vasile, Eds., RAPRA Technology, 2002, p. 39.
4. B. Harris, *Engineering Composite Materials*, 2nd edn, Institute of Materials, 1999.
5. D. Hull and T. W. Clyne, *An Introduction to Composite Materials*, 2nd edn, Cambridge University Press, 1996.

---

## Contact adhesives

---

J M MARTÍN-MARTÍNEZ

A general introduction has been given in other articles, **Rubber-Based Adhesives** and **Rubber-based Adhesives: Typical Characteristics**. Here, one of the most common types of rubber adhesives, contact adhesives, is further considered. Contact adhesives are bonded

themselves by a diffusion process in which the adhesive is applied to both surfaces to be joined. To achieve optimum diffusion of polymer chains, two requirements are necessary: (1) a high wettability of the adhesive by the smooth or rough substrate surfaces, (2) adequate viscosity (in general rheological properties) of the adhesive to penetrate into the voids and roughness of the substrate surfaces. Both requirements can be easily achieved in liquid adhesives. Once the adhesive solution is applied on the surface of the substrate, spontaneous or forced evaporation of the solvent or water must be produced to obtain a dry adhesive film. In most cases, the dry contact adhesive film contains residual solvent (about 5–10 wt%), which usually acts as a plasticizer. The time necessary to produce evaporation is called *drying time*, and it can be easily measured by touching the adhesive surface with a finger under light pressure; the drying time will be obtained when the adhesive does not stick to the finger.

Environmental conditions under which solvent release from the adhesive on the substrate is produced must be carefully controlled (see **Environment and the impact of adhesive technology**). Humidity is critical because loss of heat due to solvent evaporation may allow reaching the dew point (the evaporation of the solvent is an endothermic process), and then condensation of water on the adhesive can be produced (*moisture blooming*). The presence of water on the adhesive film causes a detrimental effect because the autoadhesion of rubber chains is greatly inhibited.

The dry adhesive films on the two substrates to be joined must be placed in contact to develop adequate autoadhesion, for example, diffusion of polymer rubber chains must be achieved across the interface between the two films to produce intimate adhesion at molecular level. The application of pressure and/or temperature for a given time allows the desired level of intimate contact (coalescence) between the two adhesive film surfaces. Obviously, the rheological and mechanical properties of the rubber adhesives will determine the degree of intimacy at the interface. Those properties can be optimized by selecting the adequate rubber grade, the nature and amount of tackifier and the amount of filler, among other factors.

The *open time* is the time by which the coalescence between two identical adhesive films drops to an unacceptable level, that is, the time after which autoadhesion and diffusion cannot be adequately produced. During the open time, several changes in the adhesive films are produced because of the loss of residual solvent, which affects the viscoelastic properties of the film (loss of plastification) and the crystallization of the rubber chains.

Natural rubber adhesives were traditionally used as contact adhesives. However, synthetic polymers are more generally used today. Polychloroprene adhesives are the most common contact adhesives based in synthetic rubber, although they recently have been displaced by polyurethane and acrylic polymers.

Further information on rubber-based adhesives is to be found in specialized articles: **Natural Rubber-Based Adhesives**, **Nitrile Rubber Adhesives**, **Polychloroprene Rubber Adhesives: Applications and Properties** and **Polychloroprene Rubber Adhesives: Modifiers and Additives**.

### Select References

- I. Skeist, Ed., *Handbook of Adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990, Several chapters.
- J. M. Martín-Martínez, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 573–675.

---

## Contact angle

---

J F PADDAY\*

### *The nature of the contact angle*

The contact angle<sup>1,2</sup> is an angle measured at the triple-phase line, between the tangents at the two surfaces of the advancing liquid; see Fig. 1 of **Wetting and spreading** for an example. The angle that is measured is a macroscopic quantity usually part of a capillary system that makes the angle measurable without much magnification. The thermodynamic contact angle used in Young's Eqn. 1 (see **Wetting and spreading**) and equations related to it (e.g. Eqns. 5–8 in **Wetting and work of adhesion**) is a microscopic quantity that is assumed to equal the measured value:

$$\gamma_{13} - \gamma_{12} = \gamma_{23} \cos \theta \quad [1]$$

Unseen surface inhomogeneities very often occur at a microscopic level and cause variations of contact angle according to whether the liquid is advancing  $\theta_a$  or receding  $\theta_r$ ; such variations caused by the triple-phase line finding contact with different effective surface energies of the solid. Such contact angle hysteresis means that measured values cannot be relied upon unless the cause of such hysteresis is known or determined. Various causes are recognized. The system may not have reached equilibrium, either thermodynamically (the triple-phase line may be moving very slowly) or thermally. A rough or porous surface gives rise to hysteresis. Heterogeneity is another cause. This may take the form of contamination with patches of material of differing surface energy or of islands of electrical charge on an insulator. Surface-active contaminants in the wetting liquid may be adsorbed on the surface: such contaminants may be in solution or in the form of microdrops of insoluble surfactant. Finally, if the liquid reacts with the solid, surface hysteresis will be observed.

The principle of measuring both advancing and receding angles and using their arithmetic mean as the thermodynamic mean is justified only when the hysteresis is produced by a regular array of inhomogeneities such as with certain types of roughness. Large unexplained differences between advancing and receding contact angles suggest that the system is not properly characterized.

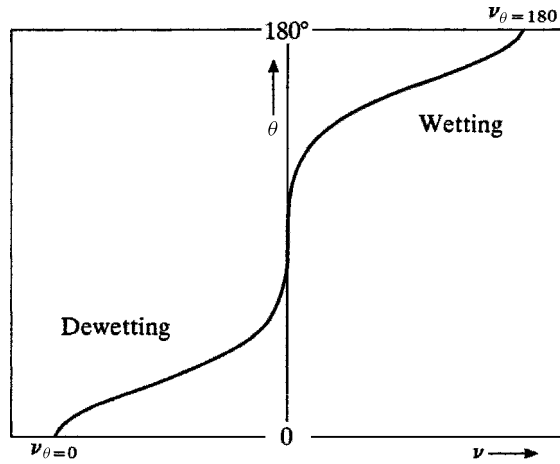
### *Contact angle at a moving line*

Contact angles are formed with wetting systems only. The liquid wetting the solid can be forced to spread by the application of some external force so as to produce "dynamic wetting", not to be confused with spreading. Further, in many systems the wetting liquid, once spread artificially, can remain in place after the external force is removed, providing the hysteresis is sufficiently large.

Dynamic wetting (**Wetting kinetics**) has been studied extensively,<sup>3</sup> and the main feature is that the contact angle changes with the speed at which the wetting line is forced across the solid surface as shown in Fig. 1. Here, it is noted that both wetting and dewetting can be forced on a system with a small amount of contact angle hysteresis.

At very low wetting speeds, the triple-phase line moves erratically with stick – slip movement, thereafter the angle increases continually with speed for the advancing line





**Fig. 1.** Contact angle as a function of the speed of wetting line movement (after reference 3)

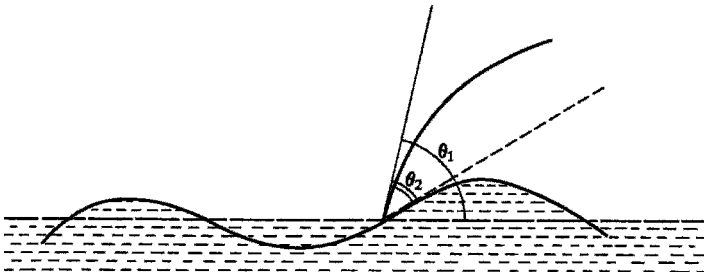
and decreases continually for the receding line until 180° or 0° is reached for each condition, respectively. Further speed increases for either advancing or receding lines result in the break-up of the line so as to form a serrated or “saw-tooth” wetting line.

*Contact angle and roughness*

The effect of roughness of the solid surface is to increase the actual area of contact between solid and liquid and also that of the unwetted solid per unit geometric area. The roughness factor,  $r$ , is defined as the real area of the solid divided by this geometrical area described by a boundary. Wenzel therefore proposed that Young’s Eqn. 1 be modified as follows:<sup>1</sup>

$$r(\gamma_{13} - \gamma_{12}) = \gamma_{23} \cos \theta \tag{2}$$

Hysteresis arises from roughness mainly because the wetting line sees a different effective macroscopic contact angle arising from the slope at the position in the groove of the wetting line, which is different for advancing and receding conditions. For each condition, the microscopic contact angle remains the same as seen in Fig. 2.



**Fig. 2.** Macroscopic,  $\theta_1$  and microscopic,  $\theta_2$ , contact angles

When the pore size of the roughness approaches molecular dimensions, the roughness factor requires modification to account for the adhesion forces changing with distance from the solid surface.

Roughness will affect spreading and wetting, and so all the equations (1–8) discussed in **Wetting and work of adhesion** require modification by the roughness factor. As spreading coefficients and the corresponding wetting energies can be positive or negative, the effect of  $r$  is to increase contact angles greater than  $90^\circ$  and decrease those less than  $90^\circ$ .

### *Contact angle and surface energy of the solid*

The spreading coefficient and the wetting energy depend critically on the magnitude of the surface energy of the solid<sup>2</sup> or the array of molecules nearest to the wetting or spreading liquid. Metals, some metal oxides and some non-metal oxides such as silica possess very high surface energies and thereby encourage spreading because the work of adhesion is large. Platinum metal forms such a surface at which most liquids spread spontaneously at room temperature.

Low-energy solids such as those of polyethylene and polytetrafluoroethylene do not encourage spreading and are termed *hydrophobic*. All these low-energy surfaces possess works of adhesion that are positive but less than the work of cohesion of the liquid, as already noted. When such low-energy solid systems possess very little hysteresis, they are described as *abhesive* because the liquid may be pulled away from the solid with ease (see **Release**).

### *Surface contamination*

The most common cause of contact angle hysteresis arises from heterogeneous contamination of the solid with islands of adsorbed or smeared low-energy impurities. High-energy surfaces attract such contamination more readily than low and often exhibit the surface of low-energy surfaces. Metals also may possess islands of oxidation that induce hysteresis. Low-energy surfaces, on the other hand, can also acquire contamination, more often with surface-active material that is amphipathic in nature.

The effect of surface-active material dissolved in the wetting liquid is to adsorb at the liquid–solid interface and decrease the interfacial tension by a large amount. Such adsorption is usually irreversible in that when the liquid is removed, a monolayer of the surfactant remains, which further adds to the hysteresis, especially so when the surfactant is an adsorbed polymer or macromolecule. The removal of surface contamination with consequent enhancement of surface energy and lowering of contact angle is a major objective of pre-treatment prior to adhesive bonding, painting or printing. Details may be found in the many articles with titles starting “Pre-treatment. . .”.

### *References*

1. A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, 6th edn, Wiley, New York, Chichester, 1997.
2. K. L. Mittal, Ed., *Contact Angle, Wettability and Adhesion*, VSP, Utrecht, 1993.
3. T. D. Blake, in *Wettability*, J. C. Berg, Ed., Marcel Dekker, New York, 1993. p. 251.

---

## Contact angle measurement

---

J F PADDAY\*

### General

The macroscopic **Contact angle**,  $\theta$ , is of considerable importance in wetting studies and, in principle, is readily measured.<sup>1,2,3</sup> The experimentalist must recall that it is measured within the advancing liquid phase. In principle, four methods of contact angle measurement are known. They are as follows

1. Direct geometric measurement;
2. Calculation from measured capillary shape properties of the system;
3. Measurement using a force balance and comparison with the surface tension;
4. Calculation from intermolecular forces.

The first three methods involve determining the macroscopic angle, whereas the fourth involves the microscopic angle. The problems of possible hysteresis are associated with the first three only and demand that both advancing and receding angles be measured several times on the same patch of solid surface. Also, the surface tension of the spreading liquid should be measured both before and after wetting or spreading so as to ensure no contamination of the liquid by interaction with the solid.

### Direct geometric measurement

Direct measurement consists of capturing an image of the three surfaces at the triple-phase line of systems shown in Fig. 1.

Very often, a reflected image of the liquid–fluid interface is seen at the solid surface, and this makes it unnecessary to determine the plane in which the solid surface lies as the angle measured is that between the liquid–liquid surface and its reflected image. Lighting the meniscus at the triple-phase boundary has been solved satisfactorily, the main problem being the interference fringe produced at a curved surface. This problem is particularly difficult when the contact angle is small ( $<25^\circ$ ). Controlled interference methods and Moiré fringes may be used to obtain greater precision. Lahooti *et al.*<sup>4</sup> discuss the effects of drop size and time-dependency on contact angle measurement.

### Capillary shape methods

The availability of high-speed computing and data processing has led to the development of indirect methods from geometric measurements of capillary shape. However, some of these methods require knowledge of the capillary constant or the values of the properties that go to make it up.

A well-known example of this method is that of measuring the radius and height of a sessile drop and then with knowledge of the capillary constant, estimate the best fit of contact angle using the tables of Bashforth and Adam. A simpler method is to determine the spreading of coefficient from the limiting height  $h$  of a very large sessile drop of

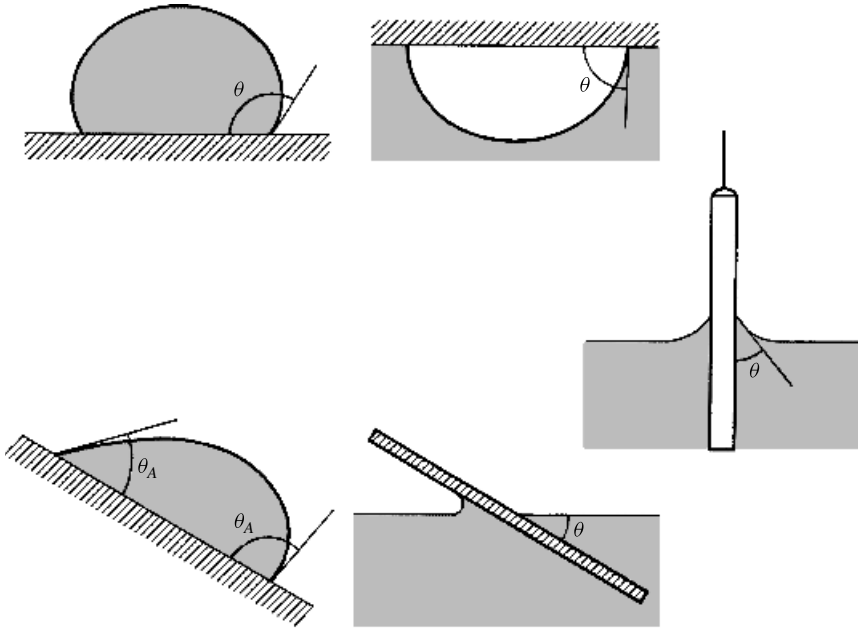


Fig. 1. Methods of measuring the contact angle

density  $\rho$ . The relationship to contact angle is given by

$$S_{C_{123}} = -\rho g h^2 / 2 = \gamma_{23} (\cos \theta - 1) \quad [1]$$

See **Wetting and work of adhesion** for the relation between spreading coefficient  $S_{C_{123}}$ , surface tension  $\gamma_{23}$  and contact angle  $\theta$ . As such limiting conditions are reached only when the drop is about 1-m diameter, it is easier to determine the height of a smaller drop and multiply the numerator by a factor,  $F$ , the value of which is determined by the ratio of two linear shape properties such as height and maximum diameter.<sup>1</sup> The contact angle is then derived from the spreading coefficient with a knowledge of the surface tension. When the capillary constant,  $a$ , given by

$$a^2 = 2\gamma_{23} / \rho g \quad [2]$$

is known, the reduced spreading coefficient is given by

$$S_{C_{123}} / \gamma_{23} = -h^2 / a^2 = (\cos \theta - 1) \quad [3]$$

#### Force balance method

The measurement of the surface tension of a liquid by the Wilhelmy – the force balance method – is widely used and well documented.<sup>1</sup> The same apparatus may be used to

measure the wetting energy directly by replacing the Wilhelmy plate ( $\theta = 0^\circ$ ) with a similar plate made of the solid to be wetting. Let the perimeter of the plate along the triple-phase line be  $L$ , and the force be  $F$ , then

$$F = \gamma_{23}L \cos \theta \quad [4]$$

Experimentally, the surface tension is measured first using a clean platinum plate. Next,  $F$  is determined for the experimental surface with a finite contact angle and finally the surface tension once again. If advancing and receding values are required, a buoyancy correction must be made to compensate for the upthrust, as the bottom edge of the plate becomes lower than the free surface of the liquid.

### References

1. J. F. Padday, *Surface and Colloid Science*, Vol. 1, E. Matejevic, Ed., Wiley-Interscience, New York, 1969, pp. 39–251.
2. A. W. Neumann and R. J. Good, *Surf. Colloid Sci.*, **11**, 31 (1979).
3. R. J. Good, in *Contact Angle, Wettability and Adhesion*, K. L. Mittal, Ed., VSP, Utrecht, 1993, p. 3.
4. S. Lahooti, O. I. del Rio, P. Cheng and A. W. Neumann, in *Applied Surface Thermodynamics*, A. W. Neumann and J. K. Spelt, Eds., Marcel Dekker, New York, 1996, p. 441.

## Contact angles and interfacial tension

---

D E PACKHAM

It seems inherently reasonable that the energy of an interface (interfacial tension) between phases 1 and 2 should be related to the individual values of **Surface energy**,  $\gamma_1$  and  $\gamma_2$ : the same molecules are responsible for each. If there actually is an interface between 1 and 2, it is, *ipso facto*, stable, so Eqns. 1 or 2 must apply

$$\gamma_{12} < \gamma_1 + \gamma_2 \quad [1]$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - \Delta \quad [2]$$

where  $\Delta$  is positive and represents the stability of the interface with respect to separate phases 1 and 2. The value of  $\Delta$  will depend on the type of bonding across the interface.

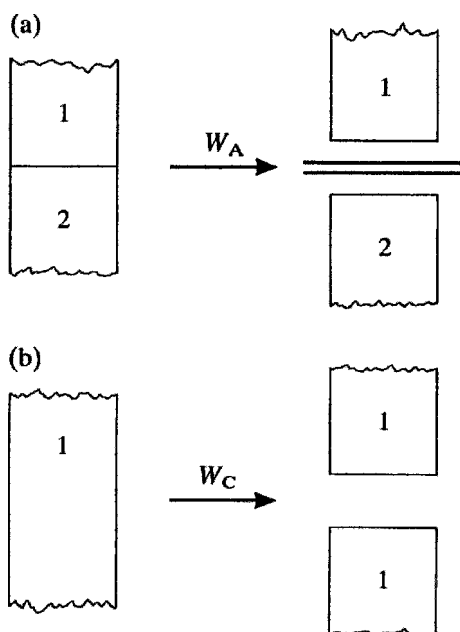
For secondary bonds, **Dispersion forces**, **Polar forces** and **Hydrogen bonding**, various explicit forms of Eqn. 2 have been proposed. Their use requires familiarity with Young's equation and the definition of the work of adhesion and the work of cohesion (Fig. 1), discussed in **Wetting and spreading**. It is convenient to quote these relationships here:

$$\gamma_{13} = \gamma_{12} + \gamma_{23} \cos \theta \quad [3a]$$

$$\gamma_{SF} = \gamma_{SL} + \gamma_{LF} \cos \theta \quad [3b]$$

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \quad [4]$$

$$W_{C_1} = 2\gamma_1 \quad [5]$$



**Fig. 1.** Representatives of the changes for which (a) work of adhesion and (b) work of cohesion are the changes in free energy

The subscripts 1 or S, 2 or L and 3 or F refer to the three phases; the letters will be used when it is desirable to refer specifically to solid S, wetting liquid L and fluid (vapour or second liquid) F.

Note that the work of adhesion is defined here as the free energy change required to separate phases 1 and 2 cleanly along the interface and to place each in a separate vacuum enclosure (Fig. 1a). It is sometimes defined in a subtly different way, see **Wetting and work of adhesion**, Eqns. 1 and 4.

It is important to realize that the work of adhesion and work of cohesion defined by Eqns. 4 and 5 refer to the hypothetical changes described: they may not, and usually will not, be closely related to practical measures of fracture energy of an adhesive bond or of a single-phase material. This is because in the context of practical fracture, much larger amounts of work are dissipated by other mechanisms, such as the plastic deformation of the materials around the fracture zone.

There is a significant difference between the terms for the solid surface energy in Young's equation,  $\gamma_{13}$  or  $\gamma_{SF}$  and  $\gamma_1$  and in Eqn. 4 of work of adhesion  $W_A$ . This is because in the former case, the solid is in equilibrium with phase 3, which may well be air saturated with vapour of liquid 2 (see **Wetting and spreading** especially Fig. 1 therein), but for the latter the solid is *in vacuo*. The difference between these two terms is the spreading pressure, see **Surface characterization by contact angles – polymers**.

Knowledge of interfacial tensions is of interest because of their direct theoretical and (less direct) practical relationship to adhesion (see **Adsorption theory of adhesion, Peel tests, Adhesion – fundamental and practical**). Three somewhat different approaches to estimating interfacial tensions by Eqn. 2 are commonly found in discussions

of adhesion. These are discussed in articles on **Good-Girifalco interaction parameter**, **Surface energy components** and **Acid–base interactions**.

### Select References

- J. C. Berg, Ed., *Wettability*, Marcel Dekker, New York, 1993.  
 K. L. Mittal, Ed., *Contact Angle, Wettability and Adhesion*, VSP, Utrecht, 1993.  
 A. W. Neumann and J. K. Spelt, Eds., *Applied Surface Thermodynamics*, Marcel Dekker, New York, 1996.  
 J. Comyn, *Adhesion Science*, Royal Society of Chemistry, 1997.

---

## Conversion coating

---

G W CRITCHLOW

Conversion coatings, commonly used in **Pre-treatment of metals prior to bonding**, are formed by a chemical reaction between an aqueous media, usually containing soluble metal salts, and a substrate to produce an insoluble passivating film. They may be chemical or electrochemically produced; when produced with an externally applied voltage, an anodic oxide is formed (see **Anodizing**).

The most commonly used types of conversion coatings are phosphates and chromates or a process based upon a combination of these two.<sup>1</sup> More recent developments have been in zirconium- and titanium-based chemistry<sup>2</sup> along with cerium-based processes.<sup>3</sup> The impetus behind the more modern conversion coatings is the replacement of hexavalent chromium, which is used in many conventional processes. Conversion coatings have been applied to most metals; the most amenable metals along with a number of applications are given in Tables 1 and 2.

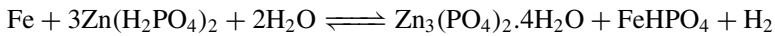
Conversion coatings, in particular phosphates, have been in existence for over a hundred years and have been extensively used since the 1930s. Conversion coatings can vary widely in thickness from a few nanometres to many micrometres with widely varied chemistry. These films tend to comprise highly complex hydrated metal oxides. Their precise chemistry can be difficult to determine or control as this is a function of many variables such as substrate type, solution composition, pH, temperature and time.

Phosphating is possibly the most widely used and useful general-purpose conversion coating process for adhesion promotion (see **Pre-treatment of steel** and **Pre-treatment of metals prior to painting**). It is used in **Rubber to metal bonding-pre-treatments**. Phosphate conversion coating solutions are based upon orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , and the primary phosphates of metals such as zinc, manganese or iron. In general terms, the deposition of a phosphate conversion coating is described by the following reaction<sup>1</sup>



The reaction is driven to the right-hand side by increased temperature and a reduction in pH. In more detail, if metal  $\text{M}^1$  is being coated in a solution containing the primary phosphate  $\text{M}^2$ , phosphates of  $\text{M}^2$ , for example  $\text{M}^2\text{HPO}_4$ , enter the coating with phosphates

of  $M^1$ . Also, phosphates of  $M^1$  enter solution and build up. Consequently, where  $M^1$  and  $M^2$  are divalent cations, the coating comprises hydrated forms of the following:  $M^1HPO_4$ ,  $M^2HPO_4$ ,  $M^1_3(PO_4)_2$  and  $M^2_3(PO_4)_2$  while the following products remain in solution:  $M^1(H_2PO_4)_2$  and  $M^2(H_2PO_4)_2$ . To illustrate this, following is a proposed reaction scheme for the zinc phosphate reaction with iron, although similar chemistry results from iron and manganese phosphate solutions:



Note that this is a highly simplified view; in reality, insoluble secondary and tertiary phosphates, oxides and hydrated material are deposited at the metal–substrate interface. The partially soluble material form an undesirable “sludge” in the processing tank.

For phosphating, a typical bath will comprise free phosphoric acid, metal phosphate and an accelerator, which might be a heavy metal salt, for example copper or nickel or an oxidizing agent. With the use of chemical or physical process acceleration, conversion coatings offer the advantage of relatively short processing times. Typical processes require a few seconds or tens of seconds to completion compared with tens of minutes for anodizing processes. These reduced timescales make conversion coatings attractive for coil-to-coil applications.

The range of structural and chemical properties provided by the many conversion coating processes is reflected in the functionality of conversion coated surfaces. In broad terms, conversion coatings offer surface passivation; increased adhesion to paints or structural materials; and improved tribological performance. Commonly found substrate-coating combinations are given in Table 1.<sup>1</sup>

The range of applications of conversion coatings is extensive; a few examples are given in Table 2.<sup>1</sup>

Conversion coatings offer many of the features identified as being desirable on a properly pre-treated metal surface; consequently, they have been applied to a range of metals for the enhancement of structural adhesion. A number of studies have demonstrated that properly optimized conversion coatings are comparable to the anodic oxides in terms of providing durability with aluminium.<sup>4</sup> Other studies have demonstrated variable adhesion performance with conversion coated aluminium adherends.<sup>5</sup> A recent study has shown phosphated medium carbon steel to give better bond durability than grit-blasted and silane-treated material.<sup>6</sup>

One issue might be the removal of the weakly bound water of crystallization invariably associated with the thicker films. For low temperature curing of applied organics, for

Table 1. Common substrate-coating combinations<sup>1</sup>

Type of coating	Substrate
Phosphate	Iron, zinc, tin
Chromate	Iron, zinc, tin, aluminium, cadmium, magnesium
Oxalate	Iron, steel, nickel
Black oxide	Iron



Table 2. Range of application of conversion coatings<sup>1</sup>

Substrate	Application
Zinc	Pre-paint
	Electronic racks
	Hardware
	Automotive parts
Aluminium	Pre-paint
	Lacquering
	Canning
	Honeycomb materials
Iron/Steel	Pre-paint
	Wire drawing
	Automotive parts

example paints, lacquers or adhesives, decomposition of the usually hydrated conversion coating is not a problem. However, above 120 to 140 °C, possibly during the cure of a single part epoxide, significant water loss can occur, potentially leading to voids present in the organic layer.

In circumstances where corrosion protection is required, chromate-based rinses are commonly applied to other conversion-coated surfaces to improve corrosion performance in applications such as pre-paint. Typically, corrosion resistance is improved by 100% with a phosphate/chromate rinse compared to that with the phosphate alone. This is reflected in measurably improved adhesion performance and reduced paint blistering.

### References

1. D. B. Freeman, *Phosphating and Metal Pre-treatment*, Woodhead Faulkner Ltd, 1986, ISBN 85941-299-7.
2. T. Schram, G. Goeminne, H. Terry, W. VanHoolst and P. VanEspen, *Trans. IMF*, **73**(3), 91–95 (1995).
3. S. M. Cohen, *Corrosion*, **51**(1), 71–78 (1995).
4. P. G. Selwood, A. Maddison and P. G. Sheasby, *Structures fabricated from aluminium components and processes involved in making these structures*, UK Patent GB 2 139 540, Published 14 November 1984.
5. J. D. Minford, *Handbook of Aluminum Bonding Technology and Data*, Marcel Dekker, 1993. ISBN 0-8247-8817-6.
6. G. W. Critchlow, P. W. Webb, C. J. Tremlett and K. Brown, *Int. J. Adhes. Adhes.*, **20**, 113–122 (2000).

---

**Corona discharge treatment**

---

D BRIGGS

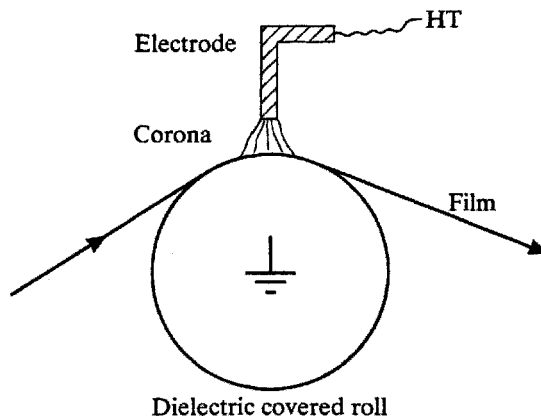
Corona discharge treatment is a form of **Plasma pre-treatment**, operated at atmospheric pressure, used widely for enhancing the adhesive characteristics of plastic materials. It is very widely used for treating plastic films (specially polyolefin films) and conical containers (tubs) but also finds application in other areas such as wire coatings and moulded composite parts.

Illustrated in Fig. 1 is the process for film treatment. The film is passed over an earthed metal roller that is covered with an insulating material (the “dielectric sleeve”). Separated from the film by  $\sim 1\text{--}2$  mm is a metal electrode, usually made from aluminium. A high-frequency (typically 10–20 kHz) generator and step-up transformer provides a high-voltage (peak typically 20 kV) to this electrode.

In each half cycle, the applied voltage increases until it exceeds the threshold value for electrical breakdown of the air gap, when the air is ionized and becomes plasma. Thus, each cycle involves current flow in each direction. In continuous operation, the discharge appears to be a random series of faint sparks (streamers) superimposed on a blue–purple glow. Discrete intense sparks are also often seen originating from localized regions of the electrode, so “corona” is not an exact description for this discharge.

The ionized air consists of ions, electrons, excited neutrals and photons in the UV-visible region. All of these are energetic enough to break C–C and C–H bonds to form radicals that via subsequent radical oxidation chemistry yield a variety of oxygen functionalities on the surface.

Taking a polyethylene surface as an example, this change in surface chemistry leads to significant increases in **Surface energy** (from 31 up to 50  $\text{mJ m}^{-2}$ ) and, hence, **Wettability and spreading** and also to a capacity for specific interactions with adhesives, inks, coatings, and so on. Particularly important seems to be the **Hydrogen bonding** capacity of enolic –OH groups, which can be formed via tautomerization of ketonic groups (–CH<sub>2</sub>CO–). Both factors are important in improving surface adhesive properties.



**Fig. 1.** Schematic diagram of the electrical discharge treatment process

The degree of surface change is a function of operating parameters such as the exposure time and the discharge power (and efficiency of coupling power from the generator into the discharge); the latter is itself related to the frequency, discharge gap, electrode cleanliness, and so on. Additive bloom to a plastic surface inhibits these changes and requires higher treatment levels to “burn off” this material so that the underlying surface can be oxidized.

### *Select References*

- M. Strobel, M. J. Walzak, J. M. Hill, A. Lin, E. Karbasheski and C. S. Lyons, A comparison of gas-phase methods of modifying polymer surfaces, in *Polymer Surface Modification*, K. L. Mittal, Ed., VSP, Utrecht, 1995, Part 3.
- T. Uehara, Corona discharge treatment of polymers, in *Adhesion Promotion Techniques*, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, New York, 1999, Chap 7.

## *Creep*

A D CROCOMBE

### *Introduction*

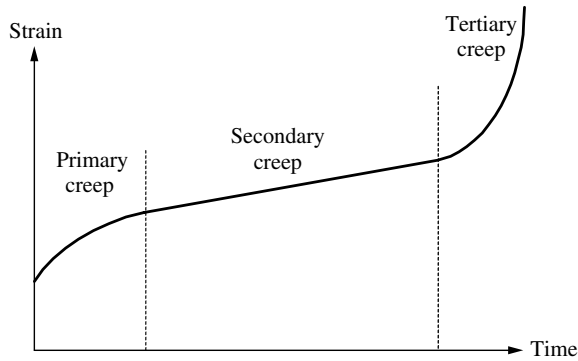
This short article begins by describing what is meant by creep and outlining typical creep behaviour and the role played by temperature. Supplementary articles include **Durability: creep rupture**, **Durability: sub-critical debonding** and **Viscoelasticity**. Various material laws that can be used to model such behaviour are then briefly presented. This article then addresses various aspects of creep in adhesively bonded structures and finishes with the interaction between creep, fracture and fatigue.

### *Definition*

Figure 1 illustrates the response to a sustained load of a material displaying creep behaviour. It can be seen that the deformation consists of two parts: an instantaneous (elastic) response and a time-dependent (creep) response. Traditionally, the time-dependent (creep) response can be divided into<sup>1</sup>

1. primary region – where the accumulation of creep strain slows
2. secondary region – where the rate of straining is essentially constant
3. tertiary region – where damage accumulates and the straining accelerates.

Creep behaviour is generally associated with metals at high temperatures in which the recovery of strain on removal of the load is negligible. This handbook is concerned with adhesives, which are generally thermo-plastic or thermo-setting polymers. On the application of sustained load, such systems can also exhibit the creep response outlined above. Unlike metals, this can be attributed to the time-dependent untangling of polymer chains.<sup>2</sup> With thermo-setting polymers, the creep response is often negligible at temperatures below the glass transition temperature. However, unlike metals, on removal of load,



**Fig. 1.** Characteristic creep behaviour

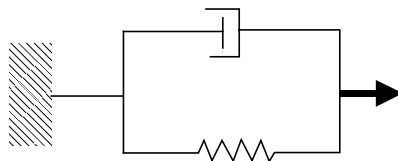
a more significant recovery of the strain can be achieved. Thus, conventional creep models can be used to model the effect of loading on polymers but not the recovery that they experience. To obtain a full representation of the polymer response, it is necessary to use more advanced visco-elastic-plastic models.<sup>3</sup> This article will generally consider the use of conventional creep models to adhesive joints at the macroscopic level.

### *Constitutive models*

Two forms of specimen are commonly used to determine the material parameters in the models outlined below: (1) bulk tensile tests and (2) thick adherend shear tests (TAST). There are two common forms of modelling creep at the macroscopic level. The first is through visco-elastic models, which can be visualized as a combination of spring and dashpot elements. The simplest of these is the Voigt model shown in Fig. 2. The constitutive equation for this model and its solution for the conditions of creep (constant stress) are given<sup>4</sup> respectively as

$$\sigma = E\varepsilon + \mu \frac{d\varepsilon}{dt} \text{ and } \varepsilon = \frac{\sigma_0}{E} \left[ 1 - e^{-\frac{t}{\mu/E}} \right]$$

More complex models can be formed by connecting a number of such elements in series. However, even these are only linear visco-elastic models in which the rate of straining is directly proportional to the stress. For polymers at typical structural levels of load, the stress-strain rate is often highly non-linear. A molecular interpretation of this can be found in a thermally activated rate process model involving motion of chain segments



**Fig. 2.** Voigt spring-dashpot model

over potential barriers.<sup>4</sup> This results in the following non-linear relationship between strain rate and stress.

$$\frac{d\varepsilon}{dt} = ke^{-\frac{\Delta H}{RT}} \sinh\left(\frac{v\sigma}{RT}\right)$$

Although it is possible to introduce non-linear visco-elastic models, the second common approach is to utilize existing metals' creep models. There are a number of models and all express the creep strain rate  $\dot{\varepsilon}^{\text{cr}}$  as a function of stress and other parameters. Popular forms are given below for primary and secondary creep, respectively.

$$\dot{\varepsilon}^{\text{cr}} = C_1\sigma^{C_2}t^{C_3}e^{-C_4/T} \quad \text{and} \quad \dot{\varepsilon}^{\text{cr}} = C_1\sigma^{C_2}e^{-C_3/T}$$

It has been found that whilst these material models give a good representation under conditions of sustained load (creep), they are not appropriate for other loading conditions in which the stresses changes, such as constant rate tests. For these loading conditions, it is necessary to use either rate-dependent yield models or more generalized visco-elastic-plastic formulations. It can be seen from the above that temperature plays an important role in creep deformation. In fact, the well-established time temperature superposition principle (TTSP) can often be applied to predict the creep response at a longer time period simply by elevating the temperature.<sup>4</sup>

### *Creep life and failure*

Failure can occur in adhesive joints that are subjected to sustained loads that are significantly lower than their instantaneous (quasi-static) failure loads. This is somewhat analogous cyclic fatigue failure, and the term "static fatigue" is sometimes employed. In practice, time-dependent creep strains accumulate and the material ruptures locally when these reach a certain level. This local rupture may give rise to subsequent catastrophic or gradual failure, depending on the configuration and hence the condition of the remaining adhesive. As one might expect, the lower the level of load, the longer the time to failure. This is illustrated in Fig. 3, which contains data from three very different configurations, manufactured using the same adhesive. In order to compare the different configurations, the load on the vertical axis has been normalized by the quasi-static failure load. It can be seen that the various data lie on a single straight line on the semi-log axes. This implies an inverse exponential relationship between the time to failure and the applied load. This is what one would expect from the molecular interpretation outlined above.

Data such as that shown in Fig. 3 can be used to generate creep load-life laws for specific adhesive systems, and these can be useful for joint design. Another important question is the validity of an endurance limit or threshold load, below which creep failure will not occur. Various researchers have investigated this, and it appears to be both material and temperature dependent.<sup>5</sup> To avoid creep failure entirely, it is recommended that the overlap length be long enough to enable the minimum adhesive stresses to be less than 10% of the maximum or yield stress. This ensures that a sufficiently large elastic zone is present, which will both limit creep strains during loading and facilitate recovery on unloading.



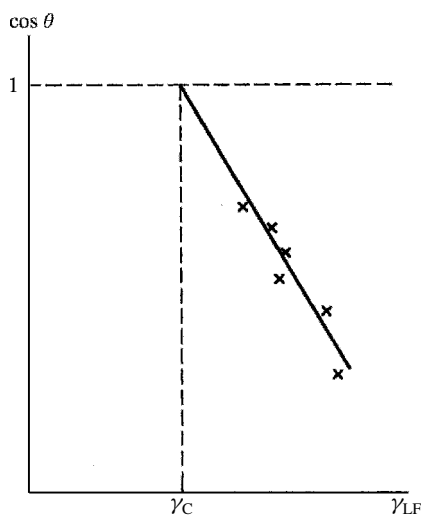
---

**Critical surface tension**


---

D E PACKHAM

The concept of critical surface tension of wetting was introduced by Zisman as a method of characterizing the nature of polymer surfaces.<sup>1</sup> It involves **Contact angle measurement** of a series of liquids on the solid surface of interest. Zisman noticed that if the cosine of the contact angle ( $\cos \theta$ ) was plotted against the surface tension of the liquid ( $\gamma_{LF}$ ), a straight line, or “narrow rectilinear band”, resulted (Fig. 1). The line was extrapolated to  $\cos \theta = 1$ , and the corresponding value of  $\gamma_{LF}$  was taken as the critical surface tension,  $\gamma_C$ ;  $\gamma_C$  then was the surface tension of the liquid that would just spread (see **Wetting and work of adhesion**) on the solid surface. Early work suggested that its value was characteristic of the solid and independent of the liquids used to establish it. Zisman regarded it as an empirical parameter “whose relative values act as one would expect of the specific surface free energies of the solids”<sup>1</sup> – values in Table 1 illustrate this point. Less cautious authors have called  $\gamma_C$  the surface energy of the solid: this is incorrect.



**Fig. 1.** Graph of cosine of contact angle  $\theta$  for a series of liquids of surface tension  $\gamma_{LF}$  on a given solid surface showing evaluation of critical surface tension  $\gamma_C$

*Table 1.* Values<sup>1</sup> of critical surface tension  
in  $\text{mJ m}^{-2}$

Polymer	$\gamma_C$
PTFE	18.5
Polyethylene	31
Polyvinyl alcohol	37
PMMA	39
Nylon 66	46

### Refinement of the concept

The availability of a wider range of experimental results and advances in the theory of polymer wettability lead to a refinement of the concept of critical surface tension. Dann<sup>2</sup> noted a pronounced curvature of some of the  $\cos \theta$  versus  $\gamma_{LF}$  plots, and the tendency for different liquids to give somewhat different values of  $\gamma_C$ . He explained these points as follows.

The theoretical relationship between  $\cos \theta$  and  $\gamma_{LF}$  for a non-polar solid, derived in **Surface energy components** (Eqn. 8), can be written

$$\cos \theta = -1 + \frac{2(\gamma_S \gamma_L^d)^{1/2}}{\gamma_{LF}} \quad [1]$$

It is clearly not linear. If  $\cos \theta$  is made unity in this equation,  $\gamma_{LF}$  becomes (by definition) the critical surface tension, giving

$$\gamma_C = (\gamma_L^d \gamma_S)^{1/2} \quad [2]$$

Two cases can be distinguished, use of a non-polar liquid and of a polar one. For a non-polar liquid,  $\gamma_L^d$  equals the surface tension, which at the condition of  $\cos \theta$  of unity, will be the critical surface tension. Thus,

$$\gamma_C = \gamma_S \quad [3]$$

However, for a polar liquid Eqn. 2 applies: inspection shows that this predicts a lower value of  $\gamma_C$  when a polar liquid is used.

Further insight comes from consideration of the **Good–Girifalco interaction parameter** theory, which gives the following equation.

$$\gamma_S = \gamma_{LF}(1 + \cos \theta)^2/4\phi^2 \quad [4]$$

When the critical condition of  $\cos \theta$  being unity is put in, it can be seen that

$$\gamma_C = \phi^2 \gamma_S \quad [5]$$

This too predicts that  $\gamma_C$  will depend on the nature of the liquids used, as this will influence the value of  $\phi$ . The critical surface tension will only be the same as the surface energy of the polymer if the interaction parameter is unity: this can occur with a non-polar liquid on a non-polar solid. More usually, the value of  $\phi$  is less than one.

### Conclusion

Despite these considerations, the critical surface tension is an empirical parameter, often quoted and relatively easy to measure, which helps characterize the surface of a low-energy solid such as a polymer. Values of this are available from review articles<sup>3</sup> and Bandrup and Immergut and Grulke's *Polymer Handbook*.<sup>4</sup> A much-simplified practical routine based on the concept is used in ASTM D-2578 to test the surface of plastic film; see **Surface characterization by contact angles – polymers**.



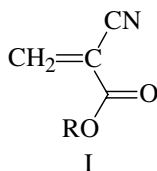
### References

1. W. A. Zisman, in *Contact Angle, Wettability and Adhesion, Advances in Chemistry Series No. 43*, R. F. Gould, Ed., American Chemical Society, 1965, p. 1.
2. J. R. Dann, *J. Colloid Interface Sci.*, **32**, 302, 321 (1970).
3. D. Briggs, D. G. Rancee and B. J. Briscoe, in *Comprehensive Polymer Science*, Vol. 2, G. Allen, Ed., Pergamon, Oxford, 1989, p. 715.
4. J. Bandrup, E. H. Immergut and E. A. Grulke, *Polymer Handbook*, 4th edn, Wiley-Interscience, 1999.

## Cyanoacrylate adhesives

J GUTHRIE

Cyanoacrylate adhesives are rapid curing “one part” adhesives based on alkyl-2-cyanoacrylate monomers (**I**).



A brief description of the chemistry of these materials is described on the article entitled **Alkyl-2-cyanoacrylates**. Commercial adhesive products are usually based on the ethyl ester but methyl, *n*-butyl, allyl  $\beta$ -methoxyethyl and  $\beta$ -ethoxyethyl are also important. Formulated adhesives consist of essentially pure monomer with relatively small amounts of property-modifying additives. The curing reaction is anionic polymerization, initiated by traces of alkaline material present on most substrate surfaces, particularly in conjunction with low levels of surface moisture (see **Chain polymerization**).

### Additives

As already stated, formulated cyanoacrylate adhesives contain low levels of additives that improve the performance profile of the product. They can be divided into two general groups: those that modify the polymerization process and those that alter the properties of the final polymer.

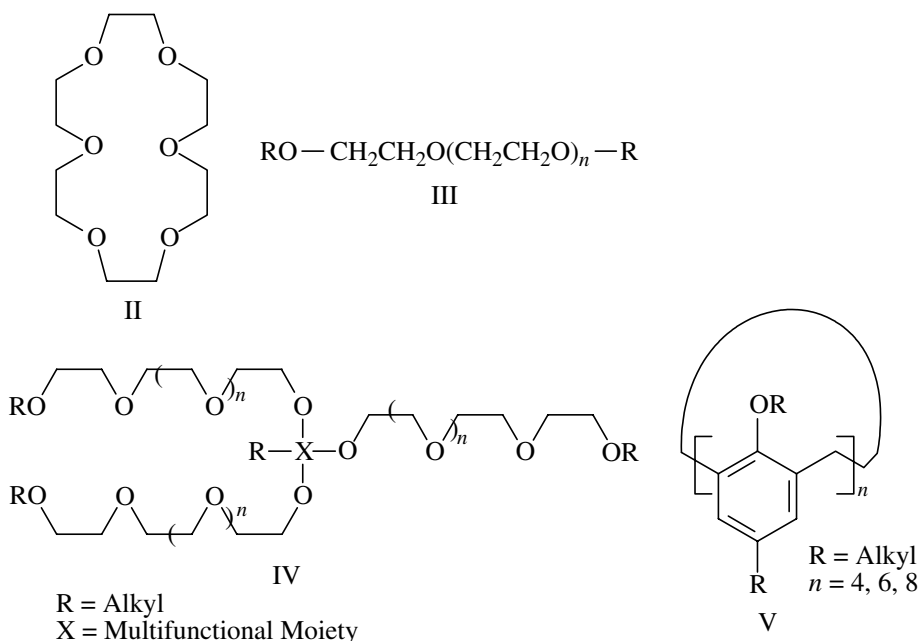
**Stabilizers** The major difficulty associated with the manufacture of cyanoacrylate adhesives is ensuring a balance between stability of the product and cure speed.

This problem has been solved by careful choice of anionic polymerization inhibitors. The materials employed are acidic compounds present at levels between 5 and 100 ppm. Table 1 shows a list of typical additives. Free radical polymerization inhibitors are also added. These are phenolic compounds such as hydroquinone or hindered phenols.

Table 1. Anionic polymerization inhibitors

Sulphur dioxide	Sulphamides
Sulphur trioxide	Cationic exchange resins
Sulphonic acids	Boric acid chelates
Sulphones	

**Accelerators** These increase the rate of polymerization. They should not be confused with polymerization initiators as they are not sufficiently nucleophilic to induce polymerization. The compounds described in the literature have one common feature, namely, they are all capable of sequestering alkali metal cations. The mechanism by which accelerators function is not clear, but it is believed to involve either increasing ion separation at the growing chain end or activation of anions on the substrate by cation sequestration to give so-called “naked” anions in the liquid adhesive. Examples of compounds used as accelerators are crown ethers (II), polyalkene oxide (III), podands (IV) and calixarenes (V).



These types of accelerators are particularly effective on porous substrates such as wood and paper.

**Adhesion promoters** The patent literature describes the use of carboxylic acids and anhydrides as adhesion promoters on metallic substrates. It is assumed that the carboxylic acid group is able to complex with the metal surface and that some degree of copolymerization takes place. There is, however, little or no experimental evidence to substantiate copolymerization. The addition of these acidic materials may also result in a reduction in cure speeds.

*Plasticizers* These are required to reduce the inherent brittleness of poly(alkyl-2-cyanoacrylates). This can be achieved by using non-copolymerizing plasticizers such as esters or higher alkyl cyanoacrylates, which copolymerize with the basic adhesive monomer. Toughness properties can be improved by the inclusion of rubber toughening materials such as ABS (acrylonitrile–butadiene–styrene) or MBS (methacrylate–butadiene–styrene) copolymers. Whichever approach is adopted, toughness is only achieved at the expense of reduced cure speed.

*Environmental performance* The durability (see **Durability – fundamentals**) of cyanoacrylate adhesive bonds is reasonably good on rubbers and some polymer substrates. However, on glass and metals, both thermal and moisture durability are low.

*Heat resistance* This can be improved by including additives in the formulation, which gives rise to a more thermally stable polymer. Examples of this approach are the use of biscyanoacrylate and bismaleimide cross-linking agents. Loss in performance may also be attributed to a temperature-induced loss in adhesion. Phthalic anhydride is believed to act as a high-temperature adhesion promoter.

*Moisture resistance* This may be increased on metal and glass substrates by including cross-linking agents, which may yield a more hydrolytically stable polymer or by using hydrophobic monomers such as fluorinated cyanoacrylates. **Silane adhesion promoters** also improve moisture durability. There is also evidence to suggest that inclusion of some of the anhydrides described above has a beneficial effect.

*Miscellaneous* Other modifications that can be made to cyanoacrylate adhesives include increasing viscosity by the addition of thickeners such as polymethyl methacrylate, cellulose esters or hydrophobic silicas. Colour can be imparted to the product by using selected dyes and pigments.

### *Applications*

Cyanoacrylate adhesives will bond a wide variety of substrates with the exception of polyolefins (unless pre-treated), Teflon and highly acidic surfaces. Porous substrates such as wood, paper and leather require the use of products containing accelerators. Formulations are now appearing that when used in conjunction with a so-called primer can give high bond strength on polyethylene and polypropylene. See **Industrial applications of adhesives**.

As with any adhesive, surface preparation is important. **Pre-treatment of metals prior to bonding** is most easily achieved by solvent degreasing and grit blasting. **Pre-treatments of polymers** usually involves cleaning in a non-solvent and optional surface abrading. Glass and ceramics require surface cleaning and drying.

*Advantages* of cyanoacrylate adhesives include rapid curing, solvent-free nature, high bond strength, versatility, solvent resistance and their comprising only one part.

*Disadvantages* of cyanoacrylate adhesives include poor thermal and moisture resistance on metals and glass, brittleness, sensitivity to surface preparation and poor cure “through

gap". In addition, there can be difficulties in handling because of the danger of bonding to the skin (see **Health and safety**).

Cyanoacrylates and acrylates are compared in the article on **Acrylic adhesives**.

### *Select References*

- H. W. Coover, D. W. Dreifus and J. T. O'Connor in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, p. 463.
- G. H. Millet, in *Structural Adhesives*, S. R. Hartshorn, Ed., Plenum Press, New York, 1986, Chap 6.
- D. C. Pepper, *J. Polym. Sci., Polym. Symp.*, **62**, 65 (1978).
- P. Klemarczyk, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, p. 847.

# D

---

## *Degreasing*

---

JOHN F WATTS

Most metal surfaces arrive from the stockholder or subcontractor with a thick layer of grease on the surface. This is often the result of mechanical forming processes, which invariably rely on some form lubricant, which although very specific at the time of processing can subsequently be described by the generic term grease. It may also have been applied as temporary protection against corrosion.

Degreasing can also be important procedures such as maintenance painting where plant that has become soiled in use must be degreased. As a preliminary to **Pre-treatment of metals prior to bonding** or **Pre-treatment of metals prior to painting**, such grease residues must be removed, or at least reduced to an acceptable level. In general, degreasing processes can be classified according to the size of the article to be cleaned, and thus, whether a dip or a spray process is more applicable, and the nature of the cleaning solution employed, which may be an organic solvent, an alkaline solution, or an emulsion of organic and aqueous solutions. All cleaning methods are improved by additional agitation, which may take the form of scrubbing a large article or using stirring or ultrasonic agitation in the case of a bath. An indication of the wide variation in degreasing performance as a function of degreasing medium and the level of agitation is provided by the data of Table 1.<sup>1</sup>

### *Solvent cleaners*

Organic solvents are effective degreasing agents in both the vapour and liquid phase. This has led to the design of degreasing tanks in which the solvent is heated to provide a vapour blanket above the liquid and articles to be cleaned are held for a short time in the vapour phase prior to immersion in the liquid. The choice of solvent has

Table 1. Efficiency of degreasing as a function of process

Degreasing method	% Cleaning efficiency
Pressure washing with detergent solution	14
Mechanical agitation in petroleum solvent	30
Vapour degreasing in trichloroethylene	35
Wire brushing in detergent solution	92
Ultrasonic agitation in detergent solution	100

been revised dramatically in the light of environmental and safety concerns, and a decade or so ago, chlorinated hydrocarbons such as trichloroethane, trichloroethylene and perchloroethylene were widely recommended as degreasing solvents for metals. For both environmental and health and safety reasons, this practice has been largely superceded and a range of proprietary solvents have been successfully introduced into the marketplace with improved environmental and safety properties: **Environment and the impact of adhesive technology.**

The effect of ultrasonic agitation on the cleaning process is impressive and the cleaning efficiency can be improved from 10% in a still solution at ambient temperature to 85%.<sup>2</sup> In the cleaning of larger articles, it is necessary to resort to wiping or scrubbing. In these cases, the problem is that of carry-over of grease from one article to another, and this can only be avoided by frequent replacement of pad or brush. Degreasing in the vapour phase is widely used but invariably in conjunction with the same, or a similar solvent, in the liquid phase and a complementary process step. The fate of the grease removed during such a process is clearly in the solvent bath itself and steps must be taken to ensure the quality of the solvent is checked on a regular basis to prevent back deposition on the material being processed.

#### *Alkaline cleaners*

Alkaline cleaners present an attractive alternative to solvent cleaners, particularly in the case of very heavy grease deposits, without the problems of unpleasant, or indeed toxic, vapours. They are used hot, the principle of an alkaline cleaner being the saponification of the grease layer by the alkali to produce carboxylate salts. Once this has occurred, the reaction products are removed from the surface by emulsification, peptization (to prevent redeposition of grease on the fresh surface) and subsequent dissolution.<sup>3</sup> In addition to the alkali itself, other chemicals are included in the formulation to aid wetting and emulsifying (trisodium phosphate, for example) and deflocculating (alkali silicates). Alkaline cleaning can be carried out by either a spray or a dip process, but once again, agitation plays an important role. The cleaning efficiency of a 5% solution of alkaline cleaner is very poor at 18% in a still solution for 24 min, but can be increased to 64% by stirring, and increased dramatically to 93% in 5 s when ultrasonic agitation is employed.<sup>4</sup>

Alkaline cleaners, particularly in the metal finishing industry, are sometimes used in conjunction with an electric potential; this process is referred to as electrolytic degreasing.

If the workpiece is made the anode, oxygen is evolved, which helps loosen grease, and may dissolve the metal itself slightly, depending on the potential involved. The cathodic version of the process is more efficient and can be adjusted to provide electrochemical reduction of the surface oxide, but the cathodic production of hydrogen can cause problems of embrittlement in some steels. A satisfactory alternative is to reverse the polarity during processing: 60 s cathodic, followed by 30 s anodic and then 20–50 s cathodic.

### *Emulsion cleaners*

The term emulsion cleaners generally refers to a commercial formulation, applied directly to the soiled article, which consists of a mixture of organic and aqueous phases; they are then rinsed off with water as an emulsion of grease, water and solvent. Although they can be used in either a spray or bath process, they find their widest use in maintenance cleaning of plant. Water itself is also used for this process in the guise of the ubiquitous steam cleaning system used for removing gross amounts of soil of all types from engineering plants. Detergent solutions may also be used but are less effective on greasy surfaces than alkaline or emulsion cleaners.

### *Efficacy of degreasing*

In the assessment of a degreasing process, gravimetric or optical methods are generally employed to determine the extent to which oils and greases have been removed. However, such methods are very insensitive when it comes to defining a few monolayers of hydrocarbon that may remain on the surface and a water break test or surface chemical analysis will be used. The question of the exact composition of metals on an atomic scale following degreasing is addressed in **Engineering surfaces of metals**.

### *References*

1. T. J. Bulat, *Met. Prog.*, **68**, 94–98 (1955).
2. R. Walker and C. L. Carter, *Product Finishing*, **37**(2), 24–28 (1984).
3. R. Walker and N. S. Holt, *Product Finishing*, **33**(4), 14–20 (1980).
4. N. S. Holt and R. Walker, *Product Finishing*, **33**(7), 12–16 (1980).

---

## *Diffusion theory of adhesion*

---

K W ALLEN

The diffusion theory of adhesion is basically a very simple concept, the original use of which is due to Voyutskii.<sup>1</sup> He was concerned with the self-adhesion (autohesion) of unvulcanized (not cross-linked) rubber (see also **Rubber-based adhesives**). He suggested that if two such polymer surfaces are in sufficiently close contact, parts of the long-chain molecules will diffuse across the interface. They will interpenetrate and eventually the interface will disappear and the two parts will have become one. It is clear that, if this

is to happen, the molecules must be relatively mobile. This means that there must not be any considerable degree of cross-linking and that the polymer must be above its **Glass transition temperature**.

This original idea was developed into a more quantitative form by Vasenin,<sup>2</sup> who applied the general theories of the diffusion of liquids to this situation. He began by considering the case where one component was oligomeric and the other was liquid, and extended this first to an oligomer and then to a polymer diffusing into itself. Eventually, he continued to the case of two different polymers interdiffusing.

The mathematics involved in all these considerations is particularly complicated and is not exact, involving several empirical factors. However, Vasenin produced expressions for the force necessary to separate two polymer surfaces.

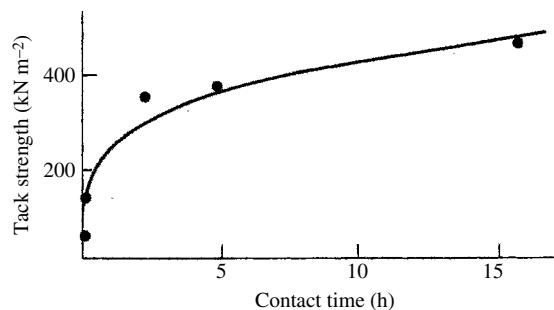
For the autohesion of a polymer to itself, this is

$$F = 11v \left\{ \left( \frac{d(2+p)}{M} \right)^{2/3} K^{1/2} \right\} r t^{1/4} \quad [1]$$

where  $F$  is the peeling force necessary to separate the two surfaces,  $v$  the vibrational frequency of a  $-\text{CH}-$ group,  $d$  the density of the polymer,  $p$  the number of chain branches in the molecule,  $M$  the molecular weight,  $r$  the rate of separation of the two surfaces,  $t$  the time of contact before testing and  $K$  a constant, characteristic of the diffusion molecule. Thus, it emerges that this force is *directly* proportional to the rate of separation and to the quarter power of the time for which the surfaces have been in contact; and *inversely* proportional to the two-thirds power of the molecular weight of the diffusing molecule.

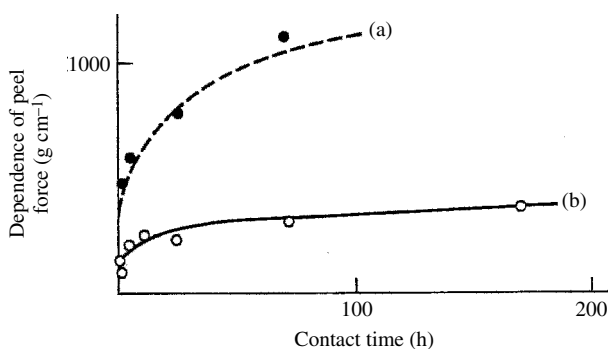
Support for Eqn. 1 is given by the agreement between theory and experiment shown in Figs. 1 and 2, where the points represent experimental results and the lines represent theoretical predictions.<sup>3</sup> In Figs. 1 and 2(b), the  $F \propto t^{1/4}$  relationship of Eqn. 1 has been fitted to the points as closely as possible. The line in Fig. 2(a) was obtained from that of Fig. 2(b) by scaling it according to the molecular weight difference using the  $M^{-2/3}$  relationship.

Much of the original work on this theory was published in Russian, which renders it less than easily accessible, but a particularly helpful review is given by Wake.<sup>3</sup>



**Fig. 1.** Dependence of tack strength ( $\text{kN m}^{-2}$ ) upon contact time (h) between nitrile rubber and natural rubber. The dots represent experimental measurements; the line is derived from Eqn. 1





**Fig. 2.** Dependence of peel force ( $\text{g cm}^{-1}$ ) upon contact time  $h$  for polyisobutylenes of molecular weight (a)  $100,000 \text{ g mol}^{-1}$  and (b)  $150,000 \text{ g mol}^{-1}$  peeled from cellophane. Dots are experimental points, lines are derived from Eqn. 1

These concepts and their development have all been criticized quite sharply, but these have almost entirely been directed to claims that were never made by the originators of the theory. A fortiori the theory applies to mutually soluble polymers (see **Compatibility**); however, see **Polymer-polymer adhesion: incompatible interfaces**.

More recently, with the development of ideas about the interpenetration of adhesives into the microstructure of metallic surfaces, there has been suggestion that the mechanism involved could be regarded as one of diffusion; but that is remote from the ideas considered here.

A comparison of different theories is given under **Theories of adhesion**. Further considerations of interdiffusion are discussed under **Solvent welding, Polymer diffusion: reptation and interdigitation** and **Polymer-polymer adhesion: weld strength**.

### References

1. S. S. Voyutskii, *Autohesion and Adhesion of High Polymers*, trans. S. Kaganoff, V. Vakula, Ed., Interscience, New York, 1963.
2. R. M. Vasenin, *RAPRA Translations 1005, 1006, 1010, 1075*, R. Moseley, Ed., RAPRA, Shrewsbury, 1960-63; *Adhesives Age*, **8**, 21, 30 (1965).
3. W. C. Wake, Ed., *Adhesion and the Formulation of Adhesives*, 2nd edn, Applied Science Publishers, London, 1982, Chap 5.

## Dispensing of adhesives

C WATSON\*

### Introduction

In many industrial situations, the use of adhesives has advantages over older methods of joining (see **Engineering design with adhesives, Industrial applications of adhesives**), but there is sometimes a reluctance to use them because of supposed difficulties

in application. They are perceived to be messy and incapable of being automatically dispensed on high-volume production lines. Modern technology has undermined the validity of both these perceptions. Effective dispensing methods are available for most adhesives, despite their diversity, which may be of chemical type (see **Adhesive classification**), of physical form (liquid, paste or solid) or a number of components. Cure times can also vary from seconds (**Cyanoacrylate adhesives**) to hours (some **Epoxide adhesives**).

A major requirement in industry is consistent quality of a manufactured article over long production runs. Accurate dispensing of the adhesive on to components to be bonded is therefore essential.

### *Basic dispensing principles*

Dispensing involves a combination of several functions depending upon the dispensing principle used. The functions relate to the control of the “bulk” product to supply energy to move it through flow pipes to a valve or dispenser nozzle. Control must be exerted over the valve to vary opening time, therefore quantity dispensed, and over the speed of movement of the dispenser nozzle relative to the component surface. All adhesives and sealants will vary in viscosity, mainly because of the variation of ambient temperature at the point of use. In order to satisfy the need of the manufacturing process, the dispenser should be so designed that variations in viscosity will not affect the accuracy or consistency of the quantity dispensed.

Two of the most difficult types of adhesives to dispense are **Cyanoacrylate adhesives** and **Anaerobic adhesives**. Cyanoacrylates cure by interaction with the surface moisture on a component part. Anaerobics remain liquid in the presence of oxygen but automatically cure once enclosed in a joint.

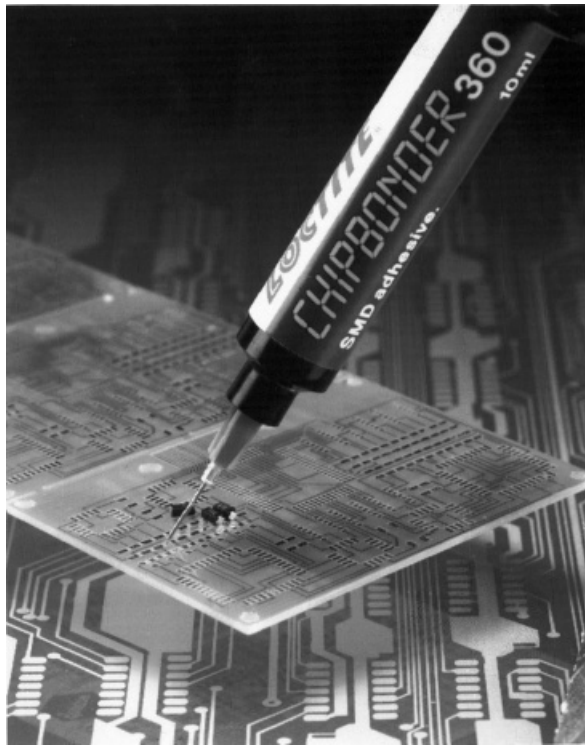
The major methods of dispensing anaerobic adhesives use pressure–time controlled valves, a cartridge and syringe system and screen printing.

Other types of adhesive may be used with some of the combinations of the above systems; the major points for consideration to be taken into account are the curing characteristics of the product, the rheology and the speed of flow required. Figures 1–5 show some typical production applications.

### *Pressure–time controlled system*

Pressure is applied to bulk liquid and timer-controlled valves meter the quantity dispensed. Figure 6 shows a typical pressure–time system for adhesives where the viscosity is up to approximately 100,000 mPa. Pressurization of the product tank pushes the adhesive through a feed line to a dispensing valve. A timer controls the opening time of the dispenser valve to obtain a metered quantity. Regulated pressure behind the product and the valve opening time control the quantity dispensed. The adhesive can be applied in dots or in bead form.

There are a number of valves that can be used with the product tank and control console. These are given under the headings below.



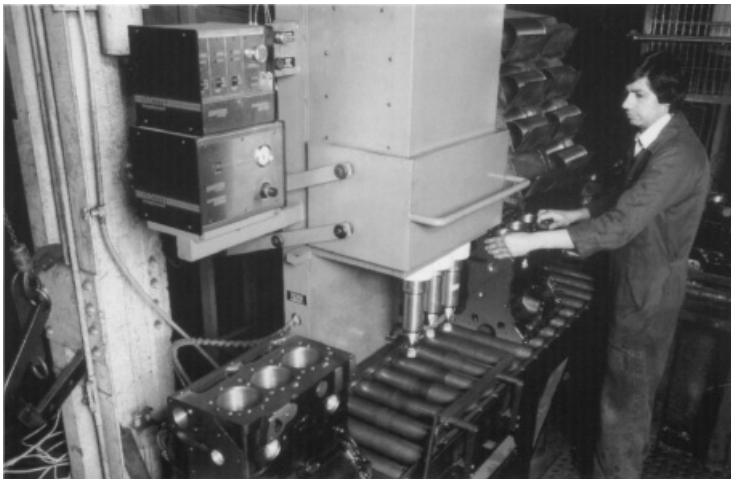
**Fig. 1.** A syringed adhesive used for bonding surface-mounted devices on to printed circuit boards



**Fig. 2.** A typical installation of an automatic machine for placement of components on to printed circuit boards. In the centre can be seen the mounted syringe for automatic application of the adhesive



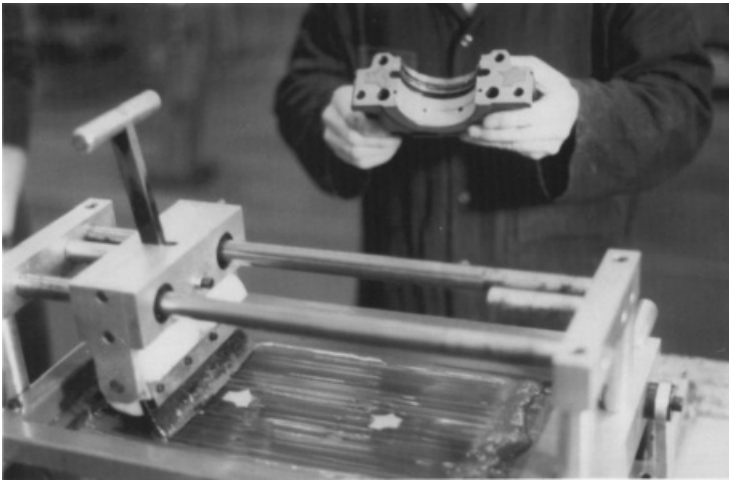
**Fig. 3.** The bench use of a dispenser for the application of cyanoacrylate to an external light switch to bond the cover to the switch base



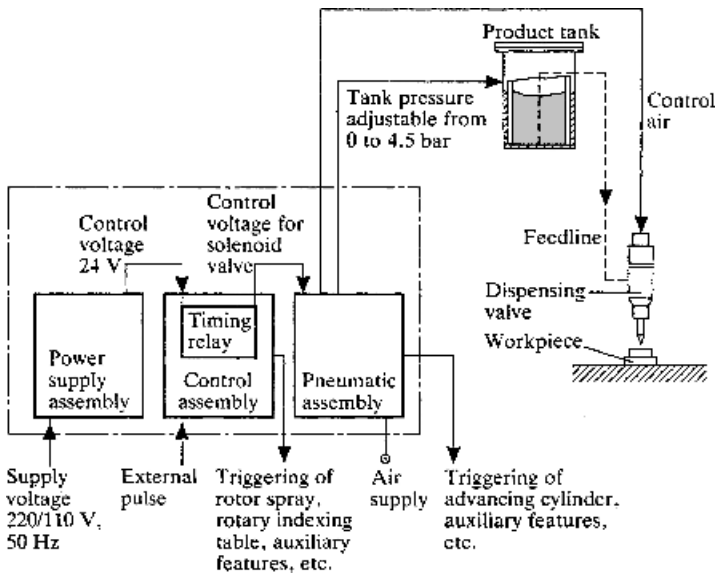
**Fig. 4.** A rotospray installation for the automatic application of an anaerobic to three bores of an engine block for the retention of cylinder liners

*Static pinch valve* The feed tube from the product tank passes underneath the pneumatic pinch cylinder. When the valve is closed, the pneumatic cylinder closes the tube. When the cylinder opens, the product flows through the tube to the dispenser nozzle.

A static pinch valve can be mounted on a bench station, or alternatively, on an automatic line. A typical bench application would be bonding the ends of a rubber extrusion to make up car door seals. In the case of an automatic line, a free-fall drop could be dispensed on to a component part located beneath the static pinch valve or, alternatively, a bead applied to a component part as it traverses beneath the pinch valve nozzle.



**Fig. 5.** The hand screen printer and a component on to which an anaerobic gasket has been printed for Jaguar



**Fig. 6.** A pressure–time typical system for dispensing adhesive

*Pressure time using advancing valve* The advancing pinch valve is utilized in operator-paced or fully automatic lines where the component part itself cannot be moved to the valve nozzle. The advancing pinch valve, which can be between a stroke of 25 and 150 mm (1 and 6 in), advances the application nozzle to the component part. The dispenser valve then opens, allowing a metered quantity of product to flow through the valve nozzle on to the component part. The valve then closes and the advancing cylinder retracts from the nozzle. In this way dots or continuous beads of product may be applied.

*Pressure time using a roto-spray unit* This unit is used to apply anaerobic products to machined bores. The unit consists of an electric motor with an integral dispenser valve. At the end of the motor shaft there is a plastic cup around the periphery of which are a number of holes.

The principle of operation is that the unit is advanced into the bore to be coated, the motor turns, the valve opens and dispenses a metered quantity of product into the roto-spray cup. The product is then thrown out centrifugally through the holes in the periphery of the cup on to the bore.

Typical applications for this dispensing system would be to coat core plugholes in an engine block, electric motor end caps for the retention of bearings and the engine block for the retention of cylinder liners.

### *Cartridge/syringe dispensers*

There are two basic methods of dispensing from a cartridge/syringe. The first is to apply an air pulse on the back of the cartridge piston, thus dispensing a certain volume of product through the dispenser nozzle. The quantity of product dispensed using pulsed air can vary with variation of air pressure. The more complex air-pulsed systems incorporate compensating devices continually to monitor and adjust the pressure.

The second principle is to have a mechanically driven piston so that an equal volume is dispensed with each cycle. Typical applications are for dispensing surface-mounted device adhesives on to printed circuit boards where up to 20,000 dots per hour are dispensed, the dispensing of anaerobic gasketing products using a robotic head, the dispensing of gel cyanoacrylates for bonding rubber gaskets to mouldings and castings.

### *Screen printing of adhesives*

In the **Automotive industry** there is a trend towards complete automation of production lines. In the application of adhesives/sealants for gasketing, the principles of dispensing have normally been to use a pressure–time system, or alternatively a cartridge system with a robotic head. However, a faster system is to screen print an anaerobic on to the surface of a component.

Here, the basic principle is to take a polyester screen and reproduce the pattern of the gasket required from the screen. Anaerobic adhesive is dispensed in metered quantities on to the screen. The component part is located below the screen, the screen advances on to the component part or the component is raised up to the screen. A squeegee traverses across the screen, automatically pushing the anaerobic product through the pattern on to the component part. Thus, completely automatic systems are being utilized to gasket component parts, replacing conventional preformed manually placed gaskets.

It is important that the potential end-user discuss his specific need with the adhesive supplier, who should be able to advise on the use of their own tailor-made or commercially available equipment to suit manufacturing process needs.

### *Select References*

- R. E. Batson, Industrial applications for adhesives, in *ASM Engineered Materials Handbook Vol. 3 Adhesives and Sealants*, M. M. Cauthier, Ed., ASM International, 1990, p. 567.

E. H. Schindel-Bidireli, *Pratique du collage Industriel*, Technique et Documentation Lavoisier, Paris, 1992.

W. A. Lees, Adhesives, in *Kempe's Engineers' Year-Book*, J. H. Stevens, Ed., CMP Information Ltd., 2002, p. 653.

### *Dispersion forces*

K W ALLEN

The origin of forces between neutral symmetrical molecules, such as hydrogen (H<sub>2</sub>) or the inert gases (e.g. A, Ne), is not obvious. Because of the symmetry of the electron configuration, there cannot be any permanent dipole; so, there can be neither dipole–dipole interactions (Keesom orientation interactions) nor dipole–molecule interaction (Debye induction interactions) (see **Polar Forces**). Further, there appears to be no Coulombic electrostatic interaction since they are electronically neutral overall, nor can there be any covalent bonding. Yet, there must be forces of some type between these molecules as the existence of liquid and solid hydrogen and argon demonstrate.

This situation was first discussed and a beginning made in explaining it by F. London in 1930. While the theory is essentially based on quantum mechanics, a plausible and helpful explanation can be given in classical terms as follows.

While a neutral molecule has an entirely symmetrical electron distribution when considered as an average over a period of time, when it is considered at an instant, the state is different. At any instant of time, the electrons will have a definite distribution, which is most unlikely to be symmetrical, so that the molecule will have an instantaneous dipole moment. This instantaneous dipole can induce a corresponding dipole moment in another adjacent molecule. So, there will be an interaction between these two molecules, which will result in forces of attraction between them. The dispersion force is then this instantaneous force of attraction averaged over all the instantaneous configurations of the electrons in the first molecule.

For two isolated molecules, the energy of interaction  $U$  is given by:

$$U = -\frac{3}{2} \cdot \frac{1}{(4\pi\epsilon_0)^2} \cdot \frac{\alpha_1\alpha_2}{r^6} \cdot \frac{I_1 I_2}{I_1 + I_2} \quad [1]$$

where  $\alpha$  are the respective polarizabilities

$I$  are the respective ionization energies

$r$  is the distance between the two molecules

The negative sign indicates that this is an attractive energy. This is often written in the form:

$$U = -A/r^6 \quad [2]$$

where  $A$  is known as the van der Waals dispersion attraction constant.

From these equations it can readily be seen that the attraction constant  $A_{12}$  between different types of molecule 1 and 2, is the geometric mean of  $A_{11}$  and  $A_{22}$ , the constants for interaction between molecules of the same type, providing that the arithmetic and

geometric means of the ionisation energies can be assumed to be the same:

$$A_{12} = (A_{11} \cdot A_{22})^{1/2} \quad [3]$$

If the molecules become very close, their electron orbitals will begin to overlap, leading to repulsion energy. This rises very sharply as the separation decreases. When this is taken into account, the complete potential energy relationship includes the Lennard–Jones potential and the relationship becomes

$$U = -A/r^6 + B/r^{12} \quad [4]$$

where the second term represents this repulsion.

This attraction will apply to all molecules irrespective of any other relationships or attractions and in addition to any other forces. Thus, this force of attraction is entirely universal and exists in all situations. Further, it has been shown that the force arising from this type of induced dipole is considerably greater than that due to the other types of dipole interactions since these effects are synchronized whereas those from separate dipoles are not. (See Table 1.)

The title “dispersion” arises because, from the more theoretical development of this concept, an important parameter, characteristic of each molecule, is involved. This constant is proportional to the dispersion of the refractive index with frequency, and this in turn is approximately proportional to the ionization energy of the molecule. Hence the title. However, since the word “Dispersion” has other connotations and could be misleading, the name “London”, the name of the man who initially developed this theory, is frequently included in the title to give “London Dispersion Forces”.

Casimir and Polder showed, in 1948, that London’s theory must be modified if the molecules are some distance (in molecular terms) apart. This is because the electrostatic forces are not propagated instantaneously but take a finite, if small, time pass between two molecules. The net result of such retarded dispersion forces is that the energy of interaction between two particles with distance between them being greater than  $\sim 20$  nm is proportional to  $r^{-7}$  instead of  $r^{-6}$ .

The relative significance of these interactions in some instances are shown in Table 1. These London dispersion interactions are of considerable importance in adhesion, and are frequently the major fact in the strengths of bonds. This is discussed under **Adsorption**

Table 1. Contribution of different types of van der Waals force to the interactive energies of some molecules

Substance	Dipole moment (D)*	Interaction energies (kJ mol <sup>-1</sup> )		
		Dipole/dipole interaction	Dipole induced interaction	Dispersion interaction
Ar	0	0	0	-1.1
CO	0.11	$-4 \times 10^5$	$-8 \times 10^{-4}$	-1.3
HCl	1.07	-0.2	-0.07	-1.8
NH <sub>3</sub>	1.47	-6.2	-0.9	-12.9
H <sub>2</sub> O	1.86	-16.1	-0.9	-5.3

\* 1 D-1 Debye unit =  $3.336 \times 10^{-30}$  Cm.



**theory of adhesion.** They also play a significant role in surface phenomena generally, such as **Contact angles and interfacial tension.** For further consideration, see **Lifshitz-Van der Waals forces.**

### *Select References*

- R. J. Good, in *Treatise on Adhesion and Adhesives* Vol 1, R. L. Patrick, Ed., Edward Arnold, London and Marcel Dekker, New York, 1969, Chap 2.
- M. Rigby, E. B. Smith, W. A. Wakeham and G. C. Maitland, *Forces between Molecules*, Clarendon Press, Oxford, 1986, Chap 1.
- T. B. Grimley, in *Aspects of Adhesion* 7, D. J. Alner and K. W. Allen, Eds., Transcripta Books, London, 1973, pp. 11–29.
- R. H. Ottewill, in *Aspects of Adhesion* 2, D. J. Alner, Ed., University of London Press, London, 1966, pp. 9–17.

## *Displacement mechanisms*

D M BREWIS

Solids will normally be covered by a thin layer of organic materials of low cohesive strength. Freshly formed high-energy surfaces, for example of metals, will rapidly adsorb organic compounds from the atmosphere (see **Surface energy**). On other occasions, metals will be covered deliberately by a fairly thick layer of protective oil or grease. Polymers will normally be covered by a layer of an additive that has migrated to the surface, or by a mould release agent, or by contamination subsequent to fabrication (see **Compatibility, Weak boundary layers**).

Sometimes, these organic layers will be removed, or at least reduced, by a **Pre-treatment**, but on many occasions, the substrates will be used “as received”. With suitable selection of adhesives, paints and printing inks, good adhesion can often be achieved with these “as-received” surfaces. For example, oily steel can be bonded satisfactorily with some **Acrylic adhesives**, hot curing **Epoxide adhesives** and **Solvent-based adhesives**; see **Selection of adhesives**.

The effect of deliberately contaminating substrates has been studied. Brewis<sup>1</sup> spread a layer of petroleum (*c.* 2  $\mu\text{m}$  thick) over HDPE, which had been etched with chromic acid. The effect on joint strength is shown in Table 1. The fact that most of the beneficial effect of the pre-treatment is retained indicates that most, if not all, the petroleum jelly has been absorbed by the epoxide adhesive.

Minford<sup>2</sup> studied the effect of contaminating aluminium with a commercial lubricant. The results are summarized in Fig. 1. It was found that the lubricant had little effect on the adhesion level until its thickness exceeded about 10  $\mu\text{m}$ . The adhesion level then fell sharply and the mode of failure (see **Stress distribution: mode of failure**) changed from cohesive within the adhesive to apparent interfacial failure. Thus the epoxide, which required a fairly long cure at a high temperature, was able to absorb quite large quantities of the lubricant.

Whether contaminants are absorbed by the mobile phase will depend on a number of factors, including the following:

Table 1. The effect of a layer of petroleum jelly (c. 2  $\mu\text{m}$  thick) on the lap shear strength of HDPE bonded with epoxide adhesive<sup>1</sup>

Surface	Joint strength (MPa)
(a) Untreated HDPE	1.8
(b) HDPE treated with chromic acid	17.6
(c) As (b) plus contaminant	12.7

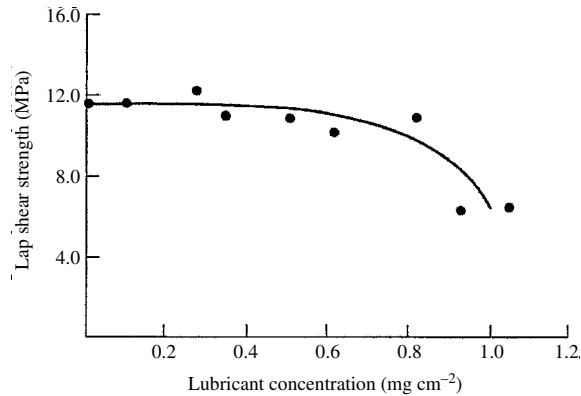


Fig. 1. The effect of lubricant concentration on the lap shear strength of aluminium joints bonded with a one-part epoxide at 177 C for 2 h

1. quantity of contaminants;
2. chemical nature of contaminant and the mobile phase, that is, their compatibility;
3. temperature;
4. time mobile phase is in its low-viscosity state.

#### References

1. D. M. Brewis, *J. Mater. Sci.*, **3**, 262 (1968).
2. J. D. Minford, *Aluminium* (Dusseldorf), **57**(10), 657 (1981).

### *Durability: creep rupture*

DAVID A DILLARD

Long-term durability of adhesively bonded joints may require resistance to a number of individual or combined degradation modes, including environmental attack, fatigue and time-dependent failures. Time-dependent failure mechanisms are often characterized using either a strength approach, involving creep and creep-rupture tests, or a fracture approach, in which debond rate is determined. In creep-rupture tests, adhesive joints are subjected to

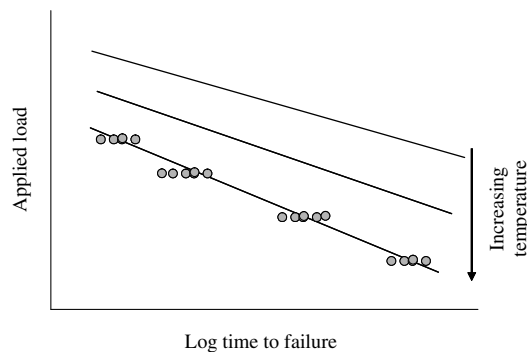
a nominally constant load. If the tests are instrumented to measure strain or deformation during the test, they are often called creep tests. The test may proceed for a chosen time period, or may be continued until complete rupture occurs. If the test is not instrumented to measure strain, but rather only determines the time at which failure occurs, the test is often called a stress rupture test.

Stress rupture tests have traditionally been widely used in adhesive bond testing. Structural adhesives are often tested in bonded lap shear configurations that are placed in spring-loaded stress tubes or other devices such as Minford rings. These loading devices are relatively inexpensive, so large numbers of specimens may be easily tested, placing them in high humidity cabinets, salt spray chambers or other environments of interest. If necessary, the load may be adjusted as the specimen creeps in order to approximate a constant load level. For semi-structural and non-structural adhesives, the loads required to conduct creep or creep-rupture tests are significantly smaller, so dead loads may often be used. A common test for pressure-sensitive adhesives, for example, employs banks of specimens loaded by small weights hanging from specimens bonded to appropriate adherends. The tape backing slides along, shearing the adhesive and debonding, until the bond fails and the weight drops, hitting a switch and stopping the timer used to measure the duration of the test. In addition to stress tubes, Minford rings, and dead load loading devices, hydraulic and pneumatic loading fixtures have also been used to measure creep and stress rupture behaviour of adhesives and adhesive joints.

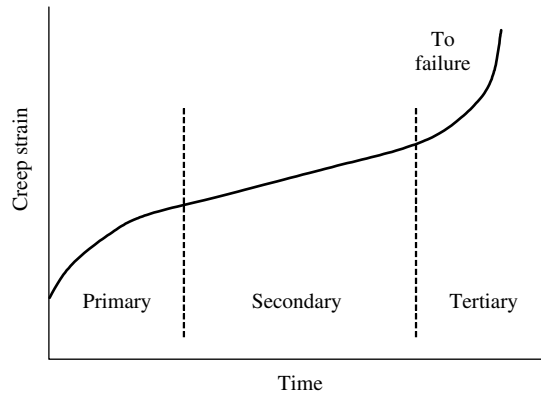
Significant scatter is often evident in time to failure data obtained from stress rupture tests conducted on either neat materials or on bonded joints. This scatter may obscure trends and frustrate the user. Results are typically plotted as load level versus the time to failure, a form that is analogous to S–N plots used in fatigue tests (see **Durability: Fatigue**). In keeping with the principles of polymer physics,<sup>1</sup> the time to failure axis should be plotted on a log scale, as illustrated in Fig. 1. Many creep-rupture models for homogeneous materials are based on forms like

$$\log(t_f) = A - B \cdot P$$

where  $t_f$  is the time to failure,  $P$  is the load level, and  $A$  and  $B$  are coefficients that may depend on temperature, environment, material system and joint configuration. These models are useful in accelerated testing procedures.<sup>2</sup>



**Fig. 1.** Schematic stress rupture data, illustrating the effect of temperature on time to failure



**Fig. 2.** Schematic creep strain plot for a butt joint bonded with a pressure-sensitive foam tape

In instrumented creep tests taken to failure, one learns not only how long specimens last but also how deformation increases throughout the creep process. For lap joints, delay times have been seen in creep tests, probably due to the increasing uniformity of the shear stress state, as predicted by the shear lag model as the creep compliance of the adhesive increases with time.<sup>3</sup> In other situations, no such delay time is seen. A schematic illustration of a creep curve for an adhesive bond consisting of a butt joint bonded with a pressure sensitive foam tape is shown in Fig. 2, exhibiting classical primary, secondary and tertiary regions of creep behaviour.

Although stress rupture tests can provide important and useful data about time-dependent failures of adhesives and adhesive joints, the data may be difficult to use for design purposes. Because these tests are strength type tests, and because the stress distributions within any common joint configurations are quite non-uniform, direct application of joint-creep rupture data to other joint designs may be problematic. An alternate approach to look at durability involves a fracture approach using subcritical debond growth (see **Durability: Subcritical Debonding**).

### References

1. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd edn, John Wiley & Sons, 1980.
2. W. Nelson, *Accelerated Testing: Statistical Models, Test Plans, and Data Analyses*, John Wiley & Sons, 1990.
3. M. E. R. Shannahan and K. W. Allen, *J. Adhes.*, **8**, 43–56, 1976.

### *Durability: fatigue*

DAVID A DILLARD

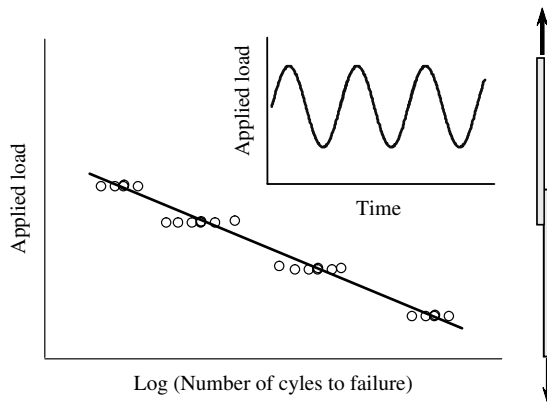
Long-term durability of adhesively bonded joints may require resistance to a number of individual or combined degradation modes, including environmental attack, fatigue

and time-dependent failures (see **Durability: fundamentals**). Fatigue-induced degradation and failure mechanisms are often characterized using either a strength approach, involving cyclic loading of bonded joints, or a fracture approach, in which debond rate is determined for fracture specimens.

The strength approach to fatigue has been used for many decades. Traditionally, carefully machined, cylindrical metal specimens were rotated while subjected to bending, effectively cycling the specimen between tension and compression. The results from many specimens are plotted as the maximum stress level versus the number of cycles to failure, the latter often on a log scale. Known as S–N plots, these have proven very popular in engineering design of monolithic components. This S–N approach has been widely employed for adhesive bond tests as well, often performing the tests in servo-hydraulic test frames. Because fatigue damage often initiates at surface defects, the surface quality is a determining factor in the fatigue life of monolithic materials, and details of spew can be important in the life of bonded joints tested in cyclic loading.<sup>1</sup> In some cases, materials exhibit an endurance limit; if the cyclic stresses do not exceed this limit, the material or joint may last an indefinite number of cycles. Statistically, fatigue life data may exhibit considerable scatter in terms of the number of cycles required for failure. Statistical methods can be employed to estimate the probability of failure or the expected reliability. As with other strength tests, however, S–N data collected on a given joint configuration may be difficult to generalize to other geometries. As such, in industry, this S–N approach is often carried out on actual prototype joints that are representative of those to be used in the final design. A variety of empirical models have been used to represent the resulting S–N behaviour and to estimate what might occur under more complex spectrum loading situations. A schematic illustration is provided in Fig. 1.

In the **Fracture mechanics** approach, subcritical debonding rate is determined, often as a function of a fracture parameter such as the applied energy release rate,  $G$ . Paris was the first to use this method, and noted that the crack growth rate per cycle was related to the energy release rate (by way of the stress intensity factor) through a power law relationship of the form

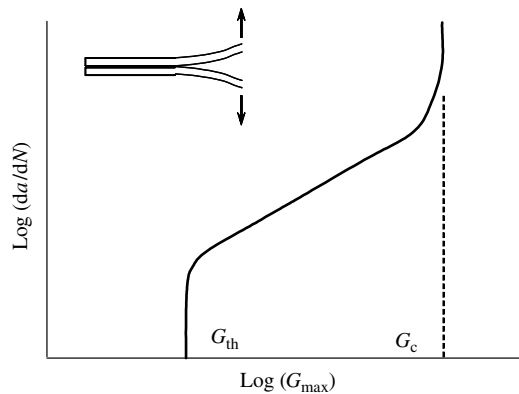
$$\frac{da}{dN} = C \cdot (\Delta G)^n$$



**Fig. 1.** Schematic illustration of S–N type plot for bonded joints loaded under cyclic loading

which is known as the Paris law.<sup>2</sup> Here  $a$  is the crack length,  $N$  is the number of cycles, and  $\Delta G$  is the range of applied energy release rate. For studies of polymers and adhesive bonds,  $G_{\max}$  is often used instead of  $\Delta G$ . The coefficient,  $C$ , and the exponent,  $n$ , are empirically determined for a given material system. This power law behaviour is illustrated schematically in Fig. 2 and is bounded on the upper end by the critical energy release rate,  $G_c$ , which would result in rapid or unstable debonding. In some material systems, the power law region may be bounded on the lower end by a threshold energy release rate,  $G_{th}$ , below which fatigue debond propagation is not observed. Being a fracture approach, data collected in this fashion can readily be applied to predict the behaviour of other flawed structures. Debond growth rate data collected from double cantilever beam specimens can be used to accurately predict the fatigue life of lap joints,<sup>3</sup> an entirely different bond configuration, suggesting the broad applicability of the method. The fracture approach outlined above focuses on the propagation of debonds, although the initiation phase can also be important in estimating bond life.<sup>4</sup>

Some material systems are relatively insensitive to test frequency. Fatigue tests on metals can often be accelerated significantly by increasing the frequency beyond that expected in service. Polymeric materials, including adhesives, are much more time and frequency dependent, however (see **Viscoelasticity**). Higher frequencies often induce hysteric heating, resulting in temperature changes that can dramatically affect the results. Because adhesives also exhibit creep, slow frequency cycling can result in poorer performance than higher frequency tests because of the viscoelastic behaviour that may result at slower test rates (see **Durability: creep rupture**). Care should be used when establishing the temperature and frequency of testing for adhesive joints. In addition, the amplitude and mean value of the loading can be important in fatigue testing. The  $R$  value, defined as the minimum load divided by the maximum load, is often a useful parameter in quantifying and comparing fatigue performance for both the S–N and debond growth approaches. For example,  $R = 1$  represents static loading,  $R = 0.1$ , a commonly used value, represents the situation where the minimum value is 10% of the maximum load, and  $R = -1$  is the fully reversed case (equal tension and compression).



**Fig. 2.** Schematic diagram of debond rate as a function of applied energy release rate

---

*References*

1. D. R. Lefebvre and D. A. Dillard, *J. Adhes.*, **70**, Part 1, 119–138 (1999).  
D. R. Lefebvre, D. A. Dillard and J. G. Dillard, *J. Adhes.*, **70**, Part 2, 139–154 (1999).
2. D. Broek, *Elementary Engineering Fracture Mechanics*, Sijthoff and Noordhoff, The Netherlands, 1978.
3. A. J. Kinloch and S. O. Osiyemi, *J. Adhes.*, **43**, 79–90 (1993).
4. Z. Zhang, J. K. Shang and F. L. Lawrence, *J. Adhes.*, **49**, 23 (1995).

---

*Durability – fundamentals*

---

G W CRITCHLOW

The durability, or permanence, of a joint or structure is a function of the entire bonding system that is, the adherend-pre-treatment-adhesive/primer combination along with the conditions to which the joint or structure is being exposed. A change in any one of these parameters can radically influence the durability of the bonding system. In general terms, durability can be considered separately for both structural and non-structural bonds.

Structural bonds are those that are expected to undergo some form of loading for a significant part of their service life while non-structural bonds remain largely unloaded, for example, in the case of paints and lacquers. An understanding of the bond failure mechanism is critically important in explaining the performance of a particular bonding system in durability tests. Surface analytical techniques such as **X-ray photoelectron spectroscopy** (XPS) are widely employed in this role.<sup>1</sup>

Failure can occur in a number of places within a bonded joint or structure, for example, (see **Stress distribution: mode of failure**):

1. cohesively within the adherends;
2. interfacially between the adherend and an altered layer resulting from any pre-treatment carried out;
3. cohesively within an altered layer resulting from pre-treatment;
4. interfacially between the pre-treatment and a primer, if present;
5. cohesively within a primer;
6. interfacially between a primer and the adhesive;
7. cohesively within the adhesive.

Mixed failure modes resulting from failure in more than one of the above regions are commonly observed. Clearly, with good design, option 1 should not occur with thick metal adherends; however, this may be required in applications such as blister packaging when polymeric laminates of thin metal foils are used.

In manufactured items, given a specified adherend material, the pre-treatment-adhesive/primer combination will be selected to optimize bond durability. **Accelerated ageing** tests will normally be used to aid their selection. For most commercially used materials, there exists a vast literature on the influence of surface pre-treatments, primers and coupling agents on bond durability as a function of various test conditions.<sup>2,3</sup> Similarly, the influence of

different adhesive types have been well studied, which effectively evaluate their mechanical response as a function of exposure time and temperature, usually in water.<sup>2,3</sup>

For non-structural bonds utilizing metal adherends, water ingress can occur over a period of many years and failure is commonly reported to occur through hydration or corrosion of the underlying metal. Failure then occurs cohesively through the usually voluminous but friable hydration or corrosion products. In this case, failure is more directly observed through blistering or delamination of the organic film. For this reason, a passivating pre-treatment is used to delay the onset of failure. **Conversion coating** such as chromates or phosphates are routinely used for this purpose with metals such as aluminium, steel, zinc coated steel and titanium while anodic oxidation might otherwise be used on aluminium or titanium. Corrosion studies are routinely used to observe the performance of different pre-treatments, and correlation is made with observed non-structural adhesion performance.

In the case of structural joints, cohesive failure of the adhesive is often observed. Indeed, in many instances, the requirement will be to engineer failure within the bulk of the adhesive layer. Modelling of the adhesive response as a function of water uptake with temperature is carried out to represent the influence of environmental exposure. With fatigued structural joints, by combining the use of fracture mechanics and appropriate modelling tools, the resultant crack propagation rates and consequently durability levels can be predicted as a function of various environmental and mechanical test parameters, such as frequency. Fatigue threshold values can be determined, which are used to predict durability performance.<sup>2,4</sup>

Often, structurally bonded metals exhibit apparent interfacial failure when viewed either optically or at higher magnifications using electron microscopy. However, when viewed on the atomic scale, for example, using XPS, it is frequently found that mechanical loading will induce failure of the boundary polymer immediately adjacent to the metal surface. With structural **Epoxy adhesives**, recent studies have shown that this boundary polymer may have chemical and mechanical properties radically different from the bulk adhesive material and which are not incorporated within current models.

In summary, the study of bond durability and, in particular, the development of predictive models is now a mature topic. Most bond durability tests provide only comparative data. Given the large number of adherend-pre-treatment-adhesive/primer combinations available and the range of exposure conditions to which a structure might be exposed, it is difficult to predict durability performance in the general case. There are limitations in the usefulness of current models once failure is observed away from the bulk adhesive.

Further information is given in articles on **Pre-treatment of metals prior to bonding, Durability: creep rupture, Durability: subcritical debonding, Weathering of adhesive joints and Weathering tests.**

### References

1. D. M. Brewis and G. W. Critchlow, *J. Adhes.*, **54**, 175–199 (1995).
2. A. J. Kinloch, *Adhesion and Adhesives: Science and Technology*, Chapman and Hall, London, 1987.
3. A. Pizzi and K. L. Mittal, Eds., *Handbook of Adhesive Technology*, Marcel Dekker Inc., New York, 1994.
4. W. K. Loh, A. D. Crocombe, M. M. Abdel Wahab and I. A. Ashcroft, *J. Adhes.*, **79**(12), 1135–1161 (2003).



---

**Durability: subcritical debonding**


---

DAVID A DILLARD

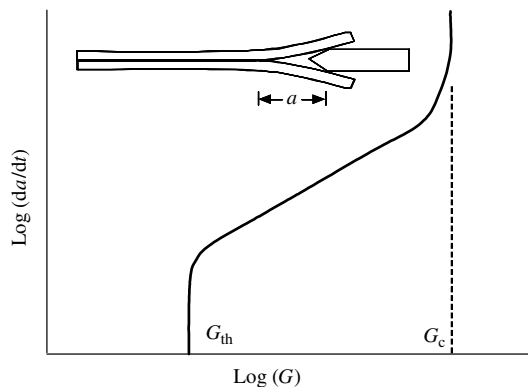
From a **Fracture mechanics** perspective, cracks can grow rapidly (approaching the order of the speed of sound) when the applied energy release rate,  $G$ , is equal to the fracture energy or critical energy release rate,  $G_c$ , of the material. Cracks may grow much more slowly in time-dependent materials, a process known as subcritical cracking or debonding. Given sufficient time, this slow, stable crack propagation can cause a flaw to reach a critical size at which failure will result.

A variety of fracture specimens may be used to collect subcritical-debond growth data. One of the most common methods is the **Wedge Test**, in which a wedge is inserted between bonded, beam-like adherends to drive a debond.<sup>1</sup> Provided the adherends do not plastically deform, or creep over time (**Durability: creep rupture**), simple formulae may be used to determine the available energy release rate (see **Fracture mechanics** and **Fracture mechanics test specimens**). Because the available energy release rate decays rapidly as the debond length,  $a$ , increases, a single specimen can provide debond rate data over a wide range of energy release rates. Dead load peel tests<sup>2</sup> have also been widely used to determine debond rate. Curvature mismatch specimens<sup>3</sup> and many other configurations have also been successfully used. Subcritical debonding can also be measured in universal test frames moving at a range of crosshead speeds.<sup>4</sup>

Subcritical debonding tests can be conducted in air or in any desired environment and temperature. Subcritical debond data is often reported on a log-log plot of debond data as a function of the applied energy release rate, as shown in Fig. 1. Many features of this graph are analogous to the Paris approach to fatigue debonding, as discussed in **Durability: fatigue**. A power law relationship may sometimes be employed to model the debond rate dependence between the threshold (below which no debonding occurs) and critical (at which rapid propagation occurs) values of energy release rate, taking the form

$$\frac{da}{dt} = C \cdot (G)^n$$

Here  $da/dt$  is the debond growth rate, and  $G$  is the applied energy release rate. The coefficient,  $C$ , and the exponent,  $n$ , are empirically determined for a given material system



**Fig. 1.** Subcritical debonding results, typical of what might be obtained with wedge specimens

and environment. If data is taken at various levels of an accelerating parameter, such as temperature or humidity level, master curves of debond rate can be generated using standard reduced time concepts. In some cases, diffusion-controlled environmental attack controls the debond rate, resulting in growth rate behaviour that is relatively independent of the applied energy release rate over some range.<sup>5</sup>

Subcritical debond data can be especially useful as a design tool for estimating adhesive bond durability. The master curve and reduced time shift factors, along with the expected energy release rate, can be used to estimate the rate of debonding that might occur in service. Being a fracture approach, data collected on a generic specimen can often be used to estimate the rate of debonding for complex bonded structures.

### *References*

1. J. Cognard, *J. Adhes.*, **20**, 1–13 (1986).
2. N. Shephard, *Measuring and Predicting Sealant Adhesion*, Master's Thesis, Virginia Tech, Blacksburg, VA, 1995.
3. T. Corson, Y.-H. Lai and D. A. Dillard, *J. Adhes.*, **33**, 107–122 (1990).
4. A. N. Gent and R. P. Petrich, *Proc. R. Soc. A*, **310**, 433–448 (1969).
5. S. Y. Kook and R. H. Dauskardt, *J. Appl. Phys.*, **91**(3), 1293–1303 (2002).

# E

---

## *Electrical adhesion*

---

K KENDALL

In 1877, Edison<sup>1</sup> patented a device based on the observation that a smooth metal electrode held at a high electrical potential adhered very strongly to a semiconducting surface. This electrical adhesion was directly related to the applied voltage, disappearing when the potential was removed. Unfortunately, the adhesion also failed when dust or scratches appeared on the semiconductor surface. As a result of these problems, there has as yet been no commercial exploitation of this invention.

However, the fact that certain materials adhere with a considerable force in an electric field is of great interest. It is also of practical effect in electrostatic precipitation of dust, in photocopying machines, in electrical control of powders flowing from hoppers and in electro-gelation of fluids.

Electrostatic precipitation is a widely used process for removing polluting particles from gas streams, for example, in power station flues or in cement kilns. The effluent dust grains become charged as the gas flows between two electrodes, then deposit in a cake on the electrode surface. This cake sticks to the electrode with a force that rises with the electric field but not simply proportional to the square of field strength as expected from the basic electrostatic equation for the cohesive stress  $\sigma$  in a dielectric:

$$\sigma = \varepsilon_0 \varepsilon_a E_a^2 / 2 \quad [1]$$

where  $\varepsilon_a$  and  $E_a$  are the average permittivity and field strength in the cake and  $\varepsilon_0$  the permittivity of free space. This equation cannot be correct because it predicts an adhesive pressure that is orders of magnitude too low. Typically, McLean<sup>2</sup> found an adhesive stress of around 100 Pa for an applied field of 1 kV mm<sup>-1</sup> with an  $E^{2/3}$  dependence.

The cause of this electrical adhesion has not been explained completely but appears to be related to the electrical conductivity of the powder. Only for particles with resistivities between  $10^4$  and  $10^9$ , ohm-metre is the adhesion apparent. Below this, the particles discharge on contact with the electrode, acquiring a charge of opposite sign and jumping off the electrode, the so-called pith-ball effect. For larger resistivities, localized electric breakdown occurs and no adhesion develops.

McLean<sup>2</sup> concluded that it was the concentration of electric field at the small contact spots between the semiconducting grains that caused the large adhesion observed. It has been shown<sup>3</sup> that this field concentration gives the correct magnitude of the adhesion stress and also the two-thirds power dependence on applied voltage. Figure 1 shows some results for the tensile stress required to break a contact between a smooth disc of semiconducting magnesium titanate and a polished steel plate as the voltage across the contact was varied. At zero potential, there was no adhesion but as the voltage was raised, the adhesion stress  $\sigma$  became substantial, giving a reasonable fit to the theoretical equation

$$\sigma = (\epsilon_0 \epsilon_a / 8\pi)^{1/3} [V E d / \pi D^2 (1 - \nu^2)]^{2/3} \quad [2]$$

where  $V$  is the applied voltage,  $E$  the elastic modulus of the material,  $\nu$  its Poisson ratio,  $d$  the contact diameter and  $D$  the disc diameter. A familiar example of electrical adhesion is the photocopier developed by Xerox. In this device, small particles of semiconductor adhere to a plate that has been selectively discharged by exposing it to light.<sup>4</sup>

Perhaps the most novel application of this electrical adhesion of solids is the control of flowing particles. For example, the phenomenon has been used to stop the flow of powder out of a silo by applying a strong field across electrodes at the open base. Alternatively, the flow was metered by pulsing the electric field in a controlled fashion.

A similar device made use of a dispersion of semiconducting particles in an insulating fluid. Winslow<sup>5</sup> in 1947 first patented such a fluid made by mixing fine silica particles in oil. This fluid flowed easily under ordinary conditions but gelled when a strong electric field, about  $2 \text{ kV mm}^{-1}$ , was applied across it. Winslow showed by microscopic study that strings of particles were formed between the electrodes when the voltage was imposed,

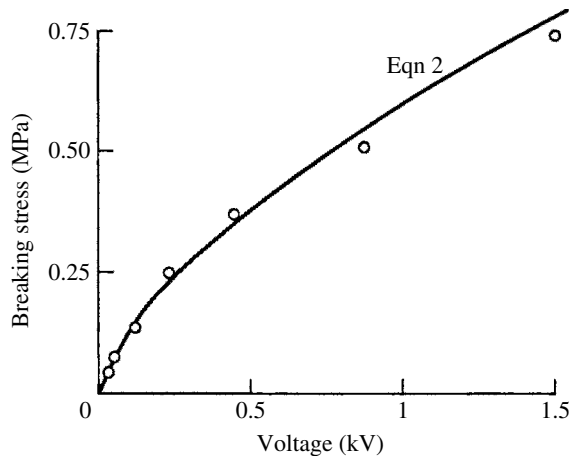


Fig. 1. Results for electrical adhesion of a ceramic disc to a metal plate

these strings effectively solidifying the fluid. Such electro-rheological fluids have been used experimentally in clutches, brakes, valves, active damper systems, and robots.<sup>6</sup>

See also **Electrostatic theory of adhesion**.

### References

1. T. A. Edison, British patent 2909 (1877).
2. K. J. McLean, *J. Air Pollut. Control Assoc.*, **27**, 1100 (1977).
3. K. Kendall, *J. Phys. D: Appl. Phys.* **23**, 1329 (1990).
4. D. S. Rimai, D. J. Quesnel, L. P. DeMejo and M. T. Regan, *J. Imaging Sci. Technol.*, **45**, 179 (2000).
5. W. M. Winlow, US Patent 2417850 (1947).
6. K. Kendall, *Molecular Adhesion and its Applications*, Kluwer, New York, 2001, 268.

---

## Electrochemical pre-treatment of polymers

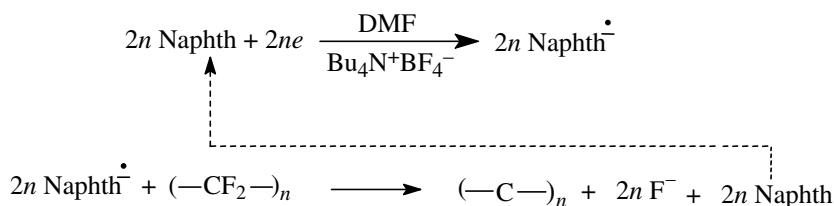
---

R H DAHM

The **Pre-treatments of polymers** is often necessary in order to form satisfactory adhesive bonds. This may be achieved for certain polymers by means of purely physical processes such as abrasion or solvent cleaning in order to remove mechanically weak material from the polymer surface and/or to provide a mechanical key for the adhesive. However, polymers made up of non-polar molecules such as polyolefins and their fully halogenated analogues often require a pre-treatment that involves chemical modification of the polymer surface in order to enable the polymer to interact or even chemically react with the adhesive. This may be achieved on the one hand by **Pre-treatments of polyolefins** with powerful oxidizing agents and on the other by treating fully halogenated materials such as PTFE with powerful reducing agents (see **Pre-treatment of fluorocarbon polymers**). Such reagents may be readily generated at the anode and cathode respectively of an electrochemical cell, and the topic will be discussed under the headings of cathodic pre-treatments and anodic pre-treatments of polymer surfaces.

### Cathodic pre-treatments

“Tetra Etch” (A L Gore Associates, Newark NJ or Flagstaff AZ), a widely used commercial process for the pre-treatment of PTFE, is based on the fact that PTFE is thermodynamically unstable in the presence of most reducing agents and may be reduced to a form of elemental carbon by exposure to solutions of radical anion salts such as sodium naphthalenide in anhydrous aprotic solvents such as tetrahydrofuran.<sup>1</sup> Dahm and Brewis showed that the pre-treatment involves transfer of electrons from the radical anion to the polymer surface, resulting in the formation of a dark brown or black surface layer of strongly adhering carbon and fluoride ion with simultaneous oxidation of the naphthalenide anion to naphthalene. They showed that the naphthalenide anion could be generated by the cathodic reduction of naphthalene in dimethyl formamide (DMF) containing tetrabutylammonium tetrafluoroborate as support electrolyte ( $\text{Bu}_4\text{N}^+\text{BF}_4^-$ ). Naphthalene was

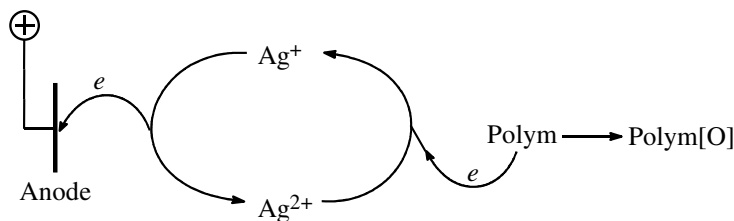


therefore made to act as an electron carrier as shown in the scheme, which represents the first recorded example of an electron carrier mediated reduction of PTFE.

Brewis and Dahm subsequently showed that the naphthalenide anion could be replaced as an electron source by a platinum cathode held at about  $-2.5$  V with respect to a saturated calomel electrode and held in direct contact with the PTFE surface. Formation of the black electronically conducting carbonaceous material would commence at the point of contact with the electrode and grow radially outwards to cover an area of approximately  $0.25$ – $0.5$   $\text{cm}^2$ . A larger area could be treated by repeated application of the point contact electrode. PTFE films treated in this way would exhibit failure loads in adhesion tests as high or even higher than those obtained using conventional sodium naphthalenide treated material.<sup>2</sup>

### Anodic pre-treatments<sup>3</sup>

More recently, these workers have turned their attention to the anodic, that is, oxidative pre-treatment of hydrocarbon-based polymers such as polypropylene (PP), polyethylene (PE) and certain synthetic elastomers such as styrene butadiene block copolymer (SBS). In the past, such materials were frequently treated with acidic dichromate solutions prior to bonding, painting or metallizing. With the advent of stricter environmental controls over the use of chromium(VI) species (see **Environment and the impact of adhesive technology**), Brewis and Dahm have developed a process aimed at replacing the chromium(VI) treatment by an environmentally more benign electrochemical process. The polymer is immersed in a dilute, acidic solution of silver(II) nitrate produced by the anodic oxidation of a dilute solution of silver nitrate in dilute nitric acid. The anodically generated silver(II) ion is a powerful oxidizing agent capable of oxidizing the surface of hydrocarbon-based polymers. The silver(II) species is reduced back to silver(I), which is returned to the anode and reoxidized to silver(II) so that there is no net consumption of silver. The process is illustrated by the following scheme:



where Polym[O] represents the treated polymer. Large increases in failure loads of lap shear joints may be obtained for PP and PE for immersion times of less than one min

at room temperature. It was also shown that PP, and to a lesser extent PE, could be treated effectively by contacting the polymer directly with a platinum electrode in dilute nitric but not in sulphuric acid. Examination of the treated surfaces by a variety of analytical techniques showed that in both cases the improvements in bondability is brought about by oxidation of the polymer surface either by the silver(II) species or, in the case of the silver-less process, by anodically generated nitrate radicals. The electrochemical treatments obviate the need for the storage of large quantities of hazardous materials and offer a viable alternative to the use of chromium(VI) compounds for the treatment of a number of hydrocarbon-based polymers.

### References

1. (a) L. Kavan, in *Chemistry and Physics of Carbon*, Vol. 23, P. A. Thrower, Ed., Marcel Dekker, New York, 1991. (b) L. Kavan, *Chem. Rev.*, **97**(8), 3061–3082 (1997).
2. (a) R. H. Dahm, in *Surface Analysis and Pre-treatment of Plastics and Metals*, D. M. Brewis, Ed., Applied Science Barking, Essex, 1982. (b) R. H. Dahm, D. J. Barker, D. M. Brewis and L. R. J. Hoy, in *Adhesion 4*, K. W. Allen, Ed., Applied Science, London, 1980, p. 215.
3. D. M. Brewis and R. H. Dahm, *Int. J. Adhes. Adhes.*, **21**(5), 397–409 (2001).

---

### Electron microscopy

---

D E PACKHAM

Whereas in **Optical microscopy** visible light is used to interact with a specimen by reflection from its surface or by transmission through its thickness, an electron microscope uses electrons in an analogous way. A heated wire cathode provides a source of electrons that are focused by electromagnetic lenses. The column of the microscope has to be evacuated as electrons are rapidly absorbed in air at atmospheric pressure.

The electrons may be scanned over the specimen and the secondary electrons collected to form an image: this occurs in **Scanning electron microscopy**, discussed elsewhere.

The interaction of electrons with matter generates X-rays. In **Electron probe microanalysis** (EPMA), these are analysed to yield information about the elemental composition of the specimen.

This article is concerned with the transmission electron microscope (TEM) in which the electrons pass through the specimen and may be focused to form an image. Because of the much smaller wavelength of electrons compared with visible light, the electron microscope has much higher resolution than an optical microscope.

The resolution<sup>1,2</sup> depends on the particular instrument and operating conditions. Broadly speaking, better resolution is obtainable with crystalline inorganic materials than with organic polymers. In favourable circumstances, a resolution of 0.2 to 0.5 nm may be obtainable.

Some transmission microscopes have X-ray detectors and so can give elemental information in a manner analogous to EPMA. In scanning transmission electron microscopes (STEM), the electron beam can be scanned. When used in conjunction with X-ray detectors, elemental information can be obtained from a very small area of the specimen. The

STEM can generally be operated in a SEM mode when it has enhanced resolution of 1.5 nm compared to 5 nm for conventional SEM.

Because of the low penetrating power of electrons, specimens for examination in transmission have to be very thin, depending on the circumstances tens or hundreds of nanometres in thickness. Surface features on thick specimens can be examined by making a thin replica. A standard technique is to evaporate a thin film of carbon on to the surface of interest, to “shadow” it by depositing an even thinner layer of platinum at a different angle, and then to remove the deposited replica, for example, by dissolution of the original specimen.

Vesely<sup>3</sup> in a short review article has described the use of a standard electron microscope modified for STEM for the microstructural analysis of polymers. To some extent the beam sensitivity of polymers is overcome as the STEM acts as an image intensifier, reducing the electron flux needed.

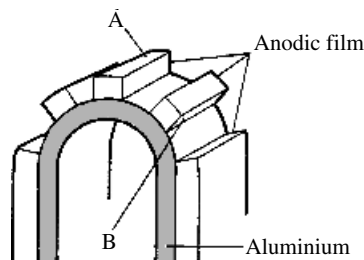
#### *Applications to problems in adhesion*

The TEM in its various forms is widely used in materials science, and some of its applications are studies of adhesion. It has helped to elucidate failure and bonding mechanisms in composites (see **Fibre matrix adhesion – carbon fibres**). An important use is in the examination of the structure of surface oxides. Several techniques have been employed.

The replica method has been used for examining the pore structure of films formed in the **Anodizing** of aluminium. Figure 1 represents a piece of anodized aluminium that had been bent, so that part of the anodic film has spalled off. The deposition and shadowing directions are indicated. Replicas made in this way show the structure of both the top surface of the anodized layer and the fracture surface; Fig. 2 shows features of the pores described in the article **Anodizing**.

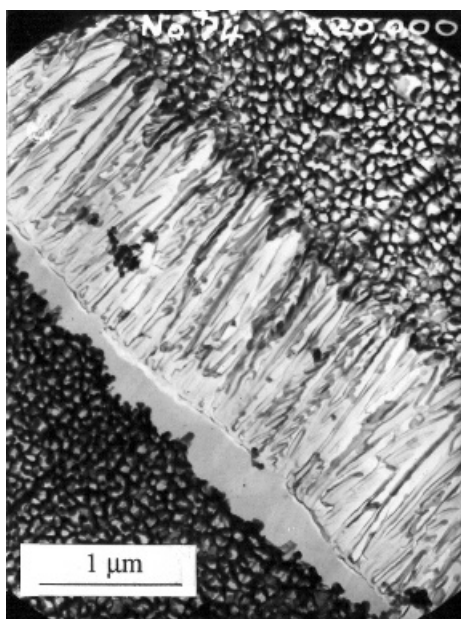
Surface oxides may also be examined directly by removing them from the base metal. Iodine in dry methanol will dissolve most metals, leaving the oxide unaffected. Electron diffraction, especially if combined with elemental analysis, provides a powerful method of studying the structure and composition of a surface layer on a metal.

Venables and colleagues have used the STEM in its SEM mode to study films formed on aluminium and titanium.<sup>4</sup> This high-resolution technique has been applied to layers produced by **Anodizing** and the **FPL etch** treatment. By producing micrographs in stereo pairs, fine details can be seen and isometric drawings produced. This has enabled



**Fig. 1.** Preparation of sections through an anodic film for replication for TEM examination: carbon deposition direction A, shadowing direction B





**Fig. 2.** Electron micrograph of an anodic layer formed on aluminium in phosphoric acid. Top right and bottom left show pore openings in the top surface and the central band shows a section through the pores

Venables to argue for the importance of mechanical interlocking (see **Mechanical theory of adhesion**) in adhesion to porous anodized surfaces.

### References

1. D. B. Williams and B. C. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*, Kluwer Academic/Plenum Publishers, 1996.
2. P. J. Goodhew, L. E. Cartwright, F. J. Humphreys and R. Beanland, *Electron Microscopy and Analysis*, Taylor & Francis, 2000.
3. D. Vesely, *Mater. World*, **10**(11), 23–24 (2002).
4. J. D. Venables, *J. Math. Sci.*, **19**, 2431 (1984).

---

### *Electron probe microanalysis*

---

B C COPE

One result of the bombardment of a material by a high-energy electron beam, as in a scanning electron microscope, is the emission of X-rays. The energy of such X-rays is characteristic of the nucleus from which they originated. Hence, if the energy of the emission is assessed, the elemental composition of the target material may be determined. This is the principle of electron probe microanalysis (EPMA).

Early electron probe microanalysers were usually stand-alone instruments, but the instrumentation currently produced normally takes the form of an add-on option to a scanning electron microscope (SEM) (see **Scanning electron microscopy**), the same beam being used to create the visible image and to generate X-rays. Thus, an area of interest may be subjected to both topographical and compositional investigation.

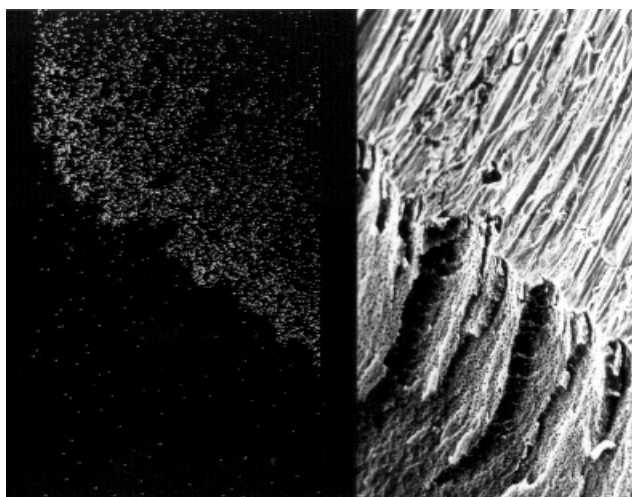
The specimen for analysis must be a solid that does not release volatiles under vacuum and which is not subject to beam damage or charging. Many polymers are therefore inherently unsuitable for investigation, although the more conductive materials may be able to be examined at low accelerating voltages. Alternatively polymers may be coated with gold and the analysis results adjusted to disregard the coating. Metals are ideally suited to the technique, especially when polished or sectioned, but some glasses, ceramics and semiconductors may yield reliable results.

Since the analysis is usually carried out in an SEM, the same limitations on specimen size apply. Most instruments are limited to samples of a centimetre or so in diameter, but particular demands sometimes lead to the construction of specialized instruments. For example, tribologists interested in automotive engine wear may commission SEM/EPMA combinations with specimen stages large enough to accommodate a substantial component of the engine at the sacrifice of the ability to orient and manipulate the specimen during examination.

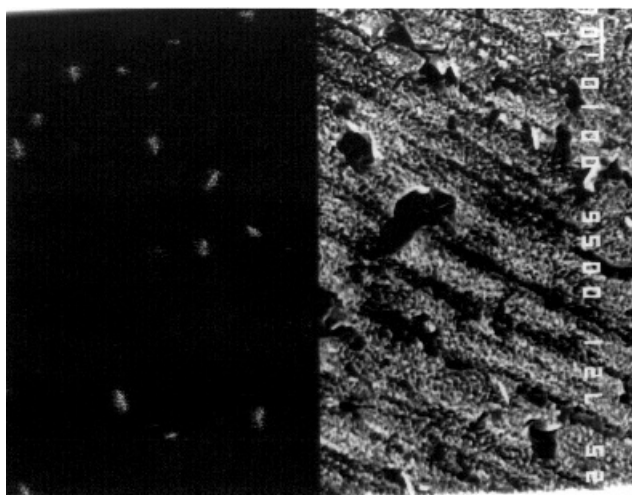
The X-rays generated may be examined by either energy-dispersive or wavelength-dispersive spectrometer. Energy-dispersive X-ray analysis (EDX) employs relatively robust equipment routinely capable of detecting elements from carbon or nitrogen upwards. Wavelength-dispersive X-ray analysis (WDX) is less commonly used, is more expensive and employs more demanding equipment, but extends sensitivity and quantification at low atomic number. Instrument parameters and the nature of the sample combine to set the volume selectivity of a particular analysis. The volume sampled can range from the order of  $1\ \mu\text{m}^3$  up to several cubic micrometres. Sensitivity varies greatly with the element in question and the matrix in which it is found, but may be around 1000 ppm for EDX and about one order of magnitude better for WDX. Although qualitative investigations are relatively straightforward, accurate quantitative work requires calibration against standards held in matrices similar to that under investigation.

The scope of EPMA in investigating problems associated with adhesion is limited by its relatively deep sampling depth ( $1\ \mu\text{m}$ ) and similar spatial resolution. However, it can be useful in studying layers on a substrate, such as those resulting from **Primers for adhesive bonding** and **Pre-treatment prior to bonding**. It can help determine the locus of failure (see **Stress distribution: mode of failure**) and show the distribution of adhesive on substrate surface. Identification of an adhesive is eased if it incorporates a filler or additive containing an element not present in other components. Figure 1 shows part of the resin side of a failure surface for rubber-toughened epoxy resin (see **Toughened adhesives**) bonded to oxidized steel. The right-hand part of the figure is the SEM image and the left-hand side is an image constructed from the iron X-ray signal. The resin in the lower region of the specimen is clear in the electron image. The upper region appears different and shows a strong iron signal in the X-ray image, indicating an area of cohesive failure within the iron oxide.

The resin side of a broken epoxy–zinc joint is shown in Fig. 2. The electron image only reveals the resin, but the zinc X-ray image also shows local concentrations of zinc in the resin. It is likely that some dendrites on the metal surface have broken



**Fig. 1.** The resin side of a broken bond between oxidized steel and rubber reinforced epoxide: right, electron image; left iron X-ray image. The top part of the specimen shows cohesive failure within the oxide. (P. J. Hine, S. EL Muddarris, D. E. Packham, unpublished micrograph, see *J. Adhesion Sci. Tech.* **1**, 69 (1987))



**Fig. 2.** The resin side of a broken bond between zinc and epoxide resin: right, electron image; left zinc X-ray image. Note the local concentrations of zinc within the resin. (P. J. Hine, S. EL Muddarris, D. E. Packham, unpublished micrograph, see *J. Adhesion* **17**, 207 (1984))

and remain embedded in the resin, giving an unusual example of a mixed failure mode (see **Microfibrous surfaces**).

A particular attribute of the SEM/EPMA instrument is the ability to present data in a striking form. The analysis may first be plotted simply as count-frequency against

energy level and a spectrum obtained with peaks indicating the presence of particular elements. A topographical micrograph may then be obtained and compared with a composition map where the concentration of a chosen element or elements may be displayed in computer-generated colour. Thus, for example, segregation in metals, the inclusion of foreign bodies or selective etching may be readily illustrated. Results may be printed out in the form of bar charts and pie charts that may be useful for presentations.

In the line scan technique, a line across the sample may be scanned and data presented as a graph or a histogram of concentration of a particular element against position

X-ray analysis facilities can also be used in transmission **Electron microscopy**.

### *Select References*

J. C. Russ, *Fundamentals of Energy Dispersive X-ray Analysis*, Butterworth, London, 1984.

P. J. Goodhew and F. J. Humphreys, *Electron Microscopy and Analysis*, 2nd edn, Taylor & Francis, London, 1988.

A. M. Jame and G. Lawes, Eds., *Scanning Electron Microscopy and Microanalysis*, ACOL/Wiley, Chichester, 1987.

---

## *Electrostatic theory of adhesion*

---

K W ALLEN

There are essentially three different situations that need to be considered under this title: adhesion of pressure-sensitive tapes to metal surfaces, adhesion of vacuum-evaporated thin films of metal on polymer surfaces and the adhesion of ultra-small particles. The first two of these will be considered here, but the third one is dealt with quite separately under the heading **Electrical Adhesion**.

The concept of regarding two surfaces that are being separated as the plates of an electrostatic condenser is due to Deryaguin *et al.*<sup>1,5</sup> as long ago as 1957. Particularly, they considered the peeling of a pressure-sensitive tape from a rigid substrate. In a quantitative development of this, the energy of a charged condenser in terms of the potential and separation of the plates is equated to the work of adhesion involved in the peeling of a tape. This is compared with conditions for an electric discharge in terms of the potential and the pressure of gas between them using a double logarithmic plot. Further, this theory predicts a variation of the work of adhesion with the pressure of the atmosphere in which it is measured. Deryaguin and his co-workers reported excellent agreement between values predicted in this way and experimental values of peel strength when a polymer (PVC or natural rubber) tape was peeled from a glass or steel surface in air or argon. However, this whole theory is subject to criticism on two fronts.

The technique for determining the various parameters in the relationships are so interdependent that the arguments are essentially cyclic and the relationships are mutually interdependent. Thus, the whole basis is flawed and the apparent agreement is inevitable. Also, it is tacitly assumed that the relationships for electric discharge in a gas (derived in quite different circumstances) applies to this situation. Secondly, attempts to repeat the various experiments have failed to reproduce Deryaguin's results satisfactorily.

However, the vital point is that this theory gives some explanation of the well-established fact that the work of adhesion does vary with the nature and pressure of the gaseous atmosphere in which it is measured, as well as for the noise and light that are emitted.

More recently, Deryaguin<sup>2</sup> has emphasized the fact that the force of attraction between the plates of a condenser is independent of their separation, in contrast to the distance–force relationships of other types of attraction. Thus, while at small distances electrostatic forces may be negligible by comparisons with others, as the distances become greater, the relative significance will change and the electrostatic forces become significant.

Considering now the adhesion of vacuum-deposited metallic films on insulator polymeric substrates, which Weaver<sup>3</sup> explored this using a **Scratch test**. He found that after deposition the interfacial strength increased with aging but this returned to its initial value when it was exposed briefly to glow discharge. This effect could be repeated a number of times. There have been a number of further investigations of the mechanism of electron transfer involving the Fermi levels. These were consolidated by some elegant work by Possart<sup>4</sup> using potential contrast **Scanning electron microscopy**. He was able to show conclusively the existence of an electron double layer at the interface between polymer and metal and to measure its magnitude. Using this data and a theoretical treatment, he provided support for the significance of this electrostatic component to adhesion, while recognizing that it was only a part of the total phenomenon, and quite possibly only a relatively small proportion of the whole.

A comparison of different theories is given under **Theories of Adhesion**.

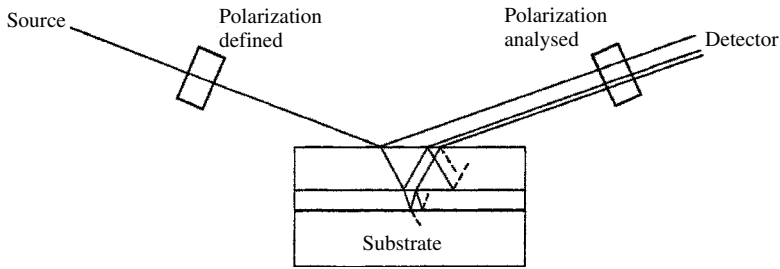
### References

1. B. V. Deryaguin, N. A. Krotova, *et al.*, *Proceedings of the 2nd International Congress on Surface Activity* Vol. III, Butterworth, London, 1957, p. 417.
2. B. V. Deryaguin and Yu. P. Toporov, in *Physicochemical Aspects of Polymer Surfaces*, K. I. Mittal, Ed., Plenum Press, New York, 1983, p. 605.
3. C. Weaver, in *Aspects of Adhesion 5*, D. J. Alner, Ed., University of London Press, London, 1969, p. 202.
4. W. Possart, *Int. J. Adhes. Adhes.*, **8**, 77, (1988).
5. B. V. Deryaguin and V. P. Smilga, *Adhesion: Fundamentals and Practice Ministry of Technology*, 1969, p. 152.

## Ellipsometry

R GREEF

Ellipsometry is a branch of oblique-incidence reflection spectroscopy, in which the change of polarization of the light is analysed, rather than just its change of intensity. It derives its name from the fact that the most general state of polarization of light is elliptical, of which the more generally known states, linearly and circularly polarized light, are particular cases. The polarization state of obliquely reflected light is controlled by the optical constants of the reflecting surface and is also very sensitive to films of foreign materials. Because ellipticities can be measured with high resolution and accuracy, sub-monolayer thicknesses can be detected, and measurements of film thickness can be made quickly and reliably.



**Fig. 1.** An ellipsometer collects the multiply-reflected light from a film-covered surface and analyses the resulting changes in its polarization. This is a very sensitive indicator of the thickness of the surface layers and of their optical properties

The technique, therefore, has found application in many diverse fields of thin-film measurements, and has the potential to be even more widely applied with the advancing capability, and declining cost, of the available instrumentation.

### Theory

The theory and practice of ellipsometry has been comprehensively treated by Azzam and Bashara.<sup>1</sup> A more practically oriented treatment can be found in two more recent books, which serve as a better starting point for the intending practitioner.<sup>2,3</sup> The following brief synopsis can only serve to highlight the main points of the technique.

The basic idea of ellipsometry is depicted in Fig. 1. Collimated light passes first through polarization optics, which define its polarization state. The beam is then incident on the test surface, which may be immersed in a transparent medium such as an electrolyte solution or etching medium. The light reflected at the specular angle is then analysed by further polarization optics.

Monochromatic light (e.g. a low-power laser) can be used as the probe beam, and instruments of this kind are still available. The applications of the monochromatic version of ellipsometry are mainly dynamic, where the time-evolution of the film growth or removal process is the principal focus. A carefully collimated white-light source can be used to obtain information across the visible spectrum, in which case the detector contains either a scanning monochromator or multi-element detector. Instrumentation is now available for carrying out ellipsometry in the IR region, which has opened up a wider range of applications, particularly in the investigation of polymer films.

The change of state of polarization caused by the reflection is described by two quantities, which are both angles:  $\Delta$ , a phase change term, and  $\psi$ , the tangent of which describes the amplitude change. For a clean, bare surface, these quantities are related to the optical constants  $n$  and  $k$  of the substrate in a one-to-one mapping. Ellipsometry is therefore one of the principal ways of evaluating the optical constants of materials.

When the surface is covered by one or more films, Fresnel analysis applied to each interface in turn followed by vector summation or the resulting multiply reflected beams leads to the Drude equations, which predict the  $\Delta$ - and  $\psi$ -values for a stack of films for which the thickness and refractive indices are known.

This classical analysis technique applies to the ideal case of isotropic films with smooth interfaces. Graded-index films can be treated by simple extension, replacing the film in the calculation by a “pile of plates”, each of uniform properties, with the individual refractive indices varying from plate to plate. Rough interfaces can also be treated in some circumstances by replacing the interface with a film of index intermediate between those of the component materials – the so-called effective medium theory. This theory is dependent on the rough surface being approximated by an intimate mixture of the grains of the component materials of a size smaller than the wavelength of the measurement light. Empirical correlations can also sometimes be found, which are useful in making qualitative predictions of the microscopic structure of rough surfaces on the basis of ellipsometric observations.

### *Instrumentation and applications*

The capabilities and value for money of instrumentation and desktop computing power continue to improve apace, which combine to make ellipsometry more accessible and powerful. Recent significant improvements include the use of CCD spectral detectors at a reasonable cost, making spectroscopic ellipsometry a more viable technique.

The inversion of the Drude equations, that is the estimation of unknown thicknesses or optical constants from ellipsometric measurements, relies upon the application of computer-intensive search and optimization methods, which are well within the capabilities of personal computers. The software for solving a wide variety of film problems is now available as part of the instrumentation package from a good number of ellipsometer manufacturers. This has resulted in the fast-widening scope of ellipsometry as reflected in the number of publications in which the technique is dominant.

Applications that are relevant to the topic of adhesion include the determination of the growth kinetics and densification of polymer films at surfaces, quality control of anodization and other surface-modification pre-treatments, measurement of adsorption and determination of molecular orientation and compaction of adsorbed layers and Langmuir–Blodgett films, detection of surface damage in plasma-etching processes and measurements of thinning of lubricant films. Metallization from the solution or vapour phase can be studied up to the stage at which the metal becomes opaque (around 40-nm thick for most metals).

Reviews of these applications are published from time to time, but because of the rapidly developing nature of the subject, they are soon outdated. The best way of locating literature references on ellipsometry at present is by computerized database search. Using the keyword fragment “ellipsomet” in conjunction with keywords for the specific application excludes almost all spurious references.

### *References*

1. R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North Holland, Amsterdam, 1977.
2. H. G. Tompkins. *A User's Guide to Ellipsometry*, Academic Press, New York, 1993.
3. H. G. Tompkins and W. A. McGahan, *Spectroscopic Ellipsometry and Reflectometry*, John Wiley & Sons, New York, 1999.

---

*Emulsion and dispersion adhesives*

---

G C PARKER

*Introduction*

Following a period of sustained growth after their introduction many years ago, the use of emulsion and dispersion adhesives is now widespread in many industrial and commercial operations. This situation is considered very likely to continue owing to the many advantages offered by these products when compared to other types of adhesive, not least in terms of environmental considerations.

*Types of emulsion adhesives*

Probably the most widely used industrial emulsion or dispersion adhesives are those based on polyvinyl acetates, commonly referred to as PVAs. These products are normally manufactured by a process referred to as emulsion polymerization whereby, basically, vinyl acetate monomer is emulsified in water and, with the use of catalysts, is polymerized. The presence of surfactants (emulsifiers) and water-soluble protective colloids facilitates this process, resulting in a stable dispersion of discrete polymer particles in the aqueous phase.

These PVAs are not normally suitable for use as adhesives in their basic unmodified state as they tend to form brittle films and have limited adhesion capabilities. They are, however, compatible with a wide range of compounding ingredients, which are capable of modifying their properties very considerably. Plasticizers and thickeners are two of the materials most commonly used in the formulation of PVA-based adhesives, but many other modifiers may be incorporated as required, resulting in a very wide range of PVA-based adhesives being available to meet the specific demands of many different applications.

It must be stressed, however, that while a substantial proportion of emulsion adhesives are based on PVA, which is referred to as a homopolymer as if it is the polymer of a single material, vinyl acetate, copolymer-based emulsions are becoming of increasing significance and importance in the marketplace.

Copolymers, as the name implies, are produced from the polymerization of two different materials. Probably one of the most widely used copolymer emulsion adhesives is that based on vinyl acetate ethylenes, commonly referred to as VAEs (see **Ethylene vinylacetate copolymers**). These are produced by the copolymerization of vinyl acetate and 10–20% ethylene, the resulting polymer base possessing some superior properties over the PVA-based emulsions referred to above. These superior properties relate principally to the increased inherent flexibility of the dry VAE film due to the internal plasticization effect of the ethylene component in the polymer, which enhances adhesion to many “difficult” surfaces. There are, however, a number of other polymers and copolymers that are used as the formulating basis for alternative specialized emulsion adhesive systems.

*Setting mechanism*

Having dealt with the basic chemistry of emulsion and dispersion adhesives, the method by which they function should now be considered.



If a thin “wet” film of emulsion adhesive is applied between two porous surfaces and these three components subjected to an adequate degree of compression, the initial state of the adhesive is one of a water phase containing discrete and stable polymer particles. Wetting of the substrate surfaces then takes place followed by the commencement of penetration of the water phase into the substrates (see **Wetting and spreading**). As this occurs, the solid content of the adhesive film rises and it becomes more viscous and tacky. Capillary forces in the substrate then continue to draw water (and, dependent on substrate porosity, possibly some polymer solids) from the adhesive until its solid content rises to the point where it coalesces into a continuous film.

Maximum bond strength will not be attained, however, until all the water present in the adhesive film and the substrates have been removed and dispersed into the atmosphere, the rate of which will be dependent upon many factors. The situation detailed above deals with two porous substrate surfaces. While this is not an essential requirement for the successful use of emulsion adhesives, it must be stressed that when these products are to be utilized in the conventional manner (i.e. bonds made using “wet” adhesive), at least one of the substrate surfaces must be porous to permit the escape of the water phase from the adhesive.

### *Methods of application*

The objective of any application system is to deposit a controlled quantity of adhesive in the correct position on a substrate at the right time. A number of types of applicators may be used to achieve this including wheel, extruder, spray, roller, dauber or printing techniques.

These different applicating systems all place differing demands on the adhesive in terms of its viscosity and rheology characteristics and also subject the adhesive to varying degrees of shear. It is important, therefore, to ensure that the properties of an adhesive are compatible with the equipment with which it is to be applied and, if high shear forces are likely to be exerted on the adhesive, that it possesses a sufficient degree of shear stability.

### *Advantages and limitations*

Some of the main advantages of emulsion adhesives include the relatively fast bond development (dependent upon specific substrate and bonding conditions) compared to that obtained with solution adhesives. The carrier phase (water) is cheap and environmentally safe (see **Health and safety** and **Environment and the impact of adhesive technology**). Copolymer systems, in particular, can be formulated to give very good adhesion to many “difficult” substrate surfaces.

Among their limitations is a slow setting speed, which is faster than that of water-based solution adhesives but is significantly slower than that of **Hot melt adhesives**. Further, when used in the conventional “wet” application mode, at least one substrate surface must be porous.

The water resistance of the dry adhesive film obtained from emulsion adhesives, while fair, tends to be adversely affected by the presence of small residual quantities of protective colloids that are water soluble. They are used as **Adhesives in the textile industry** and for bookbinding and woodworking (**Wood adhesives – basics**).

*Select References*

- A. E. Corey, P. M. Draghetti and J. Fantl, in *Handbook of Adhesives*, 2nd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1977, Chap 28.
- C. E. Blades, in *Handbook of Adhesives*, 2nd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1977, Chap 29.
- M. S. El-Aasser and J. W. Vanderhoff, Eds., *Emulsion Polymerisation of Vinyl Acetate*, Applied Science Publishers, London, 1981.

**Engineering design with adhesives**

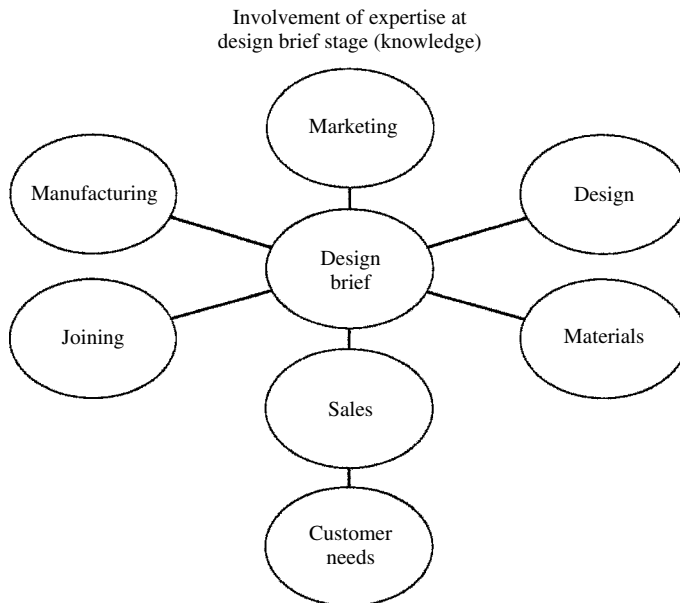
C WATSON\*

In this article are discussed ways in which adhesive technology can influence the approach of the design engineer.

Industry is, ideally, a partnership of people from quite different disciplines working together to turn a design brief into a production reality. Strong links have to be forged internally between those involved in design and manufacturing and, externally, with the suppliers of materials. Some of these are summarized in Fig. 1.

*Benefits of using adhesives for joining*

The list below gives well-established benefits that can result from the use of adhesives in preference to joining methods such as riveting, bolting, spot welding, ultrasonic welding,



**Fig. 1.** Some factors affecting engineering design

welding or mechanical clipping:

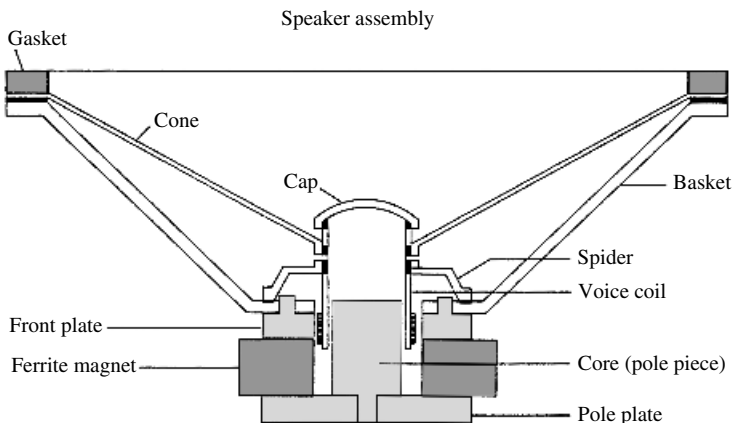
1. reduction in weight;
2. ability to join thinner materials;
3. better stress distribution over joint area;
4. improvement in joint strength;
5. ability to join dissimilar materials;
6. scope for sealing as well as joining;
7. in some cases, repairs are more readily effected;
8. increased flexibility in choice of component material;
9. elimination of extra components such as keys, circlips and so on;
10. elimination in some cases of machining operations;
11. facilitation of manufacturing process;
12. aesthetic improvement.

A number of case histories are now described illustrating the advantages available to the designer from a skilful use of adhesive technology.

*Floppy disc cover* This first example is a simple case of the manufacture of a paper floppy disc cover and illustrates the importance of the link between design and manufacturing. The designer originally chose a solvent-based adhesive (see **Solvent-based adhesives**) to bond the flaps on the three sides. The process involved applying the adhesive to both faces and waiting until the solvent flashed off – in this case 10 min. During the flash-off time, the covers had to be stored and the solvent extracted.

To achieve ease of manufacture with total continuous automation, a single component, cyanoacrylate, (see **Cyanoacrylate adhesives**) is now used. It is applied automatically to one of the joint faces and the faces mated immediately. The adhesive develops initial handling strength in 4 s.

*Loudspeaker* The loudspeaker as shown in Fig. 2 has eight or so adhesive joints. In order to meet production requirements of one every 10–15 s, it is necessary to use automatically applied fast-curing adhesives. The alternative previously employed was to use



**Fig. 2.** Loudspeaker assembled by adhesive bonding

solvent-based and/or two-component mixed products, but both were slow in terms of total process time.

Before changing to the fast-curing adhesives, one large European manufacturer was considering building a factory extension to provide extra space for “work in progress” following an increase in production demand. It can be seen from the above that “work in progress” becomes a major influence in the choice of adhesives, where performance criteria are similar.

*Coaxial assemblies* Often, the application of adhesives technology to the manufacture of such components allows the elimination of components and the machining operations, leading to a reduction in weight. Figure 3 shows a variety of cylindrical components – pulley to shaft, gear to shaft, trunnion end into roller and sprocket on to shaft.

Considering the first case, pulley to shaft, it can be seen that in order to prevent the pulley moving around the shaft a key is used. Keyways have to be cut in the pulley and the shaft, weakening both. To prevent the pulley moving along the shaft, a set screw is used, necessitating the use of additional material on the side of the pulley. Using adhesives, the design will be simpler. The key and machining of keyways could be eliminated. (This could enable a reduction in the shaft size due to elimination of stress concentration in the case of gear to shaft application.) The set screw can be eliminated and with that the integral ring. The other components could be redesigned with analogous advantages.

*Ink distributors* A world leader in office machinery has recently adopted the use of an **Anaerobic adhesive** in the manufacture of ink distributors. After an extensive study, it was found that this adhesive could save £15,000 per year in manufacturing cost by replacing solder on four joints to join shaft ends to a distributor tube. In two further joints, a slow-setting sealant has also been replaced by the fast-curing anaerobic material.

The cost of implementing the change was less than £1500. The result is a reduction in cost and an aesthetically better product manufactured more easily.



**Fig. 3.** Some coaxial components with potential for redesign involving adhesive bonding

*Flexibility in choice of component material*

Adhesives manufacturers are continually trying to develop adhesives to meet the needs of industry. One group of plastics that have been difficult to bond are polyolefins and related low-energy substrates (see **Surface energy**). They could not be bonded without elaborate surface preparation such as **Flame treatment** or **Plasma pre-treatment, Corona discharge treatment** or oxidative chemical methods.

Why then are these materials so attractive to the designer? Providing the performance criteria can be met by polyolefins, which are less costly than other plastics. According to an ICI source, polyethylene and polypropylene, cost 0.06 and 0.07 pence per cubic centimetre respectively compared with, for example, 0.40 pence per cubic centimetre for nylon.

A new primer (see **Primers for adhesive bonding**) has been developed that enables a cyanoacrylate to be used to bond polyolefins.<sup>1</sup> The primer is applied to one surface, adhesive to the other – the bond is virtually instantaneous. This will allow the designers flexibility in choice of plastics, enabling less costly polyolefins to be selected.

These are but a few examples illustrating ways in which adhesive technology can influence the approach of the design engineer in the choice of materials and manufacturing processes.

Further consideration relating mechanics to joint design are given in **Joint design: strength and fracture perspectives, Durability: creep rupture, Durability: subcritical debonding** and **Durability: fatigue**.

*References*

1. Loctite Technical Information, *New Primer for Polyolefins – Loctite 757*.

*Select References*

- J. D. Buckley and B. A. Stein Eds., *Joining Technologies for the 1990s Welding, Brazing, Soldering, Mechanical, Explosive, Solid-state, Adhesive*, Noyes Data Corporation, Park Ridge, NJ, 1986.
- R. B. Krieger, Adhesive bonding design and analysis, in *ASM Engineered Materials Handbook Vol. 3 Adhesives and Sealants*, M. M. Gauthier Ed., ASM International, 1990, p. 459.
- F. E. Penado and R. K. Dropek, *Numerical Design and Analysis*, M. M. Gauthier Ed., ASM International, 1990, p. 477.

---

*Engineering surfaces of metals*

---

JOHN F WATTS

The surfaces of metals used in practical adhesion situations are very far removed from the concept of a clean metal surface: the substrate to which adhesives and coatings manufacturers exhort us to apply their product. The surfaces of metals, unless very noble (gold or platinum), will invariably have a layer that reflects the interaction of the metal with the atmosphere. This may take the form of a simple oxide but is more likely to be of an oxyhydroxide form, and its composition may be mixed cations or the major or minor

cations of the alloy. In addition, material may be absorbed from the atmosphere to form a loosely bound surface layer (a potential weak boundary layer, see **Stress distribution: mode of failure**) or there may be extraneous material at the surface, which is merely left over from a previous processing step: lubricant from mechanical processing and temporary protectives for corrosion protection. However thorough the cleaning by **Degreasing** or **Abrasion treatment**, some of this material will invariably remain attached to the metal surface. Added to this gamut of chemistry, at the metal surface, we have various morphological and metallurgical features such as surface roughness, grain boundaries, dislocations and intermetallic precipitates; it becomes clear that the engineering surfaces of metals are very complex indeed.

As far as adhesion of an organic phase is concerned, it is the presence of an unsuspected layer at the surface of a metal that is often responsible for poor adhesion performance. The metallurgical aspects may have important secondary roles, for instance, the presence of a precipitate may interfere with the development of a uniform anodic layer on aluminium and grain boundaries may be the route by which a minor alloying element is enriched at the surface, but they are rarely responsible for poor adhesion *per se*.

In order to develop a picture of the chemistry of metal surfaces, let us first consider the interaction of the metal with atmospheric oxygen and water vapour. In a pure oxygen environment, most metals will develop a thin film, which may, or may not, confer protective properties upon the alloy depending on its composition. On exposure to the atmosphere, the situation is more complex; indeed, early descriptions of the surface of metals following atmospheric exposure indicated the presence of much adventitious material such as salts, sulphides, polar and non-polar organics, and adsorbed water in addition to metal oxides and hydroxides resulting from a chemical reaction between substrate and environment.<sup>1,2</sup> More recent work making use of the surface analysis methods of **X-ray photoelectron spectroscopy** and **Auger electron spectroscopy** has indicated that such a model, although essentially correct, is unnecessarily complicated. The oxide layer is, on some alloys (e.g. mild steel), an oxyhydroxide phase, and on others (stainless steel, for example), a mixed oxide is covered with an extremely thin layer of a hydroxide. These inorganic layers are covered with a more labile mixture of adsorbed water and organic contamination that has been deposited during a cleaning process or during subsequent air exposure.<sup>3</sup>

The method of surface cleaning employed will have a marked effect on the levels of such adventitious material<sup>4</sup>. In general, dry **Abrasion treatments** carried out with clean abrasives provide the lowest levels of contamination but invariably produce a very rough surface profile. In contrast, **Degreasing** procedures with either organic solvents or aqueous reagents tend to produce surfaces high in carbon and its associated chemisorbed water. The direct correlation between these two contaminants indicates that they are associated together at the surface perhaps by **Hydrogen bonding**.

In terms of surface cleaning or degreasing practices, the requirements are that gross levels of extraneous material are removed. This includes friable oxides, mill scale, grease, residues of corrosion inhibitors and protective wraps. This is readily achieved by the use of the appropriate surface treatment.

The remaining layers described above are more tenacious and are not easily removed. The question of whether such material remains as a discontinuity at the metal oxide/polymer interface has yet to be unequivocally resolved, but it is clear that in some cases, such as coatings stoved at elevated temperatures, the presence of water promotes the

growth of the inorganic layer (oxide, oxyhydroxide, or hydroxide) while the carbonaceous phase is absorbed by the polymer. Some adhesives are specifically designed to be applied to greasy surfaces, to reduce the process steps (and thus the costs) of the bonding process. Such grease-tolerant adhesives absorb the hydrocarbon layer and are promoted for the use of bonding mild steel strip and pressings that are encountered, for instance, in the automobile industry.

As long as a well-defined weak boundary layer is not present, it seems that most organic coatings and adhesives will at least tolerate the presence of some “contaminant” material on the metal surface. In essence, the few nanometres deposited by interaction with the atmosphere is not a problem, but many micrometers requires the use of specific cleaning steps or products designed for use on such surfaces.

### References

1. F. R. Eirich, in *Interface Conversion for Polymer Coatings*, P. Weiss and G. D. Cheever, Eds., American Elsevier Publishing Co., New York, 1968, pp. 350–374.
2. J. C. Bolger and A. S. Michaels, in *Interface Conversion for Polymer Coatings*, P. Weiss and G. D. Cheever, Eds., American Elsevier Publishing Co., New York, 1968, pp 3–52.
3. J. E. Castle, in *Corrosion Control by Coatings*, H. Leidheiser, Ed., Science Press, Princeton, 1979, pp 435–454.
4. J. E. Castle and J. F. Watts, *Corrosion Control by Organic Coatings*, NACE, Houston, 1981, pp 78–86.

---

## Environment and the impact of adhesive technology

---

D E PACKHAM

Some of the reasons for concern at a potential global environmental crisis were briefly discussed in the article on **Environmental sustainability**. Here, some of the principle environmental impacts associated with the use of adhesives are outlined.

### Resources

Most adhesives are polymers, which, at present, are derived from petroleum feedstocks. Clearly, petroleum is a non-renewable resource. Controversy attends predictions of how long reserves will last, but there are some authorities, at least, that predict a permanent downturn in production within the first or second decade of the present century.<sup>1</sup> How this will affect polymer production and use is, of course, impossible to say. Here, it is relevant to point out that there have long been adhesives in use that are obtained from animal and vegetable sources; see **Renewable sources of adhesives** and **Adhesives – historical perspective**.

Natural rubber has long been an important commercial material, and a rubber plantation is almost as effective as a virgin forest in carbon dioxide absorption.<sup>2</sup>

There is at present much interest in developing new polymers from plant sources, often using fermentation techniques or genetic modification.<sup>3,4,5</sup> Polyhydroxyalkanoates are among these materials and, depending on the length and structure of the alkyl chain,

have properties ranging from those of crystalline thermoplastics to elastomers. Their use as adhesives appears yet to be developed.<sup>6</sup> In the area of **Composite materials**, interesting work is being done involving natural fibres and also on resin matrices based on renewable sources.<sup>7</sup>

Recycling is an important means of conserving material resources. Recycling of polymers, certainly of linear polymers, is, in principle, possible.<sup>8,9</sup> In practice, successive grinding and remoulding may cause thermal degradation to an extent that the properties suffer. In addition, feedstock for recycling may consist of mixtures of different grades and compounds of the same polymer or, worse, of different polymer types (see **Compatibility**). The recycling of adhesives is even more difficult than of polymers in general as the adhesive is usually a small proportion of a larger artefact all of which should, in principle, be recycled.

### Energy

Energy consumption is unavoidable in almost all technology. Whether the source material is renewable or non-renewable, energy is used during its production and processing. Table 1 gives approximate energy contents of some polymers. Thus, considerations of energy conservation and of renewable energy generation are very much relevant to adhesive technology.<sup>10</sup> However, it is not just the energy involved in production and processing that is relevant: it is important to consider the environmental impact of an article from initial extraction of the raw materials, through manufacture and service use, to ultimate disposal – “from the cradle to the grave”. Such a “life-cycle analysis”<sup>11</sup> may suggest that weight saving and engineering efficiency associated with the use of adhesives and composites may, by saving energy during use, more than compensate for problems over recycling and disposal.

### Pollution

Some authors consider the Earth’s capacity to carry pollutants to be even more pressing a problem than those of depletion of material and energy sources. Like most industrial processes, the production and use of adhesives produces pollutants, which can have an adverse environmental effect. Much attention has been given in recent years to reducing their impact.

Table 1. Approximate energy content of some polymers (GJ tonne<sup>-1</sup>)<sup>2</sup>

Polymer	Energy consumption
Polypropylene	110
Styrene–butadiene rubber	130
Polyurethane	174
Polychloroprene	120
Natural rubber	30



Table 2. Some compounds of relevance to polymer technology with reported endocrine-disrupting properties<sup>13</sup>

Compounds	Comment
Polychlorinated compounds	Formed in some incineration processes
Alkylphenols	Stabilizers
Alkylphenol ethoxylates	Surfactants
Phthalates	Plasticizers
Bi-phenols (e.g. bisphenol-A)	Constituent of most epoxy resins

Degreasing of metals has traditionally been done with the help of chlorinated solvents. Since their implication in depletion of the ozone layer, much effort has been devoted to developing less-damaging procedures; see **Degreasing**. Indeed, it is now generally recognized that the emission of any volatile organic compound to the atmosphere is undesirable as it contributes to photochemical smog and many are implicated in the aggravation of lung diseases such as asthma. Organic vapours absorb infrared radiation and therefore act as greenhouse gases. For all these reasons, there is an increasing move away from using organic solvents and dispersing media in pre-treatment in adhesives and paints (**Emulsion and dispersion adhesives, Rubber to metal bonding–pre-treatments**). **Hot melt adhesives** and **Radiation-cured adhesives** avoid the problem of organic solvent emission.

Indeed, increasing attention has been focussed in recent years on the effects of very low concentrations in the environment of a range of organic compounds. Many have been implicated in producing physiological changes in humans and other animals.<sup>12,13</sup> For example, some mimic the action of hormones. There is evidence that residues of some compounds are xeno-oestrogenic and may disrupt the endocrine system (Table 2), depressing the human sperm count and sometimes leading to male genital deformity. Many such compounds are used as additives in adhesives and composites and, because of their fundamental **Compatibility** with the polymer phase, are likely to be released into the environment. This is an area of considerable controversy, with much dispute over the effects of low concentrations of such chemicals in the environment on humans, as opposed to their effects on test animals under laboratory conditions. It may well be that use of many additives in adhesives will be, perhaps should be, banned or much more strictly controlled in the future.

### References

1. C. B. Hatfield, *Nature*, **387**, 121 (1997).
2. W. A. Rahaman, *Rubber Dev.*, **47**, 13 (1994).
3. R. H. Marchessault, *Trends Polym. Sci.*, **4**(5), 163 (1995)
4. S. K. Moore, *Sci. Am.*, **Feb**, 23 (1997).
5. J. Evans, *Chem. Br.*, **Feb**, 41 (2000).
6. L. A. Madden, A. J. Anderson, J. Asrar, P. Berger and P. Garrett, *Polymer*, **41**, 3499 (2000).
7. S. H. Aziz and M. P. Ansell, Optimizing the properties of green composites, in Chapter 15 of "Green Composites", C. Baillie, Ed., Woodhead Publishing Ltd., 2004.

8. W. Hoyle and D. R. Karsa, Eds., *Chemical Aspects of Plastics Recycling*, Royal Society of Chemistry, London, 1997.
9. J. Scheirs, *Polymer Recycling: Science, Technology and Applications*, Wiley, 1998.
10. D. Elliott, *Energy, Society and Environmental Technology for a Sustainable Future*, Routledge, 1997.
11. N. W. van den Berg, C. E. Dutilh and G. Huppes, *Beginning LCA; A Guide into Environmental Life Cycle Assessment*, Unilever, 1995.
12. T. Colborn, D. Dumanoski and J. P. Meyers, *Our Stolen Future—Are We Threatening Our Fertility, Intelligence and Survival?—A Scientific Detective Story*, Little Brown, 1996. [Abacus 1997].
13. *Endocrine-Disrupting Substances in the Environment: What should be done?* U.K. Environment Agency, 1998.

### *Environmental sustainability*

D E PACKHAM

Adhesion science and technology are deeply involved in contemporary industrial culture. The question of environmental sustainability presents a major challenge to this culture. It is, therefore, a relevant subject for this volume.

Environmental sustainability is a concept fundamentally rooted in ethics and philosophy but has strong technological ramifications. In this article, the implications of sustainability and attitudes towards it are considered. In a further article, **Environment and the impact of adhesive technology**, practical consequences relating to the use of adhesives are discussed.

Etymologically, the term *sustainability* carries the implication of stability or equilibrium maintained “forever”, or at least for a very long time. Is the practice of contemporary industrial society consistent with such sustainability? It has been argued that it acts as if resources were infinite and it ignores the natural tendency for the disorder (entropy) of materials and of energy to increase,<sup>1</sup> that is, it ignores the implications of the laws of thermodynamics. Further, the aspiration of many politicians and economists, shared by popular sentiment, is for continuous, preferably high, growth. Yet, a few seconds’ thought will show that a constant rate of growth is, in mathematical terms, exponential growth of the form

$$P = P_0 \exp(kt)$$

where  $P$  is the size of the economy or resource at time  $t$  and  $P_0$  is its value at  $t = 0$ ;  $k$  is the growth rate. It is clear that such growth cannot be sustained in a world of finite resources. There must be limits to growth.<sup>2</sup> It is interesting to note that this was acknowledged by Adam Smith,<sup>3,4</sup> as he is so often quoted by those who advocate neo-liberal free market competition.

The limits to growth argument, briefly outlined above, clearly calls into question the validity of a belief in progress, in the sense of a continuously improving material standards of living. Such beliefs, very recent in the history of humanity, have become firmly embedded in the popular consciousness in Western industrial society over the past century or more and are now being increasingly adopted on a global scale. With such a challenge

to a deeply held dominant social paradigm, it is not surprising that the conclusions of the “limits to growth” argument are far from universally accepted. There are those who dismiss the argument as facile, countering that human ingenuity will always discover new technologies and develop new materials, which will enable us to evade its stark logic.<sup>5</sup> This belief is sometimes referred to as “cornucopian”. Others (the majority in the author’s opinion) simply do not engage with the argument and act as if they believed that continuous growth is a law of nature, as inevitable as the phenomenon of gravity. They are unreflective cornucopians.

The crisis predicted from application of the laws of thermodynamics to energy and material resources is made more urgent by the aspirations of the developing world to share in the West’s levels of prosperity. It is possible that the crisis could be considerably postponed if the growth in consumption, and consequent increase in material standard of living, is to be confined to a small, perhaps to an ever-smaller, proportion of mankind.

The position adopted by individuals on issues of sustainability depends not so much on their interpretation of the scientific evidence as on their personal philosophy and values. Irrespective of this, there seems – in the author’s perception – to be general agreement that steps should be taken to limit environmental damage and to conserve non-renewable resources. The disagreement between “limits to growth” and cornucopia (and a spectrum of positions between the extremes) is over the urgency and the extent to which change to current practice should be made.

The principle issues where the use of adhesives impacts on sustainability are considered in **Environment and the impact of adhesive technology**.

### References

1. H. E. Daly, *Steady-State Economics*, 2nd edn, Earthscan, 1992.
2. D. H. Meadows, D. L. Meadows and J. Randers, *Beyond the Limits*, Earthscan, 1992.
3. A. Smith, *An Inquiry into the Nature and Causes of the Wealth of Nations*, 1776. Critical edition R. H. Campbell and A. S. Skinner, Eds., Oxford University Press, 2 volumes 1976.
4. J. E. Alvey, *Adam Smith: Optimist or Pessimist?* Ashgate, Aldershot, 2003.
5. M. A. Cole, *Sustainable Dev.*, 7(2), 87–97 (1999).

## Epoxide adhesives

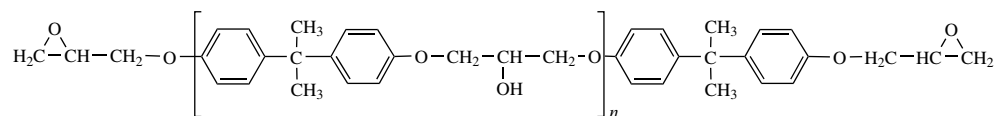
JOHN BISHOPP

Epoxy adhesives are now the “workhorse” of the industry, particularly for structural adhesives. They are amazingly versatile as far as the formulator is concerned. A large range of epoxy backbones coupled with a large number of curative chemistries means that the epoxy adhesive can be tailored to meet individual requirements such as shelf life, gap-filling properties, volatility and out-gassing characteristics during cure, shrinkage, cure temperature (between ambient and about 180 °C), service temperature (from sub zero to about 200 °C), strength requirements, environmental resistance and toughness.

Epoxide adhesives are used to bond a large range of components; their versatility means that the two adherends being bonded do not have to be of the same composition.

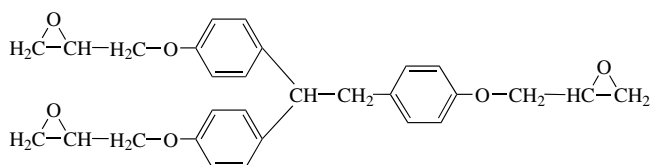


Any excess Bisphenol A in the reaction mixture will further react with the epoxy resin to give a degree of chain extension. Thus, many commercially available Bisphenol A liquid epoxies will have the following structure, where  $n = 0.15$  to  $0.25$ :

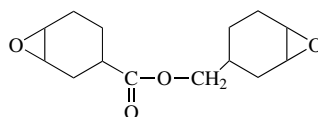


Using a deliberate excess of Bisphenol A gives rise to semi-solid to solid resins with values of  $n = 2$  to  $n = 26$ .

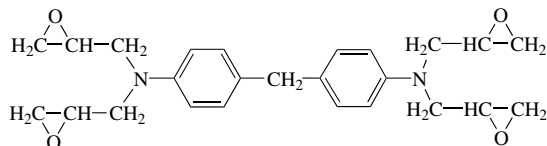
Besides a range of glycidylether resins, based on di-, tri- or tetrahydric phenols (e.g. Bisphenol A, Bisphenol F, Polyphenol A, etc.), cycloaliphatic epoxies and glycidylamine, hybrid glycidylester/glycidylamine and glycidylester resins are also commercially available.



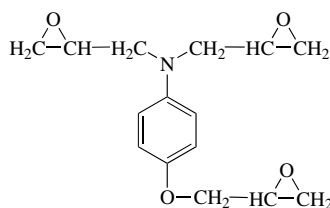
Huntsman's Tactix 742



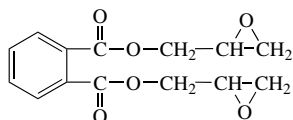
Huntsman's Araldite CY 179



Huntsman's Araldite MY 721



Huntsman's Araldite MY 0515



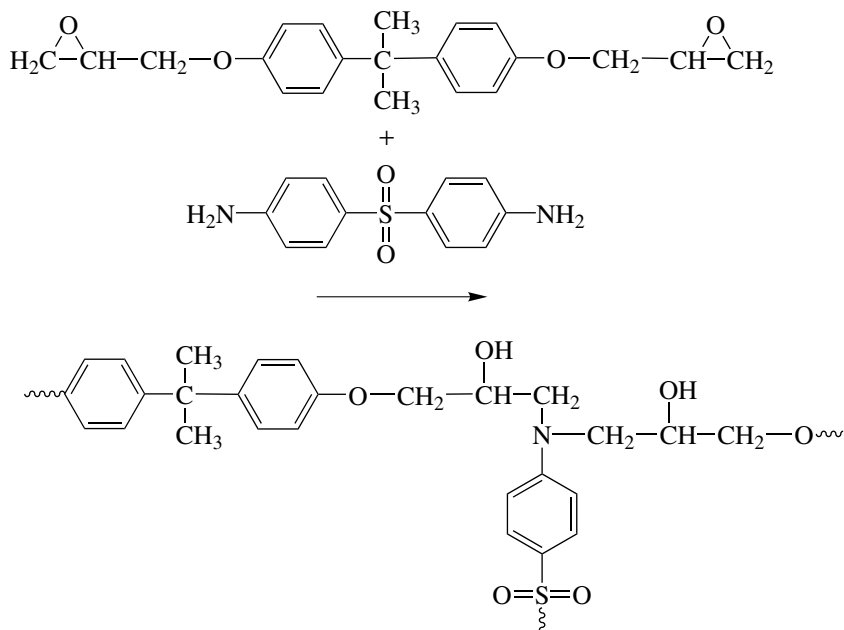
Shell's Epon A-100

### Cure of epoxies

The epoxy/oxirane ring can be opened in the presence, particularly, of active hydrogen atoms. Active hydrogen groups are contained in such materials as aliphatic and aromatic amines, alcohol groups in, for example, solid epoxy resins and phenolic resins, thiols, and aliphatic and aromatic anhydrides. The addition reaction leads to a cross-linked, infusible structure provided both materials contain at least two reactive species; one of them must contain greater than two.

Other materials such as tertiary amines, imidazoles,  $\text{BF}_3$  complexes, antimony fluoride complexes and iodonium and sulphonium salts can act as anionic or cationic initiators of the epoxy resin cure.

A typical schematic for a Bisphenol A epoxy resin cured with an aromatic amine is shown below; both active hydrogens in the amino group will react with an epoxy ring. Generally, all primary hydrogens will react first, followed by the secondary hydrogens produced by the initial reaction.



The cross-linking of these polymers is further discussed in **Epoxide adhesives: curatives**.

### Select References

- J. V. Crivello and K. Dietliker, Cationic photopolymerisation of epoxides, in *Photoinitiators for Free Radical, Cationic and Anionic Photopolymerisation*, 2nd edn, Wiley, 1998.
- Anon, *Dow Epoxy Novolac Resins*, Technical Bulletin No.296-00279-1098, Dow Chemical, 1998.
- Anon, *Epoxy Resin Curing Agents, Comparative Performance Properties*, Henkel Technical Bulletin, 1998.
- M. Goosey, M. Roth, T. Kainmuller and W. Seiz, *Epoxy Resins and Their Formulation*, Plastics for Electronics, Academic Publishers, 1999.

### Epoxide adhesives: curatives

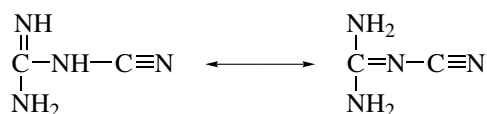
JOHN BISHOPP

Epoxide resins comprise a broad and important class of adhesives. In the article **Epoxide adhesives**, an introduction was given to some of the molecules to which the epoxy groups in these materials may be attached. The cure (cross-linking) of epoxies may be achieved

by a variety of chemical reactions, resulting in a range of different properties. This is further described below.

### Epoxy curatives/hardeners

One of the first hardeners to find commercial usage and, still today, one of the most important is the cyanoguanidine-based material called dicyandiamide.

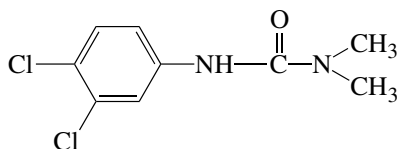


As dicyandiamide is not directly soluble in epoxy resins under a temperature of about 150 °C, it acts as an effective latent hardener, which means that it can be used in one-part adhesives, which are storage stable for about a year to eighteen months. Once it does dissolve, however, it reacts quickly and fairly exothermically. Most unaccelerated dicyandiamide-containing adhesives are cured in the region of 150 to 180 °C.

The 100% stoichiometric addition of a primary or secondary amine to cure an epoxy can be relatively easily calculated; the amount of resin containing one epoxy group will react with the amount of hardener, which contains one active hydrogen. However, dicyandiamide is, at least in part, a catalytic curative; one molecule is said to contain about 4.5 active hydrogen equivalents.

In most cases for all classes of curatives, the actual loading is generally determined by experimentation rather than simple calculation; the calculated quantity gives the formulator a good starting point.

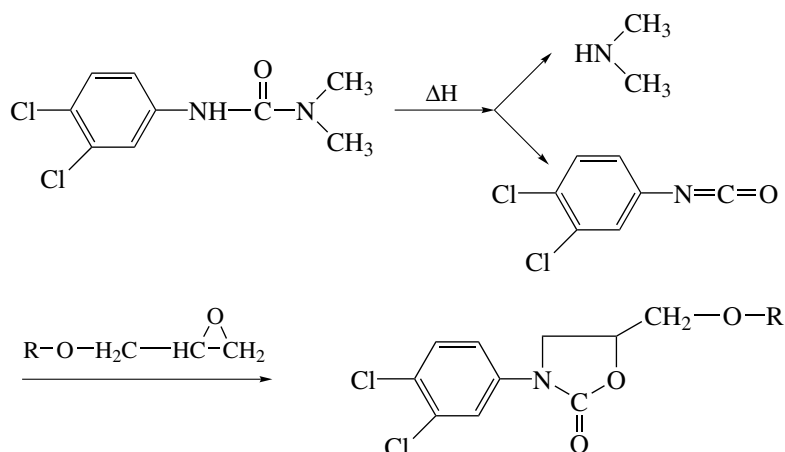
Tertiary amines are often used to accelerate the dicyandiamide cure but the most commonly found accelerators are the urones. Roughly equal loadings of dicyandiamide and a suitable urone allow the cure temperature to be reduced to 100 to 125 °C.



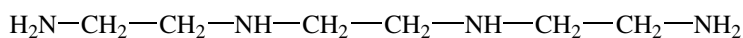
*N,N*-Dimethyl, *N'*-3,4-dichlorophenyl urea [Diuron]

One postulated reaction schematic is as follows. The urone undergoes a thermal breakdown to give a secondary amine, which will catalyse the conventional dicyandiamide cure, and an isocyanate, which will react with and cross-link with the epoxy through the formation of rigid oxazolidones.

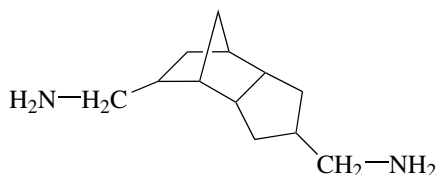
The largest group of epoxy curatives contains the aliphatic, cycloaliphatic and aromatic primary and secondary amines. Depending on the amine chosen, cure temperatures can vary from just below ambient (generally aliphatic and cycloaliphatic) to as high as 120 to 175 °C (aromatic).



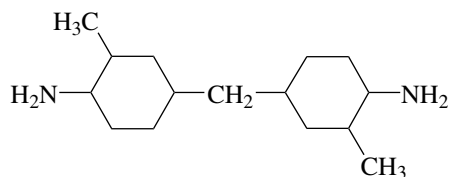
Typical of these curatives are:



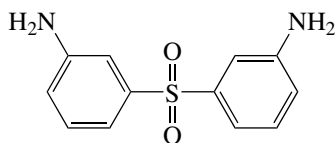
Triethylenetetramine [6-functional]



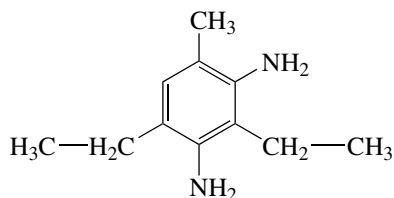
4,8-Bis(aminomethyl) tricyclo[5.2.1.0.2,6]decane [4-functional]



3,3'-Dimethyl 4,4'-diamino dicyclohexyl methane [4-functional]



3,3'-Diaminodiphenyl sulphone [4-functional]

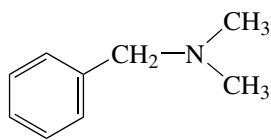


3,5-Diethyl, 2,4-diamino toluene [4-functional]

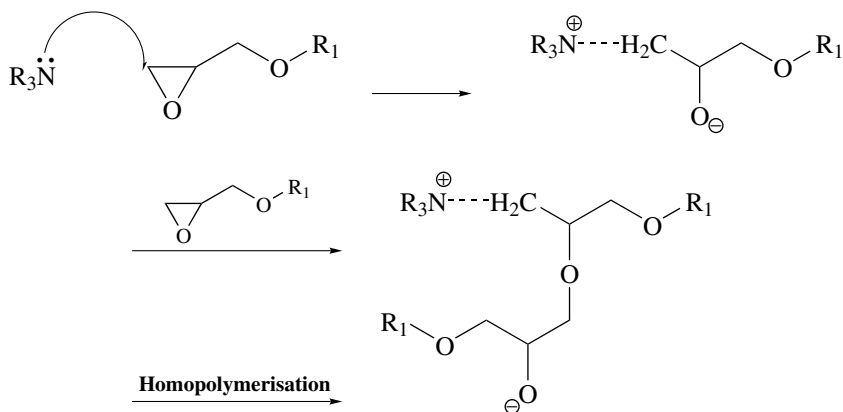
Tertiary amines such as BDMA are Lewis acids and react with epoxy resins by catalytic anionic polymerization.

They may be used as sole curatives (generally at about 1 to 6 parts per hundred of epoxy) or as accelerators for other curing agents such as dicyandiamide, polyamides, amidoamines or anhydrides. The reactivity of tertiary amines results from the unshared electron pair on the nitrogen and varies widely as the electron density around the nitrogen changes. Since there are no secondary hydroxyl groups generated, the resin may be said to homopolymerize (chain extend).

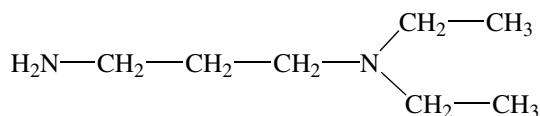




*N,N*-Dimethyl benzylamine  
[benzyl dimethylamine]

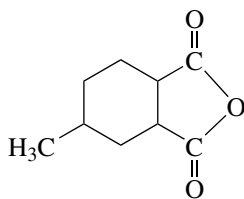


Often, both primary and tertiary amino groups are present in the same molecule; these are highly effective catalytic curatives.

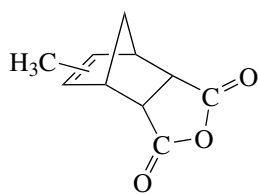


*N,N*-Diethyl, 1,3-propylenediamine [effectively between about 4- and 8-functional]

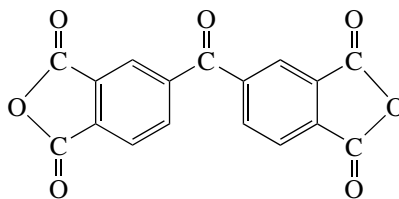
Although acid anhydrides are effective curatives for epoxies, they tend to be used in casting and moulding formulations rather than adhesives. However, when they are used, the anhydrides from dicarboxylic acids are taken as being roughly mono-functional and those from tetracarboxylic acids as being di-functional. Thus, with a conventional Bisphenol A epoxy, the empirical loadings are in the region of 80 to 120 parts per hundred parts of epoxy. Cure temperatures range from 80 to 120 to as high as 180 °C.



Methyl hexahydro  
phthalic anhydride



Methyl nadic anhydride

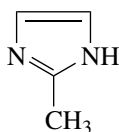


Benzophenone tetracarboxylic  
dianhydride

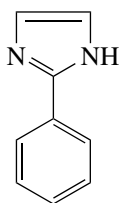
Owing to their low reactivity, it is usual to incorporate accelerators such as tertiary amines or imidazoles. Even so, the reaction mechanism is complex, as three competing reactions take place. The anhydride reacts with the epoxy hydroxyls to form half esters. The half ester containing the free carboxyl group is then available to react with an epoxide ring, which generates another hydroxyl. The newly formed hydroxyl can react with another anhydride or, in the presence of the free acid, it can react with another epoxy to form an ether linkage.

Other curatives, which react through addition mechanisms are: phenolic resins, particularly if the hydroxyl/epoxy reaction is catalysed using a tertiary amine (usually accomplished at elevated temperatures), thiols, polysulphides and mercaptans (can be formulated to give very rapid cures), polyetheramines (relatively slow cures, which can be accelerated with nonyl phenol), polyamides (less reactive than their amine counterparts) and aminoamines (characterized as having very long pot lives).

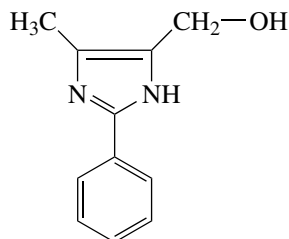
Thermal anionic initiation and cure, using tertiary amines, has already been discussed. Other curatives operating in a similar manner are the substituted imidazoles; homopolymerization being possible at loadings of <8 parts of imidazole per hundred parts of a conventional Bisphenol A epoxy.



2-Methyl imidazole



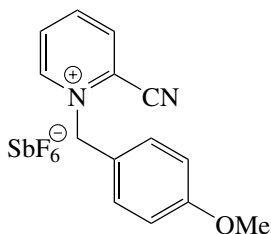
2-Phenyl imidazole

2-Phenyl, 4-methyl,  
5-hydroxymethyl imidazole

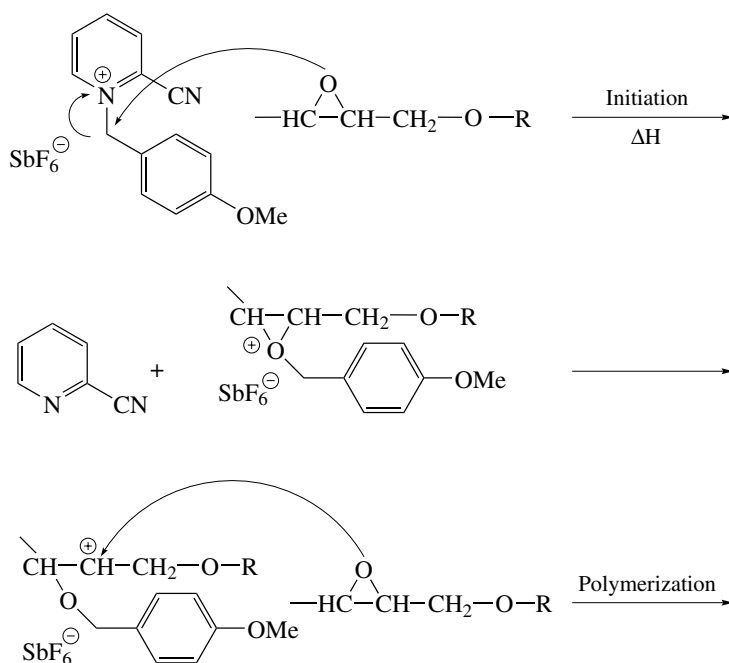
Thermal cationic cures of epoxy resins can be achieved using Lewis acids based on amine-BF<sub>3</sub> complexes.

As with the imidazoles, the reactivity of BF<sub>3</sub> complexes can be regulated by inducing steric hindrance into the molecule.

The cationic initiation of polymerization and cure, at temperatures as low as 90 °C, can also occur by the addition of, for example, antimony fluoride complexes to the adhesive.

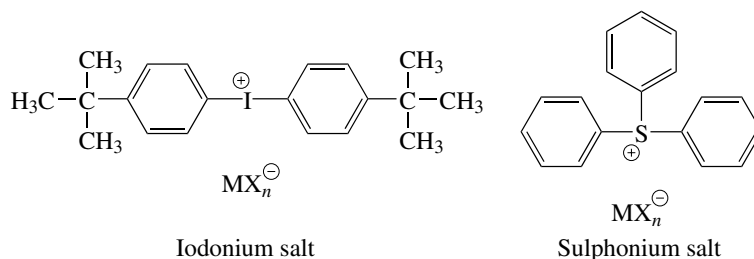


The reaction schematic is:



Under UV activation, iodonium and sulphonium salts can also be used as cationic initiators for the cure of epoxies.

Using similar initiators, epoxy formulations can be cured under electron beam conditions.



Where: M = AS, B, Sb or P and X = F or Cl

Cured epoxide adhesives form strong bonds to many substrates, but in their unmodified form tend to be brittle: **Toughened epoxy adhesives** are the subject of separate articles.

### Select References

- J. V. Crivello and K. Dietliker, Cationic photopolymerisation of epoxides, in *Photoinitiators for Free Radical, Cationic and Anionic Photopolymerisation*, 2nd edn, Wiley, 1998.
- Dow Epoxy Novolac Resins*, Technical Bulletin No.296-00279-1098, Dow Chemical, 1998.
- Epoxy Resin Curing Agents, Comparative Performance Properties*, Henkel Technical Bulletin, 1998.
- M. Goosey, M. Roth, T. Kainmuller and W. Seiz, *Epoxy Resins and Their Formulation*, Plastics for Electronics, Academic Publishers, 1999.

### *Etch primers*

N R WHITEHOUSE

Other related articles discuss **Pre-treatment of metals prior to painting**, **Paint primers** in general and **Autophoretic primers**.

Etch primers (also known as “wash” primers) are used to promote adhesion to clean metal surfaces, notably non-ferrous metals. They may also give a measure of temporary protection to ferrous metal surfaces.

Etch primers are low viscosity products that, when applied correctly, dry to form thin, translucent films (typically 10–15 μm, in thickness). Etch primers must, therefore, be overcoated (subsequently) with a fully pigmented paint system.

Traditionally, etch primers have been formulated as “one-pack” or “two-pack” products, based on polyvinyl butyral resins. In the more common “two-pack” products, the etchant (phosphoric acid) is a separate component, which is added to the resin/solvent component immediately before use. The “one-pack” products contain a small amount of chromic acid and are described as “reacted stable” formulations.

Two-pack etch primers usually contain an anti-corrosive pigment. In traditional formulations, zinc tetroxychromate was used. Current products, however, are mostly chromate-free, in response to environmental pressures. The zinc tetroxychromate has been replaced with a small amount of less toxic anti-corrosive pigments, such as zinc phosphate. Anti-corrosive performance may be compromised, to a degree, by such substitutions.

#### *Select Reference*

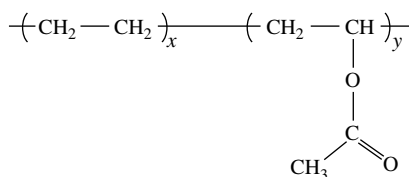
P. G. Sheasby and R. Pinner, Eds., *The Surface Treatment and Finishing of Aluminium and its Alloys*, ASM International, Materials Park, Ohio/Finishing Publications, Stevenage, 2001, Chap 14.

### *Ethylene–vinyl acetate copolymers*

D E PACKHAM

Ethylene–vinyl acetate copolymers are used in many adhesive applications.

Ethylene and vinyl acetate (EVA) are copolymerized using a radical initiator (see **Chain polymerization**). Figure 1 shows the chemical structure of EVA. The reactivity ratios of both monomers are close to unity, so copolymers have a random structure, and can be prepared with composition ranging from almost 0 to almost 100% vinyl acetate (VA).



**Fig. 1.** Structure of EVA (x and y are integers)

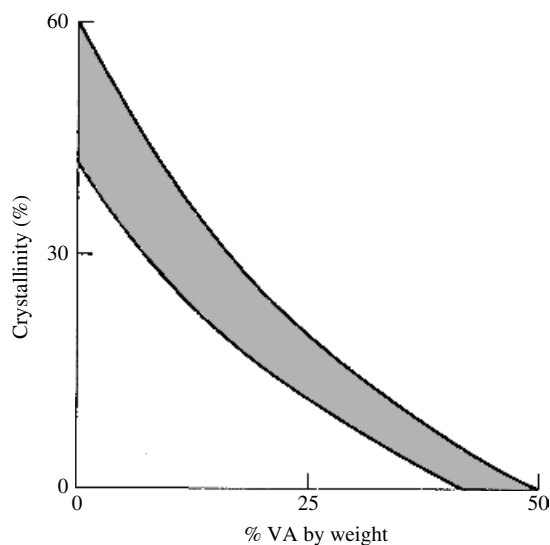
(The compositions in this article are expressed as percentages by weight.) Bulk polymerization is widely used for polymers of 40–50% VA, and an emulsion process for those over 60% VA. In the intermediate range (15–60%), solution polymerization may be used.<sup>1</sup> Both low (10–40%) and high (60–95%) VA materials have adhesive applications, the former as **Hot melt adhesives**, the latter as emulsion adhesives (see **Emulsion and dispersion adhesives**). The term “vinyl acetate–ethylene” is sometimes used to describe the copolymers rich in VA.

### Properties

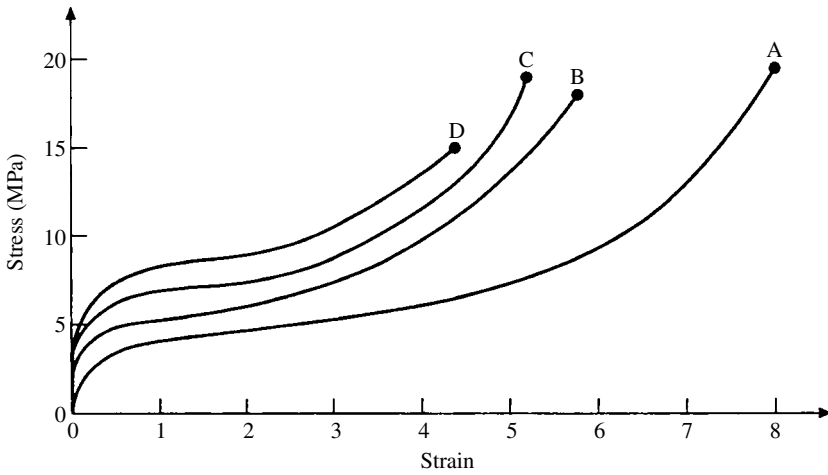
As with homopolymers, the properties of EVAs are affected by the molecular weight and degree of short- and long-chain branching. Here, particular emphasis is placed on properties that depend upon VA content.

Polyethylene is of course crystalline, and copolymers of low VA content are semi-crystalline thermoplastics, which can be thought of as modified polyethylenes. The effect of varying VA content is to vary the crystallinity and the polarity. The crystallinity depends partly on the extent of chain branching, but the VA content exerts a strong effect. As bulky VA groups are introduced into the chain, the crystallinity falls, becoming zero at around 50% VA (Fig. 2). As the crystallinity decreases, the elastic modulus and yield strength fall and the elongation at break increases (Fig. 3).

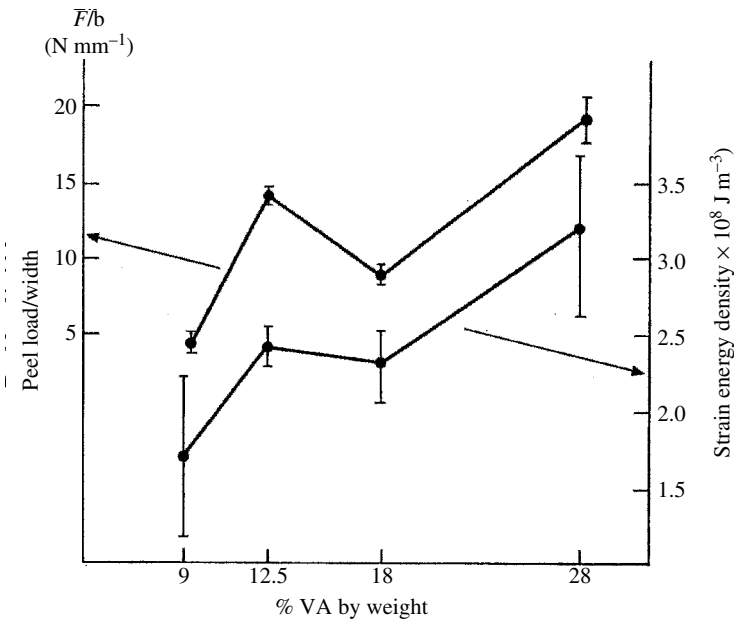
The mechanical properties of EVAs were found by Hatzinicolaou and Packham to exert a strong influence on their adhesion to metals.<sup>2</sup> Figure 4 shows a close correlation between the strain energy density of four EVAs and the peel loads when applied as hot melts to copper with a **Microfibrous surface**. Although such a straightforward connection was not found under all circumstances, the peel energies found could be rationalized using an analysis based on an extension of Eqn 7 in the article **Peel tests**.



**Fig. 2.** Envelope showing the relationship between crystallinity and vinyl acetate content (after Ref. [1])

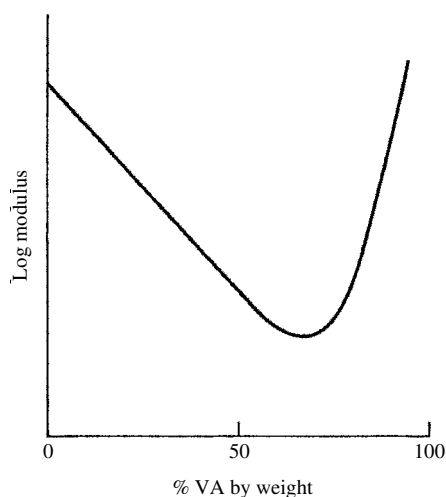


**Fig. 3.** Schematic representation of stress–strain behaviour of some EVAs, VA content weight percent A 28, B 18, C 12.5, D 9 (after Ref. [2])



**Fig. 4.** Comparison of strain energy density at failure for four EVAs with the peel loads measured for backed strips of the polymers peeled from chlorite-oxidized copper<sup>2</sup>

Polyvinyl acetate is a glassy, amorphous polymer with **Glass transition temperature** about 28 °C. The effect of increasing the proportion of ethylene is to reduce the strong forces between the chains, which, in the homopolymer, are associated with a high concentration of polar acetate groups. Consequently, the glass transition temperature falls and is as low as 25 °C for a VA content of 65%.<sup>3</sup> The properties at room



**Fig. 5.** The relationship between elastic modulus and vinyl acetate content (after Ref. [4])

temperature change as a result: modulus and tensile strength fall and extension to break increases (Fig. 5).

#### *Adhesive applications*

Low vinyl acetate content EVAs are used as **Hot melt adhesives**. A typical copolymer composition is 28% VA, but materials in the range 15–50% VA are used. They may occasionally be employed on their own,<sup>2</sup> but are most commonly blended with hydrocarbon waxes and tackifying resins such as esterified wood resins. Their uses include packaging, woodworking, (see **Wood adhesives – basic principles**), bookbinding and carpet-backing. Geddes<sup>4</sup> give some typical formulations.

High VA copolymer emulsion adhesives are often modified to suit the specific application intended, for example, with addition of plasticizers or cross-linking agents.<sup>3</sup> Applications include laminating PVC and other films, packaging and in furniture and joinery (see **Wood adhesives – hot melts**) and textile bonding: **Adhesives for textile fibre bonding** and **Adhesives in textile coating**. Discussion of some recent work on rosin-containing EVAs is given by Barrueso *et al.*<sup>5</sup>.

#### *References*

1. G. W. Gilbey, in *Developments in Rubber Technology – 3*, A. Whelan and K. S. Lee, Eds., Applied Science Publishers, London, 1982, p. 101.
2. T. A. Hatzinicolaou and D. E. Packham, *Adhesion*, **9**, 33 (1984).
3. E. F. Eastman and L. Fullhart, in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, p. 408.
4. K. Geddes, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 719.
5. M. L. Barrueso Martínez, T. D. Ferrandez Gomez, M. D. Romero Sánchez and J. M. Martín-Martínez, *J. Adhesion*, **79**, 805(2003).

---

## Extrusion coating

---

R J ASHLEY

This versatile technique is generally used where a ply of polyethylene or copolymer thereof is required in a structure. Other polymers may be used in specialized areas but the handling can become more difficult. The process is widely used within the **Packaging Industry** for the coating of paper, board, foils, cellulose film and thermoplastic films. The most common coating resin used is low-density polyethylene, but this now extends to copolymers such as **Ethylene–vinyl acetate**, ethylene–acrylic acid, polypropylene, high density polyethylene and ionomers (e.g. Surlyn). The acrylic acid–based materials and ionomers are used in areas in which enhanced adhesive strength is required, such as resistance to difficult environments.

The coatings are usually applied to a substrate to provide a heat-sealing medium, but they also serve to reduce the permeability to water vapour and to improve the mechanical properties of certain base materials.

The substrate to be coated is unwound from a braked or driven turret off-wind and passes into a priming unit (see **Primers for adhesive bonding**). The priming unit consists of a gravure applicator and a drying oven and applies chemical adhesion promoters from a solvent base. The solvent is removed from the primer coat in the oven leaving a dry coat weight in the range 0.2–1.0 g m<sup>-2</sup>. An alternative to priming is to treat the substrate by **Flame treatment** or by an electronic discharge (see **Corona discharge treatment**) which is most frequently used for plastic films (see **Pre-treatment of polyolefins**).

After priming or treating, the substrate is drawn into the primary nip of the coater, which comprises a steel cooling drum about 1 m in diameter (the chill roll) that is cooled with a high volume flow of water, and a hard rubber back-up roller that forces the substrate against the chill roll.

Molten polymer is then extruded through a straight slot die, essentially similar to that used for polymer film casting and is drawn vertically down into the primary nip. The distance between the die and nip (air gap) is critical since it influences the degree of oxidation and, subsequently, adhesion of the coating. This distance is generally between 150 and 300 mm. Recent modifications of the technique concern the use of an ozone shower or specific active species introduced to the polymer melt curtain to improve adhesion.

Since the polymer is molten when drawn into the nip, the surface of the coating conforms to that of the chill roll and both matt and polished rolls are used depending on the properties required of the final coating. The coated web passes around the drum and is peeled away by a secondary nip roller, edge trimmed and electronically treated if required for further processes.

Extrusion coating is relatively low cost for long production runs and has the advantage over adhesive laminating of polymer films in that very thin layers can be applied (especially of polyethylene). Typical coating thicknesses would be in the range 5–30 microns.

There are three major problems with the process that limit its application: (1) good gauge control is necessary, (2) adequate oxidation of the melt must be achieved for good adhesion, and (3) excessive oxidation or too high an extrusion temperature gives rise to odour problems in the coating. The use of primers contributes to achieving good adhesion levels while operating at minimum melt temperatures.



An associated technique is to use the extrusion coating in melt form as an adhesive interply between two substrates to be laminated. This is particularly useful for the lamination of paper to foil. A combination of extrusion lamination and coating can be used for the preparation of more complex structures with single machine pass.

See also **Coextrusion, Tie-layers, Packaging industry.**

*Select Reference*

R. J. Ashley, D. Briggs, K. S. Ford and R. S. A. Kelly, *Industrial Adhesion Problems*, D. M. Brewis and D. Briggs, Eds., Orbital Press, Oxford, 1985, Chap 8.

# F

---

## *Fibre composites – introduction*

---

B C COPE

Materials consisting of more than a single phase can justifiably be described as **Composite materials**. In plastic technology, the term is usually reserved for two-phase systems consisting of a reinforcing fibrous material, which is usually inorganic, but which may be polymeric, dispersed in a continuous polymeric matrix. Such materials offer exceptionally high levels of strength, stiffness and impact strength, combined with a density substantially lower than those of structural metals and alloys. Strength and stiffness arise from the properties of the reinforcing fibres, which are very small in diameter and consequently substantially free from the flaws that normally reduce the strength of brittle materials from high theoretical values to the low practical values familiar in bulk samples. The fibres are typically 50 times stronger and stiffer than the matrix, with composite strength sometimes exceeding 1000 MPa and tensile modulus exceeding 150 GPa.

The composite, then, is seen to consist of very strong and stiff fibres embedded in a matrix, which, because of the presence of stress-concentrating cracks, has a much lower strength than the fibres. The matrix serves to maintain fibre position and orientation, to transmit shear forces, to protect the fibre surface and to transfer loads to the reinforcement. For this reason, fibre–matrix adhesion is essential.

Polymer-matrix fibre-reinforced composites offer an extremely high stiffness:weight ratio to the engineer, and this factor, in combination with resistance to corrosion and relatively low tooling costs, has led to extensive use in stressed applications.

The relationship between strength and modulus of the composite and the corresponding properties of the fibre and matrix depend on the fibre length and orientation. For continuous unidirectional fibres, the modulus of the composite in the fibre direction may easily be shown to be equal to the modulus of the fibres times their volume fraction plus the modulus times the volume fraction of the matrix. This assumes that fibre–matrix

adhesion is adequate to transmit the stresses involved. The strength in the fibre direction is essentially the fibre strength times volume fraction.

The greatest volume fraction of fibre that is possible to be incorporated in most composites is not much more than 0.5, so the maximum possible strength of a composite is about 50% of the theoretical strength of the reinforcement. In practice, the attainable figure is rather less than this because of fibre imperfections, fibre damage, incomplete wetting-out and other defects. The matrix material thus contributes little directly to the strength of the composite but is essential to hold the fibres in place and to transfer shear forces.

It is obvious that in order to obtain a high volume fraction of fibre, the fibres must be unidirectional in their orientation, and are thus able to contribute nothing to the strength of the composite when it is stressed so that there is no resultant of that stress in the fibre direction. These unidirectional composites are thus immensely strong in tension, and consequently in bending, but easily split lengthwise.

For most applications, resistance to stresses in more than one direction is essential, and in these cases, a unidirectional composite is not acceptable. Strength and stiffness in both dimensions of a plane, as in a car body panel, or isotropically in all three dimensions is normally required. Consequently, the orientation of the fibres must be modified to provide resultants in the required directions. This may be achieved in two directions by the use of woven or knitted cloths or with non-woven, random felts or mats. In three dimensions, random orientation of the reinforcement is usually the only possibility. However, the maximum strength attainable drops sharply in multidirectional composites, not only because of the smaller fraction of fibres contributing to resisting the stress but also because the maximum packing density of the reinforcing fabric decreases and hence the overall volume fraction of reinforcement decreases. Despite this fall-off, the strength of the fibres is such that a very substantial reinforcement may still result.

Toughness in composites arises from the bonding between the matrix and the fibre. Under impact of loads, cracks start in the matrix and then propagate until the stress concentration preceding the crack reaches the interface between a fibre and the surrounding matrix. There, if the strength of interfacial bonding is of the right order, delamination occurs, with the dissipation of large amounts of energy. This blunting of the crack removes the source of stress concentration and prevents further propagation.

### *The fibre–matrix interface*

The optimum level of bonding between the phases of a composite is often not straightforward to determine or to achieve (see **Fibre–matrix adhesion – assessment techniques**).

High matrix and interfacial shear strength are desirable to keep the ineffective fibre length (that part of the fibre not contributing to the strength and stiffness of the composite) as low as possible. Against this, when a composite is loaded in-plane tension only, the interface should be as weak as possible to maximize strength. This situation is unusual, but may occur, for example, in filament-wound pressure vessels.

When a crack propagates in a composite, it is desirable that the interface should fail in transverse tension or in shear ahead of the crack, thus blunting it and halting its

progress. Optimum efficiency in this operation depends on a moderate level of interphase bonding, but in practice, it is difficult to achieve bonding good enough to seriously degrade impact strength.

Small fibres are inherently unstable in compression, unless well bonded to the matrix, so for good shear and compressive strength, the interface should be as strong as possible. In transverse tension, fibres act as stress concentrators and hence a weak interface is particularly deleterious.

Composites made with large-diameter isotropic fibres, such as boron, usually have a much higher compressive strength than tensile strength. Those with small-diameter isotropic fibres such as glass are usually stronger in compression than in tension, whereas those with small-diameter anisotropic fibres, such as aramids, are usually stronger in tension, with a low compressive strength that is particularly sensitive to poor interfacial bonding.

In general, a weak interfacial bond reduces tensile strength and very seriously reduces compressive and shear strengths, but toughness is increased with decreasing bond strength.

Overall, it is usually desirable to maximize interfacial bonding. The technique adopted to achieve this depends on the fibre in question. With glass, the application of a size containing a coupling agent consisting of a methacrylic chromic chloride complex or an organosilane is the usual practice. The coupling agents are designed to bond to hydroxy groups on the glass surface and to be reactive towards the appropriate thermosetting matrix resin (see **Silane adhesion promoters** and **Fibre–matrix adhesion – glass fibres**).

Carbon fibres are frequently subjected to an oxidative etching process to improve adhesion, but a size is sometimes used (see **Fibre–matrix adhesion – carbon fibres**). Sizing is generally ineffective with aramid fibres because of lack of susceptible sites, but plasma deposition of amine groups is said to improve adhesion.

Coupling agents currently in use are capable, in some circumstances, of eliminating interfacial failure and their use may more than double the flexural strength of a laminate and greatly improve its water resistance (see **Durability: fundamentals**). Their use does, however, demand control as too thick a coating or incorrect cure can lead to degradation of laminate performance. The titanates, sometimes called coupling agents, are better described as surfactants, and although they may improve dry strength they do little for wet durability.

Some of the main constituents used in these materials are discussed under **Fibre composites – matrices and fibres** and practical aspects are considered under **Fibre composites – joining** and **Fibre composites – processing techniques**.

### *Select References*

- B. Harris, *Engineering Composite Materials*, 2nd edn, IOM, London, 1999.
- D. Hull and T. W. Clyne, *An Introduction to Composite Materials*, 2nd edn, Cambridge University Press, Cambridge, 1996.
- S. K. De and J. R. White, Eds., *Short Fibre Polymer Composites*, Woodhead, Cambridge, 1996.
- C. A. Harper, Ed., *Handbook of Plastics, Elastomers and Composites*, 3rd edn, McGraw-Hill, London, 1996.
- L. A. Pilata and M. J. Mickno, *Advanced Composite Materials*, Springer-Verlag, Berlin, 1994.

---

**Fibre composites – joining**

---

K B ARMSTRONG

*Introduction*

Most of the information here is based on epoxy systems (see **Epoxy adhesives**) but should be applicable to polyester and vinyl ester resins. The joining and/or repair of thermoplastic resin composites may be more difficult, unless after cleaning it is possible to apply the necessary heat and pressure to melt the original matrix. However, the melting temperature of some thermoplastics is high: **Polyether ether ketone**, PEEK (mp 334 °C) may require processing at 375–400 °C and 6–12 MPa. When this is not possible, the low **Surface energy** must be raised using **Corona discharge treatment** or glow discharge treatments (see **Plasma pre-treatment**), or other treatment recommended by the manufacturers.

*Joints in composites*

Composites may be joined by bonding, bolting or both.<sup>1</sup> Scarf, stepped lap, supported single-lap joints are the most common, but single-lap or double-lap types are used (**Shear tests**).

*Stepped-lap joints* with glass fibre fabrics and brittle resins are easily made as each layer can be identified and peeled back. With tougher resins and stiff fibres, such as carbon-fibre fabrics and aramids, peeling back the layers is difficult, so scarf joints are more often specified in recent Structural Repair Manuals (SRMs).

*Scarf joints* should only be used if specified by the component manufacturer. Much good material must be removed to produce the taper, so skilled operatives are necessary. A layer of toughened film adhesive should be used between the scarf and the patch, or a layer of toughened two-part paste adhesive if a wet lay-up is used.

To avoid failure in the first ply of the composite, *lap joints* should be made only with toughened film or paste adhesives and a good bond area to spread the load. It is usual to “drop off” the plies one at a time near the edges of the lap so that a shallow taper is produced resulting in low transverse stresses at the edges of the patch. GMI (Paris, France) and ATACS (Seattle, USA) and other companies supply tooling that greatly assists the accurate machining of scarf and stepped-lap joints.

*Surface preparation of composites prior to bonding*

There are several important steps in this process. Firstly, the bonding surface should be solvent cleaned to remove all grease and dirt (**Degreasing**) and then all paint should be removed, taking care not to abrade into the first fibre layer. Paint removal may require a coarser grade of paper than abrasion for surface preparation for bonding (**Abrasion treatment**). Grade 150 is approved by some SRMs. Paint strippers are not recommended as they may dissolve the resin in the composite.

Secondly, the surface should be lightly abraded with grade 320 aluminium oxide or silicon carbide paper or grit blasted with 180/320 aluminium oxide grit. Again, great care must be taken not to cut into the first fibre layer. If grit blasting is used, it is essential

to use new, clean grit blasted to waste once only. The grit may be reused for other purposes but not for surface preparation. After abrasion or grit blasting, the surface dust should be removed with clean cotton pads and clean solvent until the pads remain clean. The remaining solvent should be removed with another clean, dry cotton pad. For suitable pads, see SAE AMS 3819. Acetone, methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) are suitable solvents (see **Environment and the impact of adhesive technology**). Only high quality, that is, reagent grade solvents should be used as lower grades are likely to leave residues detrimental to good bonding.

If acceptable to the component manufacturer, a “peel ply” may be bonded to a surface, which is peeled off just before bonding to another part to leave a clean, prepared, surface. Release agents should not be applied to the “peel ply” (**Release!**)! As peel plies may leave a little residual contamination, it is usually beneficial to abrade lightly after peeling and before bonding.

Thirdly, a “water break test” should then be carried out by spraying distilled or de-ionized water on to the prepared surface (**Surface characterization by contact angles – polymers and Wetting and spreading**). Careful abrasion is needed until a continuous layer of water remains for 30 s without any breaks. Once dried, the surface will then be ready for bonding.

### *Drying procedures*

All matrix resins and adhesives absorb some moisture, and a dry surface is necessary before bonding if strong and durable joints are to be made. The surface should then be dried with radiant lamps or hot air blowers for about 3 h at the intended bonding temperature or to the standard specified in the SRM for the component.<sup>2,3</sup> The prepared surfaces should not be touched by hand or anything else from the time of the “water break test” to the time of application of the adhesive. Bonding should take place as soon as possible after drying or a suitable primer should be applied within about 4 h. Once the primer is dry, the part can be stored in a sealed plastic bag for several months prior to bonding.

### *Bolted joints*

Bolted joints can be designed in many configurations especially such complex joints as the root ends of helicopter blades, which are usually made from metals. The correct torque loading on bolts is important as the clamping force suppresses transverse tensile stresses and greatly increases the strength of bolted joints.<sup>1</sup>

Simple bolted joints can only achieve an efficiency of about 40–50% of the strength of the undamaged part. Higher values require a build-up of the skin thickness in the joint area known as “padding-up” and often a stepped-lap bolted joint. Scarf joints can achieve a joint efficiency of up to 90% if a 50:1 taper ratio is used and the joint is carefully made with a good surface preparation and a strong tough adhesive. Drying, as detailed above, is necessary.

### *Bonded scarf joints*

Fatigue testing of scarf joints has shown that failure begins at the ends and at a lower load than a test-piece of the same material without a joint. Fortunately, disbond at the joint

ends gives warning of impending problems and a further repair can be made. The fatigue life of joints (bonded or bolted), and repairs therefore, needs careful consideration, and in most cases, testing is needed to establish safe performance limits.

### *Bonded lap joints*

Lap joints achieve a lower efficiency, which will vary with design and laminate thickness. If the joint strength is critical, and the repair design is not already cleared by the component manufacturer, a test is recommended to establish suitability for purpose. However, for skin repairs to lightly loaded sandwich panels and fairings, they are simple to perform and also quicker and cheaper. For sandwich panels, they are classified as “supported single-lap joints”, which have a higher joint efficiency than unsupported single-lap joints.

Bonded Lap joints are also used to repair cracked metal parts with composite patches. These patches serve to reduce the stress levels at the ends of cracks and to greatly extend the life of some metal parts.<sup>4</sup>

Other articles related to **Aerospace applications of Composite materials** include **Fibre composites – introduction** and **Fibre composites – matrices and fibres**.

### *References*

1. K. B. Armstrong, L. G. Bevan and W. F. Cole, *Care and Repair of Advanced Composites*, 2nd edn, SAE International, 400, Commonwealth Drive, Warrendale, PA, 2003. ISBN 0-7680-1062-4.
2. A. A. Baker and R. Jones, *Bonded Repair of Aircraft Structures*, Martinus Nijhoff Publishers, 1988. ISBN 90-247-3606-4.
3. K. B. Armstrong, Effect of absorbed water in CFRP composites on adhesive bonding. *Int. J. Adhes. Adhes.*, **16**(1), 21–28 (1996).
4. A. A. Baker, F. Rose and R. Jones, Eds., *Advances in the Bonded Composite Repair of Metallic Aircraft Structure*, Elsevier, 2002. ISBN 0-08-042699-9.

---

## *Fibre composites – matrices and fibres*

---

B C COPE

The general properties of polymer-based **Composite materials** and the critical influence of interfacial adhesion are considered under **Fibre composites – introduction**. The section below summarizes the range of materials that may be used as fibres and matrices, which together serve to exploit the range of properties that may be obtained from composites.

### *Fibres*

It may be shown that fibres used for reinforcement should be as small in diameter and as high in aspect ratio as possible. Very short fibres simply act as stress concentrators in all modes of stressing except compression. The upper limit to fibre length is purely a matter

of practicalities. Long fibres do not flow well and are easily damaged when the matrix is moulded, but continuous fibres can be wound into radially symmetrical structures, such as pipes, with great success. Short fibres have inferior reinforcing properties but may produce composites that are more easily moulded. The materials listed under the headings below are commonly used.

*Glass* Being both cheap and versatile, glass is by far the commonest reinforcement. Ordinary sodium silicate glass, “A-glass”, is rarely used now, as the greater durability in damp conditions of the less alkaline E-glass more than compensates for its extra cost. Other, more exotic and expensively formulated glasses, such as C-glass and S-glass, are used in advanced structural composites where their greater cost may be justified.

Glass is available in the form of rovings (untwisted bundles of strands), yarn (twisted bundles of strands), and bonded, needled, woven and knitted fabrics made from each. Yarn-based fabrics are the most expensive but yield the strongest composites. The cheapest fabric is the chemically bound, non-woven, two-dimensionally random, chopped strand mat, but where better mechanical properties are needed tapes, scrims, square weaves, twills, satins and various knitted constructions are preferred.

Surface treatments used are discussed elsewhere under **Silane adhesion promoters, Fibre–matrix adhesion – glass fibres.**

*Carbon fibre* This material, sometimes referred to as “graphite”, is much more expensive than glass, but is lighter, stiffer, and, to a degree, electrically conducting. Being black and opaque, carbon does not give the translucent composites that glass is capable of providing. Carbon-based composites may have a particularly modulus and high fatigue resistance.

As with glass, a range of cloth constructions is available. Further details of the fibres and their surface treatment are discussed under **Fibre–matrix adhesion – carbon fibres.**

*Aramids* The term “aramid” is used to describe aromatic and partially aromatic polyamides, which constitute a class of materials that are analogous to the aliphatic “nylons”. The fully aromatic polymers in this category are linear, but not thermoplastic, as they decompose before they flow sufficiently to allow shaping. However, wet spinning of fibres is possible and such materials have many “technical” applications besides being used as reinforcement.

The material most familiar as a reinforcement is probably Du Pont’s “Kevlar”, which has a very stiff chain consisting of benzene rings linked in 1,4 configuration by amide groups. Like carbon fibres, aramid fibres are lighter than glass and yield very stiff composites, which also possess adequate creep and fatigue resistance. They have the advantage over carbon of a light colour, but are less suitable for use in compression or where UV radiation is a serious problem. Kevlar and the other 1,4 aramids are particularly difficult to cut, as they have a marked tendency to fibrillate axially. This is a disadvantage in the fabrication of composites, but imparts a degree of resistance to ballistic impact.

*Boron* Elemental boron may be grown over a tungsten core into long, relatively thick fibres that may be used as reinforcing material. The fibres are extremely stiff, but their very high cost rules them out for most applications outside military aerospace projects.

*Hybrid fabrics* containing two or more fibres, are available and permit greater subtlety in reinforcement placement and orientation than may be obtained from a single fibre.



### *Matrix polymers*

Both thermosetting and thermoplastic polymers are used as matrices in composites. Thermosets have the advantages of usually being relatively low viscosity oligomeric liquids at the point at which the reinforcements are incorporated, thus improving wetting of the fibres. On cross-linking or curing, they give rigid and heat-resistant matrices.

Thermoplastics are, at the point of incorporation of reinforcement, high polymers rather than oligomers and are hence very viscous and not efficient at wetting. They give composites that, of course, soften on heating.

### *Thermosets*

*Unsaturated polyesters* The cheapest thermosetting matrix resins, the polyesters, are versatile and undemanding. They cross-link by a free radical polymerization of a reactive diluent, such as styrene. Choice of suitable cross-linking materials and techniques enables them to be hardened at temperatures from outdoor winter ambient to 150 °C. Cure times range from a few minutes to several hours depending on conditions and chemistry. Polyesters are forgiving enough to be used by amateurs, such as boat builders, and are available in chemical-resistant and flame-retardant grades for technical applications.

*Epoxy resins* Epoxy resins are monomeric or oligomeric compounds containing two or more epoxide rings that may be opened catalytically, or stoichiometrically, by reaction with multifunctional amines or carboxylic acids, to give a cross-linked network. They may be formulated to cross-link in the cold, but for optimum properties must be post-cured or cured hot (see **Epoxy adhesives**). They offer greater strength, rigidity, toughness and durability than polyesters, but at a higher price and with more difficulties in processing. Their chemical resistance is usually superior to that of polyesters. Epoxides are commonly used with the higher-priced forms of reinforcement in more “technical” applications.

*Vinyl ester resins* The vinyl ester resins are essentially epoxide resins, normally the diglycidyl ether of bisphenol A, that have been reacted with acrylic acid or its derivatives. The unsaturation in the acid residues provides sites for a cross-linking mechanism based on free radical polymerization. The retention of the bisphenol A backbone in the chain of the cross-linked polymer conserves most of the mechanical and physical properties associated with the parent epoxy. The resins thus provide a combination of ease of processing with good chemical resistance and mechanical behaviour.

*Polyimides* These expensive resins are hot cured and used primarily in aerospace and military applications in which their superior thermomechanical properties justify their cost premium (see **Polyimide adhesives**).

*Phenolic resins* Phenolics were the first synthetic polymers to become commercially available, as “Bakelite”, and were long considered to be unsuitable for composite production as their condensation curing mechanism produces water that vaporizes at the normal curing temperatures of over 100 °C. The pressure needed to prevent this water from introducing porosity into resulting laminates was sufficient seriously to degrade the reinforcing fibres. More recently, acid-catalysed and base-catalysed curing systems have made possible the

production of phenolic composites by low-pressure techniques (see **Phenolic adhesives: single-stage resoles**, **Phenolic adhesives: two-stage novolacs**). Phenolic composites are sold primarily on their fire resistance.

*Thermoplastics* Many “engineering” thermoplastics, and such marginal materials as polypropylene, are produced in glass-reinforced, and in a few cases, carbon-fibre-reinforced, grades for injection moulding and extrusion. These materials are filled with short fibres, since longer ones readily break up on passage through compounding and moulding machines, which are randomly oriented. Despite the relatively inefficient disposition of the reinforcement, these grades typically still show at least twice the stiffness of the unfilled equivalents.

Some advanced engineering thermoplastics reinforced with somewhat longer fibres and consequently possessing better mechanical properties are available for injection moulding. However, some deterioration still occurs as the fibres suffer damage in the moulding machine. **Polyether ether ketone**, PEEK, and some other advanced thermoplastics are used in the production of composite prepregs. These are thin plies of sheet material for shaping by autoclave moulding and other techniques that are made by incorporating fine cloth reinforcement or continuous unidirectional fibres in a thermoplastic matrix.

**Fibre composites – joining** and **Fibre composites – processing techniques** give details of practical aspects of these materials.

### *Select References*

- J. W. S. Hearle, *High Performance Fibres*, CRC, Cambridge, 2001.  
J. A. Brydson, *Plastics Materials*, 7th edn, Butterworth-Heinemann, Oxford, 1999.  
T. F. Starr, *Thermoset Resins for Composites*, 2nd edn, Woodhead, Cambridge, 1998.  
S. K. De and J. R. White, Eds., *Short Fibre Polymer Composites*, Woodhead, Cambridge, 1996.  
C. A. Harper, Ed., *Handbook of Plastics, Elastomers and Composites*, 3rd edn, McGraw-Hill, London, 1996.  
D. L. Chung, *Carbon Fibre Composites*, Butterworth-Heinemann, London, 1994.

---

## ***Fibre composites – processing techniques***

---

B C COPE

It is obvious that before the advantage of **Composite materials** (see **Fibre composites – introduction**) can be practically realized, they must be fabricated into components. Depending on the particular materials involved (see **Fibre composites – matrices and fibres**) and the forms required, specially developed processing methods may be necessary. Following is a brief survey of some of the more generally applicable procedures.

### *Processing techniques*

Hot-curing materials with randomly arranged reinforcement are available in grades suitable for processing by conventional compression, transfer or injection moulding. Short fibre-reinforced thermoplastics are usually injection moulded. Processes that are peculiar

to composites are necessary when dealing with continuous or cloth reinforcement. Some are outlined under the headings below.

*Pultrusion* In this analogue of extrusion, a bundle of fibres is impregnated with thermosetting resin and then pulled through a heated die where it is simultaneously shaped and cross-linked.

*Contact moulding* Contact moulding is a family of methods of shaping thermosetting composites in which no pressure, other than atmospheric, is applied as the matrix resin cures. At its simplest, contact moulding involves nothing more sophisticated than an individual with a brush and a bucket of resin that is formulated to cure at ambient temperature. Reinforcing fabric is laid on to a simple mould, made from timber, plaster or other cheap material, and then wetted out manually with liquid resin. Developments employ resin sprays or vacuum impregnation to reduce labour content and improve consistency. Very large mechanical laminating machines have been employed for specialized purposes, such as the construction of ship hulls. The processes yield components with one “good” side, that against the mould, and one unfinished and uneven one.

*Filament winding* The application of a pre-impregnated continuous length of fibre around the outside of a mandrel to produce pipes, pressure vessels and similar articles, is also a form of contact moulding. As with pultrusion, continuous reinforcement is passed through a bath of activated thermosetting resin that is cross-linked by heat, in this case on the mandrel.

*Vacuum and pressure impregnation* The manufacture of components with two “good” sides may be achieved by one of a variety of techniques in which a double-sided mould is first loaded with a preform made from reinforcing fibre and then closed before a liquid thermosetting resin complete with hardening system is drawn in under vacuum or forced in under pressure. Again, very large mouldings such as ship hulls have been produced by a variety of such techniques.

*Cold press moulding* This minor process has been used with polyesters and involves a closed mould that can be locked after a fast-setting resin has been poured onto a fibrous preform.

*Thermosetting prepregs* Thermosetting prepregs consist of reinforcement pre-impregnated with hot-curing resin fully compounded, if necessary, with hardener. Some, such as the unsaturated-polyester-based sheet moulding compound and bulk moulding compound, are processed by conventional compression moulding using very low pressures. However, when woven or knitted reinforcement is used, compression moulding may not be appropriate and is replaced by a technique in which cut-out layers of prepreg are stacked in a closed mould, which is then closed and heated in an oven or autoclave. Very large mouldings for aerospace applications are made by this technique.

*Thermoplastic prepregs* Thin plies of reinforcing tape or cloth may be incorporated into advanced engineering thermoplastics using a variety of techniques in which the matrix is softened by heat or solvent. The resulting sheets are laminated together, amalgamated and shaped by being stacked in a mould, which is then passed through an autoclaving cycle,

usually with the prepregs held against the mould by pressure applied through a flexible blanket or bag.

Some other practical aspects of the use of these materials are discussed under **Fibre composites – joining**.

### Select References

- T. G. Gutowski, Ed., *Advanced Composites Manufacturing*, Wiley, New York, 1997.  
 B. T. Åstrom, *Manufacturing of Polymer Composites*, Chapman & Hall, London, 1997.  
 P. K. Mallich and S. Newman, Eds., *Composite Materials Technology, Processes and Properties*, Hauser, Munich, 1990.

---

## *Fibre–matrix adhesion – assessment techniques*

---

F R JONES

The performance of all **Composite materials** is dependent on the adhesion between the different phases. The significance of this adhesion is discussed in **Fibre composites – introduction**: in this article some ways of measuring it are described.

The quantification of the interfacial bond strength between fibres and matrix has been recently reviewed by Favre.<sup>1</sup> A number of methods have been employed, but four tests are currently more widely used.<sup>2</sup>

### *Indirect measurements*

The most common indirect test involves the determination of interlaminar shear strength (ILSS) by a short beam shear test in three-point bending. Full specification of the test has been given by Curtis.<sup>3</sup> For typical results, see Fig. 5 of **Fibre–matrix adhesion – carbon fibres**. The disadvantage of this test is that once the interfacial shear strength exceeds the shear strength of the matrix, failure occurs predominantly in the resin and the ILSS reaches a plateau. This has been confirmed by scanning **Secondary ion mass spectrometry**.<sup>4</sup> The values of ILSS consequently vary between systems and are also subject to variabilities in the interphase structure and fibre surface chemistry.<sup>4</sup>

### *Direct measurements*

**Multiple fragmentation test** In this test, a single filament is embedded in a matrix resin and tested under tension until fragmentation into successive shorter lengths is complete and the fibre length has reached equilibrium.<sup>5,6</sup>

The interfacial shear strength  $\tau_i$  is given by a consideration of the stress transfer between fibre and matrix

$$\tau_i = \frac{d_f \sigma_{fu}(l_c)}{2l_c} \quad [1]$$

where  $d_f$  is the fibre diameter,  $l_c$  the equilibrium critical length determined in the test and  $\sigma_{fu}(l_c)$  the fibre strength at the critical length  $l_c$  for the system under consideration.

This test has a number of disadvantages as follows:

1. A tendency to select the strongest single filament from the bundle.
2. Tedious measurements of the Weibull statistics of single-filament strengths are necessary for the determination of an accurate value of the fibre strength at the critical length  $\sigma_{fu}(l_c)$ .
3. The test is limited to matrices whose failure strain is significantly greater than the fibre failure strain. This can present difficulties in comparing performance in differing matrices and environmental factors that cause matrix failure strain to decrease. The stress-transfer mechanism at the interface is further complicated by the possibility of yield in the matrix or interphase region.

Equation 1 assumes that the shear stress at the interface is constant as a result of complete interfacial debonding. With good adhesion, only partial debonding or other micro-mechanical events such as transverse matrix cracking are observed, which invalidate the assumption of a constant interfacial shear stress. As a result, alternative data reduction techniques have been developed. For example, Tripathi and Jones<sup>6</sup> developed the cumulative stress-transfer function, which deals with the limitations given above. This has been further refined by Lopattanon *et al.*<sup>7</sup> into the stress-transfer efficiency from which an ineffective length of that fibre in that resin can be determined. In this model, the matrix properties and frictional adhesion at debonds can be included in the analysis. It is also possible to use the three-phase stress-transfer model of Wu *et al.*<sup>8</sup> to include the properties of an interphase.

*Pull-out test* In this test, the force to pull a single filament out of a resin block or a micro droplet is determined. The average shear strength  $\tau_i$  can be related to the embedded length  $l_e$ :

$$\tau_i = \frac{P_f}{\pi d_f l_e} \quad [2]$$

where  $P_f$  is the maximum pull-out load.

The problems associated with this test mainly arise from the mechanism of stress transfer and the build-up of stress in the fibre from its ends.<sup>9,10</sup> Theoretical analysis is required to provide an accurate extrapolation of  $P_f/l_e$  data to determine  $\tau_{max}$ . With a strong interfacial bond  $l_e$  becomes very small. In this way, inaccuracies associated with the measurement of  $l_e$  can be mitigated.

*Microindentation or push-in test* In this experiment, a micro-indentor is used to push the fibre into the matrix. Its major advantage is that it can be applied to fibres in a polished section of a fibre composite without the need for special specimen fabrication. The interfacial shear strength is related to the displacement of the fibre into the matrix  $l_d$  and the appropriate load  $P$ :

$$l_d = \frac{2P^2}{\pi^2 d_f^3 \tau_i E_f} - \frac{2\gamma}{\tau_i} \quad [3]$$

where  $E_f$  is the fibre modulus and  $\gamma$  the fracture surface energy.

Table 1. Typical values of interfacial shear strength ( $\tau_i$ ) as measured by the various techniques

Fibre	Matrix	Treatment	$\tau_i^a$	$\tau_i^b$ (MPa)	$\tau_i^c$	$\tau_{\max}^d$	ILSS (MPa)
Aramid	Epoxy	None	–	8	–	–	55
E-glass	Epoxy	Silane	79	–	56	–	–
E-glass	Polyester	Silane	28	–	23	–	–
E-glass	Vinyl ester	Silane	18	–	–	–	51
AR-glass	Vinyl ester	Silane	14.5–16	–	–	–	41–51
AR-glass	Vinyl ester	None	14.5	–	–	–	38
Carbon HS	Epoxy	None	12	28	28	124	24–70
Carbon HS	Epoxy	100%	37–44	65	–	151	80–100

NB. These figures have been obtained from various sources.

<sup>a</sup> Fragmentation test.

<sup>b</sup> Pull-out test.

<sup>c</sup> Microindentation test – debonding strength.

<sup>d</sup> Pull-out test.

Mandell and McGarry have applied a finite-element analysis to the model. This approach has been adopted by the Dow Company for the development of a commercial instrument that records the force at which debonding occurs.<sup>11</sup>

### *Laser Raman or fluorescence spectroscopy (LRS)*

Many of the uncertainties associated with the above tests arise from the model used to calculate the stress or strain transferred between the matrix and fibre. (Laser Raman or Fluorescence Spectroscopy) LRS<sup>12</sup> is a technique for determining directly the strain in the fibre in analogy to an embedded strain gauge. The strain is probed by recording a Raman (or fluorescence) spectrum of the reinforcing fibre at increments of applied strain. The shift in the frequency at which a stress-sensitive peak occurs can be used to estimate the strain profile in the reinforcing fibre. The rate of strain development in the fibre can be used to assess the quality of the interface. Quantification still requires an appropriate stress-transfer model although a simple force-balance calculation can be used to estimate the interfacial shear stress.

As with other techniques, the approach is not universal because

1. not all reinforcing fibres have a sufficiently intense spectrum (e.g. glass and high-strength carbon fibres)
2. many matrices for testing are not transparent to the selected laser and other matrices fluoresce.
3. The time required to measure a full strain profile in the fibre at a range of applied strains limits the filament length, specimen configuration and workable applied strain to ensure that relaxation in the matrix does not dominate the data.

However, despite these limitations, the use of LRS to probe the strain in a fibre under test aids interpretation.

### *Phase-stepping technique*

In recent studies<sup>13</sup>, it has been proved possible to examine the birefringence in the matrix around a fibre-end or break. Using a phase-stepping technique<sup>13</sup>, contours of principal

stress difference can be obtained from which the interfacial shear stress can be estimated. The strength of this technique is that the decay in matrix stress perpendicular to the fibre can also be examined, enabling the effect of matrix cracks to be studied. In this way, stronger correlations between interfacial micromechanics and macromechanics should be possible.

### *Comparison of test results*

The values of  $\tau_i$  obtained by these different tests are given in Table 1. These figures are given for illustrative purposes demonstrating that competing mechanisms exist. Thus, it was always assumed that debonding occurs at the interface. Specifically with glass fibres this lead to difficulties in interpretation because the calculated interfacial shear strength often exceeded the shear strength of the matrix. It is now recognized that the “finish” applied to glass fibres creates an interphase region, which can yield (without debonding) (see **Fibre–matrix adhesion – glass fibres**). Similar variabilities in the performance of differing grades of carbon fibre are also discussed in the literature.

### *Aramid fibres*

As illustrated in Table 1, the interfacial shear strength of aramid fibre composites is generally low. Several attempts to improve the interfacial bond have been attempted. These involve grafting appropriate functional groups on to the surface of the fibres. However, the improvement is limited because the crystal structure of aramid fibres ensures that the transverse strength is low. Consequently, improvements in interfacial shear strength simply shift the locus of the failure from adhesive to cohesive within the fibre, in which case, mechanical performance is generally not improved. However, there is some benefit to the moisture sensitivity of the fibres and composites.

### *References*

1. J. P. Favre, in *Interfacial Phenomena in Composite Materials*, F. R. Jones, Ed., Butterworths, London, 1989, pp. 7–12.
2. P. I. Herrera-Franco and L. T. Drzal, *Composites*, **23**, 2 (1992).
3. P. T. Curtis, *Crag Test Methods for Engineering Properties of FRP*, RAE Technical Report 88012, 1988.
4. P. Denison, F. R. Jones, A. Brown, P. Humphrey and J. Harvey, *J. Mater. Sci.*, **23**, 2153 (1988).
5. L. T. Drzal, M. J. Rich and P. F. Lloyd, *J. Adhes.*, **16**, 1 (1982).
6. D. Tripathi and F. R. Jones, *J. Mater. Sci.*, **33**, 1 (1998).
7. N. Lopattananon, S. A. Hayes and F. R. Jones, *J. Adhes.*, **78**, 313 (2002).
8. W. Wu, I. Verpoest and J. Varna, *Composites Sci. Technol.*, **58**, 41 (1998).
9. M. J. Pitleethly and J. B. Doble, *Composites*, **21**, 389 (1990).
10. L. B. Greszczuk, *Interfaces in Composites*, ASTM STP452, pp. 42–58, 1969.
11. M. K. Tse, US Patent 4, 662, 228, 1987, Dow Chemical.
12. R. J. Young, *Key Eng. Mater.*, **116-117**, 73 (1996).
13. F. M. Zhao, S. A. Hayes, A. E. Patterson, R. J. Young and F. R. Jones, *Composites Sci. Technol.*, **63**, 1783 (2003).

---

*Fibre–matrix adhesion – carbon fibres*

---

F R JONES

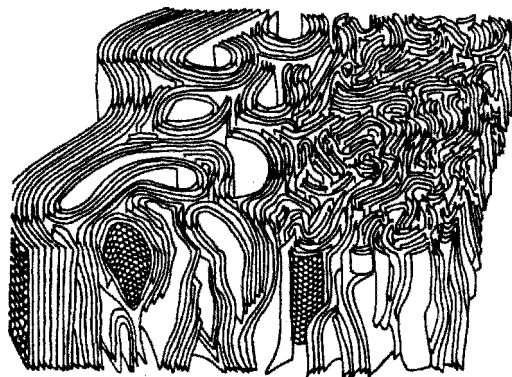
The performance of all **Composite materials** is dependent on the adhesion between the different phases. In this article, aspects relevant to carbon-fibre reinforced plastics are discussed. There is a parallel article on **Fibre–matrix adhesion – glass fibres**. A discussion of the fibre–matrix interface can be found in **Fibre composites – introduction**.

*Carbon-fibre structure*

Carbon fibres, from acrylic or polyacrylonitrile precursors, are defined by the heat-treatment temperature used for carbonization. Thus, Type I (high-modulus) fibres have experienced 2400 °C and Type II (high strength) 1500 °C. These designations arose because, for the original fibres, maximum fibre strength was achieved at the latter temperature. With the identification of the strength-limiting flaws, special acrylic fibres were developed that enabled Type A fibres of high strength to be carbonized over the temperature range 1000–1200 °C.

For intermediate modulus (IM) fibres, the precursor fibre is provided with a higher draw ratio prior to carbonization. The higher molecular orientation is maintained during carbonization to give a higher modulus while retaining the failure strain of Type A fibres.

Type I fibres are known to exhibit a core-sheath structure, with a high degree of order to the circumferential graphitic planes at the fibre surface. In Type A fibres, the graphitic structure is much less perfect so that the surface chemistry of the fibres is strongly dependent on the previous thermal history. The microstructure in the core of the fibre is predetermined by the polyacrylonitrile precursor, which forms an imperfect ladder polymer as a result of the intramolecular cyclization of the pendant nitrile groups, which occurs during the oxidation stage. Since the precursor polymer is largely atactic, these cyclized sequences occur over a short range so that on carbonization, a turbostratic structure results, as shown in Fig. 1.<sup>1</sup>



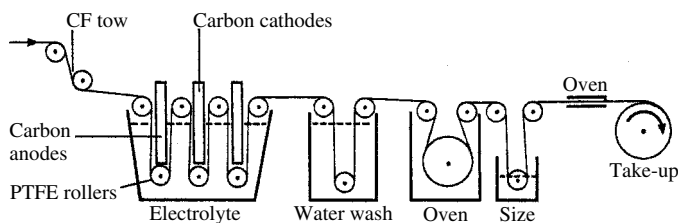
**Fig. 1.** Schematic PAN carbon-fibre structure. (After S C Bennett, D J Johnson in *Proc. 5th London Carbon and Graphite Conf.*, vol. 1, SCI, London, 1978, p. 377, reproduced with permission)



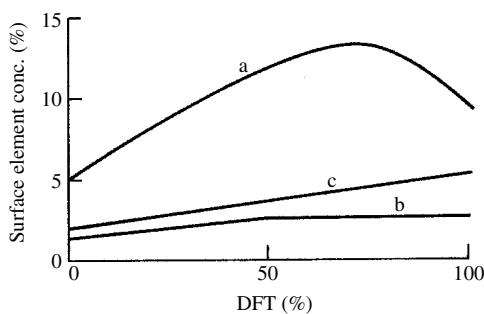
### Surface treatment

A number of surface modifications have been examined but anodic oxidation in an aqueous electrolyte (e.g. ammonium bicarbonate) is preferred. This is largely a result of the control, which can be achieved with electrochemistry as much with the convenience of adding an electrochemical bath to the production line. A typical unit is schematically given in Fig. 2. The degree of oxidation for a particular fibre type can be quantified by reference to the current density (typically  $100 \text{ C m}^{-2}$ ). However, much of the research is reported in terms of a fraction of the commercial surface treatment percent degree of fibre treatment (DFT), which is set at 100%. Variation in surface treatment can be normalized accordingly by adjusting the current density proportionally. Because of their less perfect graphitic structure, Type A fibres are more easily treated than higher modulus fibres.

*Surface microstructure, microchemistry* Surface characterization of oxidized carbon fibres has been undertaken using various techniques. It is well established that the surface oxygen concentration increases, as shown in Fig. 3. The chemical state of the oxygen has been the subject of many papers, but as shown in Fig. 3, a significant proportion exists as carboxylic acid groups. The remaining oxygen is in the form of adsorbed water, phenolic hydroxyl and/or ketonic groups. It is generally accepted that these functional groups are located at the edges of the basal planes in the graphite lattice. A correlation between surface chemistry and interfacial bond strength has been difficult to prove. A significant increase in surface area during surface treatment could not be detected. Denison and Jones<sup>2</sup> approached this problem by establishing a model segment for quantification of the surface

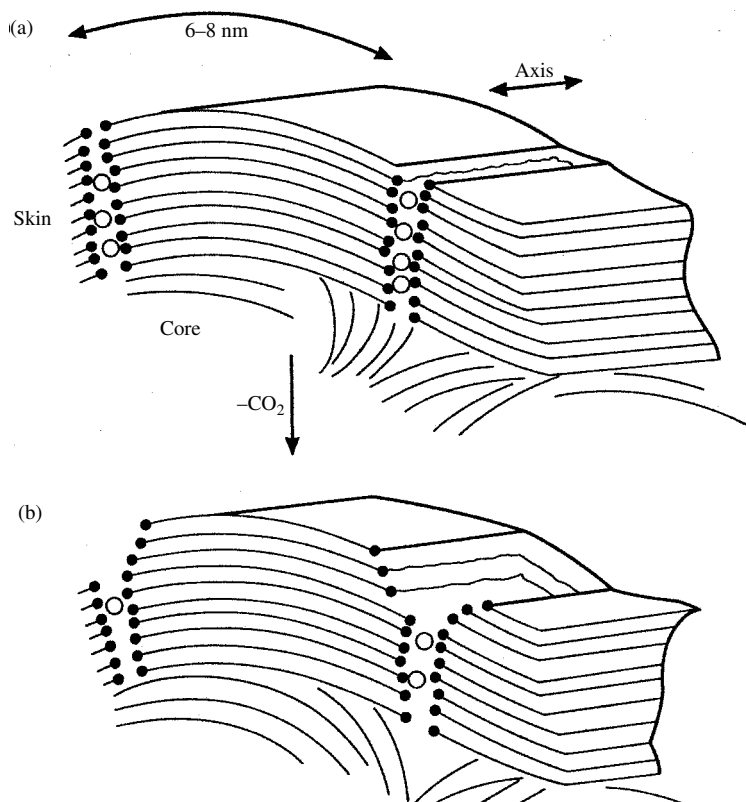


**Fig. 2.** Typical arrangement for electrochemical surface oxidation of carbon fibres



**Fig. 3.** The surface concentration of (a) oxygen atoms, (b) oxygen atoms combined as carboxylic acid groups, (c) adsorptive sites, as a fraction (in %) of 40,000 carbon atoms contained in a graphitic segment  $\approx 3.5 \text{ nm}$  thick.<sup>2</sup> DFT – degree of fibre treatment

derived groups (see **X-ray photoelectron spectroscopy**). In this way, it was possible to show that the surface of treated Type II fibres was saturated with acid groups and their average separation was smaller than theoretically possible. As a result, they postulated that the functional groups were located within the micropores in the surface. Detailed study of Type I fibres confirmed that the concentration of carboxylic acid groups rose to a maximum with surface treatment, while the dimensions of the micropores increased. Following the demonstration that thermal desorption of the oxygen-containing groups *in vacuo* at 1400 °C did not always lead to a reduction in interlaminar shear strength (see **Fibre-matrix adhesion – assessment techniques**), and that the measured acidity was not affected (i.e. the acid groups reformed by reaction with water during analysis), it was concluded that active carbons, devoid of functional groups, could also be involved in adhesive bond formation.<sup>3</sup> It has also been observed that molecular-thin layers of epoxy resins can be chemically bound to the surface.<sup>4</sup> A schematic model of the surface of Type I carbon fibres before and after surface treatment is given in Fig. 4. The spacing of these micropores is considered to be determined by the crystallite size distribution. The micropore dimension of  $\approx 0.7$  nm demonstrates that they occur at the twist boundaries between these crystallites. Transmission **Electron microscopy** of embedded fibres has



**Fig. 4.** The schematic model of Type I (high-modulus) carbon-fibre surface before (a) and after (b) electrochemical oxidation. (●) Adsorptive sites that may or may not have functional groups attached; (○) adsorbate molecules (e.g. H<sub>2</sub>O)

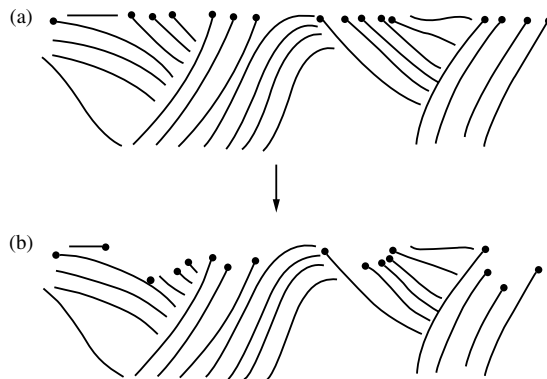
also demonstrated that the fibre–matrix adhesion occurs predominantly at the edges of the exposed basal planes. The different surface microstructures for Type A and Type I fibres have led to different interpretations; however, it is clear that the adhesion mechanism involves contributions from functional group chemistry, stereochemistry of the resin molecules and the presence of micropores whose dimensions must be large enough to allow access to the edges of the basal plane where the reactivity exists. For Type A fibres, the graphitic skin, which could be present prior to surface treatment, is etched away in the electrolytic process to expose varying degrees of perpendicularly organized basal planes. Figure 5 shows a schematic of the surface of a low modulus fibre.

Another aspect is the role of nitrogen in the surface. It was considered that the increase in its concentration after electrolytic oxidation represented exposure of nitrile residues in the “core”, but recent work by Alexander and Jones<sup>5</sup> demonstrated that the carboxyl groups that form can react with ammonium hydroxide in the aqueous electrolytes to give an amide functionality.

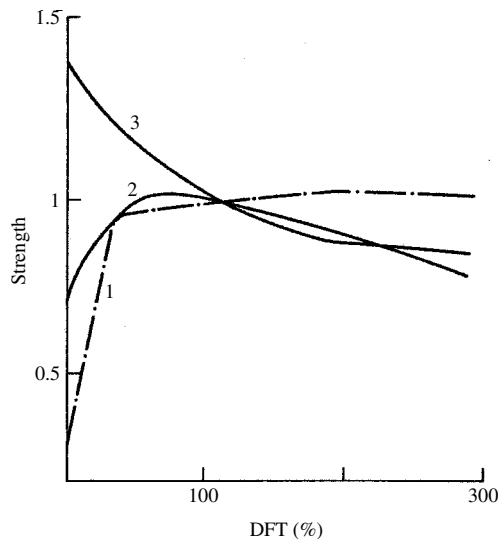
The role of chemistry in interface formation has been confirmed by coating the fibres with plasma polymers of varying functionality. Non-functional coatings destroyed the adhesion to an anhydride-cured epoxy whereas carboxyl groups were shown to be more efficient than amine groups at promoting adhesion.

After surface oxidation, the fibres are coated with a polymeric size, which is usually an epoxy resin. Whether this resin coating can be dissolved efficiently into the matrix is unclear. This aspect of the fibre–matrix interaction in carbon-fibre composites is under researched. It is generally now accepted that an interphase region forms. This can be distinct or graded depending on the solubility of the size and subsequent phase separation on curing.

*The effect of surface treatment on the mechanical properties of carbon-fibre composites* Brittle fibres in a brittle matrix can have appreciable toughness because the cracks can get diverted along the fibre–matrix interface. If the bond is weak the composite will not support loads in shear or compression, but when the bond is too strong, the material will be brittle. These aspects are illustrated in Fig. 6, where it is seen that the interlaminar shear strength reaches a plateau but the notched tensile strength decreases



**Fig. 5.** Schematic cross section of a Type A (high strength) carbon-fibre surface (a) before and (b) after electrochemical oxidation. (●) represent active and/or functionalized sites at the basal plane edges



**Fig. 6.** Effect of surface treatment (degree of fibre treatment, DFT) on the mechanical performance of Type II carbon fibre epoxy composites. (1) Interlaminar shear strength of a unidirectional composite, (2) impact strength (3) notched tensile strength, of a  $(0^\circ/+45^\circ/0^\circ)_s$  laminate

monotonically with surface treatment. Optimization and careful control of the interfacial bond strength is therefore essential for each fibre – resin system. It is also apparent from Fig. 6 that test methods other than fracture tests have to be used accurately to assess the interfacial bond strength (see **Fibre-matrix adhesion – assessment techniques**).

### References

1. J.-B. Donnet and R. C. Bansal, *Carbon Fibres*, 2nd edn, Marcel Dekker, 1989.
2. P. Denison, F. R. Jones and J. F. Watts, *J. Mater. Sci.*, **20**, 4647 (1985); *Surf. Interface Anal.*, **9**, 431 (1986); **12**, 455 (1988).
3. P. Denison, F. R. Jones, A. J. Paul and J. F. Watts, in *Interfacial Phenomenon in Composite Materials*, F. R. Jones, Ed., Butterworths, London, 1989, pp. 105–10.
4. P. Denison, F. R. Jones and J. F. Watts, in *Interfaces in Polymer, Ceramic and Metal Matrix Composites*, H. Ishida, Ed., Elsevier, New York, 1988, p. 77–85.
5. M. R. Alexander and F. R. Jones *Carbon*, **34**, 1093 (1996).

### Fibre-matrix adhesion – glass fibres

F R JONES

The properties of glass-fibre reinforced plastics, like those of all **Composite materials**, are dependent on the adhesion between the different phases; see **Fibre composites – introduction**.

### *Glass-fibre forms*

While several glass-forming compositions (see **Fibre composites – matrices and fibres**) are used to manufacture reinforcements for composites, E-glass is the most industrially important. The fibres are drawn from a low-sodium, aluminoborosilicate glass melt at 1250 °C. The drawn fibres of  $\approx 15 \mu\text{m}$  diameter are immediately cooled often with a water spray and coated with an aqueous “size” in contact with a rubber roller. The “size” or “finish” is crucial to the “handleability” of the fibres and their **compatibility** with the resin matrix. In early plants, each bushing produced approximately 200 individual filaments, which are assembled into a strand or tow. These were combined in a separate process to give rovings of appropriate tex (typically 600, 1200 or 2400 tex, “tex” is the weight in grams of a item length). When carried out in a separate stage, the rovings take on a slight twist. Without a twist these direct rovings are used for prepreg manufacture and aligned fibres composites such as pultruded sections of higher structural performance. In new plants, reinforced rhodium/platinum alloys are used for the bushings at which up to 6000 filaments can be spun. Therefore, direct rovings can be formed at the bushing.

To cater for the variety of composite fabrication techniques, fibres may be formed into woven rovings, knitted preforms or continuous random mats (CRM) or chopped into lengths of  $>20 \text{ mm}$  to  $<5 \text{ mm}$  for use in moulding compounds or assembling into chopped strand mat (CSM). For these textile processes, the polymeric component of the “size” is required to maintain strand integrity and filament strength. The random continuous and chopped strand mats require additional polymeric binders.

### *The glass-fibre “finish”*

The “finish”, which is applied as an aqueous emulsion, consists of the following: (1) adhesion promoter or coupling agent (see **Silane adhesion promoters**); (2) protective polymeric size; (3) additional polymeric binder (emulsion or powder); (4) lubricant(s). Items (2)–(4) impart good handleability and controlled wet-out kinetics with matrix resins and are therefore chosen for compatibility with the fabrication process. For specialist applications, such as environmental resistance, the chemical nature of the “size” and binder are crucial and selected accordingly (see **Durability: fundamentals**). Good economical design can be achieved by combining fibres with differing “finish” in different laminae. Typical coatings are given in Table 1.

### *Surface treatment for adhesion*

The manufacturing process described above may involve bringing hot glass into contact with water immediately prior to surface treatment. This results in a unique surface chemistry. A comparison of the bulk and surface chemistry of E-glass (Table 2) shows that the surface is silica rich. In addition, it is reported that a multimolecular layer (*c.* 20 monolayers) of water is adsorbed by **Hydrogen bonding** through surface hydroxyl groups. The adhesion promoter therefore has the following function: (1) to displace adsorbed water; (2) to create a surface that can be fully wetted with resin; (3) to develop strong interfacial bonds between the fibre and matrix, which minimize the interfacial free energy and maximize the work of adhesion (see Young’s equation in **Wetting and spreading**). Thus, the adhesion promoter has a primary role to interact with both the fibre surface and the matrix

Table 1. Typical glass-fibre finishes

Glass type	Polymeric size	Polymeric binder	Application
E	PVAc	PVAc emulsion	General-purpose roving
E	PVAc		General-purpose CSM
E	Polyester		Environmentally resistant GRP
ECR	Polyester		Environmentally resistant GRP
E. ECR, S. R	Epoxy		High-performance composites
E	Epoxy polyester copolymer	Various – powder	High-performance composites with wide range of compatibility
E. ECR	Polyester		CSM – environmental resistant GRP
			CSM – processing with controlled wet-out CRM
E	Polyurethane		Roving for thermoplastics – short-fibre moulding compounds (e.g. nylon)
C		Polyacrylate	Reinforcing veils for gel coats
		Polystyrene	Chemically resistant barrier layers

CSM = chopped strand mat, CRM = continuous random mat, GRP = glass fibre reinforced plastic, PVAc = polyvinylacetate.

Table 2. Typical bulk (ICP) and surface (XPS) elemental composition for heat cleaned polished E-glass plate<sup>b</sup> and as received non-treated, water sized fibres<sup>c</sup> (after Jones)

Element	Uncoated plate		Uncoated fibre	
	Bulk	Surface	Bulk	Surface
Si	22.3	25.1	22.8	22.4
Al	7.4	8.4	7.0	8.5
Ca	16.4	9.6	17.6	8.6
O	49.6	56.9	50.4	60.5
Mg	0.4	<sup>a</sup>	0.5	<sup>a</sup>
B	2.1	<sup>a</sup>	1.4	<sup>a</sup>
Fe	0.6	<sup>a</sup>	0.3	<sup>a</sup>

<sup>a</sup> Below the detectable limit of X-ray photoelectron spectroscopy (XPS).

<sup>b</sup> Cast from E-glass marbles.

<sup>c</sup> Commercial fibres treated only with water during manufacture.

ICP = Inductively coupled plasma technique.

and is consequently called a coupling agent. The above requirements are best achieved for most matrices, with organosilanes. However, chrome complexes and titanate coupling agents are also available.

For measurement of adhesion, see **Fibre–matrix adhesion – assessment techniques**.

### *The structure of the silane coating*

The application of organosilane coupling agents has been described by Plueddemann.<sup>1</sup> More recently, the adhesion mechanisms have been reviewed by Jones.<sup>2</sup>

The silane coupling agents have a simplified structure

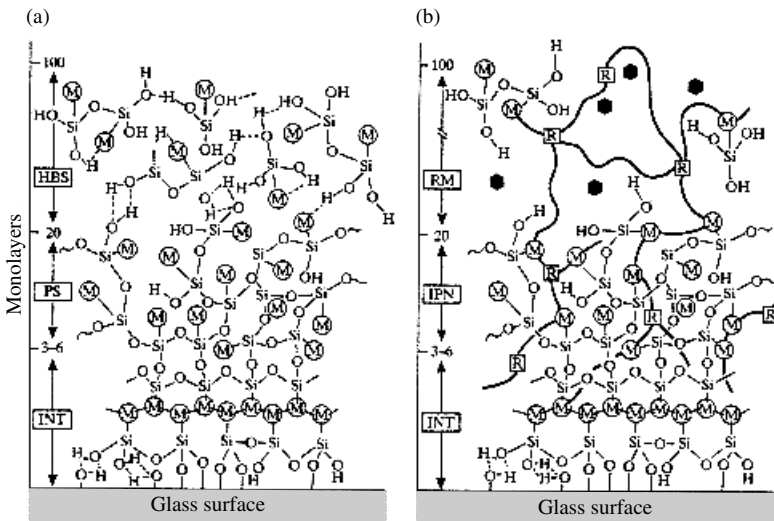


The simplistic chemical bonding theory is usually cited but cannot explain all the observations, not least the efficacy of  $\gamma$ -aminopropyltri-ethoxysilane ( $\gamma$ -APS) under conditions when chemical bonding through the amino group cannot be readily understood.

It is now clear that the adhesive bond arises from a combination of chemical bonding and the formation of an interpenetrating network between the polysiloxane and matrix resin. The former arises because the physisorbed oligomers dissolve into the resin leaving a porous structure with exposed functional groups into which the matrix resin can diffuse and copolymerize. This structure is schematically illustrated in Fig. 2. The presence of the so-called interphase has been confirmed by scanning **Secondary ion mass spectrometry** (see Thomason in Ref. [2]) and  $^{13}\text{C}$  NMR.<sup>4</sup> The latter work also confirmed the reaction of the amino group in  $\gamma$ -APS with acid in the end-groups polyamide matrix. A consequence is that the concentration of silane in the “size” emulsion can significantly influence the adhesion. The structure of the interphase in the composite is further complicated by the presence of the dissolved size and/or binder in the matrix and the interpenetrating network. As a result, the heterogeneity and thermomechanical properties of the interphase can vary with curing temperature (and glass type), leading to a modification of the stress-transfer mechanism between fibre and matrix (see also **Theories of adhesion**).

Theory (5) allows for reversible reformation of chemical bonds on drying out of aqueous conditioned specimens. The observations, which led to Plueddemann to propose this mechanism, are better explained by the effect of moisture on the yield strength on the interphase.

There is a related article on **Fibre–matrix adhesion – carbon fibres**.



**Fig. 2.** Schematic diagrams of (a) a polysiloxane deposit on glass fibre: M is the methacryloxypropyl group in  $\gamma$ -methacryloxypropyl trimethoxy silane and (b) the composite interface. Here R–M is the interpenetrating copolymer with the resin matrix (R), (●) is the dissolved binder and/or size; PS = polysiloxane, HBS = hydrogen bonded oligomeric silanes. IPN = interpenetrating network, INT = interface



### References

1. E. P. Plueddemann, *Silane Coupling Agents*, 2nd edn, Plenum Press, New York, 1991.
2. F. R. Jones, in *High-Performance Fibres*, J. W. S. Hearle, Ed., Woodhead 2001, Chap 6 pp 191–238.
3. H. Ishida and J. L. Koenig, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 1931 (1980).
4. T. L. Weeding, W. S. Veeman, L. W. Jenneskens, H. Angad Gaur, H. E. C. Schuurs and W. G. B. Huysmans, *Macromolecules*, **22**, 706 (1989).

### Filler-matrix adhesion

V KOVAČEVIĆ, S LUČIĆ BLAGOJEVIĆ AND M LESKOVAC

#### Adhesion and composites

The term “**Composite materials**” is applied to materials with interfaces. An understanding of interface is central to the science of adhesion.<sup>1</sup>

The results of most studies of adhesion and composites are interpreted in terms of the **Adsorption theory of adhesion**: the **Dispersion forces** and **Polar forces** determine the interactions between two phases, that is, the matrix and filler.

The **Surface energy** of filler and matrix are important for the adhesion properties in composites. By calculation of the surface free energy of the composite components from **Contact angle measurement**, **Inverse gas chromatography** (IGC) or other measurements, adhesion parameters can be estimated and controlled if necessary, for particular applications.<sup>2</sup> An illustration of this is given in this article.

#### Adhesion parameters in particulate-filled composites

The following parameters for adhesion between matrix (m) and filler (f) were evaluated: the work of adhesion  $W_{mf}$ , interfacial free energy,  $\gamma_{mf}$  and coefficient of wetting (spreading coefficient),  $S$ , (see **Wetting and spreading**, **Wetting and work of adhesion** and **Surface energy components**):

$$W_{mf} = \gamma_f + \gamma_m - \gamma_{mf} \quad [1]$$

$$\gamma_{mf} = \gamma_m + \gamma_f - 2(\gamma_m^d \gamma_f^d)^{1/2} - 2(\gamma_m^p \gamma_f^p)^{1/2} \quad [2]$$

$$S = \gamma_f - \gamma_m - \gamma_{mf} \quad [3]$$

where  $\gamma^d$  and  $\gamma^p$  are the dispersion and polar component of the surface energy.

From studies on effective adhesion for a given system, it is argued<sup>2</sup> that it is important to satisfy the conditions:  $W_{mf} = \max$ ;  $S \geq 0$ ;  $\gamma_{mf} = \min$ .

#### Modification of matrix/filler adhesion

The term “interfacial region” or “interphase” is often used to emphasize the gradual change of properties that occurs passing from one phase to another in composites. The

structure and properties of such an interphase between matrix and filler are important factors determining the properties of the particulate-filled composites.<sup>3</sup>

The ability to control the interface is central to successful application of adhesion in a composite. By modifying or tailoring the interface, the improved fundamental adhesion might result in the improved practical adhesion: for example, various surface treatments of ultra-high modulus polyethylene fibres used as reinforcement in polyester and epoxy composites that changed the values of both monofilament pull-out adhesion and inter-laminar shear strength.<sup>1</sup>

The pre-treatment of a filler surface changes the interface, and thus it is expected to affect the properties of adjacent phases extending some way into the bulk. There are examples of using the various surface modifiers such as acids and acid precursors, alkoxysilanes, organotitanates and related compounds, stearic acid and others.<sup>4</sup> How the surface pre-treatment of CaCO<sub>3</sub> filler by sodium stearate changed the adhesion parameters in the PVAc composite is illustrated in Table 1.<sup>2</sup> The adhesion parameters could be used to relate the interactions at the interface to the mechanical properties of the composite. For example, the small absolute decreases in the work of adhesion after the pre-treatment can lead to the proportionate large absolute decreases in fracture energy.

### Properties of composites

A quantitative characterization of the interactions at the interface should contribute significantly to the evaluation of composite mechanical behaviour.

The relation between the ultimate strength and relative amount of particulate filler is described by a number of theoretical and empirical equations. For example, the parameter  $B$  from Eqn. 4 is used for fitting the experimental data to the exponential model as a strong indicator of polymer-filler adhesion.<sup>5</sup>

$$B = (1 + LA_f \rho_f) \ln \sigma_{Ti} / \sigma_{T0} \quad [4]$$

where  $L$  is the thickness of interface,  $A_f$  and  $\rho_f$  is the specific surface area and density of filler and  $\sigma_{Ti} / \sigma_{T0}$  is a ratio between the true tensile strength of the interface and of the initial matrix polymer.

The properties of a composite reflect the interactions between phases and the interfacial region between them. The thickness of an interfacial region is much higher than the thickness of an adsorption layer in direct contact with the filler surface.<sup>3</sup> In a nanocomposite, for example, where an ultra-fine phase (1–100 nm) is involved, a significant part of polymer chains is immobilized and many polymer properties dramatically altered because of the restriction on mobility experienced by the chains in the vicinity of filler.

Table 1. Comparison of adhesion parameters in PVAc composite with untreated filler (CaCO<sub>3</sub>) and pre-treated with sodium stearate (4.5%)(CaCO<sub>3</sub>-S<sub>4,5</sub>)<sup>2</sup>

Composite	$W_{mf}$ (mJm <sup>-2</sup> )	$\gamma_{mf}$ (mJm <sup>-2</sup> )	$S$ (mJm <sup>-2</sup> )
PVAc/CaCO <sub>3</sub>	103.86	6.06	29.86
PVAc/CaCO <sub>3</sub> -S <sub>4,5</sub>	48.70	4.33	-25.30

Thus, the composite morphology is changed markedly by lowering the filler particle size. This is illustrated in Fig. 1 by the micrographs of poly (methyl methacrylate) composites containing equal volume fractions of aluminium hydroxide of differing particle size.<sup>4</sup>

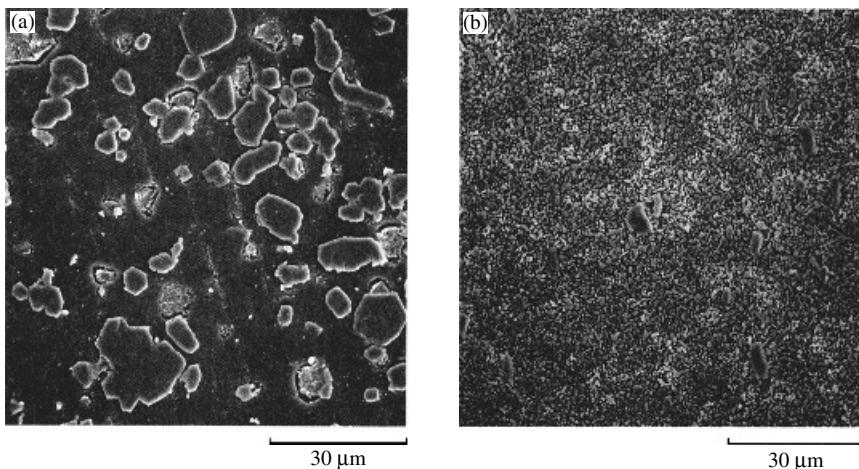
Good filler dispersion in polymer matrix is of a great importance in composites. It depends on (1) wetting of filler particles by matrix, (2) separation of filler particles during the dispersion processes, (3) distribution of filler particles in matrix.<sup>4</sup>

Adhesion between the polymer matrix and filler at the interface in the particulate-filled composites is of a key importance for the composite morphology, mechanisms of failure and the composite mechanical and other properties.

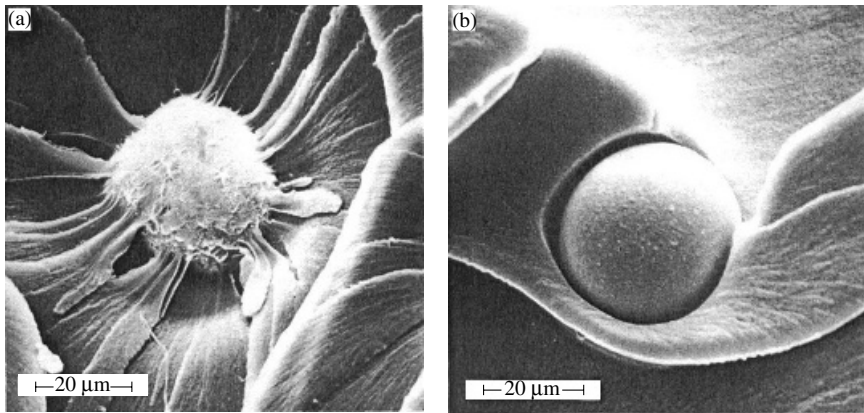
A decrease in radius of filler particles in the composite will result in an increased value of stresses needed to initiate the composite failure. Mechanisms of failure in a composite could take place in the polymer matrix by shear yielding and/or crazing, inside the aggregates of filler particles and/or at the interface matrix/filler by mechanism of dewetting. In particulate-filled composites, yielding and crazing do not depend on the work of adhesion between matrix and filler,  $W_{mf}$ , or thermal stresses,  $\sigma^T$ , but these influence the dewetting phenomenon,  $\sigma^D$  considerably, (Eqn. 5)<sup>5</sup>:

$$\sigma^D = -C_1\sigma^T + (C_2W_{mf}/R)^{1/2} \quad [5]$$

where  $R$  is radius of particles. Modification of the interfacial region provides one way of moving the locus of failure and so altering the properties. Figure 2 shows an example of dewetting at the interface of polycarbonate/glass bead composite with low interactions as a consequence of the silicone oil filler pre-treatment and the opposite effect of cohesive failure due to the strong interactions when the glass bead filler particles were pre-treated with  $\gamma$ -aminopropylsilane,<sup>6</sup> typical of **Silane adhesion promoters**.



**Fig. 1.** Scanning electron microscope images of cross sections of poly (methyl methacrylate) filled with equal volume fractions of two different particle size  $\text{Al}(\text{OH})_3$  fillers. (a) 55% coarse particles; (b) 55% fine particles



**Fig. 2.** Scanning electron micrographs of fracture surfaces of PC/glass bead composites. (a) Excellent interfacial adhesion obtained with  $\gamma$ -aminopropylsilane; (b) poor interfacial adhesion obtained with silicone oil

The possibilities of “engineering” the interface to achieve desired properties are based on understanding of the interface and the ways in which the surface of a component may alter the properties in the interfacial region and thus in the composite material as a whole.

### References

1. D. E. Packham, *J. Adhes.*, **54**, 133 (1995).
2. S. Lučić, V. Kovačević, D. E. Packham, A. Bogner and A. Geržina, *Polymer Surface Modification: Relevance to Adhesion*, Vol. 2, VSP, 505, 2000.
3. Y. S. Lipatov, *Polymer Reinforcement*, ChemTec Publishing, Toronto-Scarborough, Ontario, 1995.
4. R. Rotheron, *Particulate-Filled Polymer Composites*, Longman, Harlow, 1995.
5. B. Pukanszky, *Makromol. Chem. Macromol. Symp.* **70/71**, 213 (1993).
6. M. E. J. Dekkers and D. Heikens, *J. Mater. Sci.*, **19**, 3271 (1984).

---

## Finite element analysis

A D CROCOMBE

### Principles

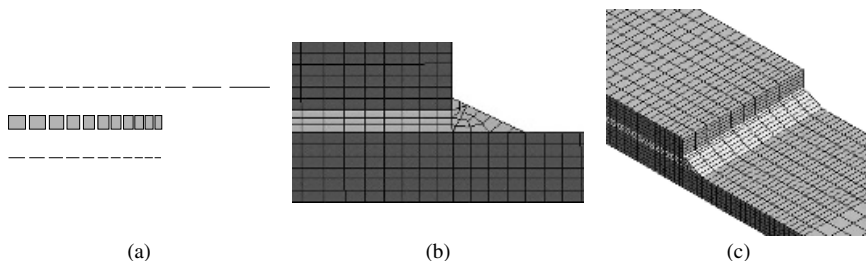
The finite element (FE) technique is an approximate numerical method for solving differential equations. Within the field of adhesive technology, it is most commonly used to determine the state of stress and strain within a bonded joint. It can also be used to determine moisture diffusion, natural frequencies of vibration and other field problems. Although this article will concentrate on the stress analysis, the same concepts can be applied to these other applications of finite element analysis. The basis of any finite element method is the discretization of the (irregular) region of interest into a number of

finite-sized (regular) elements. A trial function is defined in a piecewise manner over the elements in terms of unknown nodal parameters. The nodes are points that usually lie on the element boundaries. A finite element analysis uses variational principles to determine the optimum values of the unknown parameters at these nodes, and hence the optimum trial function. These parameters vary for different types of analyses. In a stress analysis, the parameters are displacements and from these the stresses and the strains can be determined. A simple introduction to the theoretical aspects of the finite element method can be found in Ref. [1] and more in depth reading in Ref. [2].

### *Element types and accuracy*

Within a commercial FE code, there are often more than 100 different elements. However, in broad terms, most can be classified as line, area or volume elements. As the dimensionality of the element decreases, it is necessary to supply more geometric data, that is, a solid (volume) element requires no additional data while a beam (line) element requires area, moments of area, and so on. Figure 1(a–c) illustrate the same adhesive joint modelled using various types of element. In the first, beam elements are used for the substrate connected using rigid constraints (not shown) to area elements for the adhesive. This is reasonable because the substrates can be approximated as plates subject to bending and extension. The second uses area elements for both adhesive and substrate. This enables a more accurate model to be developed, particularly at the overlap end where the beam approximation is less valid. Volume elements are used in the last figure, and although this generally requires many more nodes and elements, it is possible to gain an understanding of any widthwise variation of stresses, which could not be gained from the 2D model.

As a general rule, smaller elements should be used in regions of high stress gradients, as this will enable a more accurate trial function (and hence stress field) to be determined. Clearly, the number of elements used is a compromise between accuracy and processing time. Many FE codes have adaptive meshing facilities that continually refine the mesh until the stresses converge. A word of caution is appropriate at this stage. Convergence will occur only if the stresses are bounded. The FE models of most adhesive joints contain a point of singularity, caused by a bi-material corner.<sup>3</sup> At such points, the stresses are not bounded, convergence will not be reached and the adaptive meshing algorithms may not work properly. Conventional elements are generally classified as first order or second order. This refers to the number of nodes along an element edge (2 or 3 respectively) and hence the order of polynomial that a trial function can adopt. As a general rule, for the same computational effort, it is better to use fewer second-order elements than more first-order ones.



**Fig. 1.** (a) Beams and area elements, (b) all area elements and (c) all volume elements

*Linear and non-linear FE analyses*

The FE equations for a linear problem can be expressed simply as

$$[K][a] = [F] \text{ where } [K] = \sum [k] \text{ and } [k] = \int [B]^T [D] [B] dV$$

Generally, the “external loads”  $[F]$  are known and the stiffness matrix  $[K]$ , (which is a function of the material properties and geometry) can be found. This results in a set of  $n$  equations, which can be solved to give the  $n$  unknown nodal parameters  $[a]$ . The material properties are contained in the linear modulus matrix  $[D]$ . For an isotropic material such as a metal or polymer, the relevant properties are simply the Young’s modulus  $E$  and the Poisson’s ratio  $\nu$ . An anisotropic material such as a fibre-reinforced polymer or timber will have a different modulus and Poisson’s ratio in the different coordinate directions.<sup>4</sup>

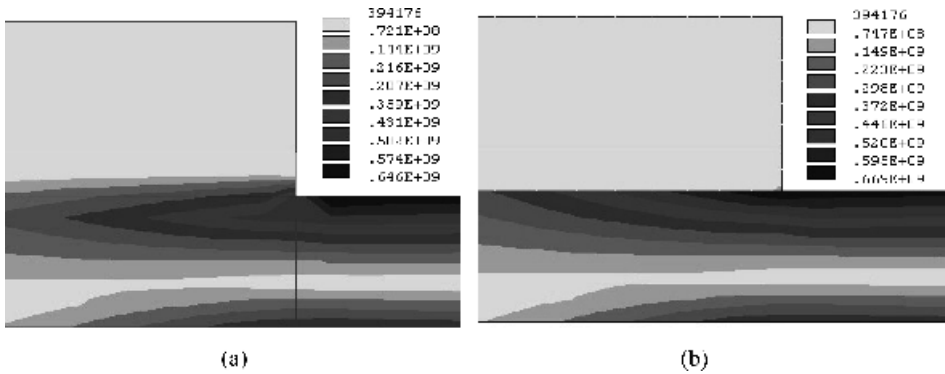
Within the field of adhesive bonding, the use of linear FE analysis is somewhat restrictive as often the response of a joint is non-linear (see **Finite element analysis: rubber**). Generally, a linear analysis can only be used when there is not a substantial change in the geometry on loading (known small displacement) and the materials remain in the linear region. Nevertheless, linear FE analyses have been applied to a wide range of bonded structures including double, single and thick lap shear, scarf, peel, double cantilever, cracked lap shear, edge-notched flexure, tubular lap, butt and many others. It is beyond the scope of this synopsis to deal adequately with this, but a good source of more details is Ref. [5] and elsewhere in this handbook. Another important application of linear FE analysis is in the field of **Fracture mechanics**, where it is necessary to evaluate parameters such as energy-release rate for non-standard configurations.

In a non-linear analysis, the stiffness matrix  $[K]$  or the external loads  $[F]$  are no longer constant but are a function of the unknown parameters  $[a]$ . In such cases, a solution must be approached iteratively using a non-linear solution technique such as Newton–Raphson.<sup>6</sup> As a result of this, solution times are generally orders of magnitude larger than equivalent linear problems. Non-linearity can arise from changes in geometry, material stiffness or loading conditions. Non-linear material behaviour can be divided into time-independent responses such as plasticity and time-dependent responses such as **Creep**.<sup>6</sup>

Material properties for the adhesive may be known but often have to be determined by test. There are a number of tests that can be used for such purposes including bulk tension and torsion, thick lap shear, napkin ring and others; see **Tensile tests** and **Testing of adhesives**.

*Pre and post processing and assessing failure*

The phases of creating a FE model and viewing the results are known as pre and post processing respectively. In most commercial FE codes, these phases can be undertaken using interactive graphics. As a FE model is complex and much data is produced, it is easy for errors to be introduced inadvertently. Thus, it is essential to assess results critically, comparing against experimental data or known “benchmark” solutions. Many FE codes average the stresses at nodes from all adjoining elements; as in homogeneous systems, this will produce the most accurate results. Bonded joints contain multi-materials and it is a common mistake to average the stresses across a material interface. Figure 2(a) and (b) illustrate the difference that this can make to the “apparent” results. In order to predict



**Fig. 2.** Examples of (a) incorrect and (b) correct averaging of adhesive stresses from the same analyses

the strength of an adhesive joint, it is necessary either to apply a failure criterion to the results or to incorporate the failure process within the FE analysis. Failure criteria that have been used include characteristic values of the adhesive stress or strain, fracture mechanics, a limit state approach and a critical bi-material stress intensity. Incorporating the failure within the analyses is a recent development but is potentially much more convenient. Various ways of evolving damage have been considered from simple removal of elements through to zero volume rupture elements.<sup>7</sup>

### References

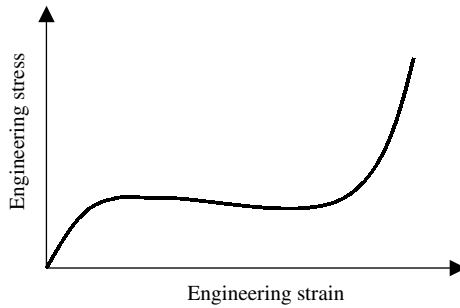
1. M. J. Fagan, *Finite element analysis, Theory and Practice*, Longman, Singapore, 1992.
2. R. D. Cooke, D. S. Malkus and M. E. Plesha, *Concepts and Applications of Finite Element Analysis*, 3rd edn, John Wiley & Sons, 1989.
3. G. P. Anderson, S. J. Bennett and K. L. DE Vries, *Analysis and Testing of Adhesive Bonds*, Academic Press, 1977.
4. J. C. Halpin, *Primer on Composite Materials Analysis*, 2nd edn, Technomic, Lancaster, PA, 1992.
5. R. D. Adams and W. C. Wake, *Structural Adhesive Joints in Engineering*, Elsevier Applied Science Publishers, 1984.
6. O. C. Zienkiewicz and R. L. Taylor, *The Finite Element Method*, Vol. 2, 4th edn, McGraw Hill, 1991.
7. M. Xie and H. Gerstle, *J. Eng. Mech.*, **121**, 1349, (1995).

### Finite element analysis: rubber

M M ABDEL WAHAB

### Hyperelasticity

A general discussion of **Finite element analysis** can be found in another article. This article is specifically concerned with hyperelastic materials. A common hyperelastic material of importance in adhesion studies and polymer technology is rubber. A hyperelastic material is a material that undergoes large strains and displacements with little changes



**Fig. 1.** Stress–strain curve for a hyperelastic material

in volume, that is, nearly incompressible material. A typical stress–strain curve for a hyperelastic material is shown in Fig. 1. Unloading follows the same path as loading, that is, fully reversible deformations. For such a material, there should exist a strain energy density function, from which the stress components can be derived through differentiation with respect to strain components. The stress components,  $S_{ij}$ , are then given by

$$S_{ij} = \frac{\partial W}{\partial \varepsilon_{ij}} \quad [1]$$

where  $W$  is the strain energy function per unit volume and  $\varepsilon_{ij}$  represents the strain components.

The mechanical behaviour of hyperelastic materials is much more complicated than that of classical materials. The material properties may differ significantly under tension, compression or shear loading conditions. Therefore, for a complete set of material data, experimental tests that cover all these modes of deformation should be carried out.

#### *Hyperelastic constitutive material models*

*Isotropic hyperelastic materials:* For this model, the strain energy density function is written in terms of the principal stress invariants<sup>1</sup> ( $I_1, I_2, I_3$ ). Equation 1 becomes

$$S_{ij} = \frac{\partial W(I_1, I_2, I_3)}{\partial \varepsilon_{ij}} = \frac{\partial W}{\partial I_1} \frac{\partial I_1}{\partial \varepsilon_{ij}} + \frac{\partial W}{\partial I_2} \frac{\partial I_2}{\partial \varepsilon_{ij}} + \frac{\partial W}{\partial I_3} \frac{\partial I_3}{\partial \varepsilon_{ij}} \quad [2]$$

*Neo-Hookean material:* This is an extension of the linear elastic Hooke's law to include large deformations. The main difference between the classical Hooke's law and the Neo-Hookean law is that in the latter the shear modulus is a function of the deformations. The strain energy density for the compressible Neo-Hookean model is given by

$$W = C_1(I_2 - 3) + \frac{1}{D_1}(V - 1)^2 \quad [3]$$

where  $C_1$  and  $D_1$  are material constants and  $V$  is the elastic volume ratio that relates the total volume ratio to the thermal volume ratio that is a function of linear thermal expansion strain. The model becomes fully incompressible if  $D_1 = 0$ .

*Mooney–Rivlin material:* Mooney<sup>2</sup> and Rivlin<sup>3</sup> developed a hyperelastic constitutive material model. The strain energy function is written in the form of series expansion of



stress invariants. The simple form of the Mooney–Rivlin model is obtained by considering the first few terms in the polynomial, that is,

$$W = C_0(I_1 - 3) + C_1(I_2 - 3) + \frac{1}{D_1}(V - 1)^2 \quad [4]$$

where  $C_0$  is material constant and again the fully incompressible model is obtained when  $D_1 = 0$ . The Neo-Hookean law is a special case of the Mooney-Rivlin law (by putting  $C_0 = 0$ ). The Mooney–Rivlin model is valid for a wide range of nearly incompressible materials like rubber and some sort of polymer.

*Blatz–Ko material:* This material law was originally developed by Blatz and Ko<sup>4</sup> to model compressible foam-type polyurethane rubbers. The strain energy for the Blatz–Ko model is given by

$$W = \frac{\mu}{2} \left( \frac{I_2}{I_3} + 2\sqrt{I_3} - 5 \right) \quad [5]$$

where  $\mu$  is the shear modulus.

#### Finite element implementation

The problem of compressibility does not appear for the case of plane stress, shell and membrane analyses because the material is free to expand in the thickness direction. Thus, no special treatment of the volumetric behaviour is required for these sorts of analyses and the use of classical finite-element formulation (displacement formulation) is good enough. However, in three-dimensional, plane strain and axisymmetric analyses, the volume of the material cannot be changed under mechanical loads and fully incompressible behaviour should be considered. In such a case, a special modelling technique using hybrid element (mixed formulation) is recommended. The mixed formulation, sometimes called U-P, displacement-pressure, is used to form the element matrices with pressure enforcing the incompressibility conditions. As the hyperelastic behaviour is non-linear (Fig. 1), an iterative FE solution is required. Moreover, because of the expected large deformations, geometric non-linearity should be taken into account during the analysis process. For further reading on this topic, reference<sup>5</sup> is recommended. Powerful softwares that have the capability to model hyperelastic materials are ABAQUS<sup>6</sup> and ANSYS.<sup>7</sup>

#### References

1. L. E. Malvern, *Introduction to the Mechanics of a Continuous Medium*, Prentice-Hall, Englewood Cliffs, NJ, 1969.
2. M. Moony, *J. Appl. Phys.*, Vol. 6, pp. 582–592, 1940.
3. R. S. Rivlin, Forty years of non-linear continuum mechanics, *Proceedings of the IX International Congress on Rheology*, Mexico, pp. 1–29, 1984.
4. P. J. Blatz and W. L. Ko, *Trans. Soc. Rheol.*, **6**, 223–251, (1962).
5. T. Belytschko, E. K. Liu and B. Moran, *Nonlinear Finite Element for Continua and Structures*, John Wiley & Sons, West Sussex, England, 2000.
6. ABAQUS 5.7, Hibbitt, Karlsson & Sorensen, Inc., 1997.
7. ANSYS 5.1, Swanson Analysis Systems, Inc., 1994.

---

**Flame treatment**

---

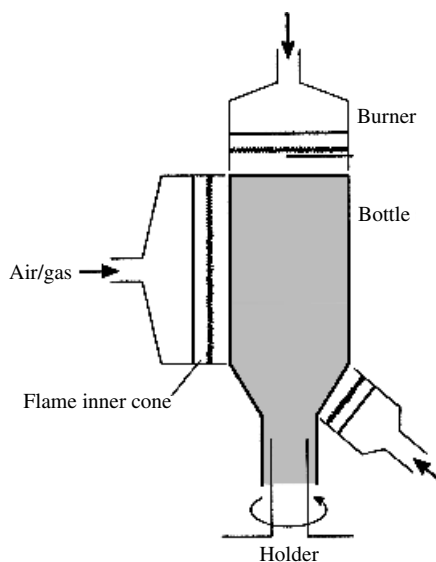
D BRIGGS

Flame treatment is mainly used for pre-treating plastic articles of fairly thick section, such as blow-moulded bottles and thermo-formed tubs. Its early application to polyolefin film treatment was not sustained because of process control difficulties and safety problems; however, these have been overcome in recent times, and flame treatment competes with **Corona discharge treatment** in this area once again.

An attractive feature is the ability to handle complex shapes, such as the bottle illustrated in Fig. 1. Each burner consists of a large number of closely spaced jets, usually in staggered rows. In the case of the bottle, treatment is achieved by bringing it into position on a line, rotating it and then moving the burners into their fixed geometry for a short time ( $<1$  s). Clearly this type of treatment is suited to robotics, and large items such as plastic car bumpers are treated in this way (to achieve good paint adhesion).

The most important variables in the process are the air: gas ratio, the air/gas flow rate, the nature of the gas, the burner-surface separation and the exposure time. The gas used is either mains (mainly methane) or bottled (propane or butane). For optimum treatment, an oxidizing flame should be used, that is, with an excess of oxygen over that required for complete combustion. For a given air: gas ratio, treatment level in a given exposure time increases as the volume of mixture burned increases. It is clearly important that the exposure time is not sufficient for the surface polymer to melt (the flame temperature is  $\sim 2000^\circ\text{C}$ ); in the case of film treatment, the film is treated as it passes over a cooled roll.

**Surface analysis** shows that very high levels of surface oxidation are possible, even under sub-optimal treatment conditions. The mechanism of oxidation is not fully understood. Both thermal and "plasma" radical oxidation are possible.



**Fig. 1.** Schematic diagram of set-up for flame treatment of blow-moulded bottles

*Select References*

- M. Strobel, M. J. Walzak, J. M. Hill, A. Lin, E. Karbasheski and C. S. Lyons, A comparison of gas-phase methods of modifying polymer surfaces, in *Polymer Surface Modification*, K. L. Mittal, Ed., VSP, Utrecht, 1995, Part 3.
- D. M. Brewis and I. Mathieson, Flame treatment of polymers to improve adhesion, in *Adhesion Promotion Techniques*, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, New York, 1999, Chap 6.

---

*FPL etch*

---

D E PACKHAM

There are many references in the literature to this method of surface preparation of aluminium. The name refers to the US Forest Products Laboratory, which published a specification based on etching the metal at *c.* 65 °C in a solution of sodium dichromate and sulphuric acid, sometimes loosely referred to as “chromic acid”. In the United Kingdom, a similar Ministry of Supply Aircraft Process Specification known as DTD 915 has been widely used. Over the years, a number of slightly different solutions (“chromic acid etches”) and procedures have been developed.<sup>1-3</sup> Clearfield gives recipes for six such solutions.<sup>1</sup>

When optimized, these are suitable preparations for both adhesive bonding and painting: their effect is to give a reproducible, oxidized surface on the aluminium. Initial adhesion is generally good, and durability fair, but not as good as with **Anodizing** pre-treatments (see **Durability: fundamentals, Pre-treatment of aluminium**).

The precise nature of the layer formed, and the subsequent adhesion and durability, depend on the composition of the solution used, the time and temperature of etching, rinsing conditions and the particular alloy being treated.<sup>1-3</sup> For example, the fresh solution does not give good results, unless it is artificially “aged” by adding some aluminium;<sup>1</sup> the presence of traces of fluoride can reduce bond durability.<sup>4</sup> Close attention to temperature control is necessary;<sup>3</sup> rinsing procedures can exert a critical effect on bond strength. Optimization of conditions, together with careful control of process variables, are therefore necessary to achieve satisfactory results.

The morphology of the surface has been studied by transmission **Electron microscopy**.<sup>4</sup> Under optimum conditions, it consists of a cell structure with oxide whiskers protruding from the surface.<sup>4</sup> It has been suggested that microscopic interlocking (see **Mechanical theory of adhesion**) appears to be a crucial factor in the adhesion.<sup>4</sup> It may be that the sensitivity to processing conditions, mentioned above, is a result of the production of a morphology with less potential for interlocking.

The use of ferric sulphate as an oxidizing agent in the place of chromates has been developed,<sup>1,3,4</sup> and overcomes some of the disposal problems associated with the toxicity of FPL and similar etching solutions (see **Health and safety**).

Chromic acid etching and other techniques are compared in **Pre-treatment of aluminium**.

---

*References*

1. H. M. Clearfield, D. K. McNamara and G. D. Davis, in *Adhesion and Adhesives*, H. L. Brinson, Ed., *Engineered Materials Handbook*, Vol. 3, ASM Ohio, 1990, p. 259.
2. ASTM D2651, *Annual Book of Standards*, American Society for Testing and Materials, Philadelphia, PA, published annually.
3. G. W. Critchlow and D. M. Brewis, Review of surface pre-treatments for aluminium alloys, *Int. J. Adhes., Adhes.* **16**, 255–275 (1996).
4. G. D. Davis and J. D. Venables, in *Adhesion Science and Engineering- 2, Surfaces, Chemistry and Applications*, Manoj. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 947.

---

*Fractals*

---

D E PACKHAM

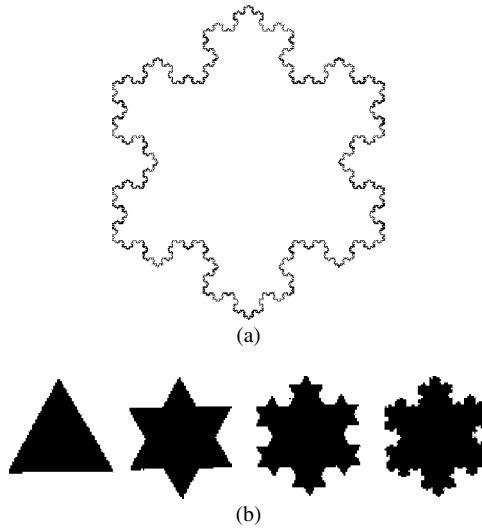
Few, if any, of the practical surfaces of concern in adhesion are smooth. Some knowledge of characterization of the **Roughness of surfaces** is necessary in understanding the theory and practice of adhesion. In recent years, it has been increasingly recognized that many engineering surfaces and many fracture surfaces are fractal in nature. For such surfaces, Euclidean concepts of dimension and of a unique surface area do not apply. In this article, an introduction is given to the nature of fractals. Further aspects are discussed in **Fractals and fractal dimension** and in **Fractals and surface roughness**.

The Euclidean abstractions – mental constructs – of the one-dimensional line, the two-dimensional surface and the three-dimensional solid are so familiar that it is easy to forget that these are idealizations that do not exist in the “real” world. Thus, no one has ever seen or drawn a line – defined as having length, but no thickness – although approximations to lines are very common: there are many on this page. This recognition may help us to come to terms with the unfamiliar nature of fractals, which may have fractional dimensions, such as 1.26186 or 2.58496 (hence the term *fractal*). Fractals too are idealizations, but they arise from concepts somewhat different from those of Euclidean geometry.

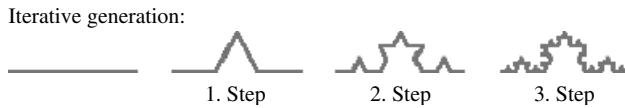
*The triadic Koch curve*

The fractal nature of surfaces is directly relevant to adhesion. However, it is easier to introduce the concept of fractals by first considering a fractal curve. A simple example is the Koch curve.<sup>1–3</sup> Figure 1(a) shows one form of the curve and Fig. 1(b) shows how that form of the curve may be developed from an equilateral triangle. The process for generating any triadic Koch curve consists in dividing a straight line into *three* parts and generating a triangular asperity as shown in step 1 of Fig. 2.<sup>4</sup> Note that the length of the line is now *four-thirds* its original length. This process is repeated *ad infinitum*: the first three steps are shown in Fig. 2. If the process is applied to an equilateral triangle, a closed curve is obtained as represented in Fig. 1.

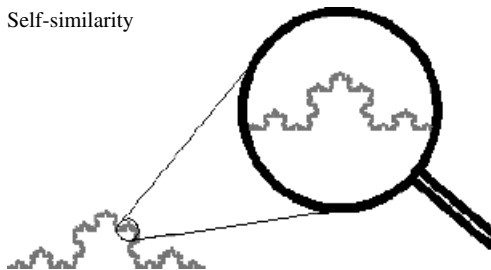
The Koch curve illustrates many features usually shown by fractals. Because the iteration is carried out to infinity generating triangles on straight lines at every stage, the



**Fig. 1.** The triadic Koch curve



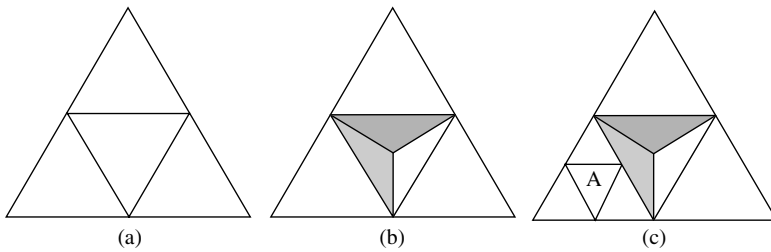
**Fig. 2.** Iterative generation of the triadic Koch curve<sup>4</sup>



**Fig. 3.** Self-similarity in the Koch curve<sup>4</sup>

curve shows similar features at all scales of magnification (Fig. 3). This is known as “self-similarity”. With some fractals, self-similarity is more approximate or perhaps statistical than literal, as shown here.

The curve is too irregular to be described in traditional geometrical language. Although confined within a finite area (see Figure 1), its length can be regarded as infinite. By selecting a measuring “rod” of a particular size, an estimate of the length of the curve could be made. The shorter the rod, the more of the features of the curve it could measure, and the greater would be the length that was recorded.



**Fig. 4.** Generation of a tetrahedral fractal surface. Step 1: (a) sides of equilateral triangle bisected, generating four smaller triangles; (b) regular tetrahedron generated on base of central triangle. (c) Step 2: regular tetrahedra generated in the 6 positions such as base of triangle labelled A

### *Length of a coastline*

The length of a coastline has often been taken as an illustration of a practical (as opposed to theoretical) fractal line. The perimeter of Britain (say), measured from a map in an atlas will be much shorter than that taken from a series of large-scale hiking maps, which reveal much finer detail of the various coves and inlets. With the large-scale map, a much shorter measuring rod is in effect being used. The process can, in principle, be repeated indefinitely. Using a large-scale architects' plan, a smaller rod size would be appropriate; an observer on the ground might use a 12-in. school ruler, or even a magnifying glass allowing a rod size of less than a millimetre. So how long is the coastline of Britain? In terms of fractal geometry, the answer is that it is indeterminate: the length depends on the size of the rod used, the length tending to infinity as the rod size tends to zero.

The situation for a fractal surface is analogous to that for a fractal line. The rod is replaced by a "measuring tile". As magnification increases, more and more surface features are revealed, and so the apparent surface area increases.

### *Fractal surfaces*

A fractal surface analogous to the triadic Koch curve could be generated by taking an equilateral triangle (in the place of the line in Fig. 2), subdividing it into four equilateral triangles, as shown in Fig. 4(a), each of side *one-half* the original and using the central triangle as a base for generation of a regular tetrahedron (Fig. 4(b)). This step has generated *six* new smaller equilateral triangles. Successive iterations repeat this process *ad infinitum*. Thus, the second step involves halving the sides of all six of the smaller equilateral triangles generated in step 1, and generating regular tetrahedra on the central triangle of each. The base of one such tetrahedron is indicated by "A" in Fig. 4(c).

Like the Koch curve, this surface shows self-similarity – similar features irrespective of the scale of magnification. The area of the surface depends on the size of the measuring tile chosen to assess it: the smaller the tile, the more of the features of the surface it could measure, and the greater would be the surface area that was recorded.

A cauliflower provides a mundane example of a fractal surface, and, as was pointed out above, many engineering surfaces are fractal in nature: their surface area tends to infinity as the tile size tends to zero.

### References

1. J. Gleick, *Chaos*, Minerva, 1997.
2. B. B. Mandelbrot, *The Fractal Geometry of Nature*, Freeman, New York, 1983.
3. C. Series, in *The New Scientist Guide to Chaos*, N. Hall, Ed., Penguin, 1992, p. 136.
4. F.-J. Elmer, University of Basel, The Pendulum Lab, <http://monet.physik.unibas.ch/~elmer/pendulum/fractal.htm> 29.7.98

---

## Fractals and fractal dimension

---

D E PACKHAM

The one-dimensional lines, two-dimensional surfaces and three-dimensional solids of Euclidean geometry are concepts so familiar to us that we tend to regard them as “common sense”. Fractals involve less familiar concepts, such as curves between two points, which have infinite length, and surfaces with infinite surface area. Fractals can be characterized by a dimension, but the dimension is fractional. For example, the triadic Koch curve (see **Fractals** Fig. 1) has a dimension of approximately 1.26186 and the surface with an infinite succession of regular tetrahedral asperities (ibid. Figure 4), a dimension of approximately 2.58496. In this article, the meaning and calculation of fractal dimension are discussed. Texts on the mathematics of fractals introduce different kinds of fractal dimension, which are beyond the scope of this article.<sup>1,2</sup> The dimension discussed here is strictly the self-similarity dimension. Further aspects of fractal dimensions are considered in **Fractals and surface roughness**.

### Fractal dimension

Suppose we apply a reduction factor  $s$ , say  $1/3$ , to a line, as shown in Fig. 1 below, we produce 3 smaller lines – “pieces” represented by  $a$ ; similarly, for a reduction factor of  $1/6$  or  $1/123$ , Table 1. Applying these reduction factors  $s$  to the side of a square, we generate  $6^2$  and  $123^2$  pieces (new squares) respectively. These values are summarized in Table 1. Similarly, it is easily seen that applying a reduction factor of  $1/3$  to the side of a cube generates  $3^3$  pieces (new cubes). The reduction factor,  $s$ , and the number of pieces generated,  $a$ , can be seen to be related to the dimension  $D$  of the of the object by

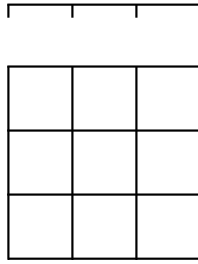
$$a = 1/s^D \tag{1}$$

$$\therefore D = \log a / \log(1/s) \tag{2}$$

Equation 2 can be used to evaluate the dimension of a fractal.

### Koch curve

Consider a triadic Koch curve (Figs. 1 and 2 in **Fractals**). At each step, the line is reduced by a factor of  $1/3$  and the length increased by  $4/3$ . After  $k$  steps, the length has increased



**Fig. 1.** Application of a reduction factor of  $1/3$  to a line and to the side of a square

*Table 1.* Summary of effect of applying various reduction factors to different objects

Object	Reduction factor $s$	Number of pieces $a$	Dimension $D$
Line	$1/3$	3	1
	$1/6$	6	1
	$1/123$	123	1
Square	$1/3$	$3^2 = 9$	2
	$1/6$	$6^2 = 36$	2
	$1/123$	$123^2 = 15,129$	2
Cube	$1/3$	$3^3 = 27$	3
	$1/6$	$6^3 = 216$	3
	$1/123$	$123^3 = 1,860,867$	3
Koch curve	$1/3$	4	$\log 4/\log 3 = 1.262$
	$1/9$	16	1.262
	$1/3^k$	$4^k$	1.262
Tetrahedral surface	$1/2$	6	$\log 6/\log 2 = 2.585$
	$1/4$	36	2.585
	$1/2^k$	$6^k$	2.585

by a factor  $(4/3)^k$  and the side reduced by a factor  $1/3^k$  (Table 2). The fractal dimension can be calculated as follows.

At step  $k$ , the number of pieces produced (here sides) is  $a$ .

$$a = \text{Total length/length of side} = [(4/3)^k l_0]/[l_0/3^k] = 4^k \quad [3]$$

$$\therefore k = \log a / \log 4 \quad [4]$$

At this stage, the reduction factor is

$$s = 1/3^k \quad [5]$$

$$\therefore \log(1/s) = k \log 3 \quad [6]$$

Eliminating  $k$  between Eqns. 4 and 6 gives

$$\log(1/s) = \log a \cdot \log 3 / \log 4 \quad [7]$$



Table 2. Generation of a Koch curve

Step:	0	1	2	3	$k$
Side	$l_0$	$l_0/3$	$l_0/3^2$	$l_0/3^3$	$l_0/3^k$
Rod size $\lambda$	$l_0/3$	$l_0/3$	$l_0/3^2$	$l_0/3^3$	$l_0/3^k$
Total length $L$	$l_0$	$4l_0/3$	$(4/3)^2 l_0$	$(4/3)^3 l_0$	$(4/3)^k l_0$

Thus, the fractal dimension of the Koch curve,

$$D = \log a / \log(1/s) = \log 4 / \log 3 = 1.2618 \tag{8}$$

*Tetrahedral surface*

The tetrahedral fractal surface (Fig. 4 in **Fractals**) can be treated analogously. At each step, the line is reduced by a factor of 1/2 and the area increased by 6/4. After  $k$  steps, the area has increased by a factor  $(6/4)^k$  and the tile size (area of triangle) reduced by a factor  $1/4^k$  (Table 3). The fractal dimension can be calculated as follows.

At step  $k$ , the number of pieces produced (here tiles) is  $a$ .

$$a = \text{Total area/area of tile} = [(6/4)^k A_0] / [A_0/4^k] = 6^k \tag{9}$$

$$\therefore k = \log a / \log 6 \tag{10}$$

At this stage, the reduction factor is

$$s = 1/2^k \tag{11}$$

$$\therefore \log(1/s) = k \log 2 \tag{12}$$

Eliminating  $k$  between 10 and 12 gives

$$\log(1/s) = \log a \cdot \log 2 / \log 6 \tag{13}$$

Thus the fractal dimension of the surface,

$$D = \log a / \log(1/s) = \log 6 / \log 2 = 2.5850 \tag{14}$$

Perhaps less laboriously, the dimension of such fractals can be seen directly from Eqn. 2. At each step of generation of the Koch curve, application of a reduction factor

Table 3. Generation of a tetrahedral fractal surface

Step:	0	1	2	3	$k$
Side	$l_0$	$l_0/2$	$l_0/2^2$	$l_0/2^3$	$l_0/2^k$
Tile area $\sigma$	$A_0/4$	$A_0/4$	$A_0/4^2$	$A_0/4^3$	$A_0/4^k$
Total area $A$	$A_0$	$6A_0/4$	$(6/4)^2 A_0$	$(6/4)^3 A_0$	$(6/4)^k A_0$

of  $1/3$  produces 4 new pieces so directly.

$$D = \log 4 / \log 3 = 1.2618$$

At each step for the tetrahedral fractal, the reduction factor of  $1/2$  leads to the generation of 6 new pieces, so

$$D = \log 6 / \log 2 = 2.5850$$

### Conclusion

Fractal curves generally have a dimension,  $D$ , between 1 and 2, fractal surfaces between 2 and 3. The value of  $D$  can be worked out knowing the mathematical procedure by which the fractal is generated. It is unlikely that such a procedure will be known for a fractal observed in nature. The evaluation of fractal dimension from experimental measurements is discussed in **Fractals and surface roughness**.

### References

1. H.-O. Peitgen, H. Jürgens and D. Saupe, *Chaos and Fractals, New Frontiers of Science*, Springer-Verlag, 1992.
2. K. Falconer, *Fractal Geometry, Mathematical Foundations and Applications*, John Wiley & Sons, 2000.

---

## *Fractals and surface roughness*

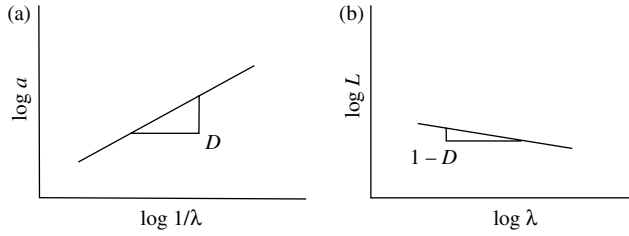
---

D E PACKHAM

**Fractals** differ fundamentally from the figures encountered in Euclidean geometry. They may be characterized by a dimension  $D$ , which for fractal curves is generally between 1 and 2, and for fractal surfaces between 2 and 3. In **Fractals and fractal dimension**, ways are presented for evaluating  $D$  for a self-similar fractal generated by repetition of an infinite number of simple mathematical operations. If an apparently fractal curve (such as the coastline of Britain) or surface (such as a fracture surface) is observed in nature, this method clearly cannot be used. What may be possible, in the first instance, is to record the total lengths of the curve measured with a series of different length measuring rods, and in the second instance, to measure the surface areas with a series of different area tiles (perhaps probe molecules). Fractal dimension can be calculated from these results.

### *Fractal curves<sup>1</sup>*

The fractal curve is measured over a range of magnifications, in effect using a series of measuring rods of different length,  $\lambda$ . A  $\log/\log$  plot of the number of rods ( $a$ ) to measure the curve versus reciprocal of rod length will be a straight line of gradient  $D$  (Fig. 1a). This can be justified by reference to the definition of dimension given in **Fractals and**



**Fig. 1.** Fractal dimension,  $D$ , for curves. Bilogarithmic plots of (a) number of rods  $a$  versus reciprocal of rod size  $\lambda$ ; (b) total measured length versus rod size

**fractal dimension** in Eqn. 2, remembering that the rod size is proportional to the reduction factor ( $s$ ). An alternative log/log plot of total measured length ( $L$ ) versus rod size will have a gradient of  $1 - D$  (Fig. 1b). This can easily be seen for the Koch curve discussed in **Fractals and fractal dimension**. The total length  $L$  and rod length  $\lambda$  are given by (Table 2 *ibid.* where  $k$  and  $l_0$  are explained):

$$L = (4/3)^k l_0 \tag{1}$$

$$\lambda = l_0/3^k \tag{2}$$

Taking logs and eliminating  $k$  between Eqn. 1 and 2 gives

$$\log L/l_0 = -(1/\log 3) \cdot \log(4/3) \cdot \log \lambda/l_0 \tag{3}$$

$$\therefore \log L/l_0 = (1 - D) \cdot \log \lambda/l_0 \tag{4}$$

remembering that  $D$  for this fractal is  $\log 4/\log 3$  (Eqn. 8 *ibid.*).

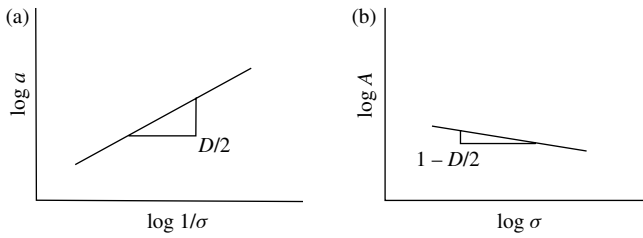
*Fractal surfaces*

Similarly, for fractal surfaces,<sup>1,2</sup> the area is measured using a series of probes (tiles) of different area. Here, the tile size,  $\sigma$  (area), is proportional to the *square* of the reduction factor:

$$\sigma \propto s^2 \tag{5}$$

*Table 1.* “Roughness factor” calculated for a fractal surface, according to the fractal dimension  $D$  and probe area  $\sigma$

$D$	Roughness factor for values of $\sigma/A_0$ as indicated:			
	$\sigma/A_0 = 10^{-4}$	$10^{-8}$	$10^{-12}$	$10^{-18}$
2	1	1	1	1
2.1	1.6	2.5	4	7.9
2.5	10	100	1000	32,000
2.8	40	1600	63,000	16,000,000



**Fig. 2.** Fractal dimension,  $D$ , for surfaces. Bilogarithmic plots of (a) number of tiles  $a$  versus reciprocal of tile size  $\sigma$ ; (b) total measured area  $A$  versus tile size

Hence, the gradient of a log/log plot of number of tiles to measure the surface versus reciprocal of tile size will be  $D/2$  (Fig. 2a):

$$\log a / \log(1/\sigma) \propto \log a / \log(1/s)^2 \propto \log a / 2 \log(1/s) = D/2 \quad [6]$$

An alternative log/log plot of total measured area versus tile size will have a gradient of  $1 - D/2$  (Fig. 2b). This can easily be seen for the tetrahedral fractal (total area  $A$  and tile size  $\sigma$ , see Table 3 in **Fractals and fractal dimension**):

$$A = (6/4)^k A_0 \quad [7]$$

$$\sigma = A_0/4^k \quad [8]$$

Taking logs and eliminating  $k$  between Eqn. 7 and 8 gives

$$\log A/A_0 = -(1/\log 4) \cdot \log(6/4) \cdot \log \sigma/A_0 \quad [9]$$

$$\therefore \log A/A_0 = (1 - D/2) \cdot \log \sigma/A_0 \quad [10]$$

remembering that  $D$  for this fractal is  $\log 6/\log 2$  (Eqn. 14 *ibid.*).

### *Roughness factor for a fractal surface*

For over sixty years, it has been customary to use the concept of the roughness factor,  $r$ , to describe **Roughness of surfaces**.<sup>3</sup> The roughness factor is defined by

$$r = A/A_0 \quad [11]$$

where  $A$  is the “true” surface area,  $A_0$  the nominal area, that is, the area of a plane surface. The roughness factor may be calculated for a fractal surface: its value varies according to the probe size and the fractal dimension.

From Eqn. 10 or Fig. 2(b),

$$\log A/A_0 = (1 - D/2) \cdot \log \sigma/A_0 \quad [10]$$

$$\text{so, } r = A/A_0 = (\sigma/A_0)^{(1-D/2)} \quad [12]$$

It is of interest to use Eqn. 12 to compute values of  $r$  for some trial values of  $D$  and  $\sigma$ . This is done in Table 1. In order to map the surface features even crudely, the probe needs to be small. It can be seen that high apparent roughness factors are readily obtained once the fractal dimension exceeds two, its value for an ideal plane.

Some examples of fractals within the context of adhesion are discussed in Ref. [3].

### References

1. A. Harrison, *Fractals in Chemistry*, Oxford University Press, 1995, p. 6.
2. D. Farin and D. Avnir in *Fractal Approach to Heterogeneous Chemistry*, D. Avnir, Ed., Wiley, 1989, p. 272.
3. D. E. Packham, in *Handbook of Adhesives Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Marcel Dekker, 2003.

---

## Fracture mechanics

---

A J KINLOCH\*

### Introduction

Adhesive joints usually fail by the initiation and propagation of flaws and, since the basic tenet of continuum fracture mechanics is that the strength of most real solids is governed by the presence of flaws, the application of such theories to adhesive joint failure has received considerable attention. The reader is referred to reviews for detailed discussions of the general principles of fracture mechanics and to on the application of fracture mechanics to the failure of adhesive joints<sup>1-5</sup>.

The main aims of the various fracture-mechanics theories are to analyse mathematically the loads at which the flaws propagate and describe the manner in which they grow. The source of naturally occurring flaws, sometimes referred to as “intrinsic flaws” may be voids, cracks, dirt particles, additive particles, inhomogeneities in the adhesive, and so on, which may be initially present at a critical size or develop during the fracture test. Fracture mechanics has proved to be particularly useful for aspects such as characterizing the toughness of adhesives, identifying mechanisms of failure and estimating the service life of “damaged” structures, the damage being in the form of cracks, air-filled voids, debonds, and so on, and having arisen, for example, from environmental attack (see **Durability: fundamentals, Weathering of adhesive joints**), fatigue loading, sub-critical impact loads (see **Impact resistance** and **Durability: fatigue**). Two main, interrelated conditions for fracture have been proposed.

### Energy-balance approach

The energy criterion arises from Griffith’s work, which supposes that fracture occurs when sufficient energy is released (from the stress field) by growth of the crack to supply the energy requirements of the new fracture surfaces. The energy released comes from stored

elastic or potential energy of the loading system and can, in principle, be calculated for any type of test-piece. This approach therefore yields a measure of the energy required to extend a crack over unit area and this is termed *the fracture energy or critical energy release rate* and is denoted by  $G_c$ . It is important to note that the value of  $G_c$  cannot usually be directly equated to that needed solely to rupture molecular bonds, since the value of  $G_c$  also encompasses the dissipative-energy losses incurred around the crack tip, that is, viscoelastic- and plastic-energy losses in the crack-tip damage zone (see **Peel tests**). In the case of bonded structures exhibiting bulk linear-elastic behaviour, the fracture criterion may be written as

$$G_c = \frac{F_c^2}{2b} \frac{dC}{da}$$

where  $F_c$  is the load at the onset of crack propagation,  $b$  is the specimen thickness,  $a$  is the crack or debond length and  $C$  is the compliance of the structure and is given by displacement/load. This equation is the foundation of many linear-elastic fracture-mechanics (LEFM) calculations of  $G_c$ , since if  $C$  is determined as a function of  $a$ , either experimentally or theoretically by an analytical or numerical technique, then  $dC/da$  may be found. If the bonded structure does not exhibit bulk linear-elastic behaviour, then the fracture energy approach is still valid, but a different form of equation to that given above is needed to describe the value of  $G_c$  in terms of the loads and displacements applied to the joint.

### *Stress-intensity factor approach*

The second approach comes from the work of Irwin, who found that the stress field around a sharp crack in a linear-elastic material could be uniquely defined by a parameter named the stress-intensity factor,  $K$ , and stated that fracture occurs when the value of  $K$  exceeds some critical value,  $K_c$ . Thus,  $K$  is a stress-field parameter independent of the material, whereas  $K_c$ , often referred to as the fracture toughness, is a measure of a material property. However, this approach becomes far more difficult to employ when the crack is either in a thin adhesive layer or is located at the adhesive–substrate interface, and the reader is referred to the references for further details on this very complex issue.

See also articles on **Fracture-mechanics test specimens**, **Blister test**, **Peel tests**, **adhesion – fundamental and practical**.

### *References*

1. J. G. Williams, *Fracture Mechanics of Polymers*, Ellis Horwood, Chichester, 1984.
2. T. L. Anderson, *Fracture Mechanics: Fundamentals and Applications*, 2nd edn, CRC Press, 1994.
3. K. M. Liechti, in *Adhesion Science and Engineering-1, The Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 2002, p. 45.
4. R. J. Sanford, *Principles of Fracture Mechanics*, Prentice Hall, 2003.
5. D. R. Moore Ed., *Application of Fracture Mechanics to Polymers, Adhesives and Composites*, Elsevier Science, 2003.

---

## Fracture mechanics test specimens

---

A J KINLOCH\*

### Introduction

A basic aim of **Fracture mechanics** is to provide a parameter for characterizing crack growth that is independent of test geometry. Therefore, in order to investigate this requirement experimentally, a wide range of different geometries have been developed in order to ascertain values of the various fracture parameters under modes II (in-plane shear) and III (anti-plane shear), as well as the more usual mode I (cleavage, or tensile, opening) case. (Although it should be noted that when a crack is propagating along a bi-material interface, the basic meaning of mode I, mode II and mode III is rather different; see Ref. [1] for a discussion on this aspect.) The reader is referred to several papers<sup>1,2</sup> for further details and to a separate article on the **Blister test** specimen.

### Flexible joints

The energy-balance approach is generally the most applicable to flexible joints since, away from the crack tip, the adhesive or substrates may not exhibit linear-elastic behaviour and so the stress-intensity factor approach is invalid. The most common test methods are shown in Fig. 1.

*Peel test* Assuming the strain in the tab is negligible (e.g. if (1) the peel forces are very low or (2) a fabric- or plastic-backed rubbery adhesive or a relatively thick metallic substrate is the peeling member) and plastic bending of the tab does not occur, then adhesive fracture energy (critical strain energy release rate) is given by

$$G_c = P(1 - \cos \alpha)$$

where  $P$  is the peel force per unit width, commonly termed the peel strength or peel energy, and  $\alpha$  is the peel angle. This is further discussed in **Peel tests** (see Fig. 1a).

*Simple-extension test-piece* Adhesive fracture energy is given by

$$G_c = (\pi/\lambda_c^{1/2})aU_{dc}$$

where  $\lambda_c$  is the extension ratio in the rubber sheet,  $a$  the crack length and  $U_{dc}$  the strain energy density in the rubber sheet at the onset of crack growth (see Fig. 1b).

*Pure-shear test specimen*  $G_c$  may be expressed as (see Fig. 1c)

$$G_c = h_a U_{dc}$$

### Rigid joints

A large number of test specimens have been designed to determine the crack growth behaviour of structural adhesive joints and some of the most common designs are shown

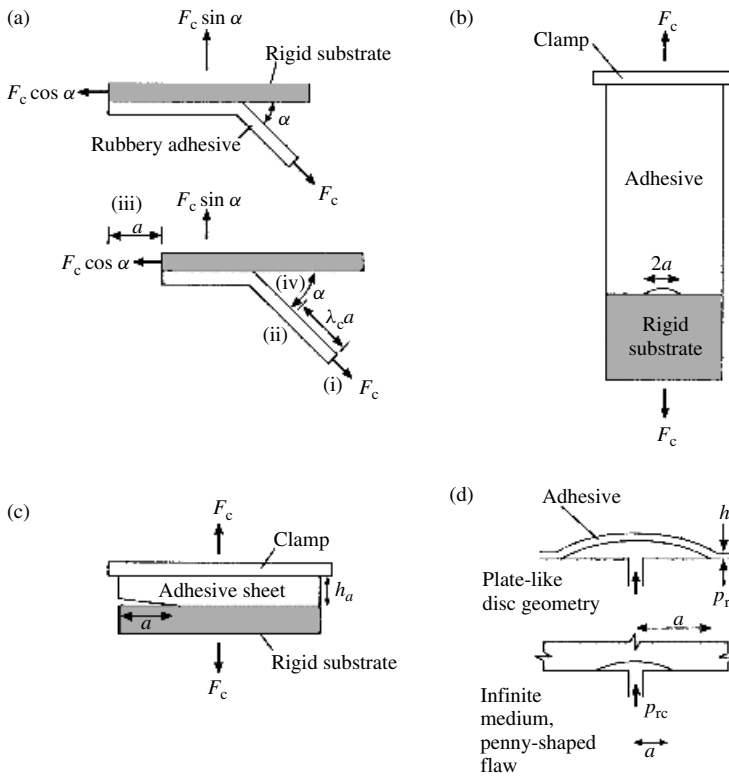


Fig. 1. Common fracture mechanics test methods

in Fig. 2. Expressions for the adhesive fracture energy  $G_c$  are given below, but it should be noted that the value of  $dC/da$  can always be determined experimentally as a function of crack length and, for linear-elastic joints, such values may then be used together with the equation stated in the article on **Fracture mechanics** in order to ascertain the value of  $G_c$ . If the stress-intensity factor at fracture is required, then either the geometry factor must be ascertained by analytical or numerical methods or it must be deduced from the value of  $G_c$ . In the latter case, it is important to use the correct modulus value. For a crack propagating in the adhesive layer, then the value of the adhesive's modulus should be used. However, when the crack propagates at, or very close to, the interface, the problem becomes complex and the reader is referred to Ref [1] for further details.

*Double cantilever beam* This gives a mode I failure when the crack is in the adhesive layer (see Fig. 2a). The value of  $dC/da$  is not constant, and under a constant load, the value of  $G_I$  increases as the crack gets longer. It is used in ASTM D 3433 specification. For linear-elastic behaviour and thin adhesive layers, the value of  $dC/da$  may be expressed analytically by

$$\frac{dC}{da} = \frac{8}{E_s b} \left| \frac{3a^2}{d^3} + \frac{1}{d} \right|$$

where  $E_s$  is the modulus of the substrate material.



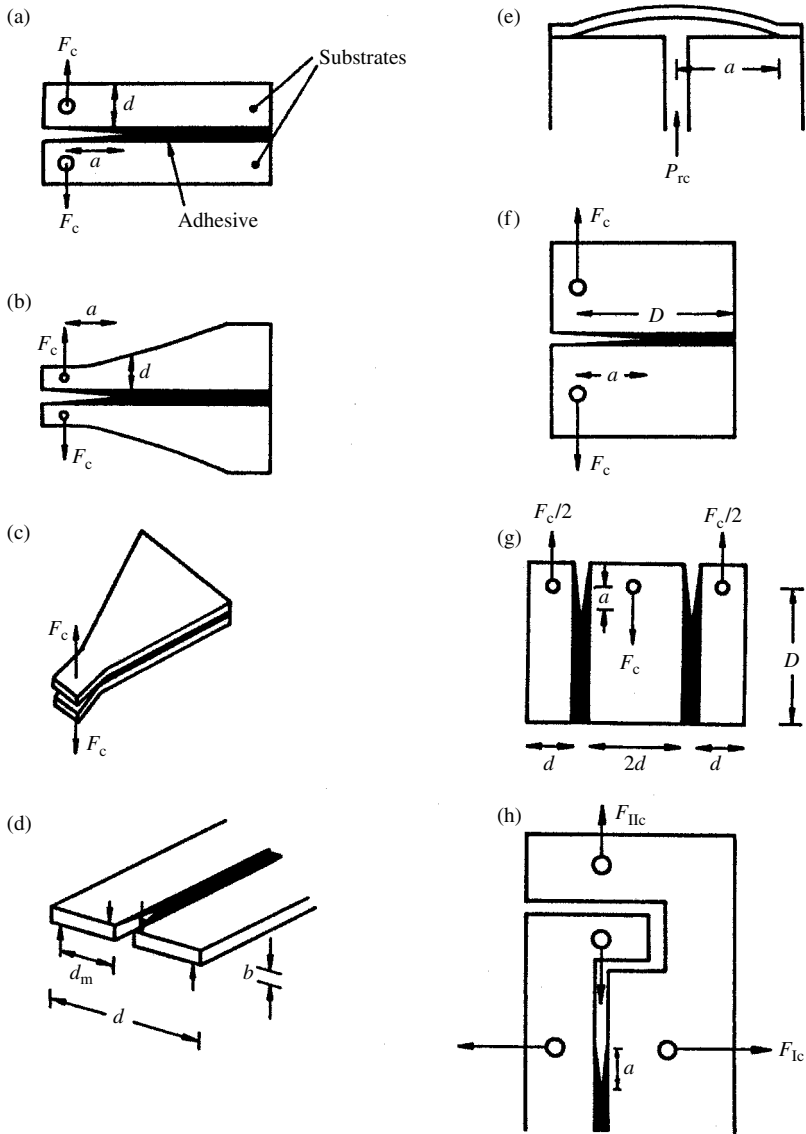


Fig. 2. Test specimen designs for determining crack growth behaviour

*Tapered double cantilever beam* This is again mode I, but the value of  $dC/da$  can be made constant by tapering of the arms of the specimen (see Fig. 2b). Thus,  $G_I$  is independent of crack length and this design is well suited to tests where the value of  $a$  is difficult to measure, for example, environmental tests (see **Durability: fundamentals**) and dynamic fatigue tests. This is also used in ASTM D 3433. The value of  $G_{Ic}$  is given by

$$G_{Ic} = \frac{(4F_c^2 m)}{E_s b^2}$$

where

$$m = \frac{3a^2}{d^3} + \frac{1}{d}$$

where  $m$  is the geometry factor and  $E_s$  is the modulus of the substrate.

*Width-tapered beam* The value of  $dC/da$  is now made constant because of a variation in width with crack length, rather than the beam height – this is very useful when using fibre-composite substrates (see Fig. 2c).

*Double-torsion* The value of  $dC/da$  is again constant and the force may be applied by a simple compression loading jig (see Fig. 2d).

*Blister test specimen* See the **Blister test** article (see Fig. 2e).

*Compact tension and compact shear* The former is a mode I specimen while the latter gives mode II (see Fig. 2f) and (see Fig. 2g).

*Independently loaded mixed-mode* Cleavage and shear loads can be applied independently to produce either mode I or mode II conditions, or a combination of both (see Fig. 2h).

## References

1. A. J. Kinloch, *Adhesion and Adhesives, Science and Technology*, Chapman and Hall, London, 1987.
2. B. R. K. Blackman and A. J. Kinloch, Fracture tests for structural adhesive joints, in *Fracture Mechanics Testing Methods for Polymers, Adhesives and Composites*, A. Pavan, D. R. Moore and J. G. Williams, Eds., Elsevier Science, Amsterdam, 2001, p. 225.

---

## Friction – adhesion aspects

---

A D ROBERTS\*

The two basic laws of friction have been known for a long time: the frictional resistance is proportional to the applied load and it is independent of the area of the sliding surfaces. Coulomb (1781) considered the possibility that friction might be due to molecular adhesion between the surfaces, but rejected the idea because if this were so the friction should be proportional to the area of the sliding bodies, whereas it was found to be independent of it. Nowadays, and especially after the classic work of Bowden and Tabor, we accept that adhesion plays a role in friction, along with other factors such as ploughing and hysteresis. Thus, in general, the frictional force involves one component associated with overcoming the adhesion between the surfaces and another related to bulk deformation such as ploughing and hysteresis. The balance between the two depends on the materials involved and the conditions of the experiment. Had Coulomb known about rubber friction, he might have taken the adhesion idea more seriously because its friction is manifestly related to the area of contact.

This article describes the adhesion component of friction by reference to rubber, an essential point being what is the real area of contact between solids when placed together. Experiments show that surfaces contain hills and valleys, which are large compared with molecular dimensions (see **Roughness of surfaces**). The majority of solids are supported on the summits of the highest hills, so that the area of intimate contact is very small. Rubber is exceptional in that, being relatively soft, it can drape over the hilltops and, with enough applied load, begin to fill the valleys so that the real area of contact begins to approach the geometric area of the sliding bodies. The use of optically smooth surfaces minimizes the micro-irregularities and makes possible investigations of how adhesion relates to friction.

### *Schallamach waves*

If an optically smooth-surfaced rubber sphere is made to slide over dry plate glass, wrinkles in the rubber surface can be seen rapidly moving across the contact zone. These have been described by Schallamach as “waves of detachment”. The rubber is in intimate contact between the waves and for this particular situation it is possible to relate the sliding friction to the interface adhesion through an expression involving a rate-dependent peel energy (see **Peel tests**). As a wave progresses across the contact region, energy  $\Gamma_p$  is required to peel rubber from the glass. Neglecting subsurface energy dissipation, then in steady-state sliding at a speed  $V$ , the frictional stress is given<sup>1</sup> by

$$F = \Gamma_p \omega / \gamma V$$

where the waves move with a speed  $\omega$  and are spaced apart by a distance  $\lambda$ . Experiments suggest this expression is accurate to about 10% over the speed range for which the waves propagate.

Waves of detachment have also been found for wet contact. In water, there is much less adhesion. The waves transport water within them through the contact zone rather than air as in dry contact. About half the wet friction can be accounted for using the above expression. The waves also occur when rubber slides on sufficiently cold ice. These observations suggest that the waves may arise for a variety of conditions and may be relevant to the performance of rubber articles possessing a smooth surface.

### *Significance of area of contact*

The friction coefficient of a reasonably smooth spherical rubber slider on a flat track can be related via the contact area to operating parameters because the geometric and real contact area are similar. If the contact area is given as a function of the normal load  $W$  by the classical theory of Hertz, and if the frictional force is proportional to this area of contact, then the friction coefficient can be written as

$$\mu = \pi \tau (9R/16E)^{2/3} W^{-1/3}$$

where  $R$  is the slider radius,  $\tau$  the interfacial shear strength and  $E$  Young’s modulus of the rubber. Knowledge of the interfacial shear strength is needed, and this will depend

upon factors such as whether surfaces are clean and dry (i.e. high adhesion), or are contaminated by dust or lubricated (low adhesion). Model experiments suggest<sup>1</sup> that friction is proportional to the Hertzian stress parameter  $R^{2/3} W^{-1/3}$  so that the above expression can be used to estimate the friction coefficient to a reasonable approximation.

With increasing surface roughness, the friction coefficient becomes less sensitive to load, and the absolute level of friction declines. No satisfactory analysis exists for the “adhesive” friction of such surfaces. The rougher a surface, the more overt the viscoelastic response of the rubber (see **Viscoelasticity**). In the absence of adhesion, the friction coefficient can depend upon load raised to a positive index due to ploughing hysteresis.

**Atomic force microscopy** provides some information on the friction of surfaces.

Friction plays a part in **Powder adhesion**.

Further information may be found in recent review articles<sup>2–4</sup>.

### References

1. A. D. Roberts Ed., *Natural Rubber Science and Technology*, Oxford University Press, Oxford, 1988.
2. R. M. Overney, *Trends Polym. Sci.* **3**(11), 359–364 (1995).
3. R. A. L. Rorrer, *Rubber Chem. Technol.* **73**(3), 486–503 (2000).
4. B. J. Briscoe and S. K. Sinha, *Materialwiss Werkst* **34**(10–11), 989–1002 (2003).

# G

---

## *Glass transition temperature*

---

D A TOD

In general, polymers are either completely amorphous or have an amorphous phase. These materials are hard, rigid glasses below a temperature known as the glass transition temperature or  $T_g$ ; above this temperature, amorphous polymers are rubbers – soft and flexible. Adhesives share with other polymers the phenomena associated with the glass transition temperature. Some, such as epoxides and acrylics (see **Epoxide adhesives, Acrylic adhesives**), are glassy at room temperature and others (e.g. **Pressure-sensitive adhesives**) are rubbery. All may pass through the glass transition when in use, and this is likely to have a dramatic effect on their properties and performance. For example, the elastic modulus of a polymer above the  $T_g$  may be a factor of over 1000 lower when compared to the modulus below the  $T_g$ .

Crystalline polymers will start to crystallize above the  $T_g$ , and if there is sufficient crystallization, this can suppress the dramatic changes in modulus as exhibited by amorphous polymers. Several other key physical properties change in the region of the  $T_g$ ; these include the coefficient of thermal expansion, specific heat capacity, refractive index and mechanical damping. The glass transition temperature is very dependent upon the structure of the polymer. Bulky side groups act to increase the  $T_g$  of a polymer, whereas hydrocarbon straight chain rubbers have low transitions. The glass transition temperature is sometimes compared with a second-order transition as it is the derivatives of a property such as volume, which changes with temperature unlike melting, which is a first-order transition where the property itself changes dramatically.<sup>1,2</sup>

Several variables affect the value of the  $T_g$ ; two of these are external pressure and internal constraints. The application of pressure will cause the  $T_g$  of a polymeric system to increase at an approximate rate of 15–35 °C kbar<sup>-1</sup>. Internal constraints such as higher filler or fibre loadings will also act to inhibit molecular motion and therefore increase the  $T_g$  of the material.

### *Methods of measurement*

It is important to appreciate the limits of practical measurement of the  $T_g$ ; a number of different experimental techniques can be used. Perhaps the commonest are dynamic mechanical spectrometry<sup>3,4</sup> and differential scanning calorimetry (see **Thermal analysis**). In the former, the mechanical response of the material is measured as a function of temperature and in the latter the heat capacity of the sample is measured. Although these different systems give similar trends, they will not give exact agreement in the absolute value of the  $T_g$ . Within each of these ranges of techniques, there are a number of different ways of defining  $T_g$ . In the dynamic mechanical tests, the peak in the loss modulus is sometimes used or the peak in the loss angle  $\tan \delta$  (see **Viscoelasticity**). A further method is to take the point of inflection of the elastic modulus–temperature curve in the glassy and transition regions and to define the  $T_g$  at this point. An example of a dynamic mechanical test upon an epoxy adhesive is shown in the article **Testing of adhesives**. The calculations of the  $T_g$  from differential scanning calorimetry can be equally difficult.

Several aspects of polymer structure act to compound these differences in measured value for  $T_g$ . Normally, the molecules in a polymer sample do not have a unique molecular weight, but there is a distribution of molecular weights and a range of different local molecular environments of chain segments. A consequence is that there is a range of values of  $T_g$  and this produces a broad peak in the properties measured. A second fundamental effect is that the  $T_g$  is sensitive to the rate at which the measurement is made. If the timescale of the measurement is long, then the apparent  $T_g$  will be lower than if the measurement were made at a very short timescale. A rough rule is that the apparent  $T_g$  will increase by a value of 3–7 °C for a decade rate of increase in test frequency.

The method of measurement of  $T_g$  is often a matter of personal choice or of available equipment. The use to which values are to be used may also influence the choice of test method. If the  $T_g$  is to be used to determine the upper operating temperature of an adhesive, then a mechanical method of measurement would be most appropriate. However, to be of most use to other workers, the exact experimental details used in determining the  $T_g$  must be quoted.

### *Effect of molecular structure*

If a polymer has a stiff backbone and bulky side groups, its glass transition will be higher than that of a linear polymer with a flexible main chain. The rigidity of the total structure will mean that high temperatures will be needed to enable molecular motion to occur. If there is a high degree of attractive forces between adjacent chains and side groups, this will also result in a high  $T_g$ . The molecular weight of the polymer will influence the  $T_g$  in a similar way: for a given polymer, a higher  $T_g$  will be exhibited by a sample of higher molecular weight. The degree of cure of a thermosetting polymer will have a major effect upon the  $T_g$ . The higher the degree of cross-linking, the higher the  $T_g$ . When **Epoxy adhesives** cross-link, there is a slight increase in density, which produces significant stresses in coatings and adhesive layers where contraction is restricted. These stresses are proportional to the temperature difference between the glass transition temperature and service temperature.

### *Effect of moisture*

All organic polymers absorb some moisture and this can act to plasticize the material.<sup>5</sup> This plasticization involves a lowering of the  $T_g$ . A useful rule of thumb that can be applied to adhesive systems is that a 1% absorption of water equates to a drop of 20 °C in the  $T_g$ . A problem exists with ambient curing structural adhesives as their transitions are not much higher than the ambient temperatures in which the adhesives are used. In time, an adhesive can absorb sufficient moisture so that its  $T_g$  is depressed and the adhesive changes from being rigid to rubber-like at its operating temperatures. Once a material is above its  $T_g$ , then it will absorb more moisture at a faster rate than it does at the lower temperatures. In adhesive joints, the effect of plasticization can be complicated. The simple plasticization of the adhesive reduces its effective strength. Moisture can also act to blunt cracks and can potentially improve the apparent durability of a joint. However, as moisture diffuses into the joint, it may attack the adhesive substrate interface, causing premature adhesive failure rather than cohesive failure in the bulk (see **Durability – fundamentals, Underwater adhesives**).

The  $T_g$  is very important in the tack of adhesive tapes. As the temperature of test is lowered, the modulus of the adhesive increases together with the viscosity. The wettability of the adhesive is reduced and the degree of **Tack** is lowered. This loss in tack is associated closely with the  $T_g$  but occurs at a higher temperature.

Plasticizers may be added deliberately to an adhesive composition to lower its  $T_g$ . This will convert a rigid material to a soft flexible system. There are many reasons to do this but often it is to match the modulus of the adhesive to the substrate being bonded. It can be shown that flexible adhesives produce joints having higher short-term strengths and fracture toughness compared to rigid adhesives.<sup>6</sup>

### *References*

1. R. N. Howard, in *Molecular Behaviour and the Development of Polymeric Materials*, A. Ledwith and A. M. North, Eds., Chapman and Hall, 1974, p. 404.
2. G. B. McKenna, in *Comprehensive Polymer Science*, Vol. 2, G. Allen and J. C. Berrington, Eds., Pergamon, Oxford, 1989, p. 311.
3. T. Murayama, *Dynamic Mechanical Analysis of Polymeric Materials*, Elsevier, Amsterdam, 1978.
4. L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1994.
5. W. W. Wright, *Composites*, **12**, 201 (1981).
6. A. Pizzi and K. L. Mittal, *Handbook of Adhesive Technology*, Marcel Dekker, New York, 2003.

---

### ***Good–Girifalco interaction parameter***

---

D E PACKHAM

A significant advance was made in the understanding of interfacial energies when Good and Girifalco<sup>1</sup> defined their interaction parameter  $\phi$  in terms of the work of adhesion

between phases 1 and 2 and the geometric mean of the work cohesion of the phases:

$$\phi = \frac{W_A}{(W_{C1}W_{C2})^{1/2}} \quad [1]$$

By incorporating the definition of  $W_A$  and  $W_C$  (see **Contact angles and interfacial tension**), Eqn. 1 can be rearranged to give the Good–Girifalco equation for interfacial tension  $\gamma_{12}$  in terms of the **Surface energy** values  $\gamma_1$  and  $\gamma_2$  of the two phases

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi(\gamma_1\gamma_2)^{1/2} \quad [2]$$

See **Contact angles and interfacial tension** for the definitions and a note on nomenclature of the surface energy terms. It is important to realize that Eqn. 2 depends only on the definitions, and so is universally valid.

#### *London dispersion forces and evaluation of $\phi$*

From the definitions of  $W_A$  and  $W_C$ , it can be seen that  $\phi$  is a function of surface energies. If the structure of a material and the molecular potential energy–separation relationships are known, the surface energy can be calculated by evaluating the work required to separate to infinity the material either side of a chosen plane. For a material in which the dominant intermolecular forces are dispersion force interactions, the Lennard-Jones potential (see **Dispersion forces** and **Polar forces**) will apply, and the calculation is relatively simple.<sup>2</sup> It gives work of cohesion on phase 1

$$W_{C1} = \frac{\pi n_1^2 A_{11}}{16r_{11}^2} \quad [3]$$

and work of adhesion between phases 1 and 2

$$W_A = \frac{\pi n_1 n_2 A_{12}}{16r_{12}^2} \quad [4]$$

where  $n_1$  and  $n_2$  are the number of molecules per unit volume in the phases 1 and 2, and  $A_{11}$  and  $A_{12}$  are van der Waals attraction constants and  $r_{11}$  and  $r_{12}$  are intermolecular separations within and between the phases indicated. Substituted into Eqn. 1, these expressions give

$$\phi = \frac{A_{12}}{(A_{11}A_{12})^{1/2}} \frac{r_1 r_2}{r_{12}^2} \quad [5]$$

As discussed in **Dispersion forces**, where substances 1 and 2 are not too dissimilar in structure.

$$A_{12} = (A_{11}A_{22})^{1/2} \quad [6]$$

The second factor in Eqn. 5 will also be close to unity for similar substances, making  $\phi$  itself unity for an “ideal” case. In general, for dispersion force interfaces between simple



liquids,  $\phi$  may be calculated from Eqn. 5 using molar volumes to evaluate the “ $r$ ” term and explicit expressions for attraction constants (see **Dispersion forces**). The method can be extended to molecules of more complex structure such as polymers, but becomes more difficult.<sup>1</sup>

Where **Polar forces** act across an interface as well as dispersion forces, the Lennard-Jones potential still applies and Eqns. 3–6 are still valid. A similar approach to the calculation of  $\phi$  is possible, but the attraction constant terms have to be summed covering the orientation and induction forces involved.<sup>1</sup>

### *Interfacial tensions and solid surface energies*

The Good–Girifalco equation (Eqn. 2) can be used directly to calculate the interfacial tension between two phases of known surface energies provided the value of the  $\phi$  is known. It can also be used to estimate solid surface energies from contact angle measurements. This is done by eliminating the interfacial tension  $\gamma_{12}$  between Eqn. 2 and Young’s equation (see **Wetting and spreading**, Eqn. 1). This gives

$$\gamma_S = \frac{\gamma_{LF}(1 + \cos \theta)^2}{4\phi^2} \quad [7]$$

In deriving this equation, it has been assumed that the spreading pressure is zero: this point is discussed under **Surface characterization by contact angles – polymers**.

Koberstein<sup>3</sup> lists some values of the interaction parameter. Somewhat different treatments of interfacial energies are discussed under **Surface energy components** and **Acid–base interactions**.

### *References*

1. R. J. Good, *J. Adhesion Sci. Technol.*, **12**, 1269 (1992).
2. B. W. Cherry, *Polymer Surfaces*, Cambridge University Press, 1981.
3. J. T. Koberstein, *Encyclopedia of Polymer Science and Engineering*, Vol. 8, John Wiley, New York, 1987, p. 255.

# H

---

## *Health and Safety*

---

MARTIN E FAKLEY

### *Introduction*

It is the duty of every employer to provide a safe place of work, maintain plant and equipment safely and ensure safe use, handling, storage and transport of articles and substances.<sup>1</sup> Furthermore under the same legislation, it is the employers' responsibility to provide adequate instruction, training and information and to conduct his undertaking in such a manner that people who are not in his employ are not exposed to risks to their health and safety. It is also the duty of employees not to endanger themselves or others by their acts or omissions and to cooperate with their employer as necessary to comply with current legislation and requirements.<sup>2</sup>

From a health and safety standpoint, all industrial adhesives are chemical-containing formulations and thus adhesive manufacturers and users are handling chemical products that fall under the Control of Substances Hazardous to Health regulations.<sup>3</sup> The main provisions of these regulations are to ensure

1. the assessing of any risk to human health;
2. prevention or control of human exposure to hazardous chemicals;
3. use of control methods to eliminate or minimize such exposures;
4. the maintenance, examination and evaluation of any such control measures;
5. the monitoring of exposure to hazardous chemicals in the workplace;
6. health surveillance of those potentially exposed to hazardous chemicals;
7. adequate provision of information, instructions and training.

In summary, before beginning an assembly process involving adhesives that may be hazardous to health, it is essential to conduct a risk assessment of the hazard presented,

that is, the type of health hazard, the amount to be used, the degree of dust or volatility of liquid; assess reasonably practicable options for eliminating or minimizing harm and document the assessment and any recommended actions.

### *Material safety data sheets*

The provision of a material safety data sheet (MSDS) in the language of the user nation, at no cost, is mandatory under current EC legislation.<sup>4</sup> The 16 sections of an MSDS are shown in Table 1.

An adhesive is considered hazardous to health if it requires labelling either as irritant, corrosive, harmful, toxic or very toxic, or if it is assigned an occupational exposure limit (OEL). Oxidizing agents and flammable compounds are intrinsically hazardous. Table 2 shows examples of hazard labels.

### *Work place best practice*

*General considerations* The work process and equipment should be so specified that there is no physical contact with the adhesive, no likelihood of eye contact, that any flammability concerns are addressed (e.g. elimination of sparking by correct electrical zoning), that procedures for adhesive clean-up and disposal are adequate and that ventilation and or extraction is sufficient. The supplier's MSDS must be available and read by all personnel likely to come into contact with adhesives (from good received to waste disposal). Skin contact should be avoided, otherwise there may be risk of dermatitis, made worse by minor skin abrasions or small cuts. In particular, chaffed, open-pore skin around collars and cuffs may be particularly sensitive.

Contamination of the work place with adhesives should be avoided and any accidental spillages correctly cleaned-up immediately by trained personnel wearing the appropriate PPE (Personal protective equipment).







Hands should never be washed with organic solvents. Eating, drinking and smoking should be prohibited in the workplace. Washing, changing and segregated clothes storage facilities should be provided. Regular laundry of work-wear and disciplined cleanliness in the workplace are advisable.

*Prevention and control of exposure* Once a particular adhesive has been specified for use, although its elimination is no longer possible (sic), steps should be taken to reduce the

Table 1. Sections of a material safety data sheet

1. Identification of the substance/preparation and of the supplier	9. Physical and chemical properties
2. Composition/information on ingredients	10. Stability and reactivity
3. Hazards identification	11. Toxicological information
4. First aid measures	12. Ecological information
5. Firefighting measures	13. Disposal considerations
6. Accidental release measures	14. Transport information
7. Handling and storage	15. Regulatory information
8. Exposure controls/personal protection	16. Other information

Table 2. Examples of classification of dangerous substances and hazard labels

Classification/Symbol	Reason	Hazard label
Flammable (F, F+)	Dangerous because of their potential to release energy rapidly and or because the resulting products are harmful in other ways	 Highly inflammable
Harmful (Xn)	Substances that if inhaled, ingested, or have entered the body through the skin present a limited risk to health	 Harmful
Irritants (Xi)	Substances that adversely affect the skin or respiratory tract. Can sensitize and/or cause allergic reaction	 Irritant
Corrosives (C)	Substances that attack chemically materials or people	 Corrosive
Toxics (T, T+)	Substances that prevent or interfere with body functions. They may overload organs such as the liver or kidneys	 Toxic
Environment (N)	Substances that were they to enter the environment would present or might present an immediate or delayed danger to one or more components of the environment	 Environment

amount capable of generating exposure, isolate the user from the source of adhesive, minimize unavoidable exposure by the adoption of engineering controls (e.g. ventilation, guards, etc.), specify the appropriate PPE (e.g. gloves, masks, work-wear) and ensure a disciplined approach to all procedures, controls and behaviours.

*Health surveillance* Where there is a reasonable likelihood that exposure to a chemical hazardous substance under working conditions may cause an identifiable or other adverse health effect, then records must be kept available for at least 40 years; employees must be allowed access to their personal health record and records of workplace monitoring must be kept for at least 5 years.

### *Conclusion*

If the above guidelines are followed, it is possible to ensure the safe use of adhesives and protect the health of those employed in their manufacture and application. Advice on storage and handling of adhesives is available from the manufacturers or general texts.<sup>5</sup>

### *References*

1. *Health and Safety at Work Act*, 1974.
2. *Essentials of Health and Safety at Work*, HSE Books, ISBN 0 7176 0716X (Key Information Source: <http://www.open.gov.uk/hse/hsehome.htm>).
3. *Control of Substances Hazardous to Health Regulations*, 1999; (Approved Code of Practice and Guidance L5, ISBN 0 7176 1670 3).
4. *EEC Commission Directive*, 91/155/EEC.
5. J. Van Twisk and S. C. Aker, Storing adhesive and sealant materials, in *Engineered Materials Handbook, Volume 3*, S. M. Copley and E. L. Langer, Eds., ASM International, 1990.

---

## *High-temperature adhesives*

---

S J SHAW\*

### *Introduction*

Adhesives are becoming increasingly used in the manufacture of a wide range of engineering components because of the substantial benefits provided by adhesive bonding in comparison with more traditional joining techniques such as riveting and welding.

Over the past decade or so, there has been a growing requirement, particularly in the aerospace industry, for adhesives capable of withstanding temperatures in excess of 150 °C for both short- and long-term applications. Epoxy resins, which currently form the basis of most structural adhesive systems, are generally formulated to yield high-temperature capabilities of approximately 50–100 °C (see **Epoxy adhesives**). Although modest improvements in this capability are possible by, for example, variation in resin/curative functionality, together with the use of certain filler materials, 150 °C is generally considered the maximum permissible working temperature. The features that impart thermal stability to a polymer are discussed in **High-temperature stability principles**.

Before going on to consider some of the adhesives capable of exhibiting high-temperature capabilities, it is important to consider what is meant by the term “high-temperature resistance”. This can be viewed in two ways. Firstly, there is the need for the adhesive to maintain mechanical properties at the intended service temperature. Second, there is

a requirement for the adhesive to maintain its structural integrity, that is, resist thermal breakdown at elevated temperature. The former is controlled primarily by the **Glass transition temperature**,  $T_g$ , while the latter is largely dependent upon the inherent thermal stability of the polymer from which the adhesive system is produced. For short-term applications, that is, short durations at elevated temperature, whereas the first requirement is of overriding importance, the latter can be, to a large degree, ignored. However, for longer-term applications, both requirements must be considered important.

### *Traditional adhesive systems*

In consideration of the types of adhesive able to exhibit high-temperature capabilities, it is convenient to divide the discussion into two main parts: first, a consideration of what could be regarded as the traditional high-temperature adhesives, that is, those that have been available for many years, and second a mention of some of the more recent developments in the high-temperature polymer area- developments designed to minimize the disadvantageous characteristics exhibited by the former types.

The traditional **Structural adhesives** capable of operating at temperatures in excess of 150 °C for both short- and long-term applications can be divided into three classes, namely: (1) phenolics, (2) polybenzimidazoles, (3) condensation polyimides (see **Phenolic adhesives: single-stage resoles**, **Phenolic adhesives: two-stage novolacs**, **Polybenzimidazoles** and **Polyimide adhesives**).

Phenolics, prepared from a reaction between phenol and formaldehyde, are rarely used alone as **Structural adhesives** because of tendencies towards both high shrinkage during cure and brittleness. Consequently, for structural adhesive applications, phenolics are usually modified with other polymers. One particular combination, the epoxy-phenolics, offer a substantial high-temperature capability, in particular, providing good strength retention for short periods of time, up to about 300 °C. For long-term use, however, a ceiling of 250 °C is advisable because of the onset of severe oxidative degradation at higher temperatures.

Similarly, **Polybenzimidazole** adhesives also offer excellent high-temperature capabilities for short-term use, with the ability to retain 50% of room temperature strength at 450 °C. Unfortunately, as with the epoxy-phenolics, this capability is not maintained under long-term, high-temperature conditions because of the susceptibility of **Polybenzimidazoles** to oxidative degradation at temperatures in excess of 250 °C.

Condensation polyimides offer the capability of retaining in the region of 50% room temperature strength at approximately 300 °C. Thermal stability, dependent on a number of factors, is such that long-term use at temperatures in the vicinity of 275 °C is feasible.

### *Recent developments*

The three adhesive types discussed above, as mentioned, exhibit substantial high-temperature capability and as such have been, and will probably continue to be, employed in various high-temperature applications. However, all three, to varying degrees, exhibit a serious disadvantage concerning processability, which, at the very least, can render them difficult to use. Although essentially discounted for high-temperature use, **Epoxy adhesives** are generally easy to use in comparison to the above-mentioned systems, and

thus, many of the recent developments in the high-temperature polymer field have had epoxy-like processability as a major goal. For convenience, these developments can be divided into the following three broad areas: (1) thermoplastic polyimides, (2) imide pre-polymers, (3) other polymers.

In all three areas, some considerable success has been achieved in fulfilling the main objective, to the extent that, in some cases, adhesive formulations based on these three categories are at, or close to, full commercialization. For more detailed accounts of these developments, see the articles entitled **Polyimide adhesives**, **Polyether ether ketone** and **Polyphenylquinoxalines**.

### *Select References*

- J. P. Critchley, G. J. Knight, W. W. Wright, *Heat Resistant Polymers*, Plenum Press, New York, 1983.
- P. M. Hergenrother, *High Performance Polym.*, **15**(1), 3–45 (2003).
- K. L. Mittal, *Polyimides – Synthesis, Characterisation and Applications*, Vols 1 and 2, Plenum Press, New York, 1984.
- S. J. Shaw, *Adhesion 10*, K. W. Allen, Ed., Applied Science Publishers, London, 1986, pp. 20–41.
- S. J. Shaw, *Mater. Sci. Tech.*, **3**, 589 (1987).

---

## *High-temperature stability: principles*

---

D E PACKHAM

A serious limitation to the use of organic polymers in general and of adhesives, in particular, is their poor resistance to thermal degradation. Considerable effort has been put into the development of **High-temperature adhesives** and examples of the materials that have been produced are described in articles on **Polybenzimidazoles**, **Polyether ether ketone**, **Polyimide adhesives** and **Polyphenylquinoxalines**. Some of the general principles used in the search for enhanced thermal stability are discussed in this article.

A very wide range of reactions is involved in polymer degradation, depending on the polymer concerned and the environment.<sup>1</sup> Main chain reaction occurs in many polymers: this often involves chain scission, but sometimes cross-linking results. In other polymers, a side chain or a substituent may be more vulnerable. Degradation often involves not one but a series of reactions leading to a complex mixture of degradation products.

Thus, generalizations about degradation are few, and there are many exceptions to them. Nevertheless, some molecular features giving thermal stability to a polymer can be described.<sup>2</sup> They are based on the recognition that degradation must start with bond breaking somewhere in the structure and that this will often initiate a series of reactions leading to a loss of desirable properties. These features are as follows:

1. only strong bonds should be incorporated in the structure;
2. no easy pathways for rearrangement should be present;
3. maximum use should be made of delocalization (resonance) stabilization;
4. where possible, polybonding should be used.

The first of these points seeks to avoid initial attack by eliminating thermally labile bonds from the structure; the second suggests one way of limiting the damage once a bond has been broken.

A powerful way of limiting the initial damage is to build stability into the partially degraded molecule: this is the rationale of the third point. The initial attack will often involve homolytic scission of a bond, giving a free radical – that is, a species with an unpaired electron. Radicals are characteristically reactive (see **Chain polymerization**), but their reactivity is reduced if the unpaired electron is not localized on a single atom. The presence of conjugated structures – structures with a number of alternating single and double bonds – allows such delocalization. The phenyl groups – the C<sub>6</sub>H<sub>5</sub> benzene ring – is a common example. If phenyl groups are linked together, delocalization may be possible over many aromatic rings, giving even greater stability.

The fourth feature mentioned, polybonding, refers to structures in which the main chain consists of more than one string of atoms, like a ladder. If one bond is broken, the chain is still held by the second, so the rate of degradation of properties is reduced.

The structures given in the articles cited on high-temperature adhesives illustrate the application of these principles. They show how frequently conjugation is used to provide radical stabilization.

### References

1. M. A. Meador, *Annu. Rev. Mater. Sci.*, **28**, 599–630 (1998).
2. P. M. Hergenrother, *High Performance Polym.*, **15**(1), 3–45 (2003).

---

## Hot melt adhesives

---

D M BREWIS

### Introduction

Hot melt adhesives are thermoplastics that are applied molten to the substrates. Depending upon the masses and temperatures of the substrates, a melt adhesive may cool very rapidly (see **Internal stress**). Setting is normally achieved in a few seconds or less, and for this reason, melt adhesives are attractive for a number of applications.

### Composition

Melt adhesives are based on thermoplastics but usually contain a number of other components. The most commonly used melt adhesives are based on **Ethylene–vinyl acetate copolymers** (EVA copolymers), but polyethylene, polyesters, polyamides and thermoplastic rubbers, for example, styrene–butadiene block copolymers, are also used. Depending upon the properties required, the vinyl acetate content in the EVA copolymer may



be varied and varying quantities of tackifying resins (e.g. rosin esters) and waxes are incorporated. Tackifying resins will affect the adhesion at elevated temperatures, the time the adhesive takes to harden and the final adhesion achieved. The main purpose of the waxes is to reduce the melt viscosity and thereby improve the wetting of the substrates.

#### *Advantages of melt adhesives*

The advantages of hot melt adhesives include the following:

1. rapid setting leading to very high production speeds;
2. much-reduced space requirements due to (a) lower warehouse volume, (b) reduced compression sections and (c) avoidance of drying areas;
3. indefinite shelf life;
4. low toxicity and fire hazards providing fuming is minimized (see **Health and safety**).

#### *Limitations of melt adhesives*

The main limitations of hot melt adhesives are their modest upper service temperature (although polyester and polyamide systems are usually much superior to EVA systems) and modest load-bearing ability.

#### *Application methods*

A wide range of application techniques is available, selection of which will be determined by assembly and performance requirements and cost. The methods include the following:

1. *Wheel system*. A wheel rotates in a reservoir of adhesive and applies a line of adhesive to a substrate. The thickness of adhesive is controlled by a doctor blade.
2. *Dauber*. Adhesive is transferred from a reservoir by a bar to particular areas of the substrate. Melt viscosity must be low to avoid stringing of the adhesive.
3. *Spring ball valve*. Adhesive is released when the substrate is pressed into contact with a sprung ball situated in the orifice of an extrusion head.
4. *Extrusion* (see **Extrusion coating**). Adhesive is forced through a die on to the substrate and may be applied as continuous or intermittent lines or bands.

#### *Uses of melt adhesives*

The widespread use of hot melt adhesives includes bookbinding (soft cover binding of books and magazines) and component assembly in electronics, consumer durables and automotive fields (see **Automotive applications**). Specialized articles discuss applications in the **Packaging industry** (e.g. carton sealing, bag making, labels), in footwear manufacture (counters and toe puffs), and in woodworking (**Wood adhesives – edgebanding**). They find employment as **Adhesives in the textile industry**.

---

*Select References*

- C. W. Paul, Hot melt adhesives, in *Adhesion Science and Engineering- 2, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002.
- A. Pizzi, Hot melt adhesives, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 739.

---

**Humidity**

---

J COMYN

Humidity is a measure of the amount of water vapour in the atmosphere and is generally quantified as relative humidity (RH), which is defined as

$$\text{RH}(\%) = \frac{\text{partial vapour pressure of water in a sample of air} \times 100}{\text{saturated vapour pressure of water at the same temperature}}$$

The saturated vapour pressure of water increases strongly with temperature.

The importance of humidity in adhesive bonding is that water in the atmosphere diffuses into adhesive bond lines and causes weakening of joints (see **Weathering of adhesive joints**). All adhesives are based on polymers and all polymers are permeable to water. There is a consensus of opinion that a common mechanism of weakening is by water attacking the interface,<sup>1</sup> and a large body of practical experience to show that weakening can be minimized by the correct application of surface pre-treatments (see **Pre-treatment of metals prior to bonding**).

There are many reports in the literature<sup>1</sup> where joints that have been exposed at high RH have weakened with time, but otherwise identical specimens stored at typical ambient laboratory humidities retain their strength. This led Gledhill, Kinloch and Shaw<sup>2</sup> to propose that there is a critical RH below which environmental weakening does not occur. One investigation<sup>3</sup> indicated that the critical RH for some epoxide-aluminium joints is about 65%.

A second aspect is that some adhesives/sealants cure by the diffusion of water vapour. This causes a sequence of chemical reactions, which leads to chain extension and possibly cross-linking by step copolymerization. Examples are some silicone and isocyanate materials, where the depth of cure is often proportional to the square root of RH, and to the square root of time<sup>4</sup> (**Moisture cure of adhesives, Silicone adhesion**).

In the laboratory, RH in relatively small containers (typically a desiccator) can be controlled by the use of saturated salt solutions. Some data over a wide range of humidities at temperatures of 22.8, 30.0 and 37.8 °C have been given by Wink and Sears.<sup>5</sup> These are self-buffering, in that, loss of water vapour results in evaporation from the liquid, and precipitation of salt. Conversely, the addition of liquid water causes some salt to be dissolved. It is important that salt crystals are present at all times.

*References*

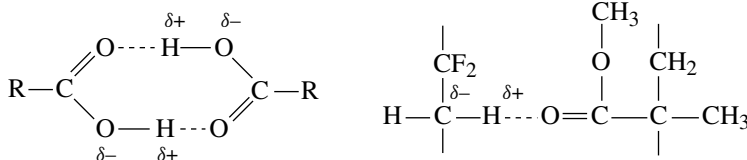
1. J. Comyn, in *Durability of Structural Adhesives*, A. J. Kinloch, Ed., Applied Science Publishers, London, 1983, Chap 3.

2. R. A. Gledhill, A. J. Kinloch and S. J. Shaw, *J. Adhesion*, **11**, 3 (1980).
3. D. M. Brewis, J. Comyn, A. K. Raval and A. J. Kinloch, *Int. J. Adhes. Adhes.*, **10**, 247 (1990).
4. J. Comyn, *Int. J. Adhes. Adhes.*, **18**, 247 (1998).
5. W. A. Wink and G. R. Sears, *TAPPI*, **33**(9), 968 (1950).

### Hydrogen bonding

D BRIGGS

Hydrogen bonding is a very important mechanism for intermolecular interaction and, therefore, adhesion (see **Bonds between atoms and molecules**). Hydrogen bonding is due to the strong interaction of hydrogen attached to one atom (such as O, N, C) by a polar covalent bond with an adjacent atom of high electronegativity (such as O, N and halogens); it is denoted by a dotted line. Thus, dimerization of carboxylic acids and interaction between molecules of PVDF and PMMA both occur by hydrogen bonding.



The strength of this interaction ( $8\text{--}35 \text{ kJ mol}^{-1}$ ) falls between that of van der Waals forces ( $4\text{--}8 \text{ kJ mol}^{-1}$ ) and full covalent bonding ( $40\text{--}400 \text{ kJ mol}^{-1}$ ).

Fowkes (following the earlier work of Drago and co-workers) has argued strongly that intermolecular interactions are due only to either van der Waals **Dispersion forces** or **Acid–base interactions**. Hydrogen–bonding is an important component of A–B interactions, often loosely referred to as specific interactions. Liquids and polymer surfaces can have one of the following three types of hydrogen-bonding capability (see **Acids**):

1. proton acceptor (electron donor or basic) such as esters, ketones, ethers or aromatics, which include such polymers as poly(methyl methacrylate), polystyrene, **Ethylene–vinyl acetate copolymers**, polycarbonate;
2. proton donor (electron acceptor or acidic) such as partially halogenated molecules, including polymers such as poly(vinyl chloride), chlorinated polyethylenes or polypropylenes, poly(vinylidene fluoride) and ethylene–acrylic acid copolymers;
3. both proton acceptor and proton donor molecules such as amides, amines and alcohols where the polyamides, polyimides and poly(vinyl alcohol) are included.

The work of adhesion between surfaces is given by

$$W_A = W_A^d + W_A^{ab}$$

where  $W_A^d$  and  $W_A^{ab}$  refer to the additive contributions from dispersion force and acid–base interactions respectively (see **Acid–base interactions**, **Contact angles and interfacial**

**tension**). Practical bond strengths can therefore be increased by maximizing  $W_A^{ab}$  and this is achieved in polymer surface pre-treatments (e.g. corona (see **Corona discharge treatment**), and **Flame treatment** of polyolefin surfaces). These result in the incorporation of highly polar groups with electron accepting or donating, and particularly H-bonding, capacity. Thus in the corona discharge treatment of polyolefins, enhanced adhesive characteristics result from the incorporation of  $-\text{CH}_2-\text{C}=\text{O}$  groups, which can enolize to  $-\text{CH}=\text{C}-\text{OH}$ , the OH group of which is a strong H-bonder. Likewise, treatment of poly(ethylene terephthalate) produces H-bonding phenolic-OH groups.

### *Select References*

- F. M. Fowkes, in *Polymer Science and Technology, Vol. 12A, Adhesion and Adsorption of Polymers*, L.-H. Lee, Ed., Plenum Press, New York, 1980, p. 43.
- D. Briggs, in *Practical Surface Analysis, Vol. 1, Auger and X-ray Photoelectron Spectroscopy*, 2nd edn, D. Briggs and M. P. Seah, Eds., John Wiley, Chichester, 1990, Chap 9.

# I

---

## *Impact resistance*

---

A MADDISON\*

The performance of bonded joints under impact conditions has particular relevance in certain applications. Automotive body structures, for example, must, if involved in a collision, collapse in a controlled manner to afford maximum protection to the occupants (see **Automotive applications**). It is therefore essential that joint integrity be maintained to permit the necessary adsorption of energy by the large-scale deformation of the structure.

It has been shown that in comparison with spot welds, rivets and a variety of self-piercing mechanical fastenings, toughened structural adhesives may yield single lap shear joints of superior energy absorption when used to bond aluminium alloy sheet; the findings were confirmed in tests on full-size bonded vehicles (see **Toughened adhesives, Structural adhesives**).

Standard test methods for the determination of impact resistance (ASTM D 950-82, ISO 9653:1998 and BS 5350, Part C4) specify the specimen geometry shown in Fig. 1, see also Appendix. While providing a simple basis for comparisons between adhesives, a number of disadvantages are associated with this configuration; for example, it does not reproduce the differential strain effects often present in real joints and it does not readily permit the evaluation of bonds to many important coated substrates.

A critical assessment of the block impact test using **Finite element analysis** has pointed out the limitations of the method.<sup>1</sup>

Finite-element methods have also been used to evaluate new test equipment to measure shear strength under impact loads.<sup>2</sup> In the equipment, two rectangular plates, bonded opposite faces of a vertical hexagonal prismatic rod, bear on a firm surface. The top of the central rod is subjected to an impact load. To prove the validity of the method, the maximum shear stress was compared with the impact shear strength, which was measured using a cylindrical butt joint subjected to impact torsional loads (see **Tensile tests**).

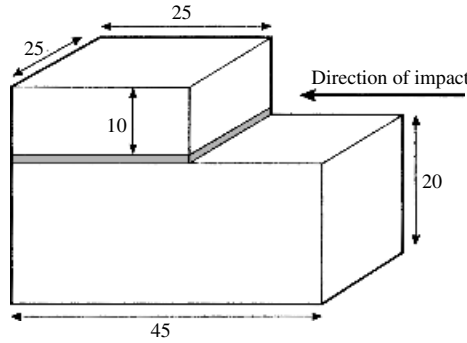


Fig. 1. Impact resistance test-piece (BS 5350 part C4): dimensions in mm

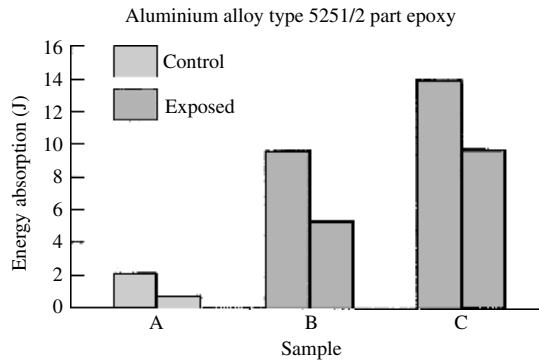


Fig. 2. Effect of pre-treatment and environmental exposure on the energy absorption of single lap shear joints. *Environment:* deionized water 50 °C. *Pre-treatments:* A degreased in acetone, then cleaned in alkali; B as A then anodize in 10 vol. percent orthophosphoric acid at 60 V r.m.s. AC for 10 s; C as B but anodized for 60 s

An important consideration in bonded structure design is the tolerance of joints to impact fatigue conditions (see **Durability: fatigue**). Recent studies suggest that a crack, once initiated, may propagate through the adhesive at low levels of applied energy.

Box team sections have been extensively employed in the evaluation of bonding and weld-bonding systems for possible application in the transport industry. Of particular value in section design and the optimization of spot-weld distribution, they provide useful indications of initial performance in more relevant geometries.

In the study of bond durability under impact conditions, **Pre-treatment of metals prior to bonding** and environmental effects have been evaluated using short diffusion path specimens derived from thin sheet adherend materials.<sup>3</sup> The results (see Fig. 2) serve to emphasize the critical role of surface treatment in the formation of strong, environmentally stable adhesive bonds.

Unfortunately, values of energy absorption obtained are invariably influenced by a number of factors, principally the properties of the adhesives and adherends, test joint geometry and the characteristics of the test machine. Given this degree of sensitivity to test conditions, appropriate experimental controls and careful interpretation of results are essential.

### References

1. R. D. Adams and J. A. Harris, *Int. J. Adhes. Adhes.*, **16**, 61–71 (1996).
2. K. Kihara, H. Isono, H. Yamabe and T. Sugibayashi, *Int. J. Adhes. Adhes.*, **23**, 253–259 (2003).
3. C. W. Critchlow and A. Maddison, *Surf. Interface Anal.*, **17**(7), 539 (1991).

---

## Industrial applications of adhesives

---

C WATSON\*

The advantages that adhesives can offer in terms of design flexibility and ease of manufacture over other methods of joining mean that adhesives find many applications throughout industry (see **Engineering design with adhesives**). In this article, it is intended to give an idea of the scope of adhesives in general industrial practice and to supplement the information to be found in more specialized articles (see **Aerospace applications, Automotive applications, Packaging industry, Rubber to metal bonding applications**).

### *Bonding cylindrical components*

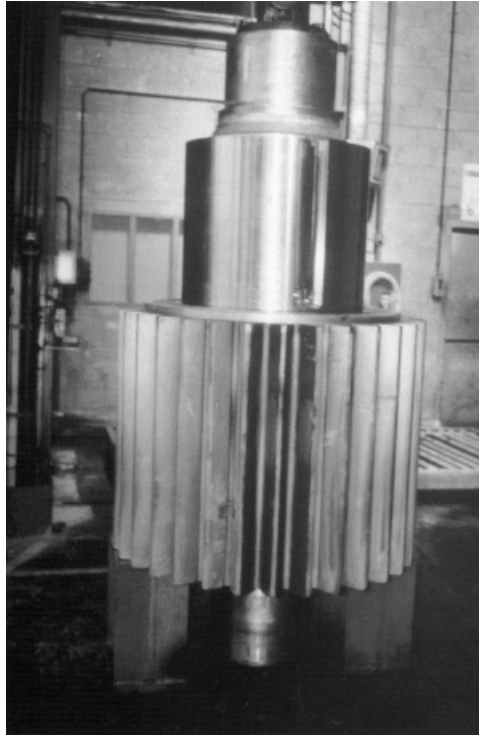
The fixing of cylindrical components is a commonly occurring requirement in industrial manufacture. In recent years, adhesives, especially **Anaerobic adhesives**, have found many applications that range across many industries replacing traditional methods. Adhesives have been used to replace brazing or welding in fixing tubes to carburettor housings and in fixing roller ends on Gestetner machines, saving £15,000 per annum. They are also used to retain bearings into housings, for instance, the spherical bearings in the flight controls of the Lynx helicopter and bearings in electric motor end caps, for instance, on Invicta vibrator motors.

*Gear to shaft bonding* Larger-scale applications include the fitting of gears to shafts in a French steel mill. Figure 1 shows the assembly, the shaft through the gear being the same size as the exposed diameter. Originally, the components were shrink fitted and could only transmit a torque of 700 kNm: when an anaerobic adhesive was employed, the torque was increased to 2800 kNm.

On a more modest scale, an increasingly important application is in car and truck gearboxes, for example, in bonding the ring gear to the differential housing (see **Joint design**).

Major benefits of this type of application are as follows: weight reduction; augmentation of mechanical fit; reduction of mechanical fit with subsequent reduction of hoop stress; ease of machining of gear teeth of separate components as opposed to machining cluster; cheaper capital outlay, for example, adhesive application assembly machine costs £100,000 compared to electron beam welding machine, which costs £500,000; easier replacement of gears.

*Cylinder liner retention* Thin-walled cylindrical components such as bushes and liners can be interference fitted into bores. This more often than not results in distortion, necessitating



**Fig. 1.** A gear in a steel mill bonded adhesively to its shaft

post machining to bring bush or liner bore back to size. Perkins Engines use an anaerobic adhesive when they manufacture the Prima diesel, for augmenting the light press fit when assembling liners to engine blocks.

Originally, in the auto industry, liners were lipped, the block recessed. The liners were assembled with a heavy interference fit. The bore was distorted and subsequently had to be honed back to size. Using adhesive technology, both these stages are eliminated.

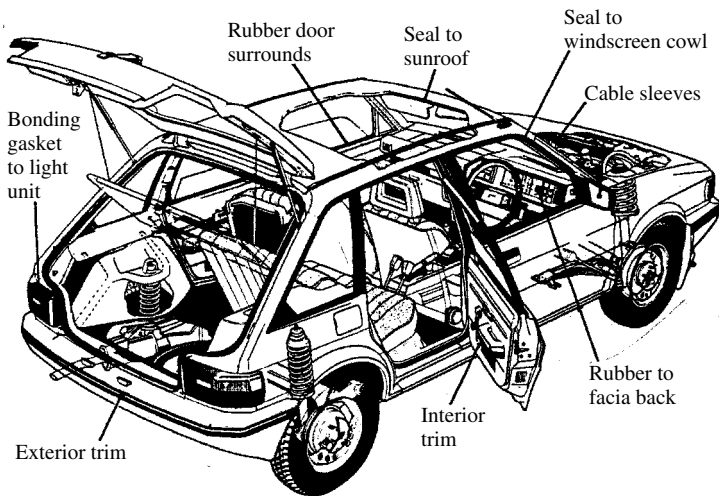
### *Non-metallic components*

Many lightweight non-metallic components are bonded with **Cyanoacrylate adhesives**. Figure 2 shows some applications on a typical car body.

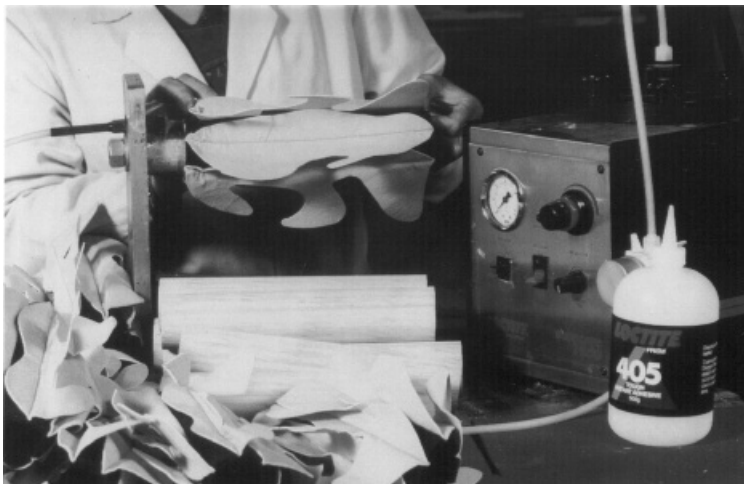
Increasing use is made of bonding for parts traditionally joined by other means. Bonding can replace stitching in attaching decorative bows to slippers; it can replace ultrasonic welding (see **Fusion welding**) for ABS torch bodies; solid rubber tyres can now be bonded to carriage wheels. Figure 3 shows a neoprene sponge rubber being bonded to a PVC tube to produce a paint roller, which gives a stippled effect.

The applications described are but a few of the many thousands of joints that are assembled using adhesives. They illustrate the varied applications and some detail of the benefits of using adhesives compared to other joining methods.





**Fig. 2.** Some typical applications of cyanoacrylate adhesives in a car body



**Fig. 3.** Neoprene sponge rubber bonded to a PVC tube to form a paint roller

The adhesives industry continues to increase the awareness of the use of adhesives so that design and manufacturing engineers may at least consider adhesives at design stage.

### Select References

- W. A. Lees (ed.), *Adhesives and the Engineer*, ASME Professional Engineering Publishing, 1989.
- E. H. Schindel-Bidineli, *Pratique du Collage Industriel*, Technique et Documentation Lavoisier, Paris, 1992.
- R. E. Batson, Industrial Applications for Adhesives, in *ASM Engineered Materials Handbook Vol. 3 Adhesives and Sealants*, ed. M. M. Gauthier ASM International, 1990, p. 567.

## Inelastic electron tunnelling spectroscopy

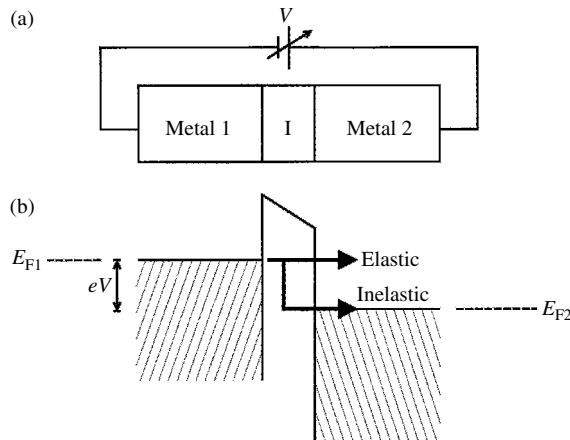
ROBERT R MALLIK

### Background

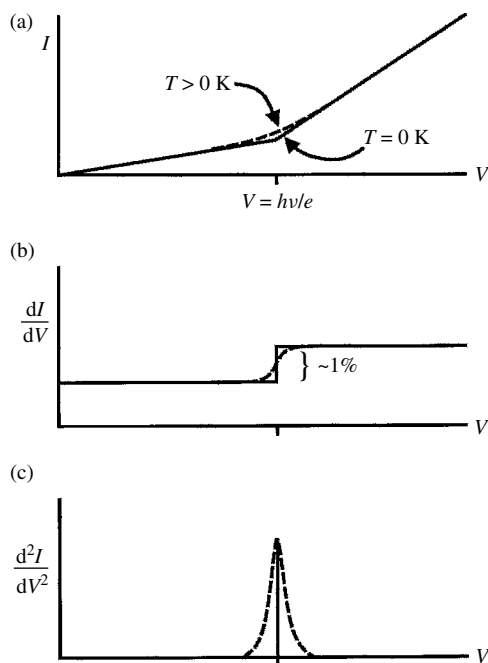
Inelastic Electron Tunnelling Spectroscopy (IETS) is now an established technique for obtaining vibrational spectra of thin films of materials.<sup>1</sup> The materials are incorporated as the insulating barrier layers in thin-film metal/insulator/metal tunnel junctions. Electrons tunnel through the barrier from the first metal to the second under the influence of an applied bias voltage. In doing so, they excite barrier vibrational modes, which form the basis for the technique. Aluminium has been the material of choice for the first metal in most cases, since it readily forms a uniformly thin oxide layer, which is well suited as a tunnel barrier. By far, the most common junctions are of the type aluminium/aluminium oxide plus adsorbed organic monolayer/lead. Since aluminium is widely used in adhesive bonding in aerospace, automotive, and packaging applications, the technique is particularly appealing for adhesion studies. Recently though, IETS has been applied to systems of adhesion promoters on glassy substrates.<sup>2</sup>

### Principles of IETS

When a dc bias voltage,  $V$ , is applied across an IET junction (Fig. 1a) the two metals' Fermi energies become offset by an amount  $eV$ , where  $e$  is the electronic charge. Electrons tunnel through the barrier from filled energy states in the first metal to empty ones in the second (Fig. 1b). Most tunnel elastically, but a small fraction ( $\sim 1\%$ ) scatter inelastically by losing energy to excite vibrational modes of the barrier. This can only occur if the electrons' energy satisfies the condition  $eV \geq h\nu$ , where  $h$  is Planck's constant, and  $\nu$  is the frequency of a particular mode. If there were elastic tunnelling only, the junction's current versus voltage ( $I-V$ ) curve would be linear to a very good approximation. However, because with increasing bias more vibrational modes become accessible to inelastically



**Fig. 1.** Bias-induced elastic and inelastic tunnelling through the insulating barrier, I, of an IET junction.  $E_{F1}$  and  $E_{F2}$  are the Fermi energies of the two metals

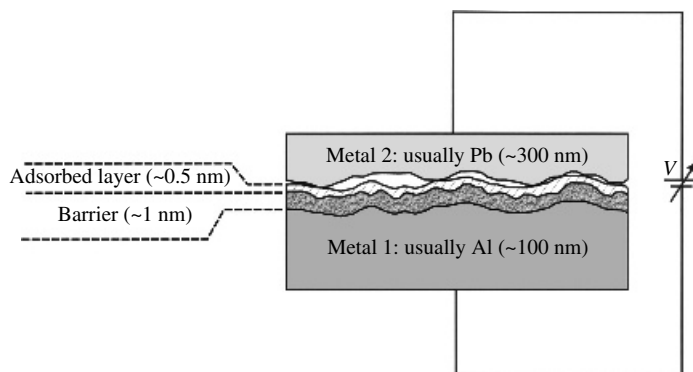


**Fig. 2.** Current-voltage and derivative curves for IET junctions. IETS peaks (c) are broadened by thermal smearing of electron energies (dashed line) and also instrumental effects (not shown)

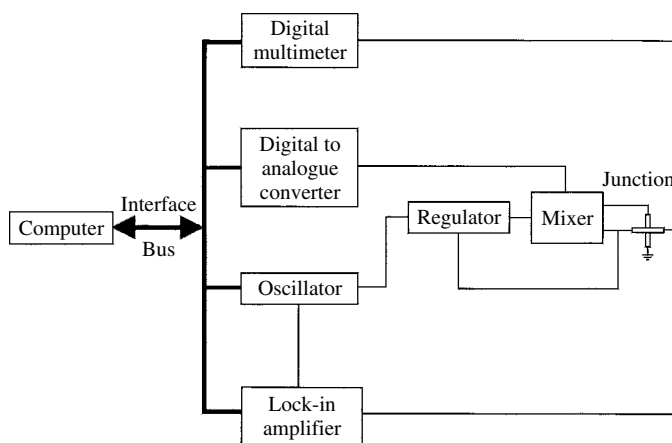
tunnelling electrons, the  $I$ - $V$  curve becomes non-linear. At a bias voltage,  $V = hv/e$ , corresponding to the onset of inelastic tunnelling, the  $I$ - $V$  curve exhibits a slight discontinuity (Fig. 2a), which is revealed more clearly as a peak in the second derivative plot  $d^2I/dV^2$  versus  $V$  (Fig. 2c). An IET spectrum is such a plot and reveals a series of peaks corresponding to the barrier's vibrational modes. IETS can be used to probe the nature of molecular adsorption since peak intensities are sensitive to bond orientation.

### Experimental methods

A schematic cross section of an IET junction is shown in Fig. 3. The metal films, whose geometries are defined by shadow masks, are vacuum evaporated onto an insulating substrate, typically glass or ceramic. Traditionally, the barrier layer is formed either by plasma oxidation of the first metal film in the vacuum chamber or by exposure to air. However, uniformly thin and continuous "artificial barriers" such as silicon, germanium and their oxides may be magnetron sputtered onto the first metal, provided low power and deposition rates are employed (roughly a few W, and 1/100th of  $\text{nm s}^{-1}$  respectively).<sup>2</sup> Required thicknesses of approximately 1–2 nm can be measured using a quartz crystal microbalance. Next, the adsorbed layer is introduced, usually by *ex-situ* exposure to a vapour or very dilute solution of the compound of interest (IETS can detect fractional monolayer coverage on surfaces). Evaporation of the second metal film completes the junction. Spectra are obtained by applying an ac modulation voltage across the junction superimposed



**Fig. 3.** Cross section of an IET junction. Approximate film thicknesses are shown



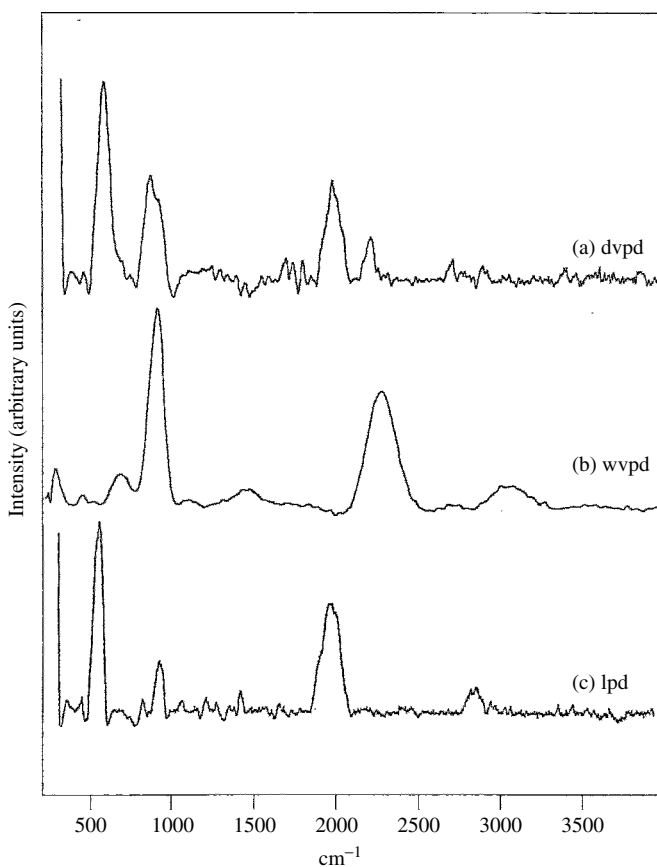
**Fig. 4.** Block diagram of a constant resolution IET spectrometer. (Figure reproduced from reference 3 by kind permission of the American Institute of Physics)

upon a dc bias ramp, simultaneously measuring the second harmonic response, and plotting this as a function of the applied bias (Fig. 4). Since commercial spectrometers are unavailable, in-house built signal mixers are required to combine the ac and dc signals. Digital lock-in amplifiers are widely used as modulation sources and for second harmonic recovery since they have excellent dynamic reserves ( $\sim 100$  dB) and ultra clean (currently 32-bit) modulation signals. Spectrometers are usually computer interfaced. Spectral resolution is determined by thermal and instrumental broadening: the full-width-at-half-maximum (FWHM) of IETS peaks is given by  $\sqrt{(5.4kT)^2 + (1.22 eV_{\text{mod}})^2}$ , where  $k$  is Boltzmann's constant,  $T$  is the Kelvin temperature, and  $V_{\text{mod}}$  is the modulation voltage.<sup>1</sup> For constant resolution, the temperature and modulation voltage must be held constant. This is typically done by immersing the samples in liquid helium to maintain a temperature of 4.2 K, and employing an ac regulator circuit<sup>3</sup> to hold the modulation voltage at  $\sim 1$  mV. Under these conditions, the FWHM is  $\sim 2$  meV ( $16 \text{ cm}^{-1}$ ). Noise is primarily  $1/f$  dependent and is minimized by operating at a modulation frequency of 10's of kHz. IET spectra are often compared to those obtained by bulk IR spectroscopy or thin-film

Multiple Reflection Absorption Infrared Spectroscopy (MRAIRS) since these techniques offer complementary information.<sup>4</sup> (See **Infrared spectroscopy**).

### *IETS studies of adhesion-related systems*

Comyn and co-workers were amongst the first to study systems of adhesives on alumina with IETS in the late 1970s and early 1980s.<sup>1</sup> Since then, other adhesive-related compounds have been studied, for example,<sup>1</sup> phenolic adhesives, ester-based polymers, and **Cyanoacrylate adhesives**, and also **Silane adhesion promoters** and phosphonic acids,<sup>5</sup> which are both used as adhesion promoters on glassy materials and metal oxides. Until recently, the materials investigated by IETS had been limited to those that adsorb on the native oxide of the first metal, usually  $\text{Al}_2\text{O}_3$ . However, it was shown starting in the early 1990s that sputtered ultra-thin artificial barriers were viable for adhesion studies.<sup>6</sup> For example, Fig. 5 shows spectra obtained for triethoxysilane (TES) adsorbed



**Fig. 5.** IET spectra of triethoxysilane (TES) adsorbed onto germania under different conditions: (a) and (b) by exposure to TES vapour under “dry” and “wet” conditions respectively, and (c) liquid phase doped from an aqueous acidic solution. (Figure reproduced from Ref. [5] by kind permission of Elsevier Science)

onto sputtered germania barriers under different conditions,<sup>2</sup> namely, by (a) exposure to neat TES vapour under relatively dry conditions (dry vapour phase doped: dvpd), or (b) in the presence of water vapour (wet vapour phase doped: wvdp), or by (c) simply pouring an aqueous acidic hydrolysed solution of TES onto the germania and spinning off the excess (liquid phase doped: lpd). Smooth polynomial backgrounds have been subtracted from all spectra for clarity. In all three spectra, the peaks ca. 2000 cm<sup>-1</sup> and 900 cm<sup>-1</sup> are due to terminal Si–H stretching and bending modes, respectively oriented perpendicular to the plane of the tunnel junction. Interestingly, when dry vapour doped, peaks due to the symmetric and asymmetric Ge–O–Ge vibrations of the germania layer are evident at 575 and 890 cm<sup>-1</sup> respectively, but no Si–O–Si peaks are present. This and the absence of ethoxy-related CH peaks ca. 3000 cm<sup>-1</sup> indicates that the TES has hydrolysed but not polymerized to form a glassy siloxane matrix on the surface. When wet vapour doped, broad Si–O–Si peaks *are* present at 726 and 1089 cm<sup>-1</sup>, indicating that the TES *has* polymerized on the surface (although the presence of weak residual ethoxy CH peaks indicate incompletely hydrolysis of the TES). Finally, and perhaps surprisingly, when liquid doped, there are no Si–O–Si peaks, indicating the TES has not polymerized, but weak CH peaks near 2850 cm<sup>-1</sup> show that the TES has hydrolysed. Ge–O–Ge peaks are visible at 550 and 900 cm<sup>-1</sup>. These results provide detailed information on the adsorption of coupling agents on model glass substrates and form the basis for further adhesion studies.

### References

1. N. M. D. Brown, in *Spectroscopy of Surfaces*, R. J. H. Clark and R. E. Hester, Eds., John Wiley & Sons, 1988, Chap 5.
2. R. R. Mallik, S. Anabtawi, B. Moore and T. A. Hartman, *Surf. Sci.*, **380**, 124 (1997).
3. T. R. Seman and R. R. Mallik, *Rev. Sci. Instrum.*, **70**(6), 2808 (1999).
4. S. Devdas and R. R. Mallik, *Int. J. Adhesion Adhesives*, **20**, 341 (2000).
5. R. Coast, M. Pikus, P. N. Henriksen and G. A. Nitowski, *J. Adhesion Sci. Technol.*, **10**(2), 101 (1996).
6. R. R. Mallik, W. J. Kulnis and T. Butler, *J. Appl. Phys.*, **70**(75), 3703 (1991).

### Infrared spectroscopy

F J BOERIO

Infrared spectroscopy, including Fourier-transform infrared (FTIR) spectroscopy, is one of the oldest and most widely used analytical techniques in adhesion-related research. Transmission infrared spectroscopy has been used to identify compounds used in formulating adhesives and to follow curing reactions. Attenuated total reflection (ATR) (see **Infrared spectroscopy: attenuated total reflection**) has been used to probe the surface composition of polymers that have been surface modified by an etching process or by deposition of a film. More recently, reflection-absorption infrared spectroscopy (see **Infrared spectroscopy: RAIR**) has been used to characterize thin films on the surfaces of reflecting substrates.

IR has numerous characteristics that make it an appropriate technique for investigations related to adhesion science. Most importantly, infrared spectroscopy is sensitive to functional groups whereas other techniques are mostly sensitive to elements. Therefore, the technique can provide a great deal of information about curing reactions of adhesives and about other chemical reactions that are relevant to adhesion. The technique is also non-destructive since virtually no sample degradation occurs when a specimen is illuminated with infrared radiation. Using the ATR technique, maps and depth profiles can be constructed to show the distribution of functional groups across the surface of a sample or with distance away from the surface of the sample and into the bulk. In RAIR, monolayer and even sub-monolayer sensitivity are almost routine, making the technique extremely useful for investigating surface processes on metals, such as corrosion or adsorption of components of adhesive systems. The cost of an FTIR system is low, especially when compared to that of instruments needed for surface characterization by vacuum techniques. Finally, the technique is quantitative.

The main disadvantages of IR spectroscopy are that depth profiling is not possible in RAIR and that surface sensitivity in ATR is limited to approximately the wavelength of infrared radiation or about 1  $\mu\text{m}$ . In addition, the spatial resolution of conventional infrared techniques is limited by diffraction effects and is only approximately a few tens of micrometers.

In an FTIR spectrometer, a source (e.g., a resistively heated ceramic rod) emits infrared radiation that is focused onto an interferometer whose main components consist of a beamsplitter, fixed mirror, movable mirror and detector. The beamsplitter divides the beam into two beams. One beam is reflected off the beamsplitter toward the fixed mirror and is then reflected back through the beamsplitter to the detector. The other beam is transmitted through the beamsplitter toward the movable mirror and is then reflected off of the beamsplitter and to the detector.

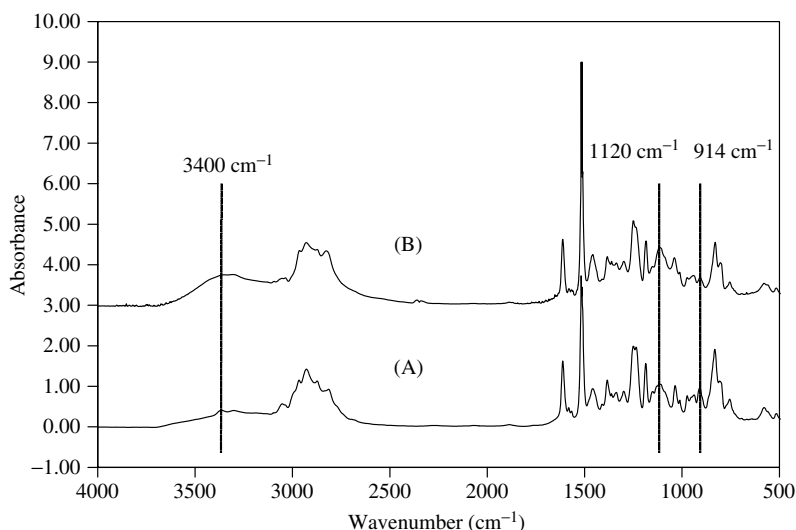
The intensity measured by the detector depends on the difference in path length that the two beams travel to reach the detector. Since one of the mirrors can be moved or scanned, the intensity reaching the detector can be measured as a function of retardation ( $\delta$ ) or the difference in path length between the two beams. The output of the detector can be displayed as an interferogram consisting of a plot of intensity versus retardation. If an absorbing sample is placed between the beamsplitter and the detector, the appearance of the interferogram is altered to some extent. In that case, the Fourier-transform of the interferogram can be calculated to obtain the infrared absorption spectrum of the sample.

The infrared absorption spectrum of a material is usually presented as a plot of absorbance ( $A$ ) versus wave number ( $1/\lambda$ ) for wave numbers between approximately 4000 and 400  $\text{cm}^{-1}$ . Absorbance is defined as  $-\log(I/I_0)$ , where  $I_0$  is the intensity of the radiation incident on the sample at any wavelength and  $I$  is the intensity transmitted by the sample.  $I$  and  $I_0$  are related by Beer's law, which can be written as

$$I/I_0 = 10^{-\epsilon Cd}$$

or as

$$I/I_0 = e^{-\alpha d}$$



**Fig. 1.** Transmission infrared spectra of an epoxide adhesive (A) before and (B) after curing with diamino-diphenyl sulphone

In these expressions,  $\varepsilon$  is the absorptivity of the sample at any wavelength,  $C$  is the concentration of absorbing species,  $d$  is the thickness of the sample, and  $\alpha$  is the absorption constant of the sample at any wavelength. The absorption constant is related to  $k_1$ , the complex part of the refractive index of the sample, by the expression

$$\alpha = 4\pi k_1/\lambda$$

From these expressions, it can be seen that in transmission, the absorbance of an absorption band is directly proportional to  $k_1$ .

As indicated above, one of the most important characteristics of infrared spectroscopy is that functional groups usually absorb at about the same frequency regardless of the molecule in which they are found. As a result, infrared spectroscopy can be used to follow curing reactions in adhesives or degradation reactions, such as hydrolysis, that may eventually result in the failure of an adhesive. A good example of the use of infrared spectroscopy in adhesion science involves the curing of **Epoxide adhesive** with an amine curing agent. Figure 1 shows the transmission infrared spectrum of the adhesive as a function of time at room temperature. The band near  $914\text{ cm}^{-1}$  is related to the epoxide groups and decreases in intensity as a function of curing time. The band near  $3400\text{ cm}^{-1}$  is related to hydroxyl groups produced during curing and increases in intensity as a function of curing time.

### Select References

- P. R. Griffiths, *Chemical Infrared Fourier Transform Spectroscopy*, John Wiley & Sons, New York, 1975.  
 J. L. Koenig, *Spectroscopy of Polymers*, 2nd edn, American Chemical Society, Washington, DC, 1999.



---

**Infrared spectroscopy: attenuated total reflection**


---

F J BOERIO

In order to characterize the surface regions of a sample that has been modified in some way, as is usually the case in adhesion-related investigations, some sort of a reflection experiment is required. Reflection **Infrared spectroscopy** may be done using attenuated total reflection (ATR) when the sample is a relatively soft material with *low* refractive index. In ATR, a prism of a material with a relatively *high* refractive index is placed in intimate contact with the sample and infrared radiation is reflected off the prism/sample interface. The angle of incidence is related to the angle of refraction (the angle that the beam transmitted into the sample makes with the normal to the interface) by Snell's law:

$$n_0 \sin(\theta_0) = n_1 \sin(\theta_1) \quad [1]$$

In this expression,  $n_0$  is the refractive index of the prism,  $\theta_0$  is the angle of incidence,  $n_1$  is the refractive index of the sample, and  $\theta_1$  is the angle of refraction. Since  $n_0$  is greater than  $n_1$ ,  $\theta_1$  is greater than  $\theta_0$ . This means that for some values of  $\theta_0$  greater than a critical angle  $\theta_c$ , the angle of refraction is greater than  $90^\circ$  and there is no travelling wave transmitted into the sample. The critical angle can be calculated by setting  $\theta_1 = 90^\circ$  in Eqn. 1 and rearranging:

$$\sin(\theta_c) = n_1/n_0 \quad [2]$$

Although there is no travelling wave in the sample when  $\theta_0 > \theta_c$ , there is an "evanescent" wave having amplitude that decreases exponentially as a function of distance away from the prism/sample interface. The "penetration depth" ( $\delta$ ) is the distance that it takes for the evanescent wave in the sample to decrease to  $1/e$  times its value at the interface and is given by the expression

$$\delta = \lambda_0 / \{2\pi n_0 [\sin^2(\theta_0) - (n_1/n_0)^2]^{1/2}\} \quad [3]$$

where  $\lambda_0$  is the wavelength of the infrared radiation. From Eqn. 3, it is evident that the depth of penetration is closely related to the refractive index of the prism and to the wavelength of the radiation and that  $\delta$  increases as wavelength increases. Some values of the penetration depth at  $3.0 \mu\text{m}$  for typical prism materials and for a polymer with refractive index equal to 1.5 (as for polyethylene) are given in Table 1.

Table 1. Penetration depth at a wavelength of  $3.0 \mu\text{m}$  and an angle of incidence of  $45^\circ$  for typical prism materials and for a sample with refractive index equal to 1.5

Prism material	Refractive index	Angle of incidence (in degrees)	Penetration depth (in $\mu\text{m}$ ) at $\lambda_0 = 3.0 \mu\text{m}$	Penetration depth (in $\mu\text{m}$ ) at $\lambda_0 = 10.0 \mu\text{m}$
Germanium	4.0	45	0.20	0.66
Silicon	3.5	45	0.24	0.80
KRS-5	2.4	45	0.60	2.00

As long as  $\theta_0 > \theta_c$  and the sample is not absorbing, the reflectivity of the prism/sample interface will be total. However, at wavelengths where the sample is absorbing, the reflectivity will be “attenuated” or less than total. Thus, an absorption spectrum that is similar to that obtained in transmission can be produced in ATR.

The refractive index of the sample can be written as a complex number  $n_1 = n_1 - ik_1$ . At wavelengths where the sample is not absorbing,  $k_1$ , the absorption constant, equals zero. However, at wavelengths where the sample is absorbing,  $k_1$  is non-zero. In transmission spectroscopy, the intensity of an absorption band depends mostly on  $k_1$  while in ATR the intensity of the same band is a complex function of  $n_1$  and  $k_1$ . Nevertheless, there will be absorption bands in ATR at wavelengths where  $k_1 \neq 0$ . It should be recalled from the previous chapter that absorption bands in transmission occur when  $k_1 \neq 0$ . Thus, bands are expected at the same wavelengths in transmission and in ATR but their intensities may be dissimilar.

As indicated above, the penetration depth is on the order of a micrometer. That means that in ATR, absorption of infrared radiation mostly occurs within a distance  $\delta$  of the surface and ATR is not as surface sensitive as some other surface analysis techniques. However, ATR, like all forms of infrared spectroscopy, is very sensitive to functional groups and is a powerful technique for characterizing the surface regions of polymers.

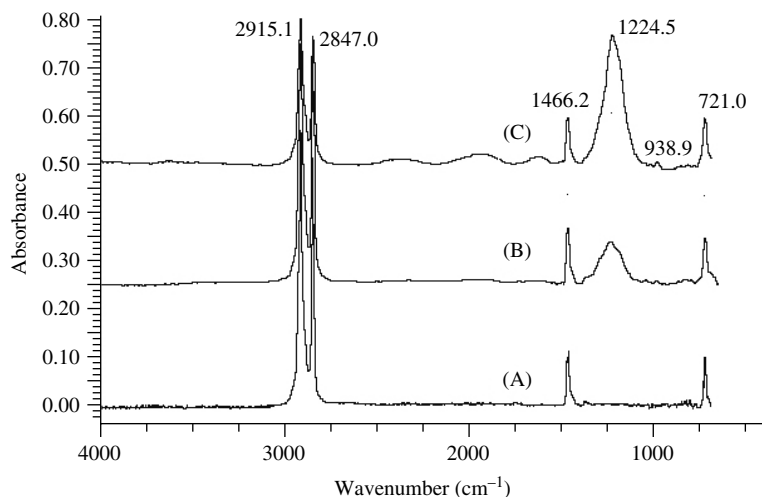
ATR infrared spectroscopy can be used to construct a depth profile showing the way in which the surface composition of a polymer changes as a function of distance away from the surface and into the polymer. As long as the polymer is not a very strong absorber, the absorbance of an infrared band in ATR is

$$A(\delta) = \int \alpha(z) \exp(-\delta z) dz \quad [3]$$

In this expression,  $z$  is the distance from the surface into the sample,  $\alpha(z)$  is the absorption coefficient, and  $\delta$ , the depth of penetration, is given by Eqn. 2. A depth profile can be obtained for a given functional group by determining  $\alpha(z)$ , which is the inverse Laplace transform of  $A(\delta)$ , for an absorption band characteristic of that functional group.

Figure 1 shows ATR spectra obtained from polyethylene substrates ( $n_1 \cong 1.52$ ) that were coated with plasma-polymerized fluorocarbon films having different thickness. The ATR spectra were acquired using a germanium prism ( $n_0 = 4.0$ ) and an angle of incidence equal to  $45^\circ$ . Using Eqn. 3, the depth of penetration in polyethylene was estimated to be approximately  $0.67 \mu\text{m}$  at a wavelength of  $10.0 \mu\text{m}$ . The spectrum of the uncoated polyethylene substrate was characterized by bands near  $2915$ ,  $2847$ ,  $1466$ , and  $721 \text{ cm}^{-1}$ . When a substrate was coated with a film having thickness ( $0.06 \mu\text{m}$ ) much less than the penetration depth, most absorption still occurred in the substrate. In this case, the ATR spectrum was characterized by the four bands related to the substrate plus a new relatively weak band near  $1224 \text{ cm}^{-1}$  that was related to the fluorocarbon film. When a substrate was coated with a film having thickness ( $0.32 \mu\text{m}$ ) similar to the depth of penetration, most absorption occurred in the film and the band near  $1224 \text{ cm}^{-1}$  was much stronger than that at  $1466 \text{ cm}^{-1}$ .

Thin films on reflecting substrates may be characterized by reflecting parallel-polarized infrared radiation off of the surface: see **Infrared spectroscopy: RAIR**.



**Fig. 1.** ATR infrared spectra obtained from an (A) uncoated polyethylene substrate and from polyethylene substrates coated with plasma-polymerized fluorocarbon films having thickness of (B) 0.06 and (C) 0.32  $\mu\text{m}$

### Select Reference

N. J. Harrick, *Internal Reflection Spectroscopy*, Interscience Publishers, New York, 1967.

## Infrared spectroscopy: RAIR

F J BOERIO

### Reflection-absorption infrared spectroscopy (RAIR)

One of the most important applications of **Infrared spectroscopy** in adhesion research concerns thin films formed on metal substrates. A wide variety of films may be studied, including air-formed oxides, anodic oxides, plasma-polymerized films, and films formed by adsorption of polymers or low molecular weight organic compounds. The structure and composition of the films may be determined, including that of the film/substrate “interphase”.

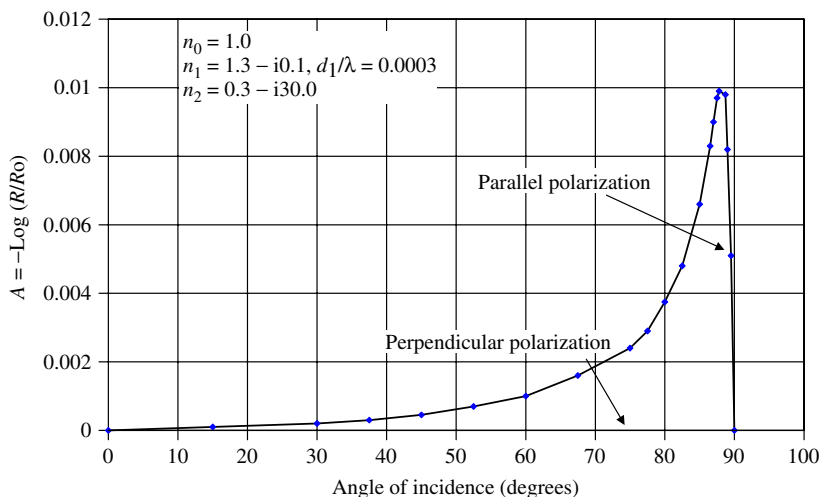
Since infrared radiation cannot be transmitted through any significant thickness of a reflecting material, a reflection experiment is required to obtain the infrared spectrum of a thin film on a substrate such as a metal. Reflection-absorption infrared spectroscopy (RAIR) is the name given to the technique for characterizing thin films on reflecting substrates by reflecting parallel-polarized infrared radiation off of the surface at large angles of incidence.

The reasons for using parallel-polarized radiation and large angles of incidence in RAIR are as follows. In RAIR, the incident and reflected beams of infrared radiation combine to form a standing wave that has nearly zero electric field amplitude at the surface of the reflecting substrate for all angles of incidence and for radiation polarized

perpendicular to the plane of incidence; since the electric field amplitude is nearly zero at the substrate surface, there is no significant absorption by a thin film on the surface when using *perpendicular* polarized radiation. A similar situation occurs for radiation polarized *parallel* to the plane of incidence and *angles of incidence less than about 45°*. However, when the radiation is polarized *parallel* to the plane of incidence and the *angle of incidence is greater than about 45°*, the electric field amplitude at the surface increases rapidly as a function of angle of incidence and *reaches a maximum at approximately 85°*. As a result, significant infrared absorption can occur in thin films on reflecting substrates when the radiation is polarized parallel to the plane of incidence and the angle of incidence is approximately 85°.

Figure 1 shows a plot of RAIR band intensity versus angle of incidence ( $\theta_0$ ) for a typical polymer film with a carbonyl absorption band at approximately  $1740\text{ cm}^{-1}$ . It is evident that band size is negligible for parallel-polarized radiation and small values of  $\theta_0$  but increases significantly at larger angles and reaches a maximum near  $\theta_0 = 85^\circ$ . When the infrared radiation is polarized perpendicular to the plane of incidence, band size is always negligible.

A powerful characteristic of RAIR spectroscopy is that the technique can be used to determine the orientation of surface species. The reason for this is as follows. When parallel-polarized infrared radiation is reflected off of a substrate at a large angle of incidence, the electric field vector ( $\mathbf{E}$ ) of the standing wave formed by the incident and reflected waves is perpendicular to the substrate surface. Since the intensity of an infrared absorption band is proportional to  $I \sim (\mathbf{E} \cdot \mathbf{M})^2$ , where  $\mathbf{M}$  is the “transition moment”, it can be seen that the intensity of a band is maximum when  $\mathbf{E}$  and  $\mathbf{M}$  are parallel

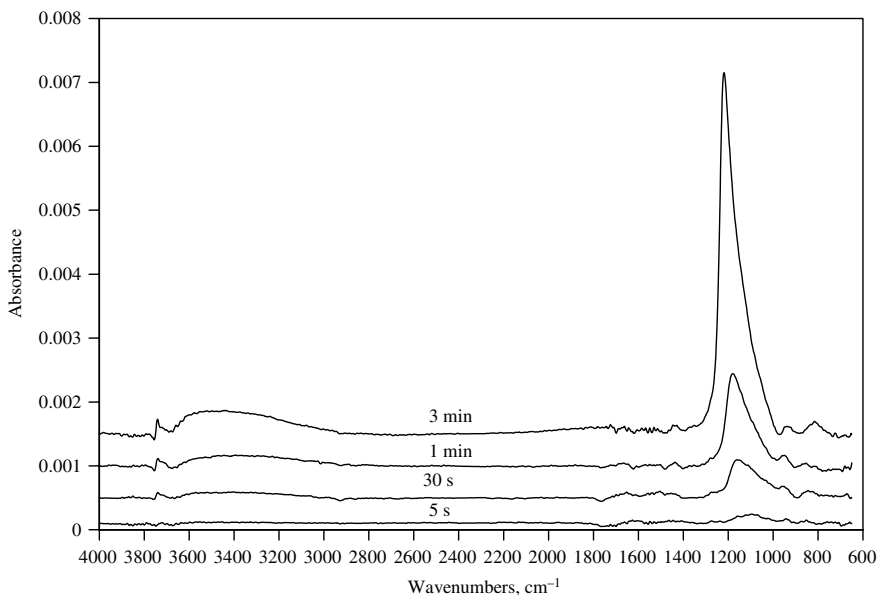


**Fig. 1.** A plot of RAIR band size versus angle of incidence. Reproduced by permission of Oxford University Press from F. J. Boerio, W. W. Zhao, and J. T. Young, in “Multidimensional Spectroscopy of Polymers”, ACS Symposium Series #598, American Chemical Society, Washington, DC, 1995, p. 8

(i.e. both perpendicular to the surface).  $I$  is a minimum when  $\mathbf{M}$  is parallel to the surface.

Since the angle of incidence is very large in RAIR, a large area of the substrate (typically several square centimeters) is usually examined and the spatial resolution of the technique is limited. However, several manufacturers have developed objective lenses that enable RAIR spectra to be acquired using an infrared microscope. These lenses make it possible to obtain RAIR spectra from areas as small as about  $25\ \mu\text{m}$  in diameter and to use RAIR for failure analysis of adhesive bonds.

An interesting example of the application of RAIR spectroscopy in adhesion science is shown in Fig. 2, where the spectra of plasma-polymerized silica-like films that are used as primers for structural adhesive bonding are presented (FJB).<sup>1</sup> For relatively long deposition times and thick films, the spectrum consisted of a very strong band near  $1230\ \text{cm}^{-1}$  and weaker bands near  $3740$ ,  $3650$ ,  $3450$  and  $940\ \text{cm}^{-1}$ . The band near  $1230\ \text{cm}^{-1}$  was related to the longitudinal optical (LO) Si–O–Si stretching mode. The band near  $3740\ \text{cm}^{-1}$  was attributed to free silanol groups while the band near  $3650\ \text{cm}^{-1}$  was attributed to isolated silanol groups in which the hydrogen atom was hydrogen-bonded to the oxygen atom of an Si–O–Si group. The band near  $3450\ \text{cm}^{-1}$  was attributed to adjacent silanol groups in which the hydrogen atom of one was hydrogen-bonded to the oxygen atom of another. The weak band near  $940\ \text{cm}^{-1}$  was attributed to Si–O stretching of silanol groups. As the film thickness was decreased, these bands all decreased in



**Fig. 2.** RAIR spectra of plasma-polymerized silica-like films deposited onto aluminium substrates for different times and thus at different thickness. Copyright (2002) from (Journal of Adhesion) by (F. J. Boerio). Reproduced by permission of Taylor & Francis, Inc., <http://www.taylorandfrancis.com>

intensity. For the thinnest films, formed in a deposition time of 5 s, a new band appeared near  $1090\text{ cm}^{-1}$  and was assigned to a unique structure found only in the film/substrate interphase; the most likely structure was an  $\text{SiO}_2$  suboxide. Formation of suboxide at the interface was favored because the free energy of formation of the metal oxide was greater than that of the monomer, which was hexamethyldisiloxane in this case.

### Reference

1. F. J. Boerio, Surface analysis applied to adhesion science, in *Adhesion Science and Engineering*, vol. 2, Surfaces, Chemistry and Applications A. V. Pocius and M. Chaudhury, Eds., Elsevier Science Publishers, New York, 2002, Ch. 6.

---

### Internal stress

---

K KENDALL

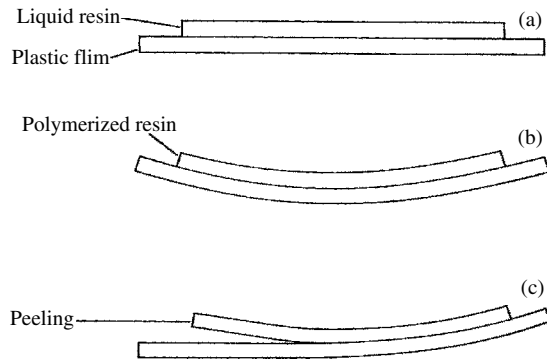
Adhesive joints often contain internal stress, that is, stress that is caused by internal movements as the joint is made, not by externally applied forces. These stresses are also called residual stresses because they remain in the joint after all external stresses have been removed. Such internal stresses are important because they cause premature failure, or even spontaneous fracture of the joint. However, in particular circumstances, an adhesive joint can be strengthened by inserting appropriate internal stress, just as glass is strengthened by blowing cold air on its surface during solidification, to promote residual compressive surface stress.

The most common form of internal stress arises from shrinkage of the adhesive. For example, a resin adhesive may shrink by several volume percent during polymerization, while the adherends remain constant in size. Obviously, this shrinkage has to be accommodated in some way, usually by the appearance of internal stress within the adhesive, and also within the surrounding adherends. The internal stress depends on the amount of shrinkage, the geometry of the joint and the relative elasticity of adhesive and adherends. The internal stress may be high enough to rupture the joint without applying any external load.

Internal stress can also be produced with **Hot melt adhesives** where the adhesive shrinks more on cooling than the adherend. In this case, there may also be a difference in thermal expansion coefficient between the two adherends, and this difference causes additional internal stress in the joint. Such internal stress is seen most dramatically in bimetallic strips used in thermostats, where the internal stress causes large bending of the joined materials. **Solvent-based adhesives** also produce internal stress when shrinkage occurs during solvent evaporation.

The simplest way to visualize internal stresses is by observing the distortions that accompany them, as in the bimetallic strip example above. For example, coating a resin adhesive on to a strip of plastic film (Fig. 1a) and then polymerizing it, causes bending of the composite strip (Fig. 1b) as a result of polymerization shrinkage in the adhesive layer.

This bending shows that internal stresses exist both in the adhesive and the adherend, and allows calculation of the stress levels once the dimensions and elastic moduli of the



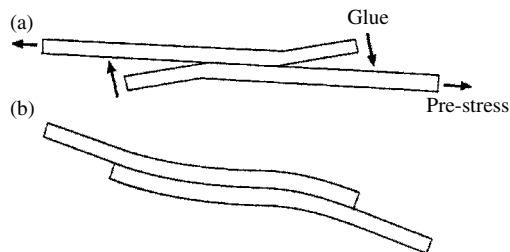
**Fig. 1.** Visualizing the effects of internal stress caused by polymerization shrinkage of the resin adhesive

materials are known. If the distortion is sufficiently large, then failure of the adhesive interface may be observed by the peeling mechanism shown in Fig. 1(c) even without the application of any external force. It has been demonstrated by a **Fracture mechanics** argument<sup>1</sup> that peeling is always assisted by internal stress, whether tensile or compressive, because the stored elastic energy released by splitting the joint can drive the crack through the interface. The strength reduction is proportional to the adhesive thickness, to its elastic modulus and to the square of shrinkage strain.

This theory allows the design of adhesive joints with resistance to internal stress. The most important objective is to minimize shrinkage by appropriate choice of polymer. An alternative approach is to add filler to the polymer to reduce shrinkage (see **Filler–matrix adhesion**). Use of a compliant or rubbery adhesive reduces the internal stress. Weakening of the joint is minimized by using the smallest possible volume of adhesive when making the joint.

Although peeling failure is always assisted by internal stress, lap joint failure may be inhibited by judicious insertion of internal stress.<sup>2,3</sup> This is most simply achieved by pre-stressing the sheets before gluing the laps in place (Fig. 2). A factor 3 improvement in lap joint strength is possible by this method.

**Paint service properties and adhesion** includes a discussion of internal stress in paint films.



**Fig. 2.** Strengthening a lap joint by introducing internal stress during formation of the joint: (a) pre-stressing and glueing of laps; (b) final shape of joint after release of pre-stress

## References

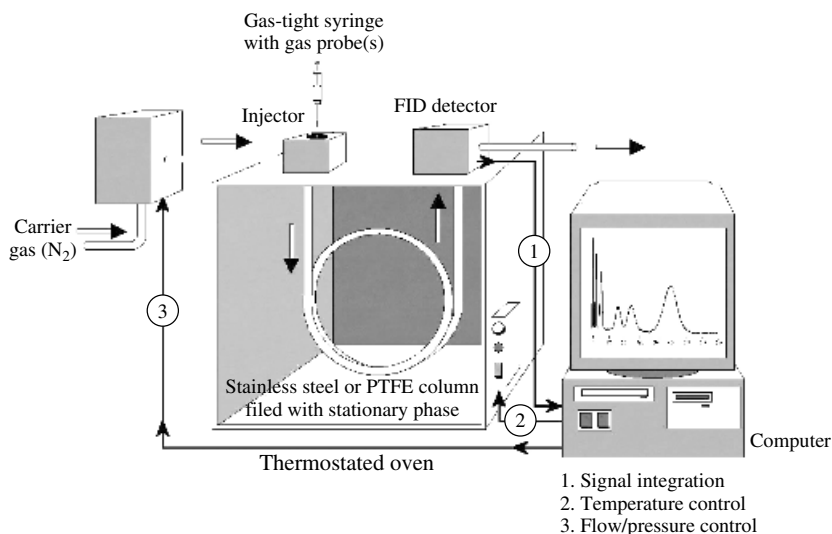
1. K Kendall, *J Phys D Appl Phys* **6**, 1782 (1973).
2. K Kendall, *Molecular Adhesion and its Applications*, Kluwer, New York 2001, 338.
3. M. D Drory and J. W Hutchinson, *Proc R Soc Lond* **A452**, 2319 (1996).

### *Inverse gas chromatography*

MARIE-LAURE ABEL AND JOHN F WATTS

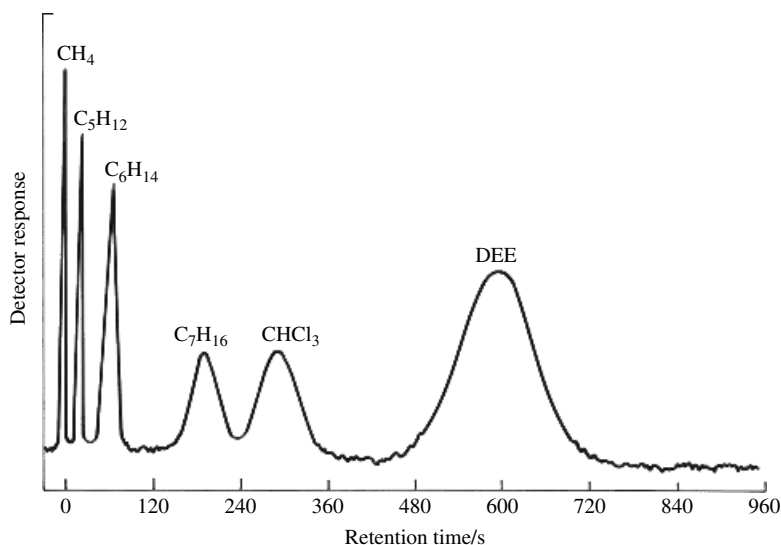
In the understanding of adhesion, the determination of **Surface energy** and characterization of the acid–base properties of the substrate is often important (see **Acid–base interactions: introduction**). This may be carried out by the study of wetting and spreading phenomena such as the **Contact angle**: these can be measured by a variety of techniques including the sessile drop method and dynamic contact angle analysis (the Wilhelmy plate approach, see **Contact angle measurement**). One method of substrate characterization that is gaining increasing popularity is that of inverse gas chromatography (IGC), which makes use of conventional gas chromatography (GC) equipment, operated in an unconventional way. The technique enables acid–base or donor–acceptor interactions (see **Acid–base interactions: introduction**) to be studied. This article gives a short account of the experimental arrangements. In **Inverse gas chromatography and acid–base interactions**, some of the methods used for relating IGC results to acid–base parameters are discussed.

The term *inverse* indicates that the material of interest is the stationary phase in the GC column rather than the volatile probe injected into the column. The experiment itself is very straightforward and is readily carried out using standard GC equipment. A schematic diagram of the IGC experiment is shown in Fig. 1. A column (of stainless steel or PTFE,



**Fig. 1.** Schematic representation of IGC experimental set-up





**Fig. 2.** Inverse gas chromatogram of hydrated alumina. Five interacting probes plus methane were injected simultaneously.<sup>1</sup> DEE – diethyl ether (Reproduced by permission of The Royal Society of Chemistry)

typically 1/8 in. -ca. 3 mm- internal diameter), packed with the solid of interest, is placed between the injector and the detector of the GC and the analytical measurements consist of injecting volatile probes with known properties through the column with an inert carrier gas (usually nitrogen). The retention time for each probe is related to the surface properties of the stationary phase. The usual practice is to carry out a series of injections for a homologous series of non-polar probes such as the *n*-alkanes. This gives information about the interactions associated with **Dispersion forces** (some authors talk in terms of **Lifshitz–van der Waals forces**). These results are then compared with those acquired using probes of known acid–base properties (such as chloroform, tetrahydrofuran and diethyl ether). A typical chromatogram for five probes and methane (injected as a non-interacting marker to define zero time) is shown in Fig. 2,<sup>1</sup> and the stationary phase is hydrated alumina. The *n*-alkane probes are pentane, hexane and heptane, while trichloromethane and diethyl ether (DEE) are used as a Lewis acid and base respectively. Note that the retention time for the alkanes increases with chain length (more CH<sub>2</sub> groups increase the dispersion force adsorption). The, still longer, retention times for the acidic and basic probes is a result of their additional acid–base adsorption, see Eqn. 4 in **Acid–base interactions**.

Further details of this method are given in the relevant texts.<sup>2,3</sup> IGC can be used for the characterization of inorganic surfaces such as pigments or fillers and even oxidized metal powders,<sup>4</sup> polymers,<sup>5</sup> the adsorption of organic molecules on inorganic surfaces,<sup>1</sup> carbon fibres<sup>6</sup> as well as many other materials. The only requirements to carrying out IGC appear to be a modest level of thermal stability as the chromatography column is always conditioned at a slightly elevated temperature, which can be as low as 50 °C, and the ability to present the material under test in coarse particulate/granular form (ca. 100 μm). The latter is readily achieved when dealing with fine powders by compaction, comminution

and sieving to obtain the required size fraction. This will provide information regarding surface properties; bulk properties can also be investigated by taking monolithic samples and converting to particles. For this reason, fibrous materials should not be chopped up as the results will then be a convolution of surface and bulk (from the fibre-ends) properties. In the case of carbon fibres (diameter ca. 6  $\mu\text{m}$ ), several tows of fibres are pulled through the GC column using a metal draw-wire, and as long as the packing density in the column is around 70% or better, reliable data can be obtained.

In adhesion studies, IGC is generally carried out at infinite dilution so that the adsorption energy depends entirely on interaction between probe and substrate, unaffected by interaction between probe molecules. Under these conditions, the adsorption of the probes follows Henry's law (amount adsorbed is proportional to concentration of probe) and can be described usefully as a zero coverage method. In this regime, Henry's Law applies rigorously, as the quantity of vapour is small ( $10^{-6}$ – $10^{-7}$  mol) and the surface area of the stationary phase (the sample under test) is higher than a planar solid as a finely divided sample, (particulate size  $\sim 100$   $\mu\text{m}$ ), is always used.

The inert carrier gas sweeps the adsorbed probe from the chromatographic column and the time required for complete desorption is recorded (either by analogue or digital means); this parameter is the retention time for the probe,  $t_R$ . For given experimental circumstances, this retention time  $t_R$  is proportional to the retention volume for the probe  $V_R$ :

$$V_R = DFt_R \quad [1]$$

where  $D$  and  $F$  are a pressure gradient correction factor and the corrected flow rate respectively. The net retention volume (also called *relative retention volume*),  $V_N$ , is the difference between retention volumes of probe and  $V_0$ , that of the non-interacting reference marker (usually methane):

$$V_N = V_R - V_0 = DF(t_R - t_0) = DFt_N \quad [2]$$

where  $t_0$  is the retention time of the marker and  $t_N$  is the net retention time of the solute (probe gas).

Some relations between the net retention volume and the acid–base characteristics of the adsorbent are discussed in **Inverse gas chromatography and acid–base interactions**.

### References

1. M. M. Chehimi, M.-L. Abel, J. F. Watts and R. P. Digby, *J. Mater. Chem.*, **11**, 533 (2001).
2. E. Pefferkorn, Ed., *Interfacial Phenomena in Chromatography*, Marcel Dekker Inc, New York, 1999. pp. 1–171, Part 1 Stationary Phase Characteristics.
3. D. R. Lloyd, T. C. Ward and H. P. Schreiber, Eds., *Inverse Gas Chromatography: Characterisation of Polymers and other Materials*, ACS Symposium Series Vol 391, American Chemical Society, Washington, DC, 1989.
4. J. H. Burness and J. G. Dillard, *Langmuir*, **7**, 1713 (1991).
5. E. Pigois-Landureau and M. M. Chehimi, *J. Appl. Polym. Sci.*, **49**, 183 (1993).
6. P. E. Vickers, J. F. Watts, C. Perruchot and M. M. Chehimi, *Carbon*, **38**, 675 (2000).

---

**Inverse gas chromatography and acid–base interactions**


---

MARIE-LAURE ABEL AND JOHN F WATTS

Inverse gas chromatography (IGC) is increasingly used to characterize the **Surface energy** of a solid, particularly its acid–base characteristics (**Surface energy components, Acid–base interactions**). In **Inverse gas chromatography**, a short description of the experimental arrangements is presented, and the meaning of net retention volume,  $V_N$ , given. In this article, some ways are discussed in which retention volume measurements may be used to characterize acid–base properties of a solid.

In adhesion studies, IGC is generally carried out at infinite dilution so that the adsorption energy depends entirely on interaction between probe and substrate, unaffected by interaction between probe molecules. Under these conditions,  $V_N$  will be proportional to the surface partition coefficient between mobile and stationary phase,  $K_S$ , and thus

$$V_N = K_S A c \quad [1]$$

where  $A$  is the total surface area of solid phase and  $c$  is a constant that depends on factors such as the weight of the stationary phase and the reference adsorption state.<sup>1</sup> Since  $K_S$  is essentially an equilibrium constant, it is related to the standard free energy of adsorption,  $\Delta G_a$ , by

$$-\Delta G_a = RT \ln K_S = RT \ln V_N + c' \quad [2]$$

where  $R$  is the gas constant,  $T$  is absolute temperature and  $c'$  is a constant related to  $c$  and  $A$ .

When the net retention volumes  $V_N$  are measured for a homologous series of alkane probes, a linear relationship is found when  $RT \ln V_N$  is plotted against the number of carbon atoms in the probe (or against the boiling points of the probes). From Eqn. 2, the gradient of this line represents the increment of standard free energy of adsorption,  $\Delta G_{CH_2}$  associated with a methylene group adsorbed on the particular solid involved.

Dorris and Gray<sup>2</sup> established a method to determine the dispersion force component of the solid surface energy,  $\gamma_s^d$  using  $\Delta G_{CH_2}$ . The free energy will be related to the work of adhesion ( $W_A$ ) via the product of Avogadro's number  $N$  and the surface area of a  $CH_2$  group  $a_{CH_2}$  ( $6 \text{ \AA}^2$ ). Moreover, for dispersion force interaction (see **Surface energy components**)

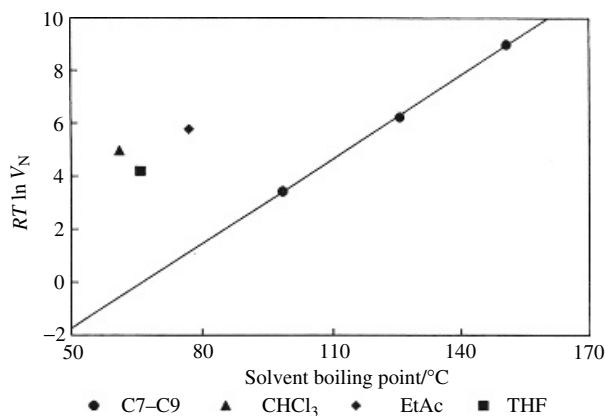
$$W_A = 2(\gamma_{CH_2} \gamma_s^d)^{1/2} \quad [3]$$

It follows that  $\gamma_s^d$  can be obtained from

$$\Delta G_{CH_2} = 2N a_{CH_2} (\gamma_{CH_2})^{1/2} (\gamma_s^d)^{1/2} \quad [4]$$

where  $\gamma_{CH_2}$  is the surface free energy of a solid containing only methylene groups such as polyethylene consequently only dispersion interactions are present ( $\gamma_{CH_2} = 36.8 - 0.058t$   $\text{mJ m}^{-2}$ ,  $t$  is temperature in  $^\circ\text{C}$ ).

If acid–base properties are sought, a similar plot may be constructed as a function of boiling points of the molecular probes,  $T_b$  (although other parameters can be used). The stronger adsorption of the acid–base probes is reflected in a deviation from the



**Fig. 1.** Adsorption of *n*-alkanes and polar probes (trichloromethane, ethyl acetate and tetrahydrofuran) on a photocured aromatic methacrylate resin<sup>8</sup> (The ordinate is numerically equivalent to  $\Delta G_a$  in  $\text{kJ mol}^{-1}$ )

“alkane” straight line as shown in Fig. 1. For polar probes interacting specifically with the stationary phase,  $\Delta G$  values are expected to show a positive deviation from the linear correlation defined by the *n*-alkanes. Assuming that dispersion and acid–base (AB) interactions are additive (**Surface energy components**), the subtraction of  $\Delta G_a^{\text{AB}}$  from  $\Delta G_a$  is straightforward and corresponds to the vertical distance between the *n*-alkane reference line (which gives  $\Delta G_S^{\text{d}}$ ) and the molecular probe of interest. Thus,

$$-\Delta G_a^{\text{AB}} = -(\Delta G - \Delta G_S^{\text{d}}) = RT \ln(V_N/V_{N_{\text{ref}}}) \quad [5]$$

where  $V_{N_{\text{ref}}}$  is the theoretical net retention volume for a hypothetical reference *n*-alkane having the same boiling point as the molecular probe.

#### *Gutmann's acceptor and donor numbers*

Thus, the approach just described enables the solid under investigation to be characterized in terms of  $\Delta G_{\text{CH}_2}$  for the *n*-alkane series and dispersion  $\Delta G_a^{\text{d}}$  and acid–base  $\Delta G_a^{\text{AB}}$  adsorption free energies for a range of selected molecular probes.

Gutmann<sup>3</sup> proposed that acid–base characteristics could be represented by a donor number, generally designated as DN (a single symbol, not a product) and an acceptor number AN\*. DN represents the base properties of the molecule and is essentially a molar heat of reaction with a reference acid, under standardized conditions. AN\* represents the acid properties of the molecule. The asterisk in AN\* indicates that the original Gutmann values have been corrected for dispersion force interactions and are expressed as molar enthalpies.<sup>4</sup> Jensen has discussed limitations of the Gutmann DN/AN theory.<sup>5</sup>

These concepts may be used to analyse the results of IGC, hence evaluating the relative acid–base properties of solids under investigation. Saint Flour and Papirer<sup>6</sup> argued that the acid–base component of the free energy of adsorption was related to the acceptor and

Table 1. Selection of acid–base probes used in IGC: boiling point ( $T_b$ ) and Gutmann donor (DN) and acceptor (AN\*) numbers<sup>1,4</sup>

Probe	$T_b/^\circ\text{C}$	DN/kJ mol <sup>-1</sup>	AN*/kJ mol <sup>-1</sup>	Characteristic
Diethyl ether	34.6	80.3	5.9	Basic
Dichloromethane	40.0	0.0	16.3	Acidic
Dichloroethane	57.3	0.0	7.5	Acidic
Trichloromethane	61.2	0.0	22.6	Acidic
Tetrahydrofuran	66.0	83.7	2.1	Basic
Ethyl acetate	77.1	71.7	6.3	Predominantly basic
<i>t</i> -Butanol	82.3	Unknown	31.8	Acidic
Dioxane	101.0	61.9	0.0	Basic

donor numbers. Schultz *et al.*<sup>7</sup> and later the present authors<sup>8,9</sup> have developed these ideas to give

$$-\Delta G_a^{\text{AB}} = K_{\text{D}}\text{AN}^* + K_{\text{A}}\text{DN} \quad [6]$$

where  $K_{\text{A}}$  and  $K_{\text{D}}$  are numbers representing respectively the acceptor and donor properties of the solid phase. Thus, for the material under test, a plot of  $-\Delta G_a^{\text{AB}}/\text{AN}^*$  versus (DN/AN\*) produces a linear correlation, of which the slope and intercepts are  $K_{\text{A}}$  and  $K_{\text{D}}$  respectively. These parameters are particularly useful in the comparison of similar materials in terms of small changes in acid–base properties<sup>8</sup> and the adsorption of polymeric molecules onto polymer substrates.<sup>9</sup>

A selection of typical probes used to assess surface characteristics, along with their relative acidic and basic properties (indicated by AN\* and DN parameters respectively) and boiling points, is presented in Table 1 compiled from published data.<sup>1,4</sup>

In summary, IGC is a simple, relatively inexpensive approach using standard GC instrumentation to obtain the surface thermodynamic properties of solids. The theoretical interpretation of the experimental results is now well established, and the deduction of acid–base properties of materials can now be regarded as being routine. IGC provides a complementary method to the use of wetting liquids, inasmuch as it probes the microscopic properties of the solid surface, (as the probe molecules are invariably small and in the gaseous phase, and are at infinite dilution, i.e. there is no interaction between adjacent probe molecules on the solid surface or in the gas phase), while the use of liquids in techniques such as dynamic contact angle analysis probes the macroscopic properties.

## References

1. J. C. Berg, in *Wettability*, J. C. Berg, Ed., Marcel Dekker, New York, 1993, p. 75.
2. G. M. Dorris and D. G. Gray, *J. Colloid. Int. Sci.*, **77**, 353 (1980).
3. V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978.
4. M. N. Belgacem and A. Gandini, in *Interfacial Phenomena in Chromatography*, E. Pefferkorn, Ed., Marcel Dekker, New York, 1999, p. 41.
5. W. B. Jensen, in *Acid-base Interactions: Relevance to Adhesion Science and Technology*, K. L. Mittal and H. R. Anderson, Eds., VSP, Utrecht, 1991, p. 11.
6. C. Saint Flour and E. Papirer, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 666 (1982).
7. J. Schultz, L. Lavielle, and C. Martin, *J. Adhesion*, **23**, 45 (1987).
8. A. M. Taylor, J. F. Watts, M.-L. Abel and M. M. Chehimi, *Int. J. Adhes. Adhes.*, **15**, 3 (1995).
9. M. M. Chehimi, M.-L. Abel and Z. Sahrroui, *J. Adhes. Sci. Tech.*, **10**, 287 (1996).

# J

---

## *JKR theory*

---

K KENDALL

The JKR theory<sup>1</sup> was developed in the early 1970s to account for the adhesion between spherical bodies, especially fine particles (see **Powder Adhesion**), making elastic contact. Previously, most studies of elastic contacts had presumed that bodies like steel railway wheels behaved as though adhesion was zero.<sup>2</sup> In other words, no adhesion interaction seemed to be acting in most engineering contact situations. Negligible adhesion force is generally detected as a wheel is lifted from a rail, and the size of the contact spot between wheel and rail can usually be predicted accurately from the laws of elastic deformation, without any molecular attractive forces.

Of course, it had been known for several centuries that short-range adhesion forces between molecules should act when elastic bodies make intimate contact. Newton had written in his book *Opticks* published in 1704 that “Particles attract one another by some Force, which in immediate Contact is exceeding strong. . . . and reaches not far from the particles with any sensible effect”, and he had produced some limited experimental evidence based on the contact of polished glass lenses.<sup>3</sup> He had seen a “black spot” where the glass surfaces deformed to make good contact and had also found sporadic adhesion. However, it was clear that small amounts of contamination or surface roughness could readily reduce the molecular attractive interactions at the contact to very small values,<sup>4</sup> such that the contacts did not exhibit significant adhesion.

This was the situation analysed and published by Hertz in 1882.<sup>5</sup> Hertz was a twenty-three-year-old assistant to Helmholtz in Berlin when he was stimulated by Newton’s results and derived the elastic theory of sphere contact in his Christmas vacation in 1880.<sup>2</sup> He found that the spot diameter  $d$  increased with the cube root of load  $F$ , showed that the elastic modulus  $E$ , Poisson’s ratio  $\nu$  and sphere diameter  $D$  were also important, and verified his equation

$$d^3 = 3(1-\nu^2)FD/E \quad [1]$$

which applies to equal spheres, by measuring contact spots for glass and metal spheres, as shown in Fig. 1.

For spheres of different diameters  $D_1$  and  $D_2$  and materials of different elastic constants,  $E_1, E_2$  and so on, the effective diameter  $D = 2D_1D_2/(D_1 + D_2)$  and effective modulus  $E/(1 - \nu^2) = 2E_1E_2/(E_1 + E_2)$  could be substituted into Eqn. 1, where  $E_1 = E_1/(1 - \nu_1^2)$  and  $E_2 = E_2/(1 - \nu_2^2)$ .

Hertz understood that the spheres pressed into each other to give a hemispherical pressure distribution across the black spot, with maximum pressure  $P$  in the middle, falling as  $P(1 - z^2/d^2)^{1/2}$  to zero pressure at the edge of the contact spot, where  $z$  was the diameter of a concentric circle within the contact spot of diameter  $d$ . The contact size was zero at zero load and there was no adhesion.

However, Eqn. (1) was not consistent with the experiments of Bradley,<sup>6,7</sup> who found that small adhering spheres made from molten silica, less than 1 mm diameter, would stick together rather well, requiring a tensile load to pull them apart. Bradley showed that the adhesive force, that is the force required to pull the two equal spheres apart, was proportional to sphere diameter. The spheres were still deforming, but now the pressure was generated by van der Waals molecular attractions at the contact spot and not by the external load (see **Adhesion – fundamental and practical, Bonds between atoms and molecules, Lifshitz-van der Waals forces**). The simplest way to take this into account was to assume that the molecular attractions were acting like an external load and to use Eqn. (1) to describe the results, as Derjaguin<sup>8</sup> did in 1934. This basic thermodynamic argument was correct because it equated the work done by the surface attractions against the work of deformation in the elastic spheres. However, the deformation Derjaguin used was not correct because he did not take into account the effect of surface attractions on the pressure distribution at the contact. Johnson<sup>2</sup> had shown that the pressure distribution within an adhesive contact could be described by adding two simple stress distributions together as shown in Fig. 2. However, he was puzzled by the resulting infinite stresses at the edge of the contact, which he therefore expected to fail under the high tension.

But infinite stress is always present in cracking problems and poses no difficulty if an energy-balance theory of crack equilibrium is used (see **Fracture Mechanics**). Applying this method to the above stress distribution gave the following equation, the so-called JKR equation, for the elastic contact spot diameter  $d$  of equal spheres, diameter  $D$  and

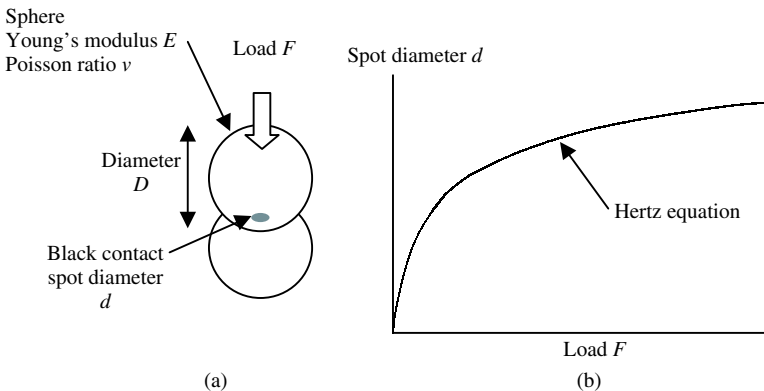
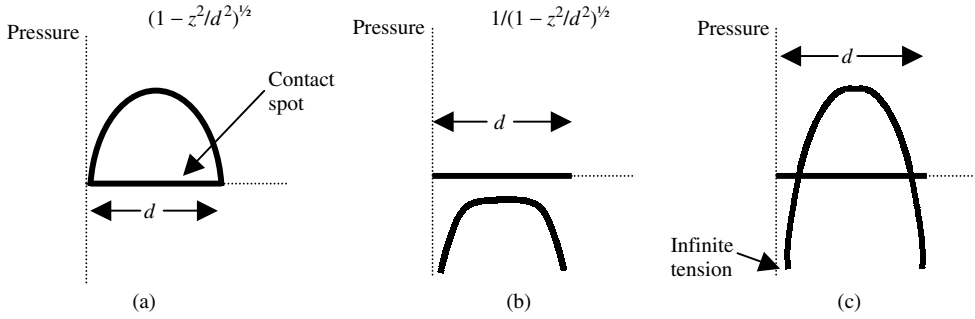


Fig. 1. (a) Two elastic spheres pressed into contact; (b) increase in spot diameter with load



**Fig. 2.** (a) Hemispherical compressive stress at Hertzian contact spot; (b) rigid punch tensile stress distribution; (c) resultant pressure distribution obtained by adding (a) and (b)

elastic constants  $E$  and  $\nu$ , with short-range work of adhesion  $W$ :

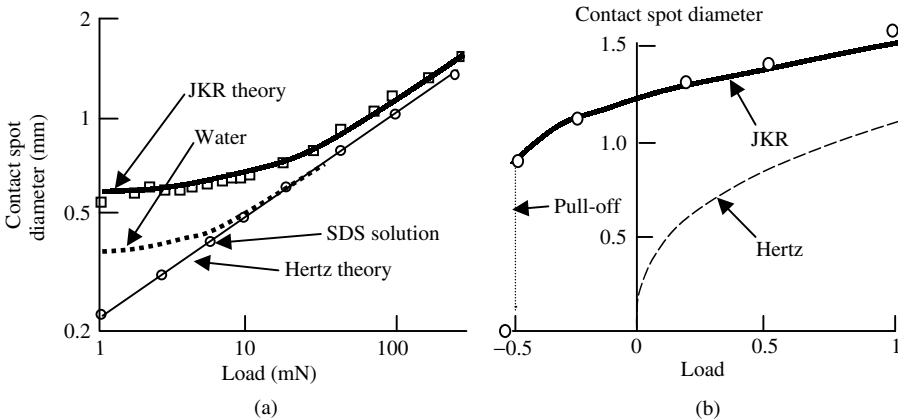
$$d^3 = 3(1 - \nu^2)D\{F + 3\pi WD/4 + [3\pi WDF/2 + (3\pi WD/4)^2]^{1/2}\}/E \quad [2]$$

Results on rubber/rubber and gelatin/poly(methyl methacrylate) contacts fitted Eqn. 2 extremely well, as shown in Fig. 3, and allowed the work of adhesion to be measured. It turned out later that a similar mathematical argument had been produced by Spurling in 1964, but he had found no experimental evidence to support his theory.<sup>4</sup>

From the contact spot size  $d_0$  at zero load, where

$$d_0^3 = 9\pi WD^2(1 - \nu^2)/2E \quad [3]$$

the work of adhesion fitting the results for dry rubber contact was  $71 \text{ mJ m}^{-2}$  and that for gelatin on poly(methyl methacrylate) was  $105 \text{ mJ m}^{-2}$ . When water was present at



**Fig. 3.** (a) Results for contacts between two rubber spheres, measured optically,<sup>1</sup> on log scale; (b) results for gelatin to glass contact plotted on linear scale showing tensile loads



the rubber contact, the work of adhesion dropped to  $6.8 \text{ mJ m}^{-2}$ , and this was consistent with Young's equation for the contact angle of  $66^\circ$  measured for water droplets sitting on the smooth rubber. This was the first time that Young's equation had been verified by direct measurement. When 0.01 molar sodium dodecyl sulphate (SDS) solution was the immersion medium, the rubber contact size fitted the Hertz equation down to the lowest loads obtainable, showing that the work of adhesion was less than  $1 \text{ mJ m}^{-2}$ . This was consistent with the wetting behaviour of the soap solution on the rubber surface.

When tensile loads were applied to pull the two spheres apart, an equilibrium contact spot size could be obtained at certain loads, but below a critical contact size, equilibrium could no longer be found and the surfaces then came apart rather quickly at a load given by

$$F = -3\pi WD/8 \quad [4]$$

where  $D$  was the diameter of the equal spheres.

The JKR equation is usually employed to interpret the results of the **Surface forces apparatus** and of **Atomic force microscopy**, which may be employed to study adhesion between two surfaces.

### References

1. K. L. Johnson, K. Kendall and A. D. Roberts, *Proc. R. Soc. Lond.*, **A324**, 301 (1971).
2. K. L. Johnson, *Contact Mechanics*, Cambridge University Press, Cambridge, 1985.
3. I. Newton, *Opticks*, 1704, reprinted by Dover, 1952, p. 397.
4. K. Kendall, *Molecular Adhesion and its Applications*, Kluwer, New York, 2001.
5. H. Hertz, in *Miscellaneous Papers*, P. Lenard, Ed., Macmillan, London, 1896, p. 146.
6. R. S. Bradley, *Philos. Mag.* **13**, 853 (1932).
7. R. S. Bradley, *Trans. Faraday Soc.* **32**, 1088 (1936).
8. B. V. Derjaguin, N. A. Krotova and V. P. Smilga, *Adhesion of Solids*, (translated by R.K. Johnson), Consultants Bureau, London, 1978, pp. 423–442.

---

## Joint design – cylindrical joints

---

C WATSON\*

Most adhesive joint configurations are either “flat” or “cylindrical”: this article is concerned with the latter type. Broader aspects of design are discussed in **Joint design – general**.

### Cylindrical joints

Some typical cylindrical joints are gear to shaft, rotor to shaft, bearing into housing, tube into casting, cylinder liner into engine block, pulley to shaft, fan to shaft, trunnions into rollers and bushings into housings.

Traditional methods of holding cylindrical components together, apart from adhesives, are mechanical fit (press fit or shrink fit), keys, circlips, set screws, splines, welding

and bolting. As far as the designer is concerned, the traditional methods work – most of the time. However, traditional methods may be heavier and cost more. Also, mechanical fits are not always strong enough, and ingress of moisture into a joint can lead to fretting corrosion.

Adhesive bonding can eliminate extra parts, reduce machining operations and ease manufacture in some instances.

### Designing cylindrical joints

The following calculations apply to **Anaerobic adhesives** and use of a computer-aided design program called RETCALC.<sup>1</sup> The program could be modified for application to other adhesives provided that appropriate data for their properties were inserted.

Anaerobic adhesives can be used to retain cylindrical components in conjunction with a clearance fit or an interference fit.

*Using anaerobic adhesives with a clearance fit*<sup>1-3</sup> The axial force to break a joint can be expressed as

$$F = A\tau f \quad [1]$$

where  $F$  is the breaking force,  $A$  the surface area of bond,  $\tau$  the shear strength of adhesive and  $f$  the product of a number of correction factors, determined empirically, to take into account deviations from the simple theory on which the equation is based.

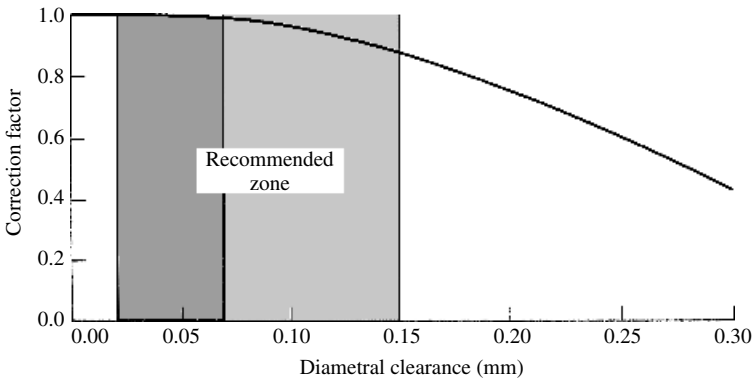
The operating temperature will affect the shear strength of the adhesive: this can be allowed for by use of a suitable factor. Different substrates have different mechanical properties: the substrate factor is unity for mild steel, but varies from 0.3 to 0.8 for aluminium, according to the alloy.

Three further factors are introduced to allow for joints of differing dimensions. The “geometry factor” varies according to the length to diameter ratio and the bonding area. A “diametrical clearance” factor falls below unity as the clearance increases above about 0.07 mm (Fig. 1). The type of assembly – whether a clearance fit, press fit or shrink fit – is allowed for via an “assembly factor” (Table 1). Data are available for certain types of adhesives.<sup>1,2</sup>

*Using anaerobic adhesive with an interference fit* The theory for a clearance fit can simply be modified by adding a frictional force term to the term for ultimate load of the adhesive

Table 1. Factor  $f_t$ : assembly factor

Type of assembly	Clearance fit	Press fit	Shrink fit
Assembly factor	1.0	0.5	1.2
In clearance fit	Adhesive fully fills joint		
In press fit	Some adhesive is scraped off during assembly		
In shrink fit	Adhesive fills joint and is maintained under compressive load		



**Fig. 1.** Diametrical clearance factor  $f_2$  used in the design of cylindrical joints (see Eqn. 1 and text, standard = 0.05 mm)

in shear. Thus, the expression for the axial force to break the joint is

$$F = A(\tau f + P\lambda) \tag{2}$$

where  $P$  is the radial contact pressure between the faces and  $\lambda$  is the coefficient of friction;  $\lambda$  is difficult to estimate realistically, but a value of 0.2 for steel on steel is usually found to give a realistic estimate of strength. The maximum torque that the joint can transmit can be obtained by multiplying  $F$  by half the diameter of the inner component.

From the derivation of the expression for  $F$ , it is clear that they represent an estimate of the ultimate strength of the joint resulting from the application of a steadily applied load. Under dynamic or fatigue conditions, the strength of the joint would be considerably lower than the static value calculated (see **Durability: fatigue**). In order to determine the magnitude of the reduction, appropriate fatigue tests, establishing the “ $S/N$ ” curve, would have to be undertaken. These joints usually show a fatigue limit, so it is often possible to apply a safety factor to the static strength calculated. Thus, for bonded interference fit joints, torsionally loaded, a factor of 0.35 is normally adequate.

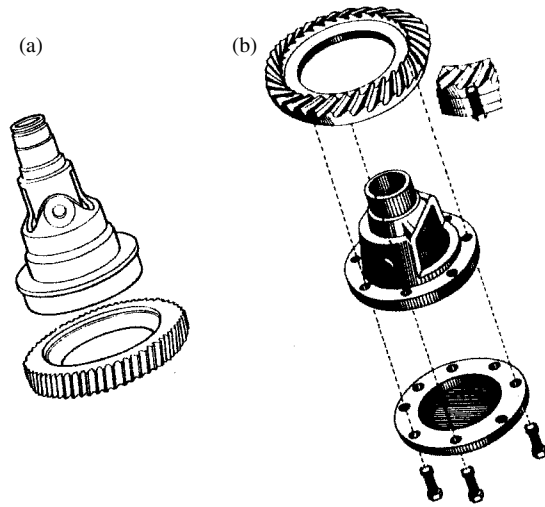
*Bonding a ring gear to a differential housing* In fitting a ring gear to differential housing on the Renault R9, the original fitting method was to use a mounting plate with mechanical fasteners (see Fig. 2a).

The Renault designers wanted to reduce weight and cost. They changed the design (see Fig. 2b) to transverse drive and shrink fitted the gear to the differential with a 0.25 mm interference. This, however, did not give the required dynamic strength of 3420 N m. Increasing the interference would have overstressed the gear. They therefore chose to use an anaerobic adhesive with a reduced shrink fit of 0.80 mm nominal, which gave the required strength. The calculation is given below.

Correction factors:

$$f_1 = 0.8 \text{ (steel on cast iron)}$$

$$f_2 = 1.2 \text{ (shrink fit, Table 1)}$$



**Fig. 2.** Fitting of ring gear to differential housing on Renault R9: (a) old design with mechanical fasteners; (b) new design with adhesive bond

$$f_3 = 0.6 \text{ (geometry factor)}$$

$$f_4 = 0.9 \text{ (temperature } 12^\circ\text{C)}$$

$$f = f_1 \times f_2 \times f_3 \times f_4 = 0.52$$

$$\tau = 25 \text{ N mm}^{-2} \text{ for Loctite adhesive}$$

$$\text{Adhesive strength} = 25 \times 0.52 = 13 \text{ N mm}^{-2}$$

$$\text{Mechanical strength} = P \times \lambda = 2.3 \text{ N mm}^{-2}$$

$$\text{Diameter} = 140 \text{ mm}$$

$$\text{Length} = 24 \text{ mm}$$

Substituting these values in the formula gives for static torque

$$3.14 \times 140 \times 24 \times \frac{140}{2} (25 \times 0.52 + 2.3) \text{ N m} = 11,300 \text{ N m}$$

$$\text{Dynamic fatigue factor} = 0.35$$

$$\begin{aligned} \text{Estimated dynamic torque} &= 11,300 \times 0.35 \text{ N m} \\ &= 3955 \text{ N m} \end{aligned}$$

$$\text{Actual required} = 3420 \text{ N m}$$

Other **Automotive applications** of adhesives discussed elsewhere.

### Conclusion

Designers should contact adhesives manufacturers who will have data for their own adhesives and can advise on joint design for flat and cylindrical joints.

### References

1. *IBM PC-compatible Software Package Retcalc*, available from Loctite Ltd, Welwyn Garden City, Herts.
2. Loctite World Design Handbook, Calculating the Strength of Bonded Cylindrical Assemblies, <http://content.loctite-europe.com/wwdh/us/i132ch07.htm> (accessed 15.4.04).
3. G. Haviland, *Machinery Adhesives for Locking, Retaining and Sealing*, Marcel Dekker, New York, 1986.

---

## Joint design – general

---

C WATSON\*

Most adhesive joint configurations can fall into one of two categories: flat joints and cylindrical joints.

For the best possible performance, joints should be specifically designed for adhesive bonding. In a few cases only can an adhesive be used on a joint not specifically designed for adhesives – mainly cylindrical joints. Bond stresses, materials, type of adhesive, surface preparation, methods of application and production requirements can then all be considered in relation to each other at the outset. The designer should consider especially the effect of shear, tension, cleavage and peel stresses upon the joint (Fig. 1) (see **Joint design: strength and fracture perspectives**).

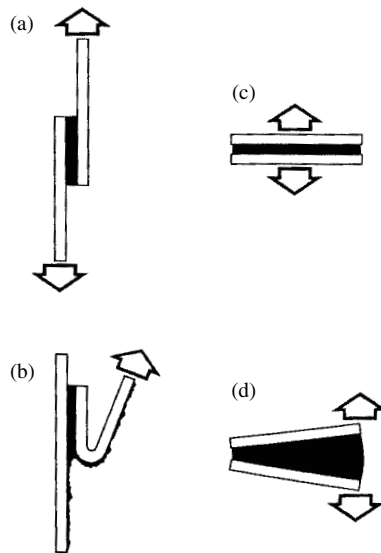
Tensile shear-loaded joints (Fig. 1a) have the highest strength (see **Shear tests**). Stress is distributed over the bond area. Joints that have load applied as a shear loading are most resistant to bond failure.

Tensile loading (Fig. 1b) will apply stress over the total bond area. However, care should be taken that joint components have the rigidity to maintain this even loading. When deflection under load occurs, a cleavage stress could arise, resulting in early bond failure (see **Tensile tests**).

Cleavage loading (Fig. 1c) will concentrate stress at one side of the joint. The bond area will have to be increased to withstand this uneven loading.

Peel strength is usually the weakest property of a joint. A wide joint will be necessary to withstand peel stress (Fig. 1d), plus the use of an adhesive with high peel strength (see **Peel test**).

For an adhesive to be used, a joint must allow the easy application of the adhesive, must allow for the adhesive to cure fully and must be designed to give uniform stress. Even in a simple face-to-face joint, it must be possible to apply adhesive to one surface and for it to remain there until the two parts are brought together and after that until curing takes place. These requirements highlight the need for a choice of thin, thick or thixotropic adhesives.



**Fig. 1.** Types of stress to which an adhesive joint may be subjected: (a) tensile shear; (b) tensile loading; (c) cleavage; (d) peel

### *Good and poor designs*

Figure 2 shows schematic diagrams of some good and poor joint designs related to the preceding comments. It can clearly be seen that the major difference between good and poor is to restrict peel–cleavage stress of the joint.

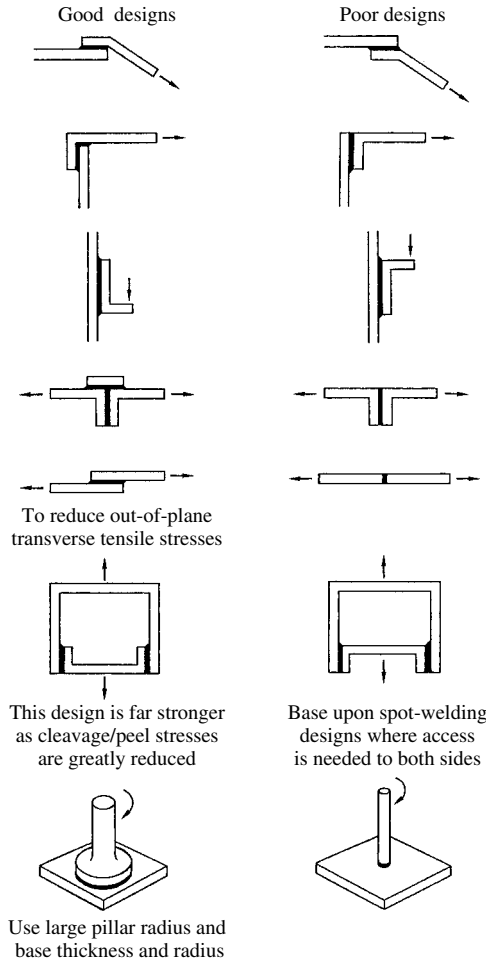
### *The bond line*

The gap between the parts, and therefore the thickness, of the adhesive film has an important bearing on the characteristics of the joint. In terms of simple strength, a thick bond line will generally be a weakening feature since the mechanical strength of the unsupported resin film is likely to be less than that of the substrates.

A thick bond line can, however, confer advantages. The adhesive is generally more flexible than the adherents or substrates. This is particularly so in most engineering applications where metals or other rigid materials can be bonded. Because of this, a thick bond line can offer a capacity to absorb some impact energy, thus increasing the strength of the bond under this type of loading.

Again, if dissimilar materials are being bonded and there is a differential change in dimensions of the two surfaces due, for example, to differential expansion by heating, then the thick film may be better able to accommodate this without being stressed to failure. Consideration of bond-line thickness leads immediately to the question of environmental resistance.

Adhesive bonds will always be susceptible to environmental attack, and it is essential that any such attack should not reduce the strength of the bond to an unacceptable level. The most important factor here is the correct choice of adhesive, but design of the joint can make a significant difference. Thus, a thick bond line offers a ready path for access



**Fig. 2.** Representations of good and bad joint design. (Reproduced with permission from A J Kinloch, *Adhesion and Adhesives: Science and Technology*, Chapman and Hall, London, 1987)

by moisture or other solvents, which might be able to diffuse through the cured adhesive (see **Durability**).

*Select References*

W. A. Lees, Ed., *Adhesives and the Engineer*, ASME Professional Engineering Publishing, 1989.  
 R. B. Krieger, Adhesive bonding design and analysis, in *ASM Engineered Materials Handbook Vol. 3 Adhesives and Sealants*, M. M. Gauthier, Ed., ASM International, 1990, p. 459.  
 F. E. Penado and R. K. Dropek, in *Numerical Design and Analysis*, M. M. Gauthier, Ed., ASM International, 1990, p. 477.  
 R. W. Johnson, in *Design Proof Testing*, M. M. Gauthier, Ed., ASM International, 1990, p. 533.  
 Loctite World Design Handbook, <http://content.loctite-europe.com/wwdh/us/a001welc.htm#top> (accessed 15.4.04)

---

**Joint design: strength and fracture perspectives**

---

DAVID A DILLARD

There are many approaches and philosophies related to engineering design, and the field of adhesive joint design is no exception. There are two basic approaches, although each has a number of variants. In the *strength* approach, one compares maximum predicted stresses or strains to some yield or ultimate values of the respective quantity. The *fracture* approach, on the other hand, is based on comparing the available strain energy release rate (or stress-intensity factor) to a critical value for the material system. From a design standpoint, both approaches have advantages and disadvantages, and both have their proponents and detractors. Traditional design methods have been based on the strength approach, and this remains the emphasis in many undergraduate engineering education programs. The fracture-mechanics approach is becoming increasingly popular, however, and has made important inroads in many design areas, as well as in fundamental and applied research.

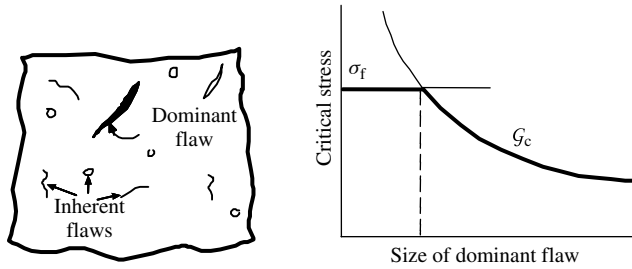
Both strength and fracture approaches rely on estimating the stress, strain, or energy state in a proposed design, and comparing this with material properties obtained on neat adhesive samples, or preferably from carefully chosen bonded joints. One reason the strength approach has worked well with monolithic materials is that material properties may be obtained on simple specimens that provide a uniform stress state throughout the test region. As such, material properties can be accurately determined because of the uniformity of the stress state. A major complication exists with tests on adhesive bonds, however, since stress states are typically highly non-uniform. Unlike tests on materials, tests of adhesive bonds are really tests of *structures*; the adhesive layer is subjected to complex stress states that complicate determination of useful adhesive properties. The effects of bond thickness, spew, inherent flaws, stress singularities, adherend behaviour and many other factors contribute to determine the breaking load of adhesive joints (see **Stress distribution: stress singularities**, **Stress distribution: bond thickness** and **Tests of adhesion**). The situation is so complex, that ASTM D 4896<sup>1</sup> states that

“Single-lap tests, like those described in Test Methods D 906, D 1002, D 2339, D 3163, D 3164, D 3165 and D 3528, are not suitable for determining the true shear strength of an adhesive. The apparent shear strength measured with a single-lap specimen is not suitable for determining allowable design stresses, nor is it suitable for designing structural joints that differ in any manner from the joints tested without thorough analysis and understanding of the joint and adhesive behaviours”. See also **Shear tests**.

Clearly, caution is needed when selecting and testing adhesive joints, and when using the properties to predict the strength of other bonded configurations. Some geometries such as the thick adherend specimen, the Arcan specimen, and the **Napkin ring test** specimen may result in somewhat more uniform stress states and may be more useful in predicting bond strength. Some success has been achieved with using properties obtained from neat adhesive coupons, particularly where bond failures are cohesive in nature. Direct comparisons of the uniaxial stress state in most neat specimens and the complex triaxial stress states present in bonded joints are tenuous at best.

Designing with **Fracture mechanics** also has limitations. Fracture energies are normally obtained in a pure loading mode (i.e. I, II or III), or at a limited number of mixed-mode conditions. Actual bonded structures are often subject to more complex mode mixtures. Although fracture energies associated with monolithic materials may be considered as material properties, this may not be the case for adhesive joints, where





**Fig. 1.** When a flaw becomes dominant, a fracture-based approach is most appropriate

bond thickness, adherend stiffness, and other factors may affect the measured properties. Fracture properties of polymers, including adhesives, are often quite sensitive to temperature, rate, diluents such as moisture, and other environmental parameters. One of the most frequently cited disadvantages to the fracture approach is the need to know or assume the size, location, and orientation of initial flaws, since fracture mechanics can only be applied to a real or assumed crack. The assumption that flaws of the largest undetectable size may occur at the worst possible location and orientation has been a cornerstone of many successful applications of fracture mechanics in engineering design.

In principle, strength and fracture-mechanics approaches may both converge. The question is really how large is the dominant flaw compared to other inherent flaws, voids, cracks or debonds present within the bonded joint. If there is no dominant flaw, concepts such as yield strength, ultimate stress or failure strain may be appropriate. If there is a dominant flaw that is larger than the defects that occur in typical test specimens, a fracture-mechanics approach offers the simplest means to evaluate the performance. Where no dominant flaw is present, fracture mechanics may still be applicable, but one must determine or estimate the size of the inherent flaws.<sup>2</sup> These two ideas are demonstrated schematically in Fig. 1.

A further discussion of the topic can be found in **Engineering design with adhesives** and other relevant considerations in **Durability: creep rupture** and **Durability: fatigue**.

### References

1. ASTM D4896, *Annual Book of ASTM Standards*, Vol. 15.06, ASTM, 419–424 2001.
2. A. J. Kinloch and S. O. Osiyemi, *J. Adhesion*, **43**, 79–90 (1993).

### Select References

- A. J. Kinloch, *Adhesion and Adhesives Science and Technology*, Chapman and Hall, 1987.
- R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*, 2nd edn, Chapman and Hall, 1997.
- G. P. Anderson, S. J. Bennett and K. L. DeVries, *Analysis and Testing of Adhesive Bonds*, Academic Press, 1977.
- L. Tong and G. P. Steven, *Analysis and Design of Structural Bonded Joints*, Kluwer Academic Publishers, 1999.

# L

---

## *Laminating*

---

R J ASHLEY

For some industries and applications, for instance in the **Packaging industry**, the use of a single web of material may not satisfy all the properties demanded. It is therefore of benefit to be able to combine the properties of several and differing materials in order to achieve the performance. A particularly useful means of tailoring exact specifications is to resort to lamination technology. This is essentially based on reel-fed operations, although some laminates may be produced by compressing sheets of material together in a hot press (e.g. decorative laminates). The methods described here rely on adhesive components coated on to a substrate forming an interface for chemical bonding to take place. The use of functionally active adhesive materials enables dissimilar substrates to be bonded satisfactorily.

There are three basic categories of adhesive bonding used, each requiring specific equipment. Selection of a particular technique depends on the nature of the substrates used and final application. There are a considerable number of adhesive laminating materials and techniques or variants upon the theme, but it can be reduced to the three basic types of material, aqueous based (see **Emulsion and dispersion adhesives**), **Solvent-based adhesives**, solventless 100% solids or **Hot melt adhesives**, and to the two basic techniques, wet and dry lamination.

Wet laminations are those in which the adhesive, based either on water or organic solvents, remain in the laminate during lamination and is dried later. Hence, the process is suited to applications in which one or more of the substrates is porous to facilitate drying of the adhesive so that solvent may permeate out of the laminate or absorb into one of the substrates. Adhesive is applied, usually by roller coating or air knife, to one of the substrates and while still wet a second substrate is combined at a nip roller. The laminate may be left to air dry or passed through a heated oven to remove solvent and build up bond strength. In general, this method is not suited to applications using plastic films,

but confined to areas in which paper and board form part of the laminate, for example, paper/foil, paper/paper. Achievement of adequate bond strength is usually indicated by fibre-tearing characteristics. The type of adhesives used is mainly the water-based natural products such as starch and dextrin, polyvinyl acetate or latexes.

Dry lamination can be used with a wider range of substrates such as coated papers, foils and plastic films. The adhesives may be water or solvent based and generally use cross-linking agents to achieve full bond strength. The adhesive film is coated on to one of the substrates generally by a roller system and the coated web passed through a drying oven to remove the solvent, leaving a slightly tacky surface. A second web may then be combined at a high temperature and pressure nip to enable good contact and flow of the adhesive. Initial tack or "green strength" should be sufficient to hold the plies together and resist forces due to relaxation of webs and full strength generally develops over about 24 h. Additional plies can be built up by successive passes through the process or several adhesive operations may be combined by using multi-head machines. The adhesives are generally solvent based although considerable development has taken place in this area to reduce the type of solvent and content. Typically, the adhesive is a two-part **Polyurethane** to achieve highest temperature and product resistance. One part will normally be a polyester resin combined with an isocyanate cross-linking agent. Over recent years, this has caused much development mainly to control residue levels and low molecular weight by-products. A wide range of adhesive compositions is available to satisfy particular bonding situations. An area of development has been the solvent-free polyurethanes that require low coat weights and special roller application systems. Initial formulations were single-part moisture-curing systems that relied on atmospheric or adsorbed moisture on substrates to achieve cross-linking, but these were replaced by two-part catalysed systems. A main advantage is that drying ovens are not required, thus resulting in cheaper equipment. Often, a solvent-free adhesive application unit will be added at the end of a multi-station printing machine so that several operations can be carried out in a single machine pass. Typical laminating equipment will have a web width of over 1 m and run at speeds in excess of 200 m min<sup>-1</sup>.

The method for hot melt adhesive lamination consists of heating the melt to a closely controlled temperature and applying to the most temperature resistant substrate by roller or similar applicator to obtain a smooth layer. Combination with a second web is achieved at a temperature-controlled nip unit followed by cooling. A pre-made film of hot melt material may be interleaved between two substrates at a high temperature nip to achieve lamination (thermal bonding). The adhesives are generally complex formulations typically based on **Ethylene-vinyl acetate copolymers** although many other polymers may be used. Cross-linkable grades have been developed to improve heat resistance of laminates.

Most of the adhesives used in laminating require a period for cross-linking and development of full bond strength. There has been some interest in the field of UV or electron beam systems where several layers can be combined and cured in-line. Progress has been limited by the availability or installation of suitable equipment and development facilities.

In many laminating operations, plastic films are used as part of the composite. Since many of these will have poor surface-wetting characteristics, especially to water, it is necessary to use surface-modification techniques in line with the laminating operation to enhance adhesion (see **Wetting and spreading**). One system commonly used is **Corona discharge treatment**.

A common procedure used to assess adhesion or bond strength in laminated materials is the **Peel test**.

### Select Reference

R. J. Ashley, D. Briggs, K. S. Ford and R. S. A. Kelly, in *Industrial Adhesion Problems*, D. M. Brewis and D. Briggs, Eds., Orbital Press, Oxford. 1985, Chap 8.

---

## *Lifshitz-van der waals forces*

---

D E PACKHAM

As discussed in the article on **Bonds between atoms and molecules**, weak forces act between molecules. These are widely referred to as van der Waals forces, and are important in many phenomena associated with adhesion, including **Wetting and spreading**. Three categories of van der Waals force are distinguished: London dispersion forces, Debye induction forces and Keesom orientation forces. These differ according to the type of dipole–dipole interaction involved (see **Dispersion forces** and **Polar forces**). The total interaction energy is often assumed to be the sum of the individual dispersion, induction and orientation interaction energies. For an assembly of molecules, pairwise addition of individual interaction energies is employed.

This approach enables the interactions between macroscopic bodies to be calculated, making assumptions about their molecular structure. The van der Waals attraction energy between individual molecules at separation  $r$  is given by

$$U = -A/r^6 \quad [1]$$

where  $A$  is the van der Waals attraction constant. Explicit forms for  $A$  are given for the different types of van der Waals force in articles on **Dispersion forces** and **Polar forces**. Assuming additivity, expressions for interaction energies,  $W$ , can be derived<sup>1</sup> for two spheres

$$W = -(H/6D)(R_1 R_2 / \{R_1 + R_2\}) \quad [2]$$

a sphere and a flat surface

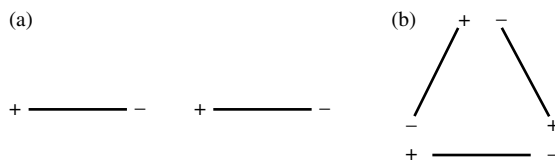
$$W = -HR/6D \quad [3]$$

two parallel surfaces

$$W/A_s = -H/12\pi D^2 \quad [4]$$

where  $D$  is the distance between the surfaces,  $R$ ,  $R_1$  and  $R_2$  are radii of the spheres and  $A_s$  is surface area. The proportionality constant  $H$  is the Hamaker constant, which, in this theory, is related to the van der Waals attraction constant,  $A$ , and the densities,  $\rho_1$  and  $\rho_2$  (molecules per unit volume) of the two bodies concerned:

$$H = \pi^2 A \rho_1 \rho_2 \quad [5]$$



**Fig. 1.** Lowest energy configuration of (a) two isolated dipoles, (b) three dipoles. With increasing numbers of dipoles, more complex structures will occur

It is increasingly argued that such pairwise addition is invalid in condensed phases, solids and liquids where the molecules are in close proximity.<sup>1-3</sup> The polarizability of a molecule will be altered by the proximity of other molecules. Moreover, a collection of dipoles cannot take up the lowest energy head to tail configuration of an isolated pair, Fig. 1. From this it follows that summations of interaction energies, such as those given in **Dispersion forces** and **Polar forces** derived for isolated molecules in a gas, will not give good results when applied to solids and liquids.

Lifshitz avoided this problem of additivity by developing a continuum theory of van der Waals forces that used quantum field theory. Simple accounts of the theory are given by Israelachvili<sup>1</sup> and Adamson.<sup>3</sup> Being a continuum theory, it does not involve the distinctions associated with the names of London, Debye and Keesom, which follow from considerations of molecular structure. The expressions for interaction between macroscopic bodies (e.g. Eqns. 2-4) remain valid, except that the Hamaker constant has to be calculated in an entirely different way.

Considerations, such as these, have lead Good<sup>2</sup> and others to use the term “Lifshitz-van der Waals forces” when referring in the context of **Contact angles and interfacial tension** and **Surface energy components** to weak interactions between molecules.

### References

1. J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd Edn, Academic Press, 1991.
2. R. J. Good, *J. Adhes. Sci. Technol.*, **12**(6), 1269 (1992).
3. A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, 6th edn, Wiley, Chichester, NY, 1997.

# M

---

## *Mechanical theory of adhesion*

---

K W ALLEN

### *Introduction*

One of the first clear statements of a mechanical explanation for adhesive phenomena is due to McBain and Hopkins, who in 1926 concluded that joints might be of two types. In one of these, a mechanical type of mere embedding existed. Thus, the idea grew of an interlocking of the adhesive with the texture of the surface and of the advantage of a rough surface. It was a statement of the simple and intuitive explanation that practical men had evolved for themselves over a considerable period. It sufficed so long as the materials being joined were simple fibrous materials such as wood or leather, although it had shortcomings even for these. Once adhesives were used, with even modest success, for smooth impervious surfaces it was clearly inadequate, at least for these materials. Nevertheless, it persisted (and persists now) to a surprising extent. It is now apparent that this concept has to be considered on two different scales.

### *Interlocking on a macro scale*

While it is now clear that a mechanical interlocking cannot be an adequate explanation of all adhesion, there are several instances where it is of major importance on a macroscopic scale.

The classical work of Borroff and Wake in 1949<sup>1</sup> on the adhesion between the textile cords and the rubber casing in automobile tyres demonstrated that the only significant factor was the penetration of the fibre ends into the rubber. These fibre ends originated from the natural textile fibre (usually cotton), and it was their absence in synthetic fibres (e.g. nylon monofilament) that caused the difficulty in using these for this product. Any specific interaction between the rubber and the fibre was insignificant and only affected

the length of fibre end that must be embedded. There was no significant penetration of the rubber between the strands of the yarn. The bond strength between rubber and cord depended solely upon the number of fibre ends involved and the depth to which they were embedded.

Rather similar is the case of adhesion to leather, which is of particular importance in the footwear industry. It has been shown that the fibres of the surface must be separated and raised so that they become embedded in the adhesive layer if a satisfactory bond is to be achieved.

A quite different example is the process known as “electroless” plating of plastics. There are a number of plastic materials that may be coated with a thin layer of metal by this process. The base materials are usually either high-impact polystyrene or ABS (acrylonitrile–butadiene–styrene), both of which have a continuous phase of glassy polymer with an elastomer dispersed in it. The process involves first an etching with chromic acid, which oxidizes and removes the elastomer from the surface layer to leave a porous, spongy structure. Then an initial metal layer (usually copper) is deposited by chemical reduction. Once this has been established, it is built up and an appropriate metallic surface layer is added by conventional electroplating. A very extensive study by Perrins and Pettett<sup>2</sup> showed that there are two mechanisms simultaneously involved in this adhesion: one a chemical relationship between the metal and the plastic, the other, a mechanical interlocking between the metal and the porous surface, which is controlled by the topography of the plastic surface.

Reference should also be made to **Thermal spray coatings used for adhesion and Wood adhesives – basics**.

### *Interlocking on a micro scale*

For a considerable period, it was common practice to dismiss mechanical interlocking as a “hook and eye” conception and as irrelevant; however, that view has changed more recently. The beginning of this change can be traced to Packham’s work<sup>3,4</sup> on the adhesion of molten polyethylene to aluminium. He was exploring the effects of various treatments of the aluminium surface on the adhesion, and particularly the effects of various oxidation processes. It was well known that by **Anodizing** aluminium in an acidic electrolyte, the oxide film produced consisted of a dense layer next to the metal covered by a porous layer. The pores were regular in size and shape and were orientated with their axis normal to the surface of the metal. These pores had diameters in the range 120–330 Å and their size and number was governed by the conditions of anodizing. Packham showed a direct relationship between the adhesive bond strength and the size and surface density of these pores. Further, he obtained electron micrographs of polymer surfaces that had been in contact with the aluminium oxide, which showed clusters of tufts. These tufts were 500–2000 Å in diameter and each consisted of a cluster of whiskers that had aggregated together. These individual whiskers had originally been inside the pores in the oxide film. Evidently, the adhesion involved the penetration of polymer into the pores to give a mechanical interlocking.

More recently, as much more sophisticated techniques of **Electron microscopy** have been developed for examining the features of surfaces, Venables and his colleagues<sup>5</sup> have revealed the detailed morphology of aluminium surfaces that have been prepared by various well-established techniques for adhesive bonding (see **Anodizing, FPL etch**,

**Pre-treatment of aluminium**). These surfaces all had whiskers of oxide on the outermost parts; and in some cases, depending upon the details of the treatment, there were also pores similar to those already described. These whiskers were 100–400 Å long and 50–100 Å in diameter and the pores were about 400 Å in diameter. Their work quite clearly implies that there is a double interlocking, with the whiskers being embedded in adhesive and with the adhesive penetrating the pores. Thus, the region between metal and adhesive has the character of a composite. The mechanism of failure depends upon a viscoelastic deformation of the polymer–adhesive together with a rupture of the other adhesive bonds that have been formed.

It is now quite clear that mechanical interlocking has a significant role in the adhesive process, but all the features involved are on a very much smaller scale than was once imagined. While on a macroscopic scale interlocking may be of little relevance, on a microscopic scale it is vital.

A comparison of different theories is given under **Theories of adhesion**.

### References

1. E. M. Borroff and W. C. Wake, *Trans. Inst. Rubber Inst.*, **25**, 199, 210 (1949).
2. L. E. Perrins and K. Pettett, *Plast. and Polym.*, **39**, 391 (1971).
3. K. Bright, B. W. Malpas and D. E. Packham, *Nature*, **223**, 1360 (1969).
4. D. E. Packham, in *Aspects of Adhesion 7*, D. J. Alner and K. W. Allen, Eds., Transcripta, London, 1973, p. 51.
5. J. D. Venables, in *Adhesion 7*, K. W. Allen, Ed., Applied Science Publishers, 1982, Chap 4; *J. Mater. Sci.*, **19**, 2431 (1984).

## Metallizing plastics

R H DAHM

The first plastic to be metallized on a commercial scale was ABS, which is used as a replacement for the much heavier zinc alloy die castings widely used in the motor industry. Many other polymers are now coated not only for decorative purposes such as bathroom fittings but also for the production of objects where the specific properties of metals such as electrical conductivity, high reflectivity and good barrier properties are combined with those of polymers such as toughness, flexibility, corrosion resistance and low cost. The techniques used to produce highly adherent metal deposits may be divided into two major groups, dry methods and wet methods.

### Dry methods

In dry methods<sup>1,2</sup> the metal is deposited from the vapour phase to produce generally thin coats such as those found in laminates associated with the **Packaging industry**, electromagnetic shielding of electrical equipment, capacitors, recording tape, CDs and optical reflectors as well as decorative trim panels, to mention just a few of the applications. The coating metal is evaporated under vacuum by one of several methods such as resistance



heating, which is commonly used in the reel-to-reel aluminizing of polymer film. A number of materials such as tungsten are difficult to melt by resistance heating but may be rapidly evaporated by bombardment with a beam of accelerated electrons. Two metals, for example cobalt and nickel, may be evaporated simultaneously using two separate electron guns as in the continuous coating of videotape with Co/Ni films at rates of up to  $10^3$  mm s<sup>-1</sup>. Arc evaporators also produce a relatively high ion flux, which has the effect of modifying the polymer surface, resulting in improved adhesion especially for difficult to coat materials such as propylene carbonate, poly(tetrafluoroethylene) and polypropylene materials, which normally require a separate surface pre-treatment (see **Pre-treatments of polymers**). Relatively high deposition rates, even of objects with complex shapes, may be achieved using magnetron-assisted ion sputtering, where metal evaporation is achieved by bombarding the metal target with inert gas ions produced in a glow discharge. Vapour deposition techniques are undergoing continuous development and the process is likely to gain in importance in the light of increasingly severe environmental legislation.

#### *Wet methods*

Wet chemical processes<sup>2-4</sup> are still widely used for the deposition of thicker, typically 25–30- $\mu$ m thick, coatings. The technique is widely used for the production of printed circuit boards<sup>5</sup> and is effective for coating the inside of hollow objects. Several steps are involved, including a preliminary surface pre-treatment, which may consist of a chemical etch, although UV excimer and **Plasma pre-treatments**<sup>6</sup> to roughen the surface and/or improve **Wetting and spreading** are increasingly used mainly because of their lower environmental impact. The areas to be coated are then activated using either the two-step or the one-step process. In the former process, the surface is sensitized by treatment with a dilute acidic stannous chloride solution followed by activation with a dilute acidic solution of palladium(II) chloride. In the one-step process, a single solution containing both the stannous and the palladium salts are used. This results in the deposition of colloidal particles containing some palladium metal on the substrate surface. The article is then immersed in a solution of the metal salt (typically 2–8 g L<sup>-1</sup>) also containing a reducing agent such as sodium hypophosphite, sodium borohydride, hydrazine, formaldehyde, and so on. The palladium nuclei catalyse the release of electrons from the reducing agent and their transfer to the metal cations, including any residual palladium(II) cations, resulting in the deposition and growth of the metal film. The electroless plating solutions, which are stabilized by the addition of chelating agents and careful control of pH must be replenished from time to time until the build-up of impurities is such that the whole solution must be replaced. The deposition rate is typically 2–10  $\mu$ m h<sup>-1</sup>.

The metals most commonly plated are copper and nickel. The deposits may be thickened by conventional electroplating with either the same or a different metal. The process has been applied successfully to many polymers other than ABS including polypropylene, polyesters, polyamides, PTFE and glass-filled epoxy resins. Selective deposition may be achieved by applying the sensitizing solution using normal printing techniques followed by exposure to the remaining processing solutions. In a novel approach, the artwork of an electrical circuit was transferred to PET based transparent film using an ordinary photocopier. The film was then treated with alcoholic potassium hydroxide solution followed by ammoniacal silver nitrate solution. Immersion in a standard electroless copper bath produced a coherent conductive copper deposit on the printed area. Another approach

that has shown some promise for coating polyimides involves deposition of palladium nuclei by decomposition of a palladium salt deposit on the polymer surface by exposure to excimer UV radiation or to an atmospheric pressure plasma. In a related process, poly(butylene terephthalate), which does not react with conventional chromic acid etch baths, was successfully activated by irradiation with 222-nm UV light.

### References

1. A. Suchentrunk, Ed., *Metallising Plastics: A Handbook of Theory and Practice*, Finishing Publications Ltd, Stevenage, 1992.
2. K. L. Mittal, Ed., *Metallised Plastics 5&6 Fundamental and Applied Aspects*, VSP B V, Utrecht, 1998.
3. W. Goldie, *Metallic Coatings of Plastics*, Vol. 1, Electrochemical Publications Limited, Middlesex, 1968, pp. 15–73.
4. G. O. Mallory and J. B. Haju, Eds., *Electroless Plating: Fundamentals and Applications*, American Electroplaters and Surface Finishers Society, 1992.
5. K. Gilleo, *Handbook of Flexible Circuits*, Van Nostrand Reinhold, New York, 1992.
6. K. L. Mittal and A. Pizzi, Eds., *Adhesion Promoting Techniques*, Marcel Dekker, New York, 1999.

## Microfibrous surfaces

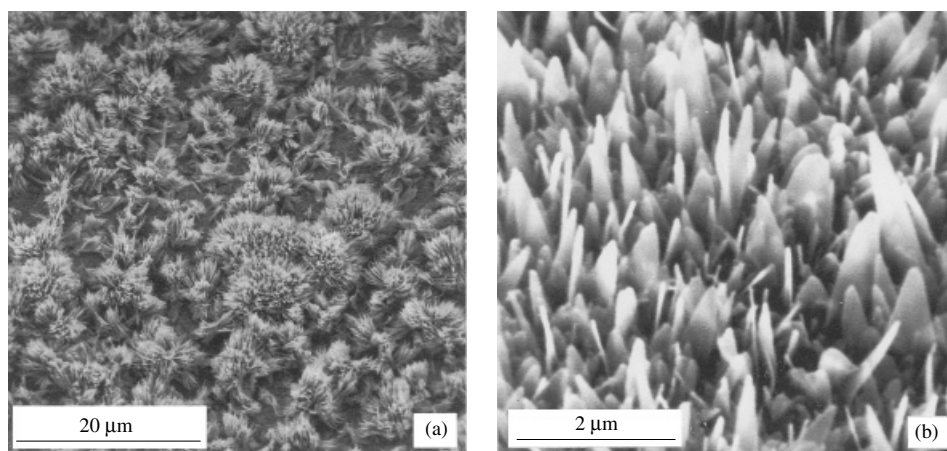
D E PACKHAM

Some form of substrate pre-treatment is almost always essential before adhesive bonding (see many articles herein entitled “**Pre-treatment of...**”). The extent to which pre-treatments increase the **Roughness of surfaces** and the connection between this and adhesion are complex issues that have interested scientists for more than 50 years (see **Mechanical theory of adhesion**). The advent of **Scanning electron microscopy** (SEM) in the late 1960s made much more detail of surface topography available. Some surfaces of metals can be seen in SEM to be covered with acicular projections with heights of the order of 1  $\mu\text{m}$  (Fig. 1). Such surfaces have been termed “microfibrous”.

### Preparation

The common feature of microfibrous surfaces is their topography, rather than their chemical nature. It is well known that certain oxidation conditions produce a whisker or blade-like oxide growth on a metal surface, rather than a film of uniform thickness. Similarly, certain conditions of electrodeposition give dendritic crystals of the deposited metal, not a smooth coating. These are ways of preparing microfibrous surfaces. Details of some typical methods are given in Ref. [1].

Needles of copper (II) oxide can be prepared on copper by oxidation of the metal at 90°C for 20 min in a solution of 3 g L<sup>-1</sup> sodium chlorite, 10 g L<sup>-1</sup> trisodium phosphate and 5 g L<sup>-1</sup> sodium hydroxide. The oxidized copper has a matt black appearance (see also **Pre-treatment of copper**).



**Fig. 1.** Scanning electron micrographs of microfibrinous oxides on (a) copper and (b) steel

A blade-like covering of oxide can be produced on mild steel by oxidation for 4.5–5 h at 450°C in a nitrogen stream that has been bubbled through water at 40°C (see Fig. 1b).

Electrodeposition of zinc from potassium zincate solution (e.g. 100 g L<sup>-1</sup> potassium hydroxide plus 0.5 g L<sup>-1</sup> of zinc oxide) on to “flat” zinc (e.g. at 130 A m<sup>-2</sup>) gives dendritic crystals on zinc on the surface of the base metal. A micrograph of such a surface is given in **Scanning electron microscopy**, Fig. 2.

### Adhesion

Microfibrous surfaces typically have a dull appearance as they scatter light. Provided the adhesion of the microfibrines to the base metal is adequate, such surfaces have potential as substrates for adhesive bonding. Examples with different polymers will be described.

Polyethylene can be applied as a hot melt coating to metals. Poor adhesion has been found with conventional pre-treatments when the polymer was stabilized with antioxidant. By contrast, adhesion to microfibrinous surfaces is good even in the presence of antioxidant (Table 1).<sup>1</sup>

The adhesion has been studied of a series of **Ethylene–vinyl acetate copolymers** applied to metals as **Hot melt adhesives**. Much higher adhesion was found to copper with a microfibrinous oxide surface than to conventionally prepared copper or steel.

*Table 1.* Effect of antioxidant concentration on the adhesion of polyethylene to “flat” and microfibrinous surfaces

Metal	Topography	Antioxidant (ppm)	Peel strength (N mm <sup>-1</sup> )
Steel	‘Flat’	Nil	2.13
		2000	0.28
Oxidized steel	Microfibrous	Nil	2.73
		2000	2.16
Oxidized copper	Microfibrous	Nil	1.47
		2000	1.44

Table 2. Fracture energy ( $G_C$ ) for zinc-epoxy single edge notched (SEN) test specimens ( $J m^{-2}$ )

Zinc surface	Percentage rubber reinforcement		
	0	7	15
'Flat'	105	300	700
Dendritic	670	2210	2550

In contrast to polyethylene and EVAs, **Epoxy adhesives** are thermosets and are much stiffer and less ductile. The adhesion fracture energy ( $G_C$ , see **Fracture mechanics**), between both unmodified and rubber-toughened epoxies (see **Toughened adhesives**) and several metals has generally been found to be much higher when microfibrinous surfaces were involved (Table 2).<sup>1</sup>

It is clear from an investigation of the locus of failure and analysis of the fracture surfaces by **X-ray photoelectron spectroscopy** that the microfibrinous surfaces lead to considerable plastic deformation of the polymer. They appear to increase the adhesion by enhanced energy dissipation during fracture<sup>2</sup> (see **Rheological theory, Peel tests**).

### References

1. D. E. Packham, *Int. J. Adhes. Adhes.*, **6**, 225 (1986).
2. D. E. Packham, The mechanical theory of adhesion – a seventy year perspective and its current status, in *1st International Congress on Adhesion Science and Technology: Invited Papers*, W. J. van Ooij and H. R. Anderson Jr, Eds., VSP Publishers, Utrecht, 1998, p. 81–108.

## Microstructure of joints

D E PACKHAM

### *The significance of microstructure*

The measured adhesion of a joint depends not only on the forces that act at the interface but also on the mechanical properties of the bulk phases, adhesive and substrate and the way they interact through the interface (see **Adhesion**). These concepts are developed in the articles **Rheological theory, Adhesion – fundamental and practical** and **Peel tests**). The microstructure of a bulk phase will usually affect its properties, so knowledge of the microstructure of the adhesive, substrate and substrate surface is relevant to an understanding of the strength and performance of an adhesive joint. In many cases, the microstructure can be altered when making the joint by altering the process variables. The advantage of this is that it gives the practitioner scope for controlling the performance of an adhesive joint between given materials; the disadvantage is that careless or poorly researched bonding procedures can give rise to adhesive bonds of far from optimum properties.

Consideration of all aspects of joint microstructure would require a scope that includes most of materials science. In this article, attention will be directed particularly to microstructural features of adhesive and of substrate surface that can be altered to affect the performance of an adhesive joint.

### *Adhesive microstructure*

A way of significantly altering the properties of a polymer is to incorporate fillers or fibres (see **Filler–matrix adhesion, Fibre composites – introduction**). The stiffness and often the toughness of the polymers are increased.

Some polymers used as adhesives, for example, polyethylene, and **Ethylene–vinyl acetate copolymers**, are crystalline and their properties will be altered by altering the degree of crystallinity or the crystalline morphology.<sup>1</sup> Cooling rates, annealing treatments and the use of nucleating agents are process variables, which it may be possible to exploit to determine adhesive joint performance.

Where the adhesive is cross-linked (see **Reaction setting adhesives, Epoxide adhesives, Phenolic adhesives: single-stage resoles, Phenolic adhesives: two-stage novolacs, Rubber-based adhesives and Rubber to metal bonding – basic techniques**), it is often easy to control properties by controlling the cross-link density.

Some important **Structural adhesives** are two-phase materials composed of dispersed rubbery particles in a glassy matrix (see **Toughened adhesives**). Optimum performance depends upon achieving the “correct” phase structure, which is achieved only by careful attention to the procedure for mixing, applying and curing the adhesive.

The presence of voids in an adhesive might be regarded as a feature of its microstructure. These are often incorporated as a result of careless mixing and exert a deleterious effect. In some circumstances, beneficial effects of voids have been found, and they can be introduced deliberately by the use of blowing agents.<sup>2</sup>

### *Microstructural features of the substrate*

The microstructure of the bulk substrate, such as the grain structure of a metal or the porosity of a ceramic, will affect substrate properties, and thence the joint performance. Of special importance to an adhesive bond is the “microstructure” of the substrate surface.

The surface structure can be altered by **Abrasion treatment** and by many other pre-treatments. These pre-treatments usually have a crucial effect on the subsequent adhesion. The mode of action of any particular pre-treatment is often a matter of speculation. Control of the chemical nature of the substrate surface, of its **Surface energy** and, through this, the **Wetting and spreading** of the adhesive are usually important; in some cases, however, the **Roughness of surfaces** has a significant influence (see **Mechanical theory of adhesion**). **Anodizing** of aluminium and titanium can produce a fine porous microstructure, which gives particularly good adhesion and durability (see **Durability: fundamentals, Pre-treatment of aluminium, Pre-treatment of titanium**). **Microfibrous surfaces** are another category where the surface structure exerts a strong effect on the adhesion.

### *Influence of the substrate on the adhesive microstructure*

Some subtle effects occur when the adhesive microstructure is altered through the influence of the substrate.

During the cooling of crystallizing **Hot melt adhesives**, the presence of the substrate can lead to surface nucleation, giving a columnar “transcrystalline” polymer morphology in the interfacial region. There have been reports that such layers influence measured adhesion, but conclusive demonstration has proved elusive.<sup>3</sup>

Many metals, especially transition metals, are well known for their catalytic activity. Some cases of such chemical influence of a metallic substrate on a curing reaction of an adhesive have been demonstrated. A well-known example, which has a considerable effect on adhesion, is the influence of brass or copper on the vulcanization of rubber (see **Rubber to metal bonding – basic techniques**).

### Conclusion

The total control of microstructure, which is used to influence the properties of materials in general, gives a valuable means of altering the performance of adhesive joints. A more extended discussion of the subject can be found in Ref. [3].

### References

1. A. S. Vaughan and D. C. Bassett, in *Comprehensive Polymer Science*, Vol. 2, G. Allen and J. C. Bevington, Eds., Pergamon, 1989.
2. T. Adam, J. R. G. Evans and D. E. Packham, *J. Adhes.*, **10**, 279 (1980).
3. D. E. Packham, Adhesives and sealants, in *Engineered Materials Handbook*, Vol. 3, H. F. Brinson, Ed., ASM, Ohio, 1990, p. 406.

---

## Moisture cure of adhesives and sealants

---

J COMYN

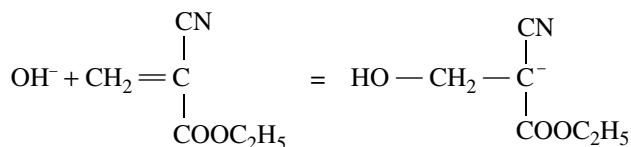
Water in the atmosphere is pure and free, and in a temperate country like the United Kingdom, the amount present, as expressed by the relative **Humidity**, remains fairly constant for most of the time. Cyanoacrylates, silicones and isocyanates are among the materials that may be available as one-part, moisture-cured adhesives. (**Cyanoacrylate adhesives, Silicone adhesion**).

The mechanism of cure is quite different for cyanoacrylates on one hand and silicones and isocyanates on the other. In the former case, cure is by **Chain polymerization** initiated by water on the surface of the substrate, while in the latter, water from the atmosphere diffuses into the adhesive or sealant and then participates in a **Step polymerization**. One consequence of this is that only catalytic quantities of water are required to cure cyanoacrylates, while much larger, stoichiometric quantities are needed for silicones and isocyanates.

### Cyanoacrylates

Cyanoacrylates are mostly supplied in polythene containers as pure monomer, with a small amount of an acidic gas (e.g. SO<sub>2</sub>) added as stabilizer. Glass is not used as a container

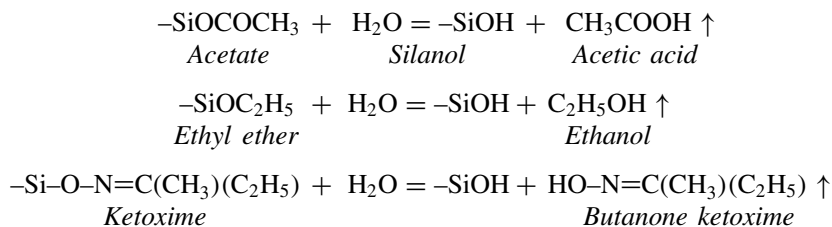
as it is alkaline and provides hydroxide ions, which initiate the anionic polymerization, as shown below for ethyl cyanoacrylate.



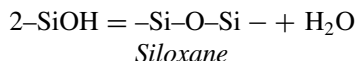
The anion that is formed is strongly stabilized by the electron-withdrawing cyanide ( $-\text{CN}$ ) and ester ( $-\text{COOC}_2\text{H}_5$ ) groups, and the stability of this anion is the fundamental reason for the rapid cure of these adhesives. The propagation reaction involves the addition of further monomer molecules to the anion. With most substrates, it is the hydroxide ions in an adsorbed layer of water that initiate polymerization.

### Silicones

Moisture-curing silicones contain polydimethylsiloxane (PDMS) with water-reactive end groups. The hydrolysis reactions with acetate, ethyl ether and butanone ketoxime end groups are as shown below.



In all cases, the silanol end groups then condense to form siloxane linkages.



Further discussion can be found in **Silicone adhesives: condensation cure**.

### Isocyanates

Moisture-curing isocyanate adhesives consist of low molecular weight, linear polymer molecules, with isocyanate ( $-\text{NCO}$ ) end groups. As shown below, some of the isocyanate groups are hydrolysed to give amine groups, and these then react with further isocyanate to give urea units that join the polymer molecules together.

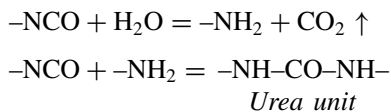
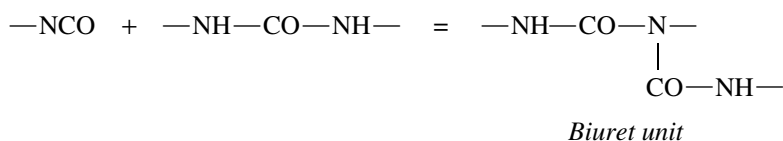


Table 1. Parameters that control the rates of moisture cure at 25°C: volume of sealant that reacts with 1 mol of water ( $V$ ), water permeability coefficient ( $P$ )

Adhesive/sealant	$V$ ( $10^{-3} \text{ m}^3 \text{ mol}^{-1}$ )	$P$ ( $10^{-13} \text{ mol s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$ )
Acetate-terminated fluorosilicone	1.33	48
Ketoxime terminated PDMS	3.92	75
Isocyanate hot melt adhesive	4.0	6.0
Isocyanate hot melt adhesive	3.7	29

Isocyanate groups then attack urea units, and the consequence is that the adhesive, which was firstly linear, now becomes branched or cross-linked.



#### Kinetics of cure for silicones and isocyanates

Cure depths ( $z$ ) at 25°C and constant humidities have been measured for the following materials – acetate-terminated fluorosilicone, PDMS with butanone ketoxime end groups, and two isocyanate hot melt adhesives. In all cases,  $z$  was found to be linear with the square root of time.

The chemical reactions are much faster than the rate of water diffusion, and their speed is shown by the rapid formation of skins and the instant smell of acetic acid from materials with acetate end groups. A partly cured layer has an outer zone that is fully cured and an inner uncured zone; there are no partially cured regions.

The cured adhesive acts as a barrier for the permeation of water to the uncured material. Any water that passes through this barrier quickly reacts with uncured material, and thus the barrier is thickened. The rate ( $dn/dt$ ) at which moles of water permeate unit cross section of the cured layer is given by Eqn. 1. Here  $p$  is the vapour pressure of water in the surroundings and  $P$  is the water permeability coefficient of cured adhesive.

$$dn/dt = Pp/z \quad [1]$$

This leads to Eqn. 2, where  $V$  is the volume of sealant that reacts with 1 mol of water.

$$z = (2VPpt)^{1/2} \quad [2]$$

This is the basic equation of cure for materials of this type, although a few systems do show modest deviations. Values of material properties that control the rate of cure are shown in Table 1.

#### Select Reference

J. Comyn, *Int. J. Adhes. Adhes.*, **18**, 247 (1998).



---

## *Mould adhesion and fouling*

---

D E PACKHAM

### *Introduction*

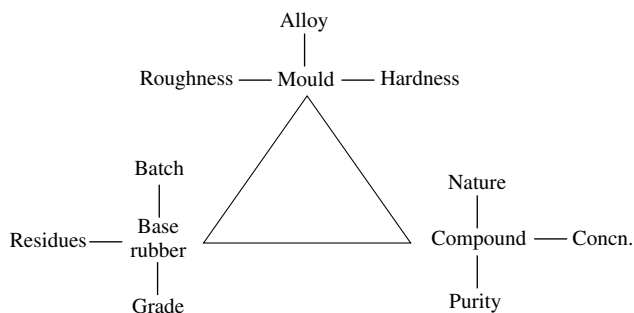
Moulding is an essential stage in the production of most polymer articles. After moulding, the article has to be released from the mould and, often, after a number of moulding cycles, the build-up of contaminants on the mould surface – mould fouling – is observed. Problems that occur in moulding include difficulty in obtaining consistent release forces and avoiding fouling. The drive for shorter moulding cycles aggravates the problem, which is sometimes so bad as to seriously hinder the introduction of automated removal of the moulded product.

There are close similarities between the moulding process and the formation of an adhesive joint. In both cases, one material (the polymer or adhesive), usually in liquid or semi-liquid form, is brought into close contact with another (the mould or substrate) and then sets. The phenomenon of mould release is in many respects the same as the phenomenon of adhesion: a moulding is almost like an adhesive bond where very low, even zero, adhesion is desired. See **Mould adhesion – measurement**.

The essential requirement for adhesion is contact between adhesive and substrate. Once this occurs, adhesion of some sort will result (see **Wetting and spreading** and **Adsorption theory of adhesion**). Contact between polymer and mould is of course the aim of moulding, so some adhesion is to be expected. Where there are appropriate chemical groups present, there may be chemical reaction forming covalent or other **Primary bonding at the interface**. Many of the materials moulded during polymer processing are chemically reactive, and it is highly likely that some of these form chemical interactions with the material of the mould. In other instances, groups may be present that are capable of forming **Hydrogen bonding**, **Acid–base interactions** or **Polar forces** interactions. Even in cases where such specific interaction does not occur, there will be at least van der Waals **Dispersion forces** between moulding and mould. Therefore, some mould sticking – which may be at a low level – is inevitable.

Mould sticking – like adhesion in general – is strongly affected by the nature of the surface layers formed during moulding. Most, probably all, polymer materials are multicomponent. The polymer itself is rarely pure and additives are incorporated. Many additives are not thermodynamically compatible with the polymer into which they are introduced. Thus, during moulding, there will be a tendency for many components of a polymer material to come to the mould surface, either as a result of surface activity or incompatibility. These considerations are important in the context of mould release. They mean that a surface layer will tend to be formed at the mould surface, of different composition from that of the bulk polymer. These surface layers will influence release. Depending on their composition, they may act as a “natural” release agent, or they may have the opposite effect.

The complexity of the effects that can occur may be judged from a study of the mould release of nitrile–butadiene rubbers (NBR) (see **Nitrile rubber adhesives**), where a complex interfacial layer including emulsifier and coagulant residues controlled the release properties. The adhesion was affected by a large number of factors, some associated with the mould surface, some with the rubber compound used and some with the base NBR (Fig. 1).



**Fig. 1.** Factors affecting the release of NBR mouldings

### Mould release agents

Difficulties of **Release**, especially of mould release, are generally reduced to acceptable levels by the use of mould release agents. These are conventionally classified into three types – sacrificial, internal and semi-permanent release agents. Silicones provide an example of *sacrificial* release agents when they are applied to the mould surface to give a release layer, which is worn away within a few mouldings and has to be applied again. *Internal* release agents, incorporated within the polymer, generally comprise surface-active molecules. Slip additives, such as stearates, are often used. These come to the polymer–mould interface during moulding, forming a weak boundary layer. *Semi-permanent* release agents are applied to the mould surface, and are usually baked on. They provide a release surface of low surface energy, which is effective over many moulding cycles, but they eventually wear away. Fluorocarbon polymers are used for this purpose.

### Mould fouling

It is clear then that residue from the polymer being moulded or from an external or internal release agent will form on the mould surface and build up over a number of moulding cycles, suffering progressive thermal degradation. The problem is more serious when moulding reactive materials like rubbers and heated moulds than when using thermoplastics or cool moulds.

Problems of mould release and fouling are endemic in the polymer processing industry. They exert a serious limitation on production rate and represent a significant cost to the industry. The large number of commercial release products available from many different manufacturers is in itself evidence that there is no facile solution to these problems.

### References

- M. J. Owen, Release agents, *Encyclopedia of Polymer Science and Engineering*, Vol. 14, Wiley-Interscience, New York, 1988, pp. 411–421.  
 D. E. Packham, *RAPRA Rev. Rep.*, **13**(6), (2002).

## Mould adhesion – measurement

D E PACKHAM

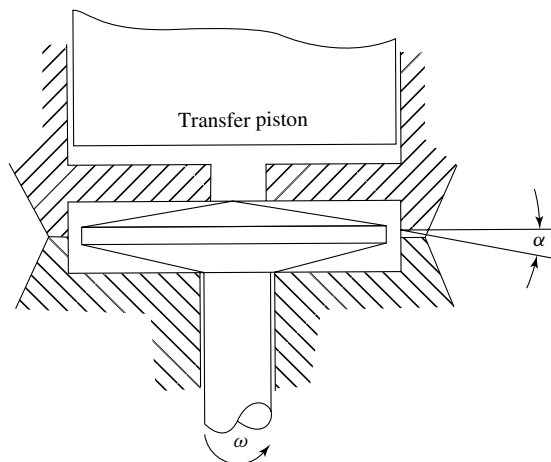
### *Assessment of release and fouling behaviour*

Measurement of the low levels of adhesion involved under conditions resembling commercial moulding produces some unusual problems (see **Mould adhesion and fouling**). Although there are many widely used **Tests of adhesion** that could be used in principle, the very low forces involved in mould release make them difficult to apply. Both the **Peel tests**, T-peel and the standard tapered double cantilever beam (TDCB) test (see **Fracture-mechanics test specimens**), have been adapted for this purpose. In the former, the time to failure under constant load was taken as a measure of sticking. A better procedure might be to measure the peel rate under a series of small peeling loads and thence to evaluate a peel energy.

The TMS rheometer has been used to study mould release in rubbers. It contains a biconical rotor (representing the mould surface). The polymer is placed in the transfer chamber, injected around the rotor and cures *in situ*, Fig. 1. The shear stress required to free the rotor is taken as the “mould-sticking index”. The rheometer has the advantage that small experimental mixes of rubber can be evaluated. Further, the rotors are easily changed, so as to evaluate changes in mould surface, and the parted surfaces are amenable to examination by XPS and other methods of surface analysis. The obvious disadvantage is that access to special equipment (the TMS rheometer) is required. The same basic concept could be adapted for the study of mould adhesion of non-elastomeric polymers.

The blister test has also been used to study mould adhesion. It requires a special mould, but could probably be used with any moulding machine. It is well suited to measuring the low levels of adhesion involved in mould release. Essentially a disc, like a beer mat, is moulded and the pressure is applied to displace it through a small hole (“penny-shaped crack”) at its centre. The detachment pressure can be related to the fracture energy.

A relatively simple way of testing mould fouling is to use a spiral mould. This enables mould fouling to be observed qualitatively, although with a little development (weighing



**Fig. 1.** TMS rheometer showing biconical rotor. The angle  $\alpha$  is  $6^\circ$

---

of inserts, for example), a quantitative measure could be obtained, if necessary. The force to detach the spiral moulding has been claimed to be a good measure of mould fouling. Obviously, the force would be directly related to mould adhesion.

#### *Select References*

- R. K. Champaneria, B. Harris, M. Lotfipour, D. E. Packham and D. M. Turner, *Plastics Rubber Process. Appl.*, **8**, 185 (1988).  
D. E. Packham, *RAPRA Rev. Rep.*, **13**(6), (2002).

# N

---

## *Napkin ring test*

---

D E PACKHAM

In conventional **Shear tests**, there is considerable non-uniformity of stress throughout the joint. The “napkin ring” test was introduced to provide a test where the variation of shear stress was minimal. It consists of two thin-walled tubes joined end to end by a thin layer of adhesive. The torque required to break the joint is recorded.

Equations have been derived relating the shear strength  $\tau$  to the torque  $T$  and the inner and outer radii of the tubes,  $r_1$  and  $r_2$  respectively.<sup>1</sup> Eqn. 1 applies to elastic failure.

$$\tau = 2Tr_2/\pi(r_2^4 - r_1^4) \quad [1]$$

When significant plastic deformation occurs during failure, the shear strength is given by

$$\tau = 3T/2\pi(r_2^3 - r_1^3) \quad [2]$$

Provided the mean radius of the cylinders  $R$  is much greater than their thickness  $t$ , both these expressions reduce to

$$\tau = T/2\pi R^2 t \quad [3]$$

Despite relative uniformity of stress, some stress concentration may occur at the edges of the adhesive (see **Shear tests**). A modification, involving rounding of edges of the tubes, has been suggested to reduce this effect.<sup>2</sup>

A variation of the test was adopted as ASTM E 229 “Standard Method of Test for Shear Strength and Shear Modulus of Structural Adhesive”, although the specification was withdrawn in 2003. The test, as a test of pure shear, is in current use in diverse areas of adhesion research.<sup>3-5</sup>

### References

1. A. J. Kinloch, *Adhesion and Adhesives, Science and Technology*, Chapman and Hall, 1987, p. 242.
2. D. W. Schmuesser, Adhesives and sealants in *Engineered Materials Handbook*, Vol. 3, H. F. Brinson, Ed., ASM, Ohio, 1990, p. 441.
3. D. E. Richardson, M. L. McLennan, G. L. Anderson, D. J. Macon and A. Batista-Rodriguez, *J. Adhes.*, **79**, 157–174 (2003).
4. J. Guilleminet, S. Bistac, P. Deprez, P. Junges and J. Schultz, *La Revue de Métallurgie-CIT/Science et Génie des Matériaux*, **98**(2), 185 (2001).
5. M. S. Kent, H. Yim, A. Matheson, C. Cogdill, G. Nelson and E. D. Reedy, *J. Adhes.*, **75**(3), 267–298 (2001).

### Natural rubber-based adhesives

JOSÉ MIGUEL MARTÍN-MARTÍNEZ

Natural rubber (NR) is the base polymer for many **Rubber-based adhesives**. This article is designed to supplement with specific information the more general treatment given in **Rubber-based adhesives: compounding** and **Rubber-based adhesives: typical characteristics**.

The chemical composition of NR mainly corresponds to *cis*-1,4-polyisoprene, Fig. 1. Significant residual unsaturation persists, even when vulcanized.

Most often, NR adhesives are supplied either as a solvent dispersion or as latex for coating onto surfaces. Viscosity can range from very low viscous solutions for spray application to higher viscous mastics suitable for troweling. NR adhesives can also be pre-coated onto fabric, paper or film to provide pressure-sensitive tapes.

NR adhesives can be divided in two types: wet bonding and dry bonding. *Wet bonding* adhesives are applied on substrates as fluid state, the bond being formed by drying. The *dry bonding* NR adhesives are pressure-sensitive adhesives because the bond is created under pressure.

### Properties

Adhesives made from the various forms of NR exhibit similar characteristics, although some properties are altered by adding curatives. They exhibit high flexibility, high resilience and fatigue resistance combined with low to moderate cost. The non-polar nature of the base NR (Fig. 1) means that there is very good water and moisture resistance and electrical insulation. In these respects, solvent-borne adhesives have an advantage

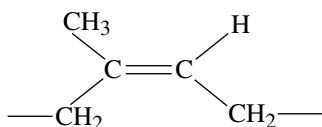


Fig. 1. Structural formula of *cis*-1,4-polyisoprene

over latex, which contains surfactants. A disadvantage of the non-polar structure is poor resistance to organic solvents and oils, although this can be partially reduced in vulcanized systems.

The residual carbon-carbon double bonds are susceptible to degradative oxidation, even after vulcanization, by oxygen and ozone attack. A consequence is brittleness upon ageing.

Tack is excellent: solvent-based compounds are very tacky, even without addition of a tackifier. Latex compounds exhibit superior self-adhesion after coated surfaces have dried.

A wide range of substrates can be bonded. The inherent tackiness of NR enables it to coat most of non-polar substrates (mainly plastics and rubbers). Thermal insulation is generally good.

*Solvent-borne adhesives* Although the NR polymer is inherently tacky, tackifying resins are generally added to improve bonding to polar surfaces. Because the solids content in these adhesives is lower than 35 wt%, they are not suitable for gap filling. The quick-grab (cements) adhesives are particular because they contain about 65% rubber and set within a few seconds under finger pressure.

*Water-borne adhesives* These contain between 40 and 80 wt% solids. They completely lack tack in the dried film and autoadhere to themselves under pressure.

#### *Additives and modifiers*

NR adhesives accept a wide variety of compounding ingredients. *Thickeners* can be added to increase the viscosity of the NR adhesives. Natural materials can be added (casein or karaya gum), but currently synthetic polymers are used (methyl cellulose and derivatives, polyacrylates).

Most of mineral *fillers* can be easily incorporated into solvent-borne and water-borne (adding adequate surfactants and wetting agents) adhesives. Hydrocarbon resins, rosin, rosin ester, coumarone indene resins, and terpene resins can be directly added to solvent-borne adhesives. For latex adhesives, resin emulsification must be produced before addition.

*Reinforcing agents* can be added to increase the cohesive strength of NR adhesives. Carbon blacks have been extensively used, but polyfunctional isocyanates are currently preferred. The isocyanate must be added to the NR adhesive immediately before use and curing is produced at room temperature. Finally, chlorinated rubber is a valued reinforcement agent for NR adhesives.

The hardness of the adhesive may be reduced by addition of *plasticizers* and oils or *softeners* (e.g. liquid polybutenes and lanolin)

Some typical rubber adhesive formulations are given in **Rubber-based adhesives: compounding**. Specific formulations for NR can be found in the references below.

#### *Adhesion characteristics*

NR adhesives perform adequately under peeling stresses. The peel strength can vary from a few  $\text{N m}^{-1}$  in PSA formulations to “substrate tear” in vulcanized compounds used in hose, belting and tyre products.

Non-vulcanizing NR adhesives typically withstand temperature ranges between  $-30^{\circ}\text{C}$  to  $65^{\circ}\text{C}$ . Vulcanized NR adhesives can perform between  $-40^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ .

The solvent-borne NR adhesives show an important mechanical component in the bonding process, and therefore bulk mechanical and rheological properties (addition of fillers is quite effective) are important. In fact, these adhesives are mainly suitable when at least one of the surfaces to be joined is water-porous (paper, concrete, leather, textiles).

### *Applications*

NR pressure-sensitive adhesives with a high tackifier content can be used as commercial tapes and surgical plasters.

*Solvent-borne NR* and quick-grab adhesives are commonly used in leather footwear manufacturing for temporary bonding and in rubber footwear as a curing laminating adhesive. Many off-the-road tires, hoses and belting use vulcanizing grade of solvent-dispersed NR.

*Latex compounds* have been typically used in paper, textile and construction. One of the most popular applications is their use in self-sealing envelopes. This application is based on the fact that when NR dries, some soluble non-rubber compounds migrate to the surface by water transport, leaving a thin film when drying is completed. This film reduces the surface tack on the rubber, and when pressed against a similar film, the non-rubber layer is displaced, allowing the two rubber surfaces to create a bond.

Other important application of NR is for bonding ceramic tiles, although this needs special compounding with clay filler and cellulose thickener.

Water-borne NR adhesives can also be used for bonding canvas and leather shoes and interior trim in some automotive applications.

Vulcanizing latex adhesives are used in the manufacture of textiles, rugs and carpets.

### *Select References*

- K. F. Gazeley and W. C. Wake, in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, Chap 9, pp. 167–184.
- S. K. De, Natural rubber-based adhesives in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 511.

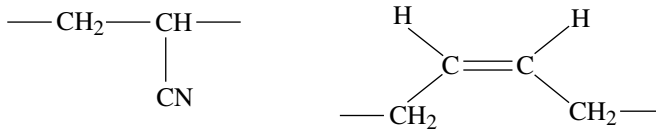
---

## *Nitrile rubber adhesives*

JOSÉ MIGUEL MARTÍN-MARTÍNEZ

Nitrile rubber, also known as nitrile–butadiene rubber (NBR), is a copolymer of acrylonitrile and butadiene (Fig. 1). As a base polymer for **Rubber-based adhesives**, it provides a number of specialized properties, which supplement those summarized in the article **Rubber-based adhesives: typical characteristics**. NBR adhesives comprise a range of materials that may differ in proportion of comonomer or may be compounded with other resins. NBR adhesives are characterized by high oil and plasticizer resistance, excellent heat resistance and high adhesion to metallic substrates.





**Fig. 1.** The repeat units in NBR: acrylonitrile (left) and butadiene (right)

There are several NBRs for adhesives and cements applications, so they should be properly selected. NBRs containing high acrylonitrile content show outstanding bonding and film properties. Mooney viscosity is related to the bond strength of NBRs, and thus, the higher the Mooney viscosity, the higher the strength of the cement adhesive.

Depending on the particular NBR, milling prior to cement preparation can be required. Milling on tight and cold mill rolls is the best way to render NBR soluble in organic solvents. Just after milling, NBR should be put in solution as solubility in milled NBR decreases as time increases.

### *Properties*

In general, the NBR adhesives show the following characteristic properties.

Although of medium-to-high cost and of low initial tack, so as to need addition of tackifiers, NBR has a number of properties needed in specific service environments. Its temperature resistance is good: if cured, NBR can easily be used at  $150\text{--}175^\circ\text{C}$ . Similarly, ageing properties, when compounded with adequate antioxidants, are excellent.

Flexibility and tensile strength are good: both properties are improved after curing. When combined with phenolic resins or epoxies, high shear strength can be obtained in joints produced with aluminium and other substrates.

As a result of its polar structure, NBR has the highest resistance to most greases, oils and non-polar solvents than any of the other elastomers. NBR adhesives are adequate to bond highly polar surfaces (steel, aluminium) but bond poorly to low-polar surfaces (polyethylene, natural rubber).

### *Additives and modifiers*

NBR is a polar polymer and shows superior compatibility with resins, compared to other elastomers. The major ingredients, in addition to the elastomer, for the NBR adhesives are given below.

*Tackifiers* Phenolic resins are added to increase strength, oil resistance and resiliency of NBR adhesives. On the other hand, tack and adhesives properties can be improved by adding chlorinated alkyl carbonates. To impart tack, hydrogenated rosin resins and coumarone-indene resins can be added.

*Plasticizers* Addition of softeners to NBR improve tack and adhesion properties. The most common plasticizers are esters (dibutyl phthalate, tricresyl phosphate), ester gums and alkyl resins.

*Fillers* They are generally added to reinforce NBR adhesives. The most common fillers are carbon blacks. Precipitated silica can be used in applications in which black colour is not acceptable, but excessive amounts tend to reduce adhesion.

*Solvents* NBRs are soluble in aromatic hydrocarbons, chlorinated hydrocarbons, ketones, esters and nitroparaffin compounds.

*Antioxidants* Amine antioxidants are generally added to NBR adhesives.

*Thickening agents* When pseudoplasticity is necessary in NBR adhesives (spread coating operations, sprayed cements), carboxylic vinyl polymers can be added.

*Curing systems* Curing agents are used when high strength and resistance against elevated temperature is a requisite in the NBR adhesives. Typical sulphur curing systems are added (sulphur/benzothiazyl disulphide/zinc oxide). Accelerators based on zinc salts of thiuram disulphides are also added when curing is desired to be produced at low temperature.

*Formulation* Nitrile rubber is compatible with phenol–formaldehyde resins, resorcinol–formaldehyde resins, vinyl chloride resins, alkyd resins, coumarone–indene resins, chlorinated rubber, epoxies and other resins, forming compositions that can be cured, providing excellent adhesives of high strength, high oil resistance and high resilience. In addition, NBR adhesives are compatible with polar adherends such as fibers, textiles, paper and wood.

Some typical rubber adhesive formulations are given in **Rubber-based adhesives: compounding**. Specific formulations for NBR can be found in the references below.

#### *Adhesion characteristics*

NBR adhesives support temperature range between 170°C and –40°C. Bond strength can run above 7 MPa and can provide structural bond to many substrates. Even without curing, NBR adhesives show excellent resistance to organic compounds, acids and alkalis.

#### *Applications*

Applications of NBR adhesives are based on the excellent elastomeric properties of the polymer coupled with its polarity, which provides good solvent resistance and compatibility with other polymers. Organic solutions of NBR are the most common adhesives, although water-borne and pre-cast films can also be used.

Quite often, NBR adhesives are used to bond various kinds of gasketing (cork, fiber, foam, rubber, metal) to rigid superstructures, such as aircraft. Films cast from solution are often used to fabricate honeycomb structures for aircraft.

Further applications are considered under three headings: (1) nitrile rubber, (2) nitrile rubber/phenolic blends, (3) nitrile rubber/epoxy blends.

*Nitrile rubber adhesives* The main application corresponds to the laminating adhesives. PVC, polyvinyl acetate and other polymeric films can be laminated to several metals

by using NBR adhesives. NBR adhesives can also be used to join medium-to-high polarity rubbers to polyamide substrates. The adhesive properties of NBR rubbers can be further improved by chemical modification using polyisocyanate or by grafting with methyl methacrylate.

NBR latices can be also used in adhesive applications. The use of latex has the advantage of avoiding the previous solution of the polymer before application and has favourable environmental treats. Compounding with a resorcinol–formaldehyde solution allows to bond nitrile rubber to cotton or rayon fabric. Nitrile latex can be mixed with PVC latex to give excellent adhesion of polypropylene carpet and plywood backings. Combinations of nitrile latices and styrene–butadiene latices provides good laminating bonds for saturated paper and woven fabrics.

*Nitrile rubber/phenolic resin blends* Blends of equal parts by weight of a nitrile rubber and a phenolic resin in methyl ethyl ketone (at a 20–30 wt% total solids content) is suitable for many adhesive purposes (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**). The more the phenolic resin in the formulation, the greater the bond strength and brittleness of the NBR adhesive. On the other hand, the higher the acrylonitrile content in the rubber, the greater the compatibility with phenolic resins and superior bonding and film properties. Lower acrylonitrile content rubbers produce adhesives with better low temperature properties.

Nitrile rubber/phenolic resin produces one of the most durable and toughest elastomeric materials developed in the adhesive industry. Further, its resistance to water as to organic solvents is excellent. For these reasons, the nitrile rubber/phenolic resin laminates are used in printed circuit board manufacturing, to bond metallic substrates between themselves (aluminium, steel) and to bond rubber to magnesium. Films of nitrile rubber/phenolic blends have also been used in the aircraft industry for bonding metal-to-metal surfaces in both plain and honeycomb sandwich constructions.

*Nitrile rubber/epoxy resin blends* The flexibility and good low temperature properties of nitrile rubber is combined with the excellent strength of epoxies in nitrile rubber/epoxy resin blends (see **Epoxide adhesives**). These blends were first developed in 1955 and found applications in laminating and structural bonding. The nitrile rubber/epoxy resin blends were developed to meet the need of more temperature-resistant adhesive for aircraft applications. A typical formulation contains the nitrile rubber and the epoxy resin, a high loading of aluminium power (to retrieve oxygen), and an amine curing agent. A unique feature of this type of adhesive is that the strengths are obtained at relatively low cure temperature (below 100°C).

Elastomers, plastics, fabrics, wood and metals can be joined themselves and to each other using nitrile rubber/epoxy resin blends cured with amines and/or acidic agents. Ethylene–propylene vulcanizates can also be joined using blends of carboxylated nitrile rubber, epoxy resin and a reactive metal filler (copper, nickel, cobalt).

It is interesting to compare the properties of NBR adhesives with those of another polar rubber: **Polychloroprene rubber adhesives: applications and properties**.

### Select References

D. E. Mackey and Ch. E. Weil, in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, Chap 11, pp. 206–226.

J. M. Martín-Martínez, in *Adhesion Science and Engineering-2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 573–675.

W. F. Harrington, Elastomeric adhesives, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 515.

---

## *Non-destructive testing of adhesively bonded structures*

---

G J CURTIS

### *Introduction*

Testing plays a crucial role in adhesion research and development. **Tests of adhesion**, described elsewhere, involve destruction of the joint: the question arises as to whether the bond strength can be measured without sacrificing the joint. In fact, it has long been the basic aim of non-destructive testing of adhesively bonded structures to determine the overall shear strength. Regrettably, this is still unattainable, principally because there is no intrinsic parameter that relates directly to strength and which can be measured non-destructively. There are, however, techniques that depend upon parameters, for example, elastic modulus, which relate indirectly to strength, under well-regulated conditions and the most valuable will be illustrated here.

### *Factors that control bond integrity*

Strength, unlike elastic modulus, is not even theoretically a readily determinable quantity. Overall elastic–plastic deformation in a structural adhesive might be describable in terms of intermolecular forces and models of viscous flow, but not at the discontinuous moment of fracture. In fact “overall” behaviour loses sight of the fact that it is normally isolated phenomena that control the magnitude of joint strength and the locus of failure (see **Stress distribution: mode of failure**). The term “isolated phenomena” refers to voids, cracks, second phase material, and so on, which can act as stress concentrators. Clearly, it would be unwise to suggest that an adhesive bond tester should merely locate and size voids and cracks, as whether or not such a defect is active depends upon where it lies in the working stress pattern of the structure.

It is useful to consider a bond to be composed of two regions; the interfacial region between the adhesive and the adherend and the region of the bulk of the adhesive, that is, the adhesive and cohesive regions. There is at least one school of thought that maintains that failure cannot occur at the true interface and that where it apparently does there is a weak layer between the two phases (see **Rheological theory**). From the non-destructive testing point of view, there is no alternative to aiming tests at both the interface and the bulk of the adhesive. To this end, two testing regimes need to be considered: manufacture and in-service use.

### *Non-destructive test methods*

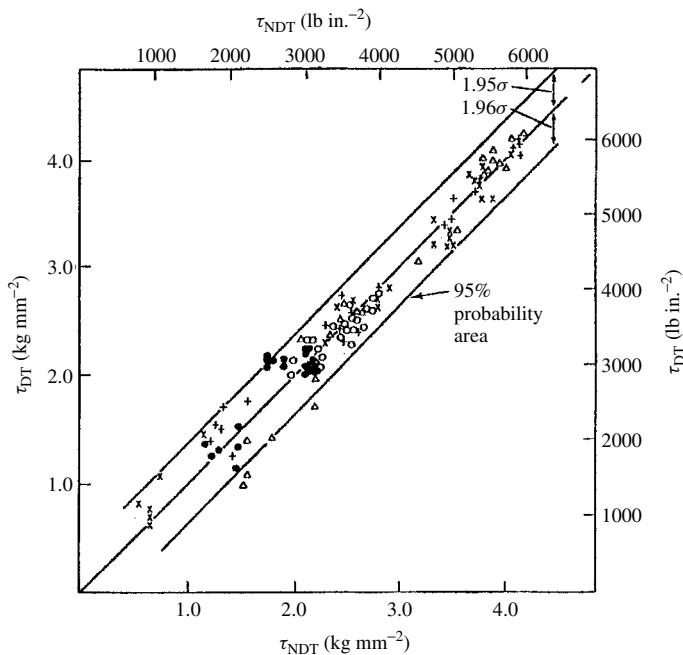
In the search for a “strength tester” almost every joint parameter that can be determined non-destructively has been studied for a correlation with bond strength. Almost every means of probing the joint has been investigated, for example elastic waves, microwaves,

thermal waves, X-rays and neutrons. All have useful features that need to be considered. Without doubt, the most useful techniques are those that make use of acoustic (elastic) waves in the joint.

An acoustic wave in a joint has four basic parameters, which can be varied by the investigator to produce desired effects and which are modified by structural features in the joint; these are amplitude, velocity, wavelength and phase. The kind of structural features that affect them are elastic modulus (e.g. shear), microporosity, macroporosity, cracks, voids and gross corrosion. Depending upon what features are to be assessed, the wavelength of the interrogating sound can be of the order of the joint thickness or, at the other extreme, of the order of the microporosity present in the adhesive. When the joint is excited into thickness resonance, for example, factors that affect the cohesive character of the joint become evident, for example, state of cure and glue-line thickness. When the joint is interrogated with a fine pencil beam of acoustic waves, factors like fabrication voids or in-service-induced cracks/non-bonds/corrosion become evident.

#### *Principal devices for production and in-service testing*

*Resonance testers* A number of devices are available. In Europe, the Fokker bond tester is commonly used. This was developed by the Fokker Aircraft Company in order to

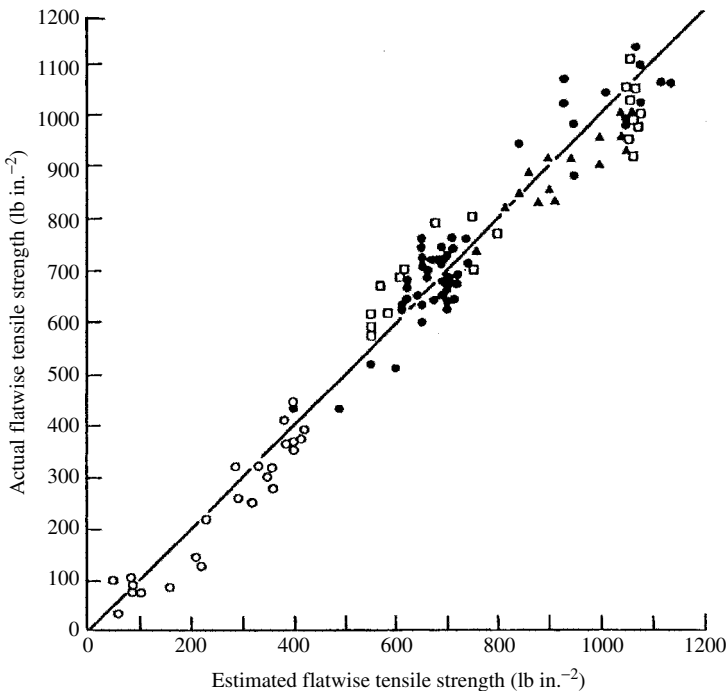


**Fig. 1.** Comparison of destructive shear strength tests on laminates with the predicted strengths using a Fokker bond tester. A series of laminates is represented where the adherend thickness  $t$  varies as follows: (●),  $t = 0.6$  mm; (○),  $t = 0.8$  mm; (×),  $t = 1.0$  mm; (+),  $t = 1.2$  mm; (△),  $t = 1.5$  mm. To construct this standard plot, 120 specimens of Dural 2024-T3 were used; 95% of all results are within the range  $\pm 0.36$  kg mm $^{-2}$ . (From R J Schliekelmann, *Non-destructive testing of adhesively bonded joints*, in *Adhesion, Fundamentals and Practice*, McClaren, London, 1966)

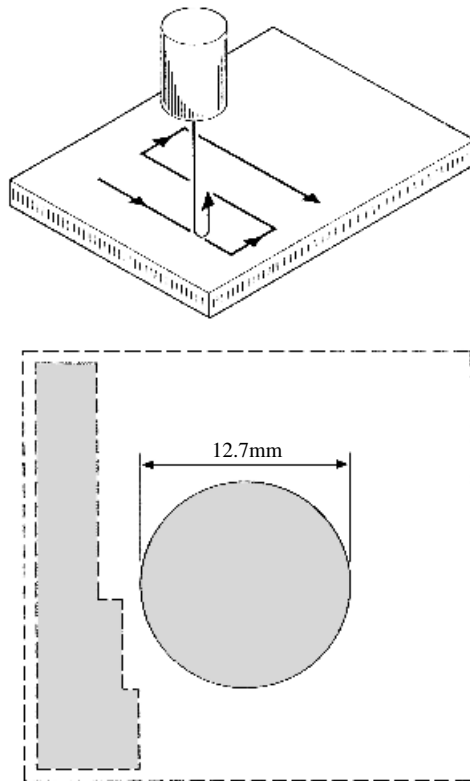
test laminates and honeycombs. Over 40 years of use and development has shown its strengths and weaknesses. Under conditions of strict fabrication control (or where they have been applied), it is capable of determining the presence of features that affect the cohesive strength of the joint. It yields “cohesive bond strength” by calibration of either the resonant frequency or amplitude of the joint with shear strength. Where the prospective failure locus is at the interface, it is less successful, and in the production regime, it is supplemented by surface-treatment quality-control tests. In the in-service regime, where gross corrosion of the interface has occurred, it can successfully detect this.

Figure 1 shows an example of the degree of correlation that can be achieved between strengths predicted by the Fokker bond tester and those determined destructively for a bonded laminate. Figure 2 shows a similar correlation for bonded honeycomb structures.

Small or large areas of laminates or honeycombs can be tested by using single or multiple acoustic probes mounted upon appropriate scanning mechanics and feeding data process and presentation equipment.



**Fig. 2.** Comparison of destructive tensile strength tests on honeycomb sandwich panels with the predicted strengths using the Fokker bond tester. A series of honeycomb constructions is represented, where the foil thicknesses and the cell sizes are both varied: (●), foil thickness 0.007 in. (0.177 mm), cell size 0.125 in. (3.175 mm); (□), foil thickness 0.003 in. (0.076 mm), cell size 0.250 in. (6.25 mm); (▲), foil thickness 0.002 in. (0.05 mm), cell size 0.1875 in. (4.762 mm); (○), foil thickness 0.001 in. (0.025 mm), cell size 0.250 in. (6.35 mm). (From R E Clemens, Paper presented at the American Society for Non-destructive Testing Technical Meeting, California, February 1962)



**Fig. 3.** An ultrasonic C-scan image of two deliberate bonding defects shown by the dark areas between the dotted boundaries, in the bond area of a step lap joint. (From J L Rose, P A Meyer, *Ultrasonic procedures for predicting adhesive bond strength*, *Mater. Evaluation*, **31** (6), 109, 1973)

*Pulse-echo testers* A vast range of general flaw detectors are available that can be used specifically for the location of voids in the glue line or at the interface. Depending upon the relative size of the acoustic beam employer and its wavelength to the size of the defect being sought, the amplitude of the beam is attenuated by their presence. Where the defects are small compared to the beam width, the overall wave amplitude is attenuated by scattering induced by the defects (to an extent depending upon their number and size relative to the wavelength). The relationship between microvoid volume fraction and wave amplitude (also wave velocity) can be determined via careful calibration. The extent of macrovoid size can be determined by scanning the beam across the joint. Figure 3 demonstrates the principle of macrovoid detection and sizing by pulse-echo testing. An acoustic transducer operating at a frequency of  $\sim 1$  MHz is coupled to the specimen by water or grease and scans rectilinearly across the bonded structure. It produces a short pulse of ultrasound, which refracts and reflects at the interfaces of the joint. A non-bond reflects back over 90% of the incident sound. The magnitude of the reflected pulse amplitude is registered on a chart recorder as a shade of grey or as colour and yields a plan view of the void area in the joint. Relatively large areas of laminates and honeycombs can be studied depending upon the scale of the scanning mechanics and coupling facilities that

can be made available. In the case of honeycombs or multiple laminates, the scan can be adjusted to show all defects anywhere in the depth of the structure or at selected depths.

### *Select References*

- G. J. Curtis, Adhesively bonded structure nondestructive testing with acoustic methods, in *Ultrasonic Testing*, J. Szilard, Ed., John Wiley, 1980.
- D. J. Hagmaier, End product non-destructive evaluation of adhesive-bonded metal joints, *Engineered Materials Handbook. Adhesives and Sealants*, Vol. 3, ASM International, 1990, pp. 743–776.
- Y. Bar-Cohen and A. K. Mal, End product non-destructive evaluation of adhesive-bonded composite joints, in *Engineered Materials Handbook. Adhesives and Sealants*. Vol. 3, ASM International, 1990, pp. 777–784.
- I. Munns, *Mater. World*, **3**(11), 527–529(1995).
- I. J. Munns and G. A. Georgiou, *Insight*, **37**(12), 941–952 (1995).
- C. Meola, G. M. Carlomagno and L. Giorleo, *J. Adhes. Sci. Technol.*, **17**(9), 1207–1222 (2003).



# O

---

## *Optical microscopy*

---

B C COPE

The average human eye is capable of resolving two points 0.1 mm apart. In order to discern or resolve features smaller than this, some form of microscopy must be used.

In the compound optical microscope, contrast is produced by the transmission through, or reflection from matter, of visible light. A positive objective lens is used to produce a real image that is viewed through and magnified by a negative eyepiece. The resolution produced by such a microscope is maximized by a reduction in the wavelength of the illuminating light to the minimum visible and an increase in the numerical aperture (decrease in the focal length) of the objective lens. The limits to the latter are set by the physical proximity of the lens and the specimen and the very shallow depth of field obtainable with very short focal length (and hence high-resolution and high-magnification) objectives. Overall, the maximum useful magnification obtainable with a dry objective (one operating in air) is around 700x, corresponding with a resolution of 0.4  $\mu\text{m}$ . Resolution is improved when the path of a light ray between the sample and the objective is through a medium of higher density. Thus, when an oil immersion objective is used with a refractive oil filling in the space between the specimen and the objective, a useful magnification of 1400x and a resolution of 0.2  $\mu\text{m}$  are obtained.

Of course, the image created by any objective may be enlarged to give an ostensibly very high magnification, but such magnification is “empty”, revealing no further detail, once the minimum resolvable distance is magnified to the resolving power of the eye.

In transmission mode, thin specimens (a few micrometres) are essential to avoid complete attenuation of the light. These may be cut using a steel or glass microtome and are mounted between a glass slide and a glass cover slip. The microscope is especially versatile in this mode as polarization may be employed to reveal contrast in birefringence generated by differences in crystallinity or strain level. Sections through adhesive joints may yield useful information when viewed in transmission, for example, on adhesive

penetration into a porous substrate (see **Roughness of surfaces**). However, the sectioning may be difficult and may introduce artefacts (i.e. visible features originating in the sample preparation method rather than in the inherent nature of the sample).

This difficulty in producing reliable sections is probably the single factor that most limits the scope of optical microscopy in adhesive studies. Adhesives and substrates that are flexible tend to deform rather than cut cleanly. Such specimens may need to be supported in a cast block of epoxide or other resin or may need to be cooled down in liquid nitrogen prior to cutting. At the other extreme, very hard samples, such as many thermosets and liquid crystal polymers, are too hard to form coherent sections by cutting and must be reduced by grinding in the same way as geological or metallurgical specimens.

Phase-contrast illumination employs special condensers and objectives that improve the visible differences between phases with similar optical characteristics. The technique may be useful in showing phase segregation in adhesive films.

The reflection technique is more limited in resolution and magnification than is transmission. Reflection optical microscopy of adhered surfaces is often revealing, but the very limited depth of field is a severe handicap. Nevertheless, examination of surfaces after testing or failure is a simple, but important, first step in determining locus of failure (see **Stress distribution: mode of failure**). Surface reflectivity of specimens is often improved by deposition of a layer of metal. The reflection microscope is especially useful when operated in dark-field mode, where topographical differences are accentuated.

The Nomarski differential interference contrast technique accentuates changes in specimen thickness and refractive index in transmission without giving the haloes round fine features that distract from the usefulness of the phase-contrast technique. In reflection, images are obtained that strongly accentuate the topographical features present.

**Scanning electron microscopy** offers vastly improved depth of field and magnification in the study of topography, but the simplicity of sample preparation, the freedom from vacuum and beam damage and the relatively modest cost of the optical microscope are attractive.

### *Select References*

- L. C. Sawyer and D. Grubb, *Polymer Microscopy*, 2nd edn, Chapman and Hall London, 1995.
- R. J. Oldfield, *Light Microscopy*, Wolfe, London, 1994.
- E. M. Slayter and H. S. Slayter, *Light and Electron Microscopy*, Cambridge University Press, Cambridge, 1992.
- D. A. Hemsley, *Applied Polymer Light microscopy*, Elsevier, London, 1989.

# P

---

## *Packaging industry*

---

R J ASHLEY

The packaging industry represents a significant market for adhesive materials. The construction of packaging materials involves the use of a wide spectrum of adhesive types and covers many methods of assembly. Some applications include coatings, which act as adhesive layers for bonding to other forms of packaging, for example, in the form of labels or tapes (gummed and pressure sensitive), or heat seal lacquers and cold seals, while some adhesives may be used to assemble the final package form, as in the case of a carton, or to prepare sophisticated laminates. The markets for packaging materials are diverse, mainly concerned with food, beverage, medical and heavy-duty industrial applications, each of which can bring stringent performance requirements and impose harsh environments under which the adhesive layer is expected to function. The nature of the differing substrates used relies on a good understanding of adhesion science to assess for surface preparation requirements and development of appropriate test procedures.

### *Materials*

In general, the adhesives used fall into categories of solvent-borne resins, water-based dispersions and solutions or solvent-free 100% solids and hot melts. Apart from coatings, methods used to produce multi-layer complexes include **Laminating**, **Extrusion coating**, **Coextrusion** and thermal bonding. Unlike other industrial sectors, the packaging industry uses a very broad range of materials as the basis for adhesives, and typical of these are the following (see **Adhesive classification**):

*Solvent-based dispersions* such as polyvinyl acetate, **Polyurethane**, polyesters, polyethers, acrylic copolymers, **Rubber-based adhesives** with tackifiers and plasticizers.

*Water-based dispersions or emulsions* such as polyvinyl acetate, acrylics, polyvinyl chloride and polyvinyl alcohol with plasticizers and tackifiers. In addition, this range can include urea formaldehyde and phenolic adhesives, resins, natural adhesives produced from starch, dextrin, casein, animal glues (see **Polyvinyl alcohol in adhesives**, **Phenolic adhesives: single-stage resoles**, **Phenolic adhesives: two-stage novolacs**, **Animal glues and technical gelatins**) and rubber latex (see **Emulsion and dispersion adhesives**).

*Solvent-free 100% solids* such as polyurethane. **Hot melt adhesives** include **Ethylene-vinyl acetate copolymers**, polyolefins, polyamides, polyesters with tackifiers and waxes. More recent additions include cross-linkable systems.

Trends over the last few years have been for a reduction in the use of **Solvent-based adhesives** in favour of water-based systems and higher solids content or 100% solids (**Environment and the impact of adhesive technology**). The use of hot melt adhesives has gained importance within the industry for use as carton assembly and labelling or tapes. The **Acrylic adhesives** have been considerably developed and have found increased use in lamination, especially in view of the advantages offered by UV or electron beam curing systems for rapid cross-linking (see **Radiation-cured adhesives**). Some of the natural adhesives such as starch and dextrin have been replaced by the synthetic polyvinyl acetate emulsions for improved tack. A revolutionary change involved use of cold seal latexes applied to polymer films for chocolate bar wrappings being linked to packaging machine developments.

While development of adhesive materials may have been rapid, their introduction and change can be slow because of a need to invest in new application equipment. Changes to systems also have implications in the investigation of process conditions. In terms of hot melts, developments have included lower temperature for application and reduced stringing for cleaner use.

The packaging industry is diverse in the range of materials used and areas where adhesives are required for bonding. Substrates include cardboard, paper, metal sheets and foils and polymeric films (plain, printed, coated and metallized). Adhesive tapes can also be based on cloth or can include fibres as reinforcements. Packaging containers can also be formed from metals, rigid plastics and glass to which a laminate may be sealed, acting as a lid. To satisfy some of the properties required of a package such as barrier, no single material may offer suitable performance, so use is made of composite structures where the properties of several materials are combined. In the form of laminates, the substrates to be bonded include paper, metal foils and most types of polymer as films. Specific uses of adhesives cover paper making, fibre board construction (cases and corrugated board), carton assembly, adhesive tapes, labels, composite tube winding, cold seals for films and envelopes and flexible packaging laminates. In addition to these areas, adhesion situations arise in the application of a coating or lacquer to a substrate, printing inks, varnishing, metallizing or heat seal applications. The nature of the surface to be bonded and the interfacial properties are of prime importance to achieve satisfactory performance, especially where the adhesive is bonding to a coating rather than to base materials. The technology may therefore also include surface modification and application of primers to enhance adhesion (see **Primers for adhesive bonding**).

### *Service requirements*

Packaging applications serve a wide range of industries from heavy-duty wrappings or sacks to containing and preserving of foodstuffs and medical products. The final materials

may be expected to perform under hostile environments such as high or low temperature, for example, deep-freeze packs and cook-in pouches, or extremes of humidity. Some of the products packed can have detrimental effects on adhesive bonds such as solvent-based polishes, cleaning agents, shampoos, essential oils and spices. Adhesive bonds can also be affected by the migration of additives (see **Rheological theory, Compatibility**) used in the plastic films, leading to failure of the package and spoilage of the products (especially foodstuffs). Some packages, for example those used in the medical applications, may be required to resist steam sterilization and irradiation. Apart from interactions with products and environment, packaging materials will also need to survive various abuse criteria that arise in the transportation systems. This may include damage via dropping, flexing or vibration, and a degree of resilience would be expected to be built into the construction.

Apart from adequately bonding various substrates together and retaining the desired shelf-life for the package, care must be taken with the selection of adhesives to suit the application involved. Problems can arise because of interaction effects between product and pack, causing odour or taint. In some cases, strict codes of practice and regulations limit the types of adhesives that may be used. There have been particular concerns over the use of some isocyanate cross-linking agents, leading to extensive migration studies of laminates in contact with foods. The two most common reference sources are the Food and Drug Administration (FDA) Register of the USA and Bundesgesundheitsamt (BGA) of Germany. In addition, local standards of good manufacturing practice apply to each country, although attempts are made to harmonize laws. These regulations have important implications in the nature of the global manufacturing and packing practices of the industry. A more recent area of regulation is the implication for recycling of materials and waste laws relating to landfill disposal (see **Environment and the impact of adhesive technology**). There is a desire to develop single material packaging to aid recycling and minimize sorting. One problem can be adhesive residues left in board where this can produce difficulties in the subsequent machine handling of a regenerated material. There may be some justification for investigation of bio adhesive systems within packaging to assist the material breakdown or recycling issues.

Residual solvents in laminates are a common source of odour and taint in products. A solvent may also act as a carrier to aid migration of additives to surfaces, leading to adhesion problems such as loss of bonding or heat seal strength. Understanding adhesion failure often requires a detailed examination of surfaces to determine the exact location, and this can be difficult as some layers may only be a few microns thick.

Suitable test programmes need to be adopted in the development of packaging materials to ensure fitness for purpose. In terms of adhesive bonding, the peel test is common but can suffer many in-house variants, causing some confusion. The use of adhesive design techniques such as finite-element analysis has not been exploited within the packaging industry, a difficulty being the thin nature of most substrates that make interpretation difficult.

See also **Laminating, Extrusion coating, Coextrusion.**

### Select References

- R. J. Ashley, *Adhesion* 7, K. W. Allen, Ed., Elsevier Applied Science Publishers, London, 1983, pp. 221–251.  
R. J. Ashley, M. A. Cochran and K. W. Allen, *Int. J. Adhes. Adhes.*, **15**(2), 101–108 (1995).

---

## Paint constitution and adhesion

---

N R WHITEHOUSE

### *Introduction*

Paints are used for protective purposes (e.g. to prevent corrosion of metals or the ingress of moisture into wood), for decorative purposes (to colour and enhance the appearance of a surface) and for functional purposes (to afford fire protection or prevent marine fouling). For all end uses, it is essential that the coating remains firmly adherent to the surface for as long as possible. The robust adhesion of paint films, therefore, under aggressive service conditions such as sunlight, atmospheric pollution, abrasion and water immersion is of primary importance.

Paints consist of a medium (the liquid part of the paint), pigments, extenders, and various additives in minor amounts. The binder, or resin, is the non-volatile, film-forming part of the medium. It ensures adhesion to the substrate and cohesion within the paint film. Film formation is determined by the binder type, and the type of binder influences film strength and other physical and chemical properties. The flexibility of some film-forming resins can be improved by the introduction of a plasticizer. Solvents reduce the viscosity of the binder, allowing a paint to be made and later applied. They form the volatile part of the medium and should evaporate during application and film formation. The solvent may be water. Pigments and extenders have a major effect on physical properties of paint films, such as hardness and water resistance. Extenders are added to formulations to reduce cost (saving expensive primary pigment) and, if chosen correctly, can improve mechanical properties and application qualities. Additives (minor components) may be included in formulations to increase shelf life and minimize sagging, for example.

### *Mechanisms of adhesion*

The adhesion of paint films is influenced primarily by the chemical composition of the binder. Films may adhere by a mix of all possible mechanisms, for example, **Dispersion forces, Acid–base interactions, Hydrogen bonding**, covalent bond formation and other specific chemical interactions, such as chelation. In addition to these molecular interactions across an interface, the micro-roughness of the substrate can contribute by increasing the surface area and points of contact (see **Mechanical theory of adhesion**). In addition, if the substrate is itself another paint film (or a plastic), chain ends of the overcoating polymer can diffuse into the substrate, provided that the binder types are mutually compatible (see **Theories of adhesion**).

### *Binders and plasticizers*

Binders in coatings include polyvinyl acetate and copolymers, polyvinyl butyral, polyesters, acrylic polymers, epoxies and polyurethanes (see **Ethylene–vinyl acetate copolymers, Acrylic adhesives, Epoxide adhesives and Polyurethane**), polyvinyl chloride, polyvinylidene fluoride and alkyds (oxygen-convertible media containing polyol esters of long-chain unsaturated acids). All these potential film-formers can adhere through dispersion forces, (which are probably weak). Many binders, however, also contain

chemical groups that can participate in the other specific interactions listed above. Hydroxyl and carboxyl groups, for example, have been shown to increase adhesion. Too many polar groups in a film, however, increase water sensitivity and, in multi-coat systems, can lead to incompatibility between coats, thereby moving the potential for adhesion failure from the primer/substrate to the primer/overcoat interface (see **Stress distribution: mode of failure**).

Chain polymers are usually plasticized for use as binders. The introduction of a plasticizer promotes good adhesion by increasing the flexibility of the film and allows more points of contact with the substrate as the solvent evaporates. The configuration of polymer molecules at the surface of a substrate will determine the number of points of contact that can be achieved. Polymer configuration is an aspect of the mechanism of coating adhesion that can be studied by Fourier transform infrared spectroscopy (see **Infrared spectroscopy**).

### *Importance of solvent*

The solvents used in coatings are hydrocarbons for alkyds, and aromatics in admixture with more polar solvents for most other media. Highly insoluble polymers, such as polyvinyl chloride and polyvinylidene fluoride, are applied as dispersions. Selection of a wrongly formulated solvent mixture may have an adverse effect on the adhesion of a film, when formed at room temperature. High boiling solvents, for example, can become trapped at the film–substrate interface for some considerable time and give rise to a soft and poorly adherent film.

Further information on the adhesion of paints can be found in the articles **Paint primers**, **Paint service properties and adhesion** and **Pre-treatment of metals prior to painting**.

### *Select References*

- J. Bentley and G. P. A. Turner, *Introduction to Paint Chemistry and Principles of Paint Technology*, 4th edn, Chapman and Hall, London, 1998.
- A. Goldschmidt and H.-J. Streitberger, *BASF Handbook on Basics of Coating Technology*, Vincentz Network, Hannover, 2003.

---

## *Paint primers*

N R WHITEHOUSE

Paint primers are the first coat of a multi-coat system to be applied to a surface. On wood, for example, an important function is to provide adequate bonding between the substrate and subsequent finishing coats, especially under damp conditions.

On metals, while promotion of adhesion of the multi-coat system is equally important, an added requirement is the control of corrosion. In metal primers, anti-corrosive properties are achieved by incorporating either pigments that are anodic to the metal substrate or pigments, such as zinc phosphate, that inhibit corrosion by other mechanisms.

The binder itself can also prevent corrosion if it has good barrier properties and a high electrical resistance.

Good adhesion of primers to metal substrates can best be achieved by ensuring cleanliness of the metal surface and by selection of generic coating primer types based on binders with chemical groups that can bond strongly to surfaces.

Specialist primers are **Autophoretic primers** and **Etch primers**, both of which react chemically with the metal surface to achieve a good bond.

### *Select Reference*

R. Lambourne and T. A. Strivens, Eds., *Paint and Surface Coatings: Theory and Practice*, 2nd edn, Woodhead Publishing, Cambridge, 1999, Chap 9.

---

## *Paint service properties and adhesion*

---

N R WHITEHOUSE

### *Introduction*

A discussion of mechanisms of adhesion and the influence of paint constitution on adhesion is given in **Paint constitution and adhesion**. In this article, aspects of paint adhesion are considered that affect the paint film once it has formed.

### *Internal stress*

Once a film has formed, its physical properties are important for the retention of adhesion. All paint films possess an **Internal stress** as a consequence of their drying and curing. Solvent-borne coatings will shrink as the solvent evaporates, beyond the point at which the bulk film appears to be rigid; coatings, which are cured thermally, acquire an internal stress by cooling through their  $T_g$  (**Glass transition temperature**). In addition, because organic coatings have coefficients of thermal expansion two to three times greater than those of metals, internal stresses arise from differential contraction on cooling (with respect to the metal substrate), from a stoving temperature to ambient, for example, or from ambient to sub-zero temperatures in a cold climate. Stresses in coatings can lead to failures. For example, repeated maintenance painting often builds up a film so thick that the cumulative stress overcomes the adhesion of the first coat to the substrate and causes the composite paint film to detach and fail.

Water penetration of coatings is usually destructive. Diffusion of water through the binder or penetration through submicroscopic cracks in the film allows water to accumulate at the coating–substrate interface. If transport of the water is driven osmotically, the resulting build up of pressure will disrupt the coating and lead to failure (see **Durability: fundamentals**).

### *Testing paint films*

Many tests have been devised for the measurement of adhesion after the film has formed. At best, the relationship of such measurements to the forces operating at the interface are



tenuous, because the tensile properties of the film constitute an interface (see **Tests of adhesion**). If the metal surface is examined spectroscopically (see **Surface analysis**), it is found invariably that a film (sometimes only a monolayer in thickness) remains firmly bonded to the substrate.

Pigmentation may increase the tensile strength of a film and give an appearance of higher adhesion in a test. It should be remembered, however, that adhesion is not affected by bulk properties, as it is an interfacial phenomenon.

Simple adhesion tests will always be informative. They can show, for example, whether or not a surface is sufficiently firm to be painted satisfactorily, or allow the progressive effects of weathering to be monitored (see **Weathering of adhesive joints, Durability**).

### *Weathering*

Exposure of a painted surface to weathering leads generally to a progressive reduction in adhesion. Adhesion promoters can be beneficial (see **Silane adhesion promoters**). Typically, these are films applied very thinly that have the ability to react with hydroxyl groups on the metal surface to form strong covalent bonds. Low molecular weight substituted silanes, for example, function in this way by making many points of contact with the metal surface.

### *Select Reference*

R. Lambourne and T. A. Strivens, Eds., *Paint and Surface Coatings: Theory and Practice*, 2nd edn, Woodhead Publishing, Cambridge, 1999, Chaps 16, 19.

---

## *Peel tests*

D E PACKHAM

A peel test, as its name suggests, is a test in which the force required to peel a flexible member is recorded and it gives a measure of adhesion. There are many varieties of the test; some are illustrated in Fig. 1. Often, the substrate is rigid and the flexible member is peeled at a defined angle, but where both materials bonded are flexible, such as laminated plastic film, a T-peel can be done (see also **Pressure-sensitive adhesives – adhesion properties**). It is possible to use the **Climbing drum peel test** for relatively rigid materials. It is evident that the “peel angle”, 90 or 180° or whatever is a formal angle between the lines of action on substrate and peeled strip, cannot be the actual angle at the point of fracture: for any given formal angle, this will vary according to the bending stiffness of the peeled member (Fig. 2).

The choice of an appropriate form of the test will often be dictated by practical considerations of the adhesive bond of interest. As with all **Tests of adhesion** it is important to standardize the test-piece dimensions and details of the test method in order to ensure that results are comparable. It is usual to express the results as a “peel strength”, the average peel force per unit width of the strip peeled. Even with this normalization, it is unwise

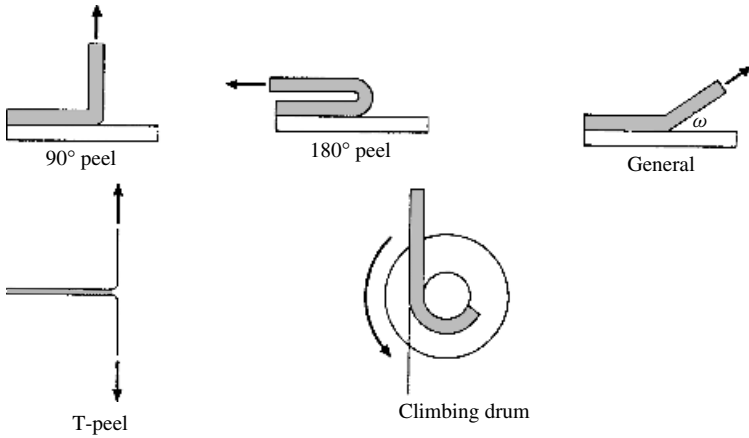


Fig. 1. Some different types of peel test



Fig. 2. Difference between the formal and actual peel angle

to alter the width peeled without checking whether there is an effect on the normalized peel strength.

In many adhesion tests, each piece tested gives only a single estimate of strength such as stress at failure in **Shear tests** and **Tensile tests**. An advantage of a peel test is that each strip peeled yields a trace, which shows how the force varies along the whole distance peeled; in taking an average, the deviation from the mean and any systematic variation along the sample can easily be seen.

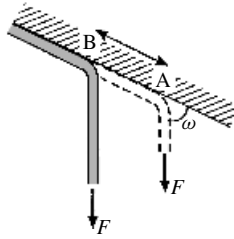
*Peel force and peel energy*

Although for many straightforward comparative purposes it is often adequate to record the results as a peel force/width, it is easy to derive an expression for the peel energy from basic mechanical principles by equating the work done by the test machine to the work done on the sample.<sup>1</sup> The result forms a basis for understanding and interpreting peel tests (see also **Fracture-mechanics test specimens**).

Consider a sample peeling a distance  $AB(= x)$  at angle  $\omega$  by the application of a force  $F$  (Fig. 3). The point of application of the force will have moved

$$l = x(1 - \cos \omega) + \Delta x \tag{1}$$

where the first term is a result of freeing a length  $x$  of strip and the second ( $\Delta x$ ) represents the extension of the feed length  $x$  caused by the force  $F$ ;  $\Delta x$  could be measured in a



**Fig. 3.** Simplified peel theory: strip peels a distance  $AB = x$

separate experiment or calculated if the tensile properties of the material of the strip were known.

The work done by the machine is then  $Fl$ , and can conveniently be written as

$$Fl = Fx(\lambda - \cos \omega) \quad [2]$$

where the expression for  $l$  has been simplified by introduction of the extension ratio  $\lambda$  (extended length/original length).

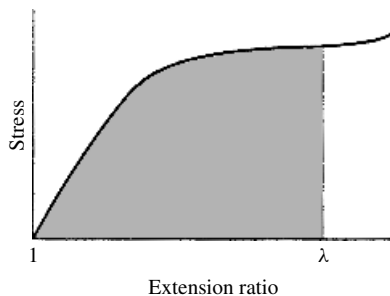
The work done on the sample can be expressed as the sum of two terms. The first is the peel energy  $P$ , which we take to be the energy (per unit area of peeled substrate surface) dissipated in the broad region of the peel front. The second is the work done in stretching the freed strip, which will be the strain-energy density  $W_\lambda$  for extension to  $\lambda$ . Here,  $W_\lambda$  can be calculated if an expression, such as Hooke's law, for the tensile stress-strain relationship for the material is known for extensions up to  $\lambda$ , otherwise it can be evaluated from the work done in an appropriate tensile test (Fig. 4). This can be used whether or not the yield point has been exceeded. Thus,

$$\text{Work done on the sample} = Pbx + W_\lambda bxt \quad [3]$$

It should be noted that as  $W_\lambda$  is expressed per unit volume, it has to be multiplied by the volume of peeled strip;  $t$  is its thickness.

By equating Eqn. 2 with Eqn. 3 we obtain, for the peel energy,

$$P = \frac{F}{b}(\lambda - \cos \omega) - W_\lambda t \quad [4]$$



**Fig. 4.** Strain-energy density is given by the area under a stress-extension ratio curve

The experimental conditions selected may well enable Eqn. 4 to be simplified. If the extension of the peeled strip is negligible, as is often the case,  $\lambda$  is unity and  $W_\lambda$  is zero; 90 and 180° are commonly chosen peel angles. Under these circumstances, Eqn. 4 reduces to

$$P_{\pi/2} = F/b \quad \text{at } 90^\circ \quad [5]$$

and

$$P_\pi = 2F/b \quad \text{at } 180^\circ \quad [6]$$

These suggest that the peel load at 90° should be twice that at 180°. This point is discussed below.

### Peel energy

An advantage of the analysis given is that it concentrates attention on the peel energy. Here  $P$  is the energy (per unit area) dissipated by all the energy-dissipating processes involved in the broad region associated with the peel front. Fracture occurs and new surfaces are created, so there will be a thermodynamic term, work of adhesion  $W_A$  or work of cohesion  $W_C$  (see **Contact angles and interfacial tension**), depending on whether failure is adhesive or cohesive (see **Stress distribution: mode of failure, Rheological theory**). To this must be added other terms according to the materials and circumstances of the experiment. These may include terms for plastic deformation of the adhesive close to the fracture surface, for viscoelastic dissipation as the peel front advances causing adhesive to be stressed and then relaxed (see **Viscoelasticity**) and for losses (plastic and/or viscoelastic) in bending the freed strip through the peel angle. Thus,  $P$  may be written as the sum of various terms:

$$P = W_A(\text{or } W_C) + \psi_{\text{plast}} + \psi_{\text{v/e}} + \psi_{\text{bend}} + \dots \quad [7]$$

### Factors affecting peel energy

Values of the thermodynamic terms ( $W_A$  and  $W_C$ ) in Eqn. 7 can usually be obtained from **Contact angle measurement** (see **Good–Girifalco interaction parameter** and **Surface energy components**). A number of analyses have sought to relate the energy dissipated plastically to the polymer properties, the thickness of the peeled strip and the peel angle.<sup>2,3</sup> In most practical circumstances, the thermodynamic terms are orders of magnitude smaller than the others: the magnitude of peel energy is largely determined by the extent of dissipation within the materials of the adhesive bond.

The thickness of the adhesive, and of any backing used, will affect the peel strength in several ways. It directly enters the strain-energy density term ( $W_\lambda t$ ) and may also alter some of the dissipation terms in Eqn. 7 by changing the actual angle at the peel front (see Fig. 2) or by altering the volume of polymer in which plastic or viscoelastic dissipation occurs. Many of the terms in Eqn. 7 will be temperature and rate dependent, so the peel strength will also depend on these variables.

### Peel angle variation

In as much as Eqn. 4 is only based on definitions and principles of mechanics, it must be correct for a given peel angle. It will predict the variation of  $P$  with peel angle if

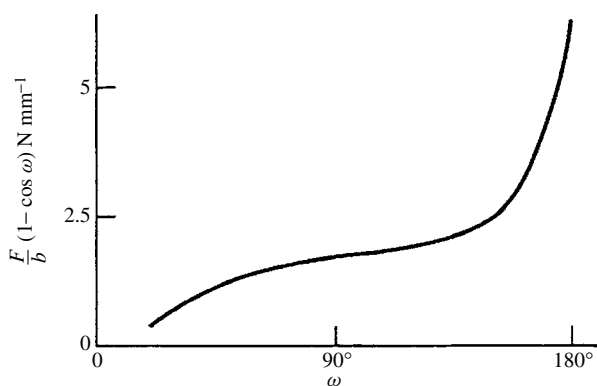


Fig. 5. Peel angle

the peel energy itself is a term independent of angle of peel. With some simple rubbery adhesives the equation is quite well followed, and the predictions of Eqns. 5 and 6 about 90 and 180° peel strengths are observed. However, most polymers are more complex mechanically than simple rubbers, and Eqns. 4, 5 and 6 do not represent their behaviour. According to Eqn. 4, the results plotted in Fig. 5 should be a horizontal straight line. They refer to the peeling of polyethylene from sulphochromated aluminium (see **FPL etch**), and show clearly that the peel energy,  $P$ , varies with angle. As the peel angle changes, bending losses will vary and the balance between shear and cleavage forces at the peel front will change, affecting energy losses at the peel front: all of these may exert a significant influence on  $P^{2,3}$  and will therefore lead to deviations of the angle dependence predicted by Eqn. 4.

### References

1. J. W. Cook, S. Edge and D. E. Packham, *Int. J. Adhes. Adhes.*, **17**, 333–337 (1997).
2. Y. Wei and J. W. Hutchinson, *Int. J. Fracture*, **93**(1–4) 315–333 (1998).
3. A. J. Kinloch and G. J. Williams, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 273–301.

### Phenolic adhesives: two-stage novolacs

JOHN BISHOPP

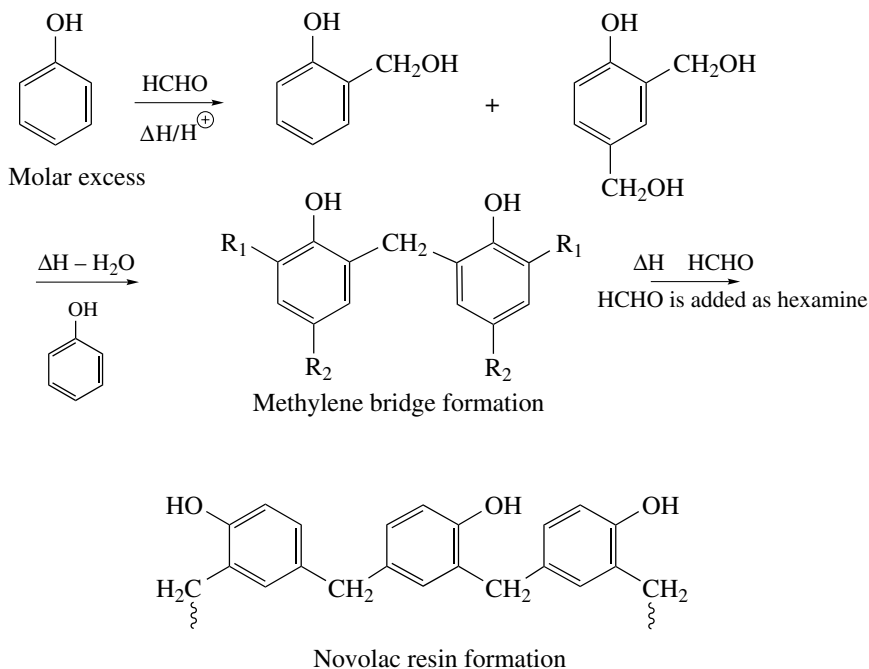
Phenolic-based adhesives are widely used in industry. Different manufacturing routes lead to two classes of phenolic adhesives, *resoles* and *novolacs*. The former are considered in **Phenolic adhesives: single-stage resoles**; this article is concerned with novolacs.

Although phenolic novolacs are most usually supplied as “lump” resins or powders, the adhesives are invariably formulated as organic solvent-based solutions; they are not generally encountered as “hot melt” adhesives.

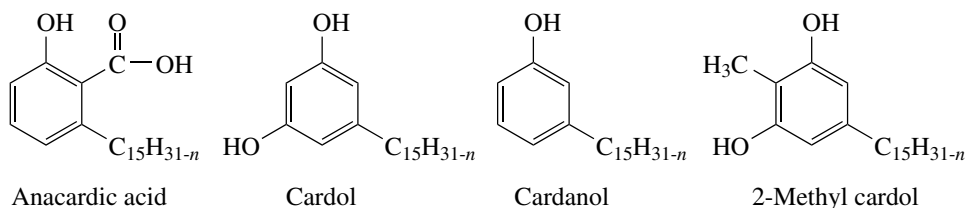
As for resoles, simple novolacs are based on phenol and formaldehyde. However, they use P:F ratios in the region of 1:0.8 (i.e. the phenol rather than the formaldehyde is now in excess) and the reaction is acidic, rather than alkaline catalysis.

Phenolic novolacs are produced by condensation reactions (**Step polymerization**), and a typical schematic is given below. It is clear that one of the major differences between novolacs and resoles is that, in their initially advanced stage, novolacs do not contain the methylol groups, which are so essential to the thermal cure of phenolic resole resins and adhesives.

To achieve cure, therefore, a “hardener” has to be added to the adhesive formulation. Suitable compounds are hexamethylene tetramine (hexamine) and paraformaldehyde as both are formaldehyde donors. In the case of the hexamine, thermal breakdown, in the presence of the water produced by the phenol/formaldehyde condensation reaction, not only yields more formaldehyde but also ammonia, which can help catalyse the reaction.



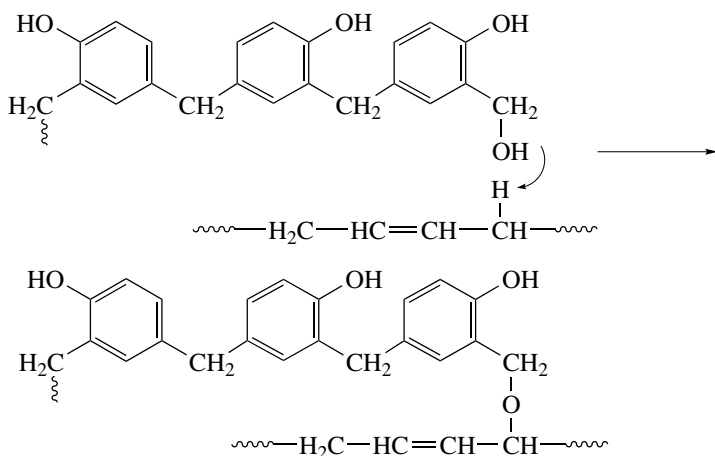
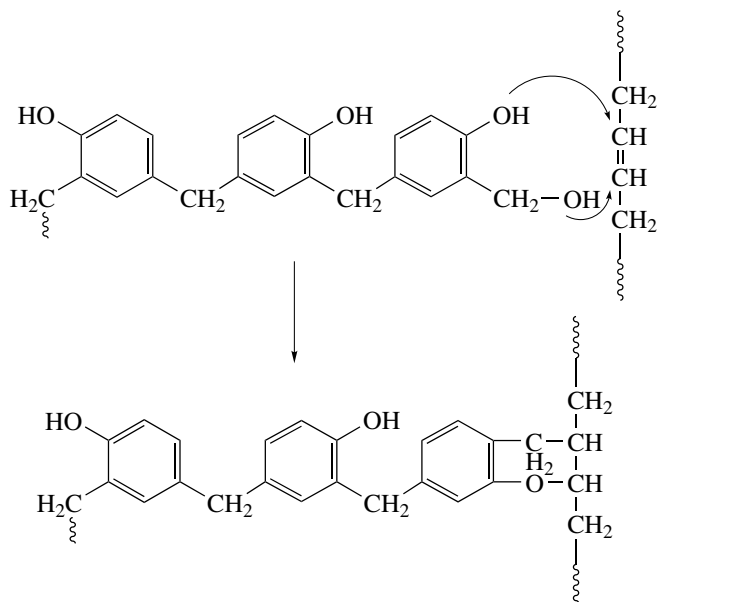
Most commercial novolacs now are far more complex, using combinations of polyhydric phenols such as resorcinol or Bisphenol A and/or highly substituted phenols such as cashewnut shell oil (CNSL) or a blend of phenol and CNSL.



[Where  $n = 0, 2, 4, 6$ ; dependant on the degree of unsaturation within each chain]

Combining the novolac resin with hexamine, at a loading of about 8 to 10 parts of hexamine to 100 parts of novolac, enables the adhesive to be cured at 150 °C within 30 to 60 min. However, some industries, particularly those involved in the manufacture of bonded automotive drum brakes, raise the cure temperature to as high as about 245 °C to enable the cure time to be reduced to about 2 min.

Again, because of the condensation reactions, which take place during cure, bonding pressures have to be high (700 kPa) to ensure that the released volatiles do not “blow” the glue line. Once again the brake bonding industry can be significantly different in that pressures of about 3 to 4 MPa can be used.



Although unmodified phenolic novolac adhesives (particularly for tyre–cord bonding) can give bonds that exhibit both excellent thermal and environmental durability, they are also inherently brittle. To reduce the shrinkage on cure and to provide stress relief within the joint, novolacs can be co-cured with, particularly, acrylonitrile butadiene elastomers.

Two reactions between the phenolic resin and the NBR are possible, but both depend on the fact that during cure some methylol groups will be available to react, preferentially, with the NBR rather than with further novolac species. The first is a condensation/addition reaction across the double bond (chroman formation) and the second is a condensation reaction with the  $\alpha$ -hydrogen atom on the elastomer.

Phenolic novolac adhesives are extensively used in **Automotive applications**: bonding friction material to steel in the production of brakes, clutches and drive shafts. They are also used as tyre–cord adhesives and in the manufacture of furniture, laminated board and grinding wheels. See also **Wood adhesives – phenolics**.

The neat novolac resins are also the precursors in the manufacture of a range of (see **Epoxy adhesives**), such as epoxy phenol novolacs and epoxy cresol novolacs epoxy resins.

### Select References

- D. M. Brewis, J. Comyn and S. T. Tredwell, *Durability of Phenolic Adhesives*, Leicester Polytechnic School of Chemistry, 1982.
- G. B. Evans, *40 Years of Structural Adhesive Bonding*, CME, 1985.
- F. L. Tobiasson, in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, pp. 316–340.
- J. A. Bishopp, *Int. J. Adhes. Adhes.*, **17**(4), 287–301 (1997).
- W. D. Detlefsen, in *Adhesion Science and Engineering–2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 869–945.
- A. Pizzi, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, Chaps 26–29, pp. 541–614.

## Phenolic adhesives: single-stage resoles

---

JOHN BISHOPP

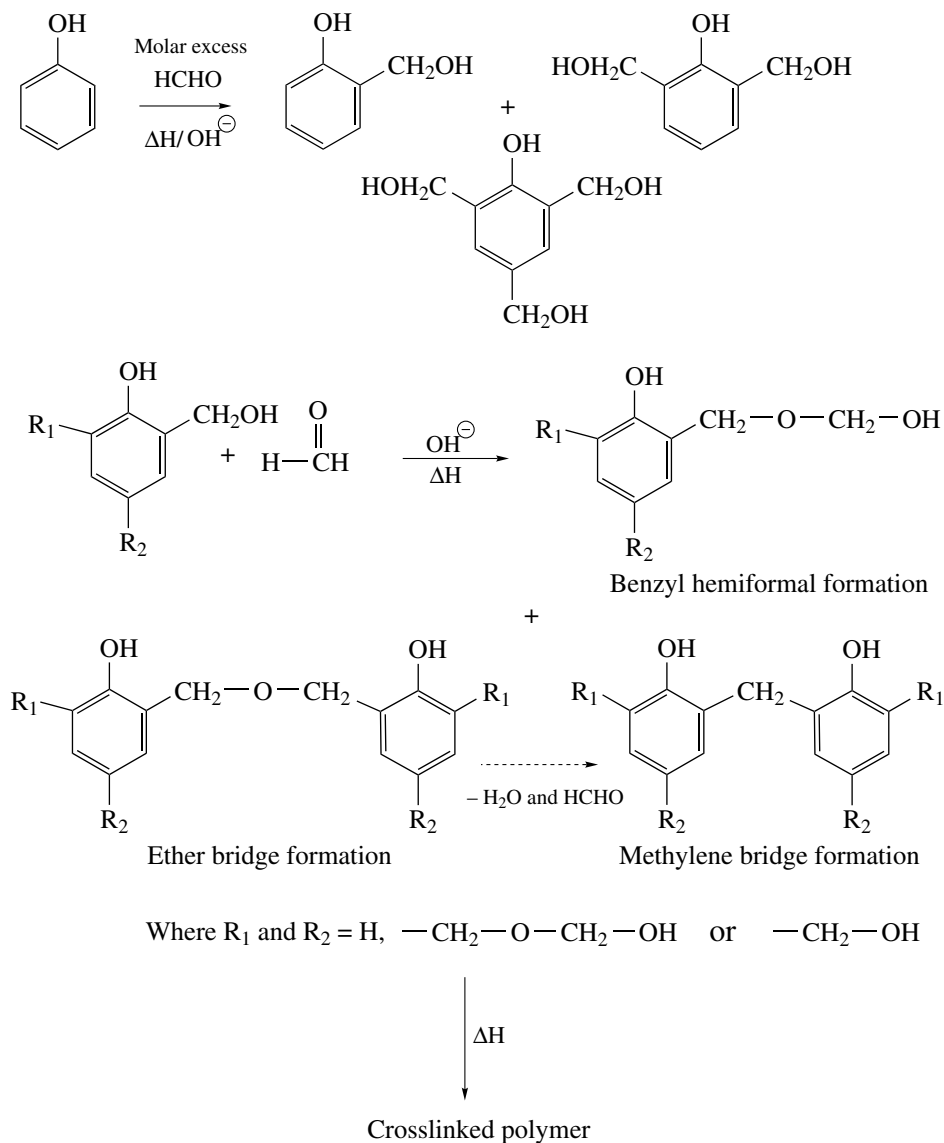
Two families of phenolic-based adhesives are to be found in industry: those formulated with phenolic *resoles* and those with *novolacs*. Although the starting chemistries for both resins are very similar, both are phenol/formaldehyde polymers, the different manufacturing routes leading to resins with significantly dissimilar properties. This article is concerned with resoles: novolacs are considered in **Phenolic adhesives: two-stage novolacs**.

### Phenolic resoles

Phenolic resoles provided the backbone chemistry for the first structural adhesives for bonding metal substrates; these were the Redux (*Research at Duxford*) range of adhesives. They are invariably supplied as solutions, usually in industrial methylated spirits or ethanol, which effectively precludes their use in “hot melt” adhesive formulations.



Simple resoles are based on phenol and catalysed with NaOH or a caustic/ammonia combination. They generally utilize phenol to formaldehyde ratios (P:F ratios) in the region of 1:1.4 to 1:1.6, which appear to be optimum for structural adhesives; ratios higher than 1:1.6 produce resins, which, for example, are used in plywood manufacture, where excellent moisture resistance is required. Phenolic resoles are produced by condensation reactions (**Step polymerization**), and a typical schematic is as follows:



The above schematic shows the formation of a resole from unmodified phenol. However, many commercial resole resins are produced from alkyl-substituted phenols and/or di-, tri- or even polyhydric phenols.

As resoles cure simply by heat activation, no hardener components need to be added to the formulation, which will cure in the region of 140 to 150 °C in 30 to 60 min; resoles are still active, albeit to a low degree, at ambient temperatures. Simple acceleration of cure can be achieved by

- raising the temperature, which reduces the cure time to as little as 5 to 15 min;
- using *p*-toluene sulphonic acid or a resorcinol/formaldehyde resin as an accelerator, which will reduce cure temperatures to the region of 120 to 130 °C or even lower.

Owing to the condensation reactions, which take place during cure, bonding pressures have to be high (700 kPa) to ensure that the released volatiles do not “blow” the glue line.

Although unmodified phenolic resole adhesives can give bonded structures that will exhibit excellent durability – both thermal oxidative resistance and resistance to harsh environments such as oil, sea water, natural weathering – they are inherently brittle. Much research work has been carried out over the years to impart some degree of toughness into these systems and at the same time to reduce the shrinkage on cure and, thus, provide some stress relief. However, toughening, in the sense understood with epoxy adhesives, is not really possible with these resins.

The best approach has been to react (**Step polymerization**) the resoles, during cure, with suitable high-molecular weight polymers such as polyvinyl acetals, epoxies, acrylonitrile butadiene rubbers (NBR) or, better, their carboxylated variants, polyurethanes and polyamides. The methylol groups on the phenolic react with the active hydrogen groups (hydroxyls or secondary amines) on the polymer.

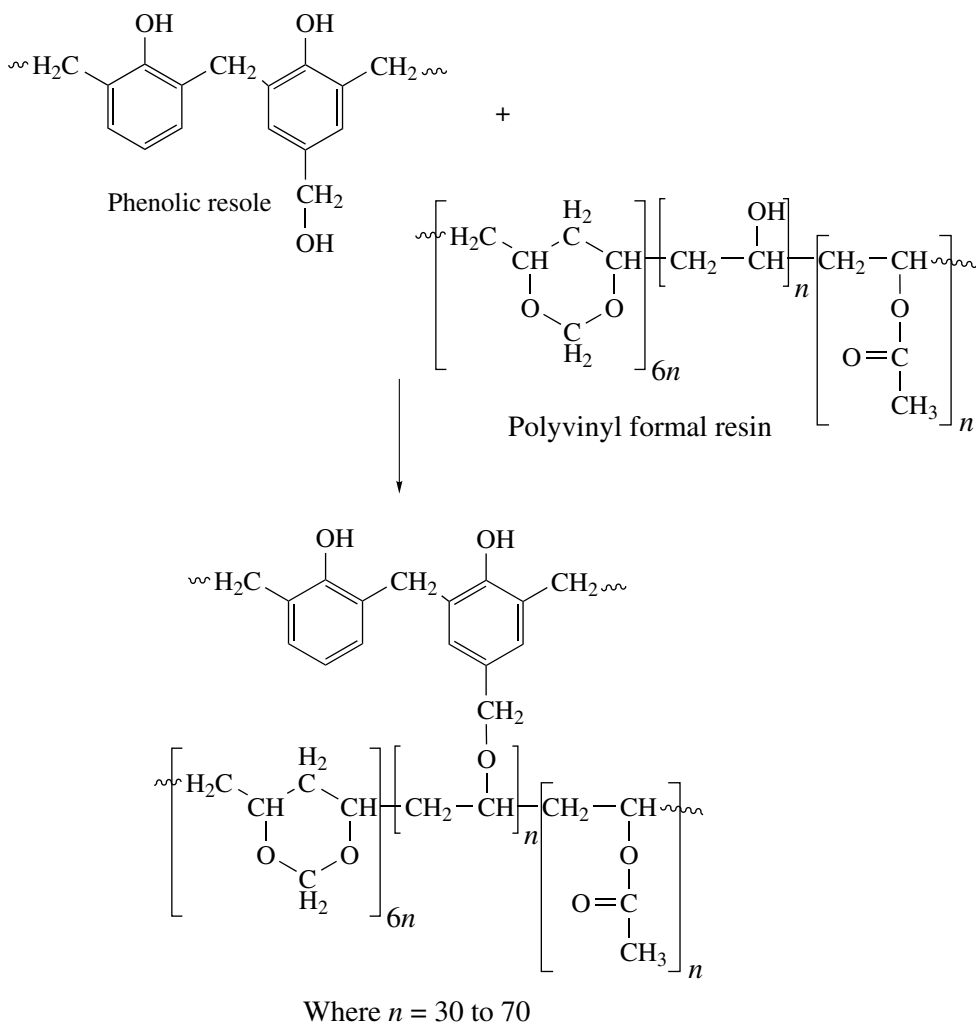
This has led to adhesives with enhanced properties and has reduced some of the inherent brittleness associated with cured resoles. Further, this has been achieved without seriously affecting their high temperature performance. A typical example is given where an acetal resin, polyvinyl formal (PVF) reacts with a resole.

Another approach is to capitalize on the fact that resoles are excellent solvents for polyamides, polyvinyl acetals, polyurethanes, epoxies, and so on. If these selfsame, tough polymers are modified by adding a less than equivalent quantity of the resole, then, indeed, tough adhesives can be formulated. However, in these combinations, where resoles are used as the modifier, the thermal properties are essentially determined by the polymer being used.

One example will suffice. Redux 64 was a resole solution to which about 15 to 20% of a PVF resin had been added. The peel performance was very low, almost non-existent, whereas thermal resistance is seen up to >200 °C. With Redux 775, on the other hand, where the resole content is only about 30 to 35%, the upper service temperature for the bonded joint is 70 to 80 °C whereas the floating roller peel performance is in the region of 8 to 10 N mm<sup>-1</sup>.

Most phenolic resole adhesives are supplied in liquid form where the adhesive is dissolved in suitable solvent(s). However, there are some exceptions where the adhesive can be supplied as a readily handleable *film*. Notable examples are Redux 775 Film (resole/PVF) and the 3 Ms range, which includes Scotch-Weld AF 6, AF 10, AF 31, AF 32, and so on (resole/NBR).

As has already been indicated, phenolic resole adhesives are renowned for their excellent environmental resistance. Both this and their good thermal oxidative resistance can, at least in part, be attributed to their high aromaticity. They can also contribute a potential



synergy in applications calling for good “fire, smoke and toxicity” (FST) performance. This makes these adhesives excellent candidates for structural bonding of “interiors” where flammability is key.

The major drawback, as far as their use in structural adhesives is concerned, is that they are difficult to use in bonded sandwich structures. Perforated honeycomb core has to be used because of the volatiles produced on cure and they do not possess good filleting behaviour. In the latter case, a core primer has to be used. The other problem is the general need to use a solvent route when formulating and/or applying these adhesives.

The first structural use of these adhesives was to bond friction material to steel in the clutches for Cromwell and Churchill tanks. Many metal-to-metal **Aerospace applications** followed in both military (Sea Hornet, F7 Cutlass, SAAB Draken) and civil (DH Dove, DH Comet, Fokker F27 to F100) aircraft. Indeed, today, they are still used in such aircrafts as the RJ 80 and the BAE SYSTEMS Hawk trainer.

Other applications include bonding in missile motors and body structures, hovercraft, **Automotive applications** including automotive drive shafts and drum and disc brakes, skis and snowboards and furniture and laminated boards. See also **Wood adhesives – phenolics**

### Select References

- D. M. Brewis, J. Comyn and S. T. Tredwell, *Durability of Phenolic Adhesives*, Leicester Polytechnic School of Chemistry, 1982.
- G. B. Evans, *40 Years of Structural Adhesive Bonding*, CME, 1985.
- F. L. Tobiasson, in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, pp. 316–340.
- J. A. Bishopp, *Int. J. Adhes. Adhes.*, **17**(4), 287–301 (1997).
- W. D. Detlefsen, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 869–945.
- A. Pizzi, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, Chaps 26–29, pp. 541–614.

## Plasma-polymerized coatings

W J VAN OOIJ

Plasma polymerization is a technique for depositing coatings of organic polymers onto any substrate. The plasma polymers can be obtained from almost any organic monomer, even those, such as ethane and other saturated hydrocarbons or fluorocarbons, that cannot be polymerized by conventional **Chain polymerization** or **Step polymerization**. When injected into a plasma, such monomers are decomposed by the high-energy electrons in the plasma and form radicals. These radicals can react with radicals already formed or adsorbed on a substrate and form a film, which grows further, as the film is continuously impacted by electrons and ions forming new radicals.<sup>1,2</sup> It should be emphasized that in a plasma only the electrons are at a high temperature. The radicals, ions and substrate are not far from room temperature. Since it requires very little power to generate a plasma in a low pressure gas (e.g. of the order of 10 W), this technique can be used to deposit coatings on polymeric substrates without damage to the substrate. It is thus a very versatile surface modification technique.

The equipment used for plasma polymerization, as well as the basic deposition mechanism, is shown in Fig. 1. Although commercial equipment is available, most researchers choose to design and construct their own equipment. All that is needed is a vacuum chamber with a pump so that a gas or vapour can flow through the chamber and a means for exciting a plasma. Typically, internal electrodes (capacitively coupled plasma) or external coils are used (inductively coupled plasma), as shown in Fig. 1. The power supply can be DC, AC (60 Hz), RF (12.56 MHz), or microwave frequency (2.35 GHz). During deposition the pressure in the chamber is, typically, of the order of 1–20 Pa and powers of 1–100 W are often used.

Polymers deposited from a plasma differ greatly from those synthesized by conventional techniques. As a result of their random three-dimensional growth mechanism, they are

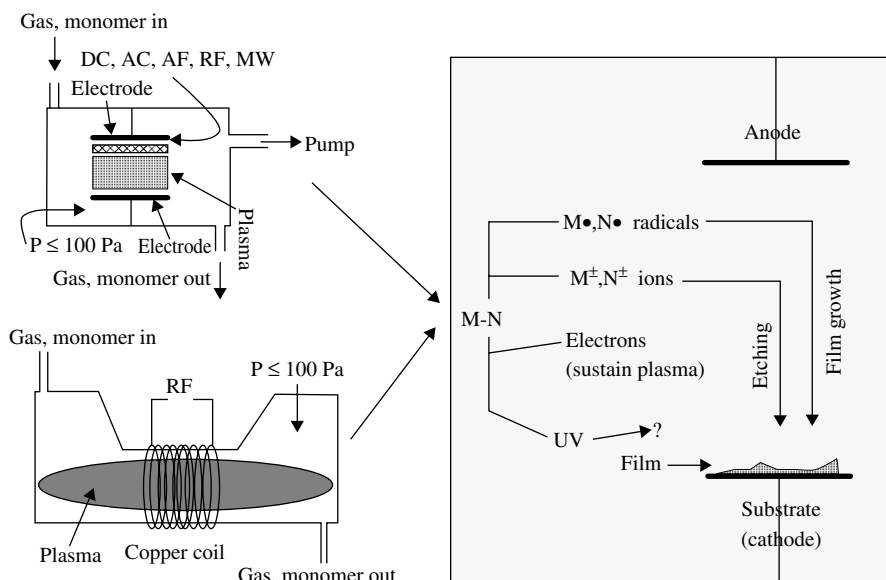


Fig. 1. Equipment and principles of plasma polymerization

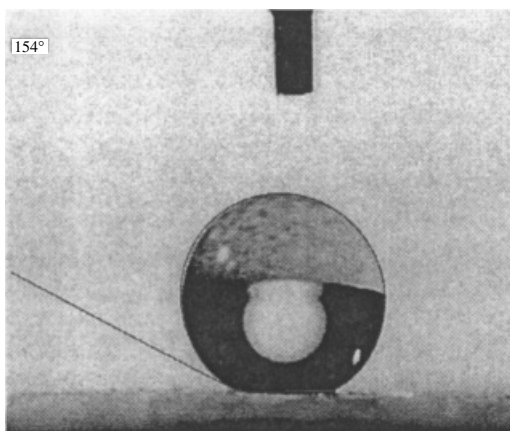
often highly cross-linked and they lack structural regularity of their repeat units. Many different functional groups are formed, functional groups are formed, depending upon the elements (such as nitrogen or oxygen) present in the monomer. Reactions with residual oxygen can also occur as well as instantaneous reactions with the atmosphere after removal from the reactor. This occurs as many plasma polymers tend to contain long-living residual radicals in their surface. As a result, they are easily oxidized in air.

The deposition rate of a plasma polymer as well as its structure is strongly dependent on the plasma conditions such as power, monomer flow rate, pressure and, to a lesser extent, substrate temperature. Higher power and lower pressure both tend to increase the intensity of the ion bombardment of the growing film, and films that are harder and more cross-linked can be obtained. Increase of the pressure and/or lowering the power leads to softer, more organic films, which may still contain some structural units of the original monomer.

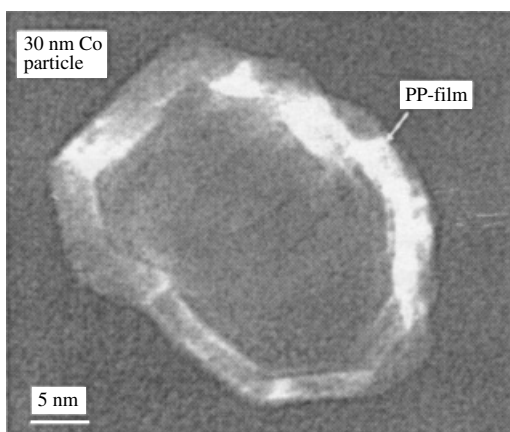
Other properties of plasma polymers that are often different from conventional polymers are greater temperature stability, lower permeability to gases and water vapour, higher modulus, lower electrical conductivity, greater resistance to chemicals, that is they are often totally insoluble in solvents. Some of these properties make plasma polymers suited for use as protective coatings. As an example, Fig. 2 shows the surface modification of filter paper by depositing a film of plasmas-polymerized  $C_6F_{14}$  on it. A water droplet had a contact angle of  $154^\circ$  on it, so water could no longer wets the filter paper.

In Fig. 3, a 30-nm nanoparticle of cobalt is shown, which had been coated with a 5-nm plasma film, also of  $PP-C_6F_{14}$ , for protection against corrosion by atmospheric moisture.

The adhesion between the plasma polymer films and most substrates is usually very good, as the substrate can be cleaned and activated *in situ* by an argon plasma prior to deposition. This plasma creates radicals in the substrate surface, which can subsequently react with radicals formed by the monomer. Whether the surface of the plasma film



**Fig. 2.** Water droplet on PP-C<sub>6</sub>F<sub>14</sub>-treated filter paper



**Fig. 3.** Cobalt nanoparticle coated with 5-nm film of PP-C<sub>6</sub>F<sub>14</sub>

adheres well to additional coatings, such as paints or adhesives, depends on the choice of monomer and the deposition conditions. If the deposition conditions are such that residual functional groups remain in the plasma film surface, adhesion can be very good. As an example, it was found in the author's laboratory that pyrrole deposited from a DC plasma on aramid tyre cords gave excellent adhesion to sulphur-vulcanized rubber if the deposition conditions were low power and high pressure (10 W, 20 Pa). When the conditions were changed to 50 W and 5 Pa, adhesion was practically lost. The former type of film contained more reactive double bonds that would interact with the sulphur curing mechanism of the rubber.<sup>3,4</sup>

### References

1. N. Inagaki, *Plasma Surface Modification and Plasma Polymerization*, Technomic Publishing Company, 1996.

2. H. Yasuda, *Plasma Polymerization*, Academic Press, Orlando, FL, 1985.
3. S. Luo and W. J. van Ooij, *J. Adhes. Sci. Technol.*, **16**, 1715 (2002).
4. W. J. van Ooij, S. Luo and S. K. Jayaseelan, *Elastomer*, **34**, 299 (1999).

---

### Plasma treatment

---

D BRIGGS

Strictly, plasma treatment encompasses any form of surface treatment in which a material is exposed to an ionized gas (plasma). This would include **Flame treatment** and **Corona discharge treatment**, but “plasma treatment” generally refers to low-pressure treatments requiring vacuum equipment. Such processes are also often referred to as glow discharge treatment.

In simple versions of such a process, power is coupled into the discharge either capacitively or inductively; in the former, the electrodes are usually inside the vacuum system with the sample resting on one of them, while in the latter the coil is external to the system. The AC power is either in the radio frequency (RF) band (almost always at the fixed frequency of 13.56 MHz) or in the microwave band (frequencies in GHz).

Depending on the gas used to generate the plasma and the plasma parameters, essentially three different forms of “treatment” are possible.

The first involves noble gas plasmas and has previously been known as “casing”. Here, the principal effect is one of surface cross-linking and elimination of potential *weak boundary layers*, but a very useful effect is the generation of a barrier layer to additive diffusion.

The second involves simple “reactive” gas plasmas (e.g. O<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, CF<sub>4</sub>). Here, the principal effect is the introduction of functional groups containing the elements present in the gas molecules. In either of these two types of treatment, a prolonged exposure will lead to ablation of material (etching) and surface texturing.

The third involves “polymerizable” gas plasmas capable of depositing a film on to the substrate (see **Plasma-polymerized coatings**). These molecules do not have to be polymerizable in the conventional sense; examples are CH<sub>4</sub>, C<sub>6</sub>F<sub>6</sub>, CH<sub>3</sub>OH. The highly cross-linked “polymer” laid down on the substrate is pinhole free even at thicknesses below 100 Å and adheres tenaciously to the substrate. Depositions using mixed gases can build up “graded” interface structures. Clearly, the scope for fine tuning surface properties is immense with this technology. Many gases can lead to either modification or deposition depending on the plasma parameters chosen (pressure, say 0.1–10 torr, flow rates, power, substrate temperature, etc.).

Plasma treatments have been used for some time to change the adhesive properties of irregular-shaped articles by batch processing, but more recently, reel-to-reel systems for film treatment have become available both out of line (inside a vacuum chamber, as in metallization) and in line (air–vacuum–air).

#### Select References

- E. M. Liston, L. Martinu and M. R. Wertheimer, Plasma surface modification of polymers for improved adhesion: a critical review, in *Plasma Surface Modification of Polymers*, M. Strobel, C. S. Lyons and K. L. Mittal, Eds., VSP, Utrecht, 1994, Part 1.

M. R. Wertheimer, L. Martinu, J. E. Klemberg-Sapieha and G. Czeremuszkina, Plasma treatment of polymers to improve adhesion, in *Adhesion Promotion Techniques*, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, New York, 1999, Chap 5.

---

### *Polar forces*

---

K W ALLEN

The attraction between two electrostatic charges of opposite sign (or repulsion between charges of the same sign), originally investigated by Coulomb in 1785, is well known. It is dependent directly upon the magnitude of each charge and inversely upon the square of the distance between them. In considering the interaction of atomic and molecular particles, this force of attraction is of importance in several situations – in materials which are ionic in nature as well as in cases where one or both particles has a dipole moment.

#### *Ionic structures*

Consider the simplest case; when there is a sufficiently great difference in electronegativity (attraction for electrons) between two atoms, then a transfer of an electron may occur to give a positively charged cation and a negatively charged anion. These two ions will then attract each other and form an ionic compound. This can be extended to cases where the particles are not simple atoms but are groups of atoms, which give rise to charged radicals.

In the solid, this will give infinite lattice with the ions occupying symmetrical positions so that there is overall electrical neutrality. In solution, the ions become separated and solvated to give a conducting electrolyte solution. Typical examples are sodium chloride and, slightly more complex, ammonium nitrate.

This type of strictly ionic bonding is not of importance in most examples of adhesion, but it needs to be reviewed here to give a satisfactory appreciation of the situation.

#### *Dipoles*

In covalent molecules, where the bonding depends upon a sharing of electrons between atoms, the distribution of electron charge density may not be symmetrical. If the electronegativity of the atoms is significantly different, then there will be a bias in this charge density toward the nucleus with the higher electronegativity. Thus, while the molecule will be overall electrically neutral, one end will carry a small negative charge (excess of electron density) and the other will carry a small positive charge (deficit of electron density). This situation is called *dipole* and the molecule is said to have a “dipole moment”.

Within the molecule, this situation is usually described in terms of the covalent bond having a partial ionic character, and this will affect its properties and behavior. Between two (or more) molecules with dipole moments, there will be additional interactions arising from these electrostatic dipoles.

The dipole moment of a molecule is represented by  $\mu$  and is expressed in Debyes (D) where  $1 \text{ D} = 1 \times 10 \text{ esu}$ . (electrostatic units) of charge centimeter. If a molecule had



a charge equivalent to one electron separated by a distance of 1 Å, then the dipole moment  $\mu$  would amount to 4.8 D. (1 D =  $3.336 \times 10^{-30}$  C m.)

Intermolecular interactions arising from dipoles can be divided into two groups: those between two molecules each of which has a dipole moment and those between two molecules only one of which has any permanent dipole moment.

### *Dipole–dipole interactions*

If two molecules each with a dipole moment are within the vicinity of each other, then there will be a mutual interaction and attraction between them depending upon the alignment between them. This is known as the “*orientation*” effect and was first investigated by Keesom in 1912. He derived a relationship for the energy between two molecules of dipole moment  $\mu_1$  and  $\mu_2$  separated by a distance  $r$ :

$$U = -\frac{2}{3} \cdot \frac{1}{(4\pi\epsilon_0)^2} \cdot \frac{\mu_1^2\mu_2^2}{r^6} \cdot \frac{1}{kT} \quad [1]$$

where  $\epsilon_0$  is permittivity of a vacuum,  $k$  is Boltzmann’s constant and  $T$  is absolute temperature.

### *Dipole–molecule interactions*

Consider the situation when a molecule with a permanent dipole moment comes near to another different molecule that does not have any dipole moment. The first will induce a dipole in the other by polarization of the electron field in that second molecule. This is known as the *induction effect* and was extensively investigated by Debye, who derived a relationship similar to that by Keesom but including polarizability terms,  $\alpha_1$  and  $\alpha_2$ :

$$U = \frac{1}{(2\pi\epsilon_0)^2} \frac{\alpha_1\mu_2^2 + \alpha_2\mu_1^2}{r^6} \quad [2]$$

This induction effect may also be effective when the second molecule itself has a dipole moment, so that it exists in the interaction between two identical molecules. Calculations indicate that, for example, with HCl, which has a dipole moment of 1.03 D, the orientation effect amounts to 3.3 and the induction effect to 1.0 kJ mol<sup>-1</sup>.

It is common for both Eqns 1 and 2 to be written in the abbreviated form

$$U = -A/r^6 \quad [3]$$

where  $A$  is the attraction constant. It is evident that

$$A_{12} = (A_{11}A_{22})^{1/2} \quad [4]$$

is an exact relationship for orientation forces and an approximate one for induction forces. (The subscripts 11 and 22 refer to interaction between like molecules, 12 to those between unlike molecules.)

The complete potential energy curve for the molecules is given by the Lennard–Jones potential

$$U = A/r^6 + B/r^{12} \quad [5]$$

where  $B$  is a constant. The second term represents the repulsion energy, which rises very rapidly with distance once the electron orbitals start to interact. Equations analogous to 3–5 apply for **Dispersion forces**.

Debye and Keesom forces together with London **Dispersion forces** are known collectively as *van der Waals forces*. See **Lifshitz-van der Waals forces** for a further discussion. They play a significant role in the **Adsorption theory of adhesion** and in surface phenomena such as **Contact angles and interfacial tension**.

### Select References

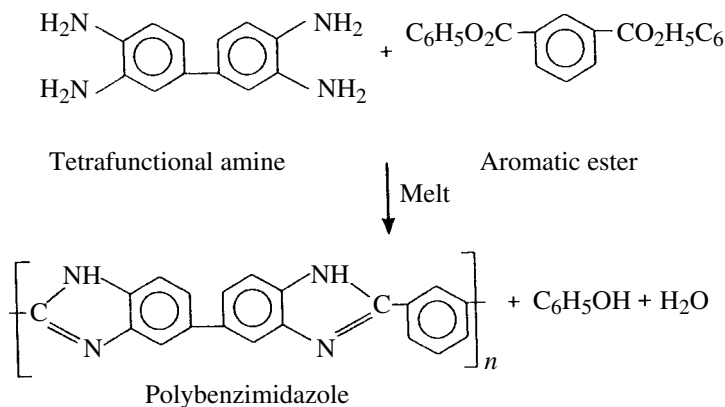
- K. W. Allen, in *Aspects of Adhesion I*, D. J. Alner, Ed., University of London Press, 1965, pp. 11–21.  
 J. A. A. Ketelaar, *Chemical Constitution*, 2nd rev. edn, Elsevier, London and New York, 1958, Chap V.  
 R. J. Good, in *Treatise on Adhesion and Adhesives*, Vol. 1, R. L. Patrick, Ed., Edward Arnold, London; Marcel Dekker, New York, 1967, Chap 2.  
 H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, Pergamon Press, Oxford, 1971.

## Polybenzimidazoles

S J SHAW\*

Initially developed in the late 1950s and early 1960s, polybenzimidazoles are prepared by reaction of tetrafunctional aromatic amines with aromatic esters (Fig. 1). They find application as **High-temperature adhesives**.

Since high-molecular-weight polybenzimidazoles exhibit, depending upon structure, fair to high levels of intractability, adhesive formulations based on them generally employ the



**Fig. 1.** Reaction scheme/structural formula for polybenzimidazole

polymeric component initially in a low-molecular-weight prepolymer (dimer or trimer) form, with the final polymerization step being conducted within the bond line. Unfortunately, this occurs by a polycondensation reaction, resulting in the liberation of both phenol and water, which can therefore result in a porous adhesive layer of low mechanical strength (see **Step polymerization**). To alleviate such problems, polybenzimidazole adhesives require bonding pressures of approximately 1.4 MPa at cure temperatures in the region of 320 °C, together with the venting of condensation products. Even under such circumstances, however, large-area bonding can remain particularly difficult.

In spite of these difficulties, it is important to note that polybenzimidazoles offer substantial high-temperature capabilities, particularly for short-duration applications with the not inconsiderable ability to retain about 50% of room temperature strength at approximately 450 °C. In fact they can be regarded as superior to all their high-temperature competitors, including both the condensation polyimides and epoxy-phenolics in this respect. Unfortunately, this capability is not maintained under long-term, high-temperature conditions because of their susceptibility to oxidative degradation at temperatures in excess of 250 °C. For this reason, post-cure operations at about 400 °C, which are often considered necessary, need to be conducted in inert atmospheres, thus adding further complexity and cost to the processing operation.

One further substantial advantage that the polybenzimidazoles enjoy over their competitors is their ability to retain good mechanical properties at temperatures as low as –190 °C.

Although in certain respects the polybenzimidazoles offer a virtually unique combination of properties, they have not enjoyed the success of other **High-temperature adhesives**. A major reason for this has undoubtedly been due to the monomeric materials required, most notably aromatic tetraamines, being both costly and difficult to obtain in the required purity. In addition, doubts concerning carcinogenic activity have also been expressed (see **Health and safety**), which, together with the adverse processability mentioned above has severely restricted their acceptance. For these reasons, commercial availability has to date been somewhat limited.

Further discussion on the general theme of high-temperature adhesives can be found in the articles entitled **Polyether ether ketones**, **Polyimide adhesives** and **Polyphenylquinoxalines**.

#### *Select References*

- S. Litrak, *Adhesive Age*, **11**(1), 17 (1968).  
J. P. Critchley, G. J. Knight and W. W. Wright, in *Heat-Resistant Polymers*, J. P. Critchley, Ed., Plenum Press, New York, 1983.  
M. A. Meador, Recent advances in the development of processable high-temperature polymers, *Ann. Rev. Mater. Sci.*, **28**, 599–630 (1998).

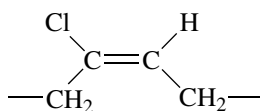
---

### ***Polychloroprene rubber adhesives: applications and properties***

---

JOSÉ MIGUEL MARTÍN-MARTÍNEZ

Polychloroprene rubber (CR), often called by the trade name *Neoprene*, possesses the characteristics of natural rubber and has the advantage of higher polarity. CR adhesives are by far the most important family of **Rubber-based adhesives**.



**Fig. 1.** Structural formula of polychloroprene

The chemical structure of CR is analogous to that of natural rubber (see **Natural rubber-based adhesives**) with the methyl group of *cis*-1,4-polyisoprene replaced by a chlorine atom, see Fig. 1.

The curing of CR adhesives is different from that for most rubber-based adhesives as it involves the labile chlorine atoms. This is reflected in the compounding ingredients. The most common room curing agent is zinc oxide, but isocyanates are also very common. Further discussion is given in **Polychloroprene rubber adhesives: modifiers and additives**.

About two-thirds of the CR adhesives are *solvent dispersions*. Solids content range from 5 to 90 wt%, the most common range is 15 to 30 wt%. Properly compounded solvent-borne CR dispersions are resistant to degradation by heat, sunlight, ozone, water, oils and chemicals. Solvent selection allows a great variation in adhesive viscosity and drying rate. Compounding with resins allows specific adhesion to many porous and non-porous substrates to be produced.

*Water-borne contact adhesives* are growing in importance because of environmental regulations, occupation health and the flammability of solvents. The solids content in the water-borne polychloroprene adhesives varies between 40 and 60 wt%, and viscosities between 15 and 500 mPa can be obtained. Although *polychloroprene latices* are water based, they are generally inflammable as the resin is dissolved in organic solvents before emulsifying. All polychloroprene latices are susceptible to coagulation by mechanical, thermal and chemical means.

### Properties

Characteristic of CR adhesives is a high green strength and, with the addition of phenolic resin, high ultimate strength (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**). They have good resilience, better than for natural rubber. Oil resistance too is better than that for natural rubber adhesives, but not as good as that for NBR. Temperature resistance and ageing properties are excellent: with proper compounding, CR adhesives can be used between  $-40$  and  $175^\circ\text{C}$ . A wide range of substrates can be joined. CR adhesives bond to almost any high-polar surface, as well as to many low-polar surfaces (including polyolefins).

### Adhesion characteristics

The properties of the *solvent-borne CR adhesives* depend on the molecular weight, degree of branching and rate of crystallization of the polymer. The ability of polychloroprene adhesives to crystallize is unique as compared to other elastomers. The higher the crystallization rate, the faster the adhesive strength development. The crystallization is responsible for the quick grab of polychloroprene adhesives. This rapid bond strength

development allows the formation of immediate dry bonds without the need for clamping or pressing.

Bond strength can vary from a temporary bond (non-curing compound) to a substrate-tearing bond (using phenolic-modified curing products). Solvent-borne CR adhesives can be formulated to have very short open times for fast production operations or to retain contact bond characteristics for up to 24 h. Heat and solvent reactivation can be used to re-impart tack to the dried surfaces.

Grafting of acrylic moieties on polychloroprene improves the adhesion properties of solvent-borne adhesives. IR and NMR spectroscopy studies have shown that the mechanism of grafting is a chain transfer as evidenced by the decrease in chlorine content in the graft copolymers. The adhesive formulation containing the graft-polychloroprene exhibited higher peel strength and shear strength in joints produced between upper leather and sole leather.

*Latex systems* derive their strength characteristics from the gel structure rather than crystallinity as in solution systems. In general, higher gel content leads to the same properties than polymers with higher crystallinity. Polymers with a higher gel content exhibit higher cohesive strength, modulus and heat resistance. Tack, open time and elongation are reduced.

### *Applications*

Applications of solvent-borne CR adhesives and polychloroprene latices will be considered separately.

*Solvent-borne CR adhesives* allow almost any two substrates to stick together. They are used as shoe adhesives for the permanent attachment of soles and the manufacture of leather goods, particularly leather shoe sole bonding and belt lamination.

Among automotive applications are bonding recreational vehicles' sidewalls and vinyl trim in panels. Truck and trailer roofs may similarly be bonded. In the construction industry, CR adhesives find uses in countertops and panel fabrication for curtain walls and partitions.

Solvent-borne CR adhesives are also used in high-pressure laminates for bonding foams to wood or fabric and for bonding metal, fibreglass and plastics.

*Polychloroprene latices* are mainly used for high-pressure lamination, for foam bonding and for vinyl substrates (such as PVC) adhesion. Also, they are used for foil lamination, carpet installation, and PVC floor tile bonding. Bonding and shaping of foams is done with highly crystallizable water-borne polychloroprene adhesives. The adhesive is sprayed on the foam and immediately the foam pieces are placed in contact. The assembly is wet-bonded because no drying is necessary as the water will dissipate into the foam.

In summary, like **Nitrile rubber adhesives** polychloroprene adhesives use a polar rubber and their properties complement one another.

### *Select References*

- R. S. Whitehouse, in *Synthetic Adhesives and Sealants*, W. C. Wake, Ed., John Wiley, Chichester, 1986, pp. 1–29.
- S. K. Guggenberger, in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, Chap 15, pp. 284–306.

W. F. Harrington, Elastomeric adhesives, *Engineered Materials Handbook. Adhesives and Sealants*, Vol. 3, ASM International, 1990, pp. 143–150.

J. M. Martín-Martínez, in *Adhesion Science and Engineering—2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 573–675.

### *Polychloroprene rubber adhesives: modifiers and additives*

JOSÉ MIGUEL MARTÍN-MARTÍNEZ

Most **Rubber-based adhesives** may be cured by a sulphur-based vulcanizing system (see **Rubber-based adhesives: compounding**), however, as mentioned in **Polychloroprene rubber adhesives: applications and properties**, CR adhesives are cross-linked by various reactions involving the labile chlorine atoms in the repeat unit. This is reflected in the additives used, as discussed below.<sup>1,2</sup>

#### *Solvent-borne CR adhesives*

The typical components of a solvent-borne CR adhesive formulation is shown in Table 1. Each component is considered below. Note that fillers are not commonly used.

*Polychloroprene elastomer* Although grades Neoprene AC and AD<sup>1,2</sup> are the most commonly used, the latter is more prevalent because of its superior viscosity stability.

*Metal oxides* Metal oxides provide several functions in solvent-borne polychloroprene adhesives. Their main function is as an *acid acceptor*. Upon ageing, small amounts of hydrochloric acid are released, which may cause discolouration and substrate degradation. Magnesium oxide (4 phr) and zinc oxide (5 phr) act synergistically in the stabilization of solvent-borne polychloroprene adhesives against this dehydrochlorination.

Table 1. Typical components of a solvent-borne CR adhesive

Component
Polychloroprene elastomer
Metal oxides
Tackifiers (resins)
Antioxidant
Solvent
Curing agents
Other modifiers

Magnesium oxide, in addition, *retards scorch* (premature cure) during mill processing of polychloroprene adhesives.

Zinc oxide is a *curing agent*, producing a room-temperature cure of solvent-borne CR adhesives, giving increased strength and improved ageing resistance.

Magnesium oxide reacts in solution with *t*-butyl phenolic resin to produce an infusible resinate, which provide *improved heat resistance*. The resinate has no melting point and decomposes above 200 °C. A small amount of water (1–2 phr) is necessary as a catalyst for the reaction.

*Tackifiers (resins)* Addition of resins to solvent-borne CR adhesives serve to improve specific adhesion and autoadhesion, increase tack retention and increase hot cohesive strength. *Para-tertiary* butyl phenolic resins are the most common resins for solvent-borne CR adhesives. In general, addition of 40–45 phr provides an adequate balance of tack and heat resistance. In general, tack decreases by increasing the phenolic resin content in the CR adhesive, and bond strength reaches a maximum at about 40 phr, decreasing for high amounts of phenolic resin (see **Phenolic adhesives: single stage resoles** and **Phenolic adhesives: two-stage novolacs**).

The high heat resistance produced by adding phenolic resins to solvent-borne CR adhesives is due to the formation of the infusible resinate (mentioned above), which reduces the thermoplasticity of the adhesive and provides good bond strength up to 80 °C. 4 phr of magnesium oxide for 40 phr of phenolic resin are sufficient to produce room-temperature reaction.

Terpene phenolic resins can also be added to solvent-borne CR adhesives to increase open tack time and to provide a softer glueline than *t*-butyl phenolic resins. To provide adequate hot bond strength, these resins are used in combination with a polyisocyanate curing agent.

Addition of a low molecular weight chlorinated rubber (containing about 65% chlorine) promotes the adhesion of solvent-borne CR adhesives to metals and plasticized PVC and improves the shear strength and creep resistance but a reduction in open time is also produced. A heat reactivation process restores tack to the polychloroprene adhesive. In this process the surface of the adhesive film is raised to 90–100 °C to destroy the crystallinity of the film and to allow diffusion to proceed more rapidly.

Isocyanates can be added to solvent-borne CR adhesive solutions as a two-part adhesive system. To improve the specific adhesion to different substrates, addition of a poly-alpha-methylstyrene resin to solvent-borne CR adhesives is quite effective.

*Antioxidant* A good antioxidant should be added to CR adhesives to avoid oxidative degradation and acid tendering of substrates. Derivatives of diphenyl amine provide good performance but staining is produced. To avoid staining, hindered phenols or bisphenols can be added. 2 phr antioxidant is sufficient in solvent-borne CR adhesives formulations.

*Solvent* Solvent affects adhesive viscosity, bond-strength development, open time, cost and ultimate strength. Blends of three solvents (aromatic, aliphatic, oxygenates – e.g. ketones, esters) are generally added, and in their selection, environmental and safety regulations must be considered.

The open tack time of the CR adhesives partially depends on the evaporation rate of the solvent blend. If a solvent evaporates slowly, the CR adhesive will retain tack longer, whereas if the solvent evaporates quickly, the cohesive strength will develop more rapidly.

*Curing agents* Curing agents are generally added to CR adhesive formulations to increase heat resistance. Thiocarbonyl and polyisocyanates can be used as curing agents. The reaction of an isocyanate with polychloroprene, which leads to improved heat resistance property, has not been fully explained.

*Other modifiers* Although they are not common, additional ingredients can be added to polychloroprene adhesive formulations to improve specific properties. *Plasticizers* can decrease the glass transition temperature, influence crystallization tendency and reduce cost. Highly *aromatic mineral oils* can be used when reduction in crystallization rate is required. *Stearic acid*, in concentrations of 0.5–1 phr, improve processability and reduce mill sticking. *Resorcinol* type resins improve adhesion to textiles and metals.

#### *Polychloroprene latex adhesives*

Many of the components are essentially the same as those shown in Table 1 for the solvent-borne CR adhesives, except that water-based ingredients have to be used and the compounding has to be particularly carefully controlled. The following ingredients can be found in most polychloroprene latex adhesives' formulations.

*Polychloroprene latex* Both anionic or nonionic latices can be used. The polymer determines the initial tack and open time, the bond-strength development and hot bond strength, the application properties and the adhesives viscosity.

*Emulsifiers* Non-compounded polychloroprene latex has good mechanical and storage stability, but the addition of other formulating ingredients may require the incorporation of additional surfactants, wetting agents or stabilizers. Surfactants are added to improve storage stability, substrate wetting and attain improved freeze resistance. Emulsifiers are used in polychloroprene latex adhesives to attain stabilization or to convert to liquid, water-insoluble chemicals (e.g. antioxidants, plasticizers) into emulsions.

*Metal oxides* 2–5 phr zinc oxide is the most effective metal oxide.

*Resins* In general, 30–60 phr are added and attention should be paid to the pH and compatibility with the emulsifier systems. The hot-bond performance is generally proportional to the softening point of the resin. *t*-butyl phenolic resins cannot be used in polychloroprene latex adhesives because of the colloidal incompatibility. Terpene, terpene phenolic, coumarone-indene, and rosin acids and esters resins can be added to polychloroprene latex adhesives' formulations.

*Antioxidant* Antioxidants similar to those for solvent-borne CR adhesives can be used. The common amount of antioxidant in latex adhesives is 2 phr.

*Thickeners* Thickeners increase the viscosity of the polychloroprene latex adhesives. Amounts up to 1 wt% of polyacrylates, methyl cellulose, alginates and polyurethane thickeners can be used. Particular attention should be paid to fluctuations in pH when thickener is added in the formulations.

*Coagulants* For some applications (e.g. plastic foam processing), "sprayable" polychloroprene latex dispersions must be used. In this process, a fast coagulation of latex particles



is important to enable immediate bonding of the substrates with exceptional high initial strength. The most common coagulants are carboxylic acids (e.g. lactic acid, citric acid) or salts of multivalent metal ions (e.g. calcium chloride, calcium nitrate, zinc sulphate, aluminium sulphate).

*Cross-linking agents* Curing agents such as aqueous suspension isocyanates produce a cross-linking reaction at room temperature and give fast bond development, but exhibit a finite pot life.

*Other ingredients* Bacterial and fungal attack can be a problem in polychloroprene latex formulations with pH below 10. It is manifested by odour, discolouration and gas evolution and 500–1500 parts per million of a biocide should be added.

### References

1. S. K. Guggenberger, in *Handbook of Adhesives*, 3rd edn, I. Skeist, Ed., Van Nostrand Reinhold, New York, 1990, Chap 15, pp. 284–306.
2. J. M. Martín-Martínez, in *Adhesion Science and Engineering–2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 573–675.

## Polyether ether ketone

D A T O D

Polyether ether ketone, poly(aryl-ether-ether-ketone) or PEEK is a highly aromatic semi-crystalline thermoplastic (Fig. 1). It is being increasingly used in a number of advanced products such as wire coatings and high-performance mouldings. PEEK is available from Victrex plc as unreinforced material, reinforced with glass and as the matrix material in a carbon-fibre composite known as APC2. The history and development of PEEK by the originators ICI Ltd has been described by Rose<sup>1</sup> and a general review of the subject has been given by Nguyen and Ishida.<sup>2</sup>

PEEK is a relatively expensive polymer, but it does have several attractive properties: high tensile strength (93 MPa at 20 °C, 37 MPa at 150 °C); high stiffness (3.6 GPa at 20 °C, 2.2 GPa at 150 °C); low inflammability; high-temperature stability; excellent chemical and radiation resistance; good fatigue, wear and abrasion resistance (see **High-temperature stability principles, Durability: fatigue**). In order to reduce the cost of the item, the polymer is frequently used as a filled system. The modulus for the unfilled grades drops sharply above the glass transition temperature (143 °C) as the material approaches its melting temperature (334 °C). This reduction in modulus is significantly reduced with the filled grades and almost removed in the continuous fibre composite versions (see **Fibre**

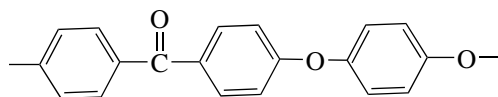


Fig. 1. The structure of the repeat unit in PEEK

**composites – introduction**). The crystallinity of thermoplastics has a major influence upon their resultant properties. The crystallites act as reinforcing particles to the amorphous matrix and they also act to make the material solvent resistant. The crystallinity and structure-mechanical properties in PEEK has been reviewed by Medellin-Rodriguez.<sup>3</sup>

Surface pre-treatment of PEEK usually involves some degree of mechanical abrasion (see **Abrasion treatment**) to provide a key and then degreasing with a suitable solvent such as 1,1,1-trichloroethane. Etching techniques have been used to good effect in adhesive bonding, and a suitable etchant for PEEK has been developed by Olley.<sup>4</sup> This is a permanent etchant based on orthophosphoric acid. Besides treatment with a blue (oxidizing) flame<sup>5</sup>, other pre-treatments such as chromic acid etching have proved effective.

PEEK has also been used as a thermoplastic **Hot melt adhesive** for bonding of titanium and to the PEEK composite APC2. Lap shear strengths at room temperature of 20 Mpa with titanium and 50 Mpa with APC2 were obtained.

### References

1. J. B. Rose, in *High Temperature Polymers: Their Origin and Development*, R. B. Seymour and G. S. Kirshenbaum, Eds., Elsevier, New York, 1986.
2. H. X. Nguyen and H. Ishida, *Polym. Compos.*, **8**, 57 (1987).
3. F. J. Medellin-Rodriguez and P. J. Phillips, *Polym. Eng. Sci.*, **30**, 860 (1990).
4. R. H. Olley, D. C. Basssett and D. J. Blundell, *Polymer*, **27**, 344 (1986).
5. A. H. Ladrock, *Adhesives Technology Handbook*, Noyes Publications, New Jersey, 1985.

## Polyimide adhesives

S J SHAW\*

### Introduction

Of the numerous polymers developed since the early 1960s that have high-temperature resistance as a primary requirement, the polyimides have by far achieved the greatest commercial success owing primarily to their ability to maintain acceptable mechanical properties at elevated temperatures together with a measure of thermal stability sufficient to allow their long-term use at temperatures in excess of 250 °C. Key application areas have included fibre-reinforced composites, surface coatings, electronic devices and, of course, as **High-temperature adhesives**.

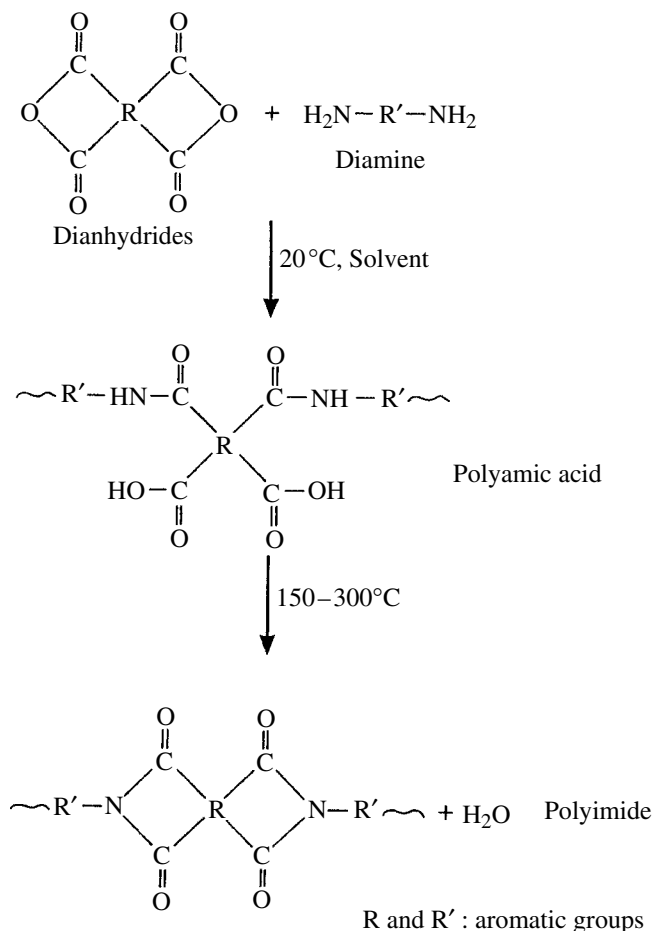
Adhesives based on polyimides that have achieved, or appear in the process of achieving, a measure of commercial acceptability can be divided into three broad classes, and it is convenient to consider briefly these major types separately. These are

1. condensation polyimides
2. thermoplastic polyimides
3. imide prepolymers.

### Condensation polyimides

Proprietary condensation polyimide adhesives are usually based upon starting materials (dianhydrides and diamines) that yield a polyimide structure having a high degree of intractability. Consequently, they are processed at an intermediate stage with conversion of an essentially soluble intermediate polymer (known as a polyamic acid) to the polyimide being conducted within the bond line (see Fig. 1). Unfortunately, evolution of water, which occurs during this conversion process, together with the need to remove solvent, provides a major processing difficulty with the possibility of porous, mechanically weak bonds (see **Step polymerization**). Although both high bonding pressures and venting techniques can alleviate such problems, there are usually quite stringent limitations on the area that can be successfully bonded using condensation polyimide adhesives.

In spite of these difficulties, these adhesives can exhibit excellent properties. For short-term applications, they can retain in excess of 50% room temperature strength at approximately 300 °C. Table 1 indicates typical joint strength values that can be achieved.



**Fig. 1.** Reaction scheme/structural formula for condensation polyimide

Table 1. Lap-shear strengths of condensation polyimide-bonded titanium joints

Temperature (°C)	Lap-shear strength (MPa)
25	26.5
100	24.5
200	22.2
300	18.5
400	12.5
500	8.5

Table 2. Influence of thermal ageing on adhesive joint strength of condensation polyimide-bonded titanium joints

Ageing time at 260 °C (h)	Lap-shear strength (MPa)
0	21.0
1000	19.5
2000	19.2
4000	17.8
40,000	20.7
0 <sup>a</sup>	17.7
1000 <sup>a</sup>	19.2
2000 <sup>a</sup>	11.0
3000 <sup>a</sup>	1.9

<sup>a</sup> Adhesive not containing arsenic thioarsenate stabilizer.

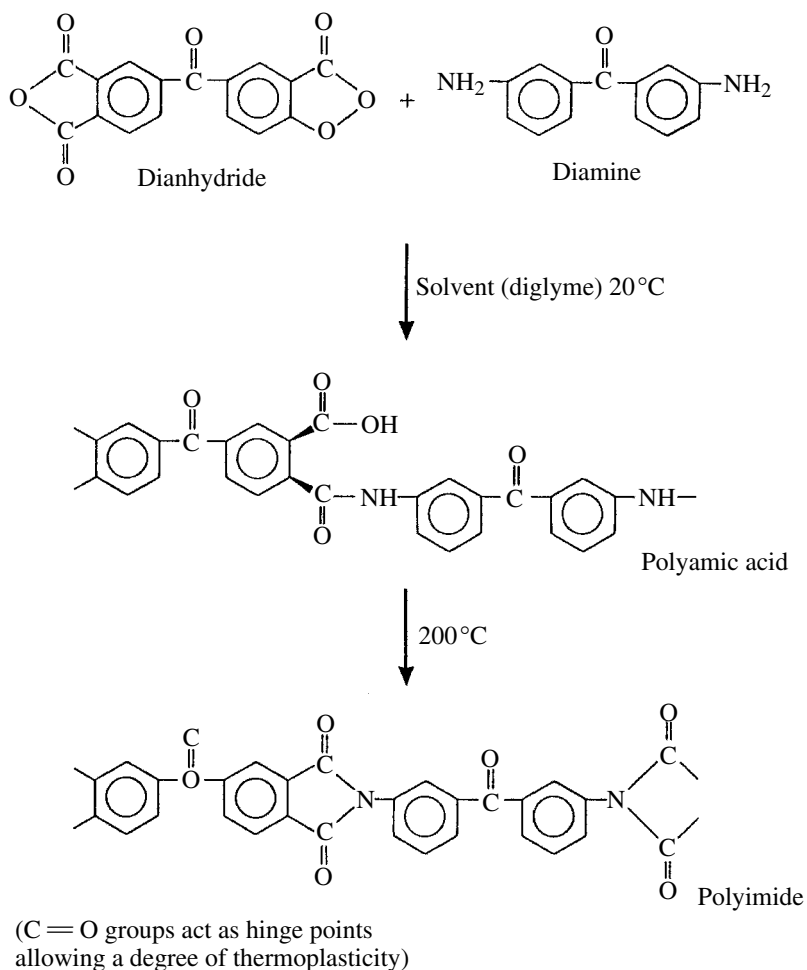
Long-term thermal stability is dependent upon a number of factors including the addition of stabilizers such as arsenic thioarsenate and the nature of the substrate. Studies have shown that, under certain circumstances, long-term use at temperatures in the vicinity of 275 °C is possible, as indicated in Table 2.

Although condensation polyimides can exhibit remarkable elevated temperature properties, their processing disadvantages have clearly limited the acceptance they would have otherwise deserved.

### *Thermoplastic polyimides*

Investigations aimed at developing polyimide-based adhesives exhibiting substantially improved processing characteristics relative to the condensation polyimides have resulted in two major success areas, one of these being thermoplastic polyimides (Fig. 2). The reaction route is essentially the same as that for condensation polyimides (see Fig. 1); the difference lies in the flexible linkages in the original dianhydride and diamine, which give greater chain flexibility in the resulting polyimide.

Many studies have shown that the imposition of molecular flexibility allows the possibility that the flexibilized polyimide could exhibit sufficient thermoplasticity above its **Glass transition temperature** for fabrication by a hot-melt process (see **Hot melt adhesives**).



**Fig. 2.** Reaction scheme/structural formula for thermoplastic polyimide (LARC-TPI)

In such circumstances, bonding using a fully imidized film could remove the need for both solvent evaporation and polyamic acid to polyimide conversion within the bond line, thus allowing the bonding of relatively large areas.

One of the most successful thermoplastic polyimides has been LARC-TPI, developed by the National Aeronautics and Space Administration (NASA) in the United States. The polymer is commercially available. Table 3 shows some of the very reasonable properties obtained from this adhesive. As indicated, the ability both to maintain mechanical properties at elevated temperatures and indeed retain mechanical integrity for long periods of time are clearly apparent.

In addition to LARC-TPI, further recent developments have included the polyimide sulphones, polysiliconeimides and polyetherimides. All three have been evaluated and have shown promise for adhesive bonding applications.

Table 3. Typical properties of LARC-TPI bonded titanium joints (see **Shear tests**)

Property Lap-shear strength (MPa)	Value
20 °C	36.5
232 °C	13.1
3000 h at 232 °C	20.7
$T_g$ (°C)	250
Decomposition temperature (°C)	520

#### Adhesives based on imide prepolymers

The concept of low-molecular-weight imide prepolymers can be viewed as an alternative route to enhanced processability. The development of such systems has been conducted on the basis of three fundamental requirements. First, the prepolymers should be of low molecular weight, allowing for the possibility of a low melting point and low viscosity. Second, imide groups should be present in the prepolymer so as to remove the particularly troublesome polyamic acid to imide conversion process mentioned previously. Third, the prepolymers should have reactive terminal groups capable of reaction by an addition mechanism so as to convert the molten prepolymer to a cross-linked polymer without the harmful evolution of volatiles.

A wide range of imide prepolymers have been developed on the basis of this approach. The various forms differ primarily in the type of terminal reactive group employed so as to convert the prepolymer to a cross-linked product. Three main types have achieved prominence and shown potential as **High-temperature adhesives**, these being prepolymers based upon norbornene, acetylene and maleimide (bismaleimide) functionality.

Studies into the first of these types, the norbornene imides, have resulted in a high-temperature adhesive system known as LARC-13, which demonstrated improved processability over condensation polyimides. Some typical results obtained from this adhesive are shown in Table 4, demonstrating its high-temperature capabilities.

An alternative approach to imide prepolymer formation using acetylenic termination as the means for further reaction was developed in the 1970s. Although various investigations have provided ample evidence of the excellent properties possible using acetylenic polyimides, current proprietary systems suffer one inherent drawback in having close melting and cure temperatures. The resulting extremely short gel times have resulted in poor lap-shear strengths (see **Shear tests**) at both ambient and elevated temperatures presumably

Table 4. Typical properties of LARC-13 bonded titanium joints

Property Lap-shear strength (MPa)	Value
20 °C	22.1
232 °C	17.9
1000 h at 232 °C	17.9
$T_g$ (°C)	300
Decomposition temperature (°C)	450

Table 5. Lap-shear data for bismaleimide-bonded aluminium joints

Temperature (°C)	Lap-shear strength (MPa)
25	20.0
232	18.6
260	12.7

because of poor wetting characteristics. There is little doubt that disappointing results of this kind have resulted in the poor acceptance of these materials to date.

Bismaleimides offer possibly the greatest benefits in terms of enhanced processability, being more akin to the easy-to-use epoxies than any of the systems described above. As a result, they have received a great deal of consideration in recent years for many potential applications. Owing to these highly promising characteristics, attempts have been made to employ bismaleimides in high-temperature adhesive formulations. In particular, a bismaleimide modified **Epoxide adhesive** has been developed that is considered capable of operating at temperatures up to approximately 280 °C, as suggested by the data shown in Table 5.

Although bismaleimides offer significant advantages over many other high-temperature systems, they do not exhibit the same degree of thermal stability and, hence, long-term performance of many other polyimide systems. As a result, they are restricted to service applications requiring a 200–300 °C long-term capability. They essentially “fill the gap” between the epoxies and the condensation and thermoplastic polyimides described earlier.

Further discussion on the general theme of high-temperature polymers and adhesives can be found in the articles entitled **Polyphenylquinoxalines**, **Polybenzimidazoles** and **Polyether ether ketones**. (See also article on **High-temperature adhesives**.)

#### Select Reference

- M. Kajiyama, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 813–822.

### *Polymer diffusion: reptation and interdigitation*

RICHARD P WOOL

Polymer–polymer interfaces are ubiquitous and adhesion plays a critical role in determining the properties, reliability and function of a broad range of materials. For example, polymer processing via injection molding (for plastic parts in **Automotive applications**) and extrusion (for plastic pipe) create many interfaces in the form of internal weldlines, where the fluid fronts coalesce and weld. Compression molding and sintering (of artificial hip joints, see **Adhesion in medicine**) requires the coalescence of pellets or powder when their surfaces contact in the mold. Drying of latex paints and coatings entails a very large number of interfaces per unit volume, as the relatively tiny (ca. 1000 Å) latex particles interdiffuse together to form a continuous film (see **Emulsion and dispersion adhesives**

and **Paint constitution and adhesion**). Construction of composites with thermoplastic matrices (aircraft bodies) requires the fibre-filled laminates to weld by an interdiffusion process at the interface (see **Aerospace applications**). Welding of two pieces of polymer by thermal or solvent bonding is a commonly encountered example of strength development at a polymer–polymer interface; tack between uncured rubber sheets during auto tyre manufacture is an important example of this kind of welding (see **Rubber to metal bonding: processing effects**).

The strength of a polymer–polymer interface (the adhesion between the two polymers) depends on the structure that develops during its formation.<sup>1,2</sup> For simplicity, consider two amorphous polymers that are brought into good contact above their **Glass transition temperatures**. The chain conformations at the interface tend to relax towards those in the bulk because of Brownian motion. Five different time regions can be identified. They are, in increasing order of relaxation time, (1) short-range Fickian diffusion of individual chain segments, (2) Rouse relaxation between chain entanglements, (3) Rouse relaxation of the whole chain, (4) reptation diffusion and (5) Fickian long-range diffusion. Some illustrative values are given in Table 1.

The fastest relaxation (1) takes place on the order of a single statistical segment, so lateral displacements are quite small, and the segments feel neither topological constraints nor chain connectivity. This diffusion is independent of molecular weight. The long-range Fickian diffusion (5) occurs at long times when the chain has lost all memory of its initial conformation and has become a random coil.

Time scales (2), (3) and (4) are important in the reptation model of polymer diffusion: (2) involves wriggling motions leading to relaxations between chain entanglements and (3) involves wriggling motions leading to relaxations of the whole chain while (4) is reptation. Reptation, has its root in *reptare*, the Latin word meaning “to creep”, and well describes the snake-like motion of interdiffusing chains.

In the reptation dynamics model, proposed by de Gennes and Edwards,<sup>3,4</sup> individual polymer chains are conjectured to move like Brownian snakes in a field (tube) of topological constraints imposed by entanglements from neighbouring chains, (Fig. 1) at  $t = 0$ . At time  $t_1$ , some end portions of the chain (these are called the “minor chains”) have already “escaped” from the initial tube by reptation.

During interdiffusion (Fig. 1), those parts of the chain that have diffused from the tube are allowed to interdiffuse across an interface plane between the two polymers in good contact.

The reptation model predicts that the relationship between relaxation time and molecular weight varies according to the mechanisms involved (Table 1). The table also gives predictions of diffusion distance for a specified styrene polymer. Generally, an interdiffusion distance of about 110 Å is necessary for maximum weld strength. It can be shown that for polymers of molecular weight significantly greater than that between chain entanglements ( $M_c$ ) (see **Polymer–polymer adhesion: molecular weight dependence**), the timescale  $t$  of importance for adhesion by interdiffusion is  $\tau_{RO} < t \leq T_r$ . (Where molecular weight is very high – greater than  $M^*$ , which is  $8M_c$  – times less than  $\tau_{RO}$  can be important.)

The molecular aspects of interdigitation of linear entangled polymers ( $M > M_c$ ) during welding of polymer interfaces are summarized for a symmetric interface in Table 2. The properties are expressed as a time-dependent function of reptation relaxation time  $T_r$  ( $T_r \sim M^3$ ). Thus, for some general property  $H$ :

$$H(t) = H_\infty(t/T_r)^{r/4} \quad [1]$$



Table 1. Chain relaxation and diffusion mechanisms: relaxation time ( $\tau$ ) and molecular weight ( $M$ ) relationships

Mechanism	Relation between relaxation time and molecular weight	Relaxation time <sup>a</sup>	Average diffusion distance <sup>a</sup> at $\tau$
Rouse relaxation between chain entanglements	$\tau_e \sim M_c^2$	10 s	30 Å
Rouse relaxation of the whole chain	$\tau_{RO} \sim M^2$	21 min	60 Å
Reptation	$T_r \sim M^3$	1860 min	110 Å

Note:  $M_c$  is molecular weight between chain entanglements. Numerical data<sup>a</sup> refer specifically to polystyrene ( $M = 245,000$ ) welded to itself at 118 °C.

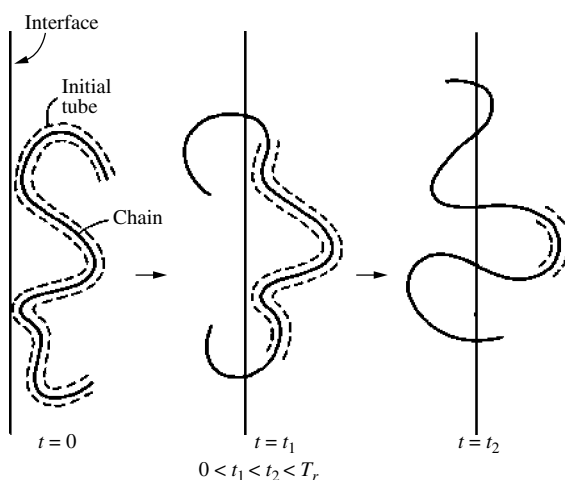


Fig. 1. Reptation: disengagement of a chain from its initial tube near the interface. Only the portion of the initial tube that still confines the part of chain is shown

$H_\infty$ , the static relation, depends on molecular weight:

$$H_\infty \sim M^{(3r-s)/4} \quad [2]$$

Values of  $r$  and  $s$ , which vary according to the property concerned, are given in Table 2.

The reptation dynamics and the interface structure relations in Table 2 have been demonstrated experimentally by a series of interdiffusion experiments with selectively deuterated HDH/DHD polymer interfaces using dynamic secondary ion mass spectroscopy (DSIMS – see **Secondary ion mass spectrometry**) and neutron reflectivity. The scaling laws for interdigitation and the complete concentration profiles for Rouse and reptation dynamics have also been calculated.<sup>1,2</sup>

The relation between the interdigitated structure and strength of polymer–polymer interfaces has been extensively investigated. Initially, as the symmetric interface wets by local Rouse segmental dynamics, we find that rapid interdiffusion occurs to distances

Table 2. Molecular aspects of interdiffusion at a polymer–polymer interface<sup>2</sup>

Molecular aspect		Dynamic relation $H(t)$	Static relation $H_\infty$	$r$	$s$
General property	$H(t)$	$t^{r/4}M^{-s/4}$	$M^{(3r-s)/4}$	$r$	$s$
Average contour length	$l(t)$	$T^{1/2}M^{-1/2}$	$M$	2	2
Number of chains	$n(t)$	$T^{1/4}M^{-5/4}$	$M^{-1/2}$	1	5
Number of bridges	$P(t)$	$t^{1/2}M^{-3/2}$	$M^0$	2	6
Average monomer diffusion depth	$X(t)$	$t^{1/4}M^{-1/4}$	$M^{1/2}$	1	1
Total number of monomers diffused	$N(t)$	$t^{3/4}M^{-7/4}$	$M^{1/2}$	3	7
Fractal diffusion front length	$N_f$	$t^{1/2}M^{-3/2}$	$M^0$	2	6

of the order of the radius of gyration of the entanglement molecular weight, ca. 30 Å. However, at this point, the interface is very weak (ca. 1 J m<sup>-2</sup>). As welding proceeds,  $\Sigma$  minor chains of length  $L$  diffuse into an interface of width  $X$  and considerable strength develops. The diffusing chains are fractal random walks and interpenetrate with chains (see **Fractals**), which are fully entangled (ignoring surface reflection configuration effects on entanglement density).

The structure of the diffuse weld interface resembles a box of width  $X$ , with fractal edges containing a gradient of interdiffused chains<sup>2</sup> as shown by Wool and Long.<sup>1,2</sup> When the local stress at a crack tip exceeds the yield stress, the deformation zone forms and the oriented craze fibrils consist of mixtures of fully entangled matrix chains and partially interpenetrated minor chains.

The consequences of the mechanisms of diffusion, discussed above, for the strength of the interfaces formed are further considered in **Polymer–polymer adhesion: models**.

### References

1. R. P. Wool, *Polymer Interfaces: Strength and Structure*, Hanser, 1995.
2. R. P. Wool, Diffusion and autohesion, in *Adhesion Science and Engineering, Vol. II, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 351.
3. P.-G. de Gennes, *J. Chem. Phys.*, **55**, 572 (1971).
4. S. F. Edwards, *J. Chem. Soc. London*, **92**, 9 (1967).

## **Polymer–polymer adhesion: incompatible interfaces**

RICHARD P WOOL

Despite macroscopic thermodynamic incompatibility (see **Compatibility**), an atomically sharp interface between two incompatible polymers will not be stable. Although there is an enthalpy debt to be paid if a chain of polymer A starts to diffuse into polymer B, there is an entropy gain. Helfand and Tagami<sup>1,2</sup> introduced a model that considered the probability that a chain of polymer A has diffused a given distance into polymer B when the interactions are characterized by the parameter  $\chi$ . They predicted that at equilibrium the “thickness”,  $d$ , of the interface would depend upon the interaction parameter and the

mean statistical segment length<sup>3,4</sup>,  $b$ , as follows

$$d = \frac{2b}{(6\chi)^{1/2}} \quad [1]$$

To understand the strength  $G$ , of an incompatible A/B interfaces as a function of their width  $d$ , we first consider the random walk of a bridge of length  $L \sim d^{1/2}$ . This length  $L$  is part of a much larger random walk chain, and is a segment, which begins on the B-side and traverses into the A-side, and returns to the B-side. In this respect, it is a bridge segment (of a larger chain) of length  $L_p$ , rather than a free chain of length  $L$ , such that the interface width is described by

$$d \sim L_p^{1/2} \quad [2]$$

The number of bridges per unit area crossing the A/B interface is  $\Sigma_p$ , which is independent of molecular weight. As  $L_p$  increases with decreasing  $\chi$  values (Eqn. 1), entanglements develop, crazes form and the percolation relation  $G \sim [p - p_c]$  applies. Here, the percolation parameter  $p$  is,

$$p \sim \Sigma_p \frac{(L_p/L_e)}{d} \quad [3]$$

where  $L_p/L_e$  is the number of entanglements per bridge. Since  $d \sim L_p^{1/2}$ , we obtain  $p \sim d$ ,  $p_c \sim d_c$ , and hence

$$G \sim [d - d_c] \quad [4]$$

Here  $d_c$  is the critical interface width corresponding to  $p_c$ , which will be of order the radius of gyration of the entanglement length, and below which no strength exists, other than that of simple pullout and surface energy terms, as described by the nail solution. Letting the normalized width  $w = d/d_c$ , this equation becomes

$$G \sim [w - 1] \quad [5]$$

The maximum strength  $G^*$  is determined by,

$$G^* \sim [w^* - 1] \quad [6]$$

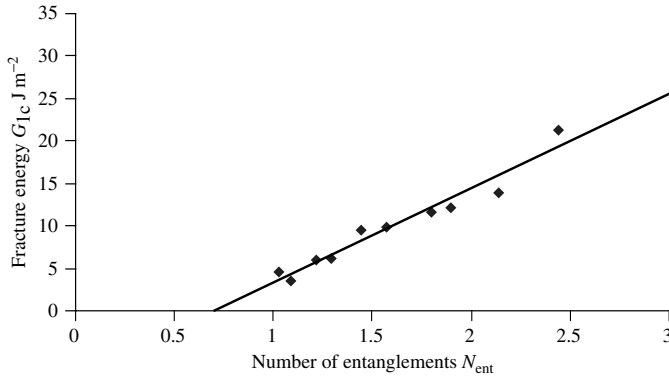
Writing the normalized width  $w = d/d_c$ , and entanglement density  $N_{\text{ent}} \sim d/L_e$ , the following relations apply:

$$\frac{G}{G^*} = \frac{(w - 1)}{(w^* - 1)} \quad [7]$$

$$\frac{G}{G^*} = \frac{[N_{\text{ent}} - N_c]}{[N^* - N_c]} \quad [8]$$

where  $w^*$  and  $N^*$  are the values at the maximum fracture energy  $G^*$ .

Figure 1 shows data of Cole *et al.*<sup>5</sup> plotted as fracture energy  $G_{\text{lc}}$  versus  $N_{\text{ent}}$ . According to Eqn. 4, a straight line relationship should be obtained with intercept  $N_c$ . The linear fit correlation coefficient was  $R^2 = 0.95$  (neglecting  $G = 0$  points) with intercept  $N_c = 0.7$ , and slope of  $11 \text{ J m}^{-2}$ .



**Fig. 1.** Fracture energy  $G_{1c}$  of bonds between immiscible polymers as a function of number of entanglements  $N_{ent}$ . Data of Cole *et al.*:<sup>5</sup> the line is a best fit to the percolation relation,  $G_{1c} \sim [N_{ent} - N_c]$

*Incompatible interfaces reinforced with  $\Sigma$  (A–B) diblocks compatibilizer chains*

The strength of an incompatible A/B interface can be considerably increased by use of an A–B diblock copolymer, the A block tending to diffuse into A, the B block into B.

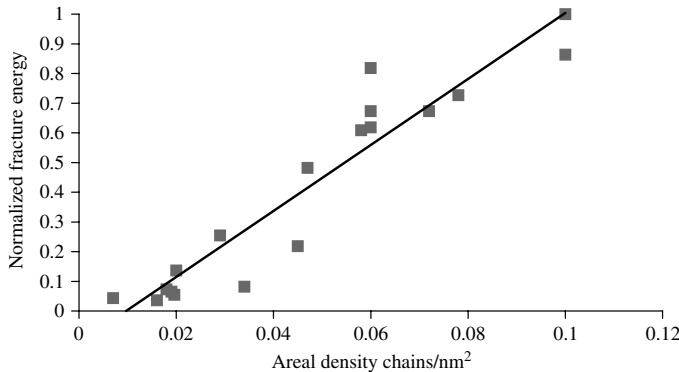
Consider an incompatible A/B interface reinforced by an areal density  $\Sigma$  of compatibilizer chains. The vector percolation theory term,  $p$ , the occupational probability of the lattice, will be proportional to the number of chains ( $\Sigma$ ) times their length ( $L$ ) divided by their thickness ( $X$ ):

$$p \sim \Sigma L / X \tag{9}$$

However the length  $L$  of the chains and the interface thickness  $X$  here are constant, so  $p \sim \Sigma$ . Similarly for  $p_c$ , the percolation threshold,  $p_c \sim \Sigma_c$ , such that  $G \sim [\Sigma - \Sigma_c]$  and hence

$$\frac{G}{G^*} = \frac{[\Sigma - \Sigma_c]}{[\Sigma^* - \Sigma_c]} \tag{10}$$

The results presented in Fig. 2 give support to this analysis.



**Fig. 2.** Fracture energy (*normalized*)  $G/G^*$  versus areal density  $\Sigma$ , of A–B diblock chains in an A/B incompatible interface, using data of Creton *et al.* The line is a least squares fit to the percolation formula,  $G/G^* \sim [\Sigma - \Sigma_c]$

Other examples of the application of reptation theory to polymer adhesion problems can be found in articles on **Polymer–polymer adhesion: weld strength** and **Polymer–polymer adhesion: molecular weight dependence**.

### References

1. E. Helfand and Y. Tagami, *J. Chem. Phys.*, **56**, 3592 (1972).
2. E. Helfand, *Macromolecules*, **25**, 1676 (1992).
3. R. P. Wool, *Polymer Interfaces: Strength and Structure*, Hanser, 1995, p. 338.
4. R. P. Wool, Diffusion and autohesion, in *Adhesion Science and Engineering, Vol. II, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 393.
5. P. J. Cole, R. F. Cook and C. W. Macosko, *Macromolecules*, **36**, 2808 (2003).

## Polymer–polymer adhesion: models

RICHARD P WOOL

In the article on **Polymer diffusion: reptation and interdigitation**, the mechanisms of interdiffusion that may occur when two polymers are brought into good contact were considered. Here, we consider how those mechanisms, and the structure they produce, may be related to the adhesion between the polymers and the strength of the interface formed.

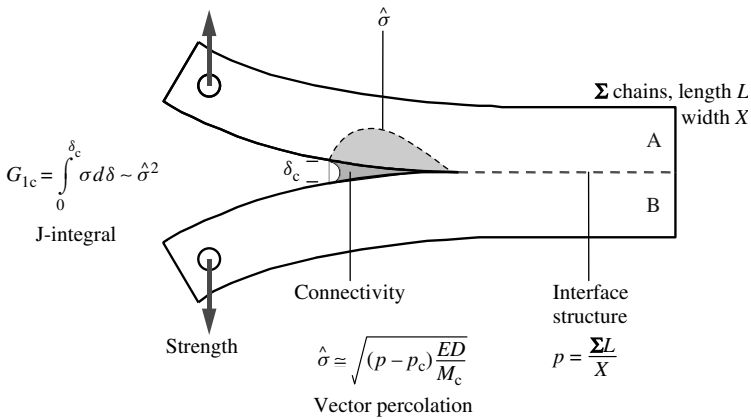
The problem of evaluating the fracture energy  $G_{1c}$  of polymer interfaces is represented in Fig. 1.<sup>1</sup> Material A is brought into contact with material B to form an A/B interface, the weld is fractured and the strength is related to the structure of the interface through microscopic deformation mechanisms. If interpenetration is limited, chain pullout and perhaps chain fracture may occur. Such an interface is weak and may be modelled using the *Nail Solution* discussed below.

For more extensive interpenetration, a crack propagates through the interface region preceded by a deformation zone at the crack tip. Extensive energy dissipation may occur giving a strong interface: this case may be treated by *Vector Percolation Theory*. For cohesive failure, the fracture energy may be determined by the J-integral method (Hutchinson<sup>2</sup>), where  $G_{1c}$  is the integral of the traction stresses with draw displacements  $\delta$ , in the cohesive zone following yielding at a local yield or craze stress  $\sigma_Y$ . The cohesive zone at the crack tip breaks down by a vector percolation process at a maximum stress value,  $\sigma_m > \sigma_Y$ . Typical ratios of  $\sigma_m/\sigma_Y$  are about 4–10.

### The nail solution: weak interfaces<sup>1</sup>

Here, the polymer–polymer laminate (see Figure 1) is modelled as a cantilever beam comprising two planks of wood, nailed together by  $\Sigma$  nails (molecular chains) per unit area with penetration length  $L$ . A simple analysis of the energy required to pullout the molecules leads to expressions for the fracture energy of the form

$$G_{1c} \sim \Sigma \text{ and } G_{1c} \sim L^2 \quad [1]$$



**Fig. 1.** The microscopic entanglement structure, at an interface or in the bulk, is related to the measured macroscopic fracture energy  $G_{1c}$ , via the vector percolation (VP) theory of breaking connectivity in the embedded plastic zone (EPZ) at the crack tip. The VP theory uses the molecular structure through  $p = \Sigma L/X$ , which determines  $\sigma \sim (p - p_c)^{1/2}$  in the EPZ, which is related to  $G_{1c} \sim \sigma^2$ , via Hutchinson’s J-integral theory<sup>1</sup>

Consideration of surface energy  $\gamma_{AB}$  and of friction  $\mu$  gives an expression

$$G_{1c} = 2 S \gamma_{AB} + \frac{1}{2} (\mu L^2 \Sigma) \tag{2}$$

where  $S$  is a factor relating to surface roughness.

Here, chain segment pullout dominated the fracture process; however, the whole chain does not pullout, rather bridge segments of length  $L \sim M^{1/2}$ . As the number of bridges  $\Sigma$  is independent of molecular weight, Eqn. 2 can be rewritten in the form

$$G_{1c} = G_o + kM \tag{3}$$

where  $G_o$  is the surface energy term.

This model is excellent when applied to very weak interfaces ( $G_{1c} \approx 1 \text{ J m}^{-2}$ ) where most of the fracture events occur in a well-defined two-dimensional plane and chain pullout dominated the fracture process. However, it is not applicable to strong interfaces ( $G_{1c} \approx 100\text{--}1000 \text{ J m}^{-2}$ ) where the fracture events occur in a three-dimensional deformation zone at the crack tip. Here, the vector percolation model is appropriate.

*Vector percolation model of fracture in nets<sup>1</sup>*

Strong interfaces develop when the energy is dissipated in a large volume containing the interface e.g. at crazes and deformation zones at crack tips, Fig. 1. During welding of linear polymer chains, interdiffusion proceeds across the polymer–polymer interface and we need to consider fracture events occurring many planes away from the original plane of contact. The long chains diffusing across the interface create fractal connectivity

between planes and this connectivity is broken by deformation mechanisms involving chain disentanglement or bond rupture.

A theory of fracture was developed for such entangled polymers that was based on the vector percolation model of Kantor and Webman.<sup>1</sup> The percolation model is used to describe connectivity between the chains and to relate the interfacial structure to the breakdown process of the deformation zone at the crack tip. Vector percolation involves the transmission of forces (vectors) through a two- or three-dimensional lattice where a certain fraction of the bonds are missing or broken. Thus, we can examine how the stiffness or strength of a lattice changes with bond fracture or disentanglement.

The material is, in effect, treated as a randomly populated lattice.<sup>3</sup> The occupational probability of the lattice is designated by  $p$ . At high values of  $p$  ( $p \rightarrow 1$ ), a connected pathway – connectivity – exists between top and bottom of the lattice. The minimum concentration (occupational probability) at which connectivity could occur in an infinite lattice is known as the percolation threshold,  $p_c$ . Many properties,  $H(p)$ , of the system follow scaling laws near  $p_c$ , which are of the form

$$H(p) \sim (p - p_c)^m \quad [4]$$

where  $m$  is a critical exponent. Thus, the modulus  $E$  is related to the lattice bond fraction  $p$ , via  $E \sim (p - p_c)^m$ . The Hamiltonian for the lattice was replaced by the engineering strain energy density function of the bulk polymer,  $U = \sigma^2/2E$ , and  $p$  was expressed in terms of the normalized entanglement density, using the entanglement molecular weight  $M_e$ . The polymer fractured critically when  $p$  approached the percolation threshold  $p_c$ , which was accomplished by utilizing the stored strain energy in the network to randomly fracture  $(p - p_c)$  bonds. The fracture energy was found to be

$$G_{1c} \sim (p - p_c) \quad [5]$$

### Virgin strength

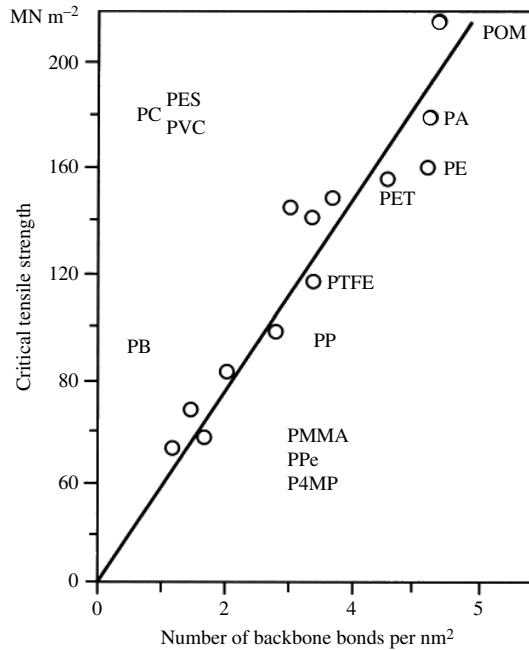
The fracture strength  $\sigma$  of amorphous and semi-crystalline polymers in the bulk can be expressed according to the Net solution as,

$$\sigma = (ED_o\rho/16 M_c)^{1/2} \quad [6]$$

where  $\rho$  is the bulk density (ca. 1 g cm<sup>-3</sup>),  $D_o$  is the bond energy (ca. 340 kJ mol<sup>-1</sup> for a C–C bond) and  $M_c$  is the entanglement molecular weight. This net solution – a first-principles approach to fracture requiring no fitting parameters – has also been found to predict accurately the fracture stress of many polymers (Fig. 2), thermosets and carbon nanotubes.

### Summary

The nail and vector percolation models of polymer–polymer adhesion have been successfully applied to many problems.<sup>1,3</sup> Some of these are treated in articles on **Polymer–polymer adhesion: weld strength**, **Polymer–polymer adhesion: molecular weight dependence** and **Polymer–polymer adhesion: incompatible interfaces**.



**Fig. 2.** Tensile fracture stress versus number of backbone bonds per monomer  $a$ , data of Vincent<sup>4</sup> The straight line is the prediction of the Vector Percolation theory, Eqn. 5, in which  $M_c \sim 1/a^2$

### References

1. R. P. Wool, Diffusion and autohesion, in *Adhesion Science and Engineering, Vol. II, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 351.
2. J. W. Hutchinson, Linking scales in fracture mechanics, in *Advances in Fracture Research, Ninth International Conference on Fracture*, B. L. Karihaloo, Ed., Elsevier, Sydney, Australia, 1997, pp. 1–14.
3. R. P. Wool, *Polymer Interfaces: Strength and Structure*, Hanser, 1995, p. 104.
4. P. I. Vincent, *Polymer*, **13**, 557 (1972).

### Polymer–polymer adhesion: molecular weight dependence

RICHARD P WOOL

Chain length (molecular weight) is an important factor in determining the strength of a polymer and the strength of polymer–polymer adhesion. In **Polymer–polymer adhesion: models**, two theories were described: the nail solution applicable to weak interfaces, that is low interpenetration (low molecular weight), and the vector percolation (VP) model for strong interfaces with extensive interpenetration (higher molecular weight). In this article, the application of these theories to molecular weight dependence of polymer–polymer adhesion is further developed.



Several characteristic molecular weights feature in treatments of chain diffusion and bond strength.<sup>1</sup> Two of these are concerned with the molecular weight at which chain entanglements become significant.  $M_e$ , sometimes referred to as the entanglement molecular weight, is the molecular weight required for the onset of the rubbery plateau observed in dynamic mechanical analysis.  $M_c$  is the critical entanglement molecular weight and corresponds to the molecular weight at the onset of the highly entangled zero-shear viscosity law,  $\eta \sim M^{3.4}$ . In terms of vector percolation theory, it is molecular weight at which  $p = p_c$ , that is at the percolation threshold  $p_c$ , the minimum concentration (occupational probability) at which connectivity could occur in an infinite lattice.  $M_e$  and  $M_c$  are related by

$$M_c = \frac{M_e}{(1 - p_c)} \quad [1]$$

Taking  $p_c \approx 1/2$  as a representative value,  $M_c \approx 2M_e$ .

A further characteristic molecular weight is  $M^*$ . This is the molecular weight at which chain disentanglement is no longer possible. It is related to  $M_c$  by  $M^* \approx 8M_c$ .

#### *Intermediate molecular weight $M_c < M < M^*$*

Fracture by disentanglement occurs in a finite molecular weight range,  $M_c < M < M^*$ , where  $M^*/M_c \approx 8$ .<sup>1</sup> Percolation theory predicts that the critical draw ratio,

$$\lambda_c = (M/M_c)^{1/2} \quad [2]$$

and the molecular weight dependence of fracture as

$$G_{1c}/G^* = 0.3 M/M_c [1 - (M_c/M)^{1/2}]^2 \quad [3]$$

$$K_{1c}/K^* = 0.55 [(M/M_c)^{1/2} - 1] \quad [4]$$

in which  $G^*$  and  $K^*$  are the fracture energy and critical stress-intensity factor respectively, at  $M^*$ .

#### *High molecular weight $M > M^*$*

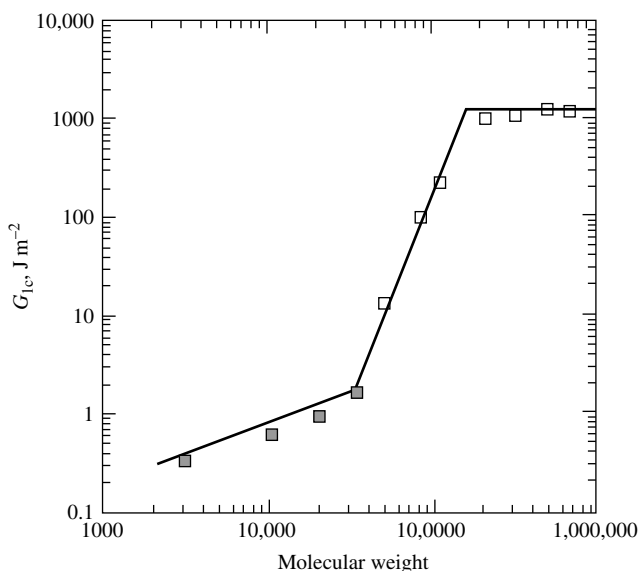
Above  $M^*$ , disentanglement is no longer significant and fracture occurs by bond rupture. The prediction of percolation theory is in accord with Flory's empirical suggestion,

$$G/G^* = [1 - M_c/M] \quad [5]$$

#### *Low molecular weight $M < M_c$*

When  $M < M_c$ , the role of entanglements is no longer present and Eqns. 2 and 3 cannot be used since  $G_{1c} = 0$  at  $M_c$ . However, the Nail solution applies for weak interfaces (see Eqn. 3 in **Polymer–polymer adhesion: models**) and the chain segments simply pullout at fracture such that  $(G_{1c} - G_o) \sim M$ , where  $G_o$  is the surface energy term, and we obtain,

$$(G_{1c} - G_o)/(G_c - G_o) = M/M_c \quad [6]$$



**Fig. 1.**  $G_{1c}$  versus molecular weight for polystyrene in the virgin state.  $M$  less than 40,000, filled squares<sup>2</sup>, higher  $M$  open squares<sup>3</sup>

where  $G_c$  is the fracture energy due to pullout at  $M_c$ . Typically, the surface energy term  $G_o$  is of order  $0.1 \text{ J m}^{-2}$  and the value of  $G_c$  at  $M_c$  is about  $1\text{--}5 \text{ J m}^{-2}$ , which compared to typical  $G_{1c}$  values for entangled polymers (ca.  $1000 \text{ J m}^{-2}$ ) is smaller by several orders of magnitude.

Figure 1 shows the molecular weight dependence of the fracture energy for polystyrene in which the three solutions are represented for the three pertinent regions involving pullout, disentanglement and bond rupture mechanisms.

1. When  $M < M_c$ , chain pullout occurs and the nail solution (Eqn. 5) applies to very fragile glasses.
2. When  $M_c < M < M^*$ , disentanglement predominates and Eqns. 2 and 3 apply such that little bond rupture occurs.
3. When  $M > M^*$ , bond rupture dominates and Eqn. 4 applies.

Articles on **Polymer–polymer adhesion: weld strength** and **Polymer–polymer adhesion: incompatible interfaces** give related examples of the application of reptation theory to polymer adhesion problems.

### References

1. R. P. Wool, Diffusion and autohesion, in *Adhesion Science and Engineering, Vol. II, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 386.
2. R. E. Robinson, *Adv. Chem. Ser.*, **154**, (1976).
3. R. P. Wool and K. M. O'Connor, *J. Appl. Phys.*, **52**, 5953 (1981).

---

**Polymer–polymer adhesion: weld strength**


---

RICHARD P WOOL

The self-adhesion (autohesion) of polymers is of considerable practical importance as many moulding operations involve the need for streams of merging polymer melt to self-adhere to form a strong bond necessary to the integrity of the moulded article. Mechanisms of polymer diffusion are discussed in **Polymer diffusion: reptation and interdigitation** and theories that relate interfacial structure to strength in **Polymer–polymer adhesion: models**. In the latter article, the vector percolation (VP) model was described, which is here applied to welding, and the practical consequences of its predictions are drawn out.<sup>1,2</sup>

Fracture of the weld occurs by disentanglement of the minor chains, or bond rupture. In the VP theory, many properties follow scaling laws dependent on the difference between  $p$ , the occupational probability of the lattice and the percolation threshold  $p_c$ , the minimum concentration (occupational probability) at which connectivity could occur in an infinite lattice. In particular, the fracture toughness, which depends on this percolation term,  $G_{1c} \sim [p - p_c]$ , determines the number of bonds to be broken, or disentangled.

Consider that  $\Sigma$  chains (per unit area), each of length  $L$ , interdiffuse in an interface of depth  $X$ . If  $L_c$  is the chain length between entanglements, there will be with  $L/L_c$  entanglements per chain. The relationship

$$p \sim \Sigma L/X \quad [1]$$

follows, and so we obtain

$$[p - p_c] \sim \{\Sigma L/X - [\Sigma L/X]_c\} \quad [2]$$

where  $p_c \sim [\Sigma L/X]_c$ . Since  $\Sigma/X \sim 1/M$  (see Table 2 in **Polymer diffusion: reptation and interdigitation**), it follows that  $p_c \sim L_c/M \approx 0$  for  $M \gg M_c$ .

The interface of depth  $X$  is composed of a fraction  $L/M$  of diffusing chains and the matrix chain fraction  $(1-L/M)$ , into which the chains are diffusing. The total stored strain energy per unit area of the interface

$$U \sim \sigma^2 X/2E \quad [3]$$

is consumed in disentangling only the  $\Sigma$  minor chains of length  $L$ , from the matrix chains, and we obtain,  $G_{1c} \sim p$  as Eqns. 3 and 4

$$G_{1c} \sim \Sigma L/X \quad [4]$$

When the stage is reached that the matrix chains disentangle or break along with the interdiffused chains,  $p = 1$  and the virgin strength is achieved. The number of diffusing chains  $\Sigma$  contributing to the strength at the interface is governed by gradient percolation, such that chains that do not straddle the interface are not counted. Since  $\Sigma \sim X/M$  (above) and  $L \sim (t/\tau)^{1/2}$ , we obtain the time dependence of welding as

$$G_{1c}(t) = G_{1c}^* (t/\tau^*)^{1/2} \quad [5]$$

where  $G_{1c}^*$  is the maximum strength obtained at  $M^* \approx 8M_c$ , and is independent of molecular weight.

If  $M < M^*$ , the welding time  $\tau$  to achieve complete strength by reptation behaves as

$$\tau \sim M^3 \quad [6]$$

(see **Polymer diffusion: reptation and interdigitation**).

For high molecular weight,  $M > M^*$ , the welding time is determined by the time required to diffuse a distance of order of the radius of gyration  $R_g$ , of  $M^*$ , such that  $\tau^* \sim M^{*2}M$ . Even though the welding time  $\tau^* \sim M$  is shorter than  $T_r \sim M^3$ , the molecular weight dependence of the welding rate remains unaffected, and we have, for all molecular weights,

$$G_{1c}(t) \sim t^{1/2} M^{-1/2} \quad [7]$$

As the interdiffusion distance  $X$  approaches  $R_g$ , the welding state becomes indistinguishable from the virgin state and Eqn. 5 converges to

$$G_{1c}/G^* = 0.3 [(M/M_c)^{1/2} - 1]^2 \quad [8]$$

when  $M < M^*$ , and to

$$G_{1c}/G^* = [1 - M_c/M] \quad [9]$$

when  $M > M^*$ .

The full interpenetration of chains (i.e.  $X$  approaches  $R_g$ ) is not necessary to achieve complete short-term strength, when  $M > M^*$  and  $\tau^* < T_r$ . However, a cautionary note: while complete strength may be obtained in terms of critical fracture measures, such as  $G_{1c}$  and  $K_{1c}$ , the durability, measured in sub-critical fracture terms, such as the fatigue crack propagation rate  $da/dN$ , may be very far from its fully healed state at  $\tau^*$ . We have shown that while the weld toughness  $K_{1c}$  increases linearly with interdiffusion depth  $X$  as  $K_{1c} \sim X$ , the fatigue crack propagation behaviour of partially healed welds behaves as<sup>2</sup>

$$da/dN \sim X^{-5} \quad [10]$$

Thus, fatigue behaviour is a very strong function of interdiffusion and underscores the penalty to pay for partial welding. Although the weld strength may be close to the virgin strength, the fatigue strength may be dramatically reduced below its maximum value. Thus, one should always design a welding time with respect to  $T_r$  to achieve maximum durability of welds and interfaces. The time to achieve complete strength  $\tau^*$  is related to the reptation time by

$$\tau^* = 64 (M_c/M)^2 T_r \quad [11]$$

such that when  $M = 8M_c$ ,  $\tau^* = T_r$ .

The significance of this can be seen by considering a specific example. The reptation time  $T_r$  can be calculated from the self-diffusion coefficient  $D$  and the end-to-end vector length  $R$ , by

$$T_r = R^2/(3\pi^2 D) \quad [12]$$

For polystyrene at 125 °C,

$$D \approx 4 \times 10^{-6} / M^2 (\text{cm}^2 \cdot \text{s}^{-1}), R^2 = 0.45 \times 10^{-16} M (\text{cm}^2)$$

such that  $T_r = 4 \times 10^{-13} M^3$  (s) and  $\tau^* = 0.0234 M$  (s). For the case where  $M = 400,000$  and  $M_c = 30,000$ , from Eqn. 11, we have  $\tau^*/T_r = 0.36$ , where  $T_r = 435$  min and  $\tau^* = 156$  min. In this example, if the maximum short-term weld strength were obtained at a welding time of 156 min, the durability as measured by  $da/dN$ , would only be about 1/5 of its virgin value, which could be obtained by complete welding at  $T_r = 435$  min. When plastic parts are being injection moulded, laminated, sintered or co-extruded, many internal weld lines are encountered, and this aspect of welding needs to be considered in designing materials with optimal durability.

Further applications of these theories can be found in **Polymer–polymer adhesion: molecular weight dependence** and **Polymer–polymer adhesion: incompatible interfaces**.

### References

1. R. P. Wool, Diffusion and autohesion, in *Adhesion Science and Engineering, Vol. II, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 390.
2. R. P. Wool, *Polymer Interfaces: Strength and Structure*, Hanser, 1995.

## Polyphenylquinoxalines

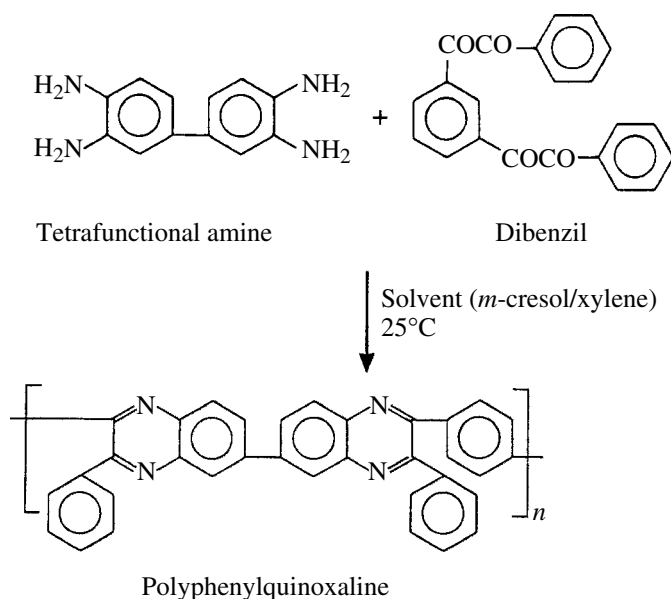
S J SHAW\*

Although the development of polyphenylquinoxalines (Fig. 1), was first reported in the late 1960s, it is only fairly recently that serious attempts have been made to exploit them as **High-temperature adhesives**. One particular adhesive system currently available on a commercial basis exists as a 20 wt% solution of the high-molecular-weight polyphenylquinoxaline polymer in a xylene–cresol solvent mixture. Bonding using this system requires three main stages, as follows:

1. application of the solution to the substrate or carrier;
2. evaporation of the solvent;
3. bonding of the substrates at approximately 400 °C and 1.4 MPa pressure.

Evaporation of the solvent leaves the polymer film, which can then be employed as essentially a “hot-melt” adhesive, requiring bonding at temperatures substantially in excess of the **Glass transition temperature** (approximately 290 °C), together with high-pressure application so as to induce polymer flow and thus allow a degree of wetting (see **Wetting and spreading**).

Some results obtained from a proprietary polyphenylquinoxaline adhesive system are given in Table 1. Although these show lap-shear strength (see **Shear tests**) deteriorating rapidly as  $T_g$  is approached, it should be noted that joint strength values have been



**Fig. 1.** Reaction scheme/structural formula for polyphenylquinoxaline

*Table 1.* Lap-shear strength values for polyphenylquinoxaline-bonded titanium joints

Test condition	Lap-shear strength (MPa)
20 °C	21.1
177 °C	20.0
232 °C	8.1
177 °C (after 3000 h at 177 °C)	24.1
232 °C (after 3000 h at 232 °C)	13.4

found to vary substantially from one study to another. For example, with titanium substrates changes in surface pre-treatment have been shown to have significant effects with room temperature lap-shear strength varying between 10 and 36 MPa. The values quoted in Table 1 may therefore represent an over-pessimistic view of the capabilities of polyphenylquinoxaline.

As with other thermoplastic-based **High-temperature adhesives**, the main advantage of the polyphenylquinoxalines is undoubtedly their ability to produce large area bonded structures free of significant bond-line porosity. Disadvantages, including the need for solvent removal together with a high-temperature, high-pressure bonding requirement, would be seen in some circumstances, however, as being particularly serious. In common with many other thermoplastic polymers, they have also shown susceptibility to gross deformation and failure at temperatures substantially below the limits set by thermal stability.

A reduction in excessive thermoplasticity requires the introduction into the polymer molecule of some means of cross-linking, and much of the research conducted into polyphenylquinoxalines in recent years has been concerned with this problem. One

approach, making use of technology developed initially with the polyimides, has involved the development of phenylquinoxaline prepolymers having acetylene terminal groups. Under the appropriate conditions, the acetylene groups react by an addition mechanism to produce a cross-linked structure exhibiting reduced thermoplasticity and hence a greater high-temperature capability. More recent studies have been concerned with the incorporation of pendant cross-linking sites distributed along the polymer chain. Most success has been achieved by the addition of so-called phenylethyl groups, which have resulted in substantial improvements in high-temperature adhesive joint strength. Although extremely promising, **High-temperature adhesives** based on these developments are not yet, to the author's knowledge, available commercially. Linear thermoplastic polyphenylquinoxalines are, however, commercially available, albeit at a high price.

Further discussion on the general theme of high-temperature polymers and adhesives can be found in the articles entitled **Polybenzimidazoles**, **Polyether ether ketones** and **Polyimide adhesives**.

### Select References

- P. M. Hergenrother, *Polym. Eng. Sci.*, **16**, 303 (1976).  
P. M. Hergenrother, *Polym. Eng. Sci.*, **21**, 1072 (1981).  
C. Hendricks and S. G. Hill, *SAMPE Quarterly*, **12**, 32 (1981).  
J. P. Critchley, G. J. Knight and W. W. Wright, in *Heat Resistant Polymers*, Plenum Press, New York, 1983.  
P. M. Hergenrother, *Polym. J.*, **19**(1), 73 (1987).  
P. M. Hergenrother, *High Performance Polymers*, **15**(1), 3–45 (2003).

---

## Polyurethane adhesives

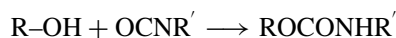
---

G C PARKER

### Introduction

A polyurethane adhesive is produced by reacting together two basic raw materials – a polyol and an isocyanate (see **Step polymerization**). The two most common polyols are based on polyether and polyester, and the two principal isocyanates used are toluene diisocyanate (TDI) and diphenyl methane diisocyanate (MDI), both of these latter products being extremely reactive.

When a polyol and an isocyanate are mixed together, the isocyanate reacts with the hydroxyl groups in the polyester/polyether polyol.



This reaction is exothermic and is stopped by cooling the vessel and introducing a vacuum before all the isocyanate has reacted. Depending on the properties required of the adhesive, between 5 and 35% of the isocyanate is left unreacted or “free”. This free isocyanate will subsequently react in the presence of moisture, or when mixed with a substance containing free hydroxyl groups, to complete the curing process.

Polyurethane adhesives can be conveniently divided into two types – solvent-free and solvent-based systems.

### *Solvent-free systems*

These adhesives are liquids with a 100% solids content and are available in both 1- and 2-component forms.

The 1-component adhesives typically contain about 15% free isocyanate. After application, the curing process is completed by exposure to atmospheric humidity and/or moisture on the substrate surface.

The 2-component adhesives comprise of one part that is 100% polyol and a second part that is a partial reaction of polyol with isocyanate. This second part typically contains approximately 30% free isocyanate. When the two components are mixed, the free isocyanate in the second part reacts with the hydroxyl groups in the first part and these two components then polymerize to form an adhesive film. With this type of product, it can be appreciated that the cure rate is not therefore moisture dependent.

The 1-component adhesives will typically form a holding bond after 24–36 h and will cure completely in a further 4–5 days. The 2-component adhesives form a holding bond after 24 h and are usually completely cured after 2–3 days.

These products are used primarily for flexible film lamination on purpose-built machines running at speeds of up to  $300 \text{ m min}^{-1}$ , although they do find certain other applications elsewhere.

**Radiation-cured adhesives** include acrylated urethanes.

### *Solvent-based systems*

These adhesives are usually 1-component systems in non-flammable solvents and are moisture curing. The solids content of the products used are varied according to the method of application. A 40–60% solids product is typical where a spray application is used, a solids content of 70–80% is common for roller coater applications and a solids content as high as 95% is typical for sealants and mastics.

When solvent-based polyurethanes are spray applied, the solvent will evaporate very rapidly and leave an adhesive film possessing a very aggressive **Tack**. These adhesives are generally applied to one surface only, and each has a finite open time during which the bond must be made if optimum bond strength is to be achieved. The tack of the applied film of adhesive will gradually diminish as the adhesive cures, and a good holding bond may be achieved in around 20 min with the fastest-curing products. Complete curing will typically take a further 24 h, thereby giving a much faster cure rate than can be expected with the solvent-free systems discussed above.

Solvent-based polyurethane adhesives find application particularly in the diverse field of product assembly operations, and are used for bonding materials such as steel, aluminium, timber products and rigid insulation. Products are available, however, that have been formulated to cure to a soft flexible adhesive film for bonding flexible materials such as fabrics and nylon scrim to flexible foams and sponge.

Consequently, major markets for these products are modular floor panels, caravan manufacture, insulated building panels, kitchen scouring pads and sound-insulation materials along with **Automotive applications** such as upholstery, door trims and head linings.



Properties of structural polyurethanes are compared with those of **Epoxide adhesives** and **Toughened acrylic adhesives** in the article on **Structural adhesives**.

### *Toxicological considerations*

The main potential hazard associated with polyurethane adhesives is due to the free isocyanate content, although the potential hazards need to be kept in perspective. All isocyanates are very reactive with moisture and will therefore react on the skin and, if inhaled, the lungs. It is now well established that TDI can cause sensitization of the respiratory tract if inhaled in quantity or over a prolonged period of time.

Compared with TDI, MDI is relatively safer in the working environment because it has a much lower vapour pressure. In practice, free MDI is unlikely to be a hazard at temperatures below 40 °C, especially if adequate extraction is provided at the point of application. If the application temperature is above 40 °C, or if the adhesive is spray applied, a vapour mist will always be formed and exhaust extraction must be used. To ensure a safe working environment, monitoring equipment should always be used to determine the level of isocyanate in the atmosphere, the maximum permitted level for MDI being 0.02 parts per million (0.2 mg m<sup>-3</sup>). See **Health and safety**.

### *Select References*

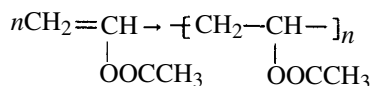
- K. C. Frisch, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, p. 759.  
 D. G. Lay and P. Cranley, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 659.

## ***Polyvinyl alcohol in adhesives***

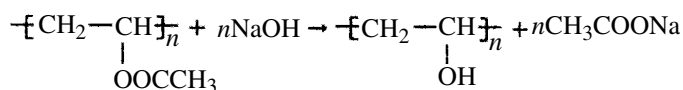
C A FINCH

Polyvinyl alcohols are a group of water-soluble polymers used in a wide variety of general-purpose and industrial adhesives to bond porous and cellulosic substrates such as paper and paperboard, wood and textiles and also some smooth surfaces such as metal foils. The polymer may be used alone, in aqueous solution, and is also employed with other polymers to modify the viscosity and rheological properties of formulations. In particular, it is used as the protective colloid component of vinyl acetate polymer and copolymer emulsions used as the base polymers of liquid “white” glues for bonding wood and paper products.

Polyvinyl alcohol is produced in large quantities by a two-stage process. First, vinyl acetate in methanol solution is polymerized to polyvinyl acetate:



This reaction is exothermic to the extent of  $5.2 \text{ kJ mol}^{-1}$  vinyl acetate. The polyvinyl acetate is hydrolysed, usually with alkali, to give polyvinyl alcohol:



There are many detailed variations on this process.

The polymer is separated from the residual methanol–methyl acetate solvent mixture (which is recovered), washed to remove residual salts (mainly sodium acetate) and dried to a fine white powder. This can be made in many grades, defined by the degree of polymerization (dp) of the original polyvinyl acetate, and by the degree of hydrolysis, usually considered to be “partly” (87–89%) or “fully” (97–99%) hydrolysed. Use of polyvinyl alcohol with higher dp (up to 2400) results in increased solution viscosity and dry film strength and increased initial “grab” to substrate: lower dp polymer is easier to dissolve but has less attractive properties. The water resistance of polymer films with 99% hydrolysis is greater than those with lower values and they are more difficult to dissolve. Such grades of polyvinyl alcohol are used as components of several types of adhesives, since they are compatible in aqueous solution with other polymers, including most starches (e.g. wheat, maize or potato (farina) starches) and dextrans (see **Compatibility**). The polymers are also compatible with some natural gums and alginates, used for remoistenable paper coating adhesives (where low dp, low-hydrolysis polyvinyl alcohol is used). Fillers such as wood flour, china clay or whiting can also be added to reduce cost. All these considerations affect the use of polyvinyl alcohols in water-based adhesives for many applications (see **Emulsion and dispersion adhesives**). However, polyvinyl alcohols have only limited compatibility with proteins, such as gelatine, animal glue and casein (see **Animal glues and technical gelatins**), and with natural rubber latex (although this can be mixed with some low-hydrolysis grades).

Polyvinyl alcohol is used in several types of wood adhesives (see **Wood adhesives – basics**). It is added at the condensation stage in the manufacture of modified urea–formaldehyde or urea–melamine–formaldehyde resins used in plywood and particleboard, to increase viscosity, and improve initial grab and the aging characteristics of the adhesive bond. In emulsion-based wood adhesives, the polymer is used in production of the emulsion, as a protective colloid, and then further polyvinyl alcohol is added in formulation of the adhesive, to improve both “open time” during formation of the adhesive bond and the resistance to “creep” (the cold flow in wood-to-wood adhesive joints under tensile load). Frequently, a mixture of different grades of the polymer is employed to control the viscosity and rheological properties of the adhesive during application. Adhesion to substrates can be improved by employing a polyvinyl acetate copolymer emulsion with 1–2% of a carboxylate-containing comonomer. Improved moisture resistance in the final adhesive bond can be attained by employing polyvinyl acetate copolymer emulsions, which contain cross-linking comonomers (*N*-methylolacrylamide is most frequently employed).

Adhesives for paper-to-paper applications are made from polyvinyl acetate emulsions, with added plasticizers, or from vinyl acetate copolymers (notably **Ethylene–vinyl acetate copolymers**) with added polyvinyl alcohol to modify viscosity, flow and coating properties, remoistenability and the rate of formation of the adhesive bond. These

properties are important for effective use of the adhesive on high-speed application equipment. In water-remoistenable adhesives, partially hydrolysed polyvinyl alcohols with low viscosity are included as a major component, usually with added humectants, such as polyalkylene oxides. A range of adhesives for production of water-resistant corrugated paperboard has been prepared from a high-viscosity fully hydrolysed polyvinyl alcohol in acid solution, slightly gelled with boric acid, used to stabilize a dispersion of finely divided calcium carbonate. Frost resistance during transport may be improved by addition of glycols or other polyols.

Many types of acrylic copolymer emulsions are used, with polyvinyl alcohol as binder and thickener, for building adhesives, bonding concrete to different substrates such as ceramic tiles, polyvinyl flooring tiles, polystyrene insulating panels, and hydrophobic films to paper.

Polyvinyl alcohol is added to acrylate copolymer emulsions, which are usually surfactant-stabilized, to alter or improve their adhesive performance. Many emulsions of this type are used as components of water-based pressure-sensitive emulsions – typically, a tacky adhesive for paper can be prepared by dissolving polyvinyl alcohol in a 2-ethylhexylacrylate copolymer emulsion.

Polyvinyl alcohol solutions are also used as adhesion binders for non-woven fabrics, screen-printing, ferrites, ceramics and some building materials. In powder form, it is also an effective binder for finely divided powders, such as pigments. Mixtures of low dp polyvinyl alcohol with ethylene glycol, however, have low adhesion to substrates and are used as peelable coatings for metals and plastics for protection during storage and transport.

### *Select References*

- C. A. Finch, *Polyvinyl Alcohol: Developments*, 2nd edn, John Wiley, Chichester, 1992.  
I. Skeist Ed., *Handbook of Adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990.

---

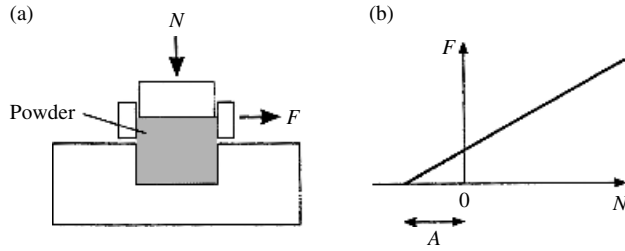
## *Powder adhesion*

K KENDALL

Fine powders stick together tenaciously. Anyone who has tried to dig through dry clay will bear witness to the powerful adhesion developed between the micrometre-diameter clay particles. Like the strength of many other adhesive systems, for example, epoxy–aluminium joints, the adhesion of these clay particles is much diminished by the addition of water, and also by the influence of pH, as when lime is added (see **Durability: fundamentals**).

Control of clay particle adhesion was perhaps the first historical example of adhesive technology for human benefit. It was discovered in Babylonian times that wet clay could be plastically shaped when its interparticle adhesion was low, then dried and used as a construction material when the adhesion between grains was raised by drying and firing.

Such understanding and control of particle adhesion is essential to many industrial processes. For example, powder adhesion is useful in making pharmaceutical tablets, which are manufactured by compressing the powder in shaped steel dies. Polymer powders



**Fig. 1.** (a) Shear box test for powder adhesion and friction; (b) plot of shear force versus load for a fine powder

made by dispersion polymerization are agglomerated into larger granules in which the fine grains stick together to allow easier handling. On a much larger scale, powdered iron ore is passed through a pelleting process before entering the blast furnace. Similarly, ceramics ranging from building bricks through to ball-bearings are made by compacting fine powders in moulds before sintering the products in a furnace. During this sintering process, the particles flow below the melting point to form extensive interparticle contacts, further enhancing the adhesion.

In contrast, particle adhesion can be a problem in certain areas; powders may refuse to flow out of hoppers, pigments may form intractable sediments in paints and dust grains may wreck electronic micro-circuitry by adhering strongly to the chips. Perhaps the most dramatic consequences of problematic particle adhesion are found during earthquakes or mudslides, when the relatively weak interparticle forces are overcome by vibration or by fluid flow. The theory of powder adhesion attempts to describe and predict such problems from first principles.

The first ever equation used to describe adhesion between solids was devised by Coulomb in 1773 to explain the movement of soils under load. In a shear box test (Fig. 1a), a powder is loaded with a normal force  $N$ , and sheared with a force  $F$ . In general, the plot of  $F$  versus  $N$  (Fig. 1(b)) does not pass through the origin but is displaced by an amount  $A$  on the horizontal axis. This displacement  $A$  represents the adhesive force pulling the particles into contact by **Dispersion forces** or other molecular attractions. Coulomb's equation describing this behaviour may be written as

$$F = \mu(A + N) \quad [1]$$

where  $\mu$  is the coefficient of friction (see **Friction – adhesion aspects**). This equation is the basis of soil mechanics as described, for example, by Bolton.<sup>1</sup>

It became apparent in the 1930s that all solid particles must attract each other unless some barrier material is interposed between the grains, the attractive force increasing as the particles approached. For two spheres of diameter  $D$  separated by a gap  $a$ , the attractive force  $A$  is given by Israelachvili<sup>2</sup> as

$$A = HD/24a^2 \quad [2]$$

where  $H$  is the Hamaker constant, about  $10^{-19}$  J. This equation has been verified by bringing very smooth mica surfaces together, or by studying the contact of fine-pointed probes using the atomic force microscope.

When the particles touch, the force of attraction rises to such a large value that deformation of the particles occurs. This may be elastic deformation as demonstrated by Johnson *et al.*,<sup>3</sup> or it may be plastic indentation as noted by Krupp.<sup>4</sup> In the elastic case, spherical particles form a small circle of intimate contact diameter  $d$ , which depends on the elastic modulus  $E$ , the Poisson ratio  $\nu$  of the material and the particle diameter  $D$  according to

$$d^3 = 9\pi WD^2(1 - \nu^2)/2E \quad [3]$$

where  $W$  is the work of adhesion of the surfaces (see **JKR theory** and **Contact angles and interfacial tension**). But the force required to separate the grains does not depend on the elasticity and is given by

$$A = 3\pi DW/8 \quad [4]$$

In practice, it is extremely difficult to measure the adhesion between two small particles, and satisfactory methods have not yet been devised. Generally, experiments are carried out on compacted pellets containing around  $10^{12}$  particles. Attempts to interpret the strength and fracture properties of such gross compacts have had mixed success. Perhaps the best technique for understanding the adhesion of these powders is to measure the elastic modulus of the compacted powder. Because this elasticity depends on the number and size of contacts between the individual grains, it is possible to estimate the work of adhesion of powders from such tests.<sup>5</sup>

### References

1. M. Bolton, *A Guide to Soil Mechanics*, Macmillan, London, 1979, Chap 4.
2. J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1985, Chap 1.
3. K. L. Johnson, K. Kendall and A. D. Roberts, *Proc. Roy. Soc. Lond.*, **A324**, 301 (1971).
4. H. Krupp, *Adv. Coll. Int. Sci.*, **1**, 111 (1967).
5. K. Kendall, *Molecular Adhesion and its Applications*, Kluwer, New York, 2001, 193.

---

## Pressure-sensitive adhesives

---

D W AUBREY\*

### *Nature of pressure-sensitive adhesives*

Pressure-sensitive adhesives are unusual materials in the sense that they are somewhere between the viscous and rubber states at room temperature, that is, their response to deformation is viscoelastic. They show sufficient liquid-like behaviour to deform or flow into contact with a smooth surface under light contact (the “bonding” process), yet they show appreciable resistance to flow during a separation or “debonding” process. The level of bond strength (force or energy of separation) depends on obtaining a rather delicate balance of viscoelastic properties in the adhesive polymer (see also **Viscoelasticity, Tack**), as well as favourable interfacial energetics (see also **Surface energy**).

The main advantages of pressure-sensitive adhesives compared with other types of adhesives are those of convenience of use. There is no storage problem, there is no mixing

or activation necessary and no waiting is involved. Often the bond is readily reversible. Disadvantages are that the adhesive strength (both peeling and shearing strengths) are low, they are unsuitable for rough surfaces and they are expensive in terms of cost per unit bond area. Some standard test methods are indicated in the Appendix.

### *Materials used as pressure-sensitive adhesives*

The selection of materials to be used is based not only on the final adhesion properties required but also on considerations of the economy of the manufacturing process for the particular pressure-sensitive product.

The most well-known type of adhesive consists of natural rubber (NR) blended with an approximately equal amount of a tackifier resin, and a small amount of antioxidant (see **Natural rubber-based adhesives**). It is applied to a suitably primed supporting member or backing, such as regenerated cellulose film (“cellophane”), as a solution in petroleum spirit. A release agent on the reverse side of the backing is commonly applied to facilitate unwinding (see **Release**). Early rosin ester tackifier resins were later largely replaced by better aging terpene resins (mainly those derived from  $\beta$ -pinene), which in turn have now been largely replaced for economic reasons by cheaper resins obtained by the cationic polymerization of petroleum fractions ( $C_4$ ,  $C_5$  and  $C_6$ ), although the terpene resins are still regarded as being excellent technically. Considerable economy of solvent may be achieved by the higher solution concentrations possible from the use of the newer thermoplastic rubbers, especially styrene–isoprene–styrene (SIS), in place of some or all of the natural rubber, and this is quite commonly practised in current solution coatings. Rigid PVC and polypropylene are now also extensively used as backing materials for general-purpose pressure-sensitive tapes, and many other plastic films and papers are used in specialized products including tapes, labels and decals.

Another type of solution coating extensively used is that based on polyacrylate (e.g. poly-2-ethyl hexyl acrylate) or an acrylate – vinyl acetate copolymer. These are generally used in high-quality tapes for their better technical properties – they are paler in colour, much better aging, and if cross-linked after coating can give very good shear strength. Other adhesive polymers used to a lesser extent in solution coating are polyvinyl alkyl ethers, polyisobutylenes, and silicones.

However, the use of organic solvents for coating is becoming increasingly unpopular and various means have been sought to eliminate the solvent (see **Environment and the impact of adhesive technology**). The use of latex rather than solution systems for rubber/resin adhesives has not resulted in commercial success because of problems of dispersion, mechanical stability, film homogeneity and cost of drying. However, latex (or “emulsion”) systems based on polyacrylate emulsions have been developed successfully as pressure-sensitive adhesives and are widely used in sheet materials and labels. These materials do not need added tackifier resins and are very stable mechanically, so the above problems are largely eliminated. They cannot be formulated, however, to give the same high adhesion and shear strength as the solution polyacrylates and are therefore not much used in tape form.

The most recent development in pressure-sensitive tape manufacture is the development of the hot-melt coating process. Almost all of the current hot-melt applied adhesives (see also **Hot-melt adhesives**) are based on SIS thermoplastic rubber, mixed with hydrocarbon tackifier resins and oils in substantial amounts, and an antioxidant in minor amounts.

Usually, the materials are mixed in an extruder and fed via a holding tank direct to the coating head. It is therefore a very fast and economical process but is not very versatile and is most suitable for large-scale production of the same basic tape or sheet. Much of the general-purpose packaging tape currently produced in the United Kingdom is made by this method.

A more complete account of the many varieties of pressure-sensitive products commercially available may be found in the first reference (see also **Pressure-sensitive adhesives – adhesion properties**).

### *Select References*

- D. Satas, Ed., *Handbook of Pressure Sensitive Adhesive Technology*, 3rd edn, Satas & Associates, 1999.
- J. Johnston, *Pressure Sensitive Adhesive Tapes: A Guide to their Function, Design, Manufacture, and Use*, Pressure Sensitive Tape Council, Northbrook, IL, 2003.
- A. I. Everaerts and L. M. Clemens, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 465–534.
- T. M. Goulding, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Ed., Marcel Dekker, 2003, pp. 839–854.

---

## *Pressure-sensitive adhesives – adhesion properties*

---

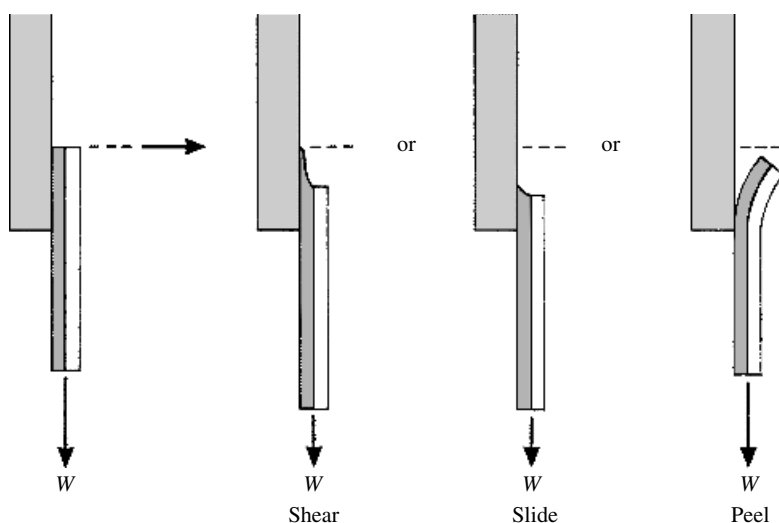
D W AUBREY\*

Pressure-sensitive adhesives are normally supported on “backing” materials and sold as tapes, labels or sheet products. Their adhesion properties are often tested in the form of tapes cut directly from such products. Since most adhesion properties are influenced by the nature and thickness of the adhesives and backing film layers, the results obtained cannot be regarded as intrinsic properties of the pressure-sensitive adhesives, but are in fact properties of the composite tape.

Standard tests used to characterize the adhesion properties of tapes are for the assessment of shear strength (see **Shear tests**) (the ability of a tape joint to resist a load applied in the shear mode), peel strength (see **Peel tests**) (the resistance of a tape joint to peeling under specified conditions) and **Tack** (the ability of a pressure-sensitive adhesive to form a bond immediately on contact with another material). There are many standard test specifications laid down by different authorities to assess these properties and many differences in detail between them (e.g. see Appendix). No attempt will be made to describe them comprehensively, but the principles of the tests will be discussed separately.

### *Shear strength tests*

Shear strength of a tape joint is often assessed in the industry by a shear adhesion or holding-power test, in which a weight (e.g. 0.5 kg) is hung on a tape bonded over a known area (e.g. 1 in.<sup>2</sup>) to a steel test plate (Fig. 1). The time taken (at a given temperature) for



**Fig. 1.** Modes of failure in the holding power test

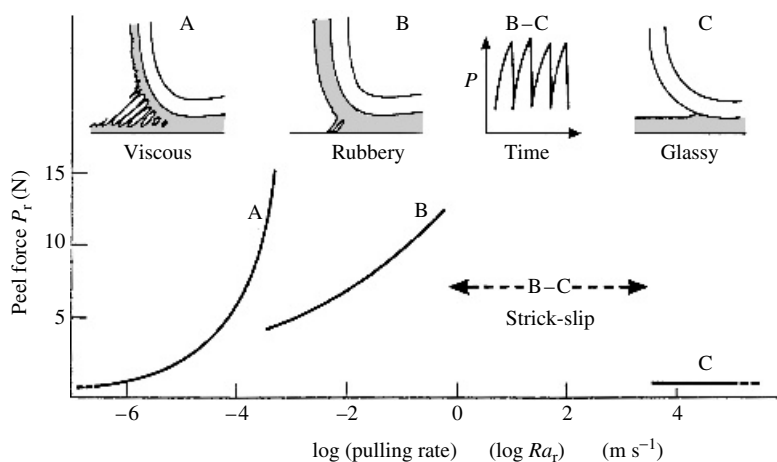
the tape either to move a certain distance or to drop from the plate is taken as the indication of shear strength. The test is commonly carried out at room temperature or at 40 °C. A typical test is described in PSTC-7.<sup>1</sup> Although it may be adequate for routine assessment of tape performance under simulated service conditions, it gives little information about intrinsic properties of the adhesive itself. This is partly because there are at least three modes of failure possible in the test (Fig. 1).

First, the adhesive may undergo a true shear failure in which viscous flow is involved; it may be possible to correct this by increasing adhesive molecular weight or cross-linking the adhesive. Second, the tape may appear to slide intact from the plate, a process, which probably involves the “waves of detachment” mechanism well known in the sliding friction of rubbers. Third, peeling may occur from the unloaded end of the tape because of low adhesion accompanied by a turning moment induced from elastic deformation of the backing, a well-known effect in lap joints generally. The latter two effects involve peeling phenomena and are best corrected by increasing the level of peel strength (see below).

### *Peel strength tests*

Peel strength is determined by pulling a tape from a test plate (usually steel, sometimes glass) at a constant rate and temperature in a tensile testing machine. Procedures for plate cleaning, bonding the tape, conditioning before test, and so on, are tightly specified and must be rigorously adhered to for reproducible results. Normally a 180° peel angle is used, as in the well-known standard tests PSTC-1<sup>1</sup> and ASTM D 903-78 but sometimes 90° or lower angles are used. Peeling at 90° is subject to less error and is probably more related to practical situations but requires more complicated test equipment than 180° peeling. Peel strength may be expressed either in force units ( $\text{N m}^{-1}$ ) or in work units ( $\text{J m}^{-2}$ ).





**Fig. 2.** Typical peel adhesion master curve<sup>2</sup> for polybutyl acrylate supported on polyester film peeled at 90° from glass. Insets show tape behaviour or force–time trace (“stick–slip”)

Peel strength for a given tape joint is very dependent on temperature and pulling rate, and it is found that peel strength measured over a comprehensive range of rates and temperatures may be treated as a viscoelastic function. Application of the time–temperature superposition principle (see **Viscoelasticity – time–temperature superposition**) either by experimental shifting or by use of the WLF equation enables master curves of peel force against pulling rate at a given temperature to be obtained over a very wide (e.g.  $10^{12}$ -fold) range of rates. Such master curves illustrate the change in viscoelastic response of the adhesive as rate and temperature is varied, and regions of steady peeling can be seen corresponding to viscous, rubbery and glassy behaviour of the adhesive (labelled A, B and C, respectively, in Fig. 2). A wide region (labelled B–C) of stick–slip peeling involves regular oscillation of peel force and is associated with a region of (theoretical) negative slope in the master curve. The master curve illustrated in Fig. 2 is for a simple amorphous uncross-linked polymer (poly-*n*-butyl acrylate) peeled at 90° from glass.<sup>2</sup>

### Tack tests

The phenomenon of **Tack** is easily understood subjectively as the bond that forms when another surface (e.g. the thumb) is pressed against the adhesive surface for a brief time. There are three kinds of tests, reviewed in detail by Everaerts and Clemens<sup>3</sup> that have been most often used to measure tack.

A probe tack test may be regarded as a “mechanical thumb” in which a disc or hemisphere of standard material (e.g. brass) is brought into contact with the adhesive surface under a fixed load for a specified dwell time (e.g. 1 s) and then removed at a specified rate. The maximum force of removal is usually taken as the tack value, although sometimes the work or energy of separation is reported. In such a test, it is important to control accurately the variables: probe material and finish, probe diameter and shape, load on probe, thickness of adhesive, dwell time, rate of debonding of probe from adhesive, and

test temperature. Types of probe-testing devices are described by Everaerts and Clemens,<sup>3</sup> and in ASTM D 2979-77.

The rolling ball test for tack usually involves allowing a stainless steel ball, diameter *c.* 12 mm, (or sometimes a table-tennis ball) to accelerate down a ramp of fixed (21.5°) inclination on to the horizontal adhesive surface. The distance travelled by the ball on the adhesive surface before arrest is taken as an inverse of tack for that surface. For a given adhesive, the ratio  $h^{2/3}d^{-1}$  is often found to be constant, where *h* is ramp height and *d* is distance travelled. Although the test is inexpensive and easy to perform, it suffers from greater variability than the probe test and interpretation of results is more difficult. Typical arrangements for the test are described in PSTC-6<sup>1</sup> and ASTM D 3121-73.

The quickstick test,<sup>1</sup> sometimes regarded as a measure of tack, involves the peeling of a loop of tape that has been allowed to contact a steel test plate for a brief time under its own weight only. It is clearly a modified form of peel test in which minimal contact between tape and plate has been achieved. As such, it will depend strongly on the stiffness of the tape-backing layer and is therefore not a property characteristic of the adhesive itself. The test is often carried out alongside the conventional peel test, requiring the same equipment. Again, it is difficult to interpret the results of this test in any fundamental way, since the act of peeling the tape will increase the contacting force because of backing leverage<sup>2</sup> and the additional contacting force from this effect will increase with the peeling force.

A more fundamental basis for the phenomenon is discussed under **Tack**.

### References

1. *Test Methods for Pressure Sensitive Adhesive Tapes*, 14th edn, Pressure Sensitive Tape Council, Northbrook, IL, 2003.
2. D. W. Aubrey in *Developments in Adhesives – 1* ed. W. C. Wake, Applied Science Publishers, London, 1977, p. 129.
3. A. I. Everaerts and L. M. Clemens, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 465–534.

---

### Pre-treatment of aluminium

---

G W CRITCHLOW

The article, **Pre-treatment of metals prior to bonding**, provides a general survey: this article is concerned with the industrially important aluminium and its alloys.

There are a large number of available pre-treatments for bonding aluminium and its alloys. These range from simple mechanical processes to highly complex and expensive multi-stage operations.<sup>1–4</sup> In general terms, the more complex processes provide the best initial levels of adhesion and, significantly, bond permanence or durability. The reason is that the more complex **Conversion coating** and, in particular, the anodic oxides on aluminium (see **FPL etch** and **Anodizing**) provide all of the desirable surface characteristics required for optimized adhesive bonding, namely, wettability, macro- and micro-roughness and corrosion resistance (see **Wetting and spreading**).

The requirements for bonded aluminium assemblies can range from the purely decorative to semi or fully load bearing. The load conditions can be static, quasi-static or fatigue (see **Durability: fatigue**). The environmental conditions to which a bonded aluminium structure can be exposed can also be highly variable ranging from dry to temperate to hot and wet or humid (see **Durability: fundamentals, Weathering of adhesive joints and Weathering tests**). The selection of an aluminium pre-bond pre-treatment will depend to some extent on the aforementioned factors but it also depends upon others such as the required adhesion performance, pre-treatment process speed, surface stability, environmental acceptability and cost.

The available processes can be broadly divided into four categories: mechanical, chemical, electrochemical and others. All of these processes are designed to modify the aluminium alloy to provide a high energy, wettable surface that is relatively free from contamination. As mentioned, the most successful also provide additional surface roughness and enhanced passivation.

Table 1 provides a brief summary of the main processes included within each category. It should be noted that within each process there are usually a number of variables such as blast media or solution type, blast pressure or treatment temperature or time. Each of these parameters might influence the effectiveness of the pre-treatment. In the general case, a particular pre-treatment will need to be optimized for a particular application to ensure satisfactory levels of adhesion.

The simplest processes involve only **Degreasing** or mechanical roughening, by **Abrasion treatment** and then cleaning of the aluminium surface. Such processes can provide a “peak and valley” morphology with an increased area over which interactions can occur (see **Roughness and adhesion**), but because of the fact that the last monolayers of organic contamination are difficult to remove, the wettability may not be particularly good and trapped air can result within the adhesive post curing. Furthermore, abraded surfaces leave only thin air-formed oxides, usually only a few nanometres thick. Such films possess poor corrosion resistance.

Conversion coated or etched aluminium surfaces are generally free from organic contamination and easily wetted. A water break test is commonly used to establish that a clean surface has been generated. Such pre-treated surfaces have been described as forming a

Table 1. Summary of the main pre-treatment processes for aluminium

Pre-treatment type	Process
Mechanical	Solvent wipe or clean by immersion or from the vapour phase Alkaline or acid degreasing Abrasion from pads Grit- or sand-blasting or honing, wet or dry Plasma or corona discharge Plasma spray or other PVD methods
Chemical	Acid etching, e.g. chromic, nitric or mixed acids Alkaline etching, usually proprietary solutions based on sodium hydroxide. Conversion coatings
Electrochemical Others	AC or DC, e.g. in weak chromic, phosphoric or sulphuric electrolytes Laser ablation CO <sub>2</sub> cryoblasting

“micro-composite interphase” with a subsequently applied adhesive. Interphase formation results in good initial adhesion and invariably reasonable durability performance. More aggressive exposure conditions such as salt spray can cause bond failure through corrosion of the underlying metal; this is more of a problem with etched adherends. The thickness of the oxide post etching is reported to be up to a few tens of nanometres. Conversion coatings can be much thicker; these are considered elsewhere.

The electrochemical processes can produce thicker, more corrosion resistant oxides than the etches (see **Anodizing**). For example, the idealized view of the structure produced by the Benough-Stuart 40 to 50 V direct current (DC) chromic acid anodize (CAA) process comprises a series of hexagonal close-packed open cells with a pore diameter of approximately 30 nm and an oxide thickness of approximately 3  $\mu\text{m}$ . The CAA provides mainly barrier protection to the underlying aluminium alloy. The other commonly used process is based on phosphoric acid anodizing (PAA) and produces a much thinner, more open film. The presence of  $\text{AlPO}_4$  in the outer layers of the PAA oxide is considered to provide a rate-limiting step to the hydration and eventual failure of this oxide. Alternating current (AC) anodic oxides form much quicker than DC films but, under the same deposition conditions, are much thinner. Typically, AC films range in thicknesses from a few nanometres to a few hundred nanometres. AC films can, however, be deposited in a single bath without the requirement for degrease, desmut and deoxidize stages unlike their dc counterparts.

Other pre-treatments find niche applications. For example, laser ablation can be used to clean and texture localized areas of a surface, leaving sensitive parts in unbonded regions unaffected.

It should also be mentioned that a particular pre-treatment may be alloy specific. For example, a relatively well-defined DC anodic oxide usually forms on a clad aluminium surface comprising a thin layer of co-extruded “pure” aluminium alloy. In contrast, a more branched, less well defined and patchy anodic oxide will form in the same electrolyte on a 2xxx series alloy surface because of the presence of second phase Al–Cu particles, which do not have the same electrochemical potential as the matrix.

In addition, organic coupling agents, hydration inhibitors and primers can be used to provide further surface stability towards either organic contamination or water to extend pre-bond surface exposure times and to improve durability. Organofunctional silanes are commonly used as coupling agents for aluminium. A number of studies have demonstrated a substantial improvement in bond durability with aluminium treated by grit-blasting plus the addition of a 1% aqueous solution of  $\gamma$ -glycidoxypropyltrimethoxy silane compared with the grit-blasted only case (see **Silane adhesion promoters**). This is generally attributed to the increased hydrolytic stability offered by the Al–O–Si bond. Hydration inhibitors are usually based on phosphonate chemistry; these can provide variable levels of adhesion.

In summary, bonding of aluminium alloys can be successfully achieved with an optimum pre-treatment/coupling agent or primer/adhesive combination. The anodic oxides are preferred in safety-critical applications in which adverse environmental and loading conditions are applied. Specifically, chromic and phosphoric acid are used in the **Aerospace applications** and defence sectors along with other electrolytes, for example, boric-sulphuric acid. AC anodizing is now the subject of much research because of its relative simplicity and short treatment times. For non-load bearing applications in extended outdoor conditions, for example, underneath paint, a conversion coating

may be adequate. Other applications, particularly when hydration is not likely to be a problem, may require less involved pre-treatments such as a simple grit-blast and degrease combination.

Reference should also be made to **Thermal spray processes**.

### References

1. J. D. Minford, *Handbook of Aluminum Bonding Technology and Data*, Marcel Dekker, 1993, ISBN 0-8247-8817-6.
2. E. W. Thrall and R. W. Shannon, Eds., *Adhesive Bonding of Aluminum Alloys*, Marcel Dekker, 1985, ISBN 0-8247-7405-1.
3. G. W. Critchlow and D. M. Brewis, *Int. J. Adhes. Adhs.*, **16**, 255–275 (1996).
4. A. C. Maloney, in *Surface Analysis and Pre-treatment of Plastics and Metals*, D. M. Brewis, Ed., Applied Science Publishers, 1982, pp. 175–197, ISBN 0-85334-992-4.

## Pre-treatment of copper

D E PACKHAM

Careful surface preparation before adhesive application is essential for consistent and successful bonding to most substrates (see **Pre-treatment of metals prior to bonding**), and this certainly applies to copper, which has a reputation for being difficult to bond. Part of the difficulty is the friability of the black copper(II) oxide, which forms on the surface in air at temperatures in the range 200–500 °C. At ambient temperatures, a thin layer of copper(I) oxide is present.

Detailed recipes for pre-treatment of copper, (which are also suitable for some copper alloys) are given in Refs. [1–4]. The simplest treatment consists of abrasion (see **Abrasion treatment**) with emery cloth followed by **Degreasing** in a chlorinated hydrocarbon solvent. Most of the treatments recommend a more elaborate routine of (1) degrease (2) etch and (3) dry. Etching solutions for use at ambient temperature include iron(III) chloride in either nitric or hydrochloric acid. Immersion for between 1 and 3 min is advised. Ammonium persulphate solution (1:3 or 1:4 parts by weight) is also used at room temperature: perhaps for times as short as 30 s.<sup>3</sup>

A two-stage etching treatment is also described: the first stage involves immersion in a iron(III) sulphate/sulphuric acid solution for 10 min at 66 °C. After rinsing, this is followed by ambient temperature treatment in sodium dichromate/sulphuric acid solution.

A proprietary treatment using “Ebonol C” is recommended, for example, by ASTM D 2651.<sup>4</sup> A similar alkaline chlorite treatment is increasingly used.<sup>3,5</sup> These involve treatment in the solution at 98 °C for periods up to 10 min. This method produces **Microfibrous surfaces** consisting essentially of a “floral” array of needle-like copper(II) oxide (see Fig. 1a in article on Microfibrous surfaces), which does adhere well to the base metal. The alkaline chlorite solution described in the article just cited gives a similar, but not identical, effect.

It is worth mentioning that microfibrous copper(II) oxide surface can also be produced by alkaline **Anodising** at elevated temperature.<sup>5</sup> Suitable conditions are 4 M sodium hydroxide at 90 °C with a current density of 143 A m<sup>-2</sup>.

Selection of a pre-treatment may well depend on striking a balance between convenience and effectiveness. A proper assessment of convenience and effectiveness will take account of the potential damage to the **Health and safety** of operators and of the general public as well as the environmental impact of disposal of waste materials (**Environment and the impact of adhesive technology**). Whichever treatment is chosen, the recipes cited (Refs. [1–4]) should be regarded as a starting point for a series of experiments aimed at optimizing the process variables for the particular application involved.

### References

1. C. M. Cotell, J. H. Sprague and F. A. Smidt, *ASM Handbook, Vol. 5 Surface Engineering*, ASM, 1994, p. 805.
2. Ciba Adhesives, *Surface Preparation and Pre-treatment of Structural Adhesives*, <http://www.on-hand.com/Manuals/SurfacePreparation.pdf> (accessed 6.4.04).
3. Araldite Bonding, *Surface preparation and pre-treatments*, [http://www.rapidchemical.com.tw/back/file/surface Pre-treatment.pdf](http://www.rapidchemical.com.tw/back/file/surface%20Pre-treatment.pdf) (accessed 6.4.04).
4. ASTM D 2651, in *Annual Book of ASTM Standards*, American Society for Testing and Materials, Philadelphia, published annually.
5. J. R. G. Evans and D. E. Packham, *J. Adhes.*, **10**, 177 (1979).

## Pre-treatment of fluorocarbon polymers

D M BREWIS

The fully fluorinated polymers, that is, polytetrafluoroethylene (PTFE) and the copolymer of tetrafluoroethylene and hexafluoroethylene (FEP) are difficult to adhere to and, to obtain satisfactory adhesion, it is usually necessary to pre-treat these polymers. With partially fluorinated polymers, it is often possible to obtain good adhesion without a pre-treatment; for example, good bond strengths have been obtained with poly(vinyl fluoride) and poly(vinylidene fluoride)<sup>1</sup> and polychlorotrifluoroethylene and the copolymer of chlorotrifluoroethylene and vinyl fluoride.<sup>2</sup>

The wide range of pre-treatments for fully fluorinated polymers has been reviewed by Dahm.<sup>3</sup> The methods available include the following:

1. immersion in a solution of an alkali metal in liquid ammonia;
2. immersion in a solution of sodium naphthalenide in tetrahydrofuran;
3. reduction with electrochemically generated tetra(alkylammonium) radical anions;
4. direct electrochemical reduction of the surface when placed in contact with a metal electrode in a non-aqueous electrolyte;
5. treatment with alkali metal amalgams;
6. exposure to an activated inert gas;
7. **Plasma pre-treatment** in air or ammonia.

Pre-treatments (1) and (2) are by far the most widely used commercially and a number of proprietary solutions are available for treatment (2). Immersion in a 1 M solution of sodium naphthalenide in tetrahydrofuran for 60 s resulted in a 15× increase in the

adhesion of PTFE to an epoxide<sup>1</sup> (see **Epoxide adhesives**). Plasmas, which are more environmentally acceptable than methods (1) and (2), can lead to substantial improvements in wettability and bondability.<sup>4</sup>

Aqueous and alcoholic solutions of group 1 hydroxides provide effective treatments for partially fluorinated polymers.<sup>5</sup> Flame treatment is also effective with these polymers.<sup>5</sup>

There is much evidence that the pre-treatments (1)–(4) lead to marked chemical changes in the surfaces of the fluorinated polymers. In particular, **X-ray photoelectron spectroscopy** (XPS) has shown that much defluorination occurs and this is accompanied by the introduction of various functional groups containing oxygen. The chemical changes caused by these pre-treatments result in a large increase in the **Surface energy** of the polymer.

The reductive treatments (1)–(5) result in the formation of a brown-black carbonaceous layer, the nature of which has been discussed elsewhere.<sup>3</sup> Long exposure to oxygen or UV or treatment with a strong oxidizing agent may result in the removal of this dark layer and the loss of the benefits of the pre-treatment.

See also **Pre-treatments of polymers** and **Surface characterization by contact angles – polymers**.

### References

1. D. M. Brewis, *Prog. Rubber Plast. Technol.*, **4**(1), 1 (1985).
2. H. Schonhorn and L. H. Sharpe, *Polym. Lett.*, **2**, 719 (1964).
3. R. H. Dahm, in *Surface Analysis and Pre-treatment of Plastics and Metals*, D. M. Brewis, Ed., Applied Science Publishers, London, 1982, p. 227.
4. D. M. Brewis and I. Mathieson, in *Mittal Festschrift*, W. J. van Ooij and H. R. Anderson Jr, Eds., VSP, Utrecht, 1998, p. 267.
5. I. Mathieson, D. M. Brewis, I. Sutherland and R. A. Cayless, *J. Adhes.*, **46**, 49 (1994).

---

### Pre-treatment of metals prior to bonding

---

G W CRITCHLOW

The importance of the surface condition prior to adhesive bonding of metal substrates has been widely reported in the literature.<sup>1–3</sup> A number of separate articles are provided, which are cross-referenced in this article or listed at the end. Here are presented a number of general comments that are applicable to all metal bonding pre-treatment procedures. The aim of the following section is, firstly, to describe the role of a metal pre-treatment and, secondly, to aid in the selection of a particular process.

A review of the literature on the subject of metal bonding will reveal that the most successful pre-treatments for this application impart the following surface characteristics: wettability, mechanical stability, roughness and corrosion resistance. Depending on the application, the relative importance of these factors may vary. A consideration of these factors follows.

Whichever theory of adhesion is applied to a particular circumstance, all depend upon intimate contact between the adhesive and the metal surface (see **Wetting and spreading**).

All metal surfaces are of high **Surface energy**, typically well over a hundred millijoules per square metre. Consequently, all adhesives should intimately “wet” clean metal surfaces on application or during the highly viscous phase prior to curing. However, the majority of metals requiring adhesive bonding are supplied in either sheet or extrusion form. Such material will invariably be contaminated with rolling oils, press lubricants, other processing aids or adventitious material that reduce the surface energy; see **Engineering surfaces of metals**. To facilitate surface wetting, this material must be either absorbed or displaced by an adhesive or otherwise removed prior to adhesive application. A number of studies have demonstrated the ability of adhesives to absorb and displace contaminants. This is of importance in **Automotive applications**, for example, where there is a demand to bond directly onto oily hot-dipped galvanized mild steel. In a general situation, this would not be advisable, and a degreasing stage would be regarded as the minimum preparation that would be carried out on a metal surface. **Degreasing** would usually be carried out using either an organic solvent or a mild alkaline etchant usually by agitated immersion or, in the case of a solvent, by condensation from the vapour phase. Solvents rarely produce atomically clean surfaces, as a monolayer or so of strongly adsorbed material is usually residual on the metal surface after cleaning. Solvents are associated with the formation of photochemical smog (**Environment and the impact of adhesive technology**). Other processes such as laser ablation or solid CO<sub>2</sub> cryoblasting have been demonstrated to be more effective.

The importance of providing a mechanically stable surface can be easily overlooked. Weakly adhered or friable oxides or hydrated oxides, for example, can be produced following processing. An example would be the mechanically weak magnesium-rich oxide formed on 5xxx series aluminium following rolling. Alternatively, an inappropriate surface pre-treatment may provide such a layer such as the chromic acid anodized layer on titanium (**Pre-treatment of titanium**), which when exposed to temperatures up to 360 °C dissolves into the metal to provide a brittle zone.<sup>4</sup> In both cases, an internal weak boundary layer would be produced within a joint. In the first case, a deoxidizing process would be carried out to remove the magnesium-rich layer. The second case highlights the importance of selecting the correct surface pre-treatment for a particular application.

The roughness of a metal surface can impact upon adhesion in three ways. If purely physical effects are considered, a macro- or micro-rough surface texture can facilitate micro-mechanical interlocking between the adhesive and the substrate (see **Roughness and adhesion** and **Mechanical theory of adhesion**). In addition, photoelastic and Moiré studies have demonstrated that the high spots on roughened surfaces act as microscopic stress raisers within joints, which are capable of redistributing an applied load within the bondline. Additionally, considering the chemistry, the establishment of a rough surface provides a potentially much increased area over which interactions can occur.

The simplest method for roughening a surface is simply by mechanical **Abrasion treatment**, usually with a specified abrasive pad or paper with selected graded grit embedded. This procedure can produce a highly rough texture, R<sub>a</sub> values are typically many micrometres, but with poor uniformity and reproducibility (**Roughness of surfaces**). Alternatively, compressed air blasting or liquid honing can be carried out with abrasive media such as graded alumina, silica or chilled iron. These processes provide a more reliable, uniformly treated surface. Usually, a mechanical treatment will be followed by a degrease stage to further clean and remove residual abrasive media. A similar macro-rough effect can also be achieved from processes such as plasma spraying.



Additionally, chemical etching from either acid or alkaline solutions, **Conversion coating** and **Anodizing** are all capable of generating highly modified surface structures compared to the untreated case. These processes alter the surface by introducing surface micro-roughness, where features may be present on the nanometre scale and above (see **Microfibrous surfaces**).

The importance of corrosion resistance or metal passivation has been highlighted in many studies concerned with the longevity or durability of bonded structures. In particular, the presence of water in the vicinity of the structure, from either the liquid or vapour phase, has been shown to produce voluminous corrosion products within the joint. Such corrosion products again provide a weak boundary layer within the joint, leading to premature failure on loading. Surface pre-treatments, sometimes in combination with corrosion resistant **Primers for adhesive bonding** or coupling agents, are used to increase the passivation properties of the metal surface when good durability is required. The aforementioned degrease and mechanical roughening processes provide no significant corrosion protection. In contrast, processes such as chromic and phosphoric acid anodizing provide barrier protection on aluminium, while chromate and sodium hydroxide anodizing are applied to titanium. These processes are used widely in defence and **Aerospace applications**. On steels, whether zinc-coated, or uncoated mild or medium carbon types, phosphate- or chromate-based conversion coatings are used for this purpose (see **Pre-treatment of steel**). Conversion coating of aluminium alloys is also used in demanding **Automotive applications** (see **Pre-treatment of aluminium and FPL etch**).

Importantly, for a particular application, and where the metals to be joined have been specified, an overall metal bonding system should be considered. Typically, this will include selection of a suitable adhesive and possibly primer or coupling agent in combination with appropriate methods of surface preparation or pre-treatment. Organofunctional silanes (see **Silane adhesion promoters**) are commonly used coupling agents, which have been demonstrated to provide covalent chemical bonds with steel or aluminium surfaces and possess epoxide or amine functionality for reaction with **Epoxide adhesives**.

In an industrial situation, the selection of a surface pre-treatment for a particular application will be determined by it being “fit for purpose”. In general terms, the best-performing surface pre-treatments, for example, the anodic oxides on aluminium or titanium, are complicated multi-stage processes, which are time consuming and require substantial investment in plant in order to be carried out.<sup>1,2</sup> In contrast, for less-demanding applications, a metal part may be simply degreased with much reduced effort and cost. In short, the application will determine the selection of a particular metal pre-treatment, in particular, whether the bonded assembly is required for structural or non-structural applications. Increasingly, modelling is used to determine, for example, the load on a particular bonded structure to help with pre-treatment selection.

There exists a range of potential pre-treatments for all of the commonly used metal substrates; the most successful processes are the subject of national and international standards documents. There are, however, legislative measures in Europe and United States to reduce the use of hexavalent chromium, a vital part of many commercial pre-treatments, throughout industry. Environmental issues are increasingly becoming the driving force behind the development of new pre-treatment processes and identification of those that are currently an option.

Further detail may be found in articles on **Pre-treatment of metals prior to painting, Pre-treatment of copper, Thermal spray processes and Rubber to metal bonding – pre-treatments.**

### References

1. J. D. Minford, *Handbook of Aluminum Bonding Technology and Data*, Marcel Dekker, 1993, ISBN 0-8247-8817-6.
2. E. W. Thrall and R. W. Shannon, Eds., *Adhesive Bonding of Aluminum Alloys*, Marcel Dekker, 1985, ISBN 0-8247-7405-1.
3. G. W. Critchlow and D. M. Brewis, *Int. J. Adhes. Adhes.*, **15**(3), 161–172 (1995).
4. H. M. Clearfield, D. K. Shafer, S. L. Vandoren and J. S. Ahearn, *J. Adhes.*, **29**, 81–102 (1989).

## *Pre-treatment of metals prior to painting*

N R WHITEHOUSE

The importance of a clean surface for painting is paramount (see **Engineering surfaces of metals**). For metallic substrates, either mechanical or chemical surface treatment is almost always needed to remove surface contamination and promote adhesion. Chemical pre-treatment of metals prior to painting is an effective method of surface conversion that can provide both corrosion resistance and improved paint adhesion. For ferrous metals, the most common chemical pre-treatment is a phosphate; for aluminium (and many other non-ferrous metals), the most effective pre-treatment is chromate. Metals must first be cleaned with an alkaline cleaner and then rinsed before they can be converted chemically in an immersion bath or by spray.

Phosphate pre-treatments may be either zinc phosphate (from zinc dihydrogen phosphate solutions) or an iron phosphate (from alkali phosphate solutions) (see **Conversion coating** and **Pre-treatment of steel**). The conversion reactions are promoted by accelerators (depolarizers), for example, bromates or molybdates in alkali phosphate baths or chlorates in zinc phosphate baths (with Ca or Ni grain-refining additions). Iron phosphate pre-treatment coatings are often described as “amorphous”. In practice, however, they are usually crystalline deposits of iron oxides and iron phosphate. Zinc phosphate pre-treatment coatings are always crystalline. A fine, dense crystal pattern of zinc phosphate on the metal surface is the ideal, as it improves both paint adhesion and corrosion resistance most effectively.

The best conversion coating for *zinc* is a zinc phosphate. A typical zinc phosphate coating, formulated for the pre-treatment of zinc, can also be effective on ferrous substrates and the pre-treatment of iron and zinc (or zinc-coated) articles on one pre-treatment line is not unusual.

For *aluminium*, the choice of pre-treatment will depend on the aluminium (or the aluminium alloy) itself and the corrosion resistance required. Chromium-containing pre-treatments have proved to be the most effective, but concern in recent years over the toxicity associated with the chemicals used is now driving forward the development of

new, chromate-free pre-treatments. The move towards more environmentally acceptable chemical pre-treatments for metals can be expected to continue.

Electrochemical processes for the pre-treatment of metals include both anodic oxidation, for example, of Cu and Al in alkali, or Ti in NaF/HF, and cathodic oxidation of Cu in sodium bicarbonate. Electrochemical pre-treatments promote adhesion by producing either a porous surface (**Anodizing** of Al), or a needle-like dendritic oxide structure. The most suitable surface structure may often be determined by the generic nature of the paint that will be applied subsequently.

A complementary discussion can be found in **Conversion coating and Pre-treatment of metals prior to bonding**.

### *Select References*

L. L. Shreir, R. A. Jarman and G. T. Burstein, Eds., *Corrosion*, 3rd edn, Butterworth-Heinemann, Oxford, 1994, Chaps 11, 15.

N. R. Roobol, *Industrial Painting: Principles and Practice*, 2nd edn, Hanser Gardner Publications, Cincinnati, 1997, Chap 8.

---

## *Pre-treatment of steel*

---

JOHN F WATTS

The pre-treatment of steel or any other metallic substrate can be taken, in the broadest sense, to refer to any method of modifying **Engineering surfaces of metals** to prepare them for the subsequent application of an organic coating or adhesive. In this category one would find the physical cleaning processes of **Degreasing** and **Abrasion treatment**, but by the term pre-treatment, some chemical modification of the surface is often implied. Such a chemical modification may simply be the dissolution of the native oxide, referred to as pickling; alternatively, pre-treatment of the steel may involve the application of a conversion coating. The most widely employed conversion coating is a phosphate pre-treatment, although other methods such as chromating are sometimes employed, but the use of the latter treatment is now controlled as a result of the production of toxic, Cr(VI) containing wastes (although non-rinse chromate treatments are being developed: see **Environment and the impact of adhesive technology**).

### *Pickling*

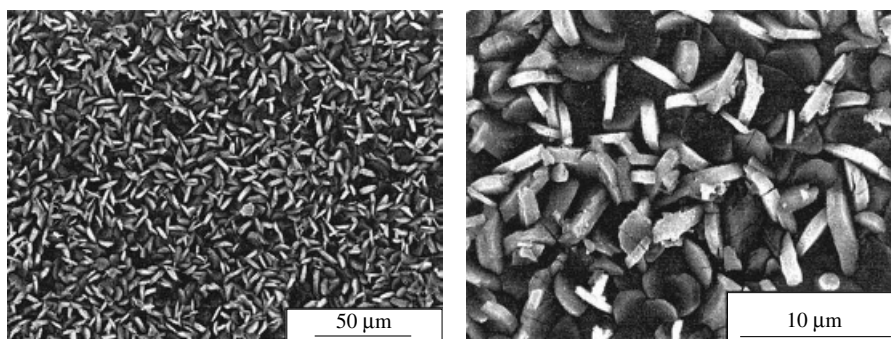
The removal of mill scale or other surface oxide layer by acid pickling is a well-established method of surface preparation for steels. The exact composition of the acid bath used varies widely, but in general, they are based on hot sulphuric acids or cold hydrochloric acids. As such, reagents will inevitably attack the underlying metal, giving rise to a rough undulating surface profile; inhibitors will usually be added. Care must of course be taken to remove all residues of acid by thorough washing and drying after treatment. The composition of the pickling solution must be carefully optimized as it will have a marked

effect on the adhesion of any organic coating or adhesive subsequently applied.<sup>1</sup> Stainless steels require rather more sophisticated pickling solutions; a widely used example is a sulphuric acid/dichromate etch, which leads to chromium enrichment in the oxide film and a subsequent improvement in adhesion.<sup>2</sup>

In the case of rusty steel surfaces or those with inorganic salt contamination (such as those resulting from storage of steel structures in marine environment), pre-treatment is readily effected with a hot dilute solution of phosphoric acid. Besides removing the oxide and etching the steel substrate slightly, it deposits a thin layer of iron phosphate on the steel. This not only provides improved corrosion-resistant properties but also leads to improved adhesion of organic coatings.<sup>3</sup> This type of treatment is a very simple example of a **Conversion coating**, that is one that is deposited on the surface by the chemical interaction between substrate and treatment bath. However, most commercially available conversion coating systems are more complex than the simple phosphoric acid wash and are designed to deposit complex mixed phosphates or chromates.

### *Conversion coatings*

The most widely used conversion coating is zinc phosphate, which is used on low-carbon steels in addition to zinc, aluminium, cadmium and tin (see **Conversion coating** and **Pre-treatment of metals prior to painting**). In this process, a steel substrate, for example, is treated in a solution of zinc phosphate and phosphoric acid (together with processing aids such as oxidizing agents) to produce a characteristic acicular intermeshed deposit on the metal surface.<sup>4</sup> The deposit is traditionally a mixture of hopeite [ $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ] 90%, phosphophyllite [ $\text{Zn}_2\text{Fe}(\text{PO}_4) \cdot 4\text{H}_2\text{O}$ ] 3%, and zinc phosphate dihydrate [ $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ] 7%. Although the various proportions of each phase are determined to a large extent by process chemistry, the concentration of phosphophyllite seems to be particularly important in terms of subsequent performance. The morphology of the deposit is shown in Fig. 1, but is critically dependent on surface cleaning procedures, temperature of application, and the nature of additions to the bath. The acicular morphology promotes good adhesion to paint films because of the large surface area generated; however, it shows poor performance in situations of **Cathodic disbondment** where the cathodically generated alkali leads to premature failure of the phosphate coating at the point where the crystals join the basal plane. For this reason, it has generally been considered to be unsuitable as a pre-treatment



**Fig. 1.** Phosphate morphology produce by a commercial process

for adhesive bonding. This may still be the case for bare steel but the performance of adhesively bonded galvanized steel is improved substantially by the use of a phosphate pre-treatment.<sup>5</sup>

### References

1. J. M. Sykes, in *Surface Analysis and Pre-treatment of Plastics and Metals*, D. M. Brewis, Ed., Applied Science Publishers, London, 1982, pp. 153–174.
2. T. Smith and R. Hank, *Treatment of AM 355 Steel for Adhesive Bonding* AD-AO 74113, 1979.
3. J. F. Watts, *J. Mater. Sci.*, **19**, 3459–3456 (1984).
4. D. B. Freeman, *Phosphating and Metal Pre-treatment*, Industrial Press Inc., New York, U.S.A. 1986.
5. M. F. Fitzpatrick and J. F. Watts, *Surf. Interf. Anal.*, **27**, 705–715 (1999).

## Pre-treatment of titanium

G W CRITCHLOW

A general survey is to be found in **Pre-treatment of metals prior to bonding**, but this article is concerned specifically with titanium.

Industrial grades of pure titanium have relatively low tensile strength in comparison to alpha-beta stabilized alloys such as Ti6Al4V. Therefore, the majority of industrial uses for titanium incorporate the alpha-beta alloys and as such these are the focus of most adhesion studies.<sup>1–4</sup> As with other metals, there is a large range of pre-treatments available for titanium and its alloys, as indicated in Table 1.

Also, in common with most metals, the majority of conventional mechanical pre-treatments, such as grit blasting, give relatively poor durability results (see **Durability: fundamentals, Weathering of adhesive joints** and **Weathering tests**). For example, **Wedge test**

Table 1. Summary of the main pre-treatment processes for titanium

Pre-treatment type	Process
Mechanical	Solvent wipe or clean by immersion or from the vapour phase Alkaline or acid degreasing Abrasion from pads Grit or sand blasting or honing, wet or dry Plasma or corona discharge Plasma spray or other PVD methods
Chemical	Air oxidation Acid etching, e.g. nitric, hydrochloric, hydrofluoric or mixed acids Alkaline etching, usually proprietary solutions, e.g. TURCO 5578 sodium hydroxide or hydrogen peroxide-based solutions Conversion coating, e.g. in phosphate-fluoride solutions
Electrochemical	DC, e.g. in chromic acid or sodium hydroxide electrolytes

joints assembled using **Epoxide adhesives** with grit-blasted adherends and tested in a boiling water environment have been demonstrated to perform substantially worse than those using chromic-acid-anodized or plasma-sprayed adherends. Crack extensions of approximately 9, <0.5 and <0.5 cm were recorded respectively following a 20-h exposure.

In many industrial applications, for example, in **Aerospace applications** and defence sectors, the titanium alloy could be exposed to hot-wet or hot-dry environments, and consequently, studies have focussed on identification of the best performing pre-treatment for particular environmental conditions and stress states.

The hydrolytic stability of a metal surface is particularly important when a bonded structure is exposed to such a hot-wet environment. Titanium does, however, offer the advantage of providing a relatively inert oxide layer, so a process such as the room temperature alkaline hydrogen peroxide (NaOH-H<sub>2</sub>O<sub>2</sub>) etch (AHPE) can be very effective. The AHPE produces a highly micro-rough, reasonably hydrolytically stable oxide that is reported to extend to 135 nm (see **Microfibrous surfaces**). Problems of control over the hydrogen peroxide content of the etch bath do, however, limit its use. The AHPE generally performs better in comparative trials than all pre-treatments other than the proprietary TURCO or Pasa Jell etches, anodizing or plasma spray.

The anodic oxides and, in particular, those based upon sodium hydroxide and chromic acid electrolytes (SHA and CAA) are regarded as being amongst the better-performing pre-treatments. These processes also produce micro-rough surfaces capable of interphase formation but they also provide thick oxides, extending up to several micrometres, for increased surface passivation and consequently potentially improved hot-wet durability performance.

There has, however, been concern raised over the stability of the CAA oxide on Ti6Al4V when exposed to dry conditions for prolonged periods (up to 1200 h) at 330 °C or shorter periods (up to 24 h) at 400 °C. A brittle zone has been shown to form at the oxide-metal interface, which results in cohesive failure of joints at low loads, below 0.7 MPa, when measured in a tensile butt test. Cohesive failure in this instance occurred within this brittle zone.

The use of **Thermal spray processes** to deposit thick layers, extending to typically 50 µm and with a surface roughness (R<sub>a</sub>) of many micrometres, of Ti6Al4V onto the same alloy has been demonstrated to be effective by a number of workers. Invariably, joints fabricated with PS pre-treated adherends perform very well in comparable durability trials, including those carried out at temperatures of 400 °C and greater. PS pre-treated adherends can give improved durability performance compared to CAA and similar results to the SHA process.

The use of primers or coupling agents based upon alkoxide or silane chemistry has been demonstrated to be potentially useful when used in combination with grit blasting or acid etching, though results are highly variable (see **Silane adhesion promoters**).

## References

1. D. K. Shaffer, H. M. Clearfield and J. S. Ahearn, in *Treatise on Adhesion and Adhesives*, Vol. 7, J. D. Minford, Ed., Marcel Dekker, New York, 1991, pp. 437-495.
2. G. W. Critchlow and D. M. Brewis, *Int. J. Adhes. Adhes.*, **15**, 161-172 (1995).
3. J. A. Filbey and J. P. Wightman, *J. Adhes.*, **28**, 1-22 (1989).
4. H. M. Clearfield, D. K. Shaffer, S. L. Vandoren and J. S. Ahearn, *J. Adhes.*, **29**, 81-102 (1989).

---

## *Pre-treatments of polymers*

---

D M BREWIS

### *Introduction*

Good adhesion to polymers is required in a number of technologies including adhesive bonding, metallizing, painting and printing. To achieve satisfactory adhesion, it is often necessary to pre-treat the polymer. The wide variety of pre-treatments available may be divided into a number of different types.

### *Solvent pre-treatments*

The poor adhesion obtained with a polymer may be due to contaminants or additives on the surface. In such a case, a wipe or dip with a suitable solvent should be the only pre-treatment required. An example is the removal of plasticizer with ethyl acetate from the surface of poly(vinyl chloride).

Such a treatment is inadequate with polyolefins and some other polymers, although immersion of polyolefins in hot chlorinated solvent vapours for a few seconds can lead to great improvements in adhesion.<sup>1</sup> This vapour treatment is discussed in the article **Pre-treatments of polyolefins**.

The properties of some polymers are seriously affected by particular organic solvents and certain polymer–solvent combinations must be avoided.

### *Mechanical pre-treatments*

Mechanical treatments such as grit blasting and the use of abrasive pads are used to improve the adhesion to thermosets, especially those of the fibre-reinforced type (see **Abrasion treatment** and **Fibre composites – joining**). The improved performance is probably due partly to the removal of contaminants from the surface and partly to the increased roughness. The latter can be beneficial owing to (1) the increased potential bonding area, (2) the possibility of mechanical keying and (3) increased plastic deformation of the adhesive or coating.<sup>2</sup> It is important to remove the particles of polymer and abrasive from the surface with a solvent wipe or with a short immersion in an ultrasonic bath. An interesting variation on grit blasting is cryoblasting, where a surface is bombarded with carbon dioxide particles. Encouraging results have been obtained with polyurethane<sup>3</sup> and PVC substrates.

An alternative pre-treatment for composites is the tear (peel) ply method. A fabric is incorporated in the composite near the surface. The fabric is pulled away just prior to bonding, exposing a clean surface, provided there is no contamination from the fabric.<sup>4</sup>

### *Oxidative pre-treatments*

The growth in the use of low-density polyethylene after the Second World War was restricted by the fact that it was very difficult to print upon or bond. This led to the development of a number of pre-treatments including the use of chromic acid, **Flame treatment** and corona discharges. Under the correct conditions, these pre-treatments are all highly effective.<sup>5</sup>

The **Corona discharge treatment** is especially suitable for the continuous treatment of plastic films, whereas the flame treatment is generally preferred for treating thicker sections such as bottles. Chromic acid is sometimes used prior to the metal plating of plastics and for treating complex shapes. These three methods are discussed in more detail in **Pre-treatments of polyolefins**.

Although these treatments were developed for low-density polyethylene, they are now used to treat other polyolefins and other types of plastic. For example, the corona treatment is used with poly(ethylene terephthalate) and chromic acid with acrylonitrile–butadiene–styrene (ABS) and polyoxymethylene.

### *Plasma treatments*

**Plasma pre-treatment** has been the subject of much research with a wide variety of polymers. In this method, power is applied to a gas or a monomer at low pressure (typically 1 torr) and a plasma, consisting of ions, electrons, atoms and free radicals, is formed. Improved adhesion may be due to a variety of mechanisms including ablation of small molecules, cross-linking or introduction of functional groups such as carbonyl and amine. With monomers, such as acrylates, grafting to the polymer surface can occur.

### *Electrochemical treatments*

Chemical modification is possible using **Electrochemical pre-treatments of polymers**, under either reductive conditions (example PTFE) or oxidative conditions (example polyethylene).

### *Summary of changes caused by pre-treatments*

The possible effects of the various pre-treatments are summarized in Table 1.

*Table 1.* Possible effects of pre-treatments for polymers

Treatment type	Possible changes to polymer surface
Solvent	<ul style="list-style-type: none"> <li>● Removal of contaminants and additives</li> <li>● Roughening (e.g. trichloroethylene vapour/polypropylene)</li> <li>● Weakening of surface regions if excessive attack by the solvent</li> </ul>
Mechanical	<ul style="list-style-type: none"> <li>● Removal of contaminants and additives</li> <li>● Roughening</li> </ul>
Oxidative	<ul style="list-style-type: none"> <li>● Removal of contaminants and additives</li> <li>● Introduction of functional groups</li> <li>● Change in topography (e.g. roughening with chromic acid treatment of polyolefins)</li> </ul>
Plasma	<ul style="list-style-type: none"> <li>● Removal of contaminants and cross-linking</li> <li>● Introduction of functional groups</li> <li>● Grafting of monomers to polymer surface</li> </ul>



### Methods to study pre-treatments

The chemical changes caused by pre-treatments may be studied by the use of contact angle measurements (see **Surface characterization by contact angles: polymers**) or preferably with surface techniques such as **X-ray photoelectron spectroscopy (XPS)**. The topographical changes are best studied by means of **Scanning electron microscopy (SEM)** or **Atomic force microscopy (AFM)**.

Other related articles are as follows: **Contact angles and interfacial tension, Infrared spectroscopy, Pre-treatment of fluorocarbon polymers, Primers for adhesive bonding, Roughness of surfaces, Surface analysis.**

### References

1. E. W. Garnish and C. G. Haskins, in *Aspects of Adhesion 5*, D. J. Alner, Ed., University of London Press, 1969, p. 259.
2. D. E. Packham, in *Adhesion Aspects of Polymeric Coatings*, K. L. Mittal, Ed., Plenum Press, New York, 1983, p. 19.
3. D. M. Brewis and I. Mathieson, *Proceedings of the 22nd Annual Meeting of the Adhesion Society*, Panama, FL, February 21–24, 1999, p. 4.
4. A. J. Kinloch, *Adhesion and Adhesives*, Chapman and Hall, London, 1987, p. 101.
5. D. M. Brewis, *Prog. Rubber Plast. Technol.*, **1**(4), 1 (1985).

## Pre-treatments of polyolefins

D M BREWIS

### Introduction

After the Second World War, it soon became apparent that low-density polyethylene (LDPE) would be a useful packaging material. However, one serious problem was the difficulty in obtaining good adhesion to the polymer. This led to much research and development to obtain effective pre-treatments for LDPE. By about 1950, a number of pre-treatments had been developed, including the use of chlorine + UV radiation, chromic acid etching, **Flame treatment** and **Corona discharge treatment**.

The first method, although effective, was soon abandoned for safety reasons, while the use of chromic acid has been largely discontinued. The other two have remained the most widely used pre-treatments, not only for LDPE but also for high-density polyethylene (HDPE) and polypropylene (PP). Other methods have been found to be effective, but for reasons of cost, safety or convenience, they have not been widely used. The pre-treatments include fuming nitric acid, potassium permanganate, ammonium peroxydisulphate, ozone, fluorine, peroxides, UV radiation, grafting of polar monomers, plasmas (see **Plasma pre-treatment**), electrochemical oxidation (see *Electrochemical pre-treatment of polymers*) and the use of solvent vapours. The corona, flame and plasma methods and the use of trichloroethylene are now discussed briefly; the latter is included because it involves a different mechanism.

### *Trichloroethylene vapour*

Garnish and Haskins<sup>1</sup> found that exposure of polypropylene to trichloroethylene vapour for 10 s resulted in a sixfold increase in joint strength using an **Epoxide adhesives**. The authors concluded that the improved adhesion was due to the removal of a weak boundary layer. However, the treatment causes the formation of a very porous surface, and an alternative explanation for the improved adhesion is the mechanical keying of the adhesive into the porous surface (see **Mechanical theory of adhesion**). Garnish and Haskins found that the optimum treatment time was about 10 s and that after 25 s the adhesion level was similar to that of the untreated polymer. This reduction is probably due to weakening of the surface region of the polypropylene.

### *Flame treatment*

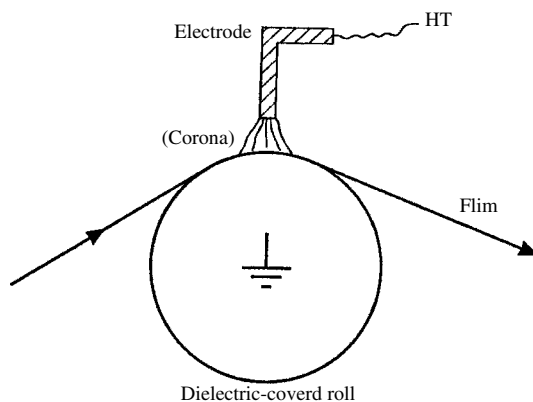
**Flame treatment** is used to improve the adhesion to relatively thick polyolefin objects. For many years, the method has been used to improve the adhesion of printing ink to polyethylene bottles. More recently, flame treatment has been used to improve the paint adhesion (see **Paint constitution and adhesion**) to polypropylene car bumpers.

The object to be treated is passed over one or more burners, each of which possesses a large number of closely spaced jets. The burners are fed with an air–hydrocarbon gas mixture whose proportions are carefully controlled. Ayres and Shofner<sup>2</sup> found that with methane the optimum treatment time for an unspecified polyolefin was 0.02 s. A study of the flame treatment of LDPE<sup>3</sup> showed very high levels of oxidation, although the oxidized layer was only 4–9 nm thick.

### *Corona discharge treatment*

The **Corona discharge treatment** has been widely used since about 1950 to treat LDPE, especially to enhance printing ink adhesion. The method has also proved to be very successful with HDPE and PP.

A schematic representation of the treatment is given in Fig. 1. The film is passed, typically at 2–4 m s<sup>-1</sup> over an earthed metal electrode covered with an insulator. The



**Fig. 1.** Schematic representation of the corona discharge treatment

distance between the electrode and the film is usually 1–2 mm. A high-frequency (10–20 kHz) generator and step-up transformer produce a high voltage, which causes the electrical breakdown of the air, with the formation of atoms, ions and electrons, which in turn leads to the formation of ozone, and so on.

**Surface analysis** has shown that the **Corona discharge treatment** leads to the introduction into the polyolefin surface of various groups, including carbonyl, carboxyl, hydroxyl and ether.<sup>4</sup>

It is known that additives such as slip agents and antioxidants can adversely affect the treatment if this is done out of line, that is, if the additives migrate before the treatment is carried out, then inferior adhesion may result. Another problem is that the effectiveness of the treatment can deteriorate over a period of a few weeks.

### *Plasma treatment*

The use of low-pressure plasmas is becoming an increasingly important method to pre-treat polyolefins. An interesting comparison of “dry” pre-treatments is given in reference.<sup>5</sup>

See also the more general article **Pre-treatments of polymers**.

### *References*

1. E. W. Garnish and C. G. Haskins, in *Aspects of Adhesion 5*, D. J. Alner, Ed., University of London Press, 1969, p. 259.
2. R. L. Ayres and D. L. Shofner, *SPE J.*, **28**(12), 51 (1972).
3. D. Briggs, D. M. Brewis and M. B. Konieczko, *J. Mater. Sci.*, **14**, 1344 (1979).
4. D. Briggs and C. R. Kendall, *Int. J. Adhes. Adhes.*, **2**(1), 13 (1982).
5. M. Strobel, M. J. Walzak, J. M. Hill, A. Lin, E. Karbasheski and C. S. Lyons, in *Polymer Surface Modification*, K. L. Mittal, Ed., VSP, utrecht, 1996, p. 233.

---

## *Primary bonding at the interface*

---

JOHN F WATTS

In considering the adhesion of an organic material to an inorganic substrate (or *vice versa*), the vast majority of systems rely on the formation of secondary bonds between the materials (see **Bonds between atoms and molecules**). Indeed, until two decades or so ago, it was universally accepted that, if the **Adsorption theory of adhesion** was relevant to a particular system, then the formation of an interfacial bond would be the result of **Dispersion forces** and **Polar forces**. In recent years, it has become clear that interfacial reactions may involve the formation of very specific bonds with their own bond angles and bond distances. One very important member of this class is **Acid–base interactions** (e.g. **Hydrogen bonding**) and the other is primary bonding. By primary bonds, we mean those that may be exclusively responsible for the bonding in a solid and which may lead to compound formation at an interface. The three types of primary forces that occur are ionic bonding (with bond energies in the range 590–1050 kJ mol<sup>-1</sup>) covalent bonding (63–710 kJ mol<sup>-1</sup>), and metallic bonding (113–347 kJ mol<sup>-1</sup>). Clearly,

in any investigation of the polymer/metal interface, we shall only be concerned with the first two categories.

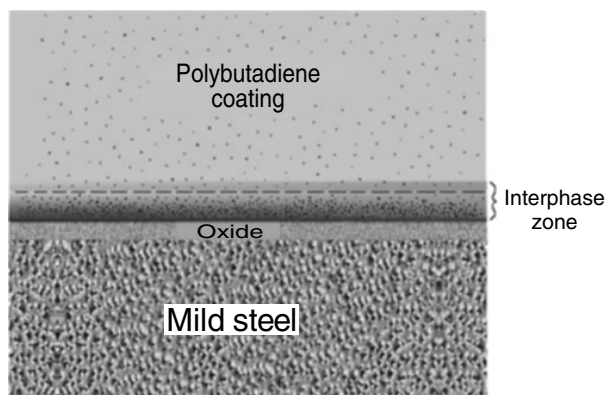
There are relatively few well-documented examples of interfacial primary bonding in the literature but it is possible to find examples in the areas of organic coatings on steel, metallized plastics and adhesion promoters. As the following examples will show, the exact definition of the chemistry resulting from primary bond formation at the interface has only become possible with the advent of surface analysis techniques. Such investigations rely heavily on XPS and ToF-SIMS for interfacial analysis.

### *Organic coatings*

Probably, the most widely investigated organic coatings system is polybutadiene,<sup>1</sup> and there is now unequivocal experimental evidence from several analytical methods that a chemical reaction occurs between the polymer and the oxidized metal substrate. An investigation by **X-ray photoelectron spectroscopy**<sup>2</sup> showed that at the interface the iron (III) oxide is reduced to iron (II) by the polymer; this is not surprising bearing in mind that the polybutadiene cures by an oxidative mechanism and thus acts as a reducing agent for the iron oxide. This reaction leads to the formation of an iron carboxylate compound at the interface, which in turn is responsible for the development of a discrete interphase as illustrated in Fig. 1. The formation of such an interphase has important ramifications in terms of the mechanical properties of the polymer/metal couple. Instead of an abrupt change in stress distribution as one sees in the case of a two-dimensional interface, there is now a gradual change across the width of the interfacial zone. In this way, the load-bearing properties of an interface can be improved by the development of an interphase.

### *Metallized plastics*

Plastics can be metallized by a variety of techniques, including **Metallizing plastics** from solution and vacuum deposition. In the case of vacuum metallization of polyimides with



**Fig. 1.** Schematic representation of the interaction between polybutadiene and mild steel. The interphase zone contains iron carboxylate

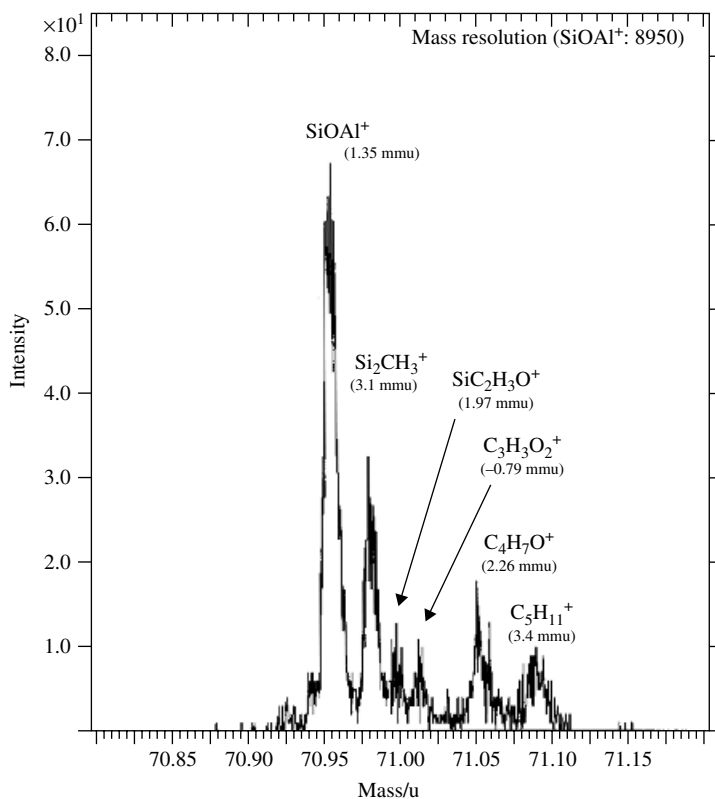
titanium, it is known that a two-stage process is involved.<sup>3</sup> In the early stages of deposition (i.e. low coverage), there is a strong interaction between the metal and the polymer by way of electron transfer from the titanium to the carbonyl oxygen of the polymer backbone. As the coverage of metal increases the Ti–C bond formation becomes involved in the reaction, a feature readily identified by **X-ray photoelectron spectroscopy** and **Auger electron spectroscopy**. At sub-monolayer coverage, the titanium is already being deposited in the metallic state, indicating that the metal–carbide complex is present as a discontinuous interfacial layer. A similar model is thought to apply for aluminium metallization.

### *Adhesion promoters*

Adhesion promoters are large organic molecules designed to improve adhesion between organic and inorganic materials. There is evidence to suggest that specific groups present in the molecule interact with one or other of the two phases to be joined. Silanes are widely used for both steel and glass substrates; XPS studies show that the silicon containing head adsorbs onto the oxide surface by a chemisorption process, and **Secondary ion mass spectrometry** has identified the formation of a Fe–O–Si bond on steel substrates. Early investigations<sup>4</sup> were carried out using mass spectrometry at unit mass resolution but later high-resolution studies<sup>5</sup> showed the assignment to be correct. On glass fibres, primary bond formation has been identified by infrared spectroscopy.<sup>6</sup>

A great deal of effort has been expended in understanding the interaction between organosilane adhesion promoters (particularly  $\gamma$  glycidoxypropyl trimethoxysilane [GPS]) and aluminium substrates, the reason being the potential for the replacement of Cr(VI) containing pre-treatments for structural adhesive bonding in the aerospace industry. The Al–O–Si<sup>+</sup> fragment in ToF-SIMS diagnostic of an interfacial covalent bond has a nominal mass of  $m/z = 71$  Da. However, as the high-resolution spectrum of Fig. 2 indicates, this region is very complex indeed and contains many other hydrocarbon- and silicon-containing fragments, in addition to a possible Al<sub>2</sub>OH<sup>+</sup> fragment from the substrate. This region has been discussed in detail elsewhere and it is clear that the Al–O–Si<sup>+</sup> fragment at  $m/z = 70.9534$  Da is present in the spectrum and increases as the interface is approached by gentle ion etching.<sup>7</sup> Once near the inorganic layer on the metal substrate, the Al<sub>2</sub>OH<sup>+</sup> fragment at  $m/z = 70.9658$  Da becomes dominant. The interfacial and solution chemistry associated with organosilane molecules applied to a variety of metal substrates for adhesion purposes has recently been reviewed by Abel *et al.*<sup>8</sup>

ToF-SIMS is the method of choice for unravelling such complex interfacial chemistry and Abel *et al.* have shown how, using diethanolamine as an epoxy analogue molecule interacting with GPS treated aluminium, a primary bond is established. This is brought about by the interaction between the nitrogen lone pair of electrons of the amine and the opening of the strained oxirane ring of the GPS molecule.<sup>9</sup> This concept of tracking such specific (primary bond) interactions by ToF-SIMS has been taken one step further by Rattana *et al.* in the study of a commercial adhesive applied to a GPS-treated aluminium.<sup>10</sup> By comparison of the spectra obtained from dilute solutions of adhesive applied to bare aluminium and aluminium treated in the recommended way,<sup>11</sup> by GPS, these authors were able to identify a fragment at  $m/z = 277$  Da resulting from the formation of a covalent bond between the curing agent with the epoxy functionality of either the epoxy component of the adhesive or the epoxy group of the GPS molecule. In the case of the GPS-treated substrate, this fragment was much more intense (by a factor of four) than for



**Fig. 2.** High resolution ToF-SIMS spectrum, of the  $m/z = 71$  Da region, of GPS applied to aluminium. The major component at  $m/z = 70.9534$  Da is attributed to the Al–O–Si<sup>+</sup> ion diagnostic of a covalent bond between the substrate and the organosilane primer

the untreated aluminium. In essence, the untreated substrate yields an interaction between curing agent and epoxy molecules in the adhesive; when a GPS primer layer is present, the additional signal at this critical mass is a result of the interaction between curing agent and GPS molecule.

Thus, when investigating the nature and mechanism of adhesion between an adhesive, coating or polymer matrix and the substrate, it is important to consider the possibility of primary bond formation in addition to the interactions that may occur as a result of **Dispersion forces** and **Polar forces**. In addition to the **Adsorption theory of adhesion**, adhesion interactions can sometimes be described by the **Diffusion theory of adhesion**, **Electrostatic theory of adhesion**, or **Mechanical theory of adhesion**. Recent work has addressed the formation of primary bonding at the interface as a feature that is desirable from a durability point of view and a phenomenon that one should aim to design into an interface. The concept of engineering the interface in such a way is relatively new, but as adhesives become more widely used in evermore demanding applications, and the performance XPS and ToF-SIMS systems continues to increase, it is anticipated that such investigations can only become more popular.

## References

1. H. Leidheiser, *J. Adhes. Sci. Tech.*, **1**, 79–98 (1987).
2. J. F. Watts and J. E. Castle, *J. Mater. Sci.*, **18**, 2987–3003 (1983).
3. F. S. Ohuchi and S. C. Freilich, *J. Vac. Sci. Tech.*, **A4**, 1039–1045 (1986).
4. M. Gettings and A. J. Kinloch, *J. Mater. Sci.*, **12**, 2511–2518 (1977).
5. S. J. Davies and J. F. Watts, *Int. J. Adhes. Adhes.*, **16**, 5–15 (1996).
6. S. S. Shyu and S. M. Chen, *J. Chin. Inst. Chem. Eng.*, **16**, 311–322 (1986).
7. M.-L. Abel, R. P. Digby, I. W. Fletcher and J. F. Watts, *Surf. Interf. Anal.*, **29**, 115–125 (2000).
8. M.-L. Abel, J. F. Watts, R. P. Digby and *J. Adhes.*, **80**, 291–312 (2004).
9. M.-L. Abel, A. Rattana and J. F. Watts, *Langmuir*, **16**, 6510–6518 (2000).
10. A. Rattana, J. D. Hermes, M.-L. Abel and J. F. Watts, *Int. J. Adhes. Adhes.*, **22**, 205–218 (2002).
11. R. P. Digby and S. J. Shaw, *Int. J. Adhes. Adhes.*, **18**, 261 (1998).

---

## Primers for adhesive bonding

---

JOHN BISHOPP

After **Pre-treatment of metals prior to bonding**, it may be several weeks before the adhesive is applied. Most pre-treated surfaces are stable for considerably less than 24 h, so protection by priming is needed. However, the effectiveness of primers, particularly of the corrosion inhibiting primers, can be very sensitive to coating thickness: a change in thickness from 2–5  $\mu\text{m}$  to above 8–10  $\mu\text{m}$  can halve the peel performance of some adhesives.

Three classes of primer are in current use: “surface protection primers”, “corrosion inhibition primers” and organosilanes, (which are claimed both to protect the surface and enhance the adhesion). By far, the greatest numbers of commercial products fall into the second class.

### *Surface protection primers*

These are usually solvent-based systems of low solids content (ca. 10%), chemically similar to the adhesive to be used. Often a primer is a simple solution of its equivalent adhesive, without insoluble fillers, and so on.

Primers are applied by brush, roller or spray gun, and dried, usually in an extracted, air-circulating oven at 60 to 80 °C. In some applications, the primed substrates are then stored in a clean, dry area until needed; in other applications, the primer is cured, by oven-stoving, at the requisite temperature. These components would then be similarly stored. In the first case, the primer co-cures with the adhesive, and in the second, the adhesives wets and bonds to the already cured primer coating. Irrespective of which route is followed, the primer protects the integrity of the pre-treated surface prior to bonding.

Surface protection primers rarely enhance the mechanical performance of the adhesive; indeed, in a few cases, a reduction in bonding strength occurs.

### Corrosion inhibiting primers

In addition to surface protection, these impart some corrosion resistance, protecting the joint against attack of moisture and electrolytic corrosion. Again, the primer may be simply dried or dried and cured before bonding.

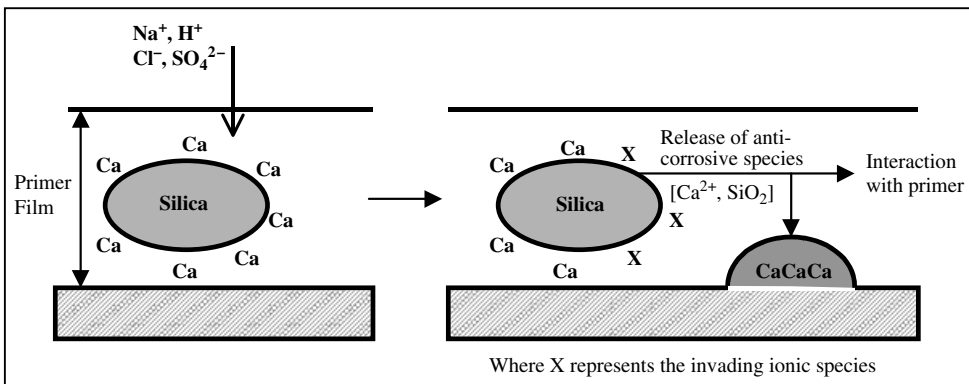
A classic example is Cytec BR-127, which is an epoxy-phenolic system dissolved in a solvents blend. Corrosion inhibition results from a significant strontium chromate loading – present as a fairly unstable suspension.

The corrosion inhibition of these heavy metal chromates depends upon their passivation of aluminium. When such a corrosion-inhibited bonded joint is attacked, a mixture of hydrated aluminium oxide and chromic oxide ( $\text{Cr}_2\text{O}_3$ ) is formed. This not only seals the “oxide” film, repairing the damage caused by the ingress of the electrolyte, but the presence of the stable chromic oxide also reduces the rate of dissolution of the aluminium oxide. The longevity of such a protection is due to the low solubility ( $\sim 1.2 \text{ g L}^{-1}$  at  $15^\circ\text{C}$ ) of the chromate in water, which means that the chromate remains “active” for a considerable period of time.

The possibility of using other inorganic compounds such as the oxides, hydroxides, phosphates and borates of calcium, magnesium and zinc to replace the potentially carcinogenic chromates has been investigated.

Another approach has been the use of suitable “ion-exchanged silicas”. In the presence of electrolytes, these give protection by releasing passivating ions that can interact not only with the matrix but also with the electrolytic species themselves and the substrate; see Fig. 1. This type of inhibitor is typified by the fact that it is completely insoluble in water and only works on demand – that is, only when invading electrolytic species are present.

Research is now strongly centred on producing primers with low volatile organic contents, by using water as the primary solvent or dispersion medium or actual water-based primers where the organic solvent content is zero. For similar reasons of **Environment and the impact of adhesive technology**, a move to non-chromate systems is also under way.

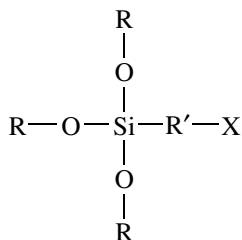


**Fig. 1.** Schematic of the corrosion inhibition reaction mechanism for ion-exchanged silicas

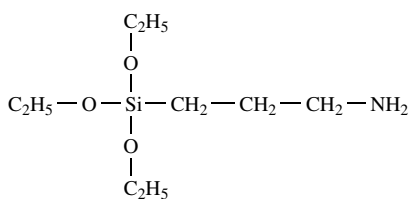


*Organosilanes*

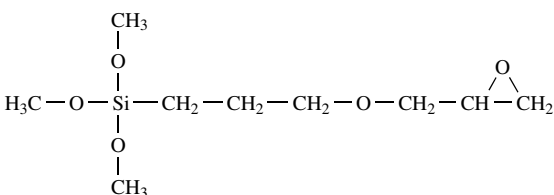
These have the structure



where R represents a simple alkyl group, which is generally methyl or ethyl, R' is an alkyl chain which is often propyl, X is the end group, which can be H but is more usually a functional group such as amino, epoxy, mercapto, ureido, isocyanato, vinyl and methacryloxy. Although some silanes encountered are complex, the two most common are  $\gamma$ -aminopropyl triethoxy silane and  $\gamma$ -glycidoxypropyl trimethoxy silane (see also **Silane adhesion promoters**).



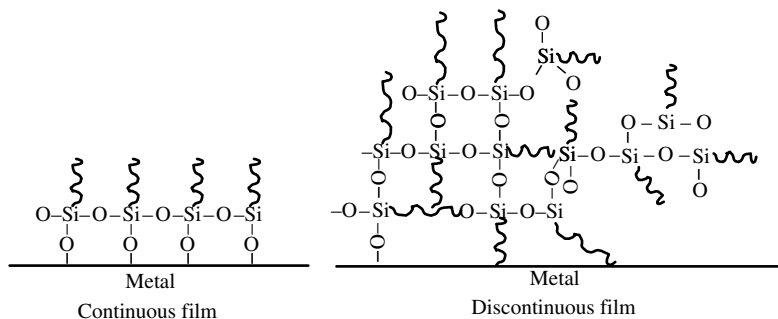
$\gamma$ -Aminopropyl triethoxy silane



$\gamma$ -Glycidoxypropyl trimethoxy silane

The alkoxy silane groups are considered to hydrolyze to form silanol groups, which can then react with the metal oxide/hydroxide surface. Further hydrolyzation can give a continuous or a randomly discontinuous film at the metal surface, see Fig. 2.

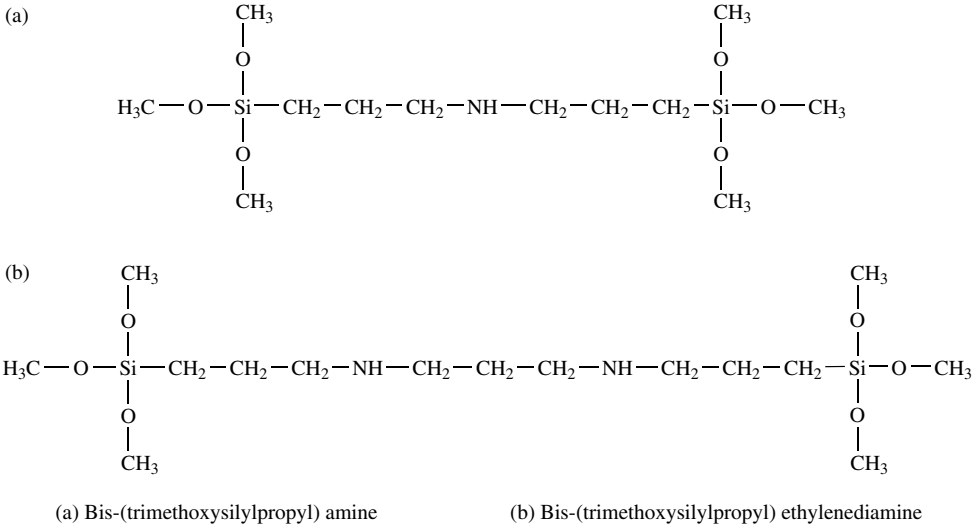
The silane concentration, the carrying medium (water or alcohol), its pH and temperature are all critical to the successful use of silanes: there are indications that low silane concentrations in water at a pH of about 5 yield optimum performance.



**Fig. 2.** Films of mono-functional silanes on metal oxide/hydroxide surfaces

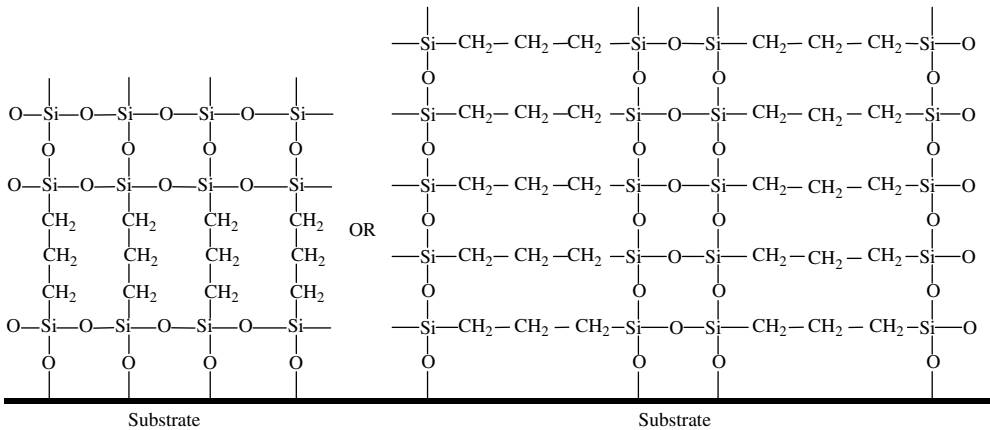
Despite considerable work over many years, silane pre-treatments or primers prior to structural bonding are still relatively rare in **Aerospace applications**. Silanes are, though, regularly used as formulating ingredients in **Epoxide adhesives** (paste and film) and primers.

More complex bis-silanes are being considered as replacements for conventional metal pre-treatment and for chromate in corrosion-inhibiting primers. van Ooij advocates the use of both mono- and di-amino based bis-silanes (see **Silanes as metal pre-treatments**):



After hydration these readily form films 400 to 500 nm thick on the metal surface, comprising continuous networks (Fig. 3), which potentially give excellent protection.

In several instances, van Ooij *et al.* have found that mixtures of mono- and bis-silanes give the best corrosion protection. As with their mono-functional counterparts, these materials are not yet in common use.



**Fig. 3.** Continuous network formations of “bis-silanes” on metal surfaces

*Select References*

- E. P. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York, 1991.
- T. Fletcher, *Polym. Paint Colour J.*, **182**, March 18th, p. 144, 1992.
- P. M. Hobbs and A. J. Kinloch, *J. Adhes.*, **66**, 203 (1998).
- W. J. van Ooij, D. Q. Zhu, G. Prasad, S. Jayaseelen, Y. Fu and N. Teredesai, *Surf. Eng.*, **16**, 386 (2000).
- W. J. van Ooij, V. Subramanian and C. Zhang, *Method of Preventing Corrosion of Metals using Silanes*, *US Patent* 6,261,638, 2001.
- M.-L. Abel, R. D. Allington, R. P. Digby, N. Porritt, S. J. Shaw and J. F. Watts, *Int. J. Adhes. Adhes.* in press.

---

*Primers for sealants*

---

G B LOWE

The term primer is used to describe any liquid preparation used to modify the surface of an adherend. While there are some primerless systems, the sealants used in construction often require primers as the surface condition may be extremely variable (See **Sealant joint design**, **Sealants in double glazing** and **Selection of joint sealants**).

For the most part, surfaces found in construction are defined as either porous or non-porous. The former covers concrete, brickwork, blockwork and so on, while the latter includes glass, metals, some plastics and so on.

Apart from determining surface type, the surface conditions have to be considered when selecting primers. For example, different primers may be required for sealing joints in water-retaining structures where- long-term water resistance is required compared to above ground application although both will have a concrete surface.

*Primers for non-porous surfaces*

Glass primers are generally dilute solutions of either a silane or silicone resin. Concentrations vary between 0.5 and 5% by weight depending on type and use. Silanes used are of the reactive side group type such as  $\gamma$ -glycidoxypropyltrimethoxysilane or aminopropyltriethoxysilane. The alkoxy group is generally short to allow rapid hydrolysis; the active group selected will depend on the polymer base of the sealant to be bonded (see **Silane adhesion promoters**).

Metal primers are similar to glass primers but at a higher concentration level. As a consequence, many manufacturers have primers at the 1–2% concentration to be suitable for both applications. Suitable silanes are described by Comyn<sup>1</sup> in the context of their evaluation as coupling agents.

*Primers for porous surfaces*

Primers for porous surfaces are generally film-forming resin solutions. They perform the dual function of preparing the surface to receive the sealant and binding any friable surface

to prevent stress damage. This is because most concrete and stone surfaces have a weak layer, which can delaminate under load.

Normal porous surface primers are based on solutions of chlorinated rubber or isocyanate prepolymer. Concentrations are higher than for non-porous surfaces and can be 20–30% by weight. A number of primers are a mixture of both polymers in order to increase the range of usage and those designed for water immersion will also incorporate a cross-linking catalyst. Special primers for use in potable water storage are based on epoxy resins cured with aliphatic amines. The porous nature of the surfaces works against the use of dilute solutions as the primer will penetrate into the matrix and become ineffective.

#### *Surface preparation for primers*

In order to prepare the surface to receive a primer, porous surfaces are roughened by wire brushing. Some workers believe that this gives a greater surface area as well as removing any loose material.

Performance of primers has been studied both in general construction and water-retaining structures.<sup>2,3</sup> Further information may be found in articles on **Selection of joint sealants**, **Sealant joint design**, **Paint primers** and **Primers for adhesive bonding**.

#### *References*

1. J. Comyn, Silane coupling agents, in *Structural adhesives*, A. J. Kinlock, Ed., Elsevier, London, 1986, Chap 8.
2. J. Beech and D. Aubrey, The influence of primers on the performance of building sealant joints, *Proceedings Adhesives, Sealants and Encapsulants Conference*, London, November, 1986.
3. Construction Industries Research and Information Association, *Report on Sealants for Potable Water*, CIRIA London 1989.

# R

---

## *Radiation-cured adhesives*

---

MARTIN E FAKLEY

### *Introduction*

The demand for ever faster assembly processes and the elimination of volatile organic compounds (VOCs) from solvent-borne adhesives (see **Environment and the impact of adhesive technology**) have led to the development of a variety of radiation curable adhesives systems.<sup>1</sup> Radiation curing utilizes electromagnetic radiation energy (Table 1) in the form of photons (UV) or electrons (EB) to effect physical and chemical change of organic chemical materials by formation of cross-linked polymer networks. The one-component, non-solvent, low-pollution, low-heat, clean air, environmentally friendly manufacturing technology offers extremely rapid curing on demand (to handling strength in substantially less than one second) and is very attractive for automated manufacture.

Infrared radiation for thermal curing is chiefly practised for pre-warming or secondary curing (i.e. to complete a thermal or other curing process). Microwave curing, an alternative to conventional thermal ovens, requires a variable frequency source to generate uniform results (because the dielectric constant of the formulation changes as cure proceeds). Radio frequency curing either requires the substrate(s) or the adhesive to inductively couple with the RF source to generate heat. These technologies are generally considered as variations of thermal curing and will not be discussed further.

### *Ultraviolet (UV) curable adhesives*

UV-curable adhesive are generally formed by **Chain polymerization**: formulations generally comprise

1. a photoinitiator – used to absorb the incident radiation and then undergo a process that leads to radical production and starts the monomers' curing;

Table 1. The electromagnetic spectrum

Radiation type	Typical wavelength (nm)	Predominant primary cure mechanism
Electron beam (EB)	$<10^{-1}$ nm from 125–150 kV source	Electronic excitation and ionization
Ultraviolet (UV)	UVA 315–380 UVB 315–280 UVC 280–100	Electronic excitation
Infrared (IR)	$10^3$ – $10^4$	Thermal
Microwave	$10^4$ – $10^6$	Thermal
Radio frequency (RF)	$>10^6$	Thermal

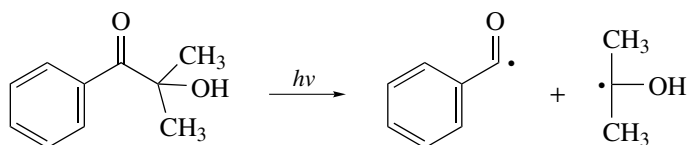
- a polymerizable oligomer (also known as a prepolymer);
- a reactive diluent, usually an acrylate and/or methacrylate;
- an amine synergist (may be part of the initiator package) to reduce the effects of oxygen inhibition;
- a pigment, for example, phthalocyanine dye, carbon black or titanium dioxide (rutile form);
- additives to improve adhesion (e.g. *N*-vinylpyrrolidone) or to control flow of the adhesive (e.g. amorphous silica).

### Photo-initiators

In general, there are two types: Type I, which undergo bond cleavage to give radicals (see Fig. 1), and Type II, usually aromatic ketones, which require a tertiary amine synergist. Following excitation, the aromatic compound attacks the synergist to give a synergist-derived radical, which in turn initiates polymerization. Cationic photo-initiators are used which, after irradiation, fragment ultimately to yield an acid, for example,  $\text{HPF}_6$ , and can catalyse ring-opening polymerization reactions of cyclo-aliphatic epoxides or of electron-rich alkenes (e.g. vinyl ethers). In both cases, polymerization occurs by a living polymer mechanism.<sup>2</sup>

### Applications

The largest application of radiation-cured adhesives is for dental procedures (see **Adhesion in dentistry: restorative materials**). Originally UV curable, these have given way to



where  $h$  is Planck's constant and  $\nu$  is frequency of the radiation

Fig. 1. Type I initiation

visible-light (VL) curing products. Other applications for radiation-curable adhesives include lamination of homo-polymers (including polyester, polycarbonate, polyethylene and cellulose acetate) and glass. Examples of hetero-laminates in packaging include paper to polyester, paper to metallicized polyester, acrylic to vinyl sheets, polyester to polyamide, polyamide to polycarbonate, glass to polyester and glass to polycarbonate. The assembly of digital video discs (DVDs) and liquid crystal displays (LCDs) are specific higher volume laminating duties.

Increasing use of UV-curable acrylates is found in the assembly of medical, automotive, electrical, electronic and optical devices. Dual cure mechanism (UV and anaerobic) adhesives are often used for the assembly of ammunition and automotive air bag inflators.

Radiation-curable **Pressure-sensitive adhesives** (PSA's) eliminate the release of organic solvents into the atmosphere and provide for easier application of the formulation onto the substrate.<sup>3</sup>

### *Safety considerations*

Any source of energetic ionizing or non-ionizing radiation is potentially hazardous if not used correctly. All UV light sources must be well shielded. Skin and eyes should always be protected from exposure to UV light.<sup>4</sup>

### *References*

1. R. S. Davidson, Ed., *Exploring the Science, Technology and Application of UV and EB Curing*, SITA Technology Limited, London, 1999, ISBN 0 947798412.
2. J. V. Crivello and K. Dietliker, in *Photoinitiators for Free Radical, Cationic & Anionic Photopolymerisation*, 2nd edn, G. Bradley, Ed., SITA Technology Limited, London, 1998, ISBN 0471 978922.
3. H. F. Huber, in *Radiation Curing in Polymer Science and Technology*, Vol. IV, J. P. Fouassier and J. F. Rabek, Eds., Elsevier Applied Science, Ondon, 1993, p. 51.
4. R. Mehnert A. Pincus and I. Janovsky, Eds., *Joint Protocol on Improved Condition of Use of UV-Technology UV & EV Curing Technology & Equipment*, John Wiley, 1998.

---

## **Reaction-setting adhesives**

---

D M BREWIS

Reaction-setting or reactive adhesives are those that harden by means of chemical reactions. These chemical reactions usually involve either **Chain polymerization** or **Step polymerization**. Depending on the functionalities of the molecules involved, either thermoplastics or thermosets are formed, the latter being much more common. Some of the reactants present **Health and safety** hazards.

Reaction-setting adhesives usually consist of two individually stable parts that react when mixed, in the cold or when heated, to form a polymer. The products are usually rigid, but some systems produce flexible products, as in the case of some polyurethanes (see **Polyurethane**). One part of a system is a monomer or a prepolymer and the other is

termed a “hardener” if the reaction proceeds stoichiometrically, or a catalyst or initiator if its function is to start a chain reaction. A common example of a stoichiometric system is the reaction between an epoxide resin and a polyfunctional amine. An example of a catalyst for acrylic systems is benzoyl peroxide plus a tertiary amine. Two-part adhesives are based on a variety of systems, including acrylics, amino resins, di-isocyanates (to form polyurethanes), epoxides (see **Epoxide adhesives**), phenolic resins (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**), silicones, anhydrides – aromatic amines (to form polyimides, see **Polyimide adhesives**).

One-part adhesives have the advantage that formulation is carried out by the adhesives manufacturer and no mixing by the user is required. However, because of problems of shelf life, only a limited range of one-part systems exists. These may harden by a variety of mechanisms, including the presence of moisture (**Cyanoacrylate adhesives**, RTV silicones and some **Polyurethane** adhesives), absence of air (**Anaerobic adhesives**), **Radiation-cured adhesives** (UV or electron beam) or by the action of heat. Clearly, the last type must be stored at a temperature low enough to provide a reasonable shelf life. The prepolymer or resin is mixed with the hardener and stored at 0 °C or lower until required. Polymerization is subsequently brought about by heating to temperatures usually in the range 120–200 °C.

The formulations of reactive adhesives can be complex. For example, an **Acrylic adhesive** might contain monomer, an elastomer, an adhesion promoter, a cross-linking agent, an initiator and a stabilizer. Details of formulations can be found in the references.

Individual reaction-setting adhesives do have disadvantages. For example, phenolic systems require high pressure during bonding. In general, reactive adhesives are more toxic than emulsion and hot melt adhesives, and they are often much more expensive than other types of adhesives. However, reactive adhesives offer a number of advantages that are essential in many applications.

Reaction-setting adhesives are usually designed to produce cross-linked structures, which provide good resistance to temperature and solvents when compared with thermoplastic adhesives. A special type of reactive adhesives, namely, the rubber-toughened acrylics and epoxides, is able to combine high peel strengths with high shear strengths.

The range of applications is very diverse, some examples being given in Table 1.

Information on particular types of adhesive may be found in articles cited above and in the following entries: **Hot melt adhesives**, **Selection of adhesives**, **Silicone adhesives: addition cure**, **Silicone adhesives: condensation cure**, **Toughened adhesives**.

Table 1. A selection of applications of reaction-setting adhesives

Application	Adhesive
Primary and secondary aircraft structures	Toughened epoxides
Assembly of steel car bodies	Phenolic/poly(vinyl formal)
Assembly of truck doors from aluminium panels	Single-part epoxides
Bonding fibre-reinforced plastics	Toughened acrylics
Mounting microchips on a printed circuit board	Polyurethanes
Assembly of computers	UV curing acrylics
Household repairs (DIY)	Cyanoacrylates
	Two-part epoxides



---

*Select References*

- I. Skeist, Ed., *Handbook of Adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990.
- Manoj K. Chaudhury and A. V. Pocius, Eds., *Adhesion Science and Engineering-2, Surfaces, Chemistry and Applications*, Elsevier, 2002.
- K. L. Mittal and A. Pizzi, Eds., *Handbook of Adhesive Technology*, 2nd edn, Marcel Dekker, 2003.

---

*Release*

---

JAMES S TONGE

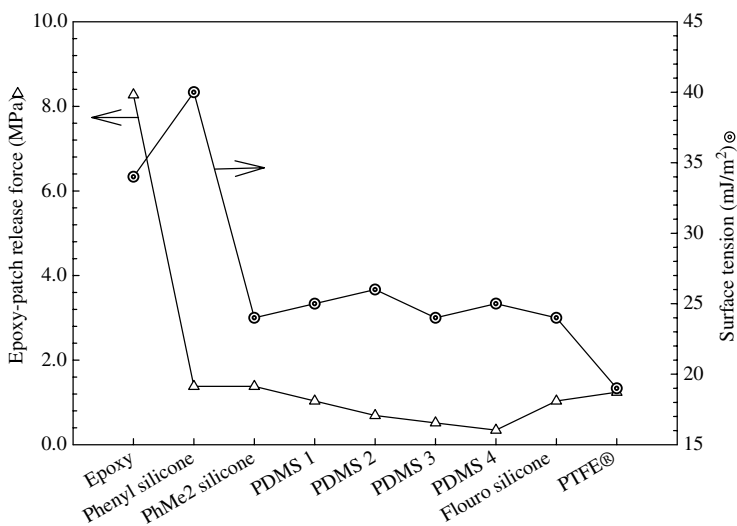
Most practitioners in the field of adhesion science and technology seek to maximize the bonding and interactions across a given substrate–coating interface. There are several commercially important applications in which the goal is to minimize, or exert a fine degree of control on, the level of adhesion. Two general families of materials can classify these release applications. In one family, the release of minimally adhering surface is achieved through a weak boundary layer, and is typified by such applications as cookware, rubber moulding and marine fouling release coatings (see **Mould adhesion and fouling**). The second family involves controlled release of pressure-sensitive adhesives from solid thin films. Both approaches have common elements in presenting a fluid, low-surface-energy interface. The divergence comes in the degree to which the interface is transferred on separation.

In the first application, either fluids are coated or solids are sprayed into a mould, or on to a surface, to make it “non-stick”. Examples of these release agents include oils (organic, fluorocarbon and silicones), soaps and waxes. The choice of any given release agent is usually governed by heat or chemical resistance, the number of release cycles and the sensitivity of the released material to the transferred release agent.

Frying pans and nuclear submarines have release coatings of a similar nature. They have a carrier coating containing a fugitive *internal release agent*. The main differences are in the heat resistance and hardness of the cookware coatings compared to silicone fouling release coatings,<sup>1</sup> which have a softer, inherently low-release poly(dimethylsiloxane) (PDMS) matrix with a fugitive fluid (see **Silicones: structures**). In both applications, the coatings act as a reservoir for the release fluid.

In the second family of release agents, a *permanent non-transferring coating* is applied to a paper or film against which **Pressure-sensitive adhesives** (PSA) are applied. The release films are used to protect the PSA until just prior to use. This class of release coatings is dominated by soft elastomeric coatings based on PDMS. Urethanes, acrylics and fluorocarbons are also used where the release requirements are not so stringent and a tougher coating is required.

Several authors from varying release disciplines have attempted to correlate surface energy either to the force required to peel off an adhesive or to biofouling.<sup>1–3</sup> As can be seen from Fig. 1, there is generally a decrease in release with progressively lower **Surface energy** substrates. The trend seems to hold as well for rigid substrates. However, soft elastomeric PDMS coatings, which have higher surface energies than a fluorinated surface such as Teflon, exhibit substantially lower release forces. It has also been shown<sup>4</sup> that within the class of PDMS release coatings, for which the surface energy remains



**Fig. 1.** Release force of Pseudo Barnacles (Epoxy studs<sup>1</sup>) from reference surfaces versus measured surface energy. The epoxy coatings is a marine anticorrosion layer; the phenyl silicone systems are typical of hard cookware coatings; PDMS 1,2,3,4 are soft PDMS-based systems with different filler types and levels, typical of fouling release coatings; the fluorosilicone is a trifluoropropylmethyl-dimethyl silicone elastomeric coating

unchanged several orders of magnitude of cross link density, changes in release force can be observed against identical PSAs. Chaudhury<sup>5</sup> ascribed this anomaly between release and surface energy to interfacial slippage. With PDMS-based PSAs, perfluorinated silicone release liners are required because of the interfacial mixing that occurs between conventional silicone release coatings and the PDMS-based PSA.

### References

1. G. G. Bausch and J. S. Tonge, Silicone technology for marine fouling release coatings systems, *Conference Proceeding of Silicone in Coatings I*, Brussels, 1996, PRA International.
2. M. J. Owen, Release agents, in *Encyclopedia of Polymer Science and Engineering*, Vol. 14, Wiley-Interscience, New York, 1988, pp. 411–421.
3. G. Swain, *J. Protect. Coat. Linings*, **16**, 26–35 (1999).
4. M. J. Owen, *J Coat. Technol.*, **53**, 49–53 (1981).
5. B. Zhang-Newby and M. K. Chaudhury, *Langmuir*, **13**, 1805–1809 (1997).

### Renewable sources of adhesives

C A FINCH

With increasing consciousness of the significance of **Environmental sustainability**, there has been much interest in renewable sources of polymers and in the **Environment and**

**the impact of adhesive technology.** Of course, in most structures and assembled articles, adhesives represent only a minor, but significant, part of the whole item, so the attributes that make an adhesive “environmentally friendly” or “green” depend principally on the attributes of the whole component, such as repulpability, biodegradability or renewability. These considerations can vary with time, and location, and with the application.

Many adhesives can be prepared from renewable resources (see **Animal glues and technical gelatins**) – the usual sources are the carbohydrates of plants (yielding starch and other related polymers), seaweed sources (alginates, etc.) and proteins (such as casein from milk), animal bone or skin and leather waste, and some forms of fish waste, soya protein (used in some wood adhesives, especially in the manufacture of plywood), and some fermentation processes. Some of these adhesive products have been employed for many centuries – traditional bookbinding is one example, and furniture has been bonded with glue obtained from bone and other animal waste. Wooden musical instruments have long been made using glue from rabbit skin “off-cuts” obtained in the manufacture of fur hats (now alternatives have to be found as fashions have changed). Many starch-based products are adequate for their purpose of bonding two surfaces together, for example, paper-to-paper bonds, where the adhesive bond need only have the strength of the paper. In practice (and in commercial use), other considerations are also important – the performance of an adhesive system in fast machine applications to the substrate, and high reliability of the resulting bond under the conditions of use are significant.

Sometimes, remoistenability is required, for example, for postage stamps and similar products, but for other purposes, resistance of the bonded article to moisture or dampness in storage is important. It can be difficult to combine in, for example, a packaging adhesive moisture resistance and the protection of the packaged contents against environmental damage in storage and transport. Materials cost and performance costs in machine application are also significant.

Large amounts of adhesive mixtures, mainly based on potato or corn (maize) starch (with plant varieties grown specifically for the purpose), are employed in paper coating, where the adhesive provides a bond between the fibrous (wood-pulp based) structure of the paper and the white china-clay-based surface layer, which can be printed. To improve performance in printing processes, these surface layers are often blended with wood rosin-based products and with polyvinyl alcohol of synthetic origin. **Polyvinyl alcohol in adhesives** (and its precursor polyvinyl acetate) can be made from ethanol obtained by the fermentation of starch – and once were so made – but the processes, carried out in dilute aqueous solution, are immensely wasteful of thermal energy.

Although it is technically possible to generate large amounts of energy from forestry operations, there is a significant cost in collection and manpower – it is expensive in terms of fuel costs to heat water to produce steam for distillation purposes. In some countries, notably Cuba, there is major production of sugar (obtained from cane grown in a sunny climate, transported to the factories by steam locomotives fuelled by sugar cane waste) but the labour input is high, and the locomotives used are very old and difficult to keep in use. However, much ethanol-based technology is still employed – in the production by distillation of vodka, gin, brandy, whisky, tequila, and so on – although all these potable spirits (from different vegetable sources) are actually, in chemical terms, flavoured ethanol–water blends, usually with some added sugar. A major part of their cost is that of taxation and bottling. Worldwide, more than 60% of ethanol is obtained from (renewable) sugar-yielding crops (less than 10% from oil). Most of it is used in

potable spirits, but vegetable alcohol is used industrially in some countries (notably India, where there is a tax-favourable regime) to make acetic acid and anhydride, vinyl acetate monomer (VAM), surfactants based on monoethylene glycol, and other chemicals. Such vinyl acetate-based polymer latexes can be employed in adhesives.

**Natural rubber-based adhesives** constitute many useful types of adhesives. They have been made from the latex that is collected from the sap of rubber trees grown in Malaysia and other countries of South East Asia. Rubber of this type was first collected from the *Hevea brasiliensis* tree – seeds from the tree were first taken from the Amazon forests in Brazil, propagated in Kew in London, and then supplied, over a century ago, to Malaya and adjacent countries, where there are now many millions of rubber trees, yielding cis-polyisoprene-based natural rubber. This has similar properties to the principal SBR synthetic rubber, derived from styrene and butadiene, both of which are obtained by the “cracking” process from crude oil, with subsequent chemical reactions. Natural rubber is obtained from the tree by tapping the bark, when the latex flows out spontaneously as the tree is wounded. This latex is about 33% solids – most natural rubber latex is concentrated to 60% and preserved with ammonia for transport and storage.

Most types of **Hot melt adhesives** used in the manufacture of laminates and in rapid **Packaging industry** applications are mineral oil-derived, hydrophobic and essentially non-dispersible, so they cannot be considered as renewable. However, some basic polymers have been prepared over the last decade from vegetable sources, which are renewable, and are adhesive, although these properties have limitations. These include poly(hydroxybutyrate/hydroxyvalerate) (PHBV), poly(lactide) (which has poor thermal stability), and starch esters. Adhesives based on sulphonated polyesters with polar petroleum waxes have improved adhesion and adequate water dispersibility. In general, however, the perfect adhesive from renewable resources with satisfactory adhesion properties remains to be discovered.

### Select References

- R. W. Hemingway, A. H. Connor and S. J. Barnham, Eds., *Adhesives from Renewable Resources*, (A C S Symposium Series No 385) 0 U P, ACS, 1989.
- F. R. van der Leij and B. Witholt, *Can. J. Microbiol.* **41**(Suppl. 1), 222 (1995).
- S. Williams and O. Peoples, *Chem. Brit.*, p. 29, Dec. (1997).
- M. C. Lubi and E. T. Thachil, *Design. Monomers Polymers*, **3**, 123–153 (2000).
- S. Parija, M. Misra and A. K. Mohanty, *J. Macromol. Sci.-Polym. Rev.*, **C41**, 175–197 (2001).
- S. P. Bunker and R. P. Wool, *Polym. Sci. Pol. Chem.*, **40**, 451–458 (2002).

---

## Repair methods

K B ARMSTRONG

### Introduction

The high cost of replacement parts made from adhesively bonded metal, metal/honeycomb, composite/honeycomb or monolithic composite laminates ensures that the interest in

repairing them is very high indeed. In **Aerospace applications** and in the case of aircraft, in particular, the cost of downtime can exceed the cost of a spare part, and if the required item is not available, then repair becomes very urgent.

Temporary repairs may be resorted to, but they mean that the work has to be done again and the second repair is usually larger than the first. This is especially true if the temporary repair is a riveted or bolted one. If the facilities are available, a permanent repair does not usually take much longer than a temporary repair, and a good permanent repair should always be made the first time, if possible.

Repairs to a structure such as an aircraft are particularly critical. Procedures have to be rigorously evaluated and specifications carefully followed. Repairs need to take account of aerodynamic considerations, mechanical clearance, lightning protection and drainage requirements, and in the case of control surfaces, weight and balance is also important.

Some areas are more critically loaded than others: each aircraft has a structural repair manual (SRM) in which established repair procedures for different areas are set out, with the maximum size and location of permitted repairs indicated.<sup>1,2</sup>

### *Surface preparation*

Good surface preparation is important in this context (see **Pre-treatment of metals prior to bonding**), as in most examples of adhesive bonding, as it influences the durability of the bond, especially in wet areas (see **Durability – fundamentals**).

With aluminium alloys, phosphoric or chromic acid anodizing are the best methods (see **Pre-treatment of aluminium, Anodizing**). Portable anodizing equipment is available: one type uses a gauze saturated with gelled electrolytes.<sup>3</sup> As an alternative, blasting with alumina grit (see **Abrasion treatment**) followed by a silane coating has been found to be quite effective. Simpler methods such as use of abrasive papers give very poor durability.

### *Choice of adhesive*

In general, the same adhesive and bonding conditions of temperature and pressure should be employed for repair as were originally used. Elevated temperatures can be achieved using lamps or heater blankets, and pressure can be applied with vacuum bags. Using the vacuum-bag techniques, described below, the atmosphere can be exploited to apply pressure to the skin in the repair of a honeycomb structure. However, it should be noted that it can be dangerous to use an adhesive curing at the original cure temperature as the remaining adhesive may soften and the internal pressure may blow the skin from the sound cells adjacent to the repair. A repair adhesive curing 25–50 °C lower should be selected.

### *Types of repair*

*Metal skins with bonded metal doublers* If the doubler has disbonded and no corrosion is present, repair may be effected by riveting. If skins are too thin for countersunk rivets, then repair by adhesive bonding may be necessary.

*Metal-skinned honeycomb panels* The type of repair will vary according to the damage. A dent in the skin, if the honeycomb is metal and it is not disbonded, may be repaired by treating the surface of the dent and some distance around, filling the dent with epoxy potting compound and bonding on an external plate to restore the buckling stiffness of the skin.

Puncture of the skin may be treated in the same way, except that the damage should be cut out to a round or elliptical hole and new honeycomb of the correct type potted in before fitting a repair plate. Many aircraft manufacturers allow very thin aluminium alloy skins to be repaired with fibreglass overlays and they provide a table relating skin thickness to the number of fibreglass layers, or rather the thickness of fibreglass required.

A common problem with honeycomb panels is disbond between the skin and the honeycomb, especially at the edges. This often leads to corrosion. Usually, both skin and honeycomb have to be replaced over the whole disbonded area. This may be done using two-part epoxy paste adhesives curing between room temperature and 80 °C or using a film adhesive curing at 120 or 180 °C. If high temperature (i.e. 120 °C and above) repairs of any size are required, then tooling may be necessary to maintain the shape of the part.

Employing a vacuum-bag technique, atmospheric pressure can be used to hold the skin to the honeycomb during cure. A “sandwich” of the new skin, a film adhesive and polyester non-woven monofilament fabric (3M-AF 3306 is satisfactory) is placed on the honeycomb. In this case, a film adhesive layer of 0.085 lb/ft<sup>2</sup> or two layers of 0.06 lb/ft<sup>2</sup> should be used. The thickness of AF 3306 should not exceed 0.003 in. The vacuum bag is sealed around the damaged area and evacuated, the non-woven fabric providing a conduit for the air pumped out.<sup>2</sup> Elevated pressure may also be required to prevent honeycomb/skin disbond adjacent to the repair area. Complete rebuilding can be done in this way.<sup>4</sup>

Temporary repairs on lightly loaded parts are sometimes made by drilling a pattern of holes through the panel at about 50 or 75 mm pitch in all directions, fitting spacers and then bonding and bolting plates on both sides. This may meet an immediate need to keep an aircraft flying, in which case it is justified, but it does mean a more extensive bonded repair at some later date.

*Composite parts* Solid composite parts may be repaired by making carefully tapered scarf joints. Hot-bonded repairs are preferred provided that the surface is first adequately dried.<sup>4,5</sup> Parts made from structural fibres, that is, carbon fibre, Kevlar or boron fibres and some glass-fibre parts require that each repair layer be of the same type as the original, or a direct equivalent, and laid up in the correct orientation.

*Composite-skinned honeycomb panels* These may use Nomex nylon paper honeycomb core, aluminium honeycomb or sometimes PVC (polyurethane or acrylic foam core). Dents are not acceptable in composite skins as they indicate fibre damage. Nomex core may split under a dent, so any such damage needs to be cut out and repaired. Nomex honeycomb can absorb considerable amounts of moisture. Wet honeycomb should be thoroughly dried or replaced. Moisture meters are available for use with Fibreglass, Kevlar or Nomex, but these meters will not work with carbon fibre because it is electrically conductive. Instruments that can indicate when carbon-fibre composites are dry enough to repair are few in number and very expensive.

### *Bolted repairs*

Bolted metal plates are sometimes used for temporary repairs to composite-skinned honeycomb panels, but a result is the need for more extensive permanent repairs.

*Permanent bolted repairs* Some aircraft such as the British Aerospace Harrier GR5 or its American counterpart, the McDonnell-Douglas AV8B, use thick monolithic composite skin and stringer structures. In such cases lighter, smaller and quicker repairs can be made using specially designed titanium plates bolted in place. Airbus and Boeing are using increasing amounts of solid laminate composite structure and the SRMs give details of bolted repairs for these. Composites and bonded metal structures are often associated with thin-skinned honeycomb parts. However, either metal or composite skins of 3 mm thickness or above can be repaired with lighter and simpler bolted joints. Adhesive bonding is preferred for materials usually significantly thinner than 3 mm.

*Composite repairs to metal parts* Alan Baker of the Aeronautical and Maritime Research Laboratories, Melbourne, Victoria, Australia, has pioneered this type of work, which has been very successful. Repairs around a fuel drain hole in the lower wing of the Mirage fighter and repairs to stringers in the wing of the Hercules transport have been particularly successful.<sup>6</sup> Carbon-fibre patches on the wing leading edge panels of Concorde have doubled the life of some of these items. For the latest information, see Ref. [6].

### *References*

1. K. B. Armstrong, *Int. J. Adhes. Adhes.*, **3**, 37 (1983).
2. K. B. Armstrong, *The Repair of Adhesively Bonded Aircraft Structures Using Vacuum Pressure*, Society for the Advancement of Material and Process Engineering Series 24, Book 2, Azusa, California, 1979, pp. 1140–1187.
3. R. E. Horton, Bonded structure repair, in *Adhesives and Sealants*, H. F. Brinson, Ed., *Engineered Materials Handbook*, Vol. 3, ASM, Ohio, 1990, pp. 799–847.
4. K. B. Armstrong, L. G. Bevan and W. F. Cole, *Base and Repair of advanced Composites*, 2nd edn, SAE International, 2003, ISBN 0-7680-1062-4.
5. H. Brown, Ed., *Composite Repairs*, SAMPE Monograph No. 1, SAMPE, Covina, 1985.
6. A. A. Baker, F. Rose and R. Jones *Advances in the Composite Repair of Metallic Aircraft Structure*, Elsevier, 2002, ISBN-0-08-042699-9.

---

## *Rheological theory*

D E PACKHAM

The **Theories of adhesion** discussed in the articles **Adsorption theory of adhesion**, **Diffusion theory of adhesion**, **Electrostatic theory of adhesion** and **Mechanical theory of adhesion** aim to describe the forces that cause the adhesive and substrate to adhere; the rheological theory is concerned with explanation of the values obtained for adhesion measured by destructive **Tests of adhesion**.

In its extreme form, as put forward by J. J. Bikerman,<sup>1</sup> the theory maintains that the measured adhesion simply reflects the rheology of the joint, especially of the adhesive, and that it can give no information about the forces acting at the interface.

Bikerman maintained that the mode of failure of an adhesive bond was always cohesive and that adhesive failure (interfacial failure, see **Stress distribution: mode of failure**) could never occur. When adhesive failure appeared to occur, more careful examination would reveal a thin layer of adhesive remaining on the substrate. When failure occurred close to the interface, it was often in a weak boundary layer.

Bikerman's theoretical arguments need not concern us in detail: they are set out in his book.<sup>1</sup> Briefly, he argued as follows:

1. that forces across an interface were the geometric mean of those in the two phases joined (see Eqn. 3 in **Dispersion forces**, Eqn. 4 in **Polar forces** and Eqn. 7 in **Surface energy components**) and therefore were necessarily stronger than the cohesive forces in the weaker phase where failure would occur;
2. that even if a crack happened to initiate at the interface, the probability of its propagating along the interface for more than a few atomic spacings was infinitesimally small.

Bikerman's theoretical arguments were often the subject of heated debate. A particularly telling critique by Good<sup>2</sup> produced some interesting discussions.<sup>3</sup>

Few would accept Bikerman's arguments in their absolute form today. Despite this, Bikerman's influence on the development of the understanding of the phenomenon of adhesion was, on the whole, benign. Much more careful examination of failure mode became more common and with it a better understanding of reasons for failure of adhesive bonds. Similarly, there is now broad agreement that the measured adhesion reflects the rheology of the joint, especially of the adhesive. However, most would argue that it also reflects the interfacial forces, although in a subtle and often obscure way. The most important advances in the subject in the last 30 years have been associated with a better understanding of the relationship between measured adhesion, interfacial forces and joint rheology.

A contemporary form of the rheological theory that would command wide support would be as follows: The measured adhesion is strongly influenced by the rheology of the joint, but also depends upon the interfacial forces. The interaction between these two factors may be obscure, but in some types of test, it is already possible to isolate and separately gauge the influence of each factor.

Some of these points are developed in the article **Adhesion – fundamental and practical**.

### References

1. J. J. Bikerman, *The Science of Adhesive Joints*, 1st edn, Academic Press, New York, 1961.
2. R. J. Good, in *Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings*, ASTM STP No. 640, K. L. Mittal, Ed., American Society for Testing and Materials, Philadelphia, 1978, p. 18.
3. R. J. Good, in *Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings*, ASTM STP No. 640, K. L. Mittal, Ed., American Society for Testing and Materials, Philadelphia, 1978, 27–9, 38–40.



---

## Roughness and adhesion

---

D E PACKHAM

The relation between **Roughness of surfaces** and adhesion is complex practical adhesion sometimes decreases, but may increase, as surface roughness gets greater (**Adhesion – fundamental and practical**).

The presence of roughness will alter the apparent contact angle (see Wenzel equation in **Contact angle**). Depending on the nature of the roughness and on the surface tension and viscosity of the adhesive, a rough surface may not be completely wetted by an adhesive that would wet a corresponding smooth one. This incomplete wetting may be the result of either thermodynamic or kinetic factors. Thermodynamic considerations show that it may not be possible for an adhesive to penetrate far into a closed pore, especially if it has an “ink bottle” (re-entrant) shape.<sup>1</sup> Further, the adhesive may set before it has time to reach an equilibrium penetration (see **Wetting kinetics**). Either way, this incomplete wetting is likely to lead to poorer adhesion.

Many **Pre-treatments of metals prior to bonding** and some **Pre-treatments of polymers** increase the roughness of the surface. This clearly occurs in **Abrasion treatment**, but it also occurs in many types of chemical etching. The enhanced adhesion after such pre-treatments is unlikely, in general, to be a consequence of the rougher surface *per se*. The enhanced surface energy, increased chemical activity of the surface or removal of weak boundary layers will often be more significant than topographical changes. However, there are now many examples recognized in which the roughness as such does appear to have a beneficial effect on adhesion.<sup>1–3</sup> Some such examples are discussed under **Mechanical theory of adhesion**, **Friction-adhesion aspects**; see also **Microfibrous surfaces** and **Anodizing**.

*How can increasing interfacial roughness increase adhesion?*

Why does increasing interfacial roughness often increase adhesion? In a simple way, this can be rationalized in terms of Eqn. 1, relating fracture energy,  $G$ , for an adhesive bond to the thermodynamic work of adhesion or of cohesion (represented by  $G_0$ ) and other energy-dissipating processes,  $\psi$

$$G = G_0 + \psi \quad [1]$$

This equation is introduced in **Adhesion – fundamental and practical**.

The *surface energy term*  $G_0$  is of the form “surface excess energy” per unit area of surface (see **Surface energy**), so may be expressed as

$$G_0 = \Delta G/A \quad [2]$$

Quite apart from any increase in  $\Delta G$  resulting from chemical changes in a surface,  $\Delta G$  will be increased as a result of roughening the surface *per se*. An atom near an asperity peak or fine fractal feature will clearly have a much greater “atomic” surface energy than a chemically similar atom in a plane crystal surface (see figures in **Microfibrous surfaces**).

Turning attention to *the area*  $A$  in Eqn. 2, it is important to remember that  $A$  refers to the formal area, the macroscopic area of the interface. For a rough surface, the “true” area will be greater, perhaps very much greater. As we move towards roughness on a

nano- and molecular scale (see **Polymer diffusion: reptation and interdigitation**), the effective increase in  $A$  can become enormous. Consequently,  $G_0$  may be raised to a very high value. Indeed, as many engineering surfaces are fractal in nature, we can only retain the concept of area at all if we accept that it can be considered as indefinitely large (see **Fractals and surface roughness**). The practical adhesion does not become infinite because the joint with a strong interfacial region will fail (cohesively) in some other region where  $G_0 + \psi$  is smaller.

It must further be remembered that  $G_0$  will often be coupled to the “other” loss terms  $\psi$  (see **Adhesion – fundamental and practical**). This means that even a modest absolute increase in  $G_0$  may lead to a much larger increase in fracture energy  $G$ .

Returning to Eqn. 1, let us now consider explicitly the *other energy absorbing processes*  $\psi$  that occur during fracture. These often make the dominant contribution to  $G$ . Where interdigitation of polymer chains is involved, these losses may include energy involved in chain pull-out or scission (see **Polymer–polymer adhesion: weld strength**). It is notable that the highest fracture energy occurs where the interdigitation is sufficiently extensive to initiate crazing or other plastic dissipation processes.

For many adhesive bonds, there is a very large difference in elastic modulus between the two phases joined. This has the effect of concentrating applied stresses at the interface, leading, for a smooth surface, to smooth crack propagation close to the interface, often giving a low fracture energy. A rough surface, especially a microfibrinous or microporous one, can be seen as causing local stress concentrations, which interfere with this smooth crack propagation. This discontinuity can lead to the deformation of larger volumes of material, leading to increased energy loss.

A high modulus gradient at the interface is also avoided in materials joined as a result of the interdiffusion of materials to form a fractal surface. The effect is to produce an interfacial composite region. This strengthens the interface and leads to a more gradual change in modulus and avoids the sharp concentrations of stress, which would occur at a smooth interface.

### References

1. D. E. Packham, in *Adhesion Science and Engineering, Vol. II, Surfaces, Chemistry and Applications*, M. K. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 317.
2. D. E. Packham, in *Handbook of Adhesives Technology*, A. Pizzi, and K. L. Mittal, Eds., 2nd edn, Marcel Dekker, 2003.
3. D. E. Packham, in *1st International Congress on Adhesion Science and Technology: Invited Papers*, W. J. van Ooij and H. R. Anderson Jr., Eds., VSP Publishers, Utrecht, 1998, p. 81.

---

### Roughness of surfaces

D E PACKHAM

It is common to talk loosely of surfaces as being “rough” or “smooth”. What is being referred to is better described by the broader term “surface texture”. Surface texture is bound to be relevant to a phenomenon such as adhesion.

Apparently smooth surfaces will often show features of roughness when examined by **Optical microscopy**, **Scanning electron microscopy** or **Atomic force microscopy**. Adhesion depends on molecular contact between adhesive and substrate (see **Wetting and spreading**), so it is important to recognize that on the molecular scale, all practical surfaces are rough: the only question is “how rough”?

### *Roughness, waviness and form*

Many surfaces of practical importance are complex: they may display features of roughness on widely differing scales. The significance of the fractal nature of some practical surfaces is increasingly recognized (**Fractals**). It is common to distinguish between the “roughness”, “waviness” and “form” of a surface.<sup>1</sup> “Waviness” is applied to undulations on which the finer roughness is imposed (Fig. 1). “Form” refers to the general shape of the surface on a still larger scale. It might refer to some curvature, perhaps irregular. The borderlines between features described by these three terms are necessarily arbitrary, but it is desirable to keep in mind whether a particular method for characterizing surface texture is sensitive to all, or only to some, of these features.

### *Characterization of surface texture*

This major topic<sup>1-5</sup> can only be briefly discussed here.

*Qualitative assessment* The usefulness of optical and electron microscopy has already been mentioned. By examination at various magnifications, they give an overall qualitative impression of the surface. The use of **Scanning probe microscopy** is discussed elsewhere. For relatively smooth surfaces, optical interference methods may be used. Among other methods, surface profilometers are important, being a popular method that can provide routine results.

The contact profilometer consists of a fine stylus that is drawn across the surface and is supposed to follow the contours. Optical profilometers do not involve contact with the surface. In some instruments, a very small spot from a bright light source is focussed on the surface. As the spot is moved across the surface, a servo system alters the height of the source so as to maintain a sharp focus. Various types of optical profilometer are discussed by Whitehouse<sup>4</sup> and by Bennett<sup>5</sup>, and are compared with contact methods.

The vertical motion of the stylus or optical system is converted into an electrical signal, which may be processed to present results in several different ways. A common form of output of a profilometer is a surface profile graph. Magnifications appropriate to the texture may be chosen, but in order to display the relatively fine features of roughness, the vertical



**Fig. 1.** Roughness and waviness. Schematic representation of roughness superimposed upon waviness

magnification is usually many times greater than the horizontal. The profile graph is then a distorted representation of the shape of the irregularities: gentle undulations are made to look like sharp Alpine peaks. A single graph gives an indication of roughness along a single line in the surface. Many instruments have the capability to make a series of traverses over an area and to produce a map showing roughness as contours or as an isometric view.

Figure 2 shows results from an optical profilometer (Proscan 2000 made by Scantron Industrial Products, Taunton, UK) for an abraded steel surface. In this instrument, laser triangulation enables fine displacements of the sample in the X, Y and Z directions to be recorded. Figure 2(a) shows a plan representation of the area scanned, Fig. 2(b) a three-dimensional representation. Surface profiles along the two lines indicated in Fig. 2(a) are given in Figs. 2(c) and (d).

*Quantitative parameters* A very large number of parameters giving a quantitative representation of surface roughness have been defined.<sup>1-5</sup> Depending on the complexity of the instrument, the profilometer output may be processed to give the value of a number of these. Some parameters characterize the vertical features of roughness, others the horizontal. The only one to be discussed here is the commonly used “roughness average”  $R_a$ . The roughness average (previously called the “centre-line average”) represents the average vertical displacement from the mean line of the surface. It is defined as

$$R_a = \frac{1}{L} \int_0^L |z| dx \tag{1}$$

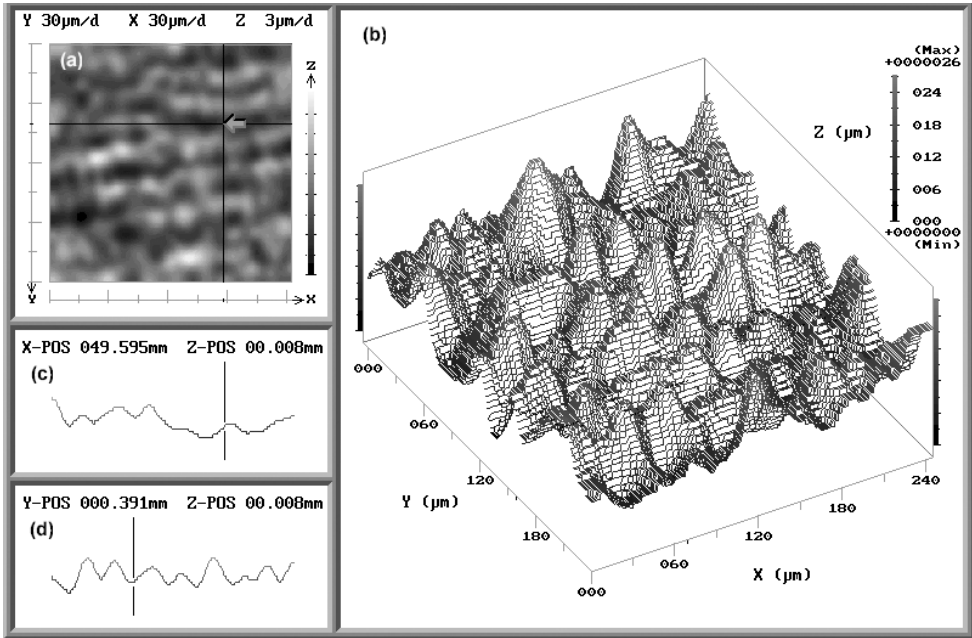


Fig. 2. Optical profilometry of an abraded steel surface. (a) Plan view, (b) three-dimensional representation, (c) and (d) surface profiles along lines indicated in (a)

Table 1. Roughness parameters for the profile in Fig. 2(d)

Symbol	Name	mm
$R_a$ (ISO)	Average roughness	0.002
$R_z$ (ISO)	10 point height	0.015
$R_z$ (DIN)	Mean peak to valley height	0.009
$R3_z$ (DB)	Mean third point height peak to valley	0.009
$R_{max}$ (DIN)	Maximum peak to valley height	0.015
$R_q$ (ISO)	Root mean square roughness	0.003
$R_{pm}$ (DIN)	Mean peak height	0.004

where  $L$  is the sampling length,  $x$  the horizontal coordinate and  $z$  the vertical coordinate. Comparing literature values for surface roughness is of little use, unless it is certain that the same parameters have been measured in each case (Table 1).

Roughness average may be the only indication of surface roughness given: it is necessary to be aware of its limitations. Surfaces may have the same roughness average but may have an entirely different distribution of peaks and valleys. Here,  $R_a$  characterizes only the vertical aspects of roughness, so surfaces with the same  $R_a$  value may differ widely in the horizontal distribution of peaks. For these reasons, surfaces with the same  $R_a$  may differ widely in surface texture.

The extent to which  $R_a$  is sensitive to the waviness of the surface depends on the relation between the waviness and the sampling length. Most profilometers enable a range of "cut-off wavelengths" to be selected, essentially altering the sample length. Thus, the same surface may give different values of  $R_a$  if they are measured at different cut-off wavelengths.

The relationship of surface roughness to adhesion is explored in the article **Roughness and adhesion**.

### References

1. H. Dignall, *Exploring surfaces*, 2nd edn, Rank Taylor Hobson, Leicester, 1986.
2. British Standards Institution, *Methods for assessment of surface texture*, B.S. 1134, Part 1, *Methods and instrumentation*, 1988, Part 2, *Guidance and general information*, British Standards Institution, 1990.
3. T. R. Thomas, Ed., *Rough Surfaces*, 2nd edn, Imperial College Press, 1998.
4. D. J. Whitehouse, *Handbook of surface metrology*, Institute of Physics, Bristol, 1994.
5. J. M. Bennett, *Meas. Sci. Technol.* **3**, 1119 (1992).

### Rubber fillers

J A LINDSAY\*

Fillers are particulate materials that are added to raw polymers to modify the polymer characteristics: they are widely used in polymer technology and play a particularly significant role in modifying the properties of rubber.<sup>1</sup> In this article, various effects of fillers are discussed, with some emphasis on the formulation of rubber for bonding to metals (see **Rubber to metal bonding – basic techniques**).

Many of the properties of a rubber can be significantly altered by incorporation of a filler; these include: cure rate, tensile properties (strength, modulus, ductility), tear strength, hysteresis and resistance to permanent set, abrasion resistance, swelling behaviour in various fluids, density and, of course, cost.

Practical experience has shown that all fillers in general use can be used in rubber compounds for bonding, during the moulding process, to almost any substrate. The use of fillers is not restricted to the rubber compound. The bonding agents employed throughout the industry also contain fillers. Certain grades of carbon black are claimed to improve adhesive strength and are set out in a patent awarded to a leading maker of bonding agents.

The earlier bonding agents were basically highly filled natural rubber solutions containing iron oxide and similar materials, together with a generous helping of sulphur. Current leading bonding agents are generally based on solutions of halogenated polymers, carbon black, basic lead – acid acceptors and dinitroso-benzene.

### *Types of filler*

Two classes of fillers may be distinguished, reinforcing and non-reinforcing. Reinforcing fillers again fall into two types, white and black. The latter are invariably carbon black, but white fillers include silica, silicates and calcium carbonate. Black fillers are the more important ones. Grades range in particle size from 10 to 500 nm and are generally classified according to size and surface area by an ASTM designation as described in ASTM D 1765. At an equivalent volume loading, reduction of particle size increases reinforcement, leading to higher tensile strength and modulus, increased abrasion and fatigue resistance and higher loss angle (see **Viscoelasticity**). The processing is also affected, mixing cycles being longer and the cure rate higher. Carbon blacks of smaller particle size are also more expensive.

The level at which any of these properties may be at its optimum varies from grade to grade. It is therefore necessary to investigate rubber formulations very thoroughly before use. This is best achieved through factorial design of experiments, results of which can then yield an optimized solution through the use of regression analysis.

The nature of carbon black is extremely complex, and different grades<sup>2</sup> differ according to their particle size, surface character (including surface area) and structure.<sup>3,4</sup> The mechanisms of reinforcement are not fully understood, but it is likely that different levels of adhesion between filler and polymer play an important part.<sup>4</sup> The **Surface energy** and structure will vary, not only between grades, but also between different parts of the same filler. Diverse chemical groups have been detected on the surfaces of carbon fillers: alcohol, phenol, quinone, lactone, carboxyl as well as free radicals. Thus, depending on the chemistry of the filler surface and of the polymer, different levels of adhesion associated with van der Waals forces or chemical bonds (see **Adsorption theory of adhesion, Dispersion forces, Polar forces**) may occur leading to different effects on the properties of the filled elastomer.<sup>4</sup> Most carbon black is produced by the furnace method of burning oil in a controlled oxygen environment. The price therefore follows that of oil.

For the automotive industry (see **Automotive applications**), the manufacture of engine mountings and anti-vibration mountings generally requires control over stiffness (or modulus), fatigue life and loss angle. If these are correct, then it is usually possible to engineer bonding processes to produce components that satisfy the specifications. A general formulation is shown in Table 1 as a basis for experiments.

Table 1. A typical experimental rubber formulation

Natural rubber (SMRCV)	100
Zinc oxide	4
Stearic acid	1
6PPD (antiozonant)	2
Microcrystalline wax	2
Carbon black	0–100
Process oil (paraffin)	0–10
Sulphenamide (CBS)	0.5–1.5
Booster (DPG)	0–0.3
Sulphur	1–3
[6PPD: <i>N</i> -(1,3-dimethylbutyl)- <i>N</i> -phenyl- <i>p</i> -phenylenediamine; CBS: cyclohexyl-2-benzothiazole sulphenamide; DPG: diphenyl guanidine.]	

*White reinforcement* This is obtained through the use of silica. Grades are defined by size surface area and method of manufacture, although there is no universally accepted grading system such as exists for carbon black. A comparison of the effects of silica and carbon black as reinforcing fillers is given in Table 2. In general, unless one needs a non-black rubber, less trouble is experienced with black reinforcement.

*Non- or semi-reinforcing fillers* These are usually added to reduce cost. In natural rubber or polychloroprene, they may be used alone, but with non-crystallizing polymers such as butadiene – acrylonitrile or styrene – butadiene copolymers, they can only be used in conjunction with a reinforcing filler. Their effect is to reduce tensile strength and elongation, tear resistance and resistance to set. The effect on modulus varies according to choice of filler, but it is always much weaker than that of a reinforcing filler.

Examples of semi-reinforcing and non-reinforcing fillers are given in Table 3. The ranking of such fillers is imprecise because it depends upon the use that may be made of them. Certain clays perform well in insulation compounds, and precipitated whittings are more than adequate to extend rubbers for components that are not subjected to high levels of stress.

### *Selection criteria for rubber bonding*

Fillers must be selected first on their ability to meet end-use requirements. These may be set out formally through specifications such as seen in SAE J200 or ASTM D 2000. Such specifications define tensile strength, hardness, age resistance, compression set, and

Table 2. Comparison of reinforcement by silicon and carbon black

Silicon better for	Carbon better for
Tear resistance	Processing (mixing)
Non-staining	Compression set resistance
Fire resistance	Mould flow
	Resilience
High modulus	Moisture absorption

Table 3. Some non-reinforcing and semi-reinforcing fillers

Filler	Reinforcing capability
Coal dust	None
Ground whiting (calcium carbonate)	None
Precipitated whiting (stearate coating)	Slight
Calcium silicate	Slight
Clays	Semi-reinforcing
Aluminium silicate	Semi-reinforcing

so on. The level of these requirements will be a good guide to filler types and grades. Tensile strengths higher than 14 MPa will certainly require a reinforcing filler at a size of 50 nm or finer (N660), and for strength above 20 MPa, a particle size of 30 nm or less is recommended (N330).<sup>2</sup> If dynamic properties are important, coarser fillers will give high resilience at equivalent levels of filler than will the finer grades.

Of equal importance to the properties of the moulded component is the influence of the filler during the mixing and moulding stages. Ease of incorporation in the rubber is important if a homogeneous mixture is to be produced. The more fine the filler, the more difficult it is to disperse.

Flow properties during moulding influence the final quality of the component. High viscosity leads to poor flow precuring of the rubber and hence to weld lines, risk of early fatigue failure and poor-quality bonds. The finer the filler, the higher the viscosity for any given volume of filler. The moisture content of any filler needs careful control. Adverse levels of moisture (>0.5%) will affect rubber cure rate, final modulus and bond strength. If these considerations are made prior to the formulation of the compound, a high quality of rubber bonding can be achieved.

### References

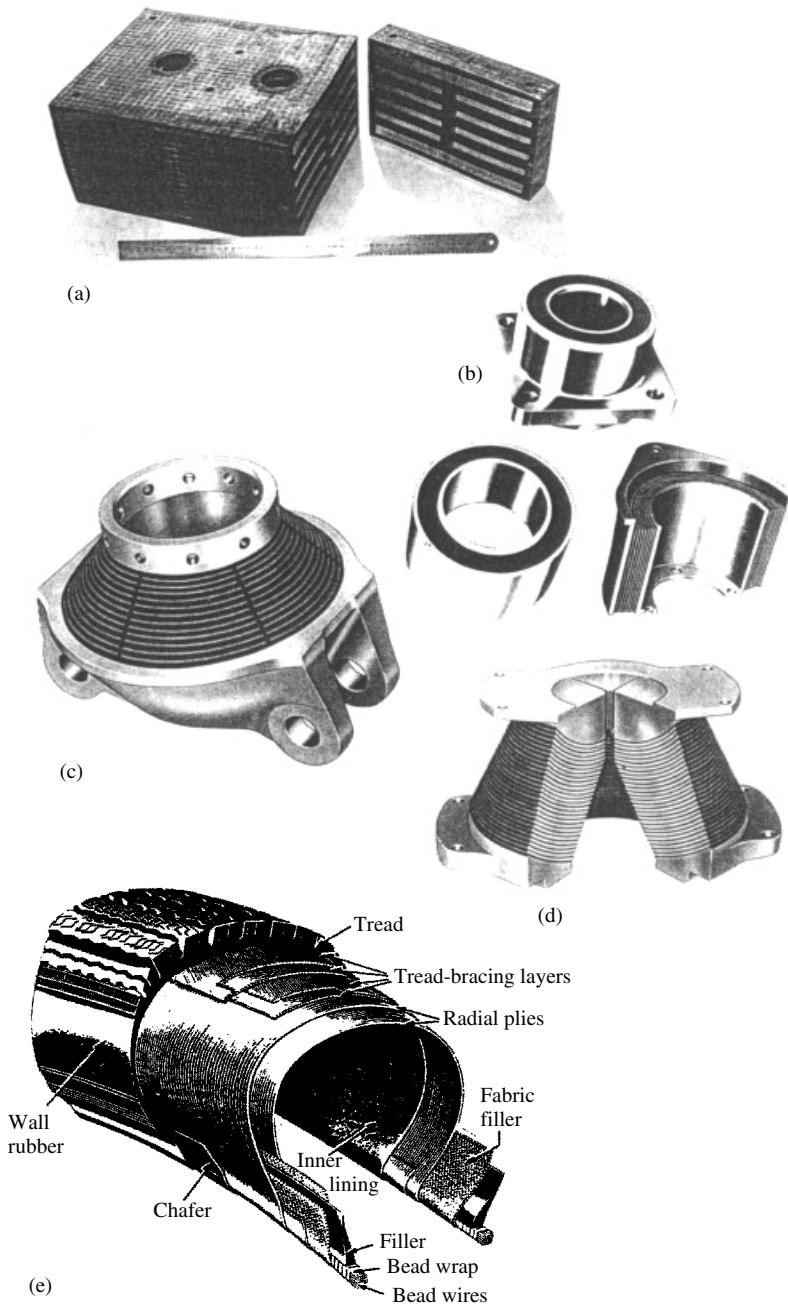
1. B. B. Boonstra, in *Rubber Technology and Manufacture*, C. M. Blow, Ed., Newnes-Butterworths, London, 1975, pp. 227–261.
2. *ASTM Book of Standards*, ASTM-D 1765, annually.
3. F. W. Barlow, *Rubber Compounding*, Marcel Dekker, New York, 1988, Chaps 9, 10.
4. W. Hofmann, *Rubber Technology Handbook*, Hanser, Munich, 1989, p. 277.

## ***Rubber to metal bonding – applications***

G J LAKE

Adhesive bonding of rubber to metal, or to other materials, occurs in many applications (Fig. 1). This may simply be for fixing purposes, as is often the case with springs and mountings, but may be a necessary part of the design. Examples in the latter category include bonding to fabric or cords (metal or polymer) in tyres, hose and many other articles where increased stiffness and strength are required; bonding to internal steel



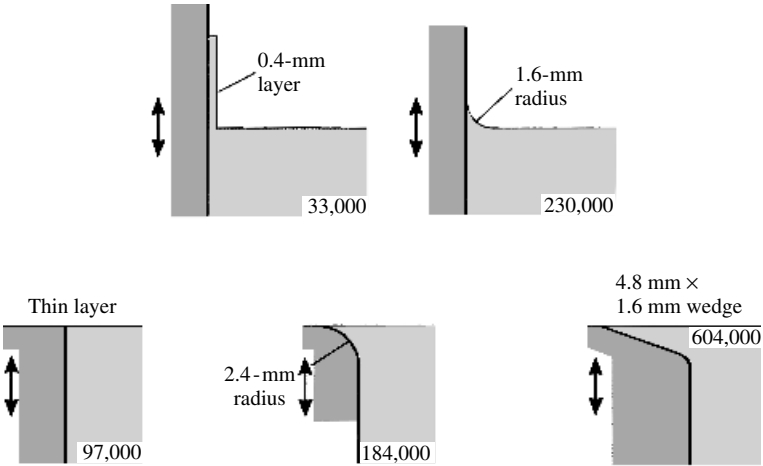


**Fig. 1.** Various articles in which rubber is bonded to metal or other materials: (a) bridge bearing; (b) cylindrical bearings; (c) conical bearing; (d) spherical segment bearing; (e) cross section of radial tyre

plates in bearings of various sorts (Fig. 1) can increase the shape factor and hence the compression stiffness without materially affecting the low shear stiffness of the rubber.<sup>1</sup> In many, though not all, such applications, the integrity of the bond is vital to satisfactory performance and life. Bonding prevents slip at load-bearing surfaces, thus ensuring reliable load – deflection characteristics. However, in some applications involving compression, friction alone may suffice to prevent slip. In addition to some types of bearing, coaxial bushes are an example where one or both metal surfaces may be unbonded. This is because hydrostatic tensile stress may arise if a bonded bush is made in a single-stage vulcanization process, owing to the difference in the thermal contraction of the rubber and metal parts on cooling. Avoidance of such stresses is very important for bonded units as otherwise internal cracking may occur at very low stress levels.<sup>1,2</sup>

The large change in modulus occurring across a boundary between rubber and a more rigid material may, in itself, give rise to stress concentrations. Avoidance of sharp corners or other features causing stress concentration is also important, as when designing with metal alone<sup>1</sup> (Fig. 2).

The environment in which an article is used may influence bond durability (see also **Durability: fundamentals**). Atmospheric ozone can cause time-dependent crack growth in vulcanized elastomers; in addition, ozone can induce failure at a bond with certain bonding agents. Although water is only slightly soluble, it can permeate elastomers by an osmotic mechanism induced by salt-like impurities. As a result, the uptake in salt water is generally less than that in pure water. Rubber to metal bond failure has been found to occur in a time-dependent manner under salt water in the presence of electrochemical activity but much more slowly, if at all, in its absence<sup>3</sup> (see also **Cathodic disbondment**). In the absence of imposed electrochemical activity, effects are likely to depend particularly on the metal used and its corrosion resistance. Provision of a bonded rubber cover layer over all metal surfaces subject to immersion is likely to enhance bond durability.



**Fig. 2.** Effect of various internal or external shapes on bond durability: the number of cycles to the development of appreciable cracks are shown for a natural rubber vulcanizate subjected to shear strains of  $\pm 100\%$  in the direction indicated (the rubber is on the right in all cases<sup>1</sup>)

Means of effecting good bonds between rubber and metal are discussed in articles on **Rubber to metal bonding – basic techniques**, **Rubber to metal bonding – pre-treatments** and **Rubber to metal bonding – testing**.

### References

1. P. B. Lindley, *Engineering Design with Natural Rubber*, Malaysian Rubber Producers' Research Association, Hertford, 1974, revised 1992.
2. G. J. Lake, A. G. Thomas, Strength, in *Engineering with Rubber: How to Design Rubber Components*, 2nd edn, A. N. Gent, Ed., Carl Hanter, Munich, 99–135, 2001, Chap 5.
3. R. P. Campion and A. Stevenson, Durability, in *Engineering with Rubber: How to Design Rubber Components?* 2nd edn, A. N. Gent, Ed., Carl Hanter, Munich, 177–221, 2001, Chap 7.

---

## **Rubber to metal bonding – basic techniques**

---

P M LEWIS

In many elastomeric products, the rubber is bonded to a metal component either for location purposes or to meet certain design requirements such as a given combination of compression and shear stiffnesses (see **Rubber to metal bonding – applications**). High rubber-to-metal bond strengths can be obtained by a number of techniques,<sup>1,2</sup> of which the most common are described below. The choice of method will depend on a number of factors including service requirements of the product, ease of assembly of components, the types of rubber and metal being bonded and, nowadays, health, safety and environmental considerations. All methods require careful surface preparation; see **Rubber to metal bonding – pre-treatments**.

### *In-vulcanization bonding*

While in-vulcanization bonding – the attainment of adhesion during the rubber-curing step – suffers from the disadvantages associated with having to incorporate and heat metal parts in moulds, it is widely used in the rubber industry for applications such as engine mountings, bushes, bridge bearings, anti-vibration building mounts and, not least, steel cord-reinforced tyres. The process is particularly well suited to bonding of complex surfaces where the flow of unvulcanized rubber ensures intimate contact with the bonding surface.

There are three principal methods of bonding the metal component to the rubber during vulcanization, given under the headings below.

*Proprietary chemical bonding agents* These are usually mixtures of an undisclosed composition, consisting of reactive ingredients suspended or dissolved in organic solvents or in aqueous dispersions or emulsions. The solids content includes resins, elastomers and fillers.<sup>1,2</sup> Cyclized, halogenated and carboxylated rubbers, rubber hydrochloride, polyisocyanates and phenolic resins have all featured in bonding agents. The systems offer a convenient and versatile means of bonding a wide range of rubbers and metals and

constitute the major method of in-vulcanization bonding for non-tyre applications. A wide variety of bonding cements are now available to cover the needs of different rubber types, vulcanizing systems, combinations of bulk fillers and oils, and different substrates as well as demanding cure conditions and different products requirements for environmental, fluid and heat resistance. For most rubbers, it is usual to use a two-coat system. In some cases, the primer may be omitted without affecting the initial bond strength, but the resistance to under-bond corrosion may be diminished. One-coat systems have been developed for some combinations of rubber and metal.

Controls on solvent emissions have stimulated the development of alternative water-based bonding systems over the last decade (see **Environment and the impact of adhesive technology**). These can be more expensive than solvent-based cements, but this cost is balanced by savings in factory solvent controls. Pre-heating the metal surfaces to above 50 °C quickens the drying process and encourages coalescence of bonding agent micelles to form a coherent layer. Manufacturers have reported some lowering in bond strength but improvements through experience and development of better aqueous systems are being made. Aware of the need for more careful handling and control of aqueous systems, many users still prefer solvent-based bonding agents for all-round performance, opting for the incineration or absorption of solvent emissions, recycling or use of alternative solvents.

Irrespective of composition, the bonding agent should be applied to the prepared metal as quickly as possible in order to prevent corrosion or contamination. Application can be carried out by brushing, dipping or spraying. Whichever method is used, a minimum thickness of bonding agent, typically 25 μm, must be obtained – 5–15 μm for a primer and 10–20 μm for a top coat. Too thin a coating can result in partial bonding but one too thick can cause delamination or flaking.

The bonding agent may be diluted with a suitable solvent, preferably the one used in the original material, or with de-ionized water in the case of aqueous systems. Use of a solvent with a lower boiling point than that used in the bonding agent may lead to premature drying during spraying or the formation of a non-coherent film of bonding agent. The use of a higher-boiling solvent may lead to incomplete drying and poor bond strength.

Once coated with the bonding system, metal components should be stored in such a way that risk of contamination or mechanical damage is minimal. However, a minimum period of storage should be specified to ensure complete drying of the primer and the top coat; typically, 30 min at room temperature should be adequate.

For most reliable results, transfer or injection moulding is preferred to compression moulding, as this ensures that a fresh rubber surface is presented to the coated metal, and the higher mix temperature improves contact with the bonding surface. Compression moulding can be used provided the rubber blanks are freshly prepared and, if necessary, freshened with a solvent wipe.

Mould design should allow for rapid filling of the cavities, but removal of bonding agent by rubber flowing over the metal surface must be avoided. Sprues and flash lines should be located away from the bonding areas, and runners in moulds should be designed to minimize the possibility of scorch. When high-temperature vulcanization is carried out, the number of cavities in the mould should be restricted to enable rapid loadings of metal parts.

As bond strength decreases with increasing temperature,<sup>3</sup> the mould should be designed to allow easy removal of components so that little or no strain is put upon the bond. Easy removal also reduces the need for mould release agents, an over-enthusiastic use of which can cause rejects.

Safe temperature ranges for bonding are specified by suppliers and are generally restricted to the range 120–180 °C, although special systems are available for high-temperature vulcanization. One factor limiting the applicability of many bonding agents is their effective lifetime at elevated temperatures. At temperatures of 170 °C and above, bond strength may be drastically reduced if coated metals are heated for more than a certain time before they come into contact with the rubber. Pre-baking to ensure a uniform state of cure becomes troublesome if mould loading and filling times exceed the safe time limits.<sup>3</sup> The problem can be minimized by loading metals into multi-cavity moulds using jigs or restricting the number of cavities in the moulds. Other precautions include reducing the mix viscosity and using wider runners and/or sprues.

The level and consistency of bond strength are influenced by the nature of the rubber; factors include the mix viscosity, level of filler, scorch safety and, in the case of sulphur-vulcanized rubbers, the amount of elemental sulphur in the vulcanizing system.

*Ebonite bonding* The adhesive layer in this case is unvulcanized ebonite (or “hard rubber”, USA) applied to the metal either as a solution or as a thin sheet.<sup>4</sup> Ebonite contains 30–50 parts sulphur per hundred parts of rubber (phr), whereas soft rubber seldom has more than 3 parts phr of this vulcanizing agent. The method dates back to the mid-nineteenth century and is most closely identified with natural rubber, but can be applied to other diene-type elastomers, including nitrile rubber.

During vulcanization, sulphur can migrate from the ebonite layer to the rubber and may result in the formation of an interlayer of highly cross-linked rubber having poor physical properties. Formation of such a layer may be avoided if a second adhesive coat consisting of the rubber mix without sulphur is applied. Since ebonite softens at higher temperatures (e.g. 80 °C in the case of a natural rubber system), the use of ebonite bonding is restricted to service temperatures near ambient.

In applications where tack of the adhesive is required, for example, tank linings or rubber-covered rollers, ebonite bonding is often found to be more suitable than proprietary bonding systems.

*Brass plating* Sulphur-vulcanized rubber will form a good bond to brass during vulcanization<sup>1,5</sup> provided

1. the brass contains between 60 and 70% copper;
2. the rubber mix contains sufficient sulphur – the maximum bond strength may require 4–6 phr sulphur, although good bonds to rubbers containing lower levels can be obtained by using an intermediate layer of a mix containing a high sulphur level; and
3. the rate of vulcanization of the rubber is adjusted to give optimum bond strength.

If the brass can be strongly bonded to a metal, brass plating can be used as a basis for rubber to metal bonding, and, under the appropriate conditions, can give excellent results.

The bond is not unduly sensitive to influences such as humidity, low mix viscosity and low vulcanizing pressures. The main drawbacks are connected with the plating process, which requires considerable investment and expertise. Brass plating has now been largely superseded by the use of proprietary bonding agents, except in the tyre industry, where bonding to brass-coated steel cords is still undertaken.<sup>5</sup>

It should not be forgotten that a poor mould design will lead to a poor bond, irrespective of the surface treatment: **Rubber to metal bonding: processing effects.**

### *Post-vulcanization bonding*

Vulcanized rubber can be bonded to metals by a number of methods using proprietary bonding agents.<sup>6</sup> The rubber must be freed from blooms, surface-bled oils or dust by washing with solvent or detergent.

Post-vulcanization (PV) bonding offers the advantage of not requiring the incorporation of metal parts into moulds, resulting in an increase in moulding productivity. On the other hand, it introduces an extra stage in the production of an article, which must be carried out by either the rubber manufacturer or the end user. As PV bonding can be carried out at lower temperatures than in-vulcanization bonding, in-built stresses in the vicinity of the bond resulting from rubber shrinkage will be lower, and thus the method can be attractive for applications such as automotive bushes.

In hot PV bonding, the bonding agents react with the rubber and no further preparation of the rubber is required. The bonding agents used are often suitable for in-vulcanization bonding, but the reverse is not true.

Rubbers can be bonded to metals at room temperature with a wide variety of bonding agents, including solvent-based or aqueous cements.<sup>7</sup> If, however, high bond strengths are required, **Cyanoacrylate adhesives** or **Epoxide adhesives** should be used, most appropriately for small articles. Cyanoacrylates do not require treatment of the rubber other than cleaning, but epoxides can only be used successfully if the rubber surface is modified prior to bonding. The modification can be carried out by chlorinating the surface with acidified hypochlorite solution or, less commonly, by dipping the rubber in sulphuric acid. Other halogen-donating materials have been patented for this treatment and are widely used in the footwear industry. Treatment with trichloroisocyanuric acid (TCICA) has also been found effective.<sup>8</sup>

For further information, see the articles **Rubber to metal bonding – testing** and **Solvent-based adhesives.**

### *References*

1. B. G. Crowther, Ed., *Handbook of Rubber Bonding*, Rapra Technology Ltd, Shrewsbury, 2001.
2. B. G. Crowther, RAPRA Rev. Rep., **8**(3), Report 87, Rapra Technology Ltd, Shrewsbury, 1996.
3. E. Cutts, in *Developments in Adhesives-2*, A. J. Kinloch, Ed., Applied Science Publishers, London, 1983, Chap 10.
4. S. Buchan, *Rubber to Metal Bonding*, Crosby Lockwood, London, 1959.
5. W. J. van Ooij, *Rubber Chem. Technol.*, **52**, 437 (1979).
6. M. A. Weih, C. F. Silverling and F. H. Sexsmith, *Rubber World*, **194**(5), 29 (1986).
7. P. B. Lindley, *NR Technol.*, **5**, 52 (1974).
8. D. Oldfield and T. E. F. Symes, *J. Adhes.*, **16**, 77 (1983).

---

## ***Rubber to metal bonding – pre-treatments***

---

P M LEWIS

Many engineering applications of rubber depend upon the polymers being bonded to metal (see **Rubber to metal bonding – applications**). Successful bonding of rubber to metal requires both the rubber and the metal to make intimate contact with the applied bonding system. To minimize risk of bond failure, surface contamination of the three components of a rubber to metal bond must be avoided. Scrupulous cleaning of the metal should be followed, as soon as possible, by application of bonding system and vulcanization or assembly. Handling of coated metals should be minimized and, when used, gloves should be changed frequently. Pre-formed vulcanized rubber and thermoplastic elastomer components should be free of blooms and, if necessary, surface treated to facilitate bonding, especially in the case of non-polar rubber types; chlorination, for example, can be effective with natural rubber.

The following methods<sup>1,2</sup> are used to clean and prepare metal surfaces prior to application of bonding agent, plating or adhesive layer. However, although careful pre-treatments are essential, a poor bond may still result if the mould design is poor; see **Rubber to metal bonding: processing effects**.

### *Degreasing*

Metal parts should be degreased with an organic solvent, for example trichloroethylene, or with an aqueous detergent wash. **Degreasing** with solvent vapour is often found most effective because it minimizes contamination, but proprietary aqueous treatments may be used satisfactorily and nowadays are increasingly preferred on health, safety and environmental grounds. If a chlorinated solvent is used, the pH should be monitored to ensure that the solvent remains neutral; otherwise, under-bond corrosion may be encountered from the build-up of acidic residues. The vapour degreasing time should be sufficient to ensure that all parts are well washed with condensate, and the efficiency of the operation should be regularly checked by wetting a part with water. If degreasing has been achieved, a coherent water film will remain on the surface.

### *Mechanical cleaning*

This operation is best carried out by grit blasting (see **Abrasion treatment**). Chilled iron, steel and alumina grits are suitable for mild steel. Alumina or a non-metallic grit is advised for stainless steel and non-ferrous substrates to avoid risk of under-bond corrosion from the galvanic action of any embedded grit particles. Compressed air used for blasting should be free from oils and water. Grit sizes are usually 30–80 mesh – anything larger in size loses its sharpness more rapidly. Grit should be cleaned of any dust contaminants resulting from its deterioration and from the prepared surface. It is usually recommended that grit blasting be followed by a second degreasing cycle.

### *Chemical cleaning*

A number of proprietary chemical cleaning treatments may be used as alternatives to degreasing with organic solvents and grit-blasting, provided care is taken to maintain

concentrations, temperatures and dwell times to within each supplier's recommendations. These treatments normally consist of an acid- or alkaline-cleaning bath and a phosphating bath, with washing after each stage (see **Conversion coating, Pre-treatment of steel and Pre-treatment of metals prior to painting**). The phosphating process introduces a modified amorphous layer, and primer should be applied within 12 h for the best results. Passivation of the phosphate layer with a chromate rinse can improve short-term corrosion resistance before bonding and enhance the environmental resistance of the bond. Phosphating treatment is commonly used for mild steel, aluminium and zinc but is not always suitable for other metals. For example, treatment with hydrochloric or chromic acid is recommended for stainless steel while treatment in a fluoride etching solution is advised for titanium.

For further information, see the articles **Rubber to metal bonding – basic techniques, Rubber to metal bonding – testing, Degreasing and Pre-treatment of metals prior to bonding**.

### *References*

1. B. G. Crowther, Ed., *Handbook of Rubber Bonding*, Rapra Technology Ltd, Shrewsbury, 2001.
2. M. Fernando, *Techniques of Bonding Rubber*, Technology Bulletin No 1, Malaysian Rubber Board, Kuala Lumpur, 1999.

---

### *Rubber to metal bonding: testing*

---

J A LINDSAY

Many widely used **Tests of adhesion** can be applied to the rubber to metal bonds: **Blister test, Fracture-mechanics test specimens, Non-destructive testing of adhesively-bonded structures, Peel tests, Shear tests, Tensile tests and Wedge test**. This particular article is concerned with those aspects that are of practical concern in the rubber-processing industry.

Bond testing can be broadly classified as either laboratory tests or product tests. In each, tests may be either qualitative or quantitative. Qualitative tests are sometimes useful for rapid screening of a wide range of conditions or materials. For optimization and specification purposes, quantitative tests need to be employed where possible.<sup>1</sup>

Methods for the production of rubber bonded components have to be established and firmly founded within strict limits of the many parameters for the control of quality. It is in the initial stages of the development of the production process that the use of suitable bond tests is vital. The test values will allow the manufacturer to discover the operational limits for all process variables and ensure that the set conditions for production do not allow a “knife-edge” situation where small changes can produce large variations in the quality of the bond. This is best achieved through the use of factorial experiment design and statistical regression analysis of the results.

It is possible, through poorly designed or maintained production systems, to make bonded components that appear to be visually satisfactory but suffer from low adhesive strength or from minor edge failures that will develop in service to a catastrophic failure. One hundred percent testing may find such failures, but the best results will always come



from the production system that can demonstrate that all the process variables have been experimentally assessed.

### *Peel tests*

The simplest type of tests to perform are **Peel tests**. In an industrial context, the test piece is a flat strip made from the substrate to which is bonded over two-thirds of its length a layer of the rubber, preferably 4–6-mm thick. The test piece is conveniently dimensioned 150 × 25 mm. The thickness of the substrate is usually of the order of 2–3 mm.

A qualitative indicator of the bond may be made by simply applying a 180° peel force to the unbonded part of the rubber by hand. It is important to examine a bonded length of 20–30 mm back from the leading bonded edge. This is achieved by applying, carefully, cross-cuts to the rubber, across the bonded front, immediately adjacent to the substrate, while maintaining the peeling force.

With a satisfactory bond, there must be no separation of the rubber from the substrate under such peel forces. A weak bond, similar to that obtained with an adhesive cellophane tape, is an immediate indication that the rubber bond is unsatisfactory. A quantitative measurements of bond strength will give results that allow assessment of the degree of change brought about by adjustment of the process conditions. The angle at which the peeling force is applied will considerably affect the result (see **Peel tests**). An angle of 30 or 45° has been recommended. A further description of the method is in ASTM D 429, Method B (see **Standards for adhesives and adhesion**).

The *advantages* are that test pieces are relatively cheap and are easily prepared. A *disadvantage* is the tendency for cohesive failure, reflecting the tear resistance of the rubber.

### *Tests in tension*

Some tests specify the use of two circular plates that may attach directly to the straining frame. Rubber is bonded between the plates, which are then separated in a mode perpendicular to the plane of the plates (see **Tensile tests**). Very high loads should be expected in this type of test. On failure of a satisfactory bond, there should be no sign of bonding agent – rubber or bonding agent – substrate separation. Details are in ASTM D 429, Method A.

The stresses in this type of test are not uniform and are not concentrated at the bond interface, which makes it difficult to judge bond quality, unless it is very poor. The mould is more expensive than that for a peel test.

### *Cone test piece*

In this test, a 25-mm diameter cylinder of rubber is moulded around two cone-shaped test pieces such that the tips of the test pieces are separated by 10 mm (ASTM D 429, Method C). It has the distinct advantage that the shape of the test piece tends to concentrate the stress towards the rubber–substrate interface. Results are sensitive to the tip radius of the cone, which must be carefully controlled.

### *Arrowhead test piece*

The arrowhead test was suggested by Aubrey *et al.*<sup>2</sup> as incorporating some of the advantages of the cone while being easier to prepare. The test piece consists of a flat arrowhead,

25-mm wide and tapering to a point with a 60° included angle, using steel strip 6-mm thick. This is bonded, using the rubber and bonding agent under test, to a 25-mm square of a similar piece of metal. Like the cone test piece, stress is concentrated at the bond interface. Unlike the cone test piece there is little sensitivity to tip radius, and test pieces can be prepared from strip metal by conventional shearing or punching techniques. Test pieces can be made readily and cheaply from all substrates that are likely to be bonded, making this test very useful for the comparison of substrates, their preparative methods and bonding agents.

#### *Obtaining consistency in test results*

As procedures for rubber to metal bonding involve a large number of steps (see **Rubber to metal bonding: basic techniques** and **Rubber to metal bonding: pre-treatments**), a wide scatter in results is not uncommon. As with all tests of adhesion, analysis of the results using techniques of **Statistics** is important. To minimize scatter, it is important to check critical properties of bonding agents and of the rubber compound. Substrate preparation and application of primer layers must be standardized with careful attention paid to the time intervals required to dry each layer. The cure of the rubber and thence the properties of the bond will be affected by the times and temperatures employed in the moulding sequence (see **Rheological theory**). For example, bonds made when the moulds are warming up will have different properties from those produced when thermal equilibrium is established: failure to control the “open time” or the mould will also lead to inconsistencies.

#### *Testing the service life*

The usual way in which the life of differently made bonds can be compared is to prepare types of test pieces and then place them in a jig, which will allow a strain to be placed upon the rubber and the bond edge (see **Durability: creep rupture**). The test pieces are then subjected to contact with a hostile environment such as hot water or salt fog (see ASTM B I 17). The resultant failures generally depend upon the type of surface preparation used and may be used to monitor these procedures.

#### *Component testing*

A range of interesting engineering components depend on rubber to metal bonding in order to function (see **Rubber to metal bonding – applications**). Components themselves may be tested to obtain a measure of how well the bond process has been carried out. The method is obviously very much dependent upon the component type and shape. Whatever be the method, observation of failure in the rubber rather than cement–rubber or cement–metal separation is the desired result. Failure in the bonding agent layer is a strong indicator that there has been a failure in the surface preparation of the substrate.<sup>3</sup>

#### *References*

1. E. Cutts, in *Developments in Adhesives*–2, A. J. Kinloch, Ed., Applied Science Publishers, London, 1981, Chap 10.

2. D. W. Aubrey, E. Southern and A. D. Harman, *Rubber – Metal Bond Testing*, London School of Polymer Technology, n.d.
3. J. A. Lindsay, *Materials World*, 7(5), 267 May 1999.

---

### ***Rubber to metal bonding: processing effects***

---

J A LINDSAY

For components made by in-vulcanization bonding, the quality of the bond formed (the “adhesion” – see **Adhesion – fundamental and practical**) depends not just on the nature of the surfaces and the properties of the rubber but also on the design of the mould in which it is formed; see **Polymer–polymer adhesion: weld strength**.

Many rubber to metal bond defects that occur can be related to intrinsic failures in mould design that generate problems such as imbalances in flow, gas trapping and scorch. Weak or failed bonds can result from the use of multi-cavity moulds if the cavities fill unevenly or too slowly. Where the mould has been designed so that the flow of rubber can entrap gases against the bond interface, bonds with little or no strength will be produced. The mould design controls the quality of the product. The reason for this is best understood by consideration of the physical factors that control bond formation.

By the use of flow modelling, these problems are avoided. Used at the initial design stage, they allow for the production of injection tools that work correctly the first time they are put in the press. There are two principle factors, namely rubber scorch and cavity pressure. Control over both of these is necessary to ensure bonds that are consistent and of high quality. To some extent, control is found through optimization of the moulding machine settings, but this will be successful only if the mould has been properly designed.<sup>1</sup>

Scorch is a property of the rubber compound that relates to the proportion of available cross-links that have been used up at any particular point in the process. When 5% of available cross-links have been completed, the rubber is said to be 100% scorched. If the rubber has reached this level before the mould is completely filled, no satisfactory bond is possible. Experimental work has shown that for consistent zero-defect production, the scorch level should not exceed 20% (1% cross-linked) before the rubber has been fully consolidated against the prepared surface to which it is to be bonded. The derivation for cross-link density from a cure rheometer trace is shown in Fig. 1.

The rate at which the level of scorch rises is governed by the time taken, at a particular temperature, for the rubber to flow through the mould into the cavity. For injection moulding, this is known as the injection time. The longer the injection time, the higher is the level of scorch (see Fig. 2). Injection time is governed by the available pressure, the rubber viscosity (temperature related) and the size of the “runners” and “gates” through which it must pass to reach the cavity. The size and shape of the cavity is a further factor.

The pressure exerted on the rubber in the cavity is related to the available pressure from the moulding machine, the speed of injection and the size of the runner through which it must flow to reach the mould cavity. The smaller the cross-sectional area of the runner, the higher is the pressure gradient between the point of injection and the cavity. If the length of the runners is the same to each cavity, there will be an equal rate of fill to all the cavities. If the path lengths are unequal, some cavities will fill before the others. Once a cavity has filled, it, and the related runner system, will rapidly achieve the full available

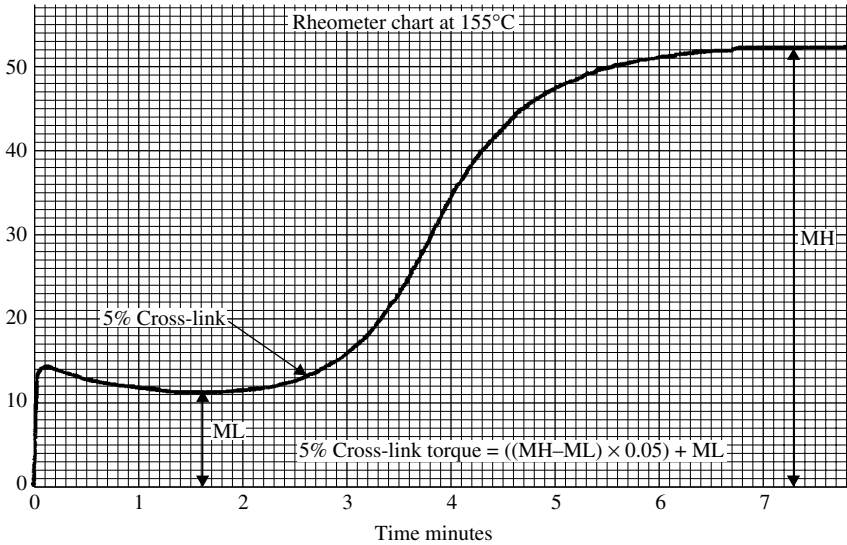


Fig. 1. Rheometer trace of torque (ordinate) versus time during cure of a rubber. Cross-link density and “scorch” can be calculated by a conventional procedure

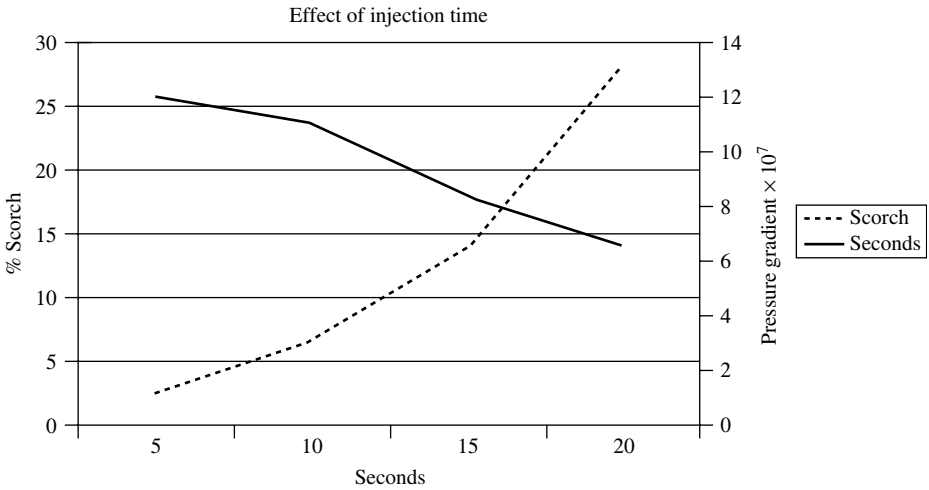


Fig. 2. Effect of pressure gradient and injection time on scorch

system pressure. For many moulds, this will mean that the over pressure generated in the runner system will cause the rubber to spill over these runners (known as flashing), so forcing the runner plate to open by several hundredths of a millimetre. This causes a loss of pressure to the partially filled cavities, resulting in some mouldings that are “light” or under filled. Associated mouldings often exhibit weak or “sellotape” bonds.

It is possible to minimize moulding problems by computer modelling of the way that the rubber flows through the mould. Commercially available programs are available for

this purpose,<sup>2-4</sup> that, in the hands of an experienced user, will allow the producer to discover the way the mould will work under a wide range of conditions before the mould has been manufactured. The effect of changes to runner sizes can be demonstrated, and through careful choice of experiments, using the computer, an optimized runner system is achieved that will allow the mould to work first time in the moulding press.

### References

1. J. A. Lindsay, *RAPRA Rev. Rep.*, **10**(1), (1999).
2. J. A. Lindsay, *Proceedings Rubber Injection Moulding: Today's Technology, Theory and Practice*, Rapra Technology Ltd, Seminar London, November 24th 1995, Papers 3, 831.
3. Fillcalc from R.A.P.R.A., Shawbury, Shewsbury, Salop, SY4 4NR.
4. Moldflow (Europe) Ltd., Central Court, Knoll Rise, Orpington, Kent, BR6 0JA.

---

### Rubber: tyre cord adhesion

---

W J VAN OOIJ

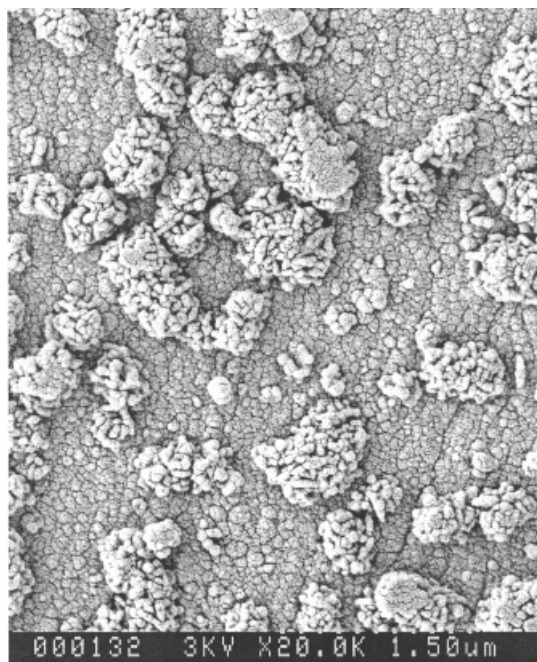
The production of tyres is among the most important of **Automotive applications** of adhesion. A modern steel-belted radial tyre contains several reinforcing materials, such as polyester and steel cords. The adhesion of the rubber compound to these cords is of critical importance for the performance and safety of the tyre. Other aspects of **Rubber to metal bonding – applications** are treated in other articles (see **Rubber to metal bonding – basic techniques**); here, the adhesion of rubber to the steel cords is discussed.

The steel cords in the belts of a tyre consist of a number of thin filaments that have been combined in a so-called cord construction. Each cord is, therefore, flexible but strong. The filament diameter varies and can be as thin as 0.15 mm. Each filament is individually coated with a thin layer of brass, typically of composition 63% Cu and the balance zinc. The brass-plating technique for bonding sulphur-vulcanized rubbers to metals has been known for many years. Currently, the tyre cord application is the only one where it is still used. In all other rubber–metal bonding operations, adhesives are used. Such adhesives cannot be used to bond the steel tyre cords to rubber, as the service temperature of the tyre belt is very high (e.g., close to 100 °C) and the bond has to withstand many dynamic cycles during the lifetime of the tyre. Only the rubber–brass bond is able to withstand the dynamic flexing at the high service temperature (see **Durability: fundamentals** and **Durability: fatigue**). Also, the high vulcanization temperature of the tyre (160 °C) eliminates adhesives as a possible bonding agent for the steel cords.

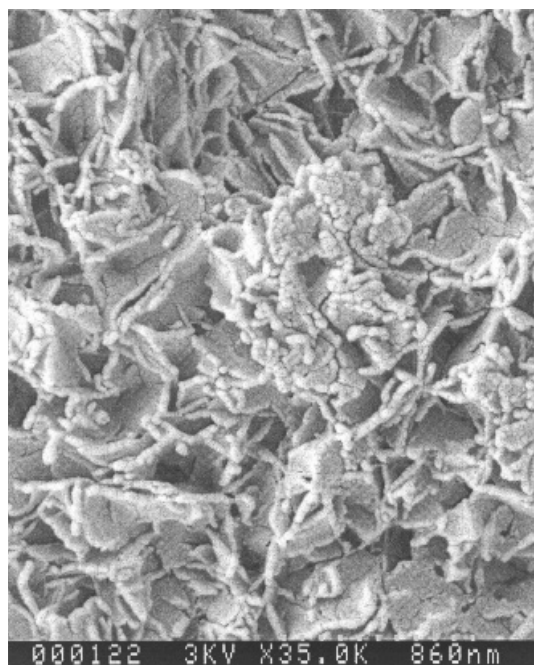
Further, in the process of manufacturing the brass-plated steel tyre cords, the brass is deposited by electroplating on the running wire, which is then drawn to its final diameter of 0.3–0.15 mm. In these drawing steps, the brass coating acts a solid lubricant. Without brass coating, the steel wires cannot be cold-drawn at high speeds through dies from 1.5 to 0.15 mm without breaking. Thus, virtually all the steel-belted radial tyres currently in use around the world contain the brass coating. Several other alloys have been proposed, but have never made it to commercialization. Modified alloys were proposed in the eighties, because tyre failures due to corrosion of the steel cords occurred frequently.

The brass–steel couple is a very unfavourable one from a corrosion standpoint. The presence of the brass coating accelerates steel corrosion when water and salt reach the cords through punctures. However, improved cord constructions and tyre designs have largely eliminated this problem. Water and salt can no longer propagate along the entire circumference of the tyre, as the rubber fills the capillaries of the cords because of the more open cord constructions that have been developed in recent years.

The brass coating on the steel reacts with components in the rubber formulation during tyre vulcanization. This mechanism has been studied extensively, and several review articles are available.<sup>1–3</sup> This reaction mechanism is unique and not exhibited by any other polymer–metal bonding system. What is so unique is that the sulphur-cured rubber compounds do not bond under the same conditions to steel, copper or zinc. Brass (and some other copper alloys) is the only metal that bonds well to such rubber compounds. During the vulcanization process (heating the tyre under pressure to about 160°C for about 15 min), the brass coating forms its own adhesive, that is, it reacts with sulphur-containing rubber intermediates and forms a sulphide film on the brass surface. This film consists of copper and zinc sulphides and is about 50–100-nm thick. It is important that this film is formed before the rubber begins to cross-link. The accelerator of the rubber is chosen such that cross-linking is delayed during the initial heating stages of the tyre. In this period, the sulphide film forms and grows into the rubber, which is very plastic in this stage. The copper sulphide film has a porous structure and hence has a very high surface area, as shown in Fig. 1 (see **Roughness and adhesion**). When the rubber cross-links and becomes elastic, the sulphide film is trapped in the rubber compound and a



**Fig. 1.** Sulphide film on brass after vulcanization of a high-sulphur rubber compound, showing the microporous structure. Magnification 20,000×



**Fig. 2.** Sulphide film on brass after aging in high humidity. Magnification 35,000×

high bond strength is obtained. Whether there are any covalent bonds between the copper sulphide crystals and the rubber remains a matter of some debate and is of scientific interest (see **Primary bonding at the interface**). The very high interfacial area by itself is sufficient to explain the high level of bonding, which exceeds the rubber tear strength under normal conditions.

The rubber–brass bond is sensitive to storage in high humidity. This so-called aged adhesion is always lower than the unaged, initial adhesion. Most of this reduction in adhesion is related to transformations in the sulphide film. The sulphide film of Fig. 1 is amorphous. During aging at high temperature or in high-humidity conditions, the film can become crystalline and brittle. The film shown in Fig. 2 is partly crystalline and contains a high level of zinc hydroxide, a product of corrosion of the brass layer underneath the sulphide film. This layer is mechanically much weaker and hence the adhesion is lower than in the case of the unaged sulphide film.

Other effects that have been reported, such as the positive effect of adding a cobalt metal–organic adhesion promoter to the rubber compound, have been shown to be related to modifications of the interfacial sulphide film.

### References

1. W. J. van Ooij, *Rubber Chem. Technol.*, **52**, 605 (1979).
2. W. J. van Ooij, *Rubber Chem. Technol.*, **57**, 421 (1984).
3. W. J. van Ooij, J. Giridhar and J. H. Ahn, *Kautschuk Gummi Kunststoffe*, **44**, 348 (1991).

---

## **Rubber-based adhesives**

---

JOSÉ MIGUEL MARTÍN-MARTÍNEZ

Rubber-based adhesives, also called elastomeric adhesives, is probably the most commonly known family of adhesives for industrial and household applications such as pressure-sensitive tapes and labels, construction, contact adhesives, hot melt packaging and bookbinding, and high-strength structural applications for aircraft, automotive and construction. In fact, about one-third of the adhesives used in the world are made from natural or synthetic rubbers. This article gives a general introduction. More specific aspects can be found in further articles listed at the end.

Compared with other adhesives systems, the formulation of the rubber-based adhesives is very complex: considerable training and practical experience is necessary before they can be successfully formulated (see **Rubber-based adhesives: compounding**). The properties of the elastomeric adhesives depend on both the chemical type and particular grade of the natural or synthetic elastomer and on the modifying additives that may be incorporated into the adhesive formulation (tackifiers, reinforcing resins, fillers, plasticizers, curing agents, etc.).

Some rubber-based adhesives need vulcanization to produce adequate ultimate strength, and the adhesion is mainly due to chemical interactions at the interface. Other rubber-based adhesives (see **Contact adhesives**) do not necessarily need vulcanization but need adequate compounding to produce the adhesive joints, mainly with porous substrates. In this case, the mechanism of diffusion dominates their adhesion properties. See **Diffusion theory of adhesion** and **Polymer diffusion: reptation and interdiffusion**.

### *Historical development*

The first elastomeric adhesive was prepared by the end of eighteenth century and was composed of naphtha solutions of natural rubber. Such adhesives are still in use in the production of temporary joints in textile, art material and footwear (where they are called “cement” adhesives). One of the early applications of the natural rubber adhesives was the laminating of textile products to impart waterproof resistance. For this application, cross-linking (vulcanization) after application of adhesive was necessary.

Adhesives made with natural rubber latex were first prepared in the middle of the nineteenth century. Organic solvents were used to prepare these adhesives, which generally contain rosins (a natural product derived from pine sap). However, the strength provided by these formulations was poor and, in general, porous substrates (e.g. paper, leather, textiles) were necessary to produce acceptable joints.

During the World War II, several new synthetic elastomers were produced, and new types of adhesives (mainly styrene–butadiene and acrylonitrile copolymers (see **Nitrile rubber adhesives**)) were manufactured to produce adequate performance in joints produced with new difficult-to-bond substrates. Furthermore, formulations to work under extreme environmental conditions (high temperature, resistance to chemicals, improved resistance to ageing) were obtained using polychloroprene (Neoprene) adhesives (see **Polychloroprene rubber adhesives: applications and properties** and **Polychloroprene rubber adhesives: modifiers and additives**). Most of those adhesives need vulcanization in order to perform properly.



Structural applications of rubber-based adhesives were also obtained using rubber-thermosetting resin blends, which provided high strength and low creep. The most common formulations contain phenolic resins and polychloroprene or nitrile rubber, and always need vulcanization.

Thermoplastic block copolymers were used for pressure rubber-sensitive and hot melt rubber adhesives from the middle sixties. These adhesives found application in packaging, disposable diapers, labels and tapes, among other industrial markets. The formulation of these adhesives generally includes an elastomer (generally containing styrene endblocks and either isoprene, butadiene or ethylene–butylene midblocks) and a tackifier (mainly a rosin derivative or hydrocarbon resin).

### *Method of application*

The viscosity of elastomeric adhesives determines their method of application. Typically, solvent-borne rubber compounds require low viscosities for application. Thus, viscosities lower than 0.6 Pa.s for spray, curtain or dip applications are required, whereas for brush application, viscosities lower than 5 Pa.s are generally used. Roll-coating technology requires viscosities between 5 and 15 Pa.s.

In recent years, the use of solvent-borne adhesives has been seriously restricted (see **Environment: sustainability**). Solvents are, in general, volatile, inflammable and toxic, in some degree. Further, solvents may react with other air-borne contaminants, contributing to smog formation and workplace exposure. These arguments allowed to limit the use of solvent-borne adhesives by different national and European regulations. Although solvent recovery systems and afterburners can be effectively attached to ventilation equipments, many factories are switching to the use of water-borne rubber adhesives, hot melts or 100% solids reactive systems, often at the expense of product performance or labour efficiency.

Because most latices have low viscosities by compounding, most of the water-borne rubber adhesives are sprayable. Thickeners such as fumed silicas can be added to increase viscosity and thixotropy. This means that, even at relatively large viscosities (over 10 Pa.s), many water-based rubber adhesives can be sprayed. Dip and curtain applications require viscosities between 0.05 and 0.3 Pa.s, whereas applications with brush works with viscosities between 1 and 50 Pa.s.

In addition to the articles cited above, further information is to be found in **Rubber-based adhesives: typical characteristics** and **Natural rubber-based adhesives**.

### *Select References*

- W. C. Wake, in *Treatise on Adhesion and Adhesives*, R. L. Patrick, Ed., Marcel Dekker, New York, 1969, Several chapters.
- N. J. De Lollis, *Adhesives, Adherends, Adhesion*, Robert E. Krieger Publisher, Malabar, FL, 1980. Chap 6, pp. 95–109.
- R. S. Whitehouse, in *Synthetic Adhesives and Sealants*, W. C. Wake, Ed., John Wiley, Chichester, 1986.
- I. Skeist, Ed., *Handbook of adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990, Several chapters.
- W. F. Harrington, Elastomeric adhesives, *Engineered Materials Handbook. Adhesives and Sealants*, Vol. 3, ASM International, 1990, pp. 143–150.

- A. V. Pocius, *Adhesion and Adhesives Technology*, Hanser, Munich, 1997, Chap 9, pp. 216–245.
- J. M. Martín-Martínez, in *Adhesion Science and Engineering—2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 573–675.
- W. F. Harrington, Elastomeric adhesives, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 515.

### **Rubber-based adhesives: compounding**

JOSÉ MIGUEL MARTÍN-MARTÍNEZ

In the general introductory article on **Rubber-based adhesives**, the complexity of formulations for these materials was emphasized. Although considerable experience is necessary for successful formulation, some introductory guidelines and typical formulations can be given: this is the purpose of this article.

Elastomeric adhesives typically contain an elastomer and a tackifying or modifying resin as key components, but in general, other ingredients are also included. The formulation of rubber-based adhesives may contain nine, or even more, different components (Table 1). Typical formulations of various types of adhesives are given in Tables 2–5.

In solvent-borne rubber adhesives, a variety of *solvents* can be chosen to control drying rate, adjust viscosity and dissolve important ingredients. *Resins* can be added to improve tack, wetting properties, heat resistance, bond strength and oxidation resistance. The most common resins used in rubber-based adhesives are rosins, rosin esters, and terpene, coumarone-indene, hydrocarbon and phenolic resins. *Plasticizers* and *softeners* reduce hardness, enhance tack and decrease cost of rubber adhesive formulations. Paraffinic oils, phthalate esters and polybutenes are typical plasticizers. *Fillers* are not often added to rubber adhesive formulations because they reduce adhesion. However they are sometimes used because they decrease cost and increase solution viscosity. Carbon black and titanium dioxide are also used to provide colour to the adhesives. Clays, calcium carbonate and silicates are also common fillers in rubber adhesive formulations. For water-borne adhesives, typically protective colloid, preservative, defoamers, wetting agents and emulsifiers are included in the formulations.

There now follows a more detailed consideration of the main features of ingredients for rubber-based adhesives.

*Table 1.* Likely components of a rubber-based adhesive

Component	Function
Elastomer	Basic polymer
Resins (tackifiers)	Increase tack
Plasticizer or softener	Increase flexibility
Fillers	Increase modulus, strength
Pigments	Colour
Curing agents	Cross-linking
Antioxidants	Stabilizer
Solvents	Lower viscosity
Emulsifiers, coagulant, biocides, etc.	

*Table 2.* Typical composition of a solvent-borne rubber adhesive. (Parts by weight per hundred parts of polymer – phr)

Component	phr
Elastomer	100
Tackifying resin	30
Magnesium oxide	4
Zinc oxide	5
Water	1
Antioxidant	2
Solvent mixture	500

*Table 3.* Typical composition of a water-borne rubber adhesive. (Parts by weight per hundred parts of polymer – phr)

Component	phr
Latex polymer	100
Surfactant	As required
Antifoam	As required
Tackifying resin	50
Thickener	As required
Zinc oxide	5
Antioxidant	2

*Table 4.* Typical formulation of a pressure-sensitive rubber adhesive. (Parts by weight per hundred parts of polymer – phr)

Component	phr
Elastomer	100
Tackifier	150
Lanolin	25
Zinc oxide	50
Antioxidant	1
Solvent mixture	400

*Table 5.* Typical formulation of hot melt rubber adhesive. (Parts by weight per hundred parts of polymer – phr)

Component	phr
Thermoplastic elastomer	100
Endblock resin	150
Midblock resin	50
Plasticizing oil	50
Antioxidant (stabilizer)	2

### *The elastomer*

The incorporation of polar side groups into the rubber structure imparts a dipolar nature, which provides oil resistance. Oil resistance is not found in rubber containing only carbon and hydrogen atoms (e.g. natural rubber). On the other hand, by making branched rubber chains rather than linear ones, low viscosity polymers for solution applications are obtained.

Several elastomers can be used in rubber-based adhesives. The elastomer provides the backbone of the adhesive, so the main performance of the adhesive is provided by the rubber properties. However, several specific properties for application are imparted by adding other ingredients in the formulations. The most common elastomers used in rubber-based adhesives are natural rubber (NR), butyl rubber (BR) and polyisobutylenes, styrene–butadiene rubber (SBR), nitrile rubber (NBR) and polychloroprene rubber (*Neoprene*) (CR).

*Natural rubber (NR)* is characterized by high cohesive strength and high tack. For use in solution adhesives, NR must be masticated sufficiently to break down gel and reduce viscosity for dissolution in suitable solvents. When low gel content is achieved, viscosity-stabilized rubbers dissolved without the need for mastication. It is usual to form the rubber into a thin layer to present a large surface to the solvent for rapid swelling (see **Natural rubber-based adhesives**).

*Butyl rubber (BR) and polyisobutylene (PIB)* are widely used in adhesives as primary elastomeric binders and as tackifiers and modifiers. The chemical structure of BR is mainly composed by long and straight carbon–hydrogen backbone. The small percentage of isobutylene provides some degree of unsaturation to allow curing, but at the same time renders BR very stable and inert to weathering, ageing and heating. BR has a good resistance to oils and to chemicals, and has very low water absorption

*Styrene–butadiene rubber (SBR)* is mainly used for tyre manufacturing and only a small amount is consumed in adhesives.

*Acrylonitrile–butadiene rubber (NBR)* (also called nitrile or nitrile butadiene rubber) shows high oils and plasticizer's resistance, excellent heat resistance, good adhesion to metallic substrates, and good compatibility with several compounding ingredients (see **Nitrile rubber adhesives**).

*Polychloroprene rubber (CR)* is the most popular and versatile of the elastomers used in adhesives: see **Polychloroprene rubber adhesives: applications and properties** and **Polychloroprene rubber adhesives: modifiers and additives**.

### *Tackifiers*

Tackifiers and modifiers are generally added to improve the adhesive performance of rubber-based adhesives, although other properties (viscosity, open time, tack) are also modified. Resins used in rubber-based adhesive formulations have the following characteristics:

1. Low molecular weight ( $M_w = 200\text{--}2000 \text{ g mol}^{-1}$ ), thermoplastic resins.
2. Viscous liquids to hard, brittle glasses at room temperature.
3. They are obtained from the derivatization of rosin or by polymerization of petroleum distillates, turpentine fractions, coal tar and pure monomers.
4. Range from water-clear to dark brown or black colour.
5. They are soluble in aliphatic and aromatic hydrocarbons as well as in many common organic solvents.

*t*-Butyl phenolic resin is a typical tackifier for solvent-borne polychloroprene adhesives. For these adhesives, rosin esters and coumarone-indene resins can also be used. For NBR adhesives, hydrogenated rosins and coumarone-indene resins can be used. For particular applications of both polychloroprene and NBR adhesives, chlorinated rubber can be added. SBR adhesives use rosins, coumarone-indene, pinene-based resins and other aromatic resins.

### *Plasticizers*

Plasticizers are substances (usually low molecular weight diluents) that are incorporated into polymeric materials to improve their workability and increase flexibility. The most important of these used in rubber adhesives are phthalates (see **Environment: sustainability**), polymeric plasticizers, and esters.

### *Fillers and pigments*

Fillers may be broadly defined as solid particulates or fibrous materials, substantially inert chemically, incorporated in polymer compositions to modify the properties and/or to reduce cost. Cost reduction is not the primary reason to incorporate fillers in adhesives but they are used to impart specific properties such as flow, improved adhesion, mechanical, thermal, electrical and optical properties, chemical and weather resistance, and rheological behaviour.

The most common fillers used in rubber base formulations are

*Silicates.* Clay and talc are the most common fillers in rubber-based adhesive formulations.

Both have platy shape, which favours the interactions with the elastomers.

*Silicas.* Only synthetic products (fumed and precipitated silicas) find use as fillers in rubber-based adhesives. Fumed and precipitated silicas are common fillers in NR- and SBR-based adhesives.

*Metal oxides.* Titanium dioxide is a common pigment, and zinc oxide and magnesium oxide are common fillers in rubber-based adhesives. Zinc oxide is a popular cross-linking agent for rubber. It is essential in the formulation of solvent-borne polychloroprene adhesives. Magnesium oxide (MgO) is used as curing agent and acid scavenger in solvent-borne polychloroprene adhesives.

*Carbon blacks.* Thermal and furnace carbon blacks are used in rubber-based adhesives.

### *Curing agents*

Rubber-based adhesives can be used without cross-linking. When necessary, essentially all the cross-linking agents normally used in the vulcanization of NR can be used to cross-link

elastomers with internal carbon–carbon double bonds. A common system, which requires heat to work, is the combination of sulphur with accelerators (zinc stearate, mercaptobenzothiazole). The use of a sulphur-based cross-linking system with zinc dibutyldithiocarbamate and/or zinc mercaptobenzothiazole allows curing at room temperature.

### *Antioxidants*

Oxidative changes induced by thermal, ozone exposition and UV light can dramatically affect service life of rubber-based adhesives. More precisely, the rubber and the tackifier are quite susceptible to oxidative degradation. This degradation can be mitigated by the incorporation of low levels of stabilizers during the fabrication process of the adhesives.

Rubber is protected against ozone attack by addition of physical and/or chemical antiozonants. Hydrocarbon waxes are the most common type of physical antiozonants, and *p*-phenylenediamines derivatives are the prevalent chemical antiozonants. Waxes bloom to the rubber surface and form a protective barrier. Since this bloom is brittle, it is broken by flexing. Therefore, waxes only protect under static conditions. A common loading for antiozonants in rubber formulations is 1.5 to 3 phr. Combinations of waxes and chemical antiozonants are generally used.

### *Solvents*

The solvent plays an important role in the performance of rubber-based adhesives. The solvent is the carrier for all components of the adhesive. Furthermore, the solvent controls the viscosity, open time, tack and adhesion of rubber-based adhesives.

A particular case in which the solvent is important is in contact adhesives, which for some time after application have enough cohesive strength and knitting ability that two surfaces coated with the adhesive have green strength immediately after they are mated. The choice of solvent in contact adhesives is critical because the solvents are chosen in such a way that a rapid evaporating solvent is used as carrier and a slower evaporating solvent provides tack during bonding.

The increase in restrictive regulations on the use of organic solvents favoured the increasing use of latex-based adhesives. Because of the slow evaporation of water, these adhesives show less tack and can suffer bacterial attack. Infrared heaters and ovens can be used to favour the evaporation of water. Often a small amount of solvent (*coalescing aide*) is added to the latex system to improve wetting and coalescence of the latex particles.

### *Select References*

1. Skeist, Ed., *Handbook of Adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990, Several chapters.
- W. F. Harrington, Elastomeric adhesives, in *Engineered Materials Handbook. Adhesives and Sealants*, Vol. 3, ASM International, 1990, pp. 143–150.
- J. M. Martín-Martínez, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 573–675.

---

**Rubber-based adhesives: typical characteristics**

---

JOSÉ MIGUEL MARTÍN-MARTÍNEZ

As discussed in other articles (see **Rubber-based adhesives**, and **Rubber-based adhesives: compounding**, it is clear that the chemical nature and molecular weight of the rubber will largely determine the properties of the adhesive. However, there are some common characteristics of most of rubber-based adhesives, which are treated here.

*Broad range of substrates for temporary or permanent assembly* Although, for many applications, curing (i.e. cross-linking or vulcanization) is not necessary, to provide high strength and, mainly, heat and chemical resistance to the joints produced with these adhesives, vulcanization is mandatory.

*Flexibility* The resilience of rubber helps to absorb the stresses applied to the joints. Therefore, these adhesives properly resist impact, shear, elongation, vibration and peel stresses.

*High peel strength* The intrinsic properties of rubbers (high ability to produce high elongation under stress) impart adequate strength to the joints under peeling forces (see **Peel tests**). However, rubber polymers show poor resistance to shear stresses.

*Versatility of formulation* Several type of elastomers can be used in elastomeric adhesives. For each family of rubber, several grades and different chemical modifications (e.g. grafting of polymers) can be achieved to impart specific properties to the joints.

*High green strength* This is one of the most important properties of the elastomeric adhesives. Natural rubber and styrene–butadiene rubber provides higher initial peel strength values. As time after joint formation progresses, polychloroprene and nitrile rubber develop much higher peel strength, particularly after a few hours. The *green* (immediate) *strength* can be defined as the ability to hold two surfaces together when first contacted and before the adhesive develops its ultimate bonding properties when fully cured. In other words, the green strength is the intrinsic capacity of elastomeric adhesives to strongly adhere to the substrates immediately after application. This unique property justifies the term “contact adhesive”, generally used to also name the elastomeric adhesives. The green strength can be modified by changing the solvent composition (for solvent-borne adhesives) and/or by incorporating ingredients in the formulations (mainly tackifiers). Green strength is essential in pressure-sensitive rubber adhesives (PSA) and in some polychloroprene rubber/phenolic resin blends.

*Variety of forms* Rubber-based adhesives can be supplied for assembly operations as solvent or water-borne dispersions, hot melts, pre-cast films, extruded tapes or reinforced films. In addition, solvent and water-borne dispersions can be supplied as single- or two-component systems.

Further information on rubber-based adhesives is to be found in specialized articles: **Natural rubber-based adhesives**, **Nitrile rubber adhesives**, **Polychloroprene rubber adhesives: applications and properties** and **Polychloroprene rubber adhesives: modifiers and additives**.

*Select References*

- I. Skeist, Ed., *Handbook of adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990, Several chapters.
- J. M. Martín-Martínez, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 573–675.
- W. F. Harrington, Elastomeric adhesives, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 515.



# S

---

## *Scanning electron microscopy*

---

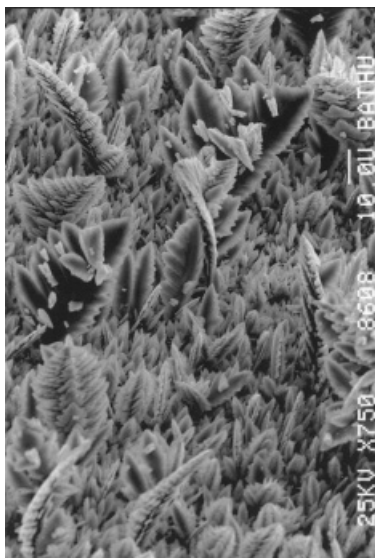
B C COPE

Electron microscopy exploits the general microscopy relationships that resolution is improved by reducing the wavelength of the illuminating radiation and depth of focus is increased by reducing the numerical aperture of the objective lens. Whereas, the resolution routinely obtained by **Optical microscopy** is typically around  $1\ \mu\text{m}$  transmission, **Electron microscopy** improves this to  $1\ \text{nm}$ . The scanning electron microscope (SEM) sacrifices some resolution for the ability to handle large, rough specimens and is routinely capable of resolving to about  $10\ \text{nm}$ . All three techniques offer improved performance under controlled conditions and with suitable specimens.

The SEM operates, in its normal secondary electron mode, by rastering an electron beam over the surface of a conducting specimen mounted in an evacuated column. The secondary electrons emitted from the surface regions of the sample are collected by a scintillator and the resulting signal is used to control the generation of an image on a cathode ray tube (CRT) display screen by modulation of the beam brightness in synchronization with the raster. Contrast results from surface topography and an image with a strong impression of spatial depth is displayed and may be recorded. Figure 1 shows the surface of zinc specially prepared for adhesive bonding by electrodeposition (see **Microfibrous surfaces**). Although the magnification ( $\times 750$ ) is within the capability of an optical microscope, the depth of field can only be obtained with the SEM. Figures in **Abrasion treatment** show contrasting micrographs of surfaces differently grit blasted.

Imaging modes other than secondary electron, such as cathodoluminescence, are available on the SEM instrument, but the only technique other than secondary electron that is likely to be of very much interest in solving adhesion problems is the use of backscattered primary electrons, which give a topographical image with some compositional contrast.

The principal advantage of the SEM over the reflectance optical microscope to the adhesives technologist perhaps lies less in the much greater magnification available and the



**Fig. 1.** Scanning electron micrograph of zinc dendrites electrodeposited onto a zinc substrate as a pre-treatment for adhesive bonding. (P. J. Hine, S. EL Muddarris, D. E. Packham, unpublished micrograph, see *J. Adhesion* **17**, 207(1987).)

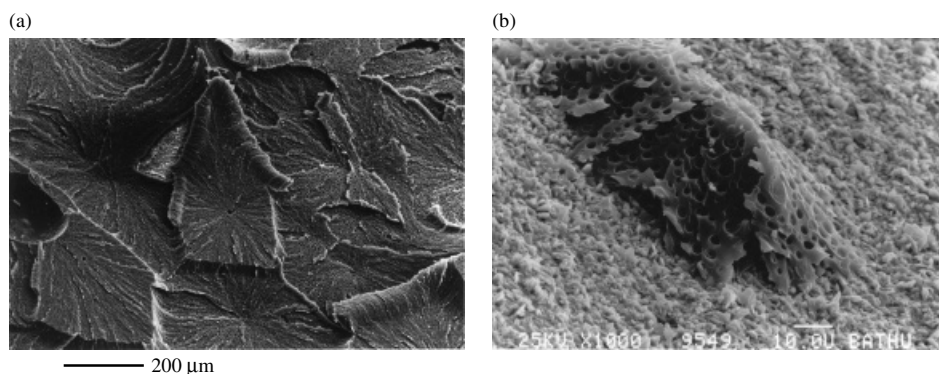
superior resolution than in the vast depth of field, which permits the study of comparatively rough surfaces.

Samples for the SEM may typically be a centimetre or so in diameter and about the same in depth. This is smaller than can be accommodated by the reflectance optical microscope but much larger than the small, ultrathin sections required for the transmission electron microscope. It is sometimes possible to work at low acceleration voltages with non-conducting specimens, but the secondary electron mode normally requires the specimen to have a conducting surface. Metals thus present no problems, but organic specimens usually need to be coated with a thin layer of gold or other metal applied by sputtering or vacuum evaporation. Careless preparation can lead to the masking of fine structure and the production of artefacts. Other changes in the specimen can occur as a result of the removal of volatiles under vacuum in the coater or the microscope, or as a consequence of “beam damage”, degradation of various kinds resulting from the concentrated input of energy from the electron beam.

Scanning electron microscopy is essentially a technique for the observation of surfaces and is thus especially applicable to the examination of adherends and failure surfaces, observations of the results of surface preparation of metals and polymers, investigations of failure modes (see **Stress distribution: mode of failure**), and examinations of finishes on fibres are typical of work reported in the literature.

Figure 2 shows fracture surfaces for bonds between zinc and rubber-toughened epoxy resin (see **Toughened adhesives**). In Fig. 2(a), there is a region of cohesive failure within the resin: the sites of bubbles, which may have initiated the fracture, can be seen. In Fig. 2(b), a piece of resin is seen adhering to what appears to be the bare zinc substrate.

There is less place for SEM work in the study of intact joints and the technique is not suited for observing sections.



**Fig. 2.** Failure surfaces of bonds between zinc and toughened epoxy resin: (a) region of cohesive failure within the resin; (b) region of apparently mixed failure. (Source as Fig. 1.)

A decade or so ago, SEM instruments were either simple and limited bench-top equipment or self-standing apparatus of room size. At that time, the image was usually recorded on 35-mm photographic film. The typical instrument is now desktop, has integrated digital image-saving and data-handling facilities, and is linked to a high-resolution printer. In many cases, facility for **Electron probe microanalysis** will be built in.

### *Select References*

- E. M. Slayter and H. S. Slayter, *Light and Electron Microscopy*, Cambridge University Press, Cambridge, 1992.
- P. J. Goodhew and F. J. Humphreys, *Electron Microscopy and Analysis*, 2nd edn, Taylor and Francis, London, 1988.
- G. Lawes and A. M. Jame, Eds., *Scanning Electron Microscopy and X-ray Microanalysis*, ACOLE-Wiley, Chichester, 1987.

---

## **Scanning probe microscopy**

---

GRAHAM LEGGETT

### *Introduction*

Conventional surface analytical methods (**X-ray photoelectron spectroscopy** or XPS and **Secondary ion mass spectrometry** or SIMS) can provide precise compositional and chemical structural information in imaging mode, but despite continuing advances in spatial resolution, they are at best capable of resolving micron-scale features. The high rate of charge and energy deposition associated with **Electron microscopy** and scanning Auger microscopy (see **Auger electron spectroscopy**) render them damaging techniques for application to polymeric systems, and their capabilities for resolving surface compositional variations are highly limited. Even for topographical characterization, stringent measures are required to facilitate imaging, leading to limited performance. Scanning

probe microscopy (SPM) has provided powerful new insights into the performance of adhesive systems. Since the development of, in particular, **Atomic force microscopy**, we have not only been able to image surface morphology with unprecedented spatial resolution but we have also been able to image variations in composition and even adhesivity with nm scale spatial resolution. New developments in near-field optics promise to facilitate genuine spectroscopic characterization with comparable spatial resolution.

### *Scanning tunnelling microscopy (STM)*

When STM (scanning tunnelling microscopy) delivered the first atomically resolved images of solid surfaces two decades ago, it was clear that a revolution had taken place in the characterization of surface structure. One of the first great triumphs of the STM was the elucidation of the Si(111) $7\times 7$  reconstruction, which had troubled surface scientists for some time. Images of beautiful structures composed of concentric rings of surface atoms left the structure in no doubt. On the basis of the phenomenon of quantum tunnelling, in which electrons tunnel through potential barriers in a classically forbidden process, the STM uses a sharp tip attached to a piezoelectric crystal to map the local density of states (LDOS) at a conducting surface. The tunnel current depends exponentially upon the separation between the tip and sample, meaning that for a sharp metal probe, the vast majority of the current flows through a small region at the apex of the tip. By varying the bias voltage between the tip and the sample, it is possible to access selectively specific electronic states (for example, to probe adatom dangling bonds on Si(111)), a mode of operation referred to as scanning tunnelling spectroscopy (STS). The principal limitation of STM is the requirement for electrical conductivity, which prevents its application to polymeric specimens except when they are coated with a conducting overlayer. In such circumstances, the resolution is clearly limited by the morphology of the overlayer.

### *Atomic force microscopy*

AFM (atomic force microscopy) was developed about five years after STM (see **Atomic force microscopy**). It relies upon the measurement of the force of interaction between a sharp tip and a sample. Being based upon the measurement of force rather than current, it is applicable in principle to any material. The technique has great versatility, and as in the case of STM, imaging may be carried out under ambient or fluid conditions. The tip is attached to a flexible cantilever, which is rastered across a sample surface. As the interaction force between the tip and the sample changes, the deflection of the cantilever varies. The cantilever deflection is readily measured (by optical deflection in most commercial systems) and is proportional to the interaction force leading to quantification, provided the spring constant of the lever is known. Either the cantilever or the sample is mounted on a piezoelectric crystal in order to exact fine control over the relative movements of the tip.

### *Near-field scanning optical microscopy (NSOM)*

Optical characterization methods suffer restricted spatial resolution due to the Abbé limit at approximately  $\lambda/2$ . Near-field scanning optical microscopy (NSOM or SNOM) developed in order to overcome this limit, using the kind of sophisticated feedback mechanisms developed for AFM and STM to scan an optical fibre, drawn to an aperture with a diameter

of as little as 50 nm, across a sample. By maintaining a very small separation between the optical aperture and the sample, it is possible to operate in the near-field regime, enabling optical characterization well beyond the Abbé limit. For example, the measurement of fluorescence with a spatial resolution of ca. 50 nm is possible. By combining the SNOM with a Raman spectrometer, it is possible to acquire spectroscopic data with similar resolution by taking advantage of the surface-enhanced Raman effect on appropriate substrates. Despite the promise that it offers, NSOM remains a less widely used technique than AFM and is generally perceived as being experimentally challenging.

Recently, there has been interest in *apertureless NSOM* methods, in which the optical fibre is replaced with a tip. The tip is either fabricated from a noble metal, or coated with one. The tip and sample are irradiated using a laser with the tip in close proximity to the sample. A surface plasmon is excited at the tip surface, and in the region directly beneath the tip, the electrostatic field experiences a strong near-field enhancement. The field associated with a surface plasmon is spatially highly confined in the region of a noble metal asperity, leading to an intense excitation of the sample in a small defined region. Published data (including apertureless Raman microscopy) suggest a spatial resolution of 25 nm is feasible, and better resolution may well be possible.

### *Scanning thermal microscopy*

In the scanning thermal microscope (SThM), the probe, which serves as both a highly miniaturized resistive heater and a temperature sensor, is a Wollaston wire, which consists of a thin platinum core (ca. 5  $\mu\text{m}$  in diameter) surrounded by a thick silver sheath (ca. 75  $\mu\text{m}$  in diameter), twisted into a loop (with a V-shaped tip) and attached to a carrier (a ceramic insulator) to form a cantilever. The silver at the apex of the tip is etched away to expose the core. When a current is passed through the wire, heating occurs primarily in the exposed platinum since this constitutes the principal resistance in the circuit. The probe is operated in a constant temperature mode, in which the power required to maintain the tip at a constant, pre-set temperature is monitored. Where the sample has a higher thermal conductivity, there will be an increase in heat flow to the sample, leading to an increase in the power required to maintain the set-point temperature; conversely, the power required is reduced for regions of low thermal conductivity. Topographical and thermal conductivity data may be acquired simultaneously. SThM has been used to characterize a variety of materials, including polymer blends, where differences in thermal characteristics may be used to image phase-separated structures. One useful modification of the technique has been to use the Wollaston wire probe to pyrolyse material from specific regions of a sample, with the products being collected by a gas chromatograph. By situating the SThM inside an infrared (IR) spectrometer, it has also been possible to conduct a highly spatially resolved **Infrared spectroscopy**. The principal drawback with SThM is the rather limited spatial resolution (a few hundred nm at best). However, the information it provides is unique.

### *Select References*

- R. Wiesendanger, *Scanning Probe Microscopy*, Springer-Verlag, Berlin, 1998.  
R. C. Dunn, *Chem. Rev.*, **99**, 2845–2890 (1999).  
H. M. Pollock and A. Hammiche, *J. Phys. D: Appl. Phys.*, **34**, R23 (2001).

### Scratch test

---

D E PACKHAM

Conventional **Tests of adhesion** are not well suited to measurement of thin films. The scratch test has been used to characterize the adhesion of thin films, such as plasma-polymerized polymers or evaporated metals, on hard substrates.

The test uses a vertically loaded stylus of a hard material such as diamond or tungsten carbide with a tip radius of the order of tens of micrometres. A micro-hardness tester may be used to make the test.<sup>1</sup> The stylus is drawn across the film a number of times, the vertical load being increased for each traverse. The critical load at which the film is just removed from the substrate is usually taken as a measure of the adhesion.<sup>2,3</sup> A European Standard has been established by the European Standards Committee CEN TC184 WGS.<sup>1</sup>

In early work on the test, it was argued that the critical load was determined only by the properties of the interface, the radius of the stylus and the hardness of the substrate.<sup>2</sup> On this basis, the scratch test would give a measure of “fundamental” adhesion (see **Adhesion – fundamental and practical**). However, there are many reports of dependency on the thickness and mechanical properties of the thin film, even several of those upon which supposedly similar styluses were used.

A simple form of the scratch test is used for assessing paint adhesion (see **Paint constitution and adhesion**). The scratch test, as described in this article, is perhaps best regarded as a useful comparative method of characterizing thin film adhesion. The test variables used should be carefully characterized and caution exercised in comparing results obtained in different laboratories.

A number of papers discussing the scratch test technique can be found in recent conference proceedings.<sup>3,4</sup>

#### References

1. European Standards Committee, *Advanced Technical Ceramics – Methods of Test for Ceramic Coatings – Part 3: Determination of Adhesion and Other Mechanical Failure Modes by a Scratch Test*, European Standard prEN 1071-3, March 5, 2001.
2. P. Benjamin and C. Weaver, *Proc. Roy. Soc.*, **A254**, 163 (1960).
3. K. L. Mittal, Ed., *Adhesion Measurement of Films and Coatings*, VSP, 1995.
4. K. L. Mittal, Ed., *Adhesion Measurement of Films and Coatings*, Vol. 2 VSP, 2001.

### Sealant joint design

---

J C BEECH\*

A preliminary article indicates the scope and types of **Sealants**. In designing a sealant joint, it is essential to select a suitable sealant with adequate capability to withstand the expected movement at the joint.

A generalized procedure for the design of a building joint employing a sealant is shown schematically in Fig. 1. In practice, the designer will be subject to constraints, which may require modification of this procedure. The design procedure must take account of the

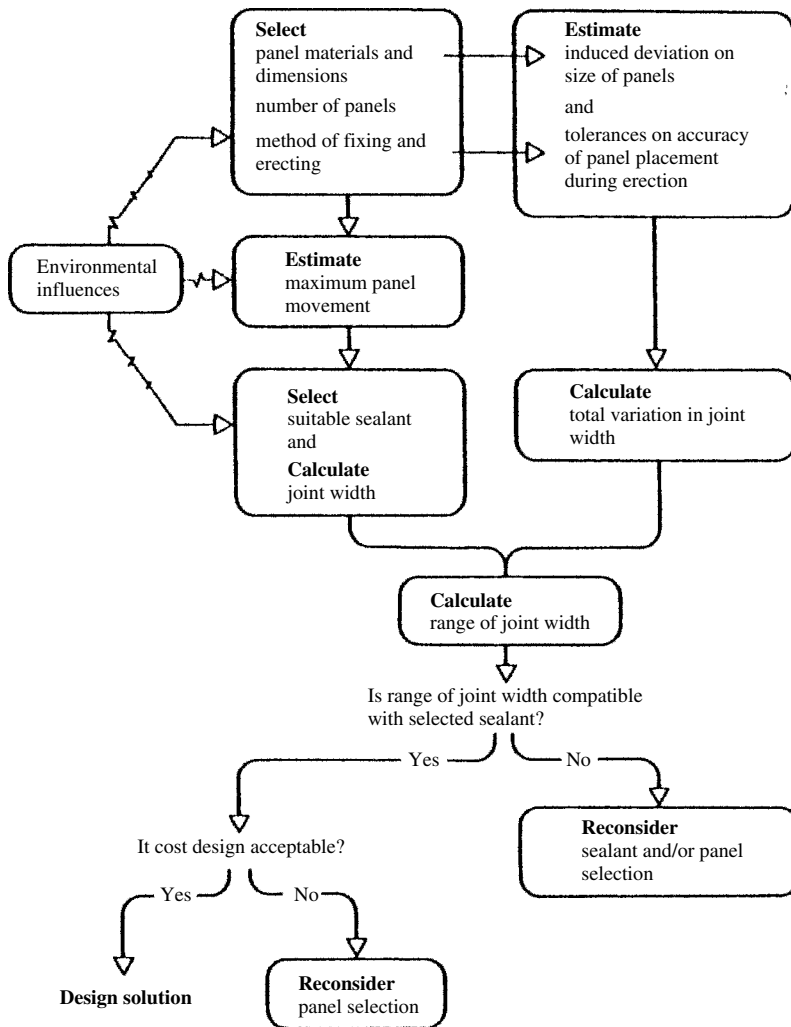


Fig. 1. Procedure for the design of a building joint employing a sealant

influence of temperature change as a primary cause of movement at the joint. Guidance is given in British Standard BS 6213<sup>1</sup> and in building research establishment (BRE) Digests 227 and 228.<sup>2</sup>

An important decision for the designer is the type of joint to use. Joints at present used for buildings of pre-cast wall panel construction are of two main types: those relying exclusively on the seal provided by the sealants and/or gaskets, known as *filled joints*; and those referred to as *open-drained joints*, in which the geometry of the joint, in conjunction with an airtight seal, is used as a two-stage defence against the weather.<sup>3</sup> These latter are usually very reliable, although additional capital costs will usually be incurred.

The two main types of filled joints are butt joints and lap joints (Fig. 2) (see **Shear tests** and **Tensile tests**); each has advantages and disadvantages. The lap joint gives the sealant some protection against the weather, and a further advantage of this type of joint

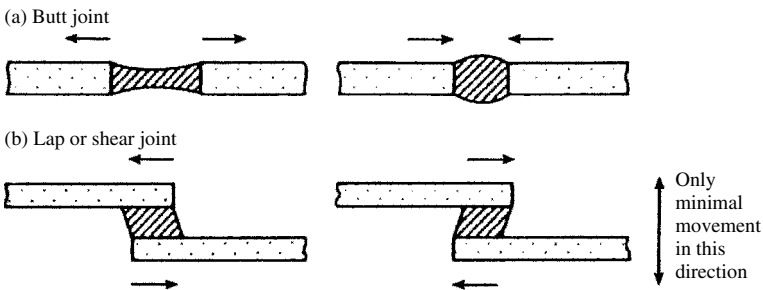
over the butt joint is that the sealant will be less prone to failure for a given amount of joint movement. This is because it is predominantly shear forces that are created during lap joint movement, and sealants more readily resist these forces than the tensile forces associated with butt joint movements. However, access to the joint to insert joint fillers and to ensure effective application of the sealant is more difficult than for the butt joint. Also, inaccuracies in component dimensions or their placing on site can mean that it is impossible to apply sufficient sealant in the joint to ensure satisfactory performance. The degradative effects of surface heat and UV light may be reduced by using a design in which the sealant is recessed within the joint. This could be simply achieved by designing a butt joint in which the sealant is applied to the back of the joint. However, in open-drained joints, the sealant is thoroughly protected from the weather by the sides of the components.

The choice of joint design should also take account of the fact that the lifetime of the chosen sealant may well be less than that of the building and that at some future date the sealant will have to be replaced. If such an operation is likely, a design of joint must be used that allows defective sealant to be removed and the joint surfaces cleaned and prepared before reapplication of fresh sealant. Because this procedure is fairly straightforward in the butt joint, this is the solution most frequently adopted by designers. In the discussion of some other aspects of joint design that follows, it is assumed that the butt joint is the option chosen.

*Component tolerances and joint widths*

When calculating the design width of joints in a building, it is essential to take account of the tolerances on the relevant dimensions of the components and the accuracy in placing them that is likely to be achieved on site.<sup>4,5</sup> For these reasons, there may, in practice, be considerable variation in the widths of a number of ostensibly identical joints. The joint width for the design must ensure that in no joint will the sealant be subjected to a level of compression or extension that, when expressed as a proportion of the achieved joint width, exceeds its movement capability. (See the **Selection of joint sealants**, where Table 1 gives maximum movement permitted for each major type of sealant.) However, considerable variation in formulation and properties may occur between different brands of the same chemical type, which may affect this value. The maximum tolerable joint movement quoted by the manufacturer should be used in joint design calculations.

A simple formula for the calculation of joint width has been derived.<sup>1</sup> The minimum joint width achieved must be sufficient to allow the sealant to be effectively gunned



**Fig. 2.** Sealant-filled joints: arrows indicate direction of movement of jointed component



into the joint. The minimum width quoted for most sealants is 5 mm. The maximum joint width achieved must not exceed that quoted as the maximum service value by the manufacturer. If it does, the sealant is likely to slump out of the joint, most probably in the period before the material fully cures, though longer-term failures of this kind may be experienced by non-setting types of sealant. Some elastomeric types of sealant may be applied to wide joints in two or more stages, the material finally being “tooled” in the normal way.

### *Sealant geometry*

After application, the sealant is forced into the joint and into good contact with the side and back surfaces by means of a wetted spatula or similar tool. This procedure is called “tooling”. It also ensures the correct front profile of the sealant surface, which should be slightly concave for elastomeric types, since this reduces stresses at the surface induced by joint movement.

The choice of the correct depth–width ratio for each type of sealant minimizes local stresses, which could promote premature failure of the sealant. The recommended depth: width ratios for different types of sealant<sup>1</sup> are: plastic 3:1 to 1:1, phaso-elastic 2:1 to 1:1, elasto-plastic 1:1 to 1:2, elastic 1:2.

Notwithstanding these recommendations, it is important to achieve a minimum depth of sealant in a joint to ensure adequate adhesion to the joint sides. For porous surfaces, this depth should be not less than 10 mm, while for non-porous materials, the minimum depth is 6 mm.

The back profile of the sealant and its correct depth are controlled by the back-up material, which is placed in the joint before sealant application. A number of readily compressible materials, such as closed-cell foamed polyethylene, are used for this purpose. It is essential that the sealant does not adhere to the back of the joint and is free to extend with joint movement. Where appropriate, therefore, a bond breaker consisting of a thin film of plastic material is inserted between the back-up material and the sealant.

### *Cure of sealants and joint movement*

Elastomeric sealants are only capable of fulfilling their functions in a building joint once the chemical reactions resulting in their cure are complete. The time taken to attain effective cure varies considerably between different types; it is longest for those sealants that rely on the diffusion of atmospheric moisture into the bulk of the material to complete the cure process. The rate of cure will obviously also depend on environmental conditions, principally air temperature and humidity, at the time of applying the sealant and for some time afterwards. One part polysulphides usually take up to 3 weeks to cure completely, and this period can be considerably longer if the air remains dry and cold. Clearly, these relatively slow-curing sealants are vulnerable to damage if subjected to deformation during the period immediately after application to the joint. This may be caused either by cyclic movements at the joints or by irreversible joint movements, such as drying, shrinkage of components or settlement of the structure.

Further information may be found in a comprehensive American compendium<sup>6</sup> and in the articles **Primers for sealants** and **Sealants in double glazing**.

---

### References

1. British Standards Institution, *Guide to the Selection of Construction Sealants*, BS 6213, BSI, London, 2000.
2. Building Research Establishment, Estimation of Thermal and Moisture Movements and Stresses: Parts 1 and 2. *BRE Digests 227 and 228*, 1979.
3. Building Research Establishment, Principles of Joint Design, *BRE Digest 137*, 1977.
4. British Standards Institution, Code of Practice for Design of Joints and Jointing in Building Construction, *BS 6093*, 1993.
5. British Standards Institution, Tolerances for Building, *BS 6954*, 1988.
6. J. T. Quinlivan and D. Arnold, Designing with adhesives and sealants, in *Engineered Materials Handbook. Adhesives and Sealants*, Vol. 3, Section 6, ASM International, 1990, p. 457.

---

### Sealants

G B LOWE

Sealants may be described as thick bed adhesives, some having plastic properties, while others used in moving joints have elastic properties. In general, the low movement accommodation systems are referred to as mastics, whereas the elastic and elasto-plastic systems are referred to as sealants. More detailed descriptions are discussed by Damusis.<sup>1</sup>

The mastic type sealants include hand-applied systems based on linseed oil (putty), gun-applied oil-based systems, using one or more drying oils and gun-applied “butyl” systems based generally on liquid polyisobutylene (PIB) with oils and solvents. These function primarily as gap fillers to prevent the ingress of dust, rain and wind in substantially non-moving joints.<sup>2,3</sup>

Intermediate movement accommodating sealants include solvent-based and emulsion-type acrylic systems, higher quality butyl/PIB blends, neoprene and styrene-butadiene (SBR) based compounds. These have sufficient movement tolerance to be used in joints subject to both settlement and thermally induced movement across the sealant. These intermediate type systems “cure” by means of solvent evaporation with some auto-oxidation, or a mixture of the two processes.

The elastomeric type sealants are chemically curing systems based on a limited variety of polymers. The best known of these being polysulfide, silicone (see **Silicones: structures**), **Polyurethane** and the modified silicones, which are urethane prepolymers with reactive silane end groups. All these are available as single- or two-part systems.

The single-part systems generally require atmospheric moisture to effect cure by inducing oxidation (e.g. single-part polysulfides cured with calcium peroxide) or condensation of a reactive end group as in the case of the polyurethanes and silicones. The cure mechanisms for these systems can be complicated and depend on a number of factors.<sup>4</sup>

Performance of sealants in construction is defined in BS EN ISO 11600 – Classification of Sealants for Building Construction – and its supporting standards. The durability of the various sealants has been the subject of a European study and the findings can be found in the RILEM proceedings.<sup>5</sup>

Specialty sealants based on modifications on the above find wide usage not only in construction but also in civil engineering, **Aerospace applications**, shipbuilding and

**Automotive applications.** A very specific use is in the field of insulation (see **Sealants in double glazing**).

Further information may be found in Ref. [6] and in articles on **Selection of joint sealants, Primers for sealants** and **Sealant joint design** together with a series of doctoral theses.<sup>7-9</sup>

### References

1. A. Damusis, Ed., *Sealants*, Van Nostrand Reinhold, New York, 1967.
2. W. R. Sharman, J. I. Fry and R. W. Whitney, *Durability Build. Mat.*, **2**, 79–90 (1983).
3. D. Aubrey and J. beech, The influence of Moisture on building joint sealants, *Build. Environ.*, **24**, 179–190 (1989).
4. G. B. Lowe, *Int. J. Adhes. Adhes.*, **17**(4), 345–349 (1997).
5. A. T. Wolf, Ed., *Durability of Building Sealants*, Rilem Publications, 1999.
6. H. F. Bronson, Ed., Adhesives and sealants, *Engineered Materials Handbook*, vol. 3 ASM, Ohio, 1999.
7. A. Pagliuca, *Adhesion and material properties of construction sealants*, Ph.D. Thesis, Brookes University, Oxford, England, 1994.
8. T. B. G. Jones, *Effect of movement during cure on the experimental performance of construction sealant materials*, Ph.D. Thesis, Brookes University, Oxford, England, 2001.
9. S. Iglauer, *Influence of backing material on sealed joint performance*, D. Phil. Thesis, Brookes University, Oxford, England, 2002.

---

## Sealants in double glazing

---

G B LOWE

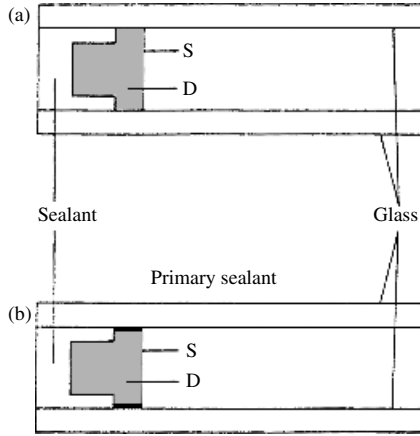
Insulating glass or double glazed units consist of two panes of glass separated by a spacer and all are held together by edge **Sealants** (Fig. 1). These sealants seek to exploit the specific properties of low moisture vapour transmission, low inert-gas transmission and high durability of the sealant used (see **Durability: fundamentals**).

The most common system for the outer or secondary sealant used is based on polysulfide polymers cured with manganese dioxide where the physical properties have been modified by the use of a low-volatility plasticizer such as a higher phthalate. Recent developments have seen an increase in the use of polyurethanes because of their higher adhesion potential. All the systems are required to have oil resistance when used in timber windows (from the glazing putt and preservatives) (see **Selection of joint sealant**).

Other systems that have been introduced include hot-applied butyl/PIB systems (HMB), warm-applied reactive urethane prepolymers and silicones. The latter has the least favourable moisture vapour transmission rate but excellent UV resistance for exposed glazing.

All the curing systems are used with a primary sealant based on poly-isobutylene (PIB), whereas the HMB systems are often used as the sole sealant (see Fig. 1b).

The durability of double glazing sealants is normally assessed by measuring the rate of moisture ingress into the cavity. This can be done by measuring the amount of water absorbed by the desiccant or by determining accurately the internal dew point. The former



**Fig. 1.** Most common insulated glass unit construction, (a) without primary sealant and (b) with primary sealant. (S = spaced, usually aluminium; D = desiccant, either zeolite or silica gel.)

measurement is known as the penetration index and is given by

$$I = \frac{T_f - T_i}{T_c - T_i}$$

where  $T_f$ ,  $T_c$  and  $T_i$  are the weight loss of the desiccant on ignition on the tested unit, the reference unit and the desiccant capacity respectively.

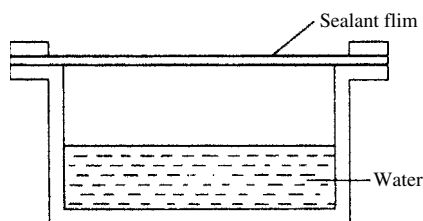
Because these systems are used in ways that are different from their construction sealant counterparts, extensive studies on long-term adhesion have been carried out to evaluate adhesion promoters capable of giving long-term (15–30 years) service life. The most successful of these have been the alkyl silanes, specifically  $\gamma$ -glycidoxypropyl-trimethoxy-silane or mercapto-propyl-trimethoxy-silane, although some workers have found amino-substituted silanes to be preferable (see **Silane adhesion promoters, Primers for sealants**).

The gas-retention qualities of the sealants have become of increased importance with the need to conserve energy. It has been found that higher molecular weight inert gases such as argon reduces heat convection and radiation within the unit, while heavy gases such as sulfur hexafluoride can reduce sound transmission.

Rates of gas loss from a unit can be determined using the European Standard EN1279 Part 3 – Long-term measurement for gas leakage rate and for gas concentration tolerances. It has been estimated that these rates are polymer dependant,<sup>1</sup> and are quoted as

Argon loss (% per annum)	
Polysulfide	0.2–0.75
Polyurethane	0.5–2.0
Silicone	10–30

The water-vapour transmission rate (WVTR) through the sealant may be measured using apparatus as shown in Fig. 2. Because of differences in details, such as film thickness and



**Fig. 2.** Determination of moisture vapour transmission. The apparatus is stored at constant temperature and humidity. Weight loss is taken as a measure of water vapour transmission rate

humidity differential, results from these are not comparable. The relative transmissions derived from a number of studies indicate the following.

	WVTR $\text{gm}^{-2} \text{day}^{-1}$
PIB/butyl	0.5–1.0
Polysulfides	1.0–2.0
Polyurethanes	1.0–3.0
Silicones	3.0–10.0

The WVTR and gas transmission must be considered along with other physical properties such as  $T_g^2$  and the long-term adhesion<sup>3</sup> for a better understanding of the sealant's potential performance.

Ageing of insulating glass units has been studied extensively.<sup>4,5</sup> As a consequence of the knowledge gained, new standards have been prepared that more accurately indicate the service life of the double glazed unit. Such standards are EN 1279 – Glass In Building – Insulating Glass Units and the American/Canadian Harmonized standard

### References

1. B. Streeter, Gas filled insulating glass sealants, *SIGMA Meeting*, New Orleans, 1989.
2. G. B. Lowe, *Dynamic Mechanical Thermal Analysis of Sealants for Insulating Glass*, Morton International, Coventry, 1988.
3. G. B. Lowe, *The Durability of Adhesion of Polysulfide Sealants to Glass*, Ph. D. Thesis, DeMontfort University, 1992.
4. S. Brolin, Penetration of water vapour into insulating glass units, *The Swedish National Test Institute Symposium*, Boras, 1989.
5. M. Schulman and M. Scherrer, *Glass Dig.*, **59**(12), 52–53 (1980).

## Secondary ion mass spectrometry (SIMS)

D BRIGGS

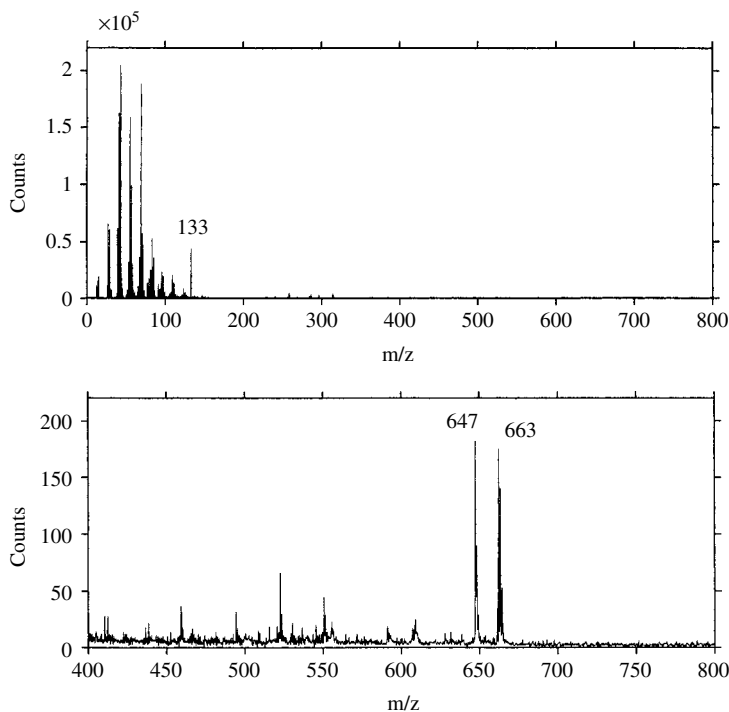
Three different experiments for surface and interface analysis are possible by SIMS (secondary ion mass spectrometry): SIMS static, dynamic and imaging SIMS.

The sample in ultra-high vacuum is bombarded with a beam of positively charged ions (e.g.  $\text{Ar}^+$ ,  $\text{O}_2^+$ ,  $\text{Ga}^+$ ,  $\text{Cs}^+$ ). Material is sputtered from the surface, mostly as neutral species but with a few percent of charged species (positive and negative secondary ions). These are collected by a mass spectrometer and mass analysed. Charging of insulators is controlled by simultaneous “flooding” with relatively low-energy electrons.

In static SIMS, the primary ion current density is very low ( $\sim 1 \text{ nA cm}^{-2}$ ) so that the spectrum is representative of undamaged surface. The aim is to optimize the collection of large fragments (cluster ions), which provide information on surface molecular structure, corresponding to only  $\sim 10 \text{ \AA}$  sampling depth. This technique is particularly valuable for identifying surface molecules, such as polymer additives and contaminants (e.g. Fig. 1).

In dynamic SIMS, the primary ion current density is very much higher (usually  $> 10 \text{ \mu A cm}^{-2}$ ) so that the surface is rapidly eroded. The intensity of elemental ions is followed as a function of time (i.e. eroded depth) to provide composition depth profiles. This technique is particularly valuable for studying buried interfaces and thin film structures.

In imaging SIMS, the two-dimensional distribution of species on the surface is studied either by scanning a focused ion beam over the surface and mapping the intensity of useful secondary ions (ion probe) or by using a defocused ion beam and imaging mass



**Fig. 1.** Positive ion ToF-SIMS spectrum from the surface of pre-treated (electrochemically oxidized) polypropylene generated by  $\text{Cs}^+$  primary ions. The intense low-mass peaks ( $m/z < 130$ ) are hydrocarbon fragments from the polymer while the peaks in the region of  $m/z$  650 are due to the antioxidant Irgaphos 168. Before pre-treatment, these peaks are not observed, showing that the antioxidant molecules migrate from the polypropylene bulk to the higher energy surface produced by electrochemical oxidation

selected species by ion–optical means (ion microscope). Imaging can be performed either in the static or dynamic mode with spatial resolutions down to 1000 Å.

The advantages of SIMS are (1) surface sensitivity ( $\sim 2$  monolayers); (2) detection limits (as low as parts per billion (ppb) in dynamic SIMS); (3) molecular specificity and high degree of structural information from both organic and inorganic materials (in static SIMS). The main disadvantage is the inherent lack of quantitation, that is there is no direct relationship between peak intensity and species concentration (as in XPS and AES)

Since about 1990, static SIMS has been transformed by the introduction of time-of-flight mass analysis, so that the term TOF-SIMS has become synonymous with modern static SIMS.

An example of an application is given in **Primers for adhesive bonding**.

### Select References

D. Briggs and M. P. Seah, Eds., *Practical Surface Analysis*, 2nd edn, Vol 2, *Ion and Neutral Spectroscopy*, Wiley, Chichester, 1992.

J. C. Vickerman and D. Briggs, Eds., *ToF-SIMS: Surface Analysis by Mass Spectrometry*, Surface-Spectra, IM Publications, Manchester, 2001.

---

## Selection of adhesives

---

D M BREWIS

### Introduction

With the exception of the pressure-sensitive type (see **Pressure-sensitive adhesives**), adhesives change from a fluid to a rigid state during bonding. This hardening process may be brought about by one of four mechanisms.

- **Solvent-based adhesives** harden by evaporation of solvent, although with porous substrates, hardening will be accelerated by capillary action.
- **Emulsion and dispersion adhesives** harden by evaporation of the dispersion medium, which is usually water; with porous substrates, hardening is again aided by capillary action.
- **Hot melt adhesives** are thermoplastics, which are heated above their softening point; hardening occurs when the molten polymer is cooled between the two substrates.
- **Reaction-setting adhesives** or reactive adhesives harden when a monomer or resin undergoes a polymerization reaction.

There are, therefore, four main types from which to select an adhesive. The choice of an adhesive depends upon several factors, which are now considered.

### Setting time

The setting time for solvent-based adhesives depends largely on the boiling point of the solvent used and can therefore be varied over a very wide range. Mixed solvents are often used to give the required evaporation rate.

With emulsion adhesives, drying can be accelerated by using heaters or by spraying the adhesives on to the substrates.

The setting times for reactive adhesives vary from a few seconds with **Cyanoacrylate adhesives** to several hours for a typical DIY epoxide cured at room temperature. For a given reactive system, the setting time can be varied by a large factor by changing the temperature and/or catalyst.

Melt adhesives can give the fastest setting rates of all and this is critical where very high production rates are required, for example, edge veneering of blockboard. However, it is possible, because of high thermal conductivity, that melt adhesives harden too rapidly to achieve good contact with the substrate. This problem can be overcome by careful formulation of the adhesive.

### *Hazards*

Adhesives may be associated with toxicity and/or inflammability and pollution hazards (see also **Health and safety**).

Harmful effects can occur because of inhalation of vapour or skin absorption. Solvent-based adhesives are probably the greatest potential problem as far as toxicity is concerned because their mode of operation involves the evaporation of large quantities of solvents. Some of the components of reaction-setting adhesives are highly toxic and very efficient ventilation is necessary. Molten polymers have very low vapour pressures. However, additives in hot melt adhesives and decomposition products may produce toxic vapours, especially if reservoirs of melt adhesives are used. Emulsion adhesives where the dispersion medium is water represent the safest group of adhesives from the toxicity viewpoint.

Fire hazards are at a minimum with emulsion adhesives and at a maximum with many solvent-based adhesives because large quantities of organic compounds are involved. Chlorinated solvents are not inflammable but have a relatively high toxicity. The adverse effect of halogenated organic compounds on the ozone layer has led to a ban or restrictions on the use of chlorinated or fluorinated solvents.

Because of toxicity, environmental considerations and inflammability problems, solvent-based adhesives are being replaced by other types of adhesives.

### *Initial performance*

The high mechanical strengths associated with many cured reaction-setting adhesives are often reflected in high lap shear strengths, which may be up to 70 MPa with some metals. **Structural adhesives** are usually of the reactive type, with **Epoxide adhesives** being especially important.

Previously, these cured adhesives had been associated with poor peel, cleavage and impact strengths (see **Tests of adhesion**). However, with the incorporation of a rubber phase into the adhesive, the fracture toughness can be much increased and high peel strengths can be obtained while retaining high shear strengths (see **Toughened adhesives**). **Toughened epoxide adhesives** and **Toughened acrylic adhesives** are discussed elsewhere in this book.

High peel strengths can be obtained with adhesives possessing moderate cohesive strengths. For example, polyurethanes and **Nitrile rubber adhesives** give high peel strengths with a wide range of flexible substrates.



### *Durability*

Adhesive joints may be subjected to a variety of adverse service conditions, including elevated temperature, organic solvents, water and stress (see **Durability: fundamentals, Durability: creep rupture**). Solvent-based, emulsion and melt adhesives are normally based on thermoplastics with fairly low softening temperatures. If a loaded joint is subjected to elevated temperature, failure may occur because of **Creep** unless the adhesive is cross-linked. Likewise, attack by organic solvents can be minimized by cross-linking. Solvent-based, emulsion and hot melt systems are available that cross-link after the initial bonding has been carried out. These systems provide improved in-service performance.

The more common environmental problem with metal joints is attack by water. In addition to alloy composition, pre-treatment and primer, durability is affected by the adhesive used (see **Pre-treatment of metals prior to bonding, Pre-treatment of polymers, Primers for adhesive bonding**). Sell<sup>1</sup> has ranked adhesives in the order of durability they provide with aluminium substrates:

nitrile-phenolics > high-temperature curing epoxides > medium-temperature curing epoxides > two-part room temperature curing epoxides > two-part **Polyurethanes**

### *Cost*

In evaluating the total cost of applying an adhesive, various factors must be considered including the following:

- the cost of the adhesive based on the area of substrate covered;
- labour costs;
- the cost of special equipment such as hot melt applicators, ovens for reactive adhesives and ventilation equipment for solvent-based adhesives;
- energy costs;
- storage costs.

### *Overall assessment*

No adhesive will be ideal with respect to all the above factors, and it is therefore necessary to decide which are the most important properties required and then to make the appropriate compromise. In particular cases, there will be other factors to consider, for example, if it is necessary to bond oily steel; then **Acrylic adhesives** might be the best choice.

Further details regarding the advantages and limitations of different adhesives are given in articles already cited and in the articles listed below. Other sources include Refs. [2–4] and works discussed in the **Appendix**. See also **Adhesive classification, Anaerobic adhesives, Cyanoacrylate adhesives, High-temperature adhesives, Rubber-based adhesives**.

### *References*

1. W. D. Sell, Some analytical techniques for durability testing of structural adhesives, Proceedings of the 19th National SAMPE Symposium, April, 1974.

2. J. Shields, *Adhesives Handbook*, 3rd edn, Butterworths, London, 1984.
3. A. Pizzi and K. L. Mittal, *Handbook of Adhesive Technology*, 2nd edn, Marcel Dekker, New York, 2003.
4. I. Skeist, Ed., *Handbook of Adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990.

---

### *Selection of joint sealants*

---

J C BEECH\*

The primary function of a joint sealant is to prevent ingress of water or particulate matter to the building or structure. It must withstand the effects of changing environmental conditions throughout its effective service life, including the effect of joint movements. To do this, it is required to maintain adhesion to the adjoining joint surfaces. Despite this, **Sealants** are not adhesives, having entirely different functions, and they must be assessed by different performance criteria.<sup>1</sup>

A large variety of different sealant products are available, ranging from plastomeric oil-based mastics that are little more than joint fillers, to high-performance elastomeric sealants, which are capable of withstanding large joint movements of up to 60% of the nominal joint width.

#### *Selection of sealants*

This is made primarily on the basis of the intended joint movement (see **Sealant joint design**), though other criteria are important such as compatibility with joint surface materials.<sup>2,3</sup> To achieve a satisfactory bond to certain surfaces under the prevailing site conditions, it may be essential to employ an appropriate primer (see **Primers for sealants**). Table 1 summarizes the types of sealants available commercially and indicates their performance characteristics.

The cheapest types of sealants, often referred to as “mastics”, are plastic in character, that is, they show little or no recovery when subjected to deformation. They have limited durability and will withstand only slight joint movement; they are most suitable for pointing around door and window frames. After application, a tough skin is formed by oxidation of the surface, protecting the material inside, which remains plastic. Progressive hardening through the bulk of the sealant leads eventually to cracking and to failure, though over-painting can considerably prolong its life.

The rest of the sealants in Table 1 are said to be elastomeric; they will all withstand some degree of joint movement and undergo change to a more or less elastic state after application. Elastomeric sealants that are predominantly plastic in character but which show limited deformations are termed *plasto-elastic*. The butyl rubber and acrylic sealants are typical of this type and are limited in their uses to joints in which moderate movement occurs and to pointing around window and doorframes. Most of these change to a plasto-elastic state by loss of volatile constituents, which can cause shrinkage, and this must be borne in mind when designing joints.

When the amplitude of joint movement is likely to be 20% or more of the joint width, it is essential to use one of the elasto-plastic or elastic types of elastomeric sealant.

Table 1. The main types of commercial joint sealants

Sealant type	Maximum tolerated movement (as % of joint width)	Character (after cure)	Typical uses	Comments	Expected service life (years)
Bituminous and rubber/bitumen	10	Plastic	In contact with bituminous materials	Poor durability in external movement joints	5
Oleo-resinous ("oil-based mastics")	10	Plastic	Pointing around window and door frames	Regular maintenance necessary	Up to 10
Butyl rubber	10	Plastic	Pointing, bedding	Properties vary with formulation	
Acrylic (solvent)	15	Plasto-elastic	Pointing, e.g. around timber frames treated with exterior wood stains, etc.	Good adhesion. May need warming before application	Up to 15
Acrylic (emulsion)	10	Plasto-elastic	Internal pointing	Low health hazard. Durability uncertain	
1-part polysulphide	25	Elasto-plastic	Movement joints in heavy structures	Slow curing: vulnerable to damage by movement until fully cured	Up to 20
1-part polyurethane	30	Elastic	Movement joints with light (e.g. metal) components	Mixed on site; so must be used within "application life". Maintenance costs low	
2-part polyurethane	30	Elasto-plastic	Both fast-moving joints in lightweight structures and slow moving joints in large heavy structures		
2-part polysulphide	30	Elastic	Joints between plastics and metal components	High initial cost. Careful surface preparation essential	
1-part silicone (low modulus)	50	Elastic			
1-part silicone (high modulus)	20	Elastic	Sanitary ware. Fast-moving joints	Unsatisfactory on porous surfaces	

Note: (1) Sealant types are listed in order of increasing initial cost; the list does not claim to be comprehensive. (2) Gun-grades are listed: for joints in horizontal surfaces, the following self-levelling types are available: (a) hot-poured bituminous and rubber/bitumen; (b) cold-poured polysulphide and polyurethane.

These also have greater inherent durability than other types of sealants; the silicones, polysulphides and polyurethanes can be expected to perform for at least 20 years when used correctly in appropriate joints. All these sealants "cure", that is, they are converted from a paste-like consistency to a rubbery state after application to the joint. This curing can be result of a catalysed chemical reaction or by reaction with atmospheric moisture.

The sealants termed “elasto-plastic” exhibit predominantly elastic behaviour but are also subject to some stress relaxation under deformation. These sealants perform well in slow-moving joints between large, heavy components of materials such as precast concrete. Stresses tend gradually to decay when the sealant is extended for long periods, so reducing the internal forces, which may cause cohesive failure of the sealant or pull it from the joint faces. Those sealants that are elastic virtually recover completely after deformation within the expected range of joint movement. They are most appropriate for use in joints between lightweight components of high thermal conductivity, such as metals and plastics, where it may be expected that the rate of movement will be fairly high.

The sealants discussed so far are primarily supplied as “gun-grades” for application to joints on vertical building surfaces. A number of types (e.g. polysulphides) are also supplied as self-levelling or pourable grades for use in horizontal surfaces; these sealants can be supplied with special properties, such as abrasion resistance for joints in traffic-bearing surfaces. Bitumen and bitumen/rubber-based sealants are also supplied for these purposes; both these types can withstand only limited movement.

### *Environmental factors*

The location of the building and of the individual joints, together with the aspect of the face of the building, will largely determine the environmental factors affecting the performance of a sealant through its lifetime in the joint (see **Durability – fundamentals**). Dark-coloured building surfaces exposed to sun in temperate climates may attain surface temperatures in excess of 70°C in summer, while in the tropics temperatures above 100°C will often occur; allowance must therefore be made for the sealant in the adjacent joints to be subjected occasionally to temperatures of this order. High temperatures will tend to accelerate certain chemical and physical changes in the sealant which, in conjunction with the cyclic movement to which it is subjected, cause gradual deterioration of the material. This degradation will be exacerbated by direct exposure to UV light. For non-curing and solvent-based sealants, this deterioration is manifest as hardening of the surface by oxidation or in shrinkage through loss of volatiles. Elastomeric sealants are prone to some surface degradation in these conditions; this may result in discoloration, chalking, crazing and, in extreme cases, surface cracking, which leads eventually to cohesive failures. The formulation and colour of these sealants will influence the kind of degradation observed in service.

Direct exposure to moisture may also have adverse effects on the performance of some sealants, either by its effects on the sealant or on the joint substrates.<sup>4</sup> Absorption of water may cause softening of the sealant material, and some acrylic-based sealants are particularly affected in this way. If absorption is followed by prolonged near-freezing temperatures, the sealant may become stiffer, leading to an increase in internal stresses as the joint opens. These stresses tend to promote failures of adhesion at the interface of the sealant and the joint surfaces. The repeated absorption of moisture by components of porous materials, such as concrete, may cause a gradual migration of soluble salts towards the sealant interface, which could lead to adhesion failure. This effect can be reduced by the application of appropriate primers to the joint faces before application of the sealant. It is essential to follow the advice of the sealant manufacturer in this respect.

For more information see articles on **Silicones: properties, Silicone adhesion** and specialized reviews on silicone<sup>5</sup> and polysulphide sealants.<sup>6</sup> **Sealants in double glazing** are the subject of a separate article.

### References

1. J. M. Klosowski and S. B. Smith, Sealant materials, in *Engineered Materials Handbook. Adhesives and Sealants*. Vol. 3, Section 3, ASM International, 1990, p. 187.
2. British Standards Institution, *Guide to Selection of Construction Sealants*, BS 6213, BSI, London, 2000.
3. Anon, *Manual of Good Practice in Sealant Application*, British Adhesives and Sealants Association and Construction Industry Research and Information Association, London, 1990.
4. J. C. Beech and C. Mansfield, The water resistance of sealants for construction, in *Building Sealants: Properties and Performance*, F. O'Connor, Ed., American Society for Testing and Materials, Philadelphia, 1990.
5. L. D. Lower and J. M. Klosowski, Silicone sealants and adhesives, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 813.
6. N. Akmal and A. M. Usmani, Polysulfide sealants and adhesives, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 531.

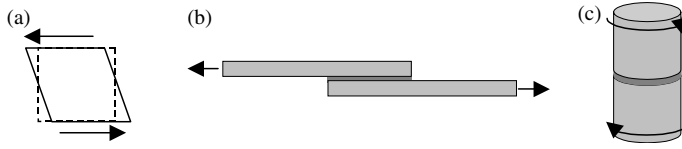
## Shear tests

A D CROCOMBE

### Introduction

Shear tests are generally carried out for one of two purposes. The first is to compare the performance of adhesives in a joint that is subjected to the most common type of loading, namely, shearing. Adhesive manufacturers use international standard test configurations whereas an adhesive user often tests a configuration that better resembles the joint under consideration. The second purpose is to determine the actual mechanical response of the adhesive for use in subsequent joint design; see **Engineering design with adhesives**. These two aspects are further discussed in the recent ASTM standard (D4896). In this article, a number of shear tests will be considered and the purpose of each discussed. Further information on these tests may be found in **Tests of adhesion, Stress distribution: shear lag solution, Stress distribution: beam on elastic foundation** and **Stress distribution: mode of failure** and also in other sources.<sup>1,2</sup> Many of the tests have been formalized in international standards and, where possible, examples have been cited from the ASTM, which is probably the most comprehensive. Where possible, the equivalent British Standard has also been cited.

Shear stresses cause sliding in an element of material as shown in Fig. 1(a). All shear tests are variants of either an overlap or a torsional joint and these are illustrated schematically in Figs. 1(b) and (c). The shear in the first is induced by transfer of the tensile/compressive load from one substrate to the other, while in the second it is caused by transfer of torsional loads from one substrate to the other. The tests have been grouped according to the manner in which the shearing has been induced.



**Fig. 1.** (a) shear deformation, (b) lap joint and (c) torsional joint

*Joints in shear by tension*

The first of these tests (D1002) is the standard metal–metal single lap joint test as portrayed in Fig. 1(b). Articles cited above illustrate that, although this is a simple configuration, rotation of the overlap causes adhesive stresses that are complex, including shear and direct (peel) stresses, both of which can be non-uniform. The non-uniformity increases with increasing adhesive stiffness and overlap length and decreasing substrate thickness. The result of this is that the test does not measure any true shear material properties. It is, however, valuable because it is simple and is typical of many bonded joint configurations. The double-lap joint (D3528) is essentially two single-lap joints, back to back. This eliminates the gross joint rotation, and generally, the strength of such configurations is more than twice the equivalent single-lap joint strength. However, the adhesive stresses still include non-uniform direct and shear components and thus this suffers the same limitations as the single-lap joint. The third test (D3165) is a variant of the first but is produced from two sheets bonded to form a laminate. This does not offer a significant improvement over the original single-lap joint except that it might be easier to produce. All but one of the other tests in the table use the single-lap joint to measure joint performance under other types of load and give joint, and not adhesive, properties.

The remaining test worthy of separate comment is the thick-lap shear test (D5656). This is an attempt to obtain true shear adhesive material data by removing the non-uniformity in the adhesive stresses by significantly increasing the thickness of the substrates in a single-lap joint. However, there are a number of limitations, which include difficulties in measuring the adhesive shear displacement accurately and also the continued presence of direct stresses in the adhesive. Further discussion of this technique can be found elsewhere.<sup>3,4</sup> Recently, another technique for measuring shear properties of adhesives by

ASTM classification	Purpose	BS classification
D1002	Static strength (single lap)	5350:C5
D3528	Static strength (double lap)	5350:C5
D3165	Static strength (laminate assy)	
D2295	Static strength, high temps	
D2557	Static strength, low temps	
D2294	Creep properties	5350:C7
D3166	Fatigue properties	
D2919	Joint durability	ISO 14615
D5656	Shear stress–strain data	ISO 11003-2

tension loading has been investigated, and is known as the *Arcan test*. A report<sup>5</sup> provides an assessment of this technique.

### *Joints in shear by compression*

When shearing the joint by application of a compressive rather than tensile load, the free substrate length is significantly reduced or eliminated to prevent buckling. Rotation of the joint is sometimes further restricted either by symmetric arrangement of the joint (D4562 axisymmetric or 5350:C15, a double lap version of D4501) or by physical constraint (D2293, D4027). In the first of these tests, a fairly standard single-lap joint is loaded in compression within a simple spring-loaded jig, thus facilitating the long-term exposure that is necessary for creep tests. The second test fixes the joint to massive carriers and uses a four-bar link to ensure that the substrates remain parallel (in principle, this could be loaded in tension or compression). As substrate deformation is minimized, this test can be used to measure adhesive material properties. The specimen can also be subjected to loading normal to the bond-line, and thus the response of the adhesive to combined loading can be obtained. The third test uses bonded blocks and provides a simple measure of compressive shear strength. The BS variant is in double-lap form and intended for very large (100-mm cubes). The final test is usually used to assess the performance of thread-locking adhesives and is the only axisymmetric configuration. Like most of the other joints in this section, the substrates are large and so the shear stress will be reasonably uniform.

ASTM Classification	Purpose	BS Classification
D2293	Creep properties	
D4027	Shear stress–strain and bi-axial failure criteria	
D4501	Shear strength – rigid substrates	5350:C15
D4562	Pin and bush shear strength	5350:G2

### *Shear by torsion*

This is generally known as the **Napkin ring test** and is a tubular version of the configuration shown in Fig. 1(c). Such tests are generally less common as they require specialized apparatus. Essentially, a moderately thin-walled cylindrical tube is made up by bonding annular discs, typically made of aluminium. This tube is then subjected to a torque and the adhesive is subjected to almost pure shear, which is almost constant if the radial thickness of the adhesive is small. As with the thick adherend test (D5656), careful extensometry is required to measure the small shear displacements that occur. Increasing the number of bonded rings will result in a larger rotational displacement. The BS variant of this test can only support a single bond-line. A version of this test is the bulk torsion test,

where a thin-walled cylinder is made completely from cured adhesive (either by casting or machining) and this is tested as an ordinary torsion specimen. As the shear displacement now occurs along the complete specimen length, rather than only the bond-line thickness, the displacements are much larger and easier to measure. Clearly, it is a simpler test, but specimen manufacture is more difficult and it is not applicable to film adhesives.

ASTM Classification	Purpose	BS Classification
E229	Shear stress–strain data	ISO 11003-1

### References

1. R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*, 2nd edn, Elsevier Applied Science Publishers, 1997.
2. A. J. Kinloch, *Adhesion and Adhesives*, Chapman and Hall, 1987.
3. R. B. Kreiger, Stress analysis concepts for adhesive bonding of aircraft primary structure, *Structural Adhesives in Engineering, Proc IMechE*, Bristol, 1986.
4. K. M. Leichi, T. Freda and T. Hayashi, Determining the constitutive and fracture properties of structural adhesives, *Proceedings of the 5th Adhesion Science Review*, Virginia Polytechnic, Blacksburg, Virginia, 1987.
5. G. D. Dean, B. C. Duncan, R. D. Adams, R. Thomas and L. Vaughn, Comparison of bulk and joints specimens for determining the shear properties of adhesives, NPL Report CMMT(B)51, National Physical Laboratory, 1996.

### Silane adhesion promoters

D G DIXON

Silanes, often referred to as organosilanes, are used as monomers, cross linkers or modifiers for polymers and are often used to coat glass, plastics and metals to modify their surface properties. In the field of adhesion, silanes are used as adhesion promoters. They can be incorporated into paints, sealants and adhesives or used as a separate surface treatment, which is applied before bonding (see **Pre-treatment of metals prior to bonding, Pre-treatment of metals prior to painting, Primers for adhesive bonding and Silanes as metal pre-treatments**). It is commonly considered that the effectiveness of the silane coupling agent is that it acts as a chemical bridge whereby one part of the molecule attaches to the substrate and another part bonds to the adhesive or polymer (see **Durability – fundamentals**). In this way, a strong and durable interface is generated that is resistant to water ingress. Plueddemann<sup>1</sup> consolidated and generated much of the early work in this area, which is still the subject of academic and industrial activity.<sup>2</sup>

The durability of adhesive bonds is critically dependent upon the surface treatment applied to the adherends, and the type of surface treatment selected for a particular application must be fit for purpose but must also be economically acceptable and practical.



Silanes have the advantage of being relatively easy to apply and can be used in small quantities; they are already used in both repair and manufacturing operations.

There are hundreds of commercially available silanes, but few have been extensively reported in the open literature. One of the most common types is  $\gamma$ -glycidoxypropyltrimethoxysilane or GPS. This has been widely investigated for the adhesive bonding of aluminium alloys and is of the general structure  $R-Si(OR')_3$  where R is an organofunctional group and R' is a group capable of hydrolysis. The silane must be hydrolysed before use, so when many silanes are applied, they are used in mixtures of water and alcohol. This choice of water and alcohol is used because the silanes do not dissolve readily in water and also because mixtures of water and alcohol wet a metal surface better. However, purely aqueous solutions appear to wet metal substrates if they have been abraded or grit blasted. A typical preparation method would be to mix a dilute solution of the silane (e.g. 2%), allow it to hydrolyse for a period of time (e.g. 1 h) and then apply it to the adherend substrate. Various application methods have been used including immersion, spraying and brushing. The treated adherend is then dried and bonded. Some procedures are strictly specific regarding the preparation, application and drying stages.

Good bond strengths and durability can be achieved with silane treatments and laboratory results can be consistent and reproducible but thorough and controlled preparation and applications practices should be followed. It is well known that the rate of hydrolysis is dependent upon the pH of the solution and that the silanes continue to change once they are mixed with water. Over-aged solutions will not produce effective coupling agents.

Specific silanes have been developed for inclusion in the formulation of paints and other coatings. These are more stable, giving a greater shelf life to the product. Silanes have also been proposed as coatings for corrosion protection.

Some silanes are also hazardous and need to be used with appropriate **Health and safety** considerations.

### References

1. E. P. Plueddemann, *Silane Coupling Agents*, 2nd edn, Plenum Publishing Corporation, New York, 1991, ISBN: 0306409577.
2. K. L. Mittal, *Silanes and Other Coupling Agents*, Vol. 2, VSP, 2000, ISBN: 9067643319.

---

### *Silanes as metal pre-treatments*

---

W J VAN OOIJ

Almost always the **Pre-treatment of metals prior to bonding** is essential to the successful use of adhesives. A more general discussion of **Primers for adhesive bonding** is given elsewhere: this article, which complements **Silane adhesion promoters**, provides detailed discussion of this important class of materials.

The term "silanes" is often loosely used to denote organofunctional silanes. Such molecules are of the type  $Y-(CH_2)_3-Si-(OX)_3$ , in which Y is an organofunctional group and OX is an ethoxy or methoxy group. In this example, the silane is a trialkoxy silane. Di- and mono alkoxy silanes and acetoxy silanes are also available commercially. This

Table 1. Some typical silanes used for metal pre-treatments

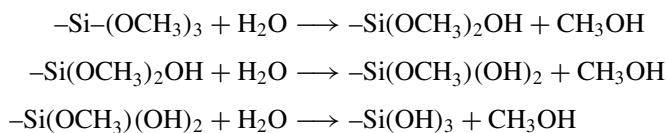
Structure	Name
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$	$\gamma$ -aminopropyltriethoxy silane
$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3$	bis-[trimethoxysilylpropyl]amine
$(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{S}_4-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$	bis-[triethoxysilylpropyl]tetrasulfide
$(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$	bis-[triethoxysilyl]ethane
$\text{H}_2\text{C}=\text{CH}-\text{Si}(\text{O}_2\text{C}_2\text{H}_5)_3$	vinyltriacetoxysilane

discussion here is limited to the trialkoxy silanes and the bis-silanes or dipodal silanes. The latter are of the type  $(\text{XO})_3-\text{Si}-(\text{CH}_2)_3\text{Y}-(\text{CH}_2)_3-(\text{Si}-\text{OX})_3$ , where the organofunctional group is now in the middle of the molecule. Some examples of several mono- and bis-silanes are given in Table 1.

Silanes have been used traditionally as additives to polymers or adhesives for cross-linking purposes.<sup>1</sup> Other large applications are as adhesion promoters between glass, glass fibres or silica particles and polymers (see **Fibre composites – introduction**). When used for adhesion purposes, they are often called coupling agents, as they are considered to couple the substrate literally to a polymer by forming covalent bonds to both. Recently, silanes have been proposed as metal pre-treatments for promoting adhesion to paints, rubbers or adhesives.<sup>2</sup> The background of this interest is an environmental one. Many pre-treatments, for example, in aerospace, consist of chromating a metal. A chromate film can give outstanding adhesion to many polymers and also provide unequalled corrosion protection of metals. In many applications, the use of chromates has recently been regulated, as they have been found to be toxic and carcinogenic. This has prompted an intensive search for chromate replacements. The use of silanes to replace chromates is a promising one, but more work needs to be done before robust treatments are available that can be used in industrial processes (see **Environment and the impact of adhesive technology** and **Environment: sustainability**).

On a laboratory scale, it has been demonstrated in recent years that thin films of silanes applied to metals can protect the metal from many forms of corrosion, including uniform corrosion, pitting corrosion, stress corrosion cracking, crevice corrosion and other forms, in addition to providing excellent and durable paint adhesion<sup>3</sup> (see **Durability – fundamentals**). Such thin films are typically of not more than 300-nm thickness. They can be applied by immersion of the metal into a dilute silane solution, for example, 5% in water or water/alcohol mixtures, as not all silanes dissolve in water. Brushing, wiping or spraying application methods can also be used.

In such solutions, the silane is typically first hydrolysed:



This hydrolysis reaction is rather slow and occurs in discrete steps with different reaction rates. The reason that the silane is commercially available as an ester (a colourless, stable

liquid) is that after hydrolysis the  $-\text{SiOH}$  groups (silanol) groups are not stable. They react with themselves and form siloxane units:



This condensation continues and a complex mixture of oligomers is eventually formed in the solution. When the degree of condensation is around 4, the silane becomes insoluble and the solution becomes cloudy. Both hydrolysis and condensation reactions are catalysed by  $\text{H}^+$  and by  $\text{OH}^-$ . Thus, they are strongly dependent on pH. For most silanes, the rate of hydrolysis is minimum at  $\text{pH} = 7$ , whereas that of the condensation reaction is minimum at  $\text{pH} = 4$ . Since the performance of silane films has been shown to be best if formed from solutions that contain the maximum number of silanol groups, the condensation reaction should be minimized and the hydrolysis maximized. Thus, the optimum pH for film deposition is 4 for most silanes.

The interaction between a silane molecule containing some silanol groups and a glass or a metal surface is believed to be through the interaction between the acidic silanol groups and the basic hydroxyl groups on the substrate surface:



However, the formation of such bonds is very difficult to demonstrate uniquely and most of the evidence presented is circumstantial or indirect (see **Primary bonding at the interface**). Other theories have also been put forward, but the covalent bond theory remains the most widely accepted one.<sup>1</sup> The remaining silane groups on the silicon atom can then condense with themselves so that a three-dimensional network is believed to be formed that is of the type shown in Fig. 1.

The bond between the polymer and the silane film is formed by a chemical reaction between the functional groups of the silane and a functional group in the polymer. However, good adhesion has also been obtained with silanes that do not contain an organofunctional group such as bis-tri[ethoxysilyl]ethane (BTSE, Table 1). In such cases, it is assumed that the penetration of the polymer into the three-dimensional siloxane network with formation of an interpenetrating network also plays a role in the adhesion mechanism.

Figure 1 can be used to explain the corrosion protection capabilities of silane films. This type of highly organized three-dimensional films is formed by bis-silanes only. A monosilane cannot form an interface containing many metallo-siloxane bonds and at the same time build the film up to a certain thickness. The film of a monosilane is, therefore, inherently porous. Thus, such films do *not* provide corrosion protection, despite the good adhesion that can be obtained with them. The more highly organized films of bis-silanes provide much better corrosion protection because they are hydrophobic and protect the interface against attack by water.<sup>2,3</sup> Such protection is necessary, as the covalent metallo-siloxane bonds are not resistant to water. When water reaches the interface, the reaction:





---

## Silicone adhesion

---

B PARBHOO

Silicone polymeric materials are used in a variety of forms such as pure fluids, emulsions, solvent-based formulations, resins, elastomers and so on. They are formulated in numerous products for various applications involving different processes across many different industries. Some of these products where adhesion plays a major role are adhesives, coatings, encapsulants, hair conditioners, **Pressure-sensitive adhesives**, mould **Release agents**, **Sealants**, skin creams and so on.

The phenomenon of adhesion in silicones goes beyond the common adhesive application where, in its strict definition, the adhesive is used to bond two different materials together. There are a variety of silicone products where by putting a silicone layer, the two newly created interfaces are very different in nature and adhesion properties. Solid/silicone and silicone/liquid interfaces are, for example, exploited in anti-fouling applications. Solid/silicone and silicone/organic polymer interfaces form the basis of release coatings for pressure-sensitive adhesives. Solid/silicone and silicone/air interfaces are used in protective coatings. In all these applications, adhesion property is essential, and in most applications, a differential strength is needed. This is well illustrated by silicone release coatings of organic PSAs where adhesion strength to the substrate has to be very high and reaching  $\text{kJ m}^{-2}$  levels and where adhesion strength at the silicone/organic interface needs to be in the range of  $\text{mJ m}^{-2}$  to  $\text{J m}^{-2}$  (see **Pressure-sensitive adhesives – adhesion properties**).

The wide choice of chemical functional groups that can be attached to silicone polymers has opened up routes to several cross-linking mechanisms. As a consequence, networks can be varied in a wide range of architectures. Cure conversion rates can proceed from a fraction of a second to hours, and in a wide range of temperatures. Silicone products respond to very demanding requirements that are dictated by applications that organic adhesives cannot respond to.

In addition, the structure of the uncured materials can be selected to fit a variety of industrial application processes. Thus, they are used in **Aerospace applications**, **Automotive applications**, as **Adhesives in the textile industry** and in building, electronic, healthcare, energy, medical, paper and personal care industries (see **Adhesion in medicine**).

The choice of the cure system can be guided by a variety of parameters that includes cure time and temperature, rheological properties in relation with the application process, surface properties of substrates, the environment the adhesive joints will be subjected to, and its subsequent durability, and of course, cost.

The performance of an adhesive product applied as a sealant, coating, potting, or adhesive joint where adhesion plays a role is determined both by its adhesive and cohesive properties. The promotion of adhesion and cohesion strength is therefore an essential step in the development of highly performing products.

Examination of the cure chemistry of silicones will reveal if organofunctional or inorganic groups can form linkages between the cross-linked network and substrates such as glass, silicon wafers, fabrics, papers, ceramics, reactive metals, plastics, silicones, and so on. Therefore, adhesion promotion by either adding a coupling agent into the silicone system and/or pre-treating the substrate may be necessary. Depending therefore on the silicone system and the substrate, silicone adhesives, sealants and coatings are formulated in *unprimed*, *primed* or *self-primed* forms.

An unprimed silicone adhesive implies that it is free of any adhesion promoter. The substrate on the other hand, may still need to be activated or primed. Adhesion relies mainly on *chemical* and/or *mechanical* mechanisms (see **Mechanical theory of adhesion** and **Primary bonding at the interface**). The chemical adhesion depends on both the reactivity of the selected silicone cure system and on the natural presence of reactive groups on the surface of the substrates.

**Primers for adhesive bonding** chemically functionalize the substrate surface to provide pathways for chemical bonding with a selected silicone cure system. The increase of chemical bond improves adhesion durability. The main disadvantage of priming the substrate is the addition of an extra step in the whole process of adhesive application. The primers are usually **Silane adhesion promoters**, a reactive alkoxy silane molecule, oligomer, or a mixture of two or more different silanes.

Another process that promotes chemical adhesion is the pre-treatment of low energy surface materials. This can be considered as a “dry” priming process, as no wet chemicals are used. **Corona discharge treatment**, dielectric barrier discharge, flame and **Plasma treatment** are widely used techniques in **Pre-treatments of polyolefins**. This reactive surface allows chemical bonding with the applied adhesive.

The ideal silicone adhesive is one that is self-primed. The adhesion promoter is included in the formulation and is generally part of the curing reaction system. This is the most desired type of adhesive as it provides adhesion without the need for a complicated pre-treatment procedure. All the art and technology of a self-priming polymeric system resides in the choice and chemical design of the adhesion promoter molecules.

Along with adhesion strength, cohesion strength is essential. The balance of these two strengths will determine the performance of the adhesive joint. The cohesive strength of a pure non-reinforced silicone network is relatively low, with the fracture energy in the region of several  $\text{J m}^{-2}$ . Inorganic fillers such as silica and calcium carbonate are added to the silicone base to transform the network into a highly elastomeric material. This results in the improvement of mechanical properties such as tensile strength, tear strength, elongation at break and hardness. The impact of bulk elastomeric properties on the performance of an adhesive is clear. Indeed, high elongation and low modulus characteristics will help absorb a lot of the stress introduced to the joint and will decouple the adherence energy.

Fillers can also be used to promote or enhance the thermal stability of the silicone adhesive. Normal silicone systems can withstand exposure to temperatures of 200°C for long hours without degradation. However, in some applications, the silicone adhesive must withstand exposure to temperatures of 280°C. This can be achieved by adding thermal stabilizers to the adhesive formulation.

Related articles are **Silicone adhesives: condensation cure** and **Silicone adhesives: addition cure**.

### Select References

- K. L. Mittal and A. Pizzi, Eds., *Adhesion Promotion Techniques – Technological Applications*, Marcel Dekker, New York, 1999.
- S. J. Clarson and J. A. Semlyen, Eds., *Siloxane Polymers, Polymer Science and Technology Series*, PTR Prentice Hall, 1993.
- B. Parbhoo, L.-A. O’Hare and S. R. Leadley, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 677–710.

---

**Silicone adhesives: addition cure**

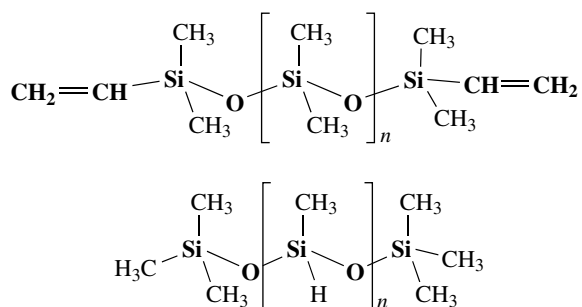

---

B PARBHOO

Part of the wide variety in **Silicone: structures** results from different curing mechanisms. Silicone adhesives may cure by addition or condensation reactions; the former is considered here, the latter in **Silicone adhesives: condensation cure**.

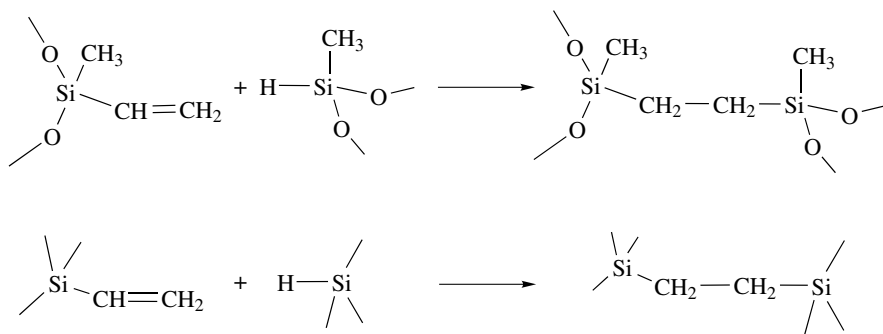
The addition cure systems have been developed for rapid processing and fast rate of deep section cure (see **Chain polymerization**). The rate of cure of addition cross-linking reactions is faster than condensation cure. No by-products are formed in the cross-linking reaction, and adhesion in most cases develops rapidly. The polymers can be selected over a wide range of chain lengths, giving formulations of a wide range of viscosities. Incorporation of fillers provides adhesive materials with excellent mechanical properties. In contrast to the condensation systems, adhesion promotion is often necessary for addition cure systems.

There are numerous applications where cure reaction by-products are not acceptable as they may contaminate other sensitive areas of the devices, and where fast deep section cure is required. These constraints have directed the choice to the platinum-catalyzed hydrosilylation addition cure system. The reaction involves the addition of a hydrido silane (SiH) to an alkenyl organic group ( $-\text{CH}=\text{CH}_2$ ), typically the vinyl or hexenyl groups. The product of the reaction is the ethylenic bridge ( $-\text{CH}_2-\text{CH}_2-$ ). The alkenyl groups are usually placed at the end of the polymer base chains in structures such as  $\text{M}^{\text{Vi}}-\text{D}_n-\text{M}^{\text{Vi}}$ . The SiH groups are usually placed in a combed structure within the polymeric or copolymeric chains called cross-linker:  $\text{M}-\text{D}_y^{\text{H}}-\text{M}$  or  $\text{M}-\text{D}_x-\text{D}_y^{\text{H}}-\text{M}$ . (The M, D, etc. nomenclature is explained in **Silicones: structures**.) Typical values of  $n$  cover a wide range from 100 to 1000, while the values of  $x$  and  $y$  vary from 3 to 100.



**Scheme 1.** Molecular structures of vinyl polymer and SiH cross-linker polysiloxanes

Products that are based on hydrosilylation cure system can be packaged in one or two parts. As the term suggests, in one-part systems, all the ingredients are formulated together. The catalytic system is inhibited by chemical means that significantly reduces or prevents the cure at room temperature. In the two-parts systems, the polymer and the cross-linker are packaged separately in so-called polymer base and cross-linker system. The catalyst, the inhibitor, the fillers and other additives, including the adhesion promoter, are formulated with one or the other parts of the package depending on their chemical reactivity. Overall, a silicone adhesive formulation based on the hydrosilylation reaction may contain seven components as described in Table 1.



**Scheme 2.** Reaction of hydrosilylation

*Table 1.* Typical components of a silicone adhesive based on hydrosilylation addition cure system

Component	Polymer/additive	Function
Polymer	Alkenyl functionalized PDMS	Backbone of silicone-cured network
Cross linker	Si-H functionalized polymer	Cross-links alkenyl PDMS
Catalyst	Platinum-based complex	Fast and controlled cure at room or high temperature
Inhibitor	Various organic or organosilicone types	Delays cure at room temperature and increases pot or bath life
Inorganic or organic filler	Silica, carbon black	Reinforces the mechanical strength
Pigment	Various metallic oxides	Colour/thermal stability
Adhesion promoter	Various silanes and proprietary complex compounds	Enhance adhesion of silicone to specific substrates. Prolonged durability

When formulating a silicone adhesive, **Sealant**, or coating, based on hydrosilylation addition cure, one must consider the following properties of the uncured product: pot life, dispensing technique, rheology, extrusion rate and cure performance. These characteristics directly affect the processing properties of the polymer base or cross-linker parts. The degree of cure conversion at the temperature of interest is determined by properties such as tack free time, cure profile and cure time. Once cured, the typical mechanical properties of the cured silicone can be evaluated, which include hardness, tear strength, tensile strength and elongation at break. In addition to required adhesive properties, considerations should be taken of thermal conductivity, thermal expansion, resistance to flammability, dielectric properties, volume resistivity and dissipation factors. Typical properties that characterize a silicone adhesive are based on standard published **Standards for adhesives and adhesion**.

Silicone adhesives and sealants are used in many advanced fields of technology where extreme environmental conditions are experienced, for example, in **Aerospace applications**, as coatings for firewalls, windshields and other thermal barriers, and for corrosion protection.

Silicone materials are successful in a wide range of applications – adhesives, sealants, coatings, encapsulants, and so on. This success is associated with mechanical properties, which range from liquid-like polymers to filled elastomeric networks and with insensitivity



to wide temperature variations. Further, they exhibit low surface energy and show potential for specific reactivity to selected substrates.

### Select References

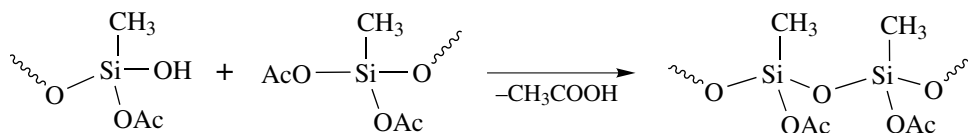
- S. J. Clarson and J. A. Semlyen, Eds., *Siloxane Polymers, Polymer Science and Technology Series*, PTR Prentice Hall, 1993.
- B. Parbhoo, L.-A. O'Hare and S. R. Leadley, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 677–710.

## Silicone adhesives: condensation cure

B PARBHOO

Silicones are widely used in industry, for example, as adhesives, **sealants** and **release agents**; see **Silicone: properties** and **Silicone adhesion**. Silicone adhesives may cure by condensation or addition reactions. The former is considered here and the latter in **Silicone adhesives: addition cure** (see also **Step polymerization**).

Condensation reaction chemistry of silicones can be divided in two sub-groups. One sub-group is the moisture condensation cure system where, as the name implies, moisture in the air is utilized for hydrolysis reactions that lead to cross-linking of the polymer chains. The cross-linking reaction proceeds from the surface into the bulk and generally takes place at room temperature. The second sub-group is based on direct condensation reactions between polymers with different functional groups (cf. Scheme 1). These latter cure systems offer adhesives with fast rate of deep section cure at both room and elevated temperature.



**Scheme 1.** Example of a condensation reaction. Ac represents the acetyl group

Silicone **Sealants** are mainly based on condensation cure chemistry and are used in the building industry as sealing, adhesive, or coating materials in view of their outstanding durability under a variety of weathering conditions. They provide a barrier against specific environmental influences, which may include humidity, rain, still or pressurized water, draughts, gases, noise, sand and dust. They can be used in the presence of many chemical compounds and can be exposed to UV radiation without showing any sign of deterioration. The transparency to light and the ability of incorporating pigments make silicones suitable as building sealants. The low chain-to-chain intermolecular interactions in PDMS result in silicone elastomers with very low modulus, which reduces permanent joint stresses and

increases longevity of assemblages. The high elastomeric property of silicone sealants gives them the ability to absorb movements. They can sustain 25–30% joint movement as expressed as the percentage of initial joint width. This allows silicone sealants to be used in applications where the adhesive is required to absorb movements of the joint without tearing apart from the substrate.

The role played by the various ingredients in the composition of sealant and, in particular, on the durability of adhesion has been discussed recently. Inert plasticizers, such as trimethylsilyl-*end*blocked-PDMS, are typically added to silicone sealant compositions in order to adjust the rheology of the uncured sealant. They result in a reduction of the modulus and hardness of the cured sealant. Differences in the durability of silicone sealants are found to be due to differences in their cure chemistry and, more specifically, to the nature and concentration of the catalyst and cross-linker. Adhesion promoters are often added in the formulation of a sealant to improve its adhesion to a substrate.

The formulation of a typical silicone adhesive based on condensation cure may contain up to 10 components as described in Table 1.

Acetoxy sealants are widely being used in a large number of applications in the construction industry. Where they are incompatible with specific substrates, they can be replaced by neutral cure systems. The alkoxy and oxime cure systems are available in either transparent (silica-filled composition only), or non-transparent/solid colour (silica- and/or chalk-filled composition containing appropriate pigment) versions. Their chemical neutrality enables these systems to offer a wide range of adhesive-bonding capabilities to

Table 1. Typical components of a silicone adhesive/sealant based on condensation cure system

Component	Typical chemical	Function
Polymer	Hydroxyl $\sim\text{SiOH}$ ,	Backbone required to form the elastomeric network
Reinforcing fillers (active)	Fumed silica ( $\text{SiO}_2$ ); Precipitated calcium carbonate ( $\text{CaCO}_3$ ); carbon black	Thixotropic reinforcing agents (non-slump), adjustment of mechanical properties (cohesion); provide toughness to the elastomer as opposed to brittle materials
Non-reinforcing fillers (passive)	Ground calcium carbonate ( $\text{CaCO}_3$ )	Reduce formulation cost; adjust rheology, and mechanical properties
Cross-linkers	Acetoxy $\sim\text{Si}(\text{OOCCH}_3)_3$ Alkoxy $\sim\text{Si}(\text{OR})_3$ Oxime $\sim\text{Si}(\text{ON}=\text{CRR}')_3$ Amine $\sim\text{Si}(\text{NHR})_3$	Cross-linking of the polymeric component; provide network structure
Catalysts	Organic complexes of Sn, Ti, Pt, Zn, Rh.	Cure the network and control of the rate of the curing process
Adhesion promoter	$\text{X}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OR})_3$	Enhances adhesion to substrates
Specific additives	Water scavenger Pigments Rheology additive Biocides	Prolonging shelf life Offering wide range of colours Adjust <i>ease-of-use</i> characteristics and features. Provide fungus growth resistance, e.g. sealing of sanitary devices and equipments

Note: Typically: R and R' =  $-\text{CH}_3$  or  $-\text{CH}_2\text{CH}_3$

X = organic functional group, for example, amino, mercapto, vinyl, epoxy, methacryloxy

metals (copper, brass, zinc, galvanized steel, aluminium), polyester powder coated metals, and all sorts of brick, concrete masonry, and marble.

Both the adhesive and sealant properties of silicones are used as **Sealants in double glazing** and in building structural glazing. The adhesive supports the glazed panels while absorbing differential movements between dissimilar materials, which can be induced by thermal fluctuations, seismic loading, or bomb blasting. The sealant improves the air and weather tightness of the structure.

The **Selection of joint sealants** and of the cure system in these applications is directed by constraints such as location of the adhesive in terms of confined space, speed and depth of cure, and so on. In general, the uncured adhesive needs to be dispensed in a well-defined and limited area and needs to stay in place without flowing during cure.

### Select References

- S. J. Clarson and J. A. Semlyen, Eds., *Siloxane Polymers, Polymer Science and Technology Series*, PTR Prentice Hall, 1993.
- B. Parbhoo, L.-A. O'Hare and S. R. Leadley, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 677–710.

---

## Silicone properties

---

B PARBHOO

Silicones are a group of polymers with varied and interesting surface properties. The complexity of their chemical constitution is described in **Silicones: structures**. In this article, some of the consequent properties are considered.

Linear PDMS (polydimethylsiloxane) polymers are colourless fluids available in a range of viscosities, depending on chain length. The value of  $n$  in the common linear trimethylsiloxy-end blocked-polydimethylsiloxane (TMS-eb-PDMS),  $(M-D_n-M)$  can vary from zero to tens of thousands, giving a range of viscosity from 0.65 to 2,500,000 cP (1 cP = 1 Pa.s) to the polymeric material. This structural property allows PDMS polymers to vary in form from “water-like” fluids to flowable gums, while retaining the same physico-chemical properties. Silicone products requiring adhesion property are generally applied in an uncured liquid state and can therefore be formulated in a wide range of viscosities.

The curing process takes advantage of the versatile chemical property of silicones. Chemical reactivity is built in the polymer and allows the formation of silicone networks of controlled molecular architectures with specific adhesion properties. The general and inherent molecular properties of the PDMS polymer are conferred to the silicone network. Pure PDMS networks are mechanically weak and do not satisfy the adhesive and cohesive requirements needed for most applications. Incorporation of fillers like silica or calcium carbonate is necessary to reinforce the silicone network (see **Composite materials**).

The low surface tension of liquid PDMS ( $20 \text{ mN m}^{-1}$ ) results from the combination of the surface properties of organic side groups and the molecular flexibility of the inorganic

backbone (see **Surface energy**). The surface tension of PDMS is one of the lowest available, which means that they wet and spread over almost any material, thus fulfilling the first requirement of any adhesive system. The low **Critical surface tension** of wetting of PDMS cross-linked surfaces ( $24 \text{ mN m}^{-1}$ ) explains one of the most familiar features of silicone polymers: their low adhesion surface property that is at the origin of **Release** property and prevent most materials from strongly adhering to them. Another significant consequence of the differences between surface tension and critical surface tension of silicones is that PDMS will wet and spread over a surface of silicone (see **Wetting and spreading**).

The molecular structure of the siloxane backbone results in a polymeric material that has a large free volume and high chain mobility. The polymer exhibits a low **Glass transition temperature** ( $T_g -125^\circ\text{C}$ ) and crystallization behaviour with a melting transition temperature ( $T_m -40^\circ\text{C}$ ). Silicone sealants do not substantially stiffen at lower service temperature. Typically, their Young's modulus is maintained within a  $\pm 25\%$  range over a temperature range of  $-40$  to  $80^\circ\text{C}$ . The large free volume and mobility of polysiloxanes give rise to a high diffusion coefficient and high permeability of gases and vapours. These properties determine the rate of cure of condensation cure adhesive formulations.

The common atmospheric agents like ultraviolet radiations, ozone, nitrogen oxides and acidic rain do not noticeably attack silicone materials. However, high-energy radiation does cross-link PDMS networks through radical chemistry of organic groups. This cross-linking increases the cohesive strength of the adhesive.

Another important property of silicones is their high thermal stability compared to common organic polymers (see **High-temperature stability principles**). TMS-eb-PDMS polymers stay unaffected when exposed to inert and oxidative atmospheres at higher temperatures than organic polymers can. Either partially replacing methyl groups by phenyl groups or by adding thermal stabilizers can further improve this outstanding thermal stability of silicone polymers. This stability towards thermal energy opened up new windows of opportunities for silicone adhesives.

The success of silicones adhesives is further due to a range of properties derived from the primary chemical structure. These include hydrophilicity/hydrophobicity balance, chemical resistance, electrical insulation, resistance to weathering, stability to extremes of temperature, resistance to thermal shocks, high elasticity, good tear strengths, capability to seal or bond materials of various natures, good electrical resistance, and so on.

In the quest for the ideal adhesive system to suit an application needs, it is essential to understand the effect of the silicone properties on the mechanisms of **Silicone adhesion**. The primary requirement for good adhesion is the creation of an intimate interface through **Wetting and spreading** of the silicone onto the substrate. The low surface tension and viscosity range of silicones satisfy this necessary condition. Therefore, the mechanical mechanism of adhesion is operative and plays a key role in adhesion of silicones to many different substrates such as leather, textile fabrics, porous metals like anodized aluminium, porous plastic and composite materials, and specialty papers like glassine, super calendered kraft and clay-coated papers.

When a polymeric and rubbery substrate is put on contact with silicones, interdiffusion of polymer chains may occur (see **Polymer diffusion: reptation and interdigitation** and **Compatibility**). The original interface becomes an interphase composed of mixtures of the two polymeric materials. Such a macromolecular interdiffusion process is limited

unless polymer chains in the adhesive and the substrate are both mobile and miscible (see **Polymer–polymer adhesion: incompatible interfaces**).

The physical bonding mechanism relies on van der Waals and London **Dispersion forces**. This omnipresent mechanism is favoured by the low surface energy and high degree of mobility of the polymeric chains. It is the basis of the **Release** property of silicone rubbers and coatings.

The chemical bonding mechanism strongly depends on both the reactivity of the selected silicone cure system and the presence of reactive groups on the surface of the substrate. The silicone adhesive can be formulated so that there is an excess of these reactive groups, which can react with the substrate to form covalent bonds. It is also possible to enhance chemical bonding through the use of adhesion promoters or chemical modification of the substrate surface. The mechanism of chemical adhesion is probably best studied and demonstrated by the use of **Silane adhesion promoters**.

Owing to the surface properties of silicones, presence of low molecular weight cyclic and linear PDMS chains, and their mobility, the formation of weak boundary layers can be formed. Typically, the locus of failure becomes truly interfacial. This mechanism has been exploited as an advantage in the release industry. It could, however, hinder strong adhesion in other areas of technologies.

The combination of the unique bulk characteristics of the silicone networks, the surface properties of the PDMS segments and the specificity and controllability of the reactive groups produces materials such as adhesives, protective encapsulants, coatings and sealants, where adhesion in one of the required property.

### Select References

- S. J. Clarson and J. A. Semlyen, Eds., *Siloxane Polymers, Polymer Science and Technology Series*, PTR Prentice Hall, 1993.
- A. Lee Smith, Ed., *The Analytical Chemistry of Silicones, Vol. 112 Chemical Analysis*, John Wiley & Sons, New York, 1991.
- B. Parbhoo, L.-A. O'Hare and S. R. Leadley, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 677–710.

## Silicone structures

B PARBHOO

Silicones are complex group of materials used as **Sealants** and adhesives (including **Pressure-sensitive adhesives**) and also find application in reducing **Mould adhesion and fouling**. In this article, the chemical structures underlying this range of properties are explored.

Silicone materials are essentially based on linear polydimethylsiloxane (PDMS) polymer. Its molecular structure,  $[-(\text{CH}_3)_2\text{SiO}]_n-$ , consists of a backbone made of siloxane (SiOSi) linkages with two methyl groups attached to the silicon atom. The combination of inorganic and organic molecular moieties results in materials that exhibit unique physical, chemical and mechanical properties.

The possibility of functionalizing PDMS polymers by replacing few of the methyl groups with a type of organofunctional groups leads to chemically reactive polymers. This built-in reactivity allows creating three-dimensional polymeric networks by reacting the polymers with appropriate cross-linkers. The process of cross-linking turns the fluidic polymer into an elastomeric material. Appropriate choice of polymer and cross-linker structures and of cross-linking reaction provide materials with a wide range of network structures and physical properties. Incorporation of adhesion and cohesion promoters and other additives results in a variety of products where adhesion varies enormously: adhesion fracture energies (see **Peel tests**) from very low ( $\text{mJ m}^{-2}$ ) to very high ( $\text{kJ m}^{-2}$ ) and where durability (see **Durability – fundamentals**) can be tailored to various product needs.

Applications requiring low adhesion take advantage of the surface properties of the methyl groups (see **Mould adhesion and fouling**). They include liquid silicone rubber (LSR) used in moulding applications, silicone **Release** coatings to dispense organic **Pressure-sensitive adhesives** (PSA) and silicone PSAs.

Product technologies that have high adhesion include elastomeric adhesives and sealants (see **Silicone adhesion** and **Rubber-based adhesives**). Their adhesive strength reflects both adhesion and cohesion properties (see **Peel tests** and **Rheological theory**). In each of these product technologies, the unique physico-chemical properties of silicones, in general, and in adhesion, in particular, originate from the atomic and chemical bond structures of the PDMS backbone.

The hydrogen, carbon, oxygen and silicon atoms in PDMS are assembled in a structure of interesting geometry. Although PDMS, polyethylene and polyether all have the basic tetrahedral geometry, the structural characteristics of PDMS are markedly different. A comparison with typical hydrocarbon and polyether readily shows the particularities of the polysiloxane. The bond lengths of C–C, C–O and Si–O are 0.154, 0.142 and 0.163 nm, respectively. The bond angles of C–C–C, C–O–C and Si–O–Si are 112, 111 and  $130^\circ$ , respectively. The polysiloxane system has the most open structure with the flattest angle and longest bond length. In contrast to hydrocarbon systems where the bond angles are fixed in a tetrahedral geometry, the Si–O–Si bond angle shows a much wider variability. This contributes to the variety and ease of interconversion of molecular configurations and leads to unique flexibility of the polysiloxane backbone. The energy required for rotation about the C–C bond in an organic polymer is  $13.8 \text{ kJ mol}^{-1}$ . In PDMS, this rotation energy is almost zero, and rotation is virtually free. As a consequence, the methyl groups are able to closely pack at the surface because of their low intermolecular forces and the large Si–O–Si bond angle. The lower Si electronegativity (1.8) versus C (2.5) leads to a very polarized Si–O bond, highly ionic and with a large bond energy of  $452 \text{ kJ mol}^{-1}$ . In contrast, the Si–C bond has energy of  $318 \text{ kJ mol}^{-1}$ , slightly lower than a C–C bond. These values partially explain the thermal stability of silicones. The Si–O bond is highly resistant to homolytic scission. On the other hand, however, heterolytic scissions are easy and facilitated by traces of acid or base.

The differences in molecular geometries between hydrocarbons, polyethers and polysiloxanes explain the large differences in their macroscopic properties.

The tetravalent silicon atom, the methyl groups and the oxygen atom allow the build-up of four basic siloxane tetrahedral-like structures:  $(\text{CH}_3)_3\text{SiO}-$ ,  $-(\text{CH}_3)_2\text{SiO}_{2/2}-$ ,  $-(\text{CH}_3)\text{SiO}_{3/2}-$ ,  $-\text{SiO}_{4/2}-$ . These are respectively denoted as M, D, T, and Q siloxy units. The fractions 2/2, 3/2 and 4/2 represent the share of each oxygen atom with a

neighbouring silicon atom in a polysiloxane network. The combination of M and D units, for example, leads to the linear PDMS and is represented as  $M-D_n-M$ . In a functionalized PDMS, where a methyl group is replaced by an organofunctional group X in D units, the symbol becomes  $D^X$ . A linear copolymer made of D and  $D^X$  units will be symbolized as  $M-D_n-D^X-M$ . The combination of M, D, T and Q units leads to a variety of polysiloxane polymeric structures. Linear, branched and hyperbranched structures result in materials in vapour, liquid or resin states and that can be inert or highly reactive.

Related articles discuss **Silicones: properties**, **Silicone adhesives: addition cure** and **Silicone adhesives: condensation cure**.

### Select References

- S. J. Clarson and J. A. Semlyen, Eds., *Siloxane Polymers, Polymer Science and Technology Series*, PTR Prentice Hall, 1993.
- A. Lee Smith, Ed., *The Analytical Chemistry of Silicones*, Vol. 112 Chemical Analysis, John Wiley & Sons, New York, 1991.
- B. Parbhoo, L.-A. O'Hare and S. R. Leadley, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 677–710.

## Solvent welding

C M WARWICK

### Introduction

Polymers may be joined by adhesive bonding or by some sort of interdiffusion (see **Polymer diffusion: reptation and interdigitation** and **Polymer–polymer adhesion: weld strength**). Diffusion may be accelerated by supplying energy (see **Welding plastics – electromagnetic radiation**, **Welding plastics – mechanical movement** and **Welding plastics – external heating**) or by use of a solvent, as in solvent welding.

Solvent welding and solvent cementing are widely used techniques for the joining of thermoplastic polymers. A small amount of solvent along the joint promotes interdiffusion of polymer chains between the substrates. This creates a permanent weld, with no additional phases or potentially weak interfaces. A solvent cement is a solution of the polymer being joined. This also promotes interdiffusion, and leaves a single-phase joint when the solvent has evaporated.

In some cases, a joint can be prepared with strength equivalent to that of the parent material. More usually, residual solvent will cause some loss of strength in the region of the weld. Nevertheless, solvent welding can give joints as strong as those produced by other techniques, and its low cost has led to use in a range of applications.<sup>1</sup> The process is used for mass production of toys and tamper-proof packaging and is widely employed for assembly of joints in PVC pipes. It is most often used to join two substrates of the same polymer where problems of **Compatibility** do not arise. However, joining of PVC to PMMA or polycarbonate has also been demonstrated.<sup>2</sup>

### *Principles of solvent welding*

The formation of a weld between two components during the solvent welding process relies on interdiffusion across the interface. As with other polymer joining techniques, this interdiffusion depends on time, temperature and pressure. The **Glass transition temperature**,  $T_g$ , of the polymer is reduced by the introduction of solvent, allowing welds to form at lower temperatures than other techniques. Solvent is applied to the two substrates to be joined and it diffuses into the surfaces. This creates a softened layer where the mobility of the polymer chains is increased. This does not occur with highly crystalline polymers, so the process is best suited to amorphous polymers. The two substrates are pressed together and held in place for a time between a few seconds and a few minutes (depending on the materials) to allow interdiffusion to create a weld. The applied pressure is then removed and the joint left for a longer period of time to allow desorption of the solvent. Generally, a solvent-affected zone (SAZ), typically between 50 and 500  $\mu\text{m}$  across, is seen on either side of the weld. As solvent is desorbed, the properties may approach those of the bulk material, but there will usually be some retained solvent, leading to a reduction in mechanical properties in the SAZ.

### *Critical parameters*

An appropriate solvent is essential to produce a strong weld. Although the process is generally robust, if too little or too much solvent is applied then a poor weld can result. Excess solvent can be allowed to evaporate before assembly of the joint. Good fit and smooth substrates help to give a strong weld.

Preheating can ensure that the substrate is dry and can accelerate diffusion of solvent into the surface. However, it is important that the solvent does not simply evaporate from the surface before the parts are brought together. Sufficient time is required for the solvent to diffuse into the substrate and for excess solvent to evaporate. Application of high pressure and a longer time can help generate a strong weld, particularly with rough substrates or if the fit is poor.

Both heat and vacuum assist in desorption of the solvent and promote a strong weld. However, to avoid incurring additional processing costs, most applications rely on desorption at ambient temperature and pressure.

### *Selection of solvent*

A wide range of amorphous or partially crystalline polymers can be joined using solvent welding. A compatible solvent with a solubility parameter matched to that of the polymer should be used. Some typical combinations of polymer and solvent are given in Table 1. Mixtures of solvents may also be used to promote strong welds.

### *Solvent cementing*

Solvent cementing describes a process in which a solution of the polymer being joined is applied to the substrates. This may be preceded by application of a primer (solvent) to the substrate to facilitate interdiffusion. Use of solvent cement can help fill gaps, allowing



Table 1. Solvent selection for solvent welding

Polymer	Solvents
Acrylic	Dichloromethane, dichloroethane
PVC	Tetrahydrofuran
Polystyrene	Toluene, dichloroethane, methyl ethyl ketone
Polysulphone	Dichloromethane
Polycarbonate	Dichloromethane
Polyamide	Phenol, resorcinol or cresols in aqueous or alcoholic solutions, calcium chloride in alcoholic solution

lower applied pressure during welding and/or greater tolerances on the parts. The higher viscosity of the solvent cement compared to solvent alone facilitates accurate dispensing and helps to avoid contamination of areas outside the joint. For these reasons, solvent cementing is widely used in applications such as joining of PVC pipes.

Many proprietary solvent cements are available. These typically contain the relevant polymer dissolved in a mixture of solvents. They usually have only a limited storage life and are prone to formation of a gel. Adding a small amount of the original solvent and mixing can recover cement that has started to gel. However, there is a risk that the resulting solution will either contain the incorrect balance of solvents, or not be fully mixed, either of which could lead to inconsistent results during welding.

### Procedure

A solvent-welded joint cannot be dismantled and can only be repositioned for a short time after the parts are brought together. Therefore, the fit of the parts should be checked before commencing, to ensure that the joint can be easily assembled. The mating surfaces are cleaned using a reagent that does not dissolve the polymer, and then a suitable solvent or solvent cement is applied. The surfaces are kept open for a short time to allow absorption of the solvent into the polymer and to allow excess solvent to evaporate. The joint is assembled and held under pressure for a short time, using anything from a light contact pressure to a load of several MPa. This achieves a low strength weld initially, which then becomes stronger as the solvent diffuses away from the weld. The time required under pressure and the time for the joint to achieve its full strength depend on the materials, solvents and geometry and can range from a few seconds to assemble the joint, to several days for full strength to develop.

A major use of solvent cementing is the joining of PVC pipes, where a permanent joint can be made between a pipe and a socket. The following 10 steps have been suggested as a practical guide to producing a satisfactory weld.<sup>3</sup>

1. Ensure that pipe ends are cut square.
2. Deburr and chamfer the pipe ends.
3. Assemble the joint in a “dry-fit” operation and make a depth-of-entry mark.
4. Preclean the parts using a suitable reagent that does not dissolve the polymer.
5. Apply the primer to both surfaces.
6. While the surfaces are still wet, apply the solvent cement to both surfaces.

7. Put a second application of cement on the pipe – enough to form a small bead when the pipe is inserted in the fitting. The joint should be left open for a short time before assembly to allow time for diffusion of the solvent into the substrate and for excess solvent to evaporate.
8. Insert the pipe into the fitting with a quarter-turn rotation to spread the cement evenly, then hold the joint in place for between 30 and 180 s.
9. Wipe off excess cement.
10. Leave the joint for at least 24 h before pressure testing.

In other applications, it may be necessary to anneal moulded parts before welding to remove internal stresses, which might otherwise cause cracking or crazing when the solvent is applied. Use of self-locating moulded parts can facilitate assembly of solvent-welded joints.

### *Benefits and drawbacks*

In comparison with some other polymer joining techniques, solvent welding can be used to assemble permanent joints in relatively large components. A wide range of joint designs can be fabricated using solvent welding, including lap, butt, scarf, socket, 90° and T joints. The process gives a low or zero visibility joint and does not introduce an additional phase to the joint. Additionally, the process is relatively simple, so the cost of capital equipment is low.

The technique cannot, however, be used for highly crystalline polymers. Residual solvent at the weld can reduce the mechanical properties of the polymer in the region of the weld, requiring long periods of desorption to achieve a strong weld. For mass-produced goods, this can mean carrying a large inventory of work in progress.

The organic solvents used are generally toxic, volatile, and in some cases inflammable (see **Environment and the impact of adhesive technology**). Attempts to find alternative solvents while retaining the simplicity of the process have been unsuccessful.<sup>4</sup> Good ventilation and housekeeping and use of appropriate personal protective equipment are therefore essential, and suppliers' instructions on use and storage should be closely followed. In particular, solvents and solvent cements should be kept in cool storage and containers should be kept sealed, and resealed if feasible between making joints. This will also help maximize storage life of solvent cements.

For these reasons, alternative techniques such as laser welding or adhesive bonding are increasingly being used for applications such as tamper-proof housings.

### *References*

1. W. V. Titow, Solvent welding of plastics, in *Adhesion-2*, K. W. Allen, Ed., Applied Science Publishers, London, 1978.
2. C. Y. Yue, *Int. J. Adhes. Adhes.*, **8**(1), 47–53 (1988).
3. T. McPherson, *Hydrocarbon Process.*, **79**(1), 65–68 (2000).
4. J. Desai, C. M. F. Barry, J. L. Mead and R. G. Stacer, Solvent welding of ABS and HIPS: a case study in methylene chloride substitution, in *ANTEC 2001 Conference Proceedings*, SPE, Eds., SPE, 2001.

---

## Solvent-based adhesives

---

J PRITCHARD

### *What are they?*

For an adhesive to work, it must start out in a fluid state to enable adequate wetting of the substrates to take place, and then the fluid state must be replaced by a solid state to enable the adhesive bond to gain strength.

Solvent-based adhesives accomplish this by having suitable solid materials dissolved in appropriate liquids. The solution is the liquid phase, which carries out the wetting of the substrates; then, by evaporation, the solvent is removed leaving a solid adhesive film.

In practice, there is a large range of materials that can be classified as solvent-based adhesives; the solvent can be either water or any of a number of organic liquids, the choice of the latter depending on what is to be dissolved, availability, cost and health and environmental considerations.

### *Aqueous solvent-based adhesives*

This class of adhesives contains some of the most traditional materials, for example, animal and fish glue and inorganic materials such as soluble silicates. Modern technology has brought other water-soluble materials into use, including modified cellulose, soluble vinyl polymers; for example, **Polyvinyl alcohol adhesives**, and a host of resins based on phenol, urea and formaldehyde (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**).

Generally, these adhesives are used where at least one of the substrates is porous or permeable to moisture vapour. The two substrates to be joined are laminated while the adhesive is still wet, and the water escapes either by initial absorption into one of the substrates or by evaporation due to permeability. See also **Emulsion and dispersion adhesives**.

*Uses of aqueous-based adhesives* Because of the need to remove water, most applications for aqueous adhesives are made with materials that are able to allow transmission of water vapour; hence, the major uses are with paper, wood and fabric (see **Adhesives in the textile industry**), either as binders or laminating adhesives. A list of applications would include the following: remoistenable gummed tape, tube winding, box manufacture, plywood manufacture, reconstituted wood products, abrasives and woodworking.

### *Organic solvent-based adhesives*

The progress of technology over the last 100 years has made available a number of organic liquids in large quantities, together with a range of synthetic solids that can be dissolved in them. Various combinations of these materials form a substantial part of the adhesives industry.

The method of use is similar to the aqueous products in that the solvent has to evaporate. If a wet laminating process is adopted, then the solvent vapour must be able to escape through one of the substrates. A special and the most important type of organic solvent-based adhesive is the so-called "contact" adhesive. This makes use of the fact that certain

elastomeric or “rubbery” solids have the property of autohesion, that is, they can stick readily to themselves, especially if compounded with resins and containing small amounts of solvents. This means that substrates may be coated with a contact adhesive and the adhesive can be allowed to dry till most of the solvent has evaporated, when the two adhesive surfaces can be brought together. Bonding takes place immediately and without much pressure. This property has meant that contact adhesives find wide use in industry for sticking many different materials together easily and without the need for clamping.

*Manufacture and compounding* The majority of organic solvent-based adhesives are based on rubbery polymers, the main ones being natural rubber, polychloroprene, butadiene–acrylonitrile, styrene–butadiene and polyisobutylene. Traditionally, the rubber was placed in a heavy-duty mixer and solvent was added slowly till a smooth solution was formed. In some cases, the rubber was milled beforehand to reduce viscosity and produce smoother solutions. Nowadays, it is possible to obtain some grades of material that only require stirring in a comparatively simple churns.

Depending on the rubber, the solvent can either be petroleum hydrocarbon of differing boiling ranges, aromatic hydrocarbon – usually toluene – or oxygenated solvents such as ketones or esters. If non-flammability is required, then chlorinated solvents are used. See also **Rubber-based adhesives**.

Various resins are added to improve adhesion to different substrates. Antioxidants will be present to improve ageing characteristics, while fillers are often added to improve performance.

*Applications of organic solvent-based adhesives* Organic solvent-based adhesives find wide application in general industry. They can be used in the footwear industry for sticking soles to uppers and a variety of other operations. The automotive industry (see **Automotive applications**) uses them for a variety of jobs including stick-on trim. Foam seat manufacturers use them in brushable and sprayable form. Paper conversion employs solvent-based permanently tacky adhesives in the manufacture of labels and sticky tapes. Wherever a variety of different materials have to be stuck together quickly and easily, then organic solvent-based adhesives will often be the answer.

#### *Advantages and disadvantages of solvent-based adhesives*

*Advantages* They are very easy to use. They can be taken directly from the can and applied with brush or scraper or applied easily by large spreading machines. They can be spray applied. Viscosities can be altered between wide limits to suit the application. Heat does not have to be applied. The standard one-can products have an extensive shelf life (12 months minimum is quite normal) and do not require expensive metering/mixing equipment. They can be compounded to stick to a wide variety of materials and can stick many dissimilar materials together: extensive surface preparation is usually unnecessary. They are easy to use and can withstand some abuse. The presence of rubbery elastomer gives tenacious impact-resistant bonds and the “contact” variety can make bonds immediately, which do not need clamping.

*Disadvantages* Water-based adhesives can take a long time to dry in cool, damp conditions. Organic solvents often constitute a risk to **Health and safety**, unless used properly

and are implicated in the formation of photochemical smog (see **Environment and the impact of adhesive technology**).

### *Select References*

- I. Skeist, Ed., *Handbook of Adhesives*, 3rd edn, Van Nostrand Reinhold, New York, 1990.  
K. L. Mittal and A. Pizzi, Eds., *Handbook of Adhesive Technology*, 2nd edn, Marcel Dekker, 2003.

---

## *Standards for adhesives and adhesion*

---

S MILLINGTON

Standards play an important part in a technology-related topic such as adhesives and adhesion. They are published by both national and international bodies and important sources of standards include the British Standards Institution (BSI), the Comité Européen de Normalisation (CEN), the American Society for Testing and Materials (ASTM) and the International Organization for Standardization (ISO). An indication of the wide scope of relevant standards can be judged from the Appendix. This list has grown considerably in recent years, mainly because of an increase in the number of European standards following the establishment of the Single European Market. It is expected that the number of standards will continue to rise as a result of the increasing importance of international standardization and as requirements are established for test methods to cover new adhesives and applications. The reason for all the effort expended on these standards lies with the increasing importance of quality assurance. To assure the quality of a material implies the need to test it, and to obtain consistent and reproducible results from such testing requires closely controlled test methods. Hence the development of standards that can be quoted by the purchaser and the supplier of the material.

Often, when disagreements or discrepancies arise relating to the testing of an adhesive to a recognized standard, the reason can be found in some uncontrolled variable between two test sites, which had resulted in a large effect upon the recorded value. It is, therefore, of paramount importance to lay down strict conditions of test in standards. This has a negative side, however, in that it encourages a test to be as simple as possible, which decreases its relationship with the conditions experienced by the material in service. Accordingly, great caution must be used when looking at the quantitative results from standard tests. For example, the bond strength attained by a structural adhesive in a simple-lap shear test at room temperature may bear no relationship to the level it achieves in service, where the substrate, the nature of the applied stresses and the environment will be totally different.

### *Adhesives standards*

In the United Kingdom, there exist relatively few British Standards for specific adhesive materials, the main ones being for wood adhesives (BS 1203 and 1204 and BS EN 204 and 301) and solvent cements (BS 6029). The tendency has been to prepare test methods for adhesives, which can then be quoted in specifications for adhesive materials issued by suppliers or users of the adhesive. The BS 5350 series (see *Methods of test for adhesives*)

contains many general methods, although, in recent years, some have been converted to, or replaced by, equivalent European standards. In addition, test methods exist for adhesives for specific applications, such as footwear, packaging, tiling and flooring. It is interesting to note, in passing, that the situation regarding adhesive tapes is quite the opposite, with most common varieties of tapes being specified by British Standards.

With adhesives, therefore, the same test method may be quoted for widely differing materials and the standards are written in such a way as to take account of this. For instance, BS 5350:Part C5, the lap shear bond strength test (see **Shear tests**), may be used to determine the bond strength of adhesives of widely different cohesive strengths on substrates of widely differing nature.

In very simple terms, tests on adhesives may be regarded as comprising three main types.

1. Tests carried out on an adhesive as a material, usually to give information concerning its application properties. Typical of these tests are viscosity, solids content and density.
2. Tests on adhesives to determine their curing or setting behaviour, for example, tack-free time, skin-over time, pot life, and so on.
3. Tests on the cured adhesive/adherend assembly to determine the bond strength attained.

A wide variety of each test exists. In addition, other tests not directly related to the quality of the adhesive may be considered. These include, to an increasing extent, tests concerned with health, safety and environmental properties, for example, flashpoint and toxicity. Mention must also be made of BS EN 923 (Adhesives – Terms and definition), which provides a useful reference to many of the terms used in the industry.

In general, the bond strength tests specified in standards are short-term, quality control tests that are not suitable for design purposes; indeed, the more recent revisions of such methods include a disclaimer to this effect. They have the advantage of simplicity, rapidity and the ability to give reproducible results. However, there is an increasing body of opinion in favour of issuing standards for more complex and long-term techniques, which could be of value to designers. Examples of such tests include cyclic load testing, crack propagation (**Wedge test**, etc.) and environmental testing. Despite the problems inherent in standardizing such tests, they will undoubtedly grow in importance in the future. One area where this has already occurred is in the specification of adhesives for the **Aerospace applications**. Here, the high emphasis placed on safety has resulted in the specification of considerable environmental testing, which must be satisfactorily completed before an adhesive can be “qualified”.

### *Formulation of standards*

Each of the standards referred to here is the responsibility of a particular British Standards Technical Committee, which is composed of representatives of adhesives suppliers and users, trade associations, research organizations and Government departments. This committee will also nominate members to attend related CEN and ISO committees. In recent years, international standardization has become the norm, with work on national standards showing a significant decrease.

In general, the procedures followed by all committees are similar. The standards are rarely, if ever, prepared “from scratch”; they are normally based upon existing methods,

such as national standards, standards published by Government departments or trade associations or, sometimes, those used by large commercial organizations. The committees discuss new standards and prepare a draft document suitable for public comment; the public in this context being primarily other parties interested or active in the relevant field. After taking such comments into account, the standard is issued, but is subject to revision at regular intervals in order to keep abreast of technical progress. This procedure, particularly at international level, is often protracted, although there have been recent efforts to speed-up the process. To avoid duplication, there is considerable incentive in BSI and CEN to adopt ISO standards where acceptable. These are then issued as “dual-numbered” European or British Standards. Unlike ISO standards, CEN standards once published are required to be adopted by member states, with the national standards that cover the same area being superseded. In common with other member states, BSI cannot work on a national standard where an equivalent already exists, or is being prepared, at CEN level.

The issue is complicated by the parallel existence of aerospace committees within BSI, and in Europe within the Association Européenne des Constructeurs de Matériel Aérospatial (AECMA). This is the European organization responsible for standardization related to aerospace materials and, hence, covers many structural applications of adhesives, as well as aircraft sealants. Standards published by AECMA, like normal European standards, are required to be adopted by member states.

### *Conclusion*

Although often undervalued, it can be seen that standardization plays an important role in the development of acceptable, reproducible test methods for adhesives and adhesion. Further information on test methods can be obtained from the general references below, from the information in the Appendix and from other specialized articles in this Handbook.

### *Select References*

- AECMA, Brussels at <http://www.aecma-stan.org> (12.1.05)
- ASTM, Pennsylvania at <http://www.astm.org> (12.1.05)
- BSI, London at <http://www.bsi-global.com> (12.1.05)
- CEN, Brussels at <http://www.cenorm.be> (12.1.05)
- ISO, Geneva at <http://www.iso.ch> (12.1.05)

---

## *Statistics*

C CHATFIELD

Statistics may be described as the science of collecting, analysing and interpreting data in the best possible way. Note that it is not just concerned with data analysis as some scientists think.

### *Random variability*

All data in the experimental sciences are subject to some “random” variability due to a variety of causes such as measurement error, natural variability in laboratory specimens, uncontrolled variation in external conditions, and so on. With careful control of the measurement process and of laboratory conditions, this variation can sometimes be kept very small. However, in other cases, it may be more substantial and then the need for statistics is more apparent. Random variation is often described, perhaps rather misleadingly, as the “error” component of variation. However, it is essential to realize that there is nothing abnormal about random variation, though the experimenter will naturally wish to reduce it as far as possible.

A major objective in statistics is to “make decisions in the presence of uncertainty” and come to conclusions about relationships despite the presence of “error terms”. These brief notes naturally cannot provide more than a brief introduction to the subject, and should be read in conjunction with an introductory text for scientists – see Select references.

### *Collecting the data*

The first step in any study is to clarify the objectives, decide which variables need to be measured and/or controlled and decide how many observations are to be taken, and how. If the data are to be collected by a technician, then clear instructions and close supervision are advisable to ensure that “good” data are collected. Poor data cannot be rescued by a statistical analysis. The topic of experimental design does not always receive the attention it deserves.

### *Analysing the data*

The first step in analysing the data is to process them into a suitable form for analysis, often by typing them into a computer. At this stage, it is advisable to have a look at the data in order to get a “feel” for them. It will usually be helpful to plot the data in any way that seems appropriate and also to calculate some simple descriptive statistics. Do not rush into a more complicated analysis before this has been done.

The simplest case is when we have, say,  $n$  observations on a single variable  $x$ . The observations will be denoted  $x_1, x_2, \dots, x_n$ . If  $x$  is a continuous variable (which can take any value in a specified range), then it is a good idea to plot a histogram of the data to see what the distribution of the variable looks like. Possible values of  $x$  are divided into different class intervals and the number of values in each interval (the frequency) is then found. The histogram plots frequency against  $x$ . One can then see if the distribution has a “bell-shaped” symmetric shape (called a normal distribution) or if one tail is longer than the other (called a skew distribution). Any extreme values, called outliers, should also be visible. If the latter are judged to be errors, then they should be excluded from the analysis. If the observed variable is discrete (so that it can for example only be a non-negative integer), then the frequencies can be plotted in the form of a bar chart.

It is also helpful to calculate a typical value (called a measure of location), which is usually the (arithmetic) mean  $\bar{x} = \sum_{i=1}^n x_i/n$ . Alternatives include the median (the middle value), which is useful if the data have a skewed distribution, and the mode (the most frequently occurring value). It is also a good idea to measure the variability



of the data with a measure of spread such as the range (largest observation minus the smallest observation) or the standard deviation,

$$s = \sqrt{\left[ \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{(n-1)} \right]}$$

Note that the square of the standard deviation  $s^2$ , called the variance, is not in the same units of measurement as the data and so is of no use as a descriptive statistic, although it has many other uses in more complicated analyses.

Having obtained some feel for the data, and revised or excluded obvious errors, a proper statistical analysis can now be carried out. There are numerous statistical techniques appropriate for different situations. Here, we can only mention the broad aims of a few selected techniques. With the advent of the computer, the details of mathematical formulae are no longer so important. What is important is to be able to choose the right technique and understand the results.

With observations on a single variable, it may be of interest to assess whether the sample mean,  $\bar{x}$ , is significantly different from a suggested population “true” value, say  $\mu$ . A procedure called a  $t$ -test essentially looks at the difference  $(\bar{x} - \mu)$  to see whether it is too large to have arisen by chance. This is the best-known example of a significance (or hypothesis) test.

The  $p$ -value, which comes from a significance test, is the probability of observing a more extreme value than the one obtained given that the null hypothesis (in this case that  $\bar{x}$  really is from a population whose true mean is  $\mu$ ) is true. It is not, as many scientists believe, the probability that the null hypothesis is true. A small  $p$ -value (usually  $<0.05$ ) is taken to be evidence against the null hypothesis, leading to its rejection.

The two-sample  $t$ -test, as the name implies, is concerned with comparing the sample means of two groups of observations. The null hypothesis is that both groups come from the same population and a “large” difference between the two sample means leads to rejection of the null hypothesis (as is intuitively obvious).

With three or more groups of observations to compare, it is incorrect to compare each pair of groups with a two-sample  $t$ -test. Instead, a one-way analysis of variance (ANOVA) should be carried out. The ANOVA technique can be generalized to deal with observations from many other types of experimental design. In each case, the analysis separates out the variation due to specified components of variation (e.g. the differences between group means in a one-way ANOVA) and the variation due to the residual or error terms. The former components of variation are then compared with the latter component to see if the systematic components are too large to have arisen by chance.

If the scientist is interested in the relationship between two variables, say  $x$  and  $y$ , and has observed  $n$  pairs of observations, say  $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$ , then it is a good idea to begin by plotting  $y$  against  $x$  to give what is called a scatter diagram. The form of the relationship (e.g. a straight line or a quadratic curve) between  $x$  and  $y$  may then be evident. If the relationship is linear, it may help to calculate a statistic, called the correlation coefficient, which measures the degree of association between the two variables. A value near zero indicates little or no relationship, while a value close to  $+1$  (or to  $-1$ ) indicates a strong positive (or negative) relationship. The technique,

called regression, is concerned with finding a regression curve to describe the relationship between a dependent variable and one or more explanatory variables.

### *Quality control*

Another important area of statistics is statistical quality control. This is concerned with the problems involved in controlling the quality of a manufactured product. Acceptance sampling is concerned with monitoring the quality of manufactured items supplied by the manufacturer to the consumer in batches. The problem is to decide whether the batch should be accepted or rejected on the basis of a sample drawn randomly from the batch. Statistical process control is concerned with detecting changes in the performance of a manufacturing process and with taking appropriate action, where necessary, in order to keep the process on target. In order to do this, control charts, such as Shewhart charts or cusum charts, are often used to plot a variable of interest against time. The recent arrival of Taguchi methods from Japan has heightened interest in quality control. These methods emphasize error prevention rather than detection and recommend the use of experimental design at the product design stage in order to get a process running near its optimum setting with minimum variability. The general philosophy of Taguchi methods is excellent although some of the detailed techniques are open to criticism.

### *Reliability*

The reliability of a product is a measure of its quality and has a variety of definitions depending on the particular situation. For example, reliability could be defined as the probability that a device will function successfully for a certain period of time. One method of measuring the reliability of a product is to test a batch of items over an extended period of time and note the failure times. This procedure is called *life-testing*. The resulting data may enable us to estimate the underlying probability distribution of failure times and/or estimate the conditional failure rate function, which describes the conditional probability of failure given that an item has survived until the particular time in question. The topic of reliability was given a major boost by the American space rocket programme, where sufficiently high reliabilities could only be obtained by adding backup items in parallel.

There are many good books on statistics, quality control and reliability, of which the following is a small selection.

### *Select References*

- R. A. Johnson, *Miller and Freunds Probability and Statistics for Engineers*, 6th edn, Prentice-Hall, New York, 2000.
- W. Q. Meaker and L. A. Escobar, *Statistical Methods for Reliability Data*, John Wiley, New York, 1998.
- D. C. Montgomery, *Introduction to Statistical Quality Control*, 3rd edn, John Wiley, New York, 1996.
- D. C. Montgomery and G. C. Runger, *Applied Statistics and Probability for Engineers*, 3rd edn, John Wiley, New York, 2002.

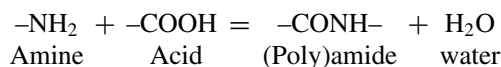
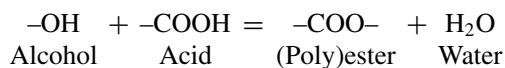
---

**Step polymerization**

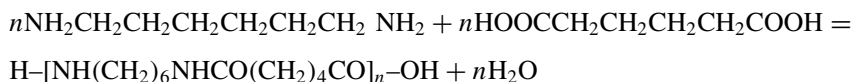

---

J COMYN

Step polymerization, also known as condensation polymerization, should be contrasted with **Chain polymerization**. In step polymerization, monomers react with one another because they contain mutually reactive chemical groups, of which there are at least two per monomer molecule. Some common groups and their reactions are given below. In many, but not all, cases, a small molecule such as water is released.



A specific example of a step polymerization is the reaction between 1,6-diaminohexane and adipic acid to form nylon 66.



Here, both monomers each contain two functional groups ( $-\text{NH}_2$  or  $-\text{COOH}$ ) and the resulting polymer is linear. In some cases, a single monomer that contains two different functional groups will self-condense. 1-hydroxypropionic acid (lactic acid) is an example. When a monomer with more than two functional groups is added, branching and eventually cross-linking will occur; this is always the case with structural adhesives.

To obtain a high molar mass product, the mixture must be stoichiometric; on the other hand, controlled deviations from stoichiometry can be used to lower the molar mass. In contrast with chain polymerization, where high molar mass molecules are formed right from the start, molar mass increases with the degree of conversion and large molecules are only formed at very high conversion. A consequence of this is that step polymers tend to have lower masses and narrower mass distributions than chain polymers.

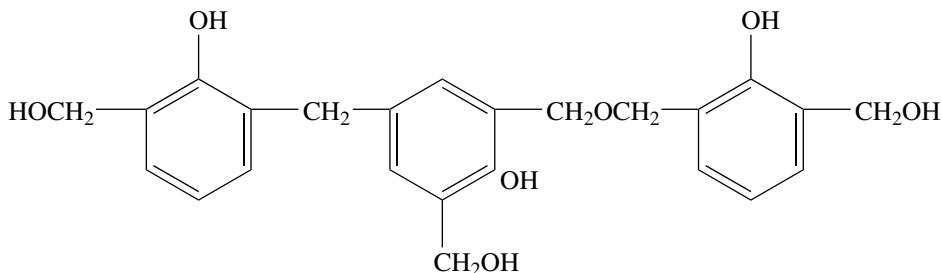
*Step polymerization in making adhesives*

Polyester and polyamide hot melt adhesives are made by step polymerization. Polysulfide **sealants** are made by reaction of sodium polysulfide with bis(2-chloroethyl formal).

*Step polymerization in curing adhesives*

Many adhesives cure by step polymerization. Structural phenolic adhesives are based on resoles, which are made by the step polymerization of phenol with excess formaldehyde under basic conditions (see **Phenolic adhesives: single-stage resoles**). They contain

phenol units bridged by  $-\text{CH}_2-$  and  $-\text{CH}_2-\text{O}-\text{CH}_2-$  groups, and there are some methylol ( $-\text{CH}_2-\text{OH}$ ) groups on the rings. A typical structure is

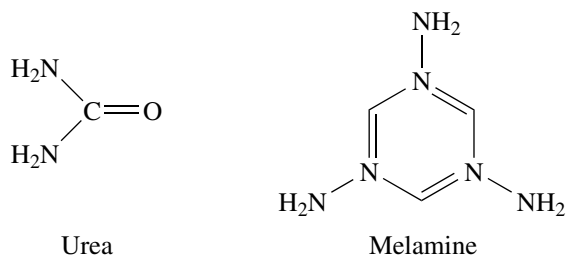


On heating to  $130-160^\circ\text{C}$ , further step polymerization takes place between methylol groups; thus,

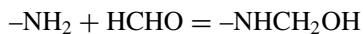


The products of this reaction are a cross-linked polymer and steam, and to avoid formation of bubbles, it is necessary to cure phenolic adhesives in a press.

The reactions of urea or melamine with formaldehyde are the basis of aminoresin wood adhesives (see **Wood adhesives – aminoplastics**).

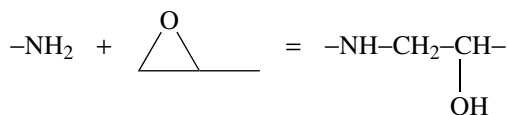


In both cases formaldehyde is first added to the amine groups to produce methylols, which later condense in the manner shown above for phenolics.

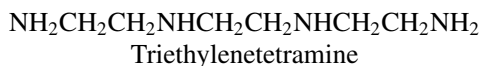


As urea is 4-functional and melamine is 6-functional, the final products are cross-linked.

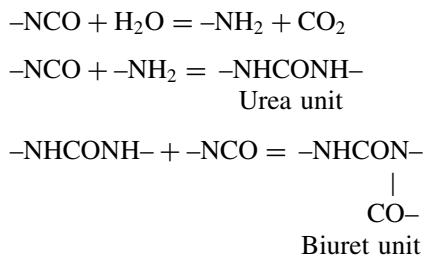
One advantage with **epoxide adhesives** is that no volatile compounds are given off during cure. Curing agents that react with epoxides by step polymerization include amines, thiols and acid anhydrides, and with the first two of these groups, each active hydrogen is capable of reacting with one epoxide in the following manner:



Triethylenetetramine is a commonly used aliphatic amine, and its high functionality (6 amine hydrogens) leads to a high level of cross-linking.

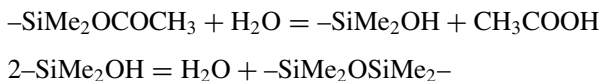


A stoichiometric mixture of an oligomeric diol and diisocyanate will react to give a **polyurethane**. However, if there is double the quantity of diisocyanate, the reaction product will be an oligomer with isocyanate end groups. Such adhesives cure by the ingress of moisture by the following sequence of reactions. (**Moisture cure of adhesives**).



The formation of urea units brings chain extension while biuret units are branch points, which ultimately lead to cross-linking.

Curing due to moisture also takes place with some **silicone adhesives** with hydrolysable end groups (acetates in the example shown below). Hydrolysis produces silanol end groups, which then react in a step polymerization.



Cure of polysulfides involves oxidative coupling of  $-\text{SH}$  groups to  $-\text{S}-\text{S}-$  often using manganese dioxide or chromates. (see **Sealants**).

### Select References

- J. Comyn, *Adhesion Science*, Royal Society of Chemistry, Cambridge, 1997.  
 R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*, 2nd edn, Chapman and Hall, London, 1997, Chap 5.  
 G. Odian, *Principles of Polymerization*, 3rd edn, John Wiley & Sons, New York, 1991.

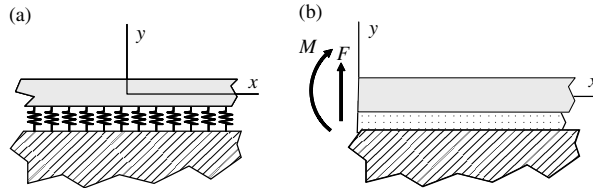
---

### Stress distribution: beam on elastic foundation

---

DAVID A DILLARD

No simple equations can be expected to predict stress states within the myriad of possible bonded joint configurations, yet several relationships have been found to be applicable



**Fig. 1.** Beam on an elastic foundation: (a) continuous beam shown on discrete elastic springs; (b) adherend loaded by applied force and moment at the end

to broad classes of adhesive bonds. Among these are the shear lag model proposed by Volkersen in 1938 (**Stress distribution: shear lag solution** and **Shear tests**), and the beam on elastic foundation model originally proposed by Winkler in 1867. Winkler, a bridge and railroad engineer teaching at the Technical University in Prague,<sup>1</sup> was interested in the deflections of a loaded rail supported by the earth, as schematically illustrated in Fig. 1(a). The solution is based on a continuous foundation, but discrete elastic springs are shown for illustration purposes. By assuming that the restoring force of the foundation was linearly proportional to the deflection, Winkler solved a fourth order differential equation, and developed solutions for a range of loading situations, as have been elaborated upon by Hetenyi.<sup>2</sup> These solutions have been used for a wide range of structural applications ranging from beams supported by the soil to floating pontoon bridges. With a slight modification, the relationship is directly applicable to adhesive bonds, with greatest accuracy where the adhesive is relatively flexible compared to the adherend.<sup>3</sup> In their seminal paper examining the effects of adherend bending on the resulting stress state for the single lap joint, Goland and Reissner<sup>4</sup> adapted the shear lag model and the beam on elastic foundation solution to estimate the shear and peel stresses, respectively, present within a single lap joint loaded in tension.

The solution to the governing differential equation for the beam on elastic foundation problem yields the deflection of the beam of the form:

$$y(x) = e^{-\lambda x}(A \cos \lambda x + B \sin \lambda x) + e^{\lambda x}(C \cos \lambda x + D \sin \lambda x)$$

where

$$\lambda = \sqrt[4]{\frac{k}{4EI}}$$

$A$ ,  $B$ ,  $C$  and  $D$  are coefficients determined by the relevant boundary conditions,  $k$  is the foundation stiffness, and  $E$  and  $I$  are the Young's modulus and second moment of area of the beam, respectively. To cast this solution in terms of adhesive bonds, the adhesive, of thickness  $h$ , is assumed to be linearly elastic with a modulus of  $E_a$ , unaffected by deformations in the surrounding material, and acting over a bond width,  $w$ , on the beam. Under these conditions, the foundation stiffness becomes

$$k = \frac{E_a}{h}w$$

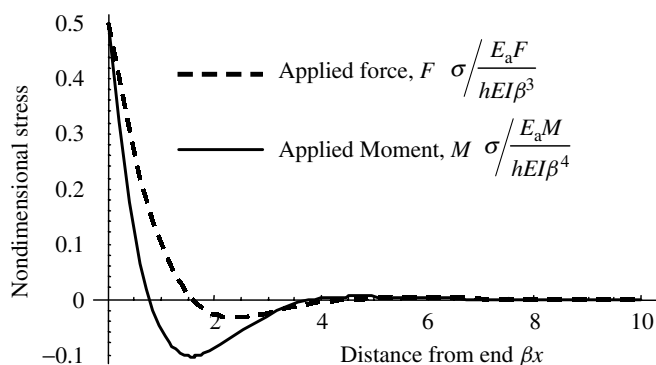


Fig. 2. Predicted stress distributions for case of an end-applied force and moment

A wide range of boundary conditions and loading conditions may be applied to obtain solutions for a variety of adhesive-related configurations. Two conditions of special importance are the cases of either a concentrated force,  $P$ , or a concentrated moment,  $M$ , applied at the end of a long bonded strip (length  $> 5/\beta$ ). The resulting expression for the peel stress is given by

$$\sigma(x) = \frac{E_a}{2hEI\beta^3} e^{-\beta x} [F \cos(\beta x) + M\beta(\cos(\beta x) - \sin(\beta x))]$$

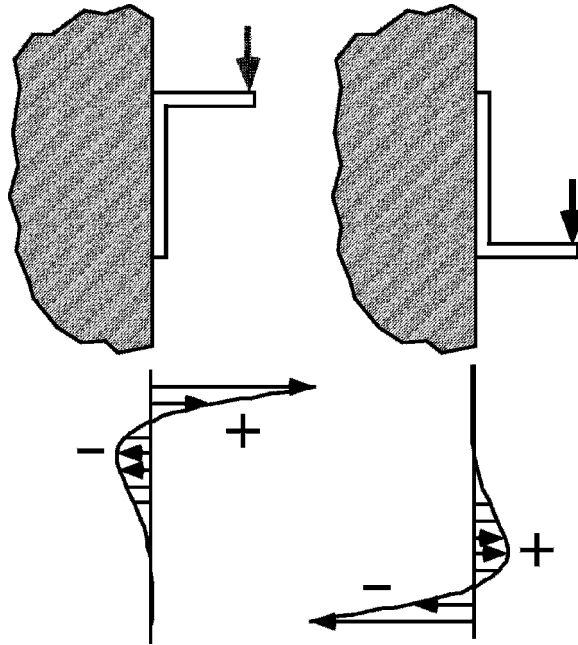
where

$$\beta = \sqrt[4]{\frac{E_a w}{4EIh}}$$

These results are plotted independently in Fig. 2, showing highly damped, oscillatory behaviour. For the case of the applied moment, one notes that the integral of the tensile peel stresses must be equal to that of the compressive stresses in order for the adherend to be in equilibrium. Thus the tensile peak at the very end of the adherend is offset by a broader compressive peak, with equivalent area, but a maximum magnitude that is only 20% of the end peak. This has important design implications, since reversing the sign of the stresses can result in a more durable design, explaining why the bracket on the right in Fig. 3 performs better than the one on the left.

The characteristic beam on elastic foundation stress distribution, as shown in Fig. 2 for the applied moment case, is frequently encountered in a wide range of adhesive bond situations. In addition to lap joints mentioned earlier, peel tests,<sup>5</sup> moisture-induced stresses,<sup>6</sup> and curvature mismatch<sup>7</sup> situations all tend to exhibit this characteristic distribution. Clearly, the beam on elastic foundation has important qualitative and, in many cases, quantitative applicability to a host of adhesively bonded joints.

Other relevant articles include **Stress distribution: bond thickness**, **Stress distribution: Poisson's ratio**, **Stress distribution: stress singularities**, **Stress distribution: shear lag solution** and **Stress distribution: mode of failure**.



**Fig. 3.** For a flexible bracket bonded to a wall, the large stress at the loaded end can be either tensile, or compressive

### References

1. L. Fryba, *Vehicle System Dynamics Supplement*, **24**, 7–12 (1995).
2. M. Hetenyi, *Beams on Elastic Foundation: Theory with Applications in the Fields of Civil and Mechanical Engineering*, University of Michigan Press, Ann Arbor, 1946.
3. R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*, 2nd edn, Chapman and Hall, 1997.
4. M. Goland and E. Reissner, *J. Appl. Mech.*, **77**, A17–A27 (1944).
5. D. H. Kaelble, *Trans. Soc. Real.*, **9**, 135 (1961).
6. Y. Weitsman, *J. Composite Materials*, **11**, 378–394 (1977).
7. T. Corson, Y.-H. Lai and D. A. Dillard, *J. Adhes.*, **33**, 107–122 (1990).

### Stress distribution: bond thickness

DAVID A DILLARD

The thickness of the adhesive layer is of importance in most adhesive joints and should be measured and controlled in **Tests of adhesion**. Adhesive layer thickness is often determined by a number of factors, some intentional in the design process and some resulting from a variety of items related to the adhesive properties and the processing steps. Factors affecting the final bond thickness include adhesive viscosity (which may fall dramatically and then rise during elevated temperature cure), clamping pressure and



uniformity, adherend stiffness, presence of a scrim cloth or other thickness limiting items, adequacy of fixtures and clamping jigs, and dimensional tolerance and stability of the adherends and bonding devices. Smaller than expected bondline thicknesses may produce insufficient wetting, excess spew and cleanup problems, while thicker than expected bonds may require more adhesive or exhibit significant voids. Either case can lead to reduced performance. Obtaining accurate control of bond-line thickness is a challenging task but can be important in the performance and appearance of the finished product.

Most designs seem to expect uniform adhesive layer thickness, although this is not always optimal. In some situations, slightly thicker adhesive layers in high stress or strain regions can relieve stress concentrations. In general, however, excessively thick bonds are to be avoided as they normally result in poorer strength.

The optimal adhesive layer thickness depends on a number of factors. Some bonds, notably **Tensile test** specimens, are stronger when the adhesive layer thickness is reduced.<sup>1,2</sup> For fracture specimens, including double cantilever beam specimens bonded with structural adhesives (see **Fracture mechanics test specimens**), optimal bond thicknesses have been identified, although the optimal thickness depends on the loading rate and test temperature.<sup>3,4</sup> Enhanced ductility plays a role in this process, and a sufficient quantity of adhesive is desired to dissipate energy (see **Peel tests**). This latter mechanism is also important in the peel energy of **Pressure-sensitive adhesives** and other systems.

Loading can be either load (or stress) controlled, displacement (or strain) controlled, or something in between. Examples include aerodynamic loads on an aircraft (see **Aerospace applications**), which tend to be load controlled, and the displacement of a sealant between relatively stiff adherends, which is displacement controlled. Because average adhesive strain, in its simplest form, is defined as displacement divided by bond thickness, strains and resulting stresses are higher in thin bondlines subjected to displacement-controlled loading scenarios. Joints loaded in such a manner often perform better with thicker bondlines. Displacement-controlled situations include thermal expansion/shrinkage of adherends, mismatched adherend expansion, and attachments bonded to pressure vessels or other adherends that are stressed.

Adhesive properties are of significant importance in optimizing bond-line thickness. To take advantage of adhesive ductility, increased adhesive thickness can increase the volume of material within which energy is dissipated. Brittle adhesives normally benefit little from increased bond-line thickness; ductile adhesives often perform better with slightly thicker bondlines.

During fabrication, many factors may be important in the resulting bond-line thickness. Thickness control depends on a number of factors. Scrim cloth offers a unique means to regulate adhesive thickness by restricting adhesive flow. These supporting layers also improve the handling properties of film adhesives. Glass beads or other thickness-control agents may be added to adhesive bonds. This method is widely used, although concerns have been expressed that stiff particles such as glass beads offer stiff load paths that may induce high stresses within the adhesive where they come in contact with the adherends, perhaps precipitating failure. Wires, shims and other spacers are commonly used in producing test coupons, with controlled bond-line thickness, but may not be practical for production joints. Preferably, these spacers are outside the test region, a method that works well for making beam-like fracture specimens provided the unsupported length of the adherends do not sag significantly under the clamping pressure.

*Select References*

1. E. D. Reedy Jr., Strength of butt and sharp-cornered joints, *Adhesion Science and Engineering – I, The Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 145–192, 2002.
2. G. P. Anderson, S. J. Bennett and K. L. DeVries, *Analysis and Testing of Adhesive Bonds*, Academic Press, 1977.
3. A. J. Kinloch and S. J. Shaw, *J. Adhes.*, **12**, 59–77 (1981).
4. W. D. Bascom, R. L. Cottingham, R. L. Jones and P. Peyser, *J. Appl. Polym. Sci.*, **19**, 2545–2562 (1975).

---

*Stress distribution: mode of failure*

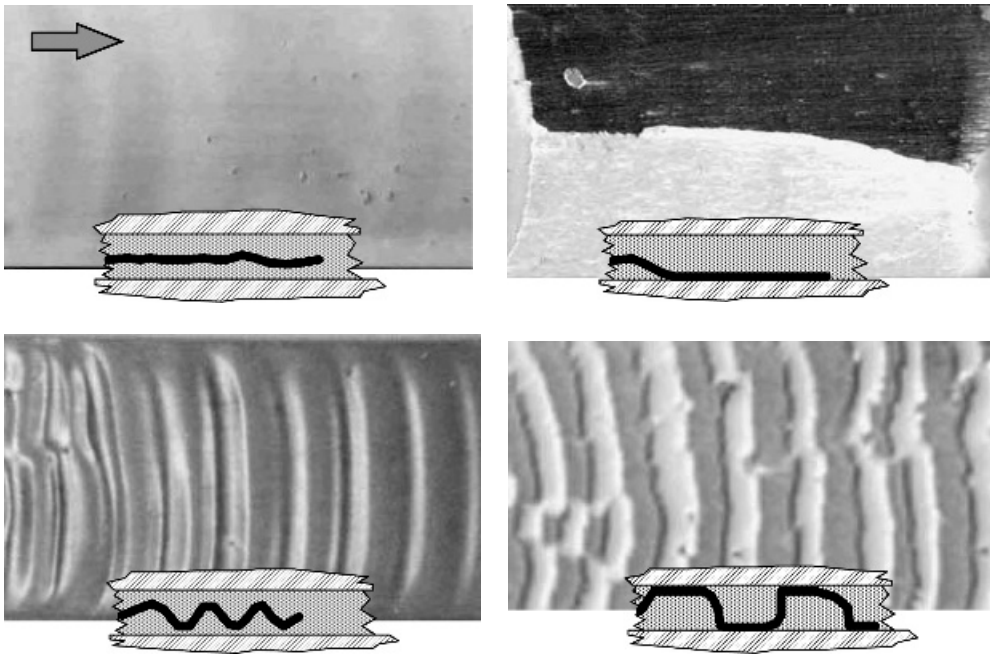
---

DAVID A DILLARD

Adhesively bonded joints may fail cohesively within the adhesive, adhesively at or very near an interface, within the adherends in some systems, or by some combination of these modes. Identifying the locus of failure can provide valuable information about weak regions where failure may initiate or propagate and is a useful procedure in diagnosing causes of failure (see **Rheological theory**). Test standards (see **Standards for adhesives and adhesion**), such as ASTM D-1002 for single lap joints (see **Shear tests**), specify that, as part of the test report, one should visually determine the percent adhesive and percent cohesive failure. Contaminants, changes in surface composition, effects of environments, locus of failure, and other important factors may be identified through surface-analysis techniques such as **X-ray photoelectron spectroscopy (XPS)**, **Auger electron spectroscopy** depth profiling, and other methods (see **Surface analysis**). Although each of these techniques can provide useful information for interpreting the cause of failure, care is required to understand the role that the imposed loading mode and test geometry may have on failure locus as well.

From childhood, we learn that chains always break at the weakest link. While this is a useful concept for understanding failure of discrete systems such as chains, the analogy breaks down for a continuum such as an adhesively bonded joint. Just as tearing perforated paper does not always result in failure through the perforations, a debond does not always initiate or propagate within the “weakest” zone. The crack path of a growing crack is determined by a number of factors in addition to the relative strength or fracture energy of the adhesive layer and the interfaces or interphases. These factors include the loading mode, the thickness of the adherends and adhesive layer, the moduli and ductility of the adherends and adhesive, the presence of localized flaws, and the residual stress state within the adhesive layer.<sup>1</sup>

As an illustration, consider Fig. 1, which shows four different failure modes for aluminum adherends bonded with a model epoxy adhesive. Simply by altering the loading mode, one can obtain cohesive failures, apparent (visually) interfacial failures, failures that oscillate within the adhesive layer, and alternating failures that jump back and forth from one interface to the other. Predicted theoretically,<sup>2</sup> this dramatic variation in locus of failure was experimentally achieved not by altering the substrates or the surface preparation but simply by changing the loading conditions for these beam-type fracture specimens.



**Fig. 1.** Altering the loading mode can result in (clockwise from top left) cohesive, interfacial, alternating, and oscillating failures

To understand the role that stress state plays in determining the mode of failure, we first note that in homogeneous, isotropic materials, cracks propagate in such a way that they grow perpendicular to the largest tensile stress direction. An arbitrary stress state can be resolved into principal directions, that is planes on which extreme values of normal stress exist but where there is no shear stress. Accordingly, a pure-shear state is equivalent to a tensile and compressive stress of the same magnitude, but rotated  $45^\circ$  with respect to the pure-shear planes. In an adhesive joint subjected to a shear state, cracks within the adhesive layer have a tendency to grow towards one interface and follow that interface as shown in the two joints in Fig. 2. Altering the direction of the shear will cause the crack to move towards the other interface. This tendency can be observed visually and with surface-analysis techniques.<sup>3</sup> Shear loading can result in interfacial failures or failures with less adhesive left on a high-quality interface.

Shear stresses can be induced by shear loading modes, but also can result from other factors such as differences in adherend thickness. For example, a debond propagating between two adherends of different thickness or different moduli will be subjected to a mild shear stress that tends to drive the debond towards the more-compliant adherend or more highly strained adherend. Common examples include **Wedge test** specimens, **Peel tests**, the **Blister test** and the asymmetric double cantilever beam (see **Fracture mechanics test specimens**). This tendency can be overcome in cases of **Pressure-sensitive adhesives** in which the backing has been specially treated to maintain strong adhesion, and removable adhesives are often formulated to release from the substrate rather than to fail cohesively. Nonetheless, these induced shear stresses provide a driving tendency that can be useful

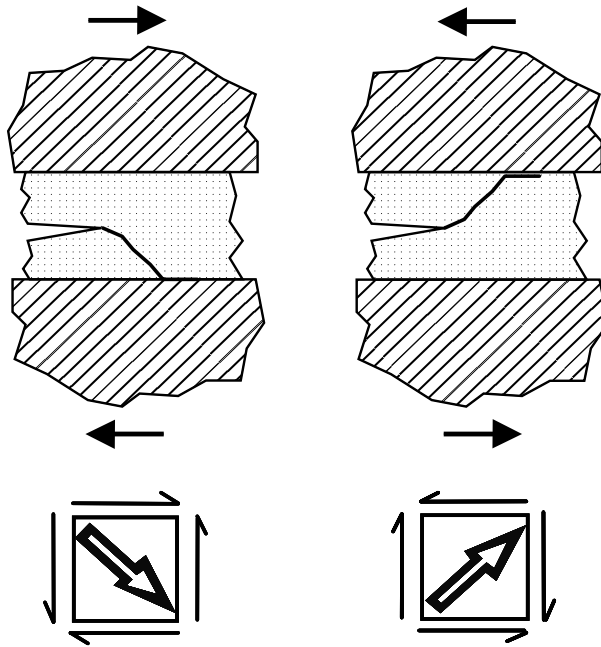


Fig. 2. Because cracks tend to grow perpendicular to the largest tensile stress, a shear stress state has a tendency to drive cracks in different directions. (Line arrows show stresses, open arrows show crack propagation tendency)

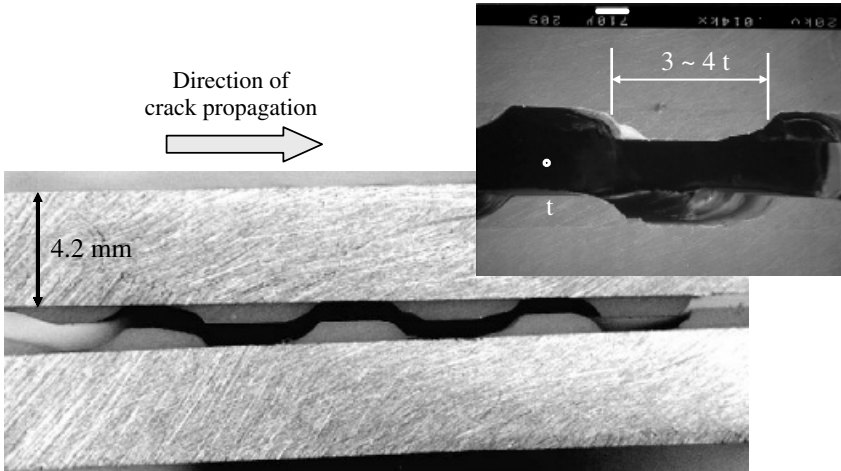


Fig. 3. Tensile stresses within the plane of the adhesive destabilize a growing debond, causing it to alternate from one adherend to the other, with a characteristic spacing of several times the adhesive thickness

in selecting appropriate test methods, or can complicate the interpretation of failure when not taken into account.

Whereas shear stresses can steer a propagating debond in a preferred direction, tensile stresses within the bond plane can destabilize growing cracks, causing them to oscillate within the adhesive layer or alternate from one adherend to the other. This effect is controlled by the T-stress, a non-singular stress that is parallel to the local crack path. If the T-stress is sufficiently tensile, the crack path is not stable and so will continuously change direction as it propagates,<sup>4</sup> as illustrated in Fig. 3. The following factors tend to increase the T-stress, and hence destabilize propagating debonds: smaller adherend thickness, larger adhesive thickness, and higher tensile residual stress within the adhesive.

In summary, the locus of failure in bonded joints is controlled by a complex interaction of the stresses and energy that drive debonding, and the spatially varying resistance of the adhesive and interfaces to failure. In some cases, failures will initiate and propagate within the weakest region, such as along a particular interface. In many cases, however, the stresses present within the adhesive layer provide a tendency to drive debonds along certain paths, which, in some cases, do not coincide with weak zones. Recognizing the importance of both the material resistance and the stress-driven tendencies is critical in making definitive claims about observed failure modes and cause of failure. **Stress distribution: bond thickness**, **Stress distribution: Poisson's ratio**, **Stress distribution: stress singularities** **Stress distribution: shear lag solution**, and **Stress distribution: beam on elastic foundation** are articles that develop these themes.

### References

1. B. Chen and D. A. Dillard, Crack path selection in adhesively bonded joints, *Adhesion Science and Engineering – I, the Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 389–442, 2002.
2. N. A. Fleck, J. W. Hutchinson, and Z. Sun, *Int. J. Solids Struct.*, **27**(13), 1683–1703 (1991).
3. B. Chen, D. A. Dillard, J. G. Dillard and R. L. Clark Jr., *Int. J. Fracture*, **114**, 167–190 (2002).
4. B. Chen and D. A. Dillard, *Int. J. Adhes. Adhes.*, **21**, 357–368 (2001).

---

### *Stress distribution: Poisson's ratio*

---

DAVID A DILLARD

Poisson's ratio is a material property defined as the negative of the transverse strain divided by the longitudinal strain under uniaxial loading conditions. Typically, pulling a material in one direction will cause it to contract in the other two perpendicular directions, resulting in a positive Poisson's ratio. The effect is relevant to the stress state in bonded joints and in **Tests of adhesion**, such as **Shear tests** and **Peel tests**. It is especially important in butt joints (see **Tensile tests**). For isotropic materials, with properties the same in all directions, one may easily show that Poisson's ratio,  $\nu$ , is bounded by  $-1 \leq \nu \leq 1/2$ . Physically, the lower bound represents a material that is infinitely stiff in shear, while the upper bound represents a material that is incompressible. Most engineering materials have positive Poisson's ratios, often ranging from 0.2 to nearly 0.5. Glassy polymers, such as

epoxies, often have Poisson's ratios on the order of  $1/3$ , while rubbery materials, such as sealants, have Poisson's ratios that approach the upper bound of  $1/2$ . As a glassy polymer is heated, one can expect Poisson's ratio to gradually increase from its glassy value to near the rubbery bound when well above its glass transition temperature. The presence of inorganic fillers can decrease Poisson's ratio, as can the presence of voids; foams have notoriously small Poisson's ratios.

Linear elastic, isotropic materials may be described with a variety of material constitutive properties, including Young's modulus, shear modulus, bulk modulus and Poisson's ratio. Only two of these are independent, but two must be known for most engineering analysis.<sup>1</sup> For example, commercial **Finite element analysis** programs often require that the user input the Young's modulus and Poisson's ratio of each material being analysed. Engineers using adhesives in their designs will often request Poisson's ratio, whereas companies producing adhesives may not routinely measure or report this property.

Since Poisson's ratio is often similar within broad classes of materials such as metals, glassy polymers and elastomers, one may often estimate Poisson's ratio when it is not available. Except for elastomers, small changes in Poisson's ratio normally result in only minimal changes in the resulting stress and strain fields in engineering structures. Many practical geometries can be approximated by 2-D plane models, whose solutions are bounded by the plane stress (assumes no stress in the out-of-plane direction) and the plane strain (assumes no strain in the out-of-plane direction) solutions. The in-plane stresses under plane strain conditions are greater than the corresponding plane stress solutions by a factor of  $1/(1 - \nu^2)$ , which for glassy polymers might be on the order of a 15% increase. Biaxial stresses within the plane of a bond, such as those induced as residual stresses due to thermal expansion mismatch, scale as  $1/(1 - \nu)$ , so a polymeric adhesive might exhibit stresses that are 30–50% higher than expected in the uniaxial case. Where the adhesive is highly constrained, stresses can scale as  $1/(1 - 2\nu)$ , resulting in even larger changes, especially significant for the case of elastomers, where Poisson's ratio approaches  $1/2$ . For this case, small changes in the fourth or fifth decimal place can have significant effects on the resulting stress state.<sup>2</sup>

In principle, Poisson's ratio should be relatively easy to measure; in practice, its determination can be challenging. For glassy polymers, biaxial strain gages mounted directly on the specimen, or biaxial extensometers can be used. Care should be used to recognize the time dependence and temperature sensitivity of these materials, however, to insure meaningful measurements. Other techniques, including measuring anticlastic bending curvatures,<sup>2</sup> have also been used. In principle, Poisson's ratio can also be determined if one knows any of the two independent constitutive properties of the material. Knowing the shear modulus and Young's modulus, for example, should allow determination of Poisson's ratio. In practice, this approach has been fraught with problems; minor errors in moduli, obtained from different test methods, can lead to unrealistic values of Poisson's ratio. Poisson's ratio is even more difficult to accurately measure for elastomeric materials. As Poisson's ratio approaches the upper bound, specialized techniques are needed to accurately measure this quantity, which often differs from  $1/2$  only in the fourth decimal place. Measuring stresses in confined configurations<sup>3</sup> is believed to be more appropriate than trying to measure the small volume changes that result.

For related topics, see **Stress distribution: bond thickness**, **Stress distribution: stress singularities**, **Stress distribution: shear lag solution**, **Stress distribution: beam on elastic foundation** and **Stress distribution: mode of failure**.

## References

1. Y.-H. Lai, D. A. Dillard and J. S. Thornton, *Trans. ASME*, **59**, 902–908 (1992);  
D. Frederick and T. S. Chang, *Continuum Mechanics*, Scientific Publishers, 1972.
2. W. G. Knauss and J. Romanko, *J. Adhes.*, **10**(4), 269–277 (1980).
3. J.-H. Yu, D. A. Dillard and D. R. Lefebvre, *Int. J. Solids Structures*, **38**, 6839–6849 (2001).

---

**Stress distribution: shear lag solution**


---

DAVID A DILLARD

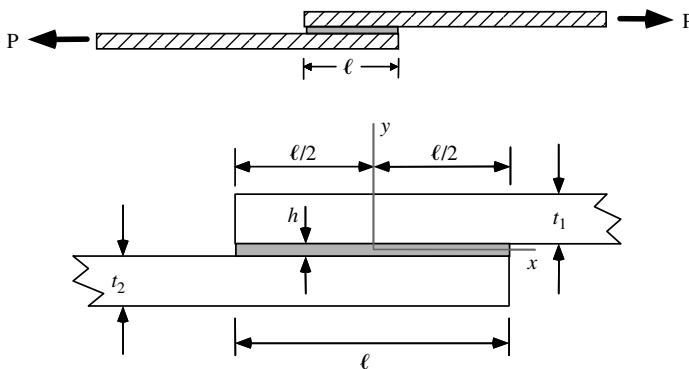
The shear lag model, proposed by Volkersen in 1938 for analysing shear stresses within adhesive joint, has found broad applicability in many engineering disciplines. It is widely used in the discussion of **Shear tests**. Ignoring the effects of adherend bending due to the eccentric load path, Volkersen considered the axial displacements of adherends in the single lap joint as shown in Fig. 1. By considering a differential element consisting of a slice of the bonded cross section, Volkersen developed a second order differential equation for the shear stress as a function of distance along the bondline.<sup>1,2</sup> The model assumes that the entire axial load was carried in the adherends, and that all the shear deformations occur within the adhesive layer and linear elasticity. The solution to the governing differential equation is of the form:

$$\tau(x) = A \cosh \omega x + B \sinh \omega x$$

where

$$\omega = \sqrt{\left[ \frac{G}{h} \left( \frac{E_1 t_1 + E_2 t_2}{E_1 t_1 E_2 t_2} \right) \right]}$$

The upper and lower adherends are denoted by subscripts 1 and 2, respectively. Each adherend has a Young's modulus  $E_i$  and a thickness  $t_i$ . The adhesive has a shear modulus of  $G$  and a thickness of  $h$ . The joint length is  $\ell$ .



**Fig. 1.** A single lap joint with relevant dimensions

Boundary conditions of special interest include the case of a mechanically applied axial load,  $P$  (load per unit width), resulting in

$$\tau(x) = \frac{P\omega}{2 \sinh\left(\frac{\omega\ell}{2}\right)} \cosh \omega x + \frac{P\omega}{2 \cosh\left(\frac{\omega\ell}{2}\right)} \left(\frac{E_2 t_2 - E_1 t_1}{E_1 t_1 + E_2 t_2}\right) \sinh \omega x$$

(illustrated in Fig. 2 for balanced adherends), and the case of a change in temperature, which is of importance when the adherends have different coefficients of thermal expansion:

$$\tau(x) = \left[ \frac{(\alpha_2 - \alpha_1)\Delta T\omega}{\left(\frac{1}{E_1 t_1} + \frac{1}{E_2 t_2}\right) \cosh(\omega\ell/2)} \right] \sinh(\omega x)$$

where  $\alpha_i$  are the coefficients of thermal expansion of the adherends. These hyperbolic sine and cosine solutions, both of which ignore adherend bending, are characteristic of this model, which is widely known as the shear lag model. This name comes from the fact that there is a spatial lag required for adherends in a long joint to reach their respective share of the load. In fact, the reciprocal of  $\omega$  has units of length, and represents the characteristic distance over which a characteristic fraction ( $1/e$ ) of the load is transferred in long joints. A stiffer adhesive decreases this characteristic shear lag distance, whereas increasing the adherend stiffness (modulus or thickness) or adhesive thickness increases this characteristic length.

The shear lag model is actually more applicable to double-lap joints than single-lap joints because of the large amount of adherend bending that occurs in the latter. In fact, Goland and Reissner,<sup>3</sup> in their seminal paper addressing adherend bending and resulting shear and peel stress state within a single lap joint, showed that the shear stresses could be as much as double the stresses predicted by Volkersen. Where such bending is not a significant factor, however, the shear lag model is very useful. Where bending occurs or other assumptions are not met, the characteristic shear lag stress distribution still may have qualitative implications. As such, the characteristic behaviour is frequently encountered in a wide range of adhesive bond situations. In addition to lap joints mentioned earlier, shear stresses around broken fibres or cracked plies in composite materials, stresses developing in reinforcing bars in concrete, shear stresses associated with torsional and bending loads in bonded airfoils and a variety of thermal mismatch situations all tend to exhibit this

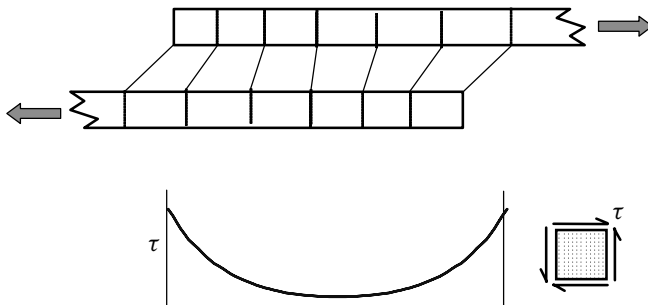


Fig. 2. Differential stretching of adherends causes characteristic shear lag stress distribution



characteristic stress distribution. Clearly, the shear lag solution has important qualitative and, in many cases, quantitative applicability to a host of adhesively bonded joints that transfer load from one adherend to the other by means of shear within the adhesive layer.

**Stress distribution: bond thickness, Stress distribution: Poisson's ratio, Stress distribution: stress singularities, Stress distribution: beam on elastic foundation and Stress distribution: mode of failure** are related articles.

### References

1. R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*, 2nd edn, Chapman and Hall, 1997.
2. D. A. Dillard, Fundamentals of stress transfer in bonded systems, in *Adhesion Science and Engineering – I, The Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 1–44, 2002.
3. M. Goland and E. Reissner, *J. Appl. Mech.*, **77**, A17–A27 (1944).

## *Stress distribution: stress singularities*

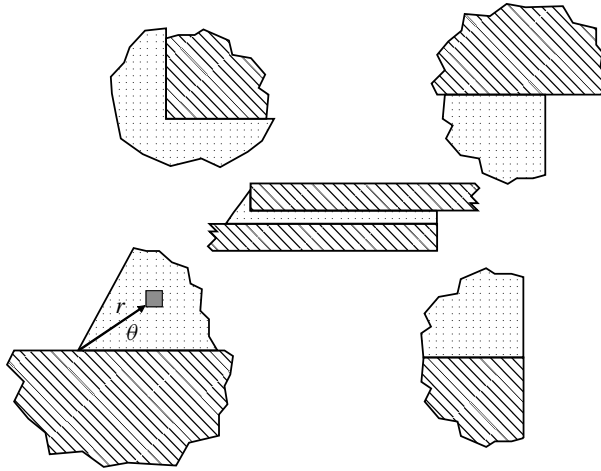
DAVID A DILLARD

The concept of stress concentration factors has been an important aspect of engineering design for decades, and has special relevance to adhesive joints (see **Fracture mechanics**). Engineers are often familiar with charts of stress concentration factors for a wide range of geometric details, including holes, fillets and notches that may occur in flat or cylindrical members subjected to axial, torsional or bending loads. The stress concentration factor, when multiplied by the nominal or far-field stress, gives the maximum stress that may occur at the edge of the geometric detail. This familiar treatment breaks down, however, when the hole becomes crack-like, when a fillet becomes a sharp corner or when a notch has a vanishingly small root radius. Mathematically, these sharp corners result in unbounded or infinite stresses at the tip of the geometry under even the smallest applied load if the material is assumed to behave in a linear-elastic fashion. These are referred to as stress singularities.<sup>1,2</sup> Although no real material can be expected to withstand infinite stresses, very large stresses and strains do result at sharp corners that are often encountered in monolithic materials and in bonded joints. Under static loading, these singularities can be expected to dramatically reduce the strength of brittle materials, although ductile systems may prove more forgiving, resulting in plastic flow around the sharp corner. From a durability standpoint, especially under fatigue loading, however, these stress singularities can be of significant importance for even more ductile materials. The higher stresses surrounding these geometric features can significantly reduce fatigue life.

Mathematically, the stress field surrounding a geometric corner, such as a crack tip, a re-entrant corner or the edge of a bi-material interface can be given as a series expansion of the form:<sup>3</sup>

$$\sigma_{ij} = Q_1 r^{\lambda_1} f_{1ij}(\theta) + Q_2 r^{\lambda_2} f_{2ij}(\theta) + \dots$$

where the  $Q_k$  coefficients are sometimes known as generalized stress-intensity factors, and  $f_{kij}$  are functions of angle with respect to the corner, as shown in Fig. 1. The radial



**Fig. 1.** Spew and re-entrant corners, such as those found in a lap joint, can result in singular stress fields

dependence on  $r$  enters through the exponents,  $\lambda_i$ , which are known as eigenvalues, and may be real, imaginary or complex, depending on the geometry and the material properties. If the real part of  $\lambda$  is less than zero, the stresses will become unbounded as the distance  $r$  from the apex of the corner goes to zero, implying singular stress fields that can reduce the strength of the structure. If the real part of the eigenvalue is positive, the stresses associated with this particular term will decay as one approaches the apex. Thus, only those eigenvalues whose real part is negative, are of concern from a stress singularity standpoint. If the eigenvalue has an imaginary component, the resulting stresses will tend to oscillate.

These singular stress fields have had an important impact on engineering design. The entire field of fracture mechanics has been built on the singular stress-field concept. For cracks in homogeneous materials, the eigenvalue has a value of  $-1/2$ , implying that stresses are proportional to  $1/\sqrt{r}$ . For cracks at bi-material interfaces, the real part of the eigenvalue remains  $-1/2$ , but an imaginary term results in oscillatory stresses as well.<sup>4</sup> For bi-material corners, the strength of the singularity is usually less than that of a crack, that is, less negative. Singular stress fields have been shown to have significant engineering design implications for bonded structures including microelectronic devices,<sup>5</sup> lap joints<sup>6</sup> and other geometries.<sup>7</sup>

Related articles are **Stress distribution: bond thickness**, **Stress distribution: Poisson's ratio**, **Stress distribution: shear lag solution**, **Stress distribution: beam on elastic foundation** and **Stress distribution: mode of failure**.

### References

1. K. M. Liechti, Fracture mechanics and singularities in bonded systems, *Adhesion Science and Engineering – I, The Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 45–76, 2002.

2. E. D. Reedy Jr., Strength of butt and sharp-cornered joints, in *Adhesion Science and Engineering – I, The Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 145–192, 2002.
3. D. R. Lefebvre and D. A. Dillard, *J. Adhes.*, **70**, 119–138 (1999).
4. G. P. Anderson, S. J. Bennett and K. L. DeVries, *Analysis and Testing of Adhesive Bonds*, Academic Press, 1977.
5. T. Hattori, S. Sakata and G. Murakami, *J. Electron. Packaging*, **111**, 243 (1989).
6. R. D. Adams and J. A. Harris, *Int. J. Adhe. Adhes.*, **7**, 69–80 (1987).
7. D. R. Lefebvre, D. A. Dillard and J. G. Dillard, *J. Adhes.*, **70**, 139–154 (1999).

---

### Structural adhesives

---

B KNEAFSEY

#### Definition

Structural adhesives are adhesives that are used to assemble structural bonds, that is, adhesives that are used to assemble load-bearing joints where the load may be either static or dynamic. These adhesives are differentiated from other adhesives in that they are normally the only load-bearing components of the structural assembly, and as such the demands and requirements of structural adhesives are greater than for most other adhesive types.

Several alternative definitions are commonly used that include the important stipulation that the adhesives must substantially maintain their load-bearing capacity within the service environment of the structures involved.<sup>1</sup> A high-performance structural adhesive should provide both rigidity for high tensile strength and the toughness and flexibility to resist high peel and impact forces of the service environment. Many structural adhesives are used in applications where the ability to withstand impact and peel stress for long periods is important. In practical terms, this means the bond strengths of structural adhesives must be at least 6–8 MPa at room temperature. Thus the adhesive joint design, (see **Engineering design with adhesives**), substrate preparation and adhesive assembly and cure conditions are extremely important to achieve the optimum performance. The importance of these factors has been reviewed extensively.<sup>2</sup>

#### Structural adhesive categories

Structural adhesives are normally categorized or subdivided into subclasses based on the resin chemistries used in their formulation, which can be in the form of solids, liquids, pastes or films.<sup>1,3</sup> The most important categories of structural adhesives are the thermoset cured adhesives based on phenolic, epoxy and polyurethane or acrylic resins and include phenolic adhesives, **Epoxy adhesives**, **Toughened epoxy adhesives**, **Polyurethane adhesives**, **Acrylic adhesives** and **Toughened acrylic adhesives**. Several of the categories can be further subdivided into both one- and two-component adhesives. The one-component structural adhesives, which can be liquids, pastes or solids (films), usually require the inclusion of added energy for activation or to effect cure in the

form of heat or radiation, for example, visible or ultraviolet light (see **Radiation-cured adhesives**). Alternatively, the cure can be activated by reaction with atmospheric components, for example, moisture or oxygen. Such adhesives usually require special packaging requirements and the cure is activated during dispensing or application. Structural adhesives specially designed for high-temperature applications include **Polyimide adhesives**, cyanate esters and bis-maleimide adhesives, which are formulated as pastes or films.

Thermoplastic structural adhesives are less significant for the more-demanding applications; however, **Cyanoacrylate adhesives** have gained considerable importance for applications at ambient temperatures and less severe environments, particularly on plastic substrates, mainly as a result of their very rapid cure speeds (seconds) and ease of application.

### *Chemistry and properties*

The cure mechanisms of structural adhesives depends on the resin chemistry and can be based on either **Chain polymerization** or **Step polymerization** reactions. The condensation cure mechanism is the most important for phenolic adhesives, **Epoxide adhesives** and **Polyurethane adhesives**, which require stoichiometric or balanced combination ratios as well as thorough mixing for maximum performance. Off-ratio mixing or incomplete mixing can alter significantly the final adhesive structure and effect the resulting properties.

Phenolic adhesives contain phenolic resins, the first successful commercial synthetic resin, which are prepared from phenols and formaldehyde giving either resol or novolac type resins depending on the ratios of the phenol and formaldehyde (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**). The resoles are prepared with excess formaldehyde under basic conditions giving self-curable water-soluble resins. The novolacs are prepared with an excess phenol under acid conditions to give stable water-insoluble resins that require catalysts, usually hexamethylene tetraamine, for curing. Both resins liberate water on curing by heat and thus are more suited to bonding porous substrates, particularly wood.

**Epoxide adhesives** comprise epoxy resin, many of which are prepared from phenols and epichlorohydrin, for example, the diglycidyl ether of bis-phenol A or bis-phenol F; usually, these resins are a mixture of molecular weights blended to fit the applications. The most-common curatives for epoxy resins are polyamines (used in stoichiometric amounts), usually a chain-extended primary aliphatic amine, for example, diethylene triamine or triethylene tetraamine or chain-extended equivalents, which react rapidly with the epoxy resin at room temperature. Aromatic amines react slowly at room temperature but rapidly at higher temperatures. Most epoxide adhesives also contain catalysts, typically, tertiary amines. Dicyanamide is the most-common curative for one-component high-temperature-cured epoxide adhesives. Mercaptans or anhydrides are used as curatives for epoxide adhesives for specialist applications, for example, for high-speed room-temperature cures or for electronic applications. A smaller number of epoxide adhesive are cured by cationic polymerization catalysed by Lewis acids photogenerated at the point of application. Lewis acid photoinitiators include diaryliodonium and triaryl sulphonium salts. See **Radiation-cured adhesives**.

**Polyurethane** adhesives comprise a polyisocyanates, polyols and chain extenders, which can be amines or alcohols. The most common polyisocyanates are based on aromatic

isocyanates toluene diisocyanates (TDI) and methylene dianiline diisocyanates (MDI). Aliphatic isocyanates include those based on hexamethylene diisocyanates and isophorone diisocyanates. The polyols are based on polyesters, polyethers and polybutadienes. The ability to design in “hard” and “soft” segments into both the polyisocyanates, the polyols and the chain extenders is a major factor in determining the toughness of polyurethane adhesives.

The acrylic structural adhesives are based on acrylate monomers and resins and are important because of their rapid cures. There are two main categories, the **Cyanoacrylate adhesives** based on cyanoacrylic acid ester, which cure by anionic polymerization and the acrylate and methacrylates, which cure by free radical catalysed **Chain polymerization**. The cyanoacrylates are unique in that the adhesives usually comprise greater than 90% cyanoacrylate ester monomers, typically, ethyl cyanoacrylate with small amounts of thickeners and cure accelerators. The adhesives are characterized by very rapid cures on most substrates and have become known to consumers as “Instant Adhesives”. The adhesives cure by anionic polymerization catalysed by moisture and base contamination on the substrates. The cured adhesives are thermoplastics and thus have poor high-temperature properties. The methacrylates cure by free radical cure mechanisms (see **Chain polymerization**). The free radicals can be generated by redox reactions, heat, radiation, including ultraviolet or visible light, and reactions catalysed by moisture or oxygen. In most two-part acrylics, the cure is initiated by redox reactions of peroxide initiators, for example, hydroperoxides with reducing agents, for example, aromatic amines. Many redox initiating systems are metal catalysed. The large range of methacrylate monomers and resins allow for a great diversity of cured properties and cure speeds to suit most applications (see **Acrylic adhesives**). Rubber tougheners can be added to improve the impact performance (see **Toughened acrylic adhesives**).

The adhesives described above are limited in their resistance to elevated temperatures for prolonged periods because of depolymerization or decomposition reactions at temperatures greater than 120–150°C. High temperature resistant structural adhesives based on polyimide, cyanate ester and bis-maleimide chemistries can withstand the higher temperatures but require more difficult cure conditions, are generally more expensive and service a smaller specialist segment of the overall structural adhesive market.

### *Applications*

Applications suitable for bonding with structural adhesives include components of aircraft fuselage, construction, machinery and automotive industries (see **Aerospace applications** and **Automotive applications**). Structural adhesives can be formulated to have low controllable viscosity or to exhibit thixotropy with anti-sag behaviour suitable for bonding joints with large gaps. Both structural acrylic and polyurethane adhesives are generally multi-component. The room-temperature curing of these adhesives makes them particularly useful for structural applications where plastics are being used, for example, the bonding of high impact plastics in automotive applications. Structural epoxides, which can be either mono-component or multi-component, are generally selected for strength and/or strength at temperature (hot strength). Typical structural applications for epoxies include numerous joints in the aerospace industry, where they are widely used.

Table 1. Comparative benefits of industrial structural adhesives (structural acrylics, polyurethanes and epoxides)

	Structural acrylic	Structural polyurethanes (with primers)	Structural epoxides	
			Two-part mixed	One-part heat cure
<i>Bond strength</i>				
Metals/ferrites	++	+	+	++
Metals/plastics	++	+	0	-
Toughness	++	+	+	+
Impact resistance	+	++	+	0
Temperature/humidity	+	-	+	++
Speed of bonding	++	-	0	-
<i>Ease of cure</i>				
Automatic application	++	-	-	++

Note: ++ great benefit, + significant benefit, 0 no benefit, - significant disadvantage.

#### *Advantages/disadvantages of structural adhesives*

Table 1 compares representative industrial structural adhesives illustrating the respective advantages and disadvantages of various generalized structural adhesives, **Polyurethane adhesives**, **Acrylic adhesives** and **Epoxide adhesives**. Often, the fast room-temperature cure of structural acrylics, together with the non-crucial mix ratio, make them ideal for an automated production line, while both the structural epoxides and structural polyurethanes, although slower curing, can often bond a more diverse range of substrates

#### *References*

1. S. R. Hartshorn, *Structural Adhesives, Chemistry and Technology*, Plenum Publishing Corporation, New York, 1986.
2. R. D. Adams and W. C. Wake, *Structural Adhesives in Engineering*, Elsevier Applied Science Publishers, London, 1984.
3. M. M. Gauthier, *Adhesives and Sealants, Engineering Materials Handbook*, Vol. 3, A S M International, 1990.

### *Surface analysis*

D BRIGGS

Surface analysis refers to the characterization of the outermost layers of materials. A series of techniques have been undergoing continuous development since the late 1960s based on ultra-high vacuum (UHV) technology. The most useful of these methods provide information on surface chemical composition and four techniques satisfy this requirement: **X-ray photoelectron spectroscopy (XPS or ESCA)**, **Auger electron spectroscopy**

Table 1. Comparison of some surface-analysis techniques

	Incident radiation	Emitted radiation	Approximate depth analysed
AES	Electrons	Electrons	3 nm
XPS	X-rays	Electrons	3 nm
SIMS	Ions	Ions	2 monolayers
ISS	Ions	Ions	Outer atom layer
EPMA	Electrons	X-rays	1 $\mu\text{m}$
ATR	IR photons	IR photons	1 $\mu\text{m}$

Note: ATR – attenuated total internal reflection IR spectroscopy.

(AES), **Secondary ion mass spectrometry (SIMS)** and ion scattering spectroscopy (ISS). The first three are described elsewhere in the book. In ISS, the energy of scattered incident ions is measured and the elemental composition of the outermost atomic layer is determined. Despite this unique capability, ISS is very much less used than the other three methods.

By combining surface analysis with ion beam sputtering (etching), a sequential or continuous monitoring of composition as a function of depth below the surface is possible. This is known as depth profiling.

Ultra-high vacuum conditions are important for two reasons. Firstly the material to be analysed is bombarded with particles or photons, and particles (electrons or ions) leaving the surface are detected; these particles suffer collisions with residual gas molecules if the pressure is  $>10^{-5}$  torr. Secondly, and more important, surfaces to be analysed can be rapidly contaminated by adsorption of residual gas molecules if the pressure is  $>10^{-9}$  torr. Hence, surface-analysis instrumentation is constructed routinely to achieve  $\sim 10^{-10}$  torr (after bake-out).

As the individual technique descriptions detail, the three techniques of XPS, AES and SIMS are highly complementary in terms of the ability to deal with materials of different types (ranging from metals to polymers), the information available from the spectra, the surface sensitivity, the elemental detection limits and degree of quantitation and the degree of spatial (lateral) resolution available.

Surface-analysis techniques have been extensively applied in both fundamental and applied adhesion studies across the whole field of materials science (see references).

Other methods of surface characterization are discussed in **Infrared spectroscopy: attenuated total reflection, Infrared spectroscopy: RAIR, Surface characterization by contact angles – metals, Surface characterization by contact angles – polymers, Critical surface tension, and Electron probe microanalysis (EPMA)**.

Some features of surface-analysis techniques are compared in Table 1.

### Select References

- D. Briggs and M. P. Seah, Eds., *Practical Surface Analysis*, Vols. 1 and 2, Wiley, Chichester, 1990.  
 J. C. Vickerman, Ed., *Surface Analysis: The Principal Techniques*, Wiley, Chichester, 1997.  
 D. Brune, R. Hellborg, H. J. Whitlow and O. Hunderi, Eds., *Surface Characterisation*, Wiley-VCH, Weinheim, 1997.

---

**Surface characterization by contact angles – metals**


---

M E R SHANAHAN

Metals and metal oxides may be considered to be high-energy solids with free **Surface energies** typically (although not always) of the order of several hundred millijoules per square metre or even more for noble metals such as platinum.<sup>1</sup> Characterization of free **Surface energy** and its components is a delicate task for several reasons. As far as the **Contact angle** methods are concerned, probably the main cause of imprecision is the difficulty of interpretation of data. Although **Contact angles** may be measured, their meaning is often vague. Is the contact angle obtained representative of thermodynamic equilibrium, or are hysteresis effects important? Is the substrate in question truly a metal or a metal oxide? Since metals tend to be of high free **Surface energy**, the equilibrium spreading pressure  $\pi_e$  cannot be ignored. A liquid drop clearly has a surrounding vapour, and this will tend to be adsorbed on to the substrate in order to lower its free energy (a problem rarely encountered with polymers). Some work has been done in UHV conditions,<sup>2</sup> but local adsorption of vapour leading to wetting hysteresis cannot presumably be avoided given the very presence of a liquid. Using classic equations such as that due to Fowkes<sup>3</sup> to evaluate **Dispersion force** interactions can also lead to errors, since an assumption of this theory is that the molecular dimensions of the two phases in contact are similar. The **Roughness of surfaces** can also perturb **Contact angles**.

Notwithstanding these drawbacks and the delicate nature of the problem, the methods described in **Surface characterization by contact angles–polymers** may be employed. Clearly, the one-liquid method is open to criticism because of potential adsorption problems, and if the substrate is indeed of high energy, virtually all liquids will spread anyway, leading to unusable **Contact angle** data. However, the two-liquid method may be attempted and indeed has been used with success in the case of aluminium.<sup>4</sup> Combining wetting measurements with corrections necessary to take into account the **Roughness of surfaces**, the surface characteristics of the metal having undergone various treatments have been evaluated. These are given in Table 1, where  $\gamma_S^D$  represents the dispersion component of the free **Surface energy** of the solid and  $I_{SW}^P$  its polar interaction with water.

The significance of acid–base interactions in **Contact angle**, and therefore free **Surface energy**, assessment is becoming more widely recognized, although their mathematical form is still somewhat in question. This aspect is probably of considerable importance in the study of metallic surfaces<sup>5</sup> (see also following article: **Surface characterization by contact angles – polymers**).

Table 1. Surface characteristics of aluminium after various treatments<sup>4</sup>

Surface treatment	$\gamma_S^D$ (mJ m <sup>-2</sup> )	$I_{SW}^P$ (mJ m <sup>-2</sup> )
Hexane extraction	42	38.7
DMF extraction	135	62.5
Phosphatization	150	18
Anodization	125	95
Sealed anodization	41	55.5



Related articles are **Adsorption theory of adhesion, Contact angles and interfacial tension, Dispersion forces, Pre-treatment of metals prior to bonding, Roughness of surfaces, Surface characterization by contact angles–polymers, Surface energy and Wetting and spreading.**

### References

1. A. J. Kinloch, in *Adhesion and Adhesives*, Chapman and Hall, London, 1987, Chap 2.
2. M. E. Schrader, *J. Phys. Chem.*, **78**, 87 (1974).
3. F. M. Fowkes, *Ind. Eng. Chem.*, **56**, 40 (1964).
4. A. Carré, J. Schultz, *J. Adhes.*, **15**, 151 (1983).
5. C. Vittoz, M. Mantel and J. C. Joud, *J. Adhes.*, **67**, 347 (1998).

### Surface characterization by contact angles – polymers

M E R SHANAHAN

Whereas the surface tension of a liquid (or the interfacial tension between a liquid and a fluid) may be measured directly by means of techniques such as that of the Wilhelmy plate or capillary rise, the lack of molecular mobility within a solid prevents the deformation necessary for detecting surface forces. As a consequence, indirect methods must be used. The most frequently employed are probably those involving the wetting of the solid by known reference liquids.

Consider a drop of a given liquid, L, resting on the surface of a solid, S, in the presence of a fluid, F (vapour or second liquid immiscible with the first, see **Wetting and spreading**). Assuming the interfacial tension liquid/fluid  $\gamma_{LF}$  to be known, measurement of the equilibrium **Contact angle**  $\theta_o$  leads to the difference between solid/fluid and solid/liquid tensions ( $\gamma_{SF} - \gamma_{SL}$ ), via Young's equation:

$$\gamma_{SF} - \gamma_{SL} = \gamma_{LS} \cos \theta_o \quad [1]$$

However, the terms  $\gamma_{SF}$  and  $\gamma_{SL}$  cannot be evaluated separately without further information. In order to go further, certain assumptions must be made. For the case of solid polymers, certain simplifications can be made.

### Critical surface tension for wetting of Zisman

Pioneering work on the evaluation of solid surface tensions was carried out by Zisman and co-workers.<sup>1</sup> The principle was to measure the **Contact angles**  $\theta_o$  of a series of liquids of decreasing surface tension  $\gamma$  on the polymer surface (see **Critical surface tension**). As the value of  $\gamma$  decreases, so does that of  $\theta_o$ , whereas  $\cos \theta_o$  increases. By plotting a graph of  $\cos \theta_o$  versus  $\gamma$ , extrapolation can be made to  $\cos \theta_o = 1$  (even if a liquid in this neighbourhood is only hypothetical). The value of  $\gamma$  for  $\cos \theta_o = 1$  is known as the critical surface tension for wetting of the solid  $\gamma_c$  and corresponds to the value of the surface tension of a liquid that will just spread spontaneously. It does not, in fact, correspond

exactly to the surface tension for wetting of the solid,  $\gamma_s$  since Young's equation predicts that

$$\gamma_{SF} - \gamma_{SL} = \gamma_c \quad [2]$$

Nevertheless, the interfacial tension between a polymer and an organic liquid is generally quite low, and as a result, to a fair approximation it can be seen that

$$\gamma_c \sim \gamma_{SF} \sim \gamma_S \quad [3]$$

where the second equivalence is a consequence of assuming negligible spreading pressure, see below. Although simple in principle, the concept of critical surface tension can be very useful. There exists a “wipe” test in which cotton wool dipped in solutions of different surface tensions are wiped over a polymer surface to observe where the liquid film break occurs (ASTM D-2578-67). The critical surface tension of the solid is situated between consecutive liquids in the series, one spreading and the next merely wetting (see **Wetting and spreading**).

#### *One-liquid method*

The original work of Zisman was developed by several workers. Using Young's equation, two problems exist. Firstly, even in a vapour atmosphere, the term  $\gamma_{SF}$  (or  $\gamma_{SV}$ ) does not correspond necessarily to the surface tension of the solid  $\gamma_s$ . Whereas  $\gamma_s$  corresponds to the surface tension of the clean solid,  $\gamma_{SV}$  refers to the same quantity after any potential adsorption (see **Adsorption theory of adhesion**) of the vapour of the liquid. The difference, always positive or zero, is called the spreading pressure  $\pi_e$ , with suffix e representing equilibrium:

$$\pi_e = \gamma_s - \gamma_{SV} \quad [4]$$

The second problem involves interpretation of the interfacial tension  $\gamma_{SL}$  (there is no difficulty concerning  $\gamma_{LF} = \gamma$  since the liquid must coexist with its vapour). The interfacial tension must be lower than the sum of the two individual surface tensions (otherwise the interface would not form) by an amount related to them (it is a consequence of the same forces that give rise to the individual surface tension). Good and Girifalco<sup>2</sup> expressed this (see **Good–Girifalco interaction parameter**) as

$$\gamma_{SL} = \gamma_s + \gamma - 2\phi(\gamma_s\gamma)^{1/2} \quad [5]$$

where  $\phi$  is the interaction parameter, which, for interfaces where only **Dispersion forces** act is close to unity. Here  $\phi$  is often difficult to calculate for interfaces of interest in adhesion. Fowkes<sup>3</sup> proposed (see **Acid–base interactions** and **Surface energy components**)

$$\gamma_{SL} = \gamma_s + \gamma - 2(\gamma_s^D \gamma^D)^{1/2} - I_{SL}^{ND} \quad [6]$$

where D refers to dispersion components of  $\gamma$ ,  $\gamma_s$  (see **Dispersion forces**) and  $I_{SL}^{ND}$  represents non-dispersion interactions (**Polar forces**, **Acid–base interactions**). Later

developments took **Acid–base interactions** into account specifically.<sup>4</sup> The proposed form for interfacial tension is

$$\gamma_{SL} = \gamma_S + \gamma - 2(\gamma_S^{LW} \gamma^{LW})^{1/2} - 2(\gamma_S^+ \gamma^-)^{1/2} - 2(\gamma_S^- \gamma^+)^{1/2} \quad [7]$$

where LW, + and – refer respectively to **Lifshitz-van der Waals forces**, electron acceptor (or acidic) and electron donor (or basic) components of surface tension. In this interpretation of  $\gamma_{SL}$ , the LW terms are assumed to regroup the dispersive and non-dispersive (polar) contributions of the earlier model.<sup>3</sup>

Developing the second approach as an example, using Eqns. 4 and 6 in Young's equation, we obtain

$$\cos \theta_o = 2(\gamma_S^D)^{1/2} \frac{(\gamma^D)^{1/2}}{\gamma} + \frac{I_{SL}^{ND}}{\gamma} - \frac{\pi_e}{\gamma} - 1 \quad [8]$$

Although  $\pi_e$  can be important for high-energy solids, it is generally negligible for low-energy solids such as polymers.

The experimental procedure is to measure equilibrium **Contact angles** of a series of liquids (showing no chemical interaction with the substrate) and to plot a graph of  $\cos \theta_o$  vs  $(\gamma^D)^{1/2}/\gamma$ . For apolar liquids (1-bromonaphthalene, tricresyl phosphate),  $I_{SL}^{ND}$  should be close to zero. A straight line passing through the corresponding data and  $-1$  has a gradient of  $2(\gamma_S^D)^{1/2}$ . For polar liquids,  $I_{SL}^{ND}$  may be readily estimated from the excess of the ordinate value above the reference apolar line. Various expressions have been proposed to break  $I_{SL}^{ND}$  into its components,<sup>5</sup> but none has yet proved entirely successful. It suffices to say that a high value of  $I_{SL}^{ND}$  for a given liquid indicates a highly polar solid.

### Two-liquid method

Following work originally done to elucidate the surface characteristics of a high-energy solid, mica,<sup>6</sup> a two-liquid method has been developed in which the vapour phase is replaced by a second liquid immiscible with the first. In general, the initial liquid is water (or formamide) and the surrounding liquid is a member of the n-alkane series. Bearing in mind that the non-dispersion interaction between the solid and the hydrocarbon will be negligible and substituting Fowkes's relation, equation 6 for both  $\gamma_{SF}$  and  $\gamma_{SL}$  in equation 1 leads to

$$\gamma_L - \gamma_F + \gamma_{LF} \cos \theta_o = 2(\gamma_S^D)^{1/2} [(\gamma_S^D)^{1/2} - (\gamma_F)^{1/2}] + I_{SL}^{ND} \quad [9]$$

(due to the apolar nature of the hydrocarbon.  $\gamma_F^D \sim \gamma_F$ ).

Experimentally, the **Contact angles** of the polar liquid on the solid surface in the presence of a series of n-alkanes are measured and a graph of

$$\gamma_L - \gamma_F + \gamma_{LF} \cos \theta_o \text{ vs } [(\gamma_L^D)^{1/2} - (\gamma_F)^{1/2}]$$

plotted. Again, the gradient is equal to  $2(\gamma_S^D)^{1/2}$  and the intersection at the origin of the abscissa gives  $I_{SL}^{ND}$ . Careful use of this method can eliminate doubt as to the importance of the undetermined  $\pi_e$  term appearing in the one-liquid method since potential adsorption of the vapour of L can be avoided.

An advantage of this method is that with a judicious choice of liquids (water for which  $\gamma_L^D = 21.6 \text{ mJ m}^{-2}$  at room temperature and n-octane for which  $\gamma_F = 21.3 \text{ mJ m}^{-2}$ ), Eqn. 9 reduces to

$$\gamma_L - \gamma_F + \gamma_{LF} \cos \theta_o \sim I_{SL}^{ND} \quad [10]$$

The non-dispersion interaction between the solid and water may be estimated immediately.

Related articles are **Adsorption theory of adhesion, Contact angles and interfacial tension, Pre-treatments of polymers, Surface energy, Wetting and spreading.**

### References

1. H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, **5**, 514 (1950).
2. L. A. Girifalco and R. J. Good, *J. Phys. Chem.*, **61**, 904 (1957).
3. F. M. Fowkes, in *Treatise on Adhesion and Adhesives I*, R. L. Patrick, Ed., Marcel Dekker, New York, 1996, Chap 9.
4. C. J. van Oss, *Interfacial Forces in Aqueous Media*, Marcel Dekker, New York, 1994.
5. S. Wu, *J. Macromol. Sci. - Revs. Macromol. Chem.*, **C10**(1), 1 (1974).
6. J. Schultz, K. Tsutsumi and J. B. Donnet, *J. Colloid Interface Sci.*, **59**, 272 (1977).

## Surface energy

---

D E PACKHAM

### *The basic concept*

The curved meniscus on a liquid, the “head” on a pint of beer and the effectiveness of soap are all phenomena that can be rationalized using the concept of surface energy. The basic idea that there is an “excess energy in the surface” of a solid or liquid can be accepted by considering the formation of the surface by breaking the bonds across what are to become the two surfaces formed. The energy to break these bonds is the surface energy.

An advantage of this mental picture of “bond breaking” is that it immediately points to a relationship between the magnitude of surface energy and the bond energy (“strength”) of the bonds that have to be broken. Thus, the surface energy for a paraffin is about  $22 \text{ mJ m}^{-2}$ , for water  $72 \text{ mJ m}^{-2}$  and for mercury  $465 \text{ mJ m}^{-2}$ , as the dominant bonds to be broken are **Dispersion forces, Hydrogen bonding** and metallic bonds respectively.

A surface cannot exist on its own: it must be part of an interface between two phases, even if one is vacuum. The term “surface energy” without qualification strictly applies to the substance concerned in contact with a vacuum. For practical purposes, the distinction between surface energy against vacuum and against air is usually neglected. The simple mental picture of surface energy’s being the energy required to break the bonds to form a surface must be refined. It is better regarded as the algebraic sum of the energy required to break the bonds to form the surface *in vacuo* and that released when any new bonds are formed on the surface when it is brought in contact with the second phase. Thus, the surface energy of a solid in contact with a vapour may well be less than that *in vacuo*,

as some components of the vapour are likely to be adsorbed on to the solid surface (this is closely connected with “spreading pressure”).

“Surface tension” is a concept closely allied with surface energy. The meniscus of mercury, for example, can be explained in terms of either the reduction of surface area, and therefore of surface energy, or of there being a surface tension – a force acting in the surface – trying to contract it. The connection between surface tension and surface energy and the precise meanings of both can be seen from thermodynamic considerations.

### *Thermodynamic aspects*

Consider a soap film held between three fixed sides of a rectangular wire frame and a frictionless wire slider of length  $l$ . Under the influence of a force  $F$ , acting at right angles to the slider, the slider moves a distance  $dx$ , and the area of the film is increased by

$$dA = ldx \quad [1]$$

The work done by the force is

$$\begin{aligned} dW &= Fdx \\ &= (F/l) \cdot ldx = (F/l)dA \end{aligned} \quad [2]$$

If the change is done at constant temperature and pressure, the increment of work will equal the increment of Gibbs free energy  $dG$ . Moreover, in elementary treatments, the surface tension  $\gamma$  is defined as the force per unit length in the surface. Thus, Eqn. 2 can be written as

$$dW = \gamma dA = dG \quad [3]$$

which leads to the thermodynamic definition of surface tension  $\gamma$  as the partial differential of the free energy of the system with respect to area:

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,P} \quad [4]$$

Now, the surface energy, more strictly the Gibbs surface free energy  $G^S$ , is the excess free energy of the system associated with the surface (per unit area), and so is defined as

$$G^S = \frac{G - G^B}{A} \quad [5]$$

where  $G$  is the total free energy of the system,  $G^B$  the value the free energy would have if all the atoms were in the environment they have in the bulk and  $A$  the surface area.

In the case of the soap film under consideration, it is only the change in area that causes a change in free energy, so  $dG$  can be equated to  $d(G^S A)$ :

$$dG = d(G^S A) = \gamma dA \quad [6]$$

therefore

$$\gamma = \frac{\partial(G^s A)}{\partial A}$$

and therefore

$$\gamma = G^s + A \left( \frac{\partial G^s}{\partial A} \right)_{T,P} \quad [7]$$

Equation 7 gives the relation between surface energy  $G^s$  and surface tension  $\gamma$ . They are equal only when  $(\partial G^s/\partial A)_{T,P}$  is zero.

The term  $\partial G^s/\partial A$  is the rate of change of surface energy per unit area with area. Thus, if  $G^s$  does not change as area increases,  $\gamma$  and  $G^s$  are equal; if  $G^s$  changes with area, they are different. If the local environment of the surface atoms remains the same, when area is increased,  $G^s$  is independent of area and equals  $\gamma$ . This is what happens in a single-component liquid. In a solid or multi-component liquid, the situation may be different. Increasing the area of a solid may involve plastic deformation of the surface, orientating the molecules and changing their local interactions. Then,  $G^s$  will change with area. In a multi-component system, changes in surface concentration of solute may occur.

In summary, the definition of surface tension is given by Eqn. 4, of surface energy by Eqn. 5 and the relation between them by Eqn. 7. (*Note:* Some authors develop these concepts in terms of the Helmholtz function rather than the Gibbs function, by supposing the soap film to be stretched at constant temperature and volume, rather than pressure.)

### Practical usage

The thermodynamic treatment given above applies strictly to single-component anisotropic solids and liquids. To take account of multi-component systems and anisotropy, further refinement is necessary.

In many practical contexts, including adhesion, values for surface energies of the solids involved cannot be measured with sufficient precision to make such distinctions worthwhile. In fact, for this reason, most of the literature, this *Handbook* included, treats “surface energy” and “surface tension” as if they were interchangeable terms. The symbol  $\gamma$  is commonly used for both.

As dimensions of surface tension and surface energy are the same (Eqns. 4 and 5), they may be expressed in the same units. The equivalent units of newtons per metre ( $\text{N m}^{-1}$ ) or joules per square metre ( $\text{J m}^{-2}$ ) can be used. Commonly, millijoules per square metre ( $\text{mJ m}^{-2}$ ) is used as it gives numbers of convenient magnitude and is identical to the dyne per centimetre or erg per square metre ( $\text{dyne cm}^{-1}$  or  $\text{erg cm}^{-2}$ ) still met in the older literature.

Solids are sometimes classified as having “high-energy surfaces” or “low-energy surfaces” according to their surface energies. Thus, low-energy surfaces have  $\gamma$  up to about  $100 \text{ mJ m}^{-2}$  and include organic surfaces, especially polymers. High-energy surfaces have  $\gamma$ -values of hundreds or thousands of millijoules per square metre and comprise hard inorganic surfaces such as metals, oxides and ceramics.

These ideas are further developed in other articles, in particular, **Surface characterization by contact angles – polymers**, **Wetting and spreading**, **Wetting and work of adhesion**, **Contact angles and interfacial tension**, **Pre-treatments of polymers** and **Pre-treatment of metals prior to bonding**.

*Select References*

- A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, 6th edn, Wiley, Chichester, 1997.  
 J. C. Berg, in *Adhesion Science and Engineering*, Vol. 2, *Surfaces, Chemistry and Applications*,  
 M. Chaudhury and A. V. Pocius, Eds., Elsevier, 2002, p. 1.

*Surface energy components*

D E PACKHAM

The magnitude of the **Surface energy** of a material depends upon the strength of the bonds that have to be broken to form the surface concerned. An extension of this idea is the suggestion of Fowkes that surface energy  $\gamma$  can be expressed as the sum of components associated with individual types of bond involved.<sup>1</sup> In general this can be expressed as

$$\gamma = \gamma^d + \gamma^p + \gamma^h + \dots \quad [1]$$

where the superscripts refer to **Dispersion forces** (d), **Polar forces** (p) and **Hydrogen bonding** (h). The number of terms in the equation and their form depend in any particular case on the structure of the substance concerned; it should be remembered that dispersion forces are universal, and so are always involved. Thus, for mercury, the surface energy could be expressed as

$$\gamma_{\text{Hg}} = \gamma_{\text{Hg}}^d + \gamma_{\text{Hg}}^m \quad [2]$$

where m refers to metallic bonding.

An important point in the use of surface energy components is the realization that for non-polar liquids, such as alkanes, only dispersion forces act between molecules, so

$$\gamma = \gamma^d \quad [3]$$

*Dispersion force interface*

Alkanes cannot exhibit metallic bonding, so it can be argued that dispersion forces comprise the only type of bond that can act across a mercury–alkane interface. Fowkes has called such an interface a “dispersion force interface” and argued that the interfacial tension was given by

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} \quad [4]$$

This equation should be compared with Eqn. 2 in **Contact angles and interfacial tension**, where the subscript notation is explained.

One justification for the geometric mean term in Eqn. 4 comes from the Good–Girifalco equation

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi(\gamma_1 \gamma_2)^{1/2} \quad [5]$$

If dispersion forces are the dominant bond type in both phase 1 and 2 and the molecules are similar in properties,  $\phi$  will be close to unity. (This is discussed in the **Good–Girifalco**

**interaction parameter.**) In these circumstances, Eqn. 1 can be regarded as a special case of Eqn. 5.

#### *Work of adhesion*

From the definition of work of adhesion  $W_A$  and work of cohesion  $W_C$  given in **Contact angles and interfacial tension**, it can be seen that the equivalent of Eqn. 1 can be written in terms of components of work of adhesion:

$$W_A = W_A^d + W_A^p + W_A^h + \dots \quad [6]$$

Further, the geometric mean assumption in Eqn. 5 is equivalent to writing

$$W_A^d = (W_{C_1}^d \cdot W_{C_2}^d)^{1/2} \quad [7]$$

This is further developed in discussing **Acid–base interactions**.

#### *Evaluation of $\gamma^d$ for liquids*

For non-polar liquids, the dispersion component is essentially the total surface tension (see Eqn. 3). For polar liquids, the dispersion component of surface tension can be obtained using Eqn. 4 after measuring both surface tensions and interfacial tension, provided that  $\gamma^d$  of the other liquid is known.

#### *Evaluation of $\gamma^d$ for solids*

Young's equation (see **Contact angles and interfacial tension** and the nomenclature described) relates **Contact angle** to surface energy terms. By measuring contact angles on a solid surface of liquids of known  $\gamma_L^d$ ,  $\gamma_S^d$  can be calculated. The solid–liquid interfacial tension  $\gamma_{SL}$  is eliminated between Eqn. 5 and the Young equation, giving

$$\gamma_S^d = \gamma_{LF}^2 (1 + \cos\theta)^2 / 4\gamma_L^d \quad [8]$$

In deriving this equation, it has been assumed that the spreading pressure is zero: this and further relevant details are discussed under **Surface characterization by contact angles – polymers**.

#### *Extension to polar components*

Equation 4 applies to an interface across which only dispersion forces act: if other forces act as well, there must be another negative term on the right-hand side, giving the further lowering of interfacial energy (see **Contact angles and interfacial tension**, Eqn. 2, and **Surface characterization by contact angles – polymers**, Eqn. 4). Over the years, it



has commonly been assumed that, in the absence of primary bonding, the non-dispersion forces across an interface could be treated as polar, that is,

$$\gamma = \gamma^d + \gamma^p \quad [9]$$

and that their contribution to the lowering of interfacial tension was also based on a geometric mean relationship<sup>2</sup>

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2} \quad [10]$$

The theory of the **Good–Girifalco interaction parameter** can be developed to give some support for this relationship.<sup>3</sup> This was not accepted by Fowkes, who argued that the principal non-dispersion interactions are **Acid–base interactions**, for which a geometric mean relationship does not apply.

#### *Lifshitz theory*

Taking cognizance of the considerations discussed under **Lifshitz-van der Waals forces**, the van der Waals force component to surface energy has often been written in recent literature as  $\gamma^{\text{LW}}$ , where LW stands for Lifshitz-van der Waals.  $\gamma^{\text{LW}}$  represents all the van der Waals force interactions, that is, in the earlier terminology, dispersion plus polar. Its contribution to the lowering of interfacial tension can be represented by a geometric mean relationship, see Eqn. 4,

$$\gamma_{12}^{\text{LW}} = \gamma_1^{\text{LW}} + \gamma_2^{\text{LW}} - 2(\gamma_1^{\text{LW}} \gamma_2^{\text{LW}})^{1/2} \quad [11]$$

The equivalent of Eqn. 9 would then be written as

$$\gamma = \gamma^{\text{LW}} + \gamma^{\text{ab}} \quad [12]$$

where  $\gamma^{\text{ab}}$  is the acid–base component of surface tension that *cannot* be represented by a geometric mean expression. This approach is further considered in the article on **Acid–base interactions**. Although opinion is now running strongly against its adequacy, much use has been made of Eqn. 10.

#### *Surface energies of solids*

Once the dispersion component of surface energy of a liquid is known, the polar component can be obtained from the surface tension using Eqn. 10. The approach based on Eqns. 9 and 10 can then be used to estimate surface energies of solids, particularly polymers, very much in the same way as  $\gamma_S^d$  values are obtained from Eqn. 8. Here,  $\gamma_{12}$  is eliminated between Eqn. 10 and the Young equation, giving

$$1 + \cos \theta = 2 \frac{(\gamma_S^d \gamma_L^d)^{1/2}}{\gamma_{\text{LF}}} + 2 \frac{(\gamma_S^p \gamma_L^p)^{1/2}}{\gamma_{\text{LF}}} \quad [13]$$

Table 1. Values of dispersion ( $\gamma^d$ ) and polar ( $\gamma^p$ ) components of surface energy

Substance	$\gamma^d(\text{mJ m}^{-2})$	$\gamma^p(\text{mJ m}^{-2})$
PTFE	18.6	0.5
Polyethylene	33.2	–
PVC	40	1.5
PMMA	35.9	4.3
Nylon 6.6	35.9	4.3

This again assumes a spreading pressure of zero; see **Surface characterization by contact angles – polymers**. The contact angles of several liquids of known  $\gamma_L^d$  and  $\gamma_L^p$  are measured on the surface of the solid of interest, giving a number of simultaneous equations of the form of Eqn. 13. These contain only two unknowns,  $\gamma_S^d$  and  $\gamma_S^p$ , so they can be evaluated. Some values of surface energy components are given in Table 1, and are given in the literature.<sup>2,4,5</sup>

The concept of surface energy components provides one route to interfacial tensions and solid surface energies and others include the **Good–Girifalco interaction parameter** and **Acid–base interactions**.

### References

1. F. W. Fowkes, B. L. Bulter, P. Schissel, G. B. Bulter, N. J. Delollis, J. S. Hartman, R. W. Hoffman, O. T. Inal, W. G. Miker and H. G. Tomphins, *Mater. Sci. Eng.*, **53**, 125 (1982).
2. D. H. Kaelble, *Physical Chemistry of Adhesion*, Wiley-Interscience, New York, 1971.
3. R. J. Good, in *Contact Angle, Wettability and Adhesion*, K. L. Mittal, Ed., VSP, 1993, p. 3.
4. D. Briggs, D. G. Rance and B. C. Briscoe, in *Comprehensive Polymer Science*, Vol. 2, G. Allen, Ed., Pergamon Press, Oxford, 1989, p. 715.
5. J. T. Koberstein, *Encyclopedia of Polymer Science and Engineering*, Vol. 8, Wiley-Interscience, New York, 1987, p. 257.

## Surface forces apparatus

ALPHONSUS V POCIUS

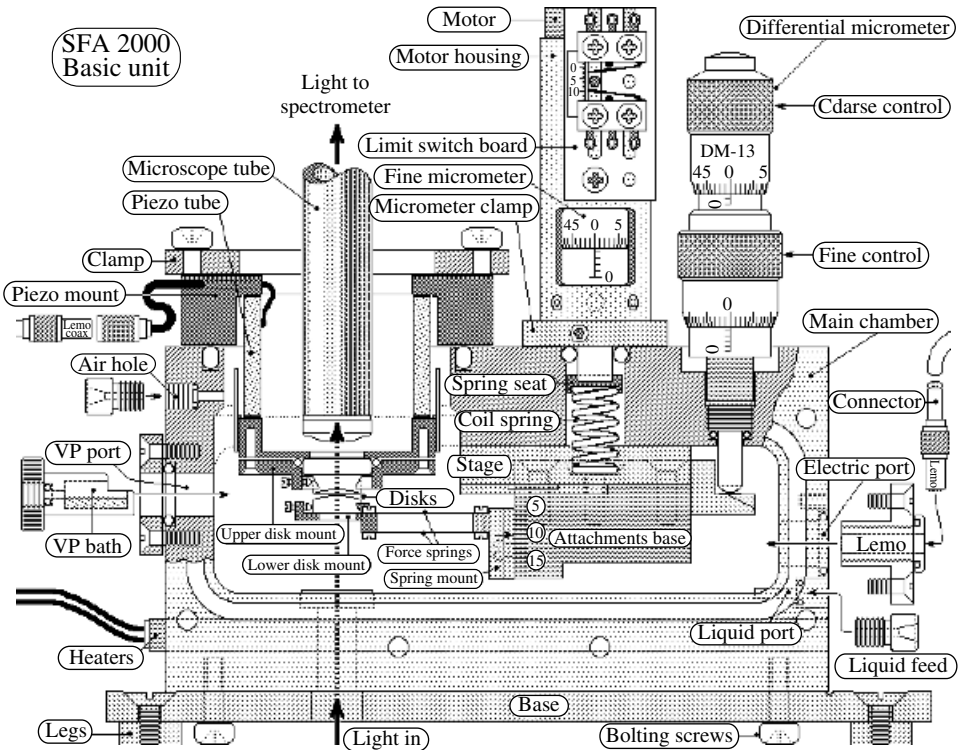
### Introduction

The study of fundamental adhesion has been hampered because standard **Tests of adhesion** provide a result that is a complicated combination of fundamental adhesion, the physical properties of the adherend and the viscoelastic/plastic character of the adhesive (see **Adhesion – fundamental and practical, Peel tests**). Our understanding of adhesion has been significantly improved with the advent of mechanical devices that are able to probe the forces of adhesion under conditions that minimize all of the confounding effects of adherend, viscoelasticity, and so on. The Surface Forces Apparatus (SFA) as developed by Israelachvili<sup>1–3</sup> and Tabor<sup>4,5</sup> is a mechanical device that has allowed adhesion scientists to directly measure the forces of adhesion under very low rate, light loading, almost equilibrium conditions. Attention is also drawn to **Atomic force microscopy**.

### Device description

A schematic diagram of the SFA is shown in Fig. 1. Basically, it consists of a stainless steel enclosure that is gasketed so that gases or liquids can be contained within the device. The bottom and the top of the device have optically clear windows arranged in such a fashion that white light can enter through the bottom of the device and exit out of the top. A spectrophotometer is an essential feature of the device. Central to the operation of the device is a sequence of hard and soft springs and microdrivers, the end of which terminates in a cantilever beam. Modern SFAs have a dual cantilever beam in order to minimize shear effects. The spring constant of the cantilever beam is determined by separate measurements of deflection under load. The device can also have one or more piezoelectric devices to drive the movement of one or both of the sample surfaces.

The operational part of the device is a pair of cylindrical lenses (called “disks” in Fig. 1). The lenses are crossed, which provides for a theoretically circular contact area. One of these lenses is fixed to the upper part of the SFA and is usually stationary (unless driven by the piezoelectric). The other lens is mounted on the end of the cantilever beam. The sample of interest is mounted on the surface of the lenses. Approximately 50 nm of silver is applied to the back of the sample before mounting. This amount of silver provides for sufficient optical transparency such that enough light can make it through both samples, both lenses, any reflecting optics and into the spectrometer for analysis.



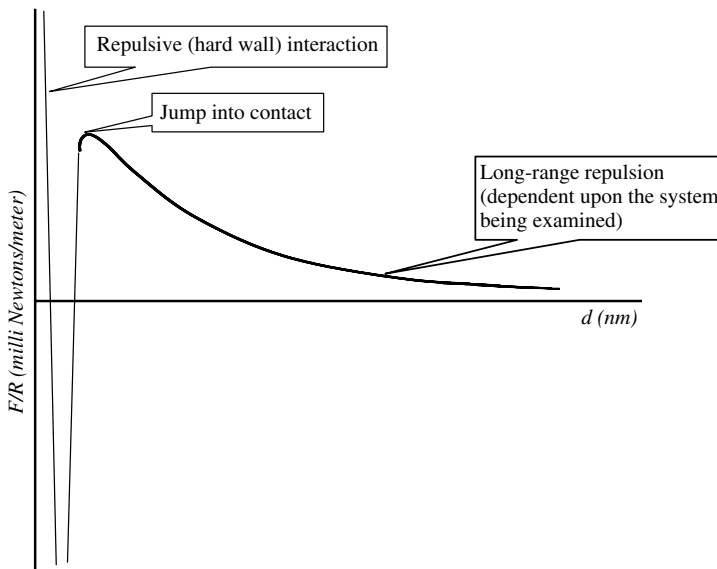
**Fig. 1.** Schematic of the SFA 2000 surface forces apparatus. (Drawing provided by Prof. J. N. Israelachvili and used with his permission)

The silvered sample is mounted on the lens using an adhesive. Very often, the adhesive is just a sugar glue, but adhesives ranging from epoxies to pressure-sensitive ones have been used. The most important consideration for the adhesive is that it is optically transparent, not affected by the medium in which the test is to be done nor should it contribute to the mechanics of the test.

Because the back of the sample is silvered, an interferometer is formed. The light exiting the SFA is projected into a spectrophotometer. The pattern seen in the spectrophotometer is called “fringes of equal chromatic order (FECO)”. The spacing between the FECO is directly related to the spacing between the silver layers.<sup>6</sup> Hence, if the sample thickness is known, then the spacing between the sample surfaces is known. If one knows the distance of separation of the sample surfaces and one also knows the spring constant of the cantilever spring, then the force between the sample surfaces can be determined using Hooke’s Law.

### Analysis methods

Measurements from the SFA have been analysed in two primary ways. In the first, the data is plotted as  $F/R$  versus  $d$ .  $F$  is the force measured as described above,  $d$  is the distance of separation between the surfaces and  $R$  is the radius of curvature of the lens/sample. A sample plot is shown in Fig. 2. The second way is the use of “contact mechanics”. This discipline analyses the deformation of elastic bodies in contact. There are two main methods for analysing contact mechanics data. One is known



**Fig. 2.** Idealized representation of a force–distance profile resulting from an SFA measurement. Items to be noted include the fact that distances are measured in nanometers or less, force is measured in mN. A jump into contact is shown. In some cases, more detailed information about molecular level forces can be obtained by examining data near to the jump into contact

as the Johnson–Kendall–Roberts<sup>7</sup> Theory (see **JKR theory**) and the other is the Derjaguin–Muller–Toporov (DMT)<sup>8</sup> Theory.

All surfaces will jump into contact at a certain distance when the derivative of the potential energy curve for the materials exceeds the spring constant of the cantilever beam. The JKR theory predicts the shape of the bodies in contact just outside the contact zone and it also predicts that the surfaces will jump out of contact at a specific non-zero contact area. One result obtainable from the SFA combined with the JKR theory comes from the force measured at the jump out of contact:

$$F_{\text{JKR}} = -\frac{3}{2} W_{\text{A}} \pi R$$

where  $F_{\text{JKR}}$  is the force measured in the SFA,  $W_{\text{A}}$  is the work of adhesion between the two surfaces and  $R$  is the radius of curvature of the sample, as discussed previously. Thus, this relatively simple measurement directly provides the work of adhesion between two solid surfaces. No other technique provides this quantity directly. The DMT theory can also provide such data. However, it is found that for most adhering materials of modulus on the order of a gigapascal or less, the JKR theory seems to fit the data better than the DMT theory. See Maugis<sup>9,10</sup> for a more detailed discussion of the application of the two theories and of this analysis.

### Surfaces

A variety of surfaces have been investigated using the SFA. No attempt is made to be exhaustive in the description of these studies.

The most widely used sample surface by far is Muscovite mica. This sample provides a surface that is atomically smooth and high modulus. In addition, because of the properties of mica, it can be cleaved to provide samples of a thickness appropriate to generate FECO of an appropriate spacing, that is, on the order of a few microns. Israelachvili and co-workers have studied mica surfaces extensively.<sup>2,11</sup> In addition, they have adsorbed various materials on mica and studied their interaction.<sup>12</sup> For example, the SFA has been used to study the force necessary to remove monolayers of small molecules from between mica surfaces.<sup>13</sup>

Horn and Smith have used the SFA to examine the contact between dissimilar high modulus materials (sapphire and mica).<sup>14</sup> Their results were drastically different from that produced by other workers in that a force of adhesion significantly in excess of  $W_{\text{A}}$  was measured. The pull-off force also exhibited an odd response. The results of the measurements indicated that charge had transferred between the two materials in contact. This work, using the SFA, provides one of the few conclusive measurements indicating the validity of the electrostatic theory of adhesion.

Many workers have examined the effect of surfactants<sup>15,16</sup> and polymers<sup>17–21</sup> adsorbed on mica. For example, polymers such as poly(vinyl pyridine) and its copolymers have been adsorbed on mica and their interfacial interactions measured in liquid media. Forces measured between these surfaces are of much longer range and provided some evidence for the “brush” conformation of polymers. Other workers have used industrially generated polymer films mounted directly to the glass lenses in the SFA and examined their adhesion

characteristics.<sup>22–24</sup> More recently, researchers have used the SFA to study the interaction of biologically important molecules at interfaces.<sup>25</sup>

### Concluding remarks

The SFA is a versatile instrument that can provide significant insight into interfacial phenomena and adhesion. Unfortunately, there are significant constraints as to the type of sample that can be used and the measurement technique can be a bit cumbersome. There is, however, no other way in which one can directly examine all of the mechanics of surfaces as they come into and out of contact.

### References

1. J. N. Israelachvili and D. Tabor, *Proc. Roy. Soc. A.*, **331**, 19 (1972).
2. J. N. Israelachvili and G. E. Adams, *J. Chem. Soc., Faraday Trans. I.*, **74**, 975 (1978).
3. J. N. Israelachvili and P. M. McQuiggan, *J. Mater. Res.*, **5**, 2223 (1990).
4. D. Tabor and R. H. S. Winterton, *Nature*, **219**, 1120 (1968).
5. D. Tabor and R. H. S. Winterton, *Proc. Royal Soc. A.*, **312**, 435 (1969).
6. J. N. Israelachvili, *J. Coll. Interface Sci.*, **44**, 259 (1973).
7. K. L. Johnson, K. Kendall and A. D. Roberts, *Proc. Royal Soc. London A.*, **324**, 301 (1971).
8. B. V. Derjaguin, V. M. Muller and Yu. P. Toporov, *J. Coll. Interface Sci.*, **53**, 314 (1975).
9. D. Maugis, *J. Coll. Interface Sci.*, **150**, 243 (1992).
10. D. Maugis and M. Barquins, *J. Phys. D: Appl. Phys.*, **11**, 1989 (1978).
11. P. M. McQuiggan and J. N. Israelachvili, *Chem. Phys. Lett.*, **149**, 469 (1988).
12. Y. L. Chen, C. A. Helm and J. N. Israelachvili, *J. Phys. Chem.*, **95**, 10736 (1991).
13. H. K. Christenson, D. W. R. Gruen, R. G. Horn and J. N. Israelachvili, *J. Chem. Phys.*, **87**, 1834 (1987).
14. R. G. Horn and D. T. Smith, *Science*, **256**, 362 (1992).
15. H. K. Christenson and P. M. Claesson, *Science*, **239**, 390 (1988).
16. H. K. Christenson and P. M. Claesson, *Adv. Coll. Interface Sci.*, **91**, 391 (2001).
17. J. Marra and M. L. Hair, *J. Coll. Interface Sci.*, **125**, 552 (1988).
18. J. Marra and M. L. Hair, *J. Phys. Chem.*, **92**, 6044 (1988).
19. N. Kawanishi, H. K. Christenson and B. W. Ninham, *J. Phys. Chem.*, **94**, 4611 (1990).
20. H.-W. Hu, J. V. Alsten and S. Granick, *Langmuir*, **5**, 270 (1989).
21. S. S. Patel and M. Tirrell, *Annu. Rev. Phys. Chem.*, **40**, 597 (1989).
22. W. W. Merrill, A. V. Pocius, B. V. Thakkar and M. Tirrell, *Langmuir*, **7**, 1975 (1991).
23. V. Mangipudi, M. Tirrell and A. V. Pocius, *J. Adh. Sci Tech.*, **8**, 1251 (1994).
24. V. Mangipudi, M. Tirrell and A. V. Pocius, *Langmuir*, **11**, 19 (1995).
25. D. Leckband and J. N. Israelachvili, *Thin Films*, **20**, 207 (1995).

### Surface nature of polymers

D BRIGGS

It is very rare for the chemical nature of the surface of a polymer to be a mere extension of that of the bulk. Even when there are no deliberate additives, for example, antioxidants, the

surface can have a different molecular weight from the bulk because of segregation of low-molecular-weight “tail” polymer and, in the case of segmented copolymers, preferential segregation of the lower energy component may occur (see **Compatibility**).

The nature of a polymer surface has an important effect on many end uses: adhesive properties such as heat sealability (see also **Wetting and spreading**), and general processing and machine-handling properties (e.g. friction and “blocking” or self-adhesion) are very sensitive to surface condition, and optical properties are affected by haze, gloss and stains. Additives in polymeric materials include agents to prevent oxidation (thermal and photochemical), to neutralize acidity, to promote fire retardance and to aid processing. These are usually intended to be well distributed throughout the bulk, but in certain circumstances, surface segregation may take place. Agents to lower surface friction, to increase surface conductivity and prevent “blocking” are intended to migrate to the surface. In some cases, they may not do so and in other cases, they may migrate across interfaces through contact with another surface. Filler and pigments particles are often surface coated, and components of this coating may pass into the matrix and hence to the surface (see **Filler–matrix adhesion**).

Surface segregation of emulsifier and stabilizer molecules used in some polymerization processes is a frequent occurrence. Common contaminants generally are lubricating oils and greases, mould release agents and various airborne materials, particularly in aerosol form (see **Mould adhesion and fouling**).

Blooms and visually similar phenomena are sometimes seen on the surfaces of rubber mouldings. These may originate from the limited solubility of a particular component of the rubber compound, or from contamination, for instance, by a *release* agent from the mould. Some blooms are deliberately contrived – hydrocarbon wax gives some protection from ozone attack. Loadman and Tidd give a useful account of the classification and analysis of blooms on rubber.

“Engineering” polymer surfaces in order to change surface properties has a long history and is increasing in sophistication (see **Corona discharge treatment, Flame treatment, Plasma pre-treatment**). Understanding structure-property relationships is vital and much research is carried out in this area using the range of **Surface analysis** techniques now available, particularly XPS and SIMS.

### Select References

- C.-M. Chan, Ed., *Polymer Surface Modification and Characterisation*, Hanser, Munich, 1994.  
F. Garbassi, M. Morra and E. Occhiello, *Polymer Surfaces*, Wiley, Chichester, 1998.  
D. Briggs, Ed., *Polymer Surface Analysis by XPS and Static SIMS*, Cambridge University Press, Cambridge, 1998.  
M. J. R. Loadman and B. K. Tidd, in *Natural Rubber, Science and Technology*, A. D. Roberts, Ed., Oxford University Press, Oxford, 1988.

# T

---

## *Tack*

---

D W AUBREY\*

When tack is significant, there is appreciable resistance to the separation of two materials brought momentarily into contact. The phenomenon may be subdivided into three distinctly different groups as given below:

1. *Cohesive tack* involves bulk flow of one or both materials during separation and applies to materials like printing inks, paints, syrups, and so on. Resistance to separation is governed by viscous flow according to the Stefan equation.
2. *Adhesive tack* involves a separation apparently at the original interface between the materials. This kind of tack applies particularly to **Pressure-sensitive adhesives**, although such adhesives may display cohesive tack under extreme conditions of rate or temperature.
3. *Autohesive tack* involves two elastomeric materials of essentially the same composition. In this case, separation may be either adhesive (usually after short times of contact) or cohesive (usually after long times of contact). It is important in the use of contact adhesives and in plying together rubber surfaces in, for example, the manufacture of tyres.

Autohesive tack differs from the other types in that it involves mutual diffusion of polymer molecules across the interface; it is discussed elsewhere (see the articles on **Diffusion theory of adhesion** and **Polymer diffusion: reptation and interdigitation**). Adhesive tack between elastomeric materials and other, usually rigid, surfaces is considered in this article.

### *Mechanism of adhesive tack*

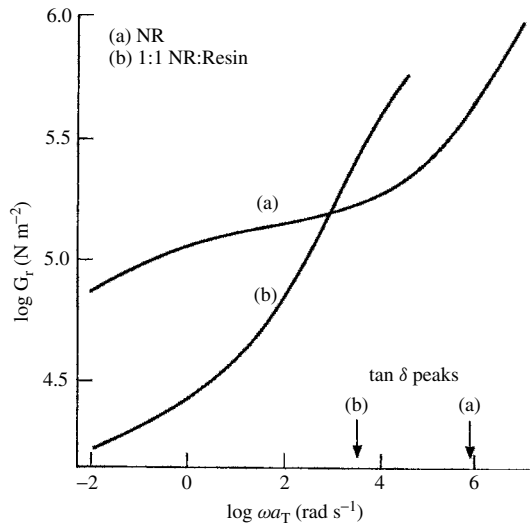
The methods used for routine assessment of tack have been described elsewhere (see **Pressure-sensitive adhesives – adhesion properties**). All these methods involve the



contact of two surfaces (adhesive and test substrate) under light pressure for a short time, followed by a separation step, the force (or energy) of separation being taken as a measure of tack. Thus, the tack phenomenon involved two processes – a bonding process in which the adhesive is allowed to deform or flow into contact with the surface for a time of the order 0.1–10 s, and a debonding process in which the adhesive separates by peeling from the surface, involving a much more localized and shorter timescale of deformation, typically  $10^{-4}$ – $10^{-6}$  s. Assuming that backing and adhesive thickness effects are eliminated, the tack value will depend on the following:

1. The ease of deformation of the adhesive during the bonding stage, that is, its shear compliance over the bonding period, which determines the degree of true interfacial contact achieved.
2. The resistance to separation of the contacted areas of interface formed in (1), determined by interfacial attractive forces, a measure of which is the thermodynamic work of adhesion.
3. The degree of deformation of the adhesive and hence the amount of energy dissipated as heat during the high-rate debonding stage, a measure of which would be  $\tan \delta$  at the appropriate rate. It depends strongly, of course, on (2).

Thus, attempts to rationalize the tack values obtained should involve for (1), knowledge of creep compliance at long times (which for high tack should be in the terminal region of the viscoelastic spectrum – see **Viscoelasticity**); for (2), knowledge of the surface energetics of the materials involved (see **Surface energy**); for (3), knowledge of  $\tan \delta$  (or equivalent parameters) at short times (which for high tack should be in the transition region of the viscoelastic spectrum – see **Viscoelasticity**).



**Fig. 1.** Master curves of (log) storage modulus  $G_r$  (against (log) frequency  $\omega$  at 296 K for (a) NR and (b) a 50/50 blend of NR with Piccolyte S115\* tackifier resin.<sup>1</sup> (\*Hercules Co. trade name)

### Mode of action of tackifier resins

Most of the study of tack has naturally involved attempts to understand the action of tackifier resins in increasing the tack of rubbers. For hydrocarbon rubbers (e.g. natural rubber, NR) and hydrocarbon tackifier resins (e.g. terpene resins such as poly- $\beta$ -pinene), it is generally found that the effects of surface energy change ((2) above) are negligible compared to the influence of the tackifier resins on the viscoelastic behaviour at both high and low rates ((1) and (3) above). This may be illustrated in a master curve of dynamic shear modulus against (log) rate (frequency),<sup>1</sup> shown diagrammatically in Fig. 1. The addition of  $\beta$ -pinene resin to NR results in a reduction in modulus (increase in compliance) in the terminal zone (at rates corresponding to the bonding step) and a shift of the transition zone (where  $\tan \delta$  is high) to lower rates (corresponding to the debonding step). Thus, the addition of a tackifier resin increases tack through its influence on both bonding and debonding processes.

Recent reviews of the basis of tack have been presented by Wool<sup>2</sup> and, in the context of **Pressure-sensitive adhesives**, by Creton and Fabre.<sup>3</sup>

### References

1. D. W. Aubrey, *Rubber Chem. Technol.*, **61**(3), 448 (1988).
2. R. P. Wool, *Polymer Interfaces: Strength and Structure*, Hanser, 1995, p. 271.
3. C. Creton and P. Fabre, in *Adhesion Science and Engineering – 2. Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, pp. 535–575.

## Tensile tests

D E PACKHAM

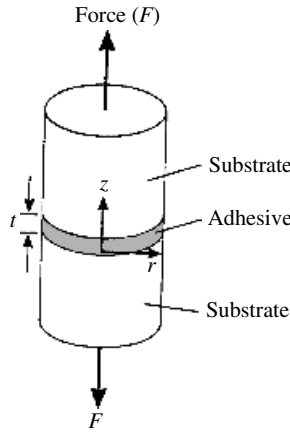
The joint is also known as the “butt joint” or “polker chip” joint. Two solid cylinders are bonded end to end, and the joint is tested by applying a force along the common axis (Fig. 1).

At first sight, it might seem a simple test to analyse with uniform tensile stress throughout the adhesive layer. In practice, the stress distribution is not uniform: the disparity of modulus and Poisson’s ratio between the cylinders and the adhesive means that shear stresses are introduced on loading (see **Stress distribution: Poisson’s ratio**). Thus, the failure stress is not independent of the dimensions of the joint.

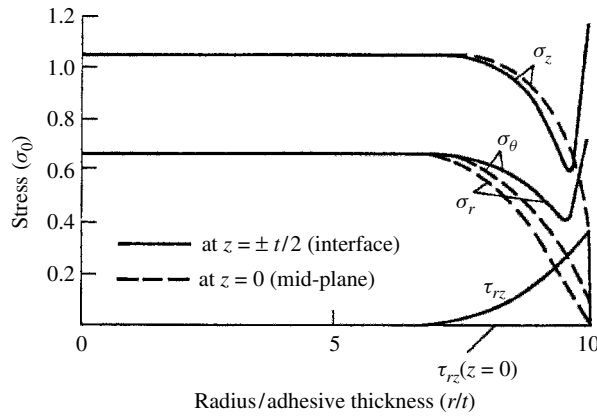
Adams, Coppendale and Peppiatt<sup>1</sup> have applied elastic **Finite-element analysis** to the joint. Figure 2 gives some typical results. The bonded area comprises two different regions. First, in the central region, the shear stress is zero and the tensile stresses are uniform, the radial  $\sigma_r$  and circumferential  $\sigma_\theta$  stresses being the same and related to the given axial stress  $\sigma_z$  by

$$\sigma_r = \sigma_\theta = \left[ \nu_a - \frac{E_a \nu_s}{E_s} \right] \left[ \frac{\sigma_z}{1 - \nu_a} \right] \quad [1]$$

where  $\nu$  is Poisson’s ratio,  $E$  is Young’s modulus and the subscripts a and s refer to adhesive and substrate respectively.



**Fig. 1.** An axially loaded butt joint



**Fig. 2.** An example of the stress distribution in an axially loaded butt joint (after Adams *et al.*)<sup>1</sup> ( $\sigma_0$  = applied average axial stress;  $E_a = 2.5$  GPa;  $E_s = 69$  GPa; aspect ratio = 20)

Second, around the periphery of the joint, both tensile and shear stresses act (see **Stress distribution: bond thickness**). As Fig. 2 shows, their magnitude depends on the aspect ratio of the joint and also varies throughout the thickness of the adhesive layer. On the adhesive – substrate interface, there is always a stress concentration at the edge of the substrate.

For a rubber adhesive, Gent<sup>2</sup> found that he could use the WLF equation to obtain a master curve of breaking stress (see **Viscoelasticity – time–temperature superposition**). He used a **Fracture mechanics** analysis to link the breaking stress to critical strain energy density.

A more detailed discussion of this test may be found in Ref. [3].

---

*References*

1. R. D. Adams, J. Coppendale and N. A. Peppiatt, *J. Strain Anal.*, **13**, 1 (1978).
2. A. N. Gent, *J. Polym. Sci.*, **A2**, 283 (1974).
3. K. L. de Vries and P. R. Bourgmeier, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, p. 225.

---

*Testing of adhesives*

---

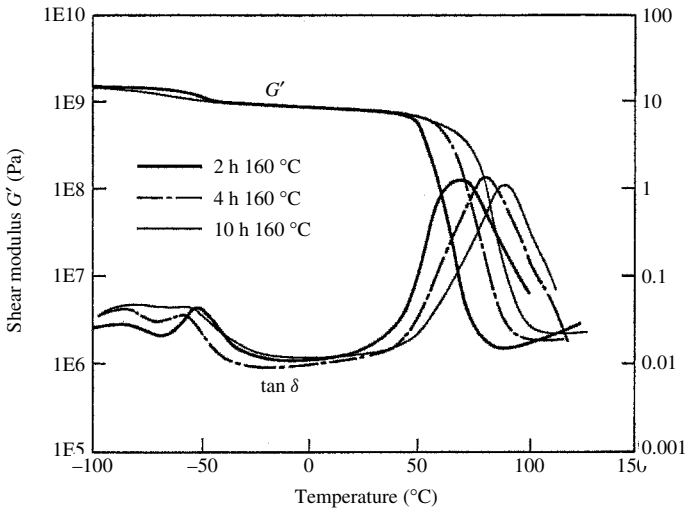
D A TOD

This article deals with the characterization of adhesives as polymers; the measurement of adhesion is dealt with in the article **Test of adhesion**.

Structural adhesives such as epoxy resins can be treated as any rigid polymer and samples can be machined from cast sheets to produce test-pieces. These can then be used to measure typical tensile properties such as failure stress and strain. Using accurate extensometry, it is possible to characterize completely the uniaxial properties of an adhesive. The **Creep** of adhesive joints is especially important for structural adhesives maintained at high temperature. It is possible to determine the creep resistance of such materials by applying suitable loads at an appropriate temperature to samples of the adhesive, and to record the deformation with time. From such data, it will soon be evident if the adhesive is suitable for use or if it will cause a joint to deform with time. It is important to remember that humidity is likely to affect the properties of the adhesive, and in a long-term creep experiment, the humidity could cause premature failure.

The effect of temperature and rate upon the properties of an adhesive can be determined using the technique of dynamic mechanical analysis. In such a test, small bars of the adhesive would be subjected to a small strain deformation at one end, and the resultant torque at the other end of the sample measured. Using suitable stimuli and analytical techniques, it is possible to resolve three properties of the material. These are the shear modulus, the loss modulus, and the loss or phase angle  $\tan \delta$  (see **Viscoelasticity**). When measured over a range of temperatures and rates, such parameters give a unique fingerprint to the usefulness of any particular polymeric system.<sup>1</sup> The effects of rate and temperature upon these properties can be combined to give one master curve using the WLF equation (see **Viscoelasticity**). Probably, the most important thermal transition in any adhesive system is the **Glass transition temperature**. Using dynamic mechanical analysis, it is possible to quickly establish this transition and its sensitivity to various parameters such as moisture uptake. The degree of cure of an adhesive can also be established with this technique, and this is shown for a typical epoxy resin in Fig. 1. This figure shows the major transition in the loss angle, which is accompanied by a rapid loss in the shear modulus at the **Glass transition temperature**. As the time of cure is increased, this transition in the adhesive increases by about 20 °C.

The cure of a thermosetting adhesive is usually measured by techniques such as cone and plate viscometry, or by a vibrating needle system. From these measurements, important characteristics such as the gelation point and the point of the final cure can be determined. The time from mixing of an adhesive to the gelation point gives the useful



**Fig. 1.** Variation of shear modulus and loss tangent with temperature for an epoxy resin cured for different times at 160 °C

life or “pot life” of the material. Various *in situ* tests are now available that can characterize the degree of cure of an adhesive; these include infrared probe techniques and dielectric techniques.

The technique of differential scanning calorimetry (see **Thermal analysis**) can also be used to provide valuable data on an adhesive. In this technique, the rate of energy input to a sample is measured as a function of temperature. The degree of cure of a resin system and its **Glass transition temperature** can be established.

The degradation temperature is very important for adhesives used at high temperature. The onset of degradation is normally established by a technique such as thermogravimetric analysis (TGA). In this technique, the weight of a sample is recorded as the temperature is increased. Eventually, the sample will begin to decompose and this will be reflected in a weight loss.

The coefficient of expansion of a polymer is very much greater than that of a metal. Such a mismatch of expansion will introduce stresses within an adhesive joint, especially if the joint is cured at an elevated temperature. The measurement of the expansion coefficient can be carried out by a variety of techniques, and one of the simplest is thermomechanical analysis (TMA), where the dimensions of a small sample are measured over a range of temperatures. The change in the sample dimension gives the variation in expansion coefficient with temperature.

The degree of cross-linking in an adhesive will give an indication of its state of cure. Several techniques can be used to establish this, and one of the commonest is the “sol-gel” technique, where the weight of an extracted portion of adhesive is compared to the un-extracted material.

In treating adhesives as polymeric materials, it is possible to use **Fracture-mechanics test specimens** to determine material properties independent of geometry. A typical sample would be the compact tension test-piece, where a sheet of material, typically 6-mm thick and 100-mm square, has a sharp crack inserted in one edge. The sample is then loaded perpendicular to the plane of the crack and the load at which crack propagation

initiates recorded. These data can then be used to generate the fracture energy of the material, which can then be used in the analysis of more complex shapes and also joint design.

An area of testing that is becoming more important is the **Impact resistance** of adhesives. The classic Charpy or Izod test methods are normally used for impact tests together with the falling or drop weight test. Generally, such instruments are becoming more highly instrumented so that subtle changes in the adhesive's material properties with high rates can be followed.

There are many other tests that can be carried out on adhesives using standard test methods for polymeric materials<sup>2-5</sup> and these should be reviewed for the most appropriate procedure (see **Standards on adhesion and adhesives**, Appendix).

### References

1. S. V. Wolfe and D. A. Tod, *J. Macromol. Sci. Chem.*, **A26**(1), 249 (1989).
2. R. P. Brown, *Handbook of Plastics Test Methods*, George Godwin, Plastics and Rubber Institute, London, 1981.
3. L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1994.
4. A. H. Landrock, *Adhesives Technology Handbook*, Noyes Publications, Park Ridge, New Jersey, 1985.
5. A. Pizzi and K. L. Mittal, *Handbook of Adhesive Technology*, Marcel Dekker, New York, 2003.

---

## Tests of adhesion

---

D A TOD

This article relates to methods of measurement of the bond strength between an adhesive and a substrate; the characterization of adhesives alone is considered in the article **Testing of adhesives**.

There are numerous different tests of adhesion that are used for five main purposes:

1. to check the quality of an adhesive to see if it falls within well-defined limits;
2. to determine the effectiveness of a surface pre-treatment;
3. to gather data for the prediction of joint performance;
4. to select an adhesive from a group for a specific application;
5. to evaluate the effect of ageing.

It will often be necessary to undertake very complex testing to yield detailed results before an adhesive joint is used in service. Once this has been done, it may be adequate for quality control purposes to use a relatively simple test, if its results are sensitive to critical factors affecting performance of the joint. When a test procedure is chosen, it is necessary to consider the nature of the adhesive; a test suitable for a rigid structural adhesive is unlikely to be useful for an elastomeric system such as an adhesive tape.

There are three commonly used test configurations: tensile, shear and peel. Probably the commonest test piece used is the lap shear test piece. This comes in two principal forms, the single- and the double-lap joints. The advantage of this test piece is that it can be easily

manufactured and quickly tested. In its simplest form, it consists of two strips of metal, approximately  $100 \times 25 \times 1.6$  mm, that are bonded together on their major surfaces with an overlap of 13 mm. After cure, the joint is pulled apart in the axis of the bond and the failure load of the joint is then calculated. Although the practical manufacture and test of this joint is simple, the stress distribution developed is complex. This leads to a situation where the measured value of joint strength is of restricted value in the design of adhesively bonded components. However, in spite of its deficiencies, this test does provide a rapid assessment of shear strength of an adhesive.

The tensile test piece can take several forms; one simple configuration consists of two right-circular cylinders whose ends are then bonded together. Such a joint is loaded to failure at right angles to the plane of the adhesive and the failure stress is determined from the loaded area and failure load.

**Peel tests** are generally used for elastomeric or rubbery adhesives. A typical version of this test would be the "T-peel test" in which two strips of a rubber would be bonded together, face to face, and the force required to pull the strips apart would be recorded. The name of the test derives from the shape of the test piece during testing when the top of the "T" are the two loaded arms and the vertical of the "T" is the remaining bonded length.

Certain tests are specifically designed to assess the effects of environmental exposure upon adhesive joints. Such a test would be the **Wedge test** in which an adhesive joint is formed out of two strips of metal bonded together, face to face. A wedge is then driven into the end of the joint to force the bonded surfaces apart and the joint is then immersed in water. The energy stored within the two strips provides a driving force for the adhesive to fail. The rate of failure of the joint will indicate the effectiveness of an adhesive and surface pre-treatment.

A completely different set of tests are referred to as **Fracture mechanics** test methods. In these tests, attempts are made to measure true material properties of the adhesive joint independent of the geometry test. Such test methodologies require careful preparation of samples so that all experimental variables are controlled. A typical parameter measured for such joints would be the adhesive fracture energy, and normally, this would be determined as a function of some parameter such as the rate or temperature of testing.

The viscoelastic (see **Viscoelasticity**) nature of the adhesives means that all joints are affected by the rate and temperature of the test. A key parameter in the testing of such joints is the **Glass transition temperature** of the adhesive. When the joints are tested below this temperature, the adhesive will be a low-strain rigid material; above this temperature, it will adopt a more rubber-like nature.

A further important parameter is the adhesive thickness within a joint. In certain adhesive systems such as rubber-toughened epoxies, there is an optimum thickness of adhesive within which energy-dissipation processes can take place. Above and below this critical size, the adhesive fracture energy will be lower.

Frequently, bulk samples of adhesives are prepared upon which various tests are conducted. It should be noted that properties from such material could be different from the properties of the adhesive formed in a joint.

Specific tests of adhesion are described in more detail under the following articles: **Blister test, Climbing drum peel test, Fracture mechanics, Napkin ring test, Peel tests, Rubber to metal bonding – testing, Shear tests, Tensile tests, Wedge test** and in Refs. [1–5]; see also **Standards for adhesives and adhesion** and Appendix.

All of these tests give a “number”, perhaps in the form of a force per unit area or an energy per unit area, which may be loosely termed the “adhesion”. It is important to realize that this number reflects the properties of the joint-substrate, adhesive, interface and the interactions between them. Thus, changes in the dimensions of a joint commonly change the value of “adhesion” measured: different tests will not necessarily rank a series of adhesives or surface treatments in the same order. It is only **Fracture mechanics** tests that make any claim to measure a fundamental property, and, even here, great care is needed in interpreting the results (see **Adhesion – fundamental and practical**).

### References

1. G. P. Anderson, S. J. Bennett and K. L. DeVries, *Analysis and Testing of Adhesive Bonds*, Academic Press, New York, 1977.
2. R. D. Adams, J. Comyn and W. C. Wake, *Structural Adhesive Joints in Engineering*, Chapman & Hall, London, 1997.
3. A. J. Kinloch, Ed., *Developments in Adhesives – 2*, Applied Science Publishers, London, 1981, Chaps 6,7,10.
4. A. V. Pocius, *Adhesion and Adhesives Technology*, Hanser, Ohio, 2002.
5. A. Pizzi and K. L. Mittal, *Handbook of Adhesive Technology*, Marcel Dekker, New York, 2003.

---

## Theories of adhesion

---

K W ALLEN

### Introduction

A distinction needs to be made between “adhesion” as measured in **Tests of Adhesion** and the mechanism on a micro- or atomic scale holding the phases together (see **Adhesion – fundamental and practical**). Here, we are concerned with fundamental adhesion. Over years, various theories have been advanced to account for the phenomena of adhesion. Ideas start from the simplest intuitive idea of the interlocking of glue with the rough surface of an adherend and have advanced through various stages of sophistication ever since. A problem that has bedevilled the whole topic has been the idea that there should be one explanation encompassing the whole range of examples. At one time, few were prepared to accept that their “pet theory”, which was perhaps satisfactory for the bonding of rough timber, was not useful for the whole range of other instances, from postage stamps to helicopter rotor blades.

It is now generally accepted that any particular case of adhesive bonding may need to be studied and explained in terms of contributions from several mechanisms. From the whole range that is available, several may contribute, each to a greater or lesser extent.

### Principal theories

The principal theories can be divided into five groups plus an additional one that is quite different: (1) mechanical theories (2) adsorption theories (3) chemical theories (4) diffusion theories (5) electrostatic theories plus pressure sensitive theories. Each of these will



be reviewed briefly and qualitatively so that their relative significance and contribution can be recognized. More detailed accounts will be found in the specialized articles indicated.

### *Mechanical theories*

The mechanical theories are the oldest and depend upon intuitive ideas. They involve the interlocking of the solidified adhesive with the roughness and irregularities of the surface of the adherend. It has sometimes been described as a “hook and eye” approach. Undoubtedly, they are significant on a macro scale for fibrous materials (e.g. paper, leather, wood). However, in recent years, a second range of significance has been recognized in which the scale of roughness and interlocking is several orders of magnitude smaller, down to something like approaching atomic dimensions. Many instances of commercial applications depend for their strength and durability upon this microscopic interlocking to give an interphase that has the nature of a composite.

### *Adsorption theories*

The adsorption theories encompass explanations that depend upon the secondary or van der Waals forces between the adhesive and the adherend (see **Bonds between atoms and molecules**). The most universal of these are the London **Dispersion forces**, which are involved, at least to some extent, in every adhesive bond. The sole requirement is that the two materials are brought into sufficiently close and intimate contact. This is achieved by ensuring that, at some stage in the bonding process, the adhesive is in the state of a mobile liquid. While these forces are relatively small, it has been shown that they are large enough to attractions considerably greater than any observed strengths. However, it has to be recognized that like gases physisorbed on a solid (from which phenomenon the title is derived) they are reasonably easily disrupted, particularly by water.

### *Chemical theories*

There are a number of instances in which, in addition to dispersion forces, primary chemical bonds are involved and provide a separate contribution to adhesive bond strength. These bonds may be simply covalent or may have a considerable degree of ionic character. This recognition has resulted from the sophisticated surface analytical techniques, which have only been readily available within the past two decades. These have revealed the fragments of bonding compounds within the fractured surfaces of broken bonds. **Acid–base interactions** and **Hydrogen bonding** may also be significant.

### *Diffusion theories*

For the specific case of two similar polymers below their glass transition temperatures in contact, there may be an interaction via the diffusion of polymer chain ends or segments across the interface, usually in both directions. The concept is straightforward and easily grasped, although the theoretical development is both difficult and complex. However, it was largely mastered some thirty years ago, mainly by Russian workers and considerable

agreement achieved between theoretical prediction and practical results. More recent work has extended the understanding of the extent and limitations of this concept (see **Polymer diffusion: reptation and interdigitation**).

### *Electrostatic theories*

The existence of an electrical double layer at the interface between a metal and a polymer adhering to it has been satisfactorily demonstrated. Undoubtedly, the electrostatic forces developed from this interaction could contribute to the total adhesive bond strength. However, the theories that have been advanced are less than rigorous and have been subject to severe criticism. Nevertheless, there are some phenomena that cannot be explained without recourse to this explanation in some form (see **Electrical adhesion**).

### *Pressure sensitive*

The familiar pressure-sensitive tapes depend, for their adhesion, upon the continuing presence of a layer of a very viscous liquid between the tape and the surface to which it is adhering. When the tape is first put on, this liquid is spread as a very thin layer by the pressure with which it is applied and hence the name **Pressure-sensitive adhesives**. The liquid is adsorbed on to the substrate; but to remove the tape, this liquid has to flow, against the resistance created by its viscosity, into the gap created by the separation. So long as the adhesive remains a viscous liquid, considerable force is needed to remove the tape. Once the liquid changes to a brittle solid, as it commonly does by various mechanisms under the action of sunlight, then the tape will peel away under its own weight (see **Rheological Theory**).

### *Examples*

A proper understanding of most practical examples of adhesion are now recognized as involving elements from several, if not all, these theories. This may best be understood by considering some examples.

First, take the case of two sheets of aluminium alloy bonded with an epoxy structural adhesive in an aeroplane. The metal will have been carefully prepared by chemical etching and **Anodizing** to give a surface with a controlled oxide layer with micropores at the outside. The adhesive in its liquid state will penetrate into these pores, so there is a degree of mechanical interlocking, but it is on a very small scale. The mechanism of this penetration may, perhaps, be considered as a diffusion process. Then there will develop forces across the interface between the adhesive and the metal. These will certainly and invariably include London **Dispersion forces** (van der Waals forces) and may also involve some forces of primary chemical bonding. The last are probably the most significant in providing the necessary strength and durability that is demanded, but the other mechanisms are also involved in various proportions.

As a second example, consider the case of wallpaper stuck to a plaster surface with a water-based cellulose adhesive. The adhesive certainly has to penetrate both surfaces by processes that are certainly a type of diffusion. As the water is lost by evaporation and

diffusion through the two materials, there will be mechanical interlocking between the solidifying adhesive and the texture of paper and plaster. Finally, there will certainly be some chemical bonds developed within the paper and probably the plaster as well.

This article, and related ones giving a more detailed explanation of individual theories (**Adsorption theory of adhesion**, **Diffusion theory of adhesion**, **Electrostatic theory of adhesion** and **Mechanical theory of adhesion**), expound what could be termed “classical” theories of adhesion. In cross-referenced articles, more recent ideas are explored. As emphasized above, the concepts of the classical theories overlap and merge seamlessly in providing a model of the empirical observations. The tendency of reducing the interpretation of adhesion phenomena to narrowly conceived theories of adhesion should be avoided, and a broader view should be adopted, using whichever blend of concepts best suits the purpose.

### Select References

- J. Comyn, *Adhesion science*, Royal Society of Chemistry, Cambridge, 1997, Chap 1.  
J. Schultz and M. Nardin, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi, Eds., Marcel Dekker, 2003, pp. 53–67.

## Thermal analysis

D E PACKHAM

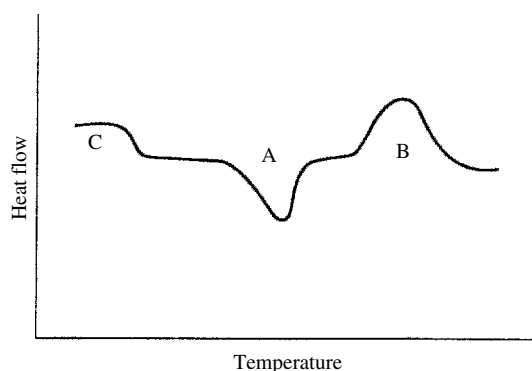
Techniques of thermal analysis play a useful role in the characterization of polymers in general and of adhesives in particular.<sup>1–3</sup> In their most common mode, some property of the adhesive is recorded as temperature changes according to a chosen programme, but isothermal operation is usually possible, the property change with time being recorded. In thermogravimetric analysis (TGA), weight changes are observed; dynamic mechanical analysis (DMA) studies the storage and loss moduli and loss tangent (see **Viscoelasticity**). The term “thermal analysis” refers *a fortiori* to differential scanning calorimetry (DSC), which measures heat flow, and is the main subject of this article.

In a typical experiment, a weighed quantity of the sample (usually around 10–15 mg) and an inert reference material are heated in the calorimeter. Any differences in thermal behaviour between the sample and reference is recorded, being obtained from the different quantities of electrical energy required to maintain both sample and reference material at the same temperature according to the selected rate of temperature change. A graph of heat flow (e.g. millijoules per second ( $\text{mJ s}^{-1}$ )) against temperature is produced.

A DSC trace might show some of the features shown in Fig. 1. The two peaks, A and B, represent enthalpy changes: the areas under them, subject to calibration of the instrument, give the enthalpy change associated with an endothermic (A) or exothermic (B) change.

### Enthalpy changes

Typical endothermic changes include melting, boiling and sublimation. Crystalline polymers are often encountered in the context of adhesion. An endothermic peak will occur



**Fig. 1.** A typical DSC trace showing an endothermic peak A, an exothermic peak B and a change in specific heat capacity C

at their crystalline melting point, and it may be possible to calculate their percentage crystallinity from the peak area.<sup>1</sup> Other endothermic peaks in adhesives may be the result of melting or volatilization of a component of the adhesive itself or of an impurity.

Exothermic peaks are sometimes associated with crystallization. In some polymers, crystallization is inevitable and will only be observed on cooling from above the crystalline melting point. Polyethylene is an example of such a polymer. In others, some silicones and some polyesters, crystallization may be inhibited by rapid cooling, so a sample may crystallize, giving an exotherm when heated in the DSC. Some polymers show more than one crystal form, each with its own crystallization and melting characteristics.

Another obvious source of exothermic peaks is chemical reaction in the sample. Curing in **Reaction-setting adhesives** can be studied by DSC. Similarly, the extent of cure of partially cured materials can be assessed. Degradation in its various forms is also likely to give rise to exothermic peaks, usually extended over a wide temperature range.

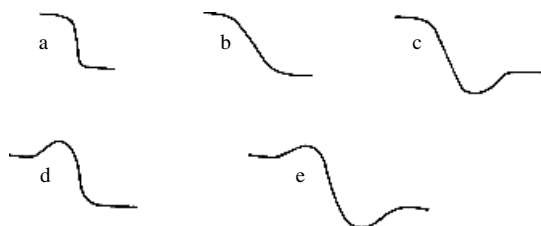
#### *Changes in specific heat capacity*

In the absence of enthalpy changes, an ideal DSC trace is a straight line the slope of which depends on the difference of specific heat capacity between sample and reference material. After calibration with a substance of reliably known specific heat (sapphire is sometimes used), the specific heat of the test material can be calculated.

In polymer materials, a step may be observed in the DSC trace, see C in Fig. 1. This represents a change in specific heat capacity at a particular temperature and usually indicates the **Glass transition temperature** ( $T_g$ ).

Vitrification is a complex process that is very sensitive to rates of heat and cooling. Lower cooling rates give lower values of  $T_g$ . The feature associated with the glass transition may not be the simple step of Fig. 1 but may take any of the forms shown in Fig. 2.

The value of  $T_g$  is affected by polymer molecular weight (see **Glass transition temperature**), so, if the polymer has a broad distribution of molecular weight, the transition recorded by the DSC will tend to be broad rather than sharp (Fig. 2b, compare Fig. 2a). The glass transition temperature would usually be taken as a temperature at the point of inflection.



**Fig. 2.** Forms that the DSC trace of a glass transition might take (axes as in Fig. 1). See text for a discussion of causes

Differences between heating and cooling lead to an “overshoot” (Fig. 2c) when the cooling rate is slower and to an “undershoot” when it is the faster (Fig. 2d). With some thermal histories, both features may be observed in the same curve (Fig. 2e).

### *Interpretation of DSC results*

The results from an unknown or poorly understood adhesive may be difficult to interpret. Curvature of the base line, perhaps combined with some of the features shown in Fig. 2(c)–(e)), may make it difficult to distinguish enthalpy changes from specific heat changes. If the thermal history is either unknown or uncontrolled, the difficulty is compounded.

It is often desirable to repeat runs of the same sample to distinguish irreversible changes such as volatilization and chemical reaction from potentially reversible ones like crystalline melting and vitrification. Similarly, results can be recorded on controlled cooling as well as on the more usual heating runs.

An understanding of the principles of crystal nucleation and growth<sup>4</sup> and of vitrification phenomena<sup>1</sup> will aid the interpretation and suggest changes in heating and cooling rates that may clarify the situation further.

It may well be impossible to interpret fully a complex DSC trace without resort to results from other experiments; DMA will reveal glass transitions, and weighing the sample after the experiment (or better still TGA) will establish whether volatile components are being lost.

Subject to these considerations, DSC provides a powerful aid to the understanding of the behaviour of adhesive systems.

Scanning thermal microscopy is discussed in the article on **Scanning probe microscopy**

### *References*

1. V. B. F. Mathot, Ed., *Calorimetry and Thermal Analysis of Polymers*, Hanser, Munich, 1994.
2. M. P. Sepe, *Thermal Analysis of Polymers (Rapra Review Report 95)* Vol. 8, No. 11, Report 95, RAPRA Technology, 1997.
3. W. Groenewoud, *Characterisation of Polymers by Thermal Analysis*, Elsevier, 2001.
4. D. E. Packham, Adhesives and sealants, *Engineered Materials Handbook*, Vol. 3, H. F. Brinson, Ed., ASM, Ohio, p. 406.

---

**Thermal spray coatings used for adhesion**

---

G D DAVIS AND R A ZATORSKI

In **Thermal spray processes** the nature of the process was described; here, applications to adhesion are presented. Thermal spray coatings for applications involving adhesion are in three general areas, metallic bond or anchor coating, ceramic bond coat, and sprayed polymer as the adhesive. In many cases, the surface modification by the deposition of a thermally sprayed coating is an alternative to environmentally hazardous methods. The thermal spray process is a dry process in which the effluent is collected in a dry cartridge system and usually recycled.

The metallic bond coat can perform several functions. Most common is as a surface modification to the substrate to provide a better surface for the adhesive. An example of this is the bondable stainless surface (BOSS) coating system of a nickel alloy combined with zinc applied by arc-plasma using powder as the feedstock. This system is applied to steel substrates and provides a rough, three-dimensional surface for adhesion of rubber liners for rollers or for internal diameter applications, such as solid rocket motors (SRMs).<sup>1,2</sup> The surface roughness of the BOSS coating is in the range of 13  $\mu\text{m}$   $R_a$  and can be adjusted for a particular application (see **Roughness of surfaces**). Thicknesses range from 0.10 to 0.30 mm. The bond strength of the coating to the steel substrate is in excess of 15 MPa. A feature of the BOSS coating is excellent corrosion protection because of the active galvanic protection of the zinc component of the coating while the nickel alloy provides the structural framework to maintain bond strength. This environmentally benign coating replaces grit blasting or chrome and phosphate conversion processes. In addition to the improved corrosion protection provided by the BOSS coating, which allows greater time between coating application and bonding or other processing, the coating is also more tolerant to surface contamination so that surface cleanliness requirements can be relaxed.

Another example is the use of a titanium plasma spray coating for **Pre-treatment of titanium** bonded structures intended for high-temperature applications.<sup>2,3</sup> Conventional oxide treatments of titanium, for example, chromic acid **Anodizing** (CAA), work well at ambient temperatures, but at significantly elevated temperatures, the oxygen in the oxide dissolves into the metal, allowing failure at the oxide-metal interface. The plasma-sprayed titanium coating remains stable at high temperatures so that bond strength is maintained.

In high-shear applications, a coating of nickel-aluminium alloy or other high-bond-strength metallic coating materials applied by two-wire arc, combustion wire or arc-plasma are used to provide a rough, three-dimensional surface for the bonding of another surface. Surface roughnesses with peak-to-valley values of over 0.3 mm are routinely produced. Thicknesses are from 0.10 to 0.38 mm. The opposing surface for bonding to these coated parts is usually a polymer that is bonded to the surface by compression methods, which can involve heat. In these instances, the polymer itself may be used as the adhesive. Composite to metallic bonds are produced by this method for inserts as well as for large area bonding needs (see **Fibre composites – joining**).

A ceramic bond coat is almost exclusively used to modify a surface for adhesive bonding. The ceramics include, but are not limited to, alumina, zirconia, titania, spinels, carbides and combinations of these materials.<sup>4</sup> The thermally sprayed bond coatings provide a rough surface on the order of 8  $\mu\text{m}$   $R_a$  that has a three-dimensional morphology. Arc-plasma is traditionally used for deposition of the ceramics for these applications.

Sprayed ceramic coatings can be made chemically active by selection of the spray parameters, which result in metastable phases within the coating. Ceramic bond coats are useful for difficult to bond materials such as ceramic components, including carbide-containing parts and refractory metals. These materials may be used in combination with a metallic bond coat on metallic substrates to mitigate stress differentials between the metallic substrate and the ceramic bond coat due to thermal or mechanical stress.

Thermoplastics and precursors for thermoset polymers are sprayed as the adhesive for metal and composite applications.<sup>2-7</sup> These include epoxies, **Polyether ether ketone** (PEEK), polyimides, liquid crystal polymers (LCP) and copolymers of urethanes. In some cases, these polymers can be combined with metals to form a composite coating. Arc-plasma and combustion thermal spraying are used to deposit these materials. Newer heated inert gas guns are starting to be used for these applications. Thicknesses range from 0.10 to 0.38 mm. The advantage of applying polymers by thermal spray include: application of the polymer in specific areas to defined thicknesses; dry application of the polymer by an environmentally benign process; and the ability to apply the polymer coating without regard to the thickness, size or geometry of the substrate. The latter is particularly important in the aerospace industry where components radically change thickness and geometry within a few centimeters.

Polymers can also be applied to components as a barrier coating for corrosion, wear or other protective applications and part of the coated surface can then be utilized as an adhesive. This is attractive as it reduces the number of manufacturing processes.

### *References*

1. G. D. Davis, G. B. Groff, L. L. Biegert and H. Heaton, *J. Adhes.*, **54**, 47 (1995).
2. G. D. Davis, G. B. Groff and R. A. Zatorski, *Surf. Int. Anal.*, **25**, 366 (1997).
3. H. M. Clearfield, D. K. Shaffer, S. L. van Doren and J. S. Ahearn, *J. Adhes.*, **29**, 81 (1989).
4. K. L. Wolfe, K. L. Kimbrough, J. G. Dillard, S. R. Harp and J. W. Grant, *J. Adhes.*, **55**, 109 (1995).
5. G. D. Davis, P. L. Whisnant, G. B. Groff, D. K. Shaffer and J. D. Venables, *Proceedings of the 41st International SAMPE Symposium*, SAMPE, Covina, 1996, p. 291.
6. J. G. Dillard, K. L. Wolfe and B. L. Holmes, *J. Adhes.*, **62**, 113 (1997).
7. J. G. Dillard, F. R. Jackson, B. L. Jackson, L. Aartun, H. A. Parvatareddy, D. A. Dillard and R. Zatorski, *J. Adhes.*, **65**, 217 (1998).

---

### *Thermal spray processes*

---

R A ZATORSKI AND G D DAVIS

The need for **Pre-treatment of metals prior to bonding**, indeed for **Pre-treatments of polymers**, is near universal. With increased consciousness of the importance of sustainability (see **Environment: sustainability**) and of the **Environment and the impact of adhesive technology**, much ingenuity has been exercised in developing pre-treatments that minimize the use of aggressive chemicals and volatile organic solvents. Thermal spray coatings are among the processes of increasing interest as pre-treatments. This

article describes the nature of the process; in **Thermal spray coatings used for adhesion**, applications are discussed.

Thermal spray deposition is a three-stage industrial process where a material is heated, accelerated and impacted onto a surface so that the material splats and cools. The sprayed materials are deposited in thin layers, usually less than 13  $\mu\text{m}$  per pass of the thermal spray device. The use of the line-of-sight additive process enables either an entire part or selected areas to be coated. Moreover the coating thickness may be varied from area to area.

Most thermal processes melt the feedstock material during processing. The molten material is accelerated in a gas stream towards the substrate in droplets ranging from 1 to 100  $\mu\text{m}$  in diameter. The individual droplets hit the surface, splat and cool at a rate of 100,000 to 1,000,000  $\text{K s}^{-1}$ . Depending on the spray device parameters and the starting material, the coatings can contain a variety of metastable phases. The flexibility provided by spray parameters and starting material can be utilized to obtain desired hardness, electrical properties, surface morphology, bond strength, corrosion protection and thermal characteristics of the coating.

Coatings, ranging from 0.01 mm to greater than 1.5-mm thick, can be thermally sprayed onto a wide variety of substrates, such as metals, ceramics and plastics including fibre-reinforced composites. The wide variety of coating materials that can be deposited include:

- refractory metals, such as molybdenum and tungsten;
- ferrous and super alloys, such as stainless steels, carbon steels, the Hastelloys and Incolloys;
- low-melting-point metals, such as aluminium and zinc alloys;
- ceramics, such as alumina, zirconia and titania;
- polymers, including thermoplastics and precursor materials for thermoset polymers.

These materials can be applied as homogeneous coatings or as multi-layers of different materials for a given application. Examples of multi-layer systems are

- metallic and ceramic layers for thermal barrier applications extensively used in turbine engines;
- multi-layer metallic systems used in restoration of machinery or other metallic systems to restore dimension;
- multi-layer metallic and carbide systems for particle erosion and restoration systems.

The different methods of thermal spraying materials are given in Table 1

In the arc-plasma process, gas is blown through an arc contained in a water-cooled torch. The resulting plasma exits the torch through nozzle, where powder is injected into the plasma stream. This method has high velocity, melts the vast majority of the particles and is most useful for high-melting-point material or where high velocity is required, such as carbides in matrices. There are usually a few oxidized or unmelted particles in the coating. The high noise levels and UV radiation require full operator protection in excess of normal arc-welding protection.

The feedstock for the plasma systems traditionally is powder. Newer wire feedstock systems are now available that reduce feedstock handling requirements and can produce lower unmelted particle and oxide content coatings with a wider processing window. Arc-plasma systems need cooling water, 40 KVA power, argon/hydrogen gases or nitrogen gas and compressed air.



Table 1. Thermal spray processes

Method; materials sprayed	Feedstock material/most common size	Typical temperature/typical velocity
Arc plasma; metals, plastics and ceramics	Powder/53 $\mu\text{m}$	10,000 °C/300 $\text{m s}^{-1}$
Arc-Plasma; metals	Wire/1.6 mm	10,000 °C/300 $\text{m s}^{-1}$
Combustion powder; metals, plastics and ceramics	Powder/53 $\mu\text{m}$	2700 °C/100 $\text{m s}^{-1}$
High-velocity Ox-fuel; metals and plastics	Powder/20 $\mu\text{m}$	2700 °C/330 $\text{m s}^{-1}$
Combustion wire; metals and plastics	Wire/3 mm	2700 °C/200 $\text{m s}^{-1}$
Arc wire; metals	(Two) wires/1.6 mm	7000 °C/200 $\text{m s}^{-1}$

The low-velocity combustion powder process uses a combustion flame of approximately 2700 °C where the powder is usually introduced in the centre of the nozzle. This low-velocity process readily melts low-to-medium-temperature materials and has some oxidized and unmelted particles in the deposited coating because of the particular nature of the feedstock. Porosity is usually higher than in other thermal spray processes because of the low velocity of this process. Required operator protection is minimal with low noise and low temperatures.

The high-velocity oxygen fuel (HVOF) spray system uses high-pressure combustion gases and compressed air in a near hypersonic, approximately 2700 °C, combustion stream to melt powdered materials. The velocity is usually in excess of the arc-plasma systems although the temperature is not as high. This process is used extensively for deposition of two-phase carbide systems, such as tungsten carbide in a nickel–chrome matrix. The advantage is that the feedstock material is heated to approximately or below the melting point and the impact of the accelerated particles fuses the particles into a coating. This greatly reduces the diffusion and dissolution of the different phases of the feedstock material. Operator protection requires effectively addressing the high noise problem as well as the standard combustion welding safety issues.

The combustion wire process uses a combustion flame approximately 2700 °C with compressed air to accelerate molten particles shedding from a centrally fed wire. The velocities are less than the HVOF systems and there is considerably less thermal energy from the system. The molten particles form from the melting wire and are therefore molten when leaving the wire and the acceleration and effective flame temperature can be adjusted. The feedstock material must be in wire or rod form. Composites, metals and ceramics can be sprayed with this system. The operator protection required is minimal.

The two-wire arc process uses two current-carrying wires whose tips intersect where an arc melts the tips. A jet of compressed air atomizes and propels the molten particles towards the surface. Most metals that can be melted in air and drawn into a wire can be sprayed with this method. The process enjoys high feedstock throughputs. In general, high temperatures of the arc melting of the wires along with the compressed atomizing air causes a higher level of oxides than the combustion wire process. Traditionally, there is a higher level of porosity in two-wire arc coatings that are being addressed by newer systems. This process needs compressed air and electrical power. Operator protection involves UV, noise and general arc-welding safety concerns.

Kinetic spray processes utilize injection of a powder into a heated gas stream passed into a converging–diverging nozzle. The powder is held below the melting point and the impact of the accelerated powder onto the substrate creates a coating. Resultant coatings are dense, have material properties similar to the starting powder and the coating are usually in compression.

The most widely used method of surface preparation for thermal spraying is thorough cleaning of debris, oil and other fluids from the substrate followed by grit blasting (see **Abrasion treatment**). The grit blast pressure and hardness, size and particle morphology of the grit affect the amount of roughening of the surface. For most applications, the grit-blasted substrates should have a surface roughness of over 10  $R_a$   $\mu\text{m}$ . For thicker coatings that usually have greater residual stresses, an effective method is to texture the surface to cause distribution of the coating stresses over a wider layer of coating and substrate interface (see **Roughness of surfaces** and **Roughness and adhesion**).

### Select References

- M. I. Boulos, P. Fauchais and E. Pfender, in *Thermal Plasmas Fundamentals and Applications*, Vol. 1, Plenum Press, 1994, Chap 1.
- M. R. Dorfman, *Adv. Mater. Proc.*, **160**(7), 47 (2002).
- M. R. Dorfman, *Adv. Mater. Proc.*, **160**(8), 47 (2002).
- M. R. Dorfman, *Adv. Mater. Proc.*, **160**(9), 49 (2002).
- H. S. Ingham, and A. P. Shepard, *Metco Flame Spray Handbook, Volume I, Wire Process*, Metco (Sultzter-Metco), Westbury, New York.
- H. S. Ingham and A. P. Shepard, *Metco Flame Spray Handbook, Volume II, Powder Process*, Metco (Sultzter-Metco), Westbury, New York.
- H. S. Ingham and A. P. Shepard, *Metco Flame Spray Handbook, Volume III, Plasma Flame Process*, Metco (Sultzter-Metco), Westbury, New York.
- L. Pawlowski, *The Science and Engineering of Thermal Spray Coatings*, Wiley, Chichester, 1995.
- Thermal Spraying, Practice, Theory and Applications*, American Welding Society (AWS), 1985.

### Tie layers

R J ASHLEY

A tie layer or coextrudable adhesive has the function of improving interfacial forces between dissimilar polymers in the **Coextrusion** process. The layer is used in cases where resins coextruded are so incompatible that effectively no bond develops between them, or where the bond between two polymers is so limited as to be impracticable (see **Compatibility**). A typical coextruded film structure may consist of five layers of the basic form: sealant layer/adhesive tie/barrier/adhesive tie/outer layer. The tie layers will generally be only a few microns thick.

Most of these tie layers are based on modified polyolefins or their copolymers. Ionomers such as Surlyn may also be used as a tie layer. The functionality of the adhesive layer derives from comonomers such as acrylic acid, methacrylic acid, maleic anhydride or vinyl acetate. Styrene–isoprene–styrene thermoplastic block copolymers blended with polyolefins can be used as tie layers. The level of addition of these grafted units is

generally between 0.5 and 15%. In the case of the polyethylene-acrylic acid materials, the low acid concentrations are used in extrusion applications.

Methods for the incorporation of the graft unit may include irradiation of the base polymer and mixing with the comonomer, or reaction as solids or solutions with free radical agents and blending techniques (see **Chain polymerization, Radiation-cured adhesives**).

An important consideration in the selection of a suitable tie layer is to match melt viscosity with that of the other polymers used in a coextruded complex. If different polymers are used on the outer and internal layers, then different tie-layer materials may be selected. A range of functional polymers may be produced where the melt viscosity is adjusted through resin blending. To assess performance of the tie layer, peel tests may be used, but this may be difficult to set up because of the very thin nature of the layers. Examination of fractured surfaces by microscopy may be required to ensure that cohesive rupture of the tie layer has been achieved to indicate a good bond as opposed to interfacial peel.

Apart from their use as tie layers in coextrusion, the modified polymers can find other adhesive applications such as improving adhesion of extrusion coatings, thermal lamination interplies, and as dispersions or powder coatings. As coatings, the modified polymers applied to metal surfaces can act as an adhesive layer to bond plastic components. A particularly useful version is to prepare a coextruded film of a non-modified base polymer such as polyethylene or polypropylene, forming the bulk of the structure, and apply a thin layer of the modified polymer to one or both external surfaces. This structure may now be used to thermally bond to a metal substrate.

#### *Select Reference*

R. J. Ashley, *Adhesion 12*, K. W. Allen, Ed., Elsevier Applied Science Publishers, London, 1988, Chap 16.

---

## *Toughened acrylic adhesives*

B KNEAFSEY

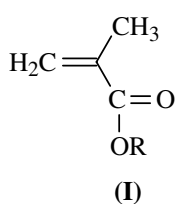

### *Introduction*

Over the last two decades, the demand for structural adhesives for the production line assembly of a wide range of components has grown considerably and has been driven by the ever-increasing diversity of new materials becoming available for component manufacture. This demand alongside further developments in the production of toughening agents has led to a renewed interest in the development of acrylic structural adhesives, in particular toughened acrylic adhesives. The changing market demands in recent years is reflected by a resurgence in patenting activity by the major adhesive manufacturers.

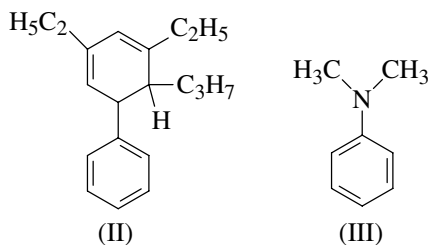
### *Chemistry and properties*

Toughened acrylic adhesives are structural adhesives and comprise mono-functional methacrylate monomers containing a dissolved rubber polymer added as a toughener, cure

accelerators and a free radical generator and optional adhesion promoters, cross-linking agents, free radical stabilizers and fillers.<sup>1,2</sup> The adhesives are one-part adhesives with an activator applied to the substrate or two part with mix ratios of 1:1 to 1:10. Cure is initiated at room temperature by a redox reaction of the cure accelerator with the free radical source (usually a peroxide or hydroperoxide) to generate the initiating species (free radicals) responsible for the adhesive cure. The adhesives cure by free-radical-catalysed **Chain polymerization**.

	Name	R
 <p>(I)</p>	Methyl	—CH <sub>3</sub>
	Hydroxyethyl	—CH <sub>2</sub> —CH <sub>2</sub> —OH
	Hydroxypropyl	—CH <sub>2</sub> —CH—CH <sub>3</sub>   OH
	Ethylhexyl	—CH—C <sub>2</sub> H <sub>5</sub>   C <sub>4</sub> H <sub>8</sub> —CH <sub>3</sub>
	Tetrahydrofurfuryl	—CH <sub>2</sub> — 

The methacrylate monomers (I) of choice for tough acrylic adhesives are selected primarily for their ability to solubilize the rubber toughening agents, volatility and speed of cure and are usually those that polymerize to give high-modulus, glassy-type polymers characterized by glass transition temperatures well in excess of room temperature (*c.* 100 °C). The monomer volatility can be used to categorize the adhesives into “high odour” adhesives, typically based on methyl methacrylate with the advantage of improved tack-free cures and “low odour” adhesives based on hydroxy alkyl methacrylates or tetrahydrofurfuryl methacrylate



The cure accelerator (a reducing agent) can be applied to the substrate as an activator, that is, as a solution in an organic solvent in the activator type toughened acrylic adhesives or can be contained in a second adhesive component (two-part adhesive). The most widely used reducing agent is the crude product, often described in patent literature as the condensation product, of aniline and butyraldehyde, the active component of which is *N*-phenyl 2-propyl 3,5-diethyl, 2 dihydropyridine (II). The aromatic amine are also

favoured as reducing agents with *NN* dimethyl para-toluidine (III) being the most important. Substituted thioureas including ethylene thiourea and benzoyl thiourea have been used as reducing agents but are now less favoured because of their toxicity. Additionally, many systems also contain transition metal catalysts to increase cure speeds.

Adhesives based on rigid, brittle polymers alone would carry high loads and give high tensile shear strength, but offer virtually no resistance to impact and peel forces. To overcome these shortcomings, toughening agents are added to the adhesive formulations. Early examples included, chlorinated polyethylene rubber (Hydralon). More recently, solubilized acrylonitrile butadiene or acrylonitrile butadiene styrene copolymers, liquid acrylonitrile rubbers copolymers and core shell tougheners have found more general acceptance. Improved fracture toughness of these adhesives is attributed to the formation of a discrete secondary phase of small rubber particles (circumference 0.1–1.0  $\mu\text{m}$ ) dispersed throughout the brittle, continuous methacrylate polymer matrix. Toughness and crack resistance is derived from the ability of these flexible particles to absorb and dissipate energy associated with propagating cracks initiated during impact and cleavage loading of the bond.<sup>3</sup> (see **Toughened adhesives**).

A significant recent innovation in the formulation of toughened acrylics is the ability to bond polyolefins (polyethylene and polypropylene) without any substrate pre-treatments. This beneficial aspect of the toughened acrylic adhesives performance is attributed mainly to newly developed and patented cure technologies and provides an unique performance feature that cannot currently be matched with any other adhesive type.<sup>4</sup>

When using single-part adhesives with a solvent-based surface activator, in most applications, it is only necessary to apply the activator to one of the surfaces to be bonded and the adhesive to the other. Once the bond is closed, cure is initiated. For close-fitting steel parts, handling strength is developed in a few minutes and full strength over a period of hours. While this approach can give very fast fixturing with good properties, a major limitation is inability to cure completely through gaps much above 1 mm, because of poor diffusion of the activator through the adhesive. This disadvantage is overcome by the use of two-part adhesives, where both parts are essentially high-viscosity adhesives, similar in appearance and are mixed either by static or dynamic mixing. The resultant mixed product is applied as a single continuous bead to one of the substrates to be bonded. Alternatively, a “non-mix” approach, unique to acrylic adhesives, of applying a continuous bead of one component on top of a continuous bead of the other, can be used. Sufficient mixing to initiate cure takes place automatically on closing the bond. In general, this method is satisfactory if bond gaps are no larger than about 1–2 mm. Above this, mixing is recommended.

Table 1 highlights typical performance parameters of toughened acrylic.

### *Applications*

Toughened acrylic adhesives can be formulated to have low, controllable viscosity, which makes possible rapid, precise dispensing (see **Dispensing of adhesives**) to parts to be bonded. The room-temperature curing or setting of these adhesives makes them particularly useful for the assembly of components in automatic or semi-automatic production lines. Examples of these are the bonding of loudspeakers (ferrite/metal and coil/cone), DC motors, bicycles, filing cabinets and general-purpose applications where some degree of toughness and impact resistance is required.

Table 1. Performance<sup>a</sup> of toughened acrylic adhesives

	Toughened acrylic	Standard anaerobic
Viscosity	3–100,000 mPa.s	1–3000 mPa.s
Speed (fixture time)	60–300 s	10–60 s
<i>Strength</i>		
Tensile shear (ASTM D1002-64)	15–30 Nmm <sup>-2</sup>	20 Nmm <sup>-2</sup>
GB steel		
<i>Toughness</i>		
T-peel (ASTM D 1876-69T)	3–8 Nmm <sup>-1</sup>	0–2 Nmm <sup>-1</sup>
GB aluminium		
Impact strength (ASTM 0950-54)	30–50 kJ m <sup>-2</sup>	10–20 kJ m <sup>-2</sup>

<sup>a</sup> Data are taken from the technical literature and are believed to be typical.<sup>4</sup>

Table 2. Comparative benefits of industrial adhesives (toughened acrylics, anaerobics, epoxies)

	Toughened acrylics	Anaerobics	Epoxies	
			Two-part mixed	One-part heat cured
<i>Bond strength</i>				
Metals/ferrites	++	++	+	++
Metals/plastics	++	–	0	–
Toughness	++	0	–	+
Impact resistance	++	–	–	0
Temperature/humidity	++	+	+	++
<i>Speed of bonding</i>	+	++	0	–
<i>Ease of cure</i>				
Automatic application	++	++	–	0

Note: ++ great benefit, + significant benefit, 0 no benefit, – significant disadvantage.

Table 2 compares toughened acrylic adhesives to two other important classes of adhesive used widely in industrial assembly operations, **Anaerobic adhesives** and **Epoxide adhesives**. The speed of bonding of anaerobics makes them ideal for metallic substrates or where toughness and impact resistance are not critical. Epoxies provide good bond strength to many substrates but are slower curing and require more accurate mixing to maintain the correct mix ratios. Toughened acrylic adhesives provide better toughness and impact resistance than anaerobics and better speed and ease of use than epoxies.

Other articles of relevance are **Toughened adhesives** and **Toughened epoxide adhesives**. In **Structural adhesives**, properties of epoxide and **Polyurethane adhesives** are compared with those of toughened acrylics.

## References

1. S. R. Hartshorn, *Structural Adhesives, Chemistry and Technology*, Plenum Publishing Corporation, New York, 1986.

2. M. M. Gauthier, *Adhesives and Sealants, Engineering Materials Handbook*, Vol. 3, A S M International, 1990.
3. 3M US Patents 5,561,910, published 16 December, 1996, DOW WO0014431A1 published 14 December, 2000, Loctite WO0234851 published 2 May 2002.
4. F. R. Martin, Acrylic adhesives, in structural adhesives – developments, in *Resins and Primers*, A. J. Kinloch, Ed., Applied Science Publishers, London, 1986, Chap 2.

---

## Toughened adhesives

---

J GUTHRIE

### *Introduction*

**Structural adhesives** function by the transformation of a liquid to a solid. In many cases, this transformation is effected by polymerization or cross-linking reactions. The resultant adhesives are often brittle, glassy solids with poor resistance to impact and peeling forces. **Impact resistance** and peel resistance can be improved by the addition of a rubber toughener to the adhesive formulation. The development of toughened adhesive technology has transformed both acrylic and epoxy adhesive technology into high-performance adhesive packages, providing important benefits in performance and durability. Toughened adhesives generally encompass both **Toughened acrylic adhesives** and **Toughened epoxide adhesives** but in theory could be applied to any curing chemistry system that results in the formation of a glassy solid.

### *Toughening mechanism*

The concept of tough adhesives is based on the principles employed to produce impact-resistant plastics. Improved impact resistance is achieved by the introduction of rubbery domains into the polymer morphology. The improved fracture toughness is attributed to the ability of the rubbery domains to absorb and dissipate energy associated with propagating cracks initiated during impact and cleavage loading of the plastic (see **Fracture mechanics**). In the simplest case, this involves the dispersion of small rubber particles in a glassy polymer matrix. Toughened adhesives consist of mono-functional and di-functional monomers or resins, adhesion promoters, stabilizers, cure accelerators, cure initiators and a dissolved rubber polymer added as a toughener. The rubber should be soluble in the adhesive but on curing should undergo phase separation to form rubber domains in the glassy matrix. Rubbers that do not undergo phase separation will simply reduce the **Glass transition temperature** of the cured adhesive and behave as flexibilizers rather than tougheners. It is also important that some degree of graft polymerization with the rubber occurs.

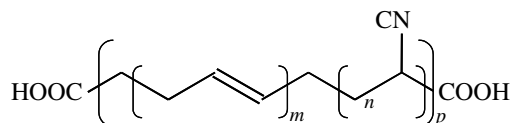
### *Toughening additives*

In the case of acrylic adhesives, the most common rubbers employed are:

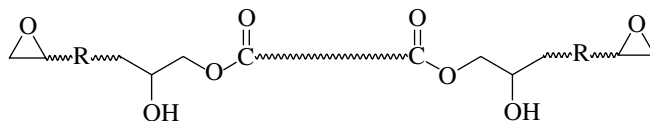
- Chlorosulphonated polyethylene – Hypalon (DuPont)

- Butadiene – acrylonitrile elastomers
- Urethane elastomers
- Polyurethane rubbers
- Acrylic elastomers
- Poly(isoprenes).

Rubber-like materials are also employed in the toughening of epoxy adhesives. These include polyacrylate rubbers and cycloaliphatic polyamides. A more interesting approach to creating rubbery domains in **Epoxy adhesives** is the introduction of rubbery segments into the adhesive matrix by co-reacting the epoxy groups in the epoxy resin with low molecular weight reactive liquid polymers (RLPs), such as liquid poly(butadiene-co-acrylonitrile) (BN) rubbers manufactured by B. F. Goodrich. Carboxy-terminated RLPs are commonly employed e.g., carboxy-terminated butadiene-acrylonitrile (CTBNs):

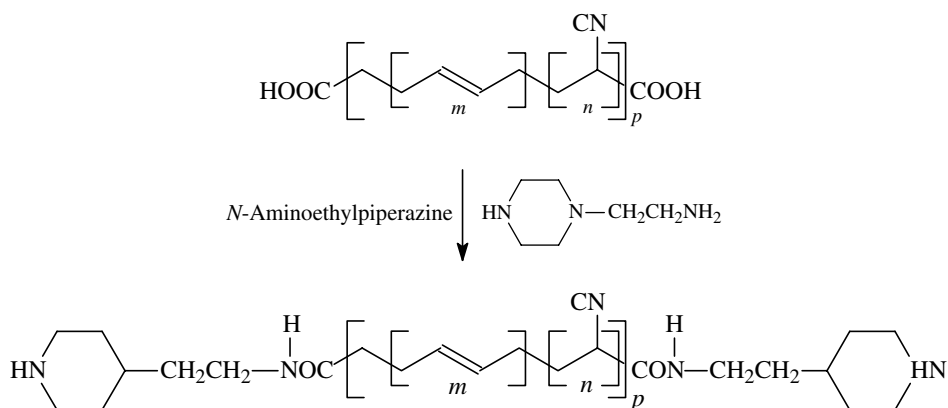


Simple formulation with the epoxy resin is not satisfactory as reactive groups such as amines present in the epoxy hardener compete with the carboxyl groups in reaction with epoxy groups (v. **Toughened epoxy adhesives**). As a result, very little RLP is incorporated into the matrix because the epoxy group has a much higher reactivity towards the hardener than the RLP. To overcome this problem, the CTBN RLP is pre-reacted with the epoxy to form an adduct:



This adduct is formulated with the epoxy resin during adhesive manufacture.

Amine-terminated RLPs (ATBNs) are used as hardeners in two-part epoxy systems. These are prepared by reacting a CTBN with *N*-aminoethylpiperazine.





The impact modifiers or toughening agents described above are all linear polymers or segments. More recently, there has been some interest in the use of Core-Shell tougheners. These materials consist of a glassy shell grafted by "seeded emulsion polymerization" onto an elastomeric core.

#### *Advantages/disadvantages of toughened adhesives*

The evolution of toughened adhesives, both acrylics and epoxies, means that adhesives that exhibit adhesion, hot strength and durability can now also maintain high impact resistance and elasticity, for example, at sub-freezing temperatures. However, in contrast to **Anaerobic adhesives** and **Cyanoacrylate adhesives**, toughened adhesives, in general, tend to be slow curing and high in viscosity, although low-viscosity toughened acrylics are now emerging.

Other articles of relevance are **Toughened acrylic adhesives**, **Epoxide adhesives**, **Structural adhesives** and **Acrylic adhesives**.

#### *Select References*

- C. D. Wright and J. M. Muggee, in *Structural Adhesives, Chemistry and Technology*, S. R. Hartshorn, Ed., Plenum Press, New York, 1986, Chap 3.
- C. W. Boeder, in *Structural Adhesives, Chemistry and Technology*, S. R. Hartshorn, Ed., Plenum Press, New York, 1986, Chap 5.
- C. B. Bucknall, *Mechanism of Rubber Toughening, in the Toughened Plastics*, Applied Science Publishers, London, 1977, Chap 7.

---

### *Toughened epoxide adhesives*

---

JOHN BISHOPP

Unmodified **Epoxide adhesives** are versatile materials, but like many polymers below their **Glass transition temperatures**, they suffer from low resistance to impact and peel forces. In **Toughened adhesives**, some means of addressing such problems were discussed in general terms. This article considers the basis of toughening in epoxies, and related articles (cross-referenced herein) discuss the types of toughening additives employed.

Since the 1960s, when it was first discovered that the toughness of cured epoxies could be improved by the addition of a reactive liquid polymer (RLP), epoxy adhesive formulators have researched into and considerably advanced the science and technology of toughening epoxy adhesives. This has led to both paste and film adhesives that possess significantly improved and better controlled physical and mechanical performance in both the uncured and cured resin, properties such as rheology, adhesion, fracture energy characteristics and thermal and environmental durability all being beneficially influenced.

The first attempts at toughening relied on reducing the inherent brittleness of the cured continuous phase of the adhesive by formulating with high-molecular-weight polymers, such as phenoxy resins, polyvinyl acetal resins (formals and butyral) and polyamides (nylons), to give some in-built flexibility to the cured matrix. Although this did improve

the peel properties and the ambient lap shear strengths, high temperature performance and, in some cases, durability was significantly compromised (see **Peel tests**, **Shear tests** and **Durability: fundamentals**).

Once the use was postulated of solid domains (second-phase particles) in polystyrene to produce a high impact plastic, it was realized that this concept could work for epoxy resins if discrete, so-called second-phase particles could be produced throughout the continuous phase of the cured adhesive matrix.

#### *Development of toughening secondary phases*

There are, essentially, three ways in which a toughening secondary phase can be induced in an epoxy adhesive: (1) discrete particles can be added to the matrix during manufacture of the adhesive, a second phase can be precipitated out of the adhesive matrix (2) during manufacture or (3) during cure. When a blend of two tougheners is used, synergy may result, giving greater toughening.

However they are produced, it is clear that any resulting toughening effect will rely heavily on particle size and distribution, the inherent particle strength and the adhesion between second phase particle and the adhesive matrix.

#### *Toughening mechanisms*

One useful, but not all embracing, definition of toughness is “. . . a means of reducing the rate of crack growth through an inherently brittle matrix without significantly affecting other properties of the continuous phase”. This leads to an increase in the stress or energy needed to reach an identified failure point. The definition of failure point is linked to the specific application and will vary as part design and material selection changes.

Some of the models used to rationalize the toughening effect associated with plastic deformation of the matrix and second-phase particle at the crack tip are represented in Fig. 1. This deformation is achieved through crack pinning and broadening, particle bridging and cavitation, crack path deflection, shear band formation and crazing or microcracking for stress relaxation at a crack tip.

In the first case, the crack meets a particle which, provided it is strong enough, stops the crack's progress and forces the tip to broaden. Crack broadening will dissipate the crack energy and, thus, will relieve the stress concentration at this critical point, and will be manifested in some form of plastic deformation round the crack tip.

In the second case, it is just possible that crack energy dissipation can occur by deformation of the second-phase particles at the tip actually deforming, while staying anchored on both sides of the crack, but its probability is low. Much more likely is that energy will be expended in deforming the particles to such an extent that they collapse in on themselves or they are pulled out of the matrix, leaving a void on one side of the crack and the deformed particle on the other.

It is unlikely that any deviation of the crack path, being deflected from one particle to the next, will be the prime cause for toughening but it will ensure that the crack will have to propagate further to reach the point of failure and hence more energy is expended.

Shear yielding in any plastically deformed zone will further protect against immediate and catastrophic crack growth and, finally, microcracking, or crazing, will help dissipate stress concentrations.

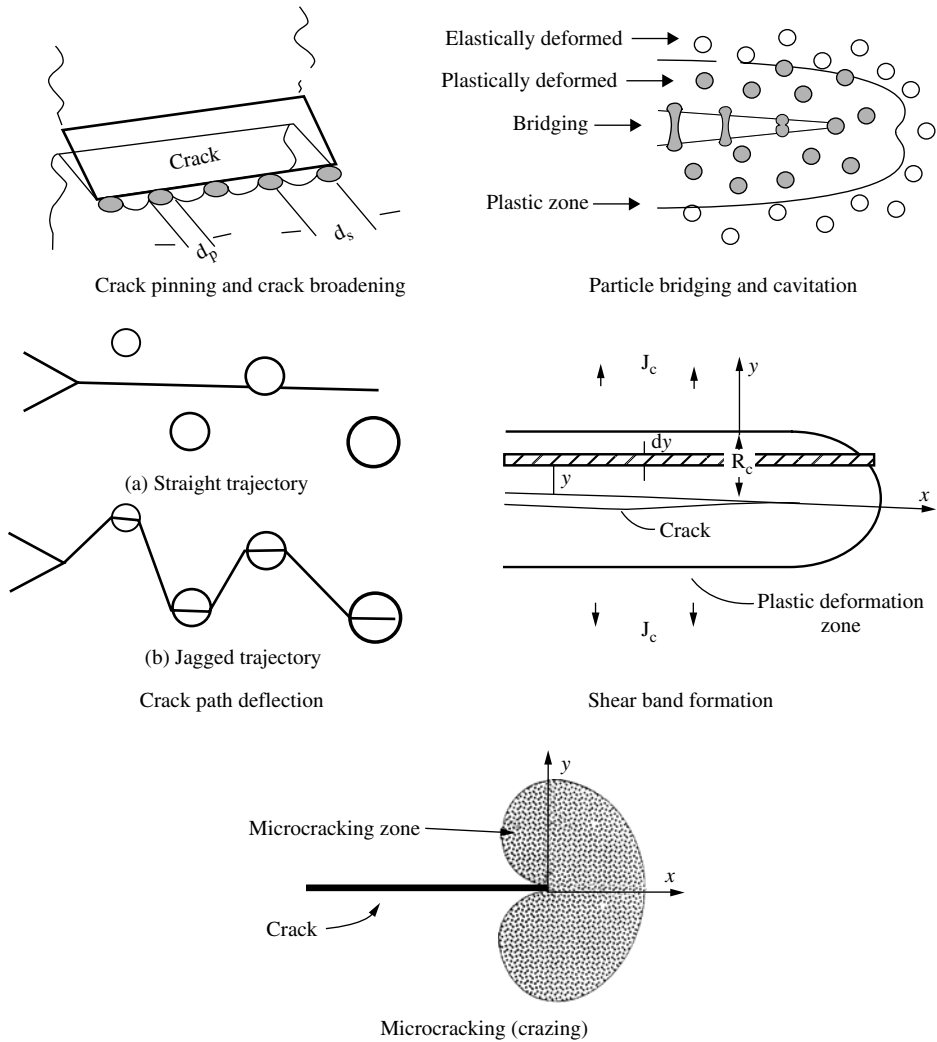


Fig. 1. Toughening mechanisms

*Additives for toughening*

The various ways in which epoxies can be toughened by introduction of a secondary phase are discussed in separate articles: **Toughened epoxide adhesives: particle formation prior to cure**, **Toughened epoxide adhesives: precipitation during cure** and **Toughened epoxide adhesives: blend synergy**.

*Use*

These materials are very much **Structural adhesives** and as such are very widely used in **Aerospace applications**, **Automotive applications** and elsewhere.

*Select References*

- C. B. Arends, *Polymer Toughening*, Marcel Dekker, 1996.  
 E. Martuscelli, P. Musto and G. Ragosta, *Advanced Routes for Polymer Toughening*, Elsevier, 1996.  
 L. Burton and J. L. Bertram, Design of tough epoxy thermosets, *Polymer Toughening*, Marcel Dekker, 1996.  
 C. K. Riew and A. J. Kinloch, Eds., *Toughened Plastics II: Novel Approaches in Science and Engineering*, American Chemical Society, 1996.  
 R. A. Pearson, H.-J. Sue and F. E. Yee, Eds., *Toughening of Plastics: Advances in Modelling and Experiments*, American Chemical Society, 2000.

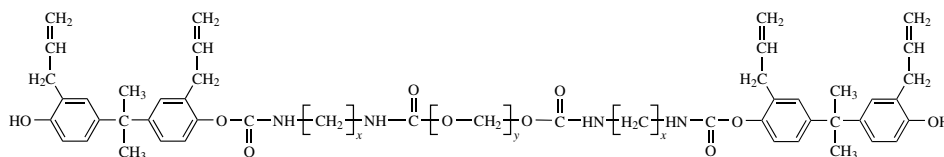
### *Toughened epoxide adhesives: blend synergy*

JOHN BISHOPP

The reasons for toughening **Epoxide adhesives** are considered in **Toughened epoxide adhesives** and some means of inducing the secondary phase in **Toughened epoxide adhesives: particle formation prior to cure** and **Toughened epoxide adhesives: precipitation during cure**. This article considers the so-called blend synergy approach in which is used a blend of two tougheners such that the resultant toughening is greater than the sum of that obtainable from each individually.

One of the first approaches was to use a blend of liquid reactive rubbers and the much higher molecular weight elastomer (carboxylated nitrile rubber). This led to a bimodal distribution of the precipitated secondary phase, which was seen as a distinct improvement over either the elastomer or the RLP on its own.

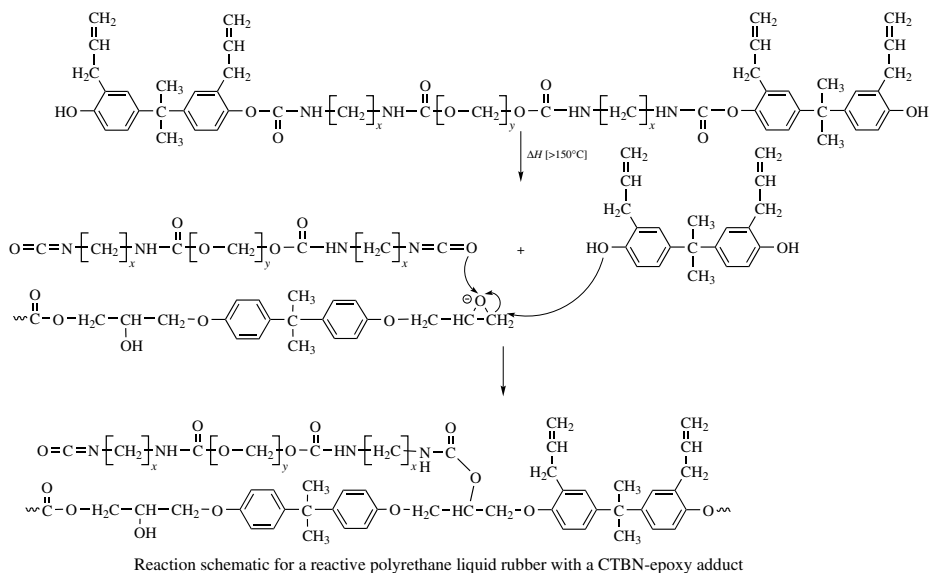
Work in the last ten years has focused on the use of a range of phenolic end-capped, low-molecular-weight polyurethanes combined with the conventional RLPs.



Typical phenolic end-capped polyurethane liquid rubber

Blend synergy appears to be the key to the improved performance seen with these systems and work has shown the importance of compatibility between the two modifying polymers in attaining this condition. The degree of compatibility can be further enhanced if both polymers contain reactive groups that can co-cure to form a microphase having interpenetrating rubber networks.

When all the conditions are optimum, particularly the polyurethane to rubber ratio, then the chemistry and nature of the precipitated phase is altered and a degree of blend synergy takes place, which leads to an improvement in the adhesive shear properties, compared with a standard CTBN-toughened system, coupled with a marked increase in peel strength, particularly under dynamic loading conditions.



Under these conditions, the nitrile rubber/epoxy adduct, instead of having a distinct separated phase, is incorporated into the polyurethane microstructure, resulting in the formation of a novel non-continuous microphase that has a bimodal distribution.

It is believed, however, that it is the polymer that is retained by the continuous phase that produces the marked changes in the physical properties of the cured matrix. It is possible that polymer is held in the continuous phase toughening the whole matrix without detriment to the system's **Glass transition temperature**,  $T_g$ , stiffness or load-bearing capabilities, but it is thought more likely that a co-continuous phase is formed that has a structure comprising discrete particles of the interpenetrated rubber networks whose particle size is on the nanometre rather than the micrometre scale. With the much higher incidence of energy-absorbing particles, it would be expected that such a zone would have a more immediate and efficient response to a propagating crack, hence leading to improved toughness.

It is also possible that the modification to the continuous phase is such as to improve the "bond" between it and the precipitated phase.

The concept of toughening on the nano scale is the subject for much current research where particles of, for example, clays, carbon fibre and carbon nano-tubes, are being evaluated as tougheners for brittle, often high-temperature epoxy matrices. In the same way as for polymeric additives, the main difficulties being experienced are those of particle exfoliation, in the case of the clays, and dispersion in the case of the carbon particles.

### Select References

- R. MÜchaupt and J. H. Powell, Third generation structural adhesives, *Proc. Adhesion '90*, Plastics and Rubber Institute, 1990.
- S. Horiuchi, C. Street, T. Ougizawa and T. Kitano, *Polymer*, **35**(24), 5283 (1994).
- R. A. Pearson, H.-J. Sue and F. E. Yee, Eds., *Toughening of Plastics: Advances in Modelling and Experiments*, American Chemical Society, 2000.
- S. Sprenger, C. Eger, A. J. Kinloch, A. Taylor, J. H. Lee and D. Egan, *Nanoadhesives: Toughness and High Strength*, Adhäsion: Special Edition, Vol. 3, Kleben & Dichten, 2003.

## Toughened epoxide adhesives: particle formation prior to cure

JOHN BISHOPP

The rationale for and uses of **Toughened adhesives** in general and of **Toughened epoxide adhesives** in particular are discussed elsewhere. **Epoxide adhesives** essentially comprise an epoxy resin and a curing agent. **Toughened epoxide adhesives** may be produced by inducing a toughening secondary phase either in the uncured resin itself or during the cross-linking process. The former method is the subject of this article. Other methods are considered in **Toughened epoxide adhesives: precipitation during cure** and **Toughened epoxide adhesives: blend synergy**.

### *Incorporating particles into the adhesive matrix*

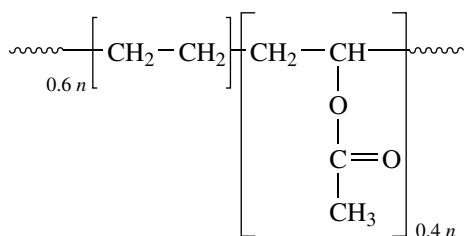
Four ways of incorporating discrete particles directly into the adhesive matrix are described.

1. *Low-melting polymers:* Soft, relatively low-melting polymers can be added to the matrix during manufacture. They melt and the mixing action breaks down the polymer droplets into particles of a suitable size, dispersing them throughout the adhesive. Once the matrix cools, the dispersed particles remain locked in place and, on cure, they act as second-phase tougheners.

There are, obviously, significant limitations with this approach. The adhesive matrix has to be solvent free and must have a high enough viscosity at temperatures above the toughening polymer's melting point to effect dispersion. Further, the polymer must not be soluble in any of the formulating ingredients and must melt at a temperature in which the stability of the adhesive is not affected.

One distinct advantage is that adhesive can, if so required, be formulated using high loadings of toughener without the rapid increase in viscosity seen with high-molecular-weight soluble polymers. Another is that they generate a consistent matrix morphology that is independent of cure conditions.

**Ethylene-vinyl acetate copolymers** (EVA) have been successfully used for this approach with the particle size of the dispersed phase ranging from about 0.5 to 5.0  $\mu\text{m}$ . To be effective as tougheners, the surface of the particle generally needs either to react with or to adhere well to the matrix; electron microscopy has confirmed the latter case to be true in the case of EVA copolymers.



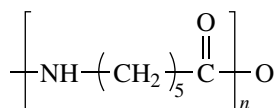
Ethylene-vinyl acetate copolymer (40% acetate content)

2. *High-molecular-weight polymers:* High-molecular-weight polymers, which are insoluble in the resin matrix and which can be produced as a powder with the correct

particle size and particle size distribution, can be simply mixed into the matrix during manufacture.

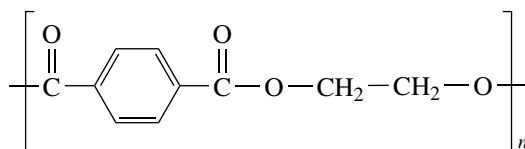
There are fewer limitations with this approach, although it is not the best toughening method for solution-based adhesives because of the possible settling out of the polymeric dispersion with time. These materials can be readily dispersed in both hot melt and paste adhesives; great care has to be taken, however, that the powder is efficiently and uniformly distributed throughout the matrix.

The comments made above, as to rheology and matrix morphology, also apply to this approach. High-molecular-weight nylon powders have been found to be effective, for example, Elf Atochem's Orgasol 1002, a Nylon 6 polymer. Depending on grade, the particle size can range from 5 to 20  $\mu\text{m}$ .



Nylon 6

Polyethylene terephthalate powder has also been found to work in a similar manner.



Polyethylene terephthalate

3. *Core-shell rubbers*: Rather than just use polymeric powders, it is now possible to formulate with pre-formed rubber particles, the so-called core-shell rubbers. These carefully designed materials enable both the particle size distribution and the volume fraction of particles in the cured resin to be closely controlled.

Here, the inner core of the particle comprises a polymer of controlled modulus, for example, a silicone rubber or a methacrylic-butadiene-styrene terpolymer. The outer shell of the particle contains reactive species that are so designed to react with the adhesive matrix being used. For example, the styrene-based core contains 1 to 2% of an alkyl aryl sulphonate as its outer shell.

Particle sizes are typically in the region of 2  $\mu\text{m}$ , and the rheological and morphological benefits, seen for other materials, again apply here.

However, these materials tend to be expensive and are probably the most difficult to disperse in the base resin. To aid in this latter area, pre-dispersed core-shell rubbers, particularly in epoxy novolac resins, are now commercially available.

4. *Latices*: Finally, it is possible to incorporate rubbery toughening agents through the use of latices. Stabilized latices of various high-molecular-weight elastomers can, with difficulty, be incorporated into the epoxy matrix. Provided all the conditions are

carefully controlled, this will result in an epoxy matrix toughened with a very fine dispersion of a rubbery toughening agent.

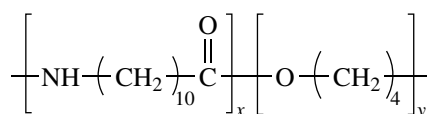
#### *Precipitation within the uncured resin matrix*

There are far fewer options for preparing the second-phase particle distribution by precipitation within the uncured resin matrix. This approach, again, is not ideal for solvent-based adhesives. Any such toughener must be soluble in the base resin system at elevated temperature and then give an even precipitation, without agglomeration, as the matrix cools back to ambient temperature.

Research along these lines has shown that the viscosity is somewhat raised, but within acceptable limits. The important consideration is that some of the polymer will, therefore, remain in the continuous phase and will affect the final thermal properties of the adhesive.

Polyether–polyamide block copolymers have been found to meet these criteria; very fine precipitates in the region of 0.5 to 2.0  $\mu\text{m}$  have been observed.

A typical polymer that behaves in this manner is a block copolymer from a polyether based on tetrahydrofuran and Nylon 11:



The benefit of such an approach is that a dispersion of the precipitated polymer can be made in liquid epoxy resin, which can then be used as a formulating ingredient in its own right in, for instance, paste adhesives.

Other means of achieving toughening is considered in articles cited above.

#### *Select References*

- H. S-Y. Hsieh, *Polym. Eng. Sci.*, **30**(9), 493 (1990).  
 L. Burton and J. L. Bertram, Design of tough epoxy thermosets, in *Polymer Toughening*, Marcel Dekker, 1996.  
 C. K. Riew and A. J. Kinloch, Eds., *Toughened Plastics II: Novel Approaches in Science and Engineering*, American Chemical Society, 1996.

---

### ***Toughened epoxide adhesives: precipitation during cure***

---

JOHN BISHOPP

The reasons for modifying **Epoxide adhesives** by introducing a toughening secondary phase are considered in **Toughened epoxide adhesives**. Here, the precipitation of the secondary phase during the curing process is discussed. This is by far the most common approach and the technique around which much research and development effort has



been expended over the years. Other toughening techniques are considered in **Toughened epoxide adhesives: particle formation prior to cure** and **Toughened epoxide adhesives: blend synergy**.

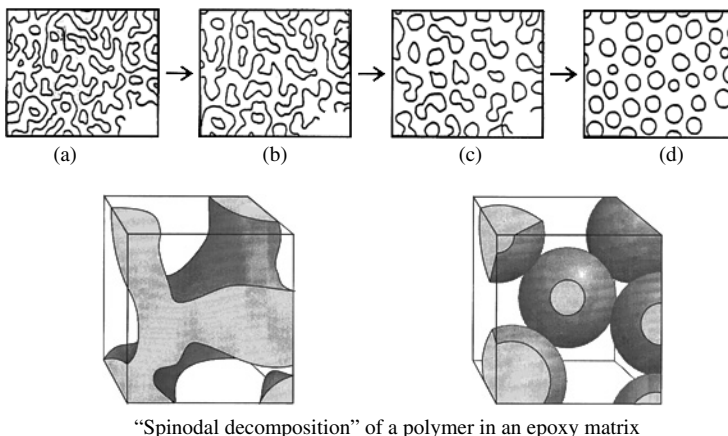
There are *three* ways of achieving precipitation during cure. The first uses the reactive liquid polymers (RLPs) – essentially, chemically active liquid rubber telomers. The second uses high-molecular-weight elastomeric polymers and the third uses high-molecular-weight thermoplastic polymers. Both elastomers and thermoplastics again ideally have reactive end or pendant groups.

Whichever approach is taken, the mechanism of toughening is essentially the same. It is best described as a type of spinodal decomposition, see Fig. 1.

Initially, the matrix starts out as an essentially compatible system (see **Compatibility**). As the cure commences, the solubility parameter of the continuous phase changes and the polymer contained in solution begins to phase separate or precipitate (a). As the curing reaction proceeds, the solubility parameters change even further, helping to ensure complete separation of the polymer from the continuous phase, and the viscosity of the continuous phase begins to rise. This viscosity increase is due to the insertion of cross-links, which begin to restrict the molecular movement of the continuous phase and “squeeze” the precipitated phase into relatively discrete domains (b and c). These domains become smaller and more distinct as the cross-linking reaction goes to completion, yielding the precipitated phase morphology associated with these adhesive systems.

Many factors influence not only how the polymer phase separates but also the size of the discrete domains and whether a bimodal particle distribution occurs. These are the basic chemistry and molecular weight of the epoxy resins present (this will significantly affect solubility parameters), the polymer loading and the rate and temperature of cure. The latter will affect the rate of change of solubility parameter and the matrix viscosity profile, both of which are important considerations.

(Bimodal distribution can be defined as the situation where particles of two distinct particle size distributions coexist in the matrix; for example, particles in the range of 0.5 to about 2.0  $\mu\text{m}$  and others in the range of 4 to 6  $\mu\text{m}$ .)



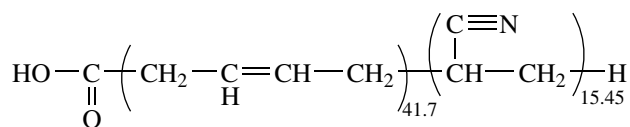
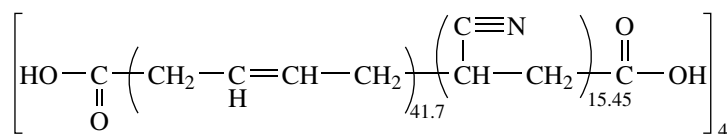
“Spinodal decomposition” of a polymer in an epoxy matrix

**Fig. 1.** Formation of second phase by spinodal decomposition

The *three* ways of achieving precipitation of the secondary phase during the curing process are now discussed.

1. *Reactive liquid polymers (RLPs)*: The liquid rubbers most often used in epoxy adhesives are those based on acrylonitrile–butadiene copolymers or on long-chain polyethers. To act as effective tougheners, however, they cannot be directly added to the formulation but have to be prereacted with some of the epoxy resin, or sometimes with the amino hardeners in two component paste adhesives (adduct formation). To achieve this, only RLPs with reactive end groups are used by the formulator.

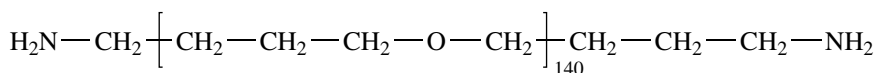
The most commonly used materials are the Hycar range from Noveon, which are butadiene, or more usually, acrylonitrile–butadiene telomers which are epoxy- (no prereaction needed), amino-, vinyl- or, as here carboxyl-terminated. These latter are the well-known “CTBN rubbers”, which have a molecular weight generally in the region of 3000 to 4000.



Hycar CTBN 1300X13

Hydroxy-terminated acrylonitrile–butadiene telomers are also available from other sources.

Another frequently encountered RLP toughener is a high-molecular-weight polyether from Dyneon LLC (Dynamar HC-1101), an amine-terminated, high viscosity, liquid polymer of molecular weight in the region of 10,000.

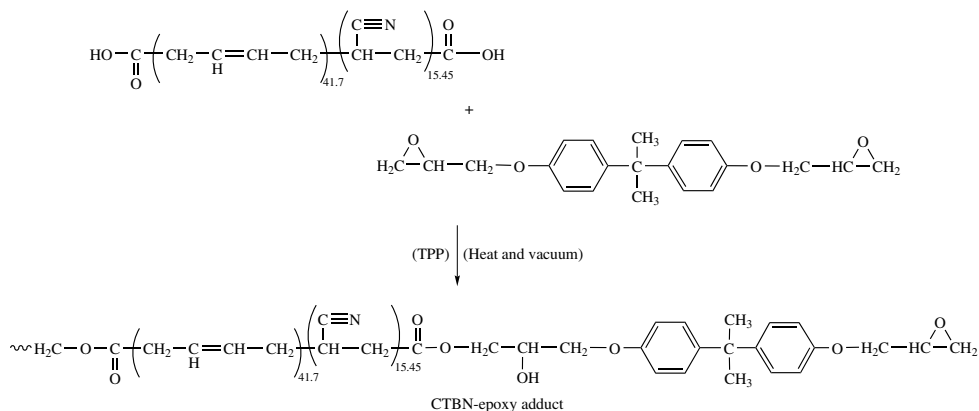


Dynamar HC-1101

The adducting processes for both these types of RLPs are very similar. The functional equivalent weight is known for each polymer and hence they can be blended with a calculated excess of epoxy resin so that the adduct, now an epoxy-terminated polymer, is formed in an epoxy resin solution. As a rule of thumb, this is generally taken as about 1 part by weight of RLP to 3 parts by weight of epoxy resin. Further, it has also been found advantageous to use a blend of liquid and solid epoxies.

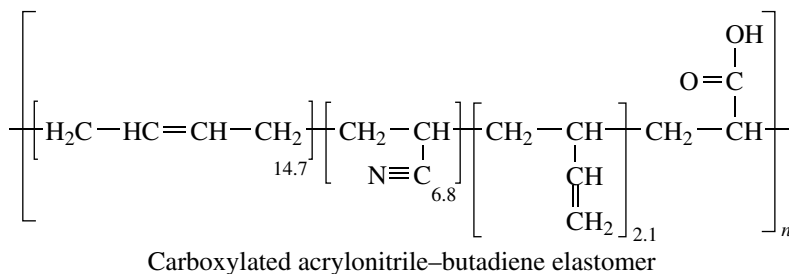
The mixture is heated *in vacuo* at about 120 to 150 °C for 1 to 2 h or the carboxyl/epoxy reaction can be catalysed with triphenyl phosphine [TPP] to reduce both reaction time and temperature.

These RLPs and their epoxy adducts are miscible with most epoxy resins, so they can easily be added to formulations with only modest increases in RT resin viscosity.



Once the rubber becomes an integral part of the cured matrix, however, decreases in strength, modulus and  $T_g$  are unavoidable unless complete secondary-phase precipitation can be assured. This means that the choice of candidate RLP, epoxy and curative must be carefully made. The acrylonitrile content of the rubber is also an important consideration; generally, as the nitrile content of a rubber increases, solubility increases and eventual particle size in the cured matrix decreases. RLP loading in the adhesive formulation is also critical, balancing out increase in toughness with any propensity for the rubber adduct to remain in the continuous phase. RLP loadings, therefore, are generally in the region of 7.5 to about 15 parts per hundred of resin.

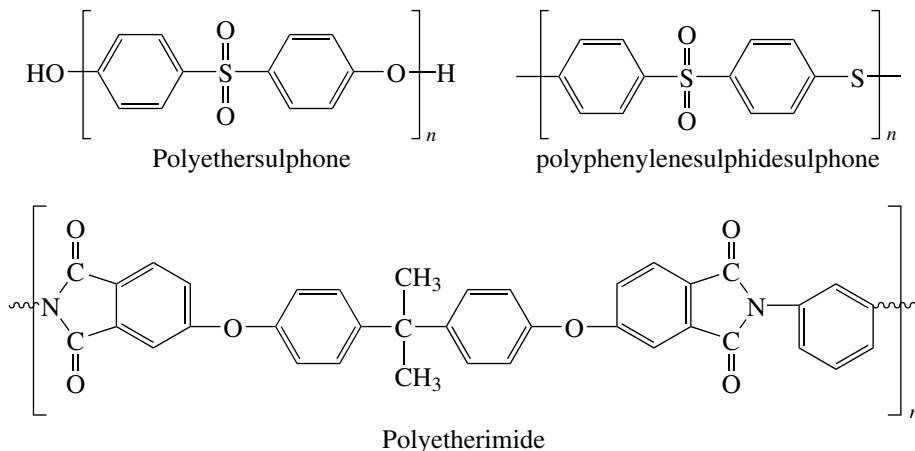
2. *Reactive elastomers:* Solid acrylonitrile–butadiene rubbers have much higher molecular weights than the liquid rubbers (200,000 to 300,000), but they can be used, as tougheners, in a like manner. Loadings are generally low (5 parts per hundred resin maximum) because of a rapid increase in resin viscosity as the rubber content increases. They can be dissolved directly into the epoxy or addition can be facilitated with a solvent that is later removed. Once again, it is important that they are prereacted with some of the epoxy. A typical material is Zeon's Nipol 1472CG.



3. *Thermoplastic modifiers:* Thermoplastics modifiers are used much like rubbers to increase the fracture toughness of epoxy resins. However, pre-reaction to form an adduct has not been found to be necessary; they are simply dissolved into the formulation either via a solution or a “hot-melt” route. They are often used at loadings as high as 50 parts of polymer to 100 parts of resin.

To be a true toughener, rather than a flexibilizer, the thermoplastic must yield the required secondary phase during cure, and this significantly limits the choice and, to obtain the most consistent performance, requires some reaction with the resins present. However, sometimes, owing to the relatively high molecular weights encountered, just the difference in solubility parameter between the polymer and the resin is enough to obtain the secondary phase.

Typical polymers used are polyethersulphone, polyphenylenesulphidesulphone, polyetherimide and polyimide.



The major benefit with this approach is that some degree of toughness can be given to inherently brittle cured epoxy matrices designed to operate at service temperatures above about 135 to 150°C, that is, highly cross-linked adhesives. Further, as most of the thermoplastics used also have  $T_g$ s at these levels or considerably above, should some polymer remain in the continuous phase after cure, the effect on the final thermal properties will not be as deleterious as with RLP or elastomeric toughening.

Other toughening techniques are discussed in the articles cited above.

### Select References

- K. Yamanaka, Y. Takagi and T. Inoue, Reaction induced phase separation in rubber-modified epoxy resins, *Polymer* **30**, 1839 (1989).
- K. Yamanaka and T. Inoue, *J. Mater. Sci.*, **25**, 241 (1990).
- Hycar Reactive Liquid Polymers*, B. F. Goodrich Technical Bulletin, 1994.
- C. B. Arends, *Polymer Toughening*, Marcel Dekker, 1996.
- E. Martuscelli, P. Musto and G. Ragosta, *Advanced Routes for Polymer Toughening*, Elsevier, 1996.
- C. K. Riew and A. J. Kinloch, Eds., *Toughened Plastics II: Novel Approaches in Science and Engineering*, American Chemical Society, 1996.
- R. A. Pearson, H.-J. Sue and F. E. Yee, Eds., *Toughening of Plastics: Advances in Modelling and Experiments*, American Chemical Society, 2000.

# U

---

## *Underwater adhesives*

---

J M LANE

### *Requirements of the adhesive*

Materials suitable for use as underwater adhesives include carefully formulated cold-curing thermosets such as **Epoxide adhesives** and **Polyurethane** adhesives. Such multi-component systems are not significantly affected by the presence of water in the uncured condition and convert from the liquid to the solid state via **Chain polymerization** in which two or more co-reactants form one polymeric product. The process does not involve the loss of solvents and does not require the presence of oxygen.

Perhaps, the earlier materials found to have a useful capacity for adhesive bonding underwater depended upon the use of a stoichiometric excess of water-scavenging polyamide hardener in an epoxide-based adhesive. This approach can lead to the production of effective joints in the short term, but formulations of this type, which are hydrophilic in the uncured state, are also likely to absorb significant amounts of water in the cured condition. It is a widely accepted view that the extent of joint weakening in susceptible joints, quite apart from the consequences of plasticization, is a function of the water-uptake characteristics of the adhesive (see **Glass transition temperature**). The consequence is therefore likely to be that such joints will show poor durability in the presence of water, when rapid uptake of water may lead to equally rapid degradation of both cohesive and interfacial properties (see **Durability: fundamentals**).

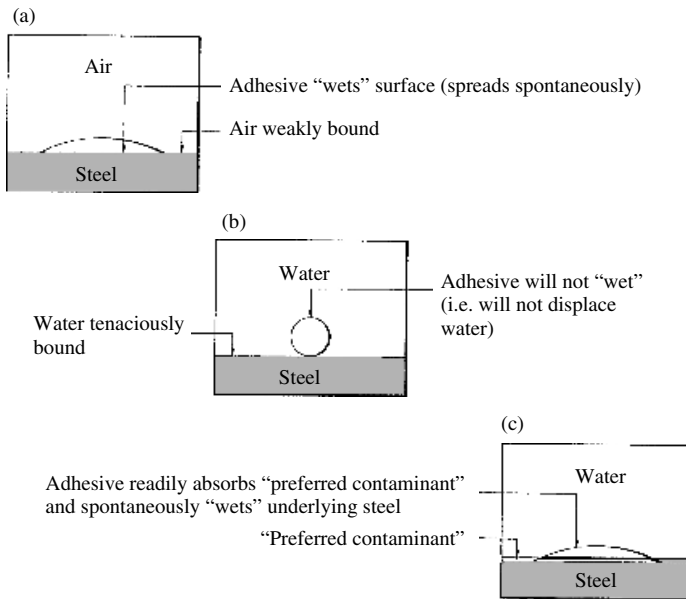
It is more satisfactory to choose an essentially hydrophobic adhesive in which water is only sparingly soluble and which has a low diffusion coefficient, and this was the approach chosen by the Admiralty Research Establishment when researching in this area.<sup>1,2</sup>

Wetting requirements

This requirement represents perhaps the greatest challenge in the underwater application of adhesives, particularly where high **Surface energy** substrates are concerned. Such materials are typified by metals, metal oxides and ceramics and are representative of most useful structural materials with the notable exception of glass and other fibre-reinforced organic composites.

The nature of the problem, as well as the solution to it, is represented in Fig. 1. The figure shows the circumstances in which adhesive joints are normally made with the substrate and adhesive surrounded by air. In the making of adhesive joints, the presence of air is seldom even considered, for the perfectly good reason that it does not represent a problem. However, the fact is that all surfaces are contaminated by the permanent gases, but they are only weakly adsorbed (see **Adsorption theory of Adhesion**) and are readily displaced by adhesive, which then spreads freely and spontaneously over the substrate surface. In this way, intimate contact is achieved between liquid adhesive and solid substrate and adhesion results. Various **Theories of adhesion** are discussed elsewhere, but all require that adhesive and adherend are in intimate contact. For example, attractive intermolecular forces (van der Waals, see **Dispersion forces, Polar forces**) can operate only over short ranges ( $\sim 1$  nm) and chemical interaction between adhesive and adherend also requires the two reactants to be in close contact.

However, Fig. 1 also shows that when the fluid air is replaced by the fluid water, a more serious problem is presented. Water, because of its relatively high surface tension (when compared with liquid organic-based adhesive for example), is much more strongly adsorbed by highly energetic surfaces and is a much more difficult contaminant to displace.



**Fig. 1.** Schematic representations of an adhesive in contact with a steel substrate (a) in air, (b) in water, (c) in water in the presence of a "sacrificial pre-treatment"

The use of mechanical action during the application of the adhesive to displace water from these surfaces is extremely inefficient and weak, and variable joints are often the result.

One approach to the solution of this problem, adopted by the Admiralty Research Establishment at Holton Heath, is to apply a so-called sacrificial pre-treatment to the substrate surface prior to the application of adhesive. The method involves the displacement of water and the deposition of a hydrophobic, but adhesive-compatible (see **Compatibility**), film over the surface to be adhesively bonded.<sup>3</sup> The consequence is that those favourable circumstances, taken for granted when bonding in the atmosphere, are re-created under water and adhesive spreads spontaneously over the surface and the essential close contact between adhesive and substrate is achieved. The sacrificial pre-treatment is so-called because it is absorbed and/or displaced by the adhesive, which then gains access to the substrate surface itself. Suitable pre-treatments may be in the form of liquids that are made up of a mixture of suitable surfactants and other components with appropriate solubility parameters (see **Compatibility**). This may be applied to freshly cleaned, preferably grit-blasted surfaces by spraying through a suitably designed hood when it performs the dual function of providing a wettable surface for the adhesive and also of protecting the metal surface against corrosion for a limited period until the adhesive may be applied. Alternatively, they may be solids, which can be applied simultaneously with the cleaning process if appropriate characteristics are possessed by the matrix materials used in the bristles of abrasive brushes, for example. When this technique is used, the thickness of the deposited layer is a function of the ratio of matrix to abrasive and also of application temperature.

Figure 2 shows, in the form of histograms, the strengths achieved with steel/steel tensile butt joints made under water both with and without the use of a sacrificial pre-treatment. The lower of the two histograms shows that, where adhesive is applied under water immediately after grit blasting, the achieved joint strength is low and extremely variable. These results clearly demonstrate the unpredictability of using purely mechanical means to displace water from energetic substrates (in this case mild steel) and the consequent incomplete wetting of the substrate by the adhesive. With joints made in this way, failures appear to be exclusively interfacial between adhesive and adherend. In the upper histogram, Fig. 2 also shows that, where the displacement of water is energetically favourable after the application of a liquid sacrificial pre-treatment, joint strengths are some three to four times higher with a greatly reduced variation at a level of around 5%. The failure of joints made in this way is usually cohesive within the adhesive layer.

Where less energetic surfaces are to be bonded, such as those presented by polymeric materials used as matrices for fibre-reinforced composites or as surface coatings, the problems are much reduced, as it will no longer be energetically favourable for water to occupy the surface. Provided the substrate is wettable by the adhesive, there will be no great problem in producing a reliable adhesive joint. By way of illustration, untreated polyethylene will be no easier to bond under water than it is in the atmosphere, but glass-reinforced polyester will be readily jointed in this way. Even when saturated with water, useful adhesive joints may still be made with this latter material.

### *Durability considerations*

The question of the durability of adhesive joints in the underwater environment is clearly one of great importance because water is widely recognized as a major threat to their

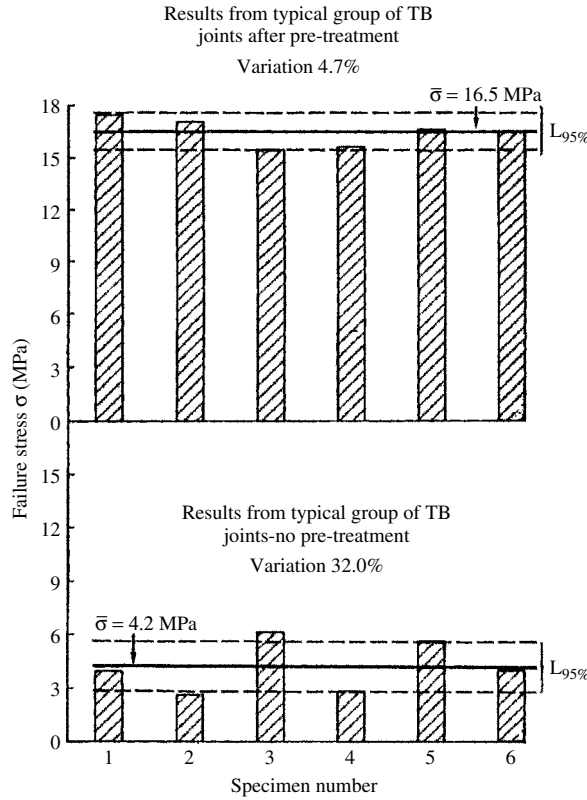


Fig. 2. Influence of a “sacrificial pre-treatment” for steel on the strength of tensile butt joints made under water with an epoxy-amine adhesive

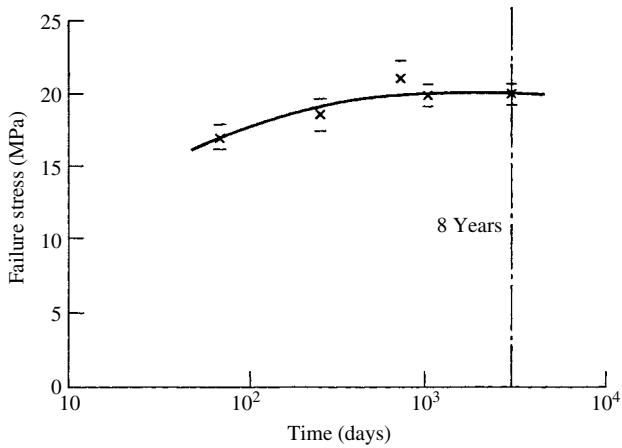
integrity (see **Durability: fundamentals**). However, joints to polymeric substrates will generally experience degradation only as the result of a weakening of the adhesive following plasticization by dissolved water. Where energetic substrates are bonded, degradation may also occur as a result of displacement of adhesive by water.

The degree of disbonding by water may also be minimized, provided water gains access to the water-sensitive interface via diffusion through the adhesive, by selecting an adhesive with a low water solubility and a low diffusion coefficient as recommended earlier. This approach, coupled with careful joint design, may provide adequate durability, but where greater resistance to hydrolytic attack is required, use of coupling agents would be advised (see **Silane adhesion promoters, Silanes as metal pre-treatments and Primers for adhesive bonding**). Figure 3 shows graphically the effect of prolonged exposure to sea water on steel/steel tensile butt joints using the WRA4501 adhesive system, which is based on an amine-cured epoxide resin (see **Tensile tests, Epoxide adhesives**).

### Applications

In recent years, underwater adhesives technology has been further developed and is now being used in offshore applications for the oil and gas industries. Underwater repairs





**Fig. 3.** Influence of exposure to sea water on the strength of tensile butt joints made between steel with an epoxy-amine adhesive

involving structural adhesive bonding and sealing have been undertaken using both diver-assisted and remotely operated vehicle (ROV) procedures.<sup>4,5</sup>

### References

1. M. R. Bowditch, J. D. Clarke and K. J. Stannard, The strength and durability of adhesive joints made underwater, in *Adhesion 11*, K. W. Allen, Ed., Elsevier Applied Science Publishers, London, 1987.
2. M. R. Bowditch and R. A. Oliver, An underwater adhesive repair method for offshore structures, in *Polymers in Offshore Engineering*, Conference proceedings, Plastics and Rubber Institute, London, 1988.
3. M. R. Bowditch, Formation of metal/resin bonds, UK Patent Specification 2 083 3778, 24 Mar. 1982.
4. M. R. Bowditch and J. M. Lane, Underwater repair of pressurised systems, in *European Coatings*, Vol. 76, 2000, p. 57.
5. M. R. Bowditch and J. M. Lane, The development of resin systems and processes for underwater bonding and sealing, *Procedures of the 24th Annual Meeting of the Adhesion Society*, Williamsburg, 2001.

# V

---

## *Viscoelasticity*

---

D W AUBREY\*

Viscoelasticity is concerned primarily with polymer deformation, not polymer or adhesive fracture processes. Its importance in adhesion processes lies in the fact that the deformation that accompanies adhesive fracture can make an important contribution to the overall joint strengths.

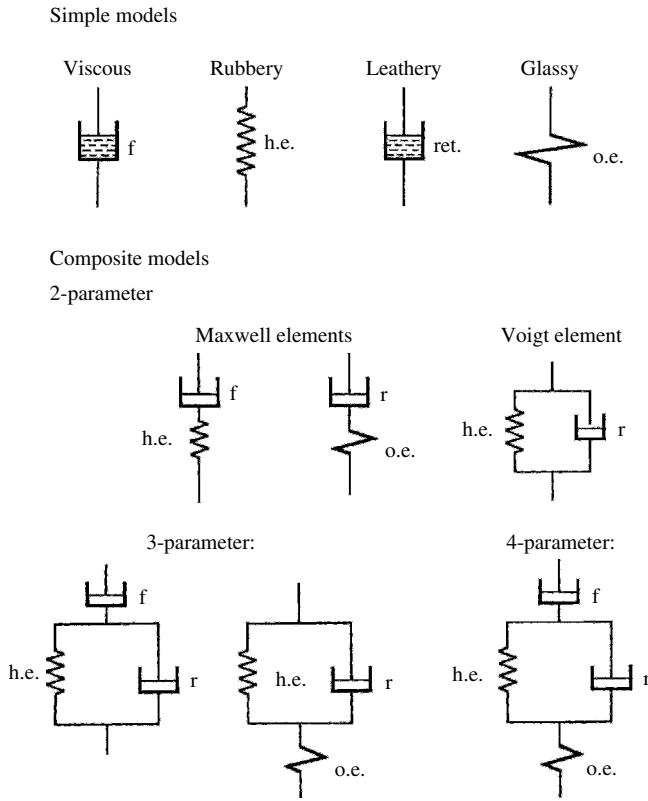
The simplest type of viscoelastic behaviour as shown by single-phase amorphous polymers is described in this article. Polymers that crystallize or form multiple phases such as blends, block copolymers, particulate or fibre-filled polymers show more complex behaviour, since each amorphous region will show its own viscoelastic response to deformation.

As its name implies, viscoelasticity involves a blend of liquid-like viscous properties with solid-like elastic properties. In order to make any progress with characterizing viscoelastic behaviour, these two aspects of behaviour must be considered separately.

### *Types of response in polymers*

Amorphous, uncross-linked polymers can exhibit various combinations of two kinds of elastic response and two kinds of viscous response to deformation. These responses are represented in Fig. 1 by mechanical analogues consisting of elastic springs and dashpots filled with viscous liquids.

Glassy response, dominated by extension and compression of secondary intermolecular bonds, is shown at the lowest temperatures. It is elastic in the same way as all rigid solids (e.g. snooker balls) are elastic and is represented in Fig. 1 as an “ordinary elastic” spring of high Young’s modulus  $E$  (stress/strain).



**Fig. 1.** Mechanical analogues for viscoelastic behaviour of polymers (f = flow; h.e. = highly elastic; ret. = retardation; o.e. = ordinary elastic)

*Leathery (“transition”) response* This is shown at somewhat higher temperatures, where segments of polymer chains, but not whole polymer chains, gain sufficient thermal energy to move under a deforming force. This is a viscous process, the viscosity  $\eta$  (shear stress/shear strain rate) depending on the frictional resistance to segmental motion. It is represented by a retardation dashpot (Fig. 1). The temperature at which the midpoint of this region falls is often taken as the **Glass transition temperature**,  $T_g$ , and is a characteristic temperature for a polymer, enabling different polymers to be compared in the same viscoelastic state.

*High elastic (“rubbery”) response* This arises at still higher temperatures, where the frictional resistance to segmental motion becomes negligible. It involves recoverable deformation in which the polymer chains are deformed from their equilibrium configurations against a network of molecular entanglements. It is represented by a high elastic spring (Fig. 1) that is of much lower modulus than the ordinary elastic spring.

*Viscous flow (“terminal”) response* This is seen at the highest temperatures. Under these conditions, the entanglements have sufficient thermal energy to become undone, and the flow of whole molecules can occur. This is the same kind of flow that arises in all

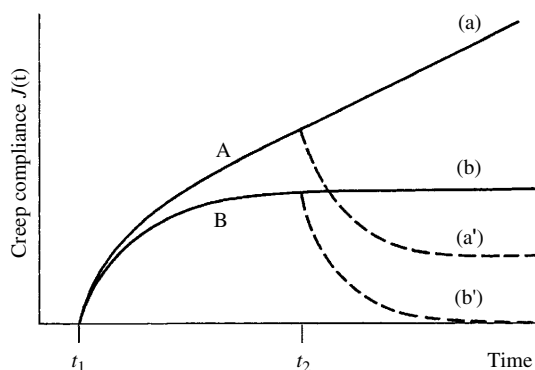
liquids and is represented by a flow dashpot (Fig. 1) of much higher viscosity than the retardation dashpot.

The modulus of an elastic spring is substantially independent of the temperature or rate at which it is measured and the work done in deforming it is all stored and recoverable. The stiffness of a dashpot, on the other hand, is markedly dependent on temperature or rate of deformation and the work of deformation is all dissipated as heat. Thus, depending on the relative contributions of springs and dashpots to its behaviour, a polymer will show various degrees of temperature and rate dependence in its properties, and various proportions of input energy dissipation as heat (hysteresis). Depending on the rate and temperature, it is common practice to approximate polymer behaviour by adopting one of the various composite mechanical analogues shown in Fig. 1. Of these, the four-parameter model is probably the most versatile, since this can be simplified to any of the other models by allowing the dashpot viscosities to range between infinitesimal and infinite.

### Viscoelastic parameters

Viscoelastic characteristics of polymers may be measured by either static or dynamic mechanical tests. The most common static methods are by measurement of creep, the time-dependent deformation of a polymer sample under constant load, or stress relaxation, the time-dependent load required to maintain a polymer sample at a constant extent of deformation. The results of such tests are expressed as the time-dependent parameters, creep compliance  $J(t)$  (instantaneous strain/stress) and stress relaxation modulus  $G(t)$  (instantaneous stress/strain) respectively. The more important of these, from the point of view of adhesive joints, is creep compliance (see also **Pressure-sensitive adhesives – adhesion properties**). Typical curves of creep and creep recovery for an uncross-linked rubber (approximated by a three-parameter model) and a cross-linked rubber (approximated by a Voigt element) are shown in Fig. 2.

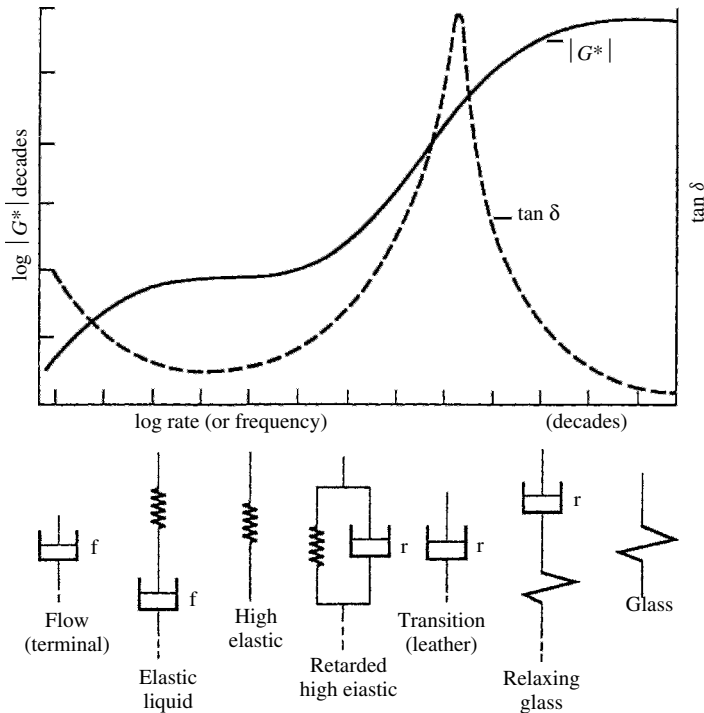
According to the Boltzmann superposition principle, the final creep deformation caused by a series of step loading and unloading increments such as those of Fig. 2 is predictable by the summation of the individual creep responses from each increment.



**Fig. 2.** Creep (curves (a) and (b)) and creep recovery (curves (a') and (b')) for (A) an uncross-linked rubber and (B) a cross-linked rubber ( $t_1$  – load applied;  $t_2$  – load removed)

Viscoelastic response of polymers can also be measured by dynamic tests, in which the response of the polymer is measured under an imposed sinusoidal oscillatory deformation of variable frequency. Because of the viscoelastic nature of the polymer, there is a lag in phase angle  $\delta$  between stress and strain. The extreme values of  $\delta$  would be zero, for a purely elastic material, and  $\pi/2$  for a purely viscous one. Typical instruments for studying dynamic mechanical properties are the torsion pendulum, the Weissenberg rheogoniometer, the dynamic mechanical thermal analyser (DMTA) and the vibrating reed. Such methods give values for viscoelastic parameters such as a “complex” Young’s modulus  $E^*$  or shear modulus  $G^*$  and differentiate between an elastic contribution  $E'$  or  $G'$  (“storage” modulus) and a viscous contribution  $E''$  or  $G''$  (“loss modulus”). These are related by, for example,  $E^* = E' + iE''$ , where  $i = (-1)^{1/2}$ . The “absolute” modulus  $|E^*|$  or  $|G^*|$  is sometimes used. It is given by  $|E^*| = \sqrt{[E'^2 + E''^2]}$ . The ratio  $E''/E'$  or  $G''/G'$ , equals  $\tan \delta$ , the dissipation factor (or loss factor), and gives a measure of energy dissipated by hysteresis and is, of course, at a maximum when viscous (dashpot) processes are involved. There is, of course, a close analogy between the formal treatment of dynamic viscoelasticity and of alternating electric current.

By application of the principle of time–temperature equivalence (see **Viscoelastic properties – time–temperature superposition**), the results of dynamic tests may be expressed as a master curve, either in the form of a viscoelastic function (e.g.  $\log G'$ ) against temperature  $T$  at constant frequency  $\omega$  of measurement or in the form of



**Fig. 3.** Illustration of the changes in absolute shear modulus  $|G^*|$  and dissipation factor  $\tan \delta$  with frequency at constant temperature for a simple amorphous polymer. Models show the changes in viscoelastic state

viscoelastic function (e.g.  $\log G'$ ) against frequency ( $\log \omega$ ) at constant temperature  $T$ . The latter presentation is more useful for adhesive materials, since it is more common to vary rates of joint fracture at constant temperature than vice versa.

We are now in a position to illustrate the various regions of viscoelastic behaviour with an idealized curve of, for example, the magnitude of the absolute dynamic shear modulus  $|G^*|$  against frequency ( $\log \omega$ ) at a constant standard temperature (Fig. 3). On the same abscissa, the energy dissipation ( $\tan \delta$ ) and applicable mechanical models are also shown.

Figure 3 illustrates the ideal viscoelastic behaviour for a simple amorphous polymer. It shows how the regions of rate (and temperature) independence coincide with elastic (spring) behaviour (where  $|G^*| \approx G'$ ), and regions of high rate (and temperature) dependence coincide with viscous (dashpot) response (where  $|G^*| \approx G''$ ).

Energy loss through viscoelastic dissipation usually contributes to the fracture energy of an adhesive bond: sometimes that contribution is dominant. Adhesives are often designed to operate in the regions where viscoelastic losses ( $\tan \delta$ ) are high. Further discussion can be found under **Adhesion – fundamental and practical**, **Peel tests** and **Tensile tests**; see also **Creep** and **Durability: creep rupture**.

### Select References

- I. M. Ward and D. W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers*, Wiley, 1993.  
 E. Riande, *Polymer Viscoelasticity*, Marcel Dekker, 1999.  
 Yn-Hwang Lin, *Polymer Viscoelasticity*, World Scientific, 2003.  
 A. Berker, in *Adhesion Science and Engineering- 1, the Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 2002, p. 451.

## Viscoelasticity – time–temperature superposition

D W AUBREY\*

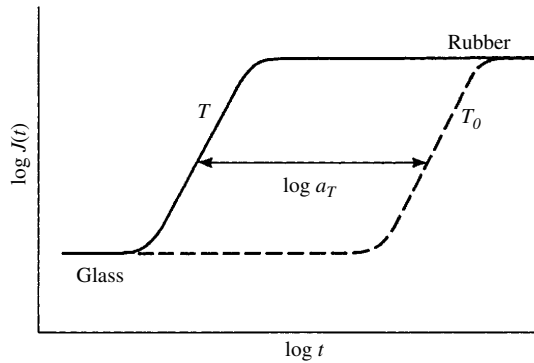
### Time–temperature equivalence

Because of the nature of viscoelastic relaxation processes (discussed briefly under **Viscoelasticity**), the effect of increasing the temperature is equivalent to allowing more time in a given test. The equivalence is expressed in general in relation to a chosen standard temperature  $T_0$  by a shift factor  $a_T$  defined as the ratio

$$a_T = \frac{\text{Time } t \text{ for a given viscoelastic response at temperature } T}{\text{Time } t_0 \text{ for the same viscoelastic response at temperature } T_0}$$

Thus, a given creep compliance value  $J(t)$  (see **Viscoelasticity**) for a cross-linked rubber may be obtained after a short time  $t$  at a higher temperature  $T$  or a longer time  $t_0$  at a lower temperature  $T_0$  (Fig. 1).

A typical shift is such that the effect of increase of 1 decade of  $t$  is approximately equivalent to an increase of  $8\text{--}12^\circ$  in  $T$ . It is therefore more convenient to use a logarithmic scale for the time (or rate) axis.



**Fig. 1.** Creep compliance at two different temperatures illustrating shift factor  $a_T$

A knowledge of the shift factor–temperature relationship therefore allows a viscoelastic function to be plotted either against deformation time (or inversely against rate) at a standard temperature  $T_0$  or against temperature at a standard time (or rate) of deformation. However, a modulus–(log) frequency curve (see Fig. 3 under **Viscoelasticity**) is not the exact inverse of the modulus–temperature curve because there are non-viscoelastic effects that also cause the modulus to change with temperature. The most important of these is the dependence of modulus on temperature in the high elastic region, and to correct for this, the “reduced” version of the measured viscoelastic function is used. For example, the reduced storage shear modulus would be given by

$$G'_r = G' \frac{T_0 \rho_0}{T \rho}$$

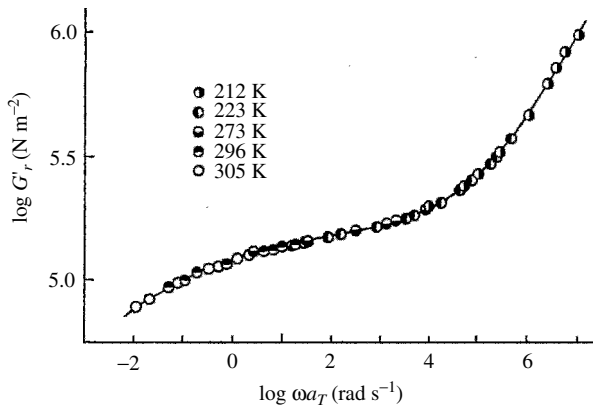
where  $T$ ,  $T_0$  are absolute test and standard temperatures, and  $\rho$ ,  $\rho_0$  the corresponding densities. The density component of this correction is very small and is often neglected.

#### *Experimental time–temperature superposition*

The experimental application of the time–temperature superposition principle will be described by reference to the formation of a shear modulus–(log) frequency master curve.

First, measurements are made of dynamic storage shear modulus  $G'$  over a range of frequencies at each of several temperatures, using an oscillatory method such as DMTA. Values are “reduced” to  $G'_r$  (see above), then data points are plotted as  $\log_{10} G'_r$  against  $\log_{10}$  frequency  $\omega$  on sheets of transparent paper, one sheet for each temperature. The abscissae for the various test temperatures  $T$  are then shifted horizontally along a common axis until data points for adjacent temperatures superimpose. The amount of horizontal shifting of each abscissa relative to that for the standard reference temperature  $T_0$  gives the value of shift factor as  $\log_{10} a_T$  for that particular temperature. The superimposed data points then form the master curve of  $\log_{10} G'_r$  against  $\log_{10} \omega a_T$  at the standard reference temperature  $T_0$  (Fig. 2).

A great advantage of such master curves is that the dependence of viscoelastic function against frequency is shown over a much wider range of rates (typically  $10^{10}$ -fold)



**Fig. 2.** Experimentally superposed results of (reduced) dynamic shear modulus obtained at various temperatures and frequencies

than are directly accessible with any viscoelastic measuring method (typically  $10^3$ -fold). All viscoelastic functions including moduli, compliances, viscosities, loss functions, and so on, are amenable to this treatment. In addition, fracture and adhesion processes in which viscoelastic deformations are prominently involved are commonly subjected to time–temperature superposition for clearer presentation and better understanding.

#### *Use of the WLF equation in time–temperature superposition*

If the values of shift factor  $\log_{10} a_T$ , obtained as above, are plotted against test temperature  $T$ , a smooth curve is obtained. Williams, Landel and Ferry (1955) showed that the same shift factor–temperature relationship was obtained from the experimental shifting of results from a large number of amorphous polymers. The empirical relationship thus obtained is known as the WLF equation, and can be used in one of the two forms:

$$\log_{10} a_T = \frac{-C_1^s(T - T_s)}{C_2^s + T - T_s}$$

where  $C_1^s = 8.86$ ,  $C_2^s = 101.6$  K,

$$\log_{10} a_T = \frac{-C_1^g(T - T_g)}{C_2^g + T - T_g}$$

where  $C_1^g = 17.44$ ,  $C_2^g = 51.6$  K.

The values of  $C_1$  and  $C_2$  shown are referred to as universal, since they have been shown experimentally to apply to a large number of polymers. If natural logarithms are used, values for  $C_1^s$  or  $C_1^g$  are multiplied by 2.303.

Here,  $T_s$  is a specific reference temperature at which all amorphous polymers are in the same viscoelastic state. It was arbitrarily chosen by Williams, Landel and Ferry as  $T_s = 243$  K for polyisobutylene and, in general, is given approximately by  $T_g + 50$  K.



The equation is now probably more used in the form with the glass transition temperature  $T_g$  as the viscoelastic reference temperature. It holds well over the range  $T_g$  to  $T_s + 100$  K ( $T_g \pm 50$  K).

The WLF equation can clearly be used as an alternative to the experimental shifting procedure described above, provided that a value for  $T_s$  (or  $T_g$ ) is known. There is some risk attached to the direct use of the WLF equation, however, since there is variation of the values of  $C_1$  and  $C_2$  for different polymers, and  $T_s$  (or  $T_g$ ) values may not be accurate. A better procedure would be to determine  $C_1$  and  $C_2$  values by experimental shifting and then use the WLF equation, with these values, for subsequent shifts. Using this procedure, the WLF equation can be used with confidence for results in viscoelastic regions where experimental shifting fails (e.g. where an absence of slope makes experimental shifting impossible).

It will be clear that the direct use of the WLF equation will produce a master curve with either  $T_s$  or  $T_g$  as its reference temperature  $T_0$ . It may be, however, that the master curve is required at some other temperature (e.g. room temperature). In such a case, it is a relatively simple matter to calculate the constants ( $C_1^0$  and  $C_2^0$ ) for any chosen reference temperature  $T_0$ .

The general form of the WLF equation may be predicted from considerations of free volume, and physical significance can be attached to the constants  $C_1$  and  $C_2$ .

#### *Time–temperature superposition and adhesion*

The viscoelastic contribution to the fracture energy in an adhesion test is, in principle, rate and temperature-dependent. Where this contribution is significant, it has been possible to nationalise adhesion measurements using the WLF transform—see **Adhesion – fundamental and practical, Pressure-sensitive adhesives – adhesion properties and Tensile tests**.

#### *Select References*

- I. M. Ward and D. W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers*, Wiley 1993.
- A. Berker, in *Adhesion Science and Engineering- 1, the Mechanics of Adhesion*, D. A. Dillard and A. V. Pocius, Eds., Elsevier, 2002, p. 451.

# W

---

## *Weathering of adhesive joints*

---

J P SARGENT

Adhesive bonding offers an efficient means of joining components, offering many advantages over traditional fastening methods; however, its Achilles' heel is the deterioration in strength as a result of weathering. Designers are usually concerned not with the as-manufactured strength of a bonded joint, but with the lowest level to which the strength will fall over the lifetime of the component because of the adverse effects of the ambient environment. Ensuring such long-term bond integrity requires the selection of a suitable "adhesive system" comprising adhesive, adherends, surface pre-treatment and primers.

Those factors that are responsible for weathering and degradation in the bond performance are often related to elevated temperatures, the presence of water, corrosive salt solution environments, solvents and creep (see **Durability: creep rupture** and **Durability – fundamentals**). When metallic substrates such as aluminium are used, then the most vulnerable region is usually the interface between adhesive or primer and the adherend, as result of the ingress of water. Interfacial regions between adhesive and substrate composed of GRP, CFRP or plastics are usually considered far less susceptible to interfacial failure (see **Fibre composites – matrices and fibres**). It is believed that this difference in performance has its origins in the differing thermodynamic work of adhesion (see **Wetting and work of adhesion, Underwater adhesives**) that exists between a metal or metal oxide (which has a high free energy surface) and that of a polymer (which has a low free energy surface).

The presence of moisture can give rise to both primary corrosion of the adherends, particularly if untreated cut edges are exposed to the environment, or lack of stability of the interfacial bond that is responsible for promoting initial bond strength – though the full details of the resulting bond deterioration are probably not fully understood. Since diffusion is considered to be the main mechanism by which water gains access to the bond region, then increasing water path lengths, for example, retaining spew fillets, will result in less rapid water ingress and increased timescales for bond deterioration. Well-known

analytical solutions are available to predict water concentration profiles for some of the simpler geometries if the diffusion coefficient is known. Moderate temperature increase results in increased values for the diffusion coefficient according to the Arrhenius rate law. The presence of water will reduce the **Glass transition temperature** and reduce the yield stress of the adhesive, giving rise to increased plastic deformation when under stress. If temperatures are too high, then the adhesive will also suffer irreversible changes such as cracking, crazing or hydrolysis.

Sufficiently good adherend surface pre-treatment that is “fit for purpose” is important in conferring adequate interfacial bond strength (see **Pre-treatment of metals prior to bonding**). For the most demanding **Aerospace applications** involving structural joints with aluminium alloys, then a durable, stable oxide structure is required, which is produced via grit blasting, etching (see **FPL etch**) and **Anodizing**. This process, is however, costly, time consuming and frequently makes use of toxic, environmentally unfriendly processes (see **Environment and the impact of adhesive technology**). For less demanding applications, where the structural loads are smaller, the lifetimes shorter, and the consequences of failure less severe, less expensive user-friendly treatments may be suitable.

Ideally, the choice and design of an adhesive system should be made using knowledge of the failure mechanism(s) and the considered use of selected test methods for measuring weathering performance. Given that the lifetime of bonded components can be many years, recourse is often made to the use of **Accelerated ageing** regimes for adhesive system selection in order to reduce timescales, frequently making use of increased temperatures in corrosive salt-spray environments under significant stress levels. However, the degree of confidence with which such accelerated procedures can be used for extrapolation does rely on the extent to which the accelerated test faithfully reproduces the failure mechanism and stress state actually responsible for in-service deterioration. This usually requires a comparison with specimens that have weathered as a result of in-service performance (see **Weathering tests**).

Common test geometries used for accelerated testing regimes that are used to rank the performance of an adhesive system include the “Boeing” **Wedge test**, the **Peel test** and the single-lap **Shear test**. The wedge test is a simple test based on the double cantilever beam used in **Fracture mechanics** testing. It has the advantage that it is self-stressed on insertion of the wedge, it is relatively easy to analyse, and does not tie up the use of expensive testing machines, so many specimens can be easily tested. If crack growth can be associated with interfacial failure, then the test can easily discriminate poor adhesion associated with poor joint performance in relatively short times, though debate exists as to its ability to discriminate between those better quality joints with very good surface pre-treatments. In addition, it should be noted that in the absence of any reliable predictive models with a validated failure criteria that encompasses a full understanding of the kinetics of degradation, extrapolation of results from any of the geometries used for accelerated testing to different geometries and loading situations, other than as a ranking exercise, should be undertaken with caution.

### *Select References*

- A. J. Kinloch, *Adhesion and Adhesives*, Chapman and Hall, London, 1987, ISBN: 0-412-27440-X, Chap 8.

---

The Performance of Adhesive Joints, *Environmental Durability of Adhesive Bonds*, MTS Adhesives, Project 3, Reports No. 1, 2, 5, 8, 1993–1996, AEA Technology, Harwell, U.K.  
*Adhesives and Sealants*, Vol. 3, Section 7, *Engineered Materials Handbook*, ASM International, 1990, ISBN: 0-87170-281-9.

---

### Weathering tests

---

S TREDWELL\*

The practical importance and theoretical complexity of environmental deterioration of adhesive bonds has resulted in extensive research on many aspects of the problem of **Weathering of adhesive joints**.

Several different test methods have been used to investigate the durability of bonded joints. By far, the largest single problem facing adhesive scientists and technologists today is that of the long-term durability of adhesive bonds exposed to natural environments, that is, weathering. **Structural adhesives** are used extensively in aerospace construction (see **Aerospace applications**), principally with aluminium alloys, and aircraft are required to function throughout a service life of several decades, in many diverse natural environments ranging from low-temperature arctic conditions to tropical, high-humidity climates.

Much work has been undertaken on the **Accelerated ageing** of adhesive joints. Although the results of such work are valuable, there is no substitute for testing of joints after exposure to a range of actual climatic conditions. Among the most severe climates are tropical dry and tropical wet climates.

The investment needed in terms of cost and time means that few such comprehensive programmes are undertaken in the short-term culture of contemporary industry. Still important are classic reports of such weathering trials undertaken by UK government laboratories.<sup>1,2</sup> These involved bonded aluminium double overlap joints, stressed and unstressed, peel and honeycomb specimens (see **Peel tests**). These were exposed at the Royal Aircraft Establishment (RAE), Farnborough (temperate), and at the Joint Tropical Research Unit (JTRU) sites at Innisfail (hot–wet) and Cloncurry (hot–dry), Australia. Periods of up to 6 years were employed, exposing a variety of adhesive systems to the different climates.

The durability of the bonded joints was greatly influenced by the nature of the adhesive; the best performers in all climates were epoxy–novolak and nitrile–phenolic formulations. A tropical, hot–wet climate was the most damaging to bonded structures and the combination of high humidity and applied stress was particularly deleterious. During exposure to natural environments, the failure mode of aluminium joints was found to change gradually from wholly cohesive, within the adhesive, to include increasing amounts of interfacial failure (see **Stress distribution: mode of failure**).

A summary of the progress in evaluating adhesive bond performance over a 25-year period has been published by Minford.<sup>3</sup> More recent papers relating to Farnborough work include a comparison of anodized and chromate etch treatments for clad aluminium<sup>4</sup> (the durability of the former was superior, see also **FPL etch, Anodizing, Pre-treatment of aluminium**) and a comparison of the natural weathering and accelerated ageing of joints.<sup>5</sup>

Further information can be found in other articles on **Durability: fundamentals**, **Epoxy adhesives** and **Pre-treatment of metals prior to bonding**.

### References

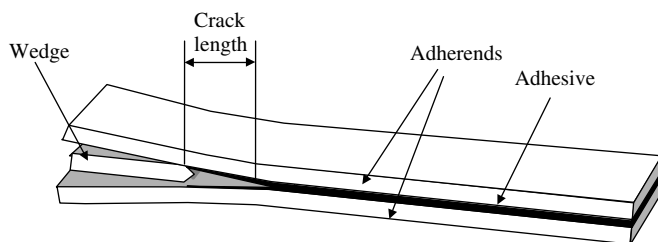
1. M. D. G. Hockney, *Technical Reports* (a) 70081 (1979); (b) 72100 (1972); (c) 73013 (1973), RAE, Farnborough.
2. J. L. Cotter, in *Developments in Adhesives – 1*, W. C. Wake, Ed., Applied Science Publishers, London, 1977.
3. J. D. Minford, in *Treatise on Adhesion and Adhesives*, Vol. 5, R. C. Patrick, Ed., Marcel Dekker, New York, 1981, Chap 3.
4. B. M. Parker, *Int. J Adhes. Adhes.*, **13**, 47–51 (1993).
5. I. A. Ashcroft, R. P. Digby and S. J. Shaw, *J. Adhes.* **75**, 175–201 (2001).

### Wedge test

D G DIXON

The wedge test, also known as the wedge cleavage test or Boeing wedge test, is a rapid quality test to assess the durability of adhesive bonds (see **Durability – fundamentals** and **Weathering of adhesive joints**) and particularly the effectiveness of **Pre-treatment of metals prior to bonding**. The method is described in an ASTM standard<sup>1</sup> for aluminium, but it has been used as a research tool to evaluate bonding treatments in a range of materials.

The test specimen consists of two sheet metal adherends with the required surface treatment to be bonded together. When the adhesive is cured, a metal wedge is inserted into one end of the specimen, forcing the adherends apart. This is shown in Fig. 1. At this stage, the crack length is measured and then the specimen is exposed to a warm, wet environment (e.g. 50°C, 98% relative humidity); crack growth is then measured periodically at the edge of the specimen. Some investigators use condensing humidity, but if controlled **Humidity** is required, this can be achieved by placing the specimen over a saturated solution of a particular salt. Tables of controlled humidities produced using this method are available in the literature. An even simpler approach is to immerse the specimen in warm water. It is necessary to abrade or polish the edge of the specimen to reveal the bond line before the test commences to allow easy viewing of the crack.



**Fig. 1.** Schematic of the wedge test specimen with the wedge inserted

The ASTM standard specifies that the metal adherends are bonded as a sheet and then cut into individual specimens. If the specimens are used in very long term exposures, the cut edges will be susceptible to corrosion, which may then lead to premature failure, so short-term tests are probably to be recommended. Although this may not always be the case, it has been found that the crack growth trends indicated by a 24-h exposure are maintained after much longer exposures, so a short test period is usually suitable.

When used as a quality control test for a given type and thickness of adherend, the wedge test is a useful way to evaluate the effectiveness of a particular surface pre-treatment such as **Anodizing** and is rugged enough to be used in a range of industrial settings, using a simple pass criterion that would require a maximum crack growth in a given period of time. It is easily possible to measure crack lengths to within 0.5 mm with the aid of a magnifying glass and this level of precision allows a useful calculation of  $G_I$ , the fracture energy, to be made, provided that there has been no plastic deformation in the adherends (see **Fracture mechanics**).

A simple equation to calculate fracture energy is

$$G_I = \frac{3Ed^2h^3}{16(a + 0.6h)^4}$$

where  $E$  is the Young's modulus of the adherend material,  $d$  is the wedge thickness,  $a$  is the crack length and  $h$  is the adherend thickness.

This value provides an estimate of the toughness of the joint and makes the wedge test a useful tool for the rapid evaluation of adhesive systems. It should not be used as the sole test to determine the suitability of an adhesive or pre-treatment but it will usually reveal poor durability performance in a short time.

The wedge test can provide further information if the fracture surfaces are examined. **Surface analysis** and microscopy can be used to determine the locus of failure and provide clues to assist in the development of adhesive materials or surface treatment processes.

### References

1. ASTM D3762-79 Standard test method for adhesive-bonded durability of aluminium.

---

## Welding plastics – electromagnetic radiation

---

A L BUXTON

### Introduction

Polymers and composites can be joined by welding, adhesive bonding and mechanical fastening. The choice of process is affected by the material to be joined, the joint configuration, the strength of joint required, the level of seal required, the process cost and speed and the production quantity. Welding processes rely on heat at the joint to melt the adjacent polymer, with a weld forming on cooling. Therefore, welding is only an

option with thermoplastic polymers and composites, while thermoset systems must rely on adhesive bonding or mechanical fastening to join them.

There are around 20 different methods of welding plastics, which can be split into three general classifications:

- techniques employing an external heat source;
- techniques in which heat is generated by mechanical movement;
- techniques that directly employ electromagnetism.

A selection of these techniques is also applicable to polymer composites (see **Fibre composites – joining**). However, since composites gain their superior properties from the reinforcement, the weld is inevitably the weak point in the system as the fibre will be discontinuous across the joint interface. All the welding processes are governed by the parameters time, temperature and pressure. In order to achieve high-quality welds, careful optimization of the welding parameters is required for each application.

Other articles are concerned with **Welding plastics – external heat source**, **Welding plastics – mechanical movement**, **Polymer–polymer adhesion: weld strength**, **Solvent welding** and **Wood bonding by vibration welding**. This article provides an overview of welding processes that use an external heat source, and considers the factors affecting the choice of process. Examples of industrial applications are given throughout.

### *Resistive implant welding*

In resistive implant welding, heat is generated through the introduction of an electrically conductive implant at the joint, through which a high electric current is passed. Implants commonly consist of copper mesh or carbon fibres. The implant heats up because of resistive losses, softening the surrounding plastic. The application of pressure at the joint fuses the two parts together and on cooling, a weld is formed.

The implant remains at the weld, which rules out the use of resistive implant welding for some applications and it has the disadvantage of requiring a consumable implant. It is useful for the joining of composites, where the implant could be manufactured from the prepreg, thus forming a homogeneous joint. Resistive implant welding is particularly suited to the joining and repair of gas and water pipes since it can be performed in the field. In the pipe joining industry, it is referred to as electrofusion welding.

### *Induction welding*

Induction welding is similar to resistive implant welding in that a conductive implant is required. However, in this case, the heat is generated by an induction field set up either by eddy currents or because of hysteresis losses. A work coil connected to a power supply is placed in close proximity to the joint. As electric current at high frequency passes through the work coil, a dynamic magnetic field is generated whose flux links to the implant. As the implant heats up, the surrounding thermoplastic softens and melts. If pressure is applied to the joint, a weld forms as the joint cools. Induction welding is ideal for attaching metallized tops to plastic bottles. It is also applicable to a range of composite materials.

### *High-frequency welding*

High-frequency (HF) welding, also known as radio frequency (RF) welding or dielectric welding, is a method of joining thin sheets of polar thermoplastic material together. It uses high frequency (13 to 100 MHz) electromagnetic energy to fuse together the materials. A rapidly alternating electric field is set up between two metal-welding bars. The electric field causes the polar molecules found in some thermoplastics to oscillate and orient themselves with respect to the field. The energy generated by this process causes a temperature increase, resulting in the melting of the materials. Combined with the pressure applied by the clamping of the welding bars, this causes a weld to be formed.

RF welding relies on the vibration and orientation of charged molecules within the polymer chain to generate heat; consequently, its use is restricted to plastics containing polar molecules. Polyvinylchloride (PVC) and polyurethanes are the most common thermoplastics to be welded by the RF process. It is possible to RF weld other polymers including nylon, PET, EVA and some ABS resins, but special conditions are required, for example, nylon and PET are weldable if preheated welding bars are used in addition to the RF power. Owing to the impending restrictions in the use of PVC, a special grade of polyolefin has been developed that also has the capability to be RF welded.

A wide range of products is manufactured using high frequency welding. Examples include ring binders and stationary wallets, inflatable items such as beach balls and life jackets, large items including tents and lorry covers, blood bags and colostomy bags for the medical industry and automotive components such as air bags and sun visors.

### *Laser welding*

Laser welding was first demonstrated on thermoplastics in the 1970s, but has only recently found a place in industrial scale situations. The technique, suitable for joining both sheet film and moulded thermoplastics, uses a laser beam to melt the plastic in the joint region. The laser generates an intense beam of radiation (usually in the infrared area of the electromagnetic spectrum), which is focused onto the material to be joined. This excites a resonant frequency in the molecule, resulting in heating of the surrounding material. Two forms of laser welding exist: CO<sub>2</sub> laser welding and transmission laser welding. CO<sub>2</sub> laser radiation is readily absorbed by plastics, allowing joints to be made at high speeds, but limiting the depth of penetration of the beam, thus restricting the technique to film applications. The radiation produced by Nd:YAG and diode lasers is less readily absorbed by plastics, but these lasers are suitable for performing transmission laser welding. In this operation, it is necessary for one of the plastics to be transmissive to laser light and the other to absorb the laser energy, to ensure that the beam energy is concentrated at the joint region. Alternatively, an opaque surface coating may be applied at the joint, to weld two transmissive plastics. Transmission laser welding is capable of welding thicker parts than CO<sub>2</sub> welding, and since the heat affected zone is confined to the joint region, no marking of the outer surfaces occurs.

Laser welding is a high-volume production process with the advantage of creating no vibrations and generating minimal weld flash. The benefits of a laser system include a controllable beam power, reducing the risk of distortion or damage to components; precise focusing of the laser beam allowing accurate joints to be formed; and a non-contact process that is both clean and hygienic. Laser welding may be performed in a single shot or continuous manner, but the materials to be joined require clamping. Weld



speeds depend on polymer absorption. It is possible to create joints in plastics over 1-mm thick (with transmission laser welding) at up to at least  $20 \text{ m min}^{-1}$  while rates of up to  $750 \text{ m min}^{-1}$  are achievable in the  $\text{CO}_2$  laser welding of films. Transmission laser welding could be used for composite materials, although the transmission properties of those containing carbon fibres are probably too low to make the process viable.

Conventional transmission laser welding of plastics uses a broad-spectrum absorber, which results in a grey or black colour in the lower part. To allow all black parts to be welded, additive suppliers have therefore developed materials that are transmissive at NIR wavelengths but give a black colour at visible wavelengths. Subsequently, matched pairs of additives have been developed to allow a range of coloured parts to be welded, with a colorant in the upper part that transmits NIR wavelengths and a colorant in the lower part that absorbs at these wavelengths. Both colorants are selected to have the same appearance in the visible spectrum.

Clearweld is a further enhancement of the transmission laser welding process that provides designers with a tool to laser weld clear, coloured or opaque thermoplastics. Clearweld uses materials capable of strong absorption in the NIR spectrum which impart minimal colour. It can be used in number of ways, including, but not limited to, a coating at the joint line, inclusion within the substrate or application as a consumable film. Compared with previous technologies, it offers complete freedom in the choice of colour, reflectivity and transparency of the work pieces at visible wavelengths.

Laser welding has proved to be particularly effective in the welding of thermoplastic films in a lap joint configuration. The speeds attainable make it especially suitable for use in the packaging industry, while biomedical applications exploit the cleanliness of the process. Developments in dye and additive technology have extended its applicability to applications where the final appearance of the joint is important, notably in the automotive, medical and textile fields. Applications are being developed in the areas of food packaging, medical devices and packaging, electronic displays, and fabrics.

### *Infrared welding*

Two different approaches to infrared welding have emerged, both based around the principle of hot-plate welding (see **Welding plastics – external heat source**). One is to use tungsten filament line heaters as the heat source; the other, which is commercially available, is to use an electrically heated metal plate. Both systems involve bringing the two plastic parts to be joined in close proximity to the infrared source for sufficient time for the parts to become molten, withdrawing the source and then pushing the parts together to form a weld.

Infrared welding has a number of advantages over hot-plate welding: weld times are reduced, the joints are free from contamination (since it is a non-contact process) and low-modulus materials can be welded (since there is little or no shearing of the parts during heating).

The current application for infrared welding is in the joining of plastic pipes, but it has the potential to be used in many areas where hotplate welding is currently used, and has been demonstrated on composites.

### *Microwave welding*

The possibility of using microwaves to weld thermoplastics has existed since the development of the magnetron in the 1940s. In 1993, TWI built a research facility to explore

the feasibility of exploiting such an operation. The modified multimode cavity, similar in nature to a microwave oven, operates at a frequency of 2.45 GHz and has the capability to apply pressure to a joint.

Most thermoplastics do not experience a temperature rise when irradiated by microwaves. However, the insertion of a microwave-susceptible implant at the joint line allows local heating to take place. If the joint is subjected simultaneously to microwaves and an applied pressure, melting of the surrounding plastic results and a weld is formed. Suitable implants include metals, carbon or a conducting polymer. The particular advantage of microwave welding over other forms of welding is its capability to irradiate the entire component and consequently produce complex three-dimensional joints. Welds are typically created in less than one minute.

The technique is still in the development stages, and as such, there are currently no reported industrial applications. However, it is anticipated that microwave welding may prove to be suitable for joining automotive under-body components and domestic appliance parts.

### *Select References*

R. J. Wise, *Thermal Welding of Polymers*, Abington Publishing, Cambridge, 1999.  
*Handbook of Plastics Joining*, Plastics Design Library, New York, 1997.

---

## *Welding plastics – external heat source*

---

A L BUXTON

### *Introduction*

There are around 20 different methods of welding plastics, which can be split into three general classifications:

- techniques employing an external heat source;
- techniques in which heat is generated by mechanical movement;
- techniques that directly employ electromagnetism.

This article provides an overview of welding processes that use an external heat source and considers the factors affecting the choice of process. Examples of industrial applications are given throughout. Other articles are concerned with **Welding plastics – electromagnetic radiation**, **Welding plastics – mechanical movement**, **Polymer–polymer adhesion: weld strength**, **Solvent welding** and **Wood bonding by vibration welding**.

### *Hot-plate welding*

In hot-plate welding, the parts to be welded are held in fixtures, which press them against either side of a heated platen. Once the parts are sufficiently molten, the platen is removed. The components are then pressed together and held until they cool. Hot-plate welding is a

versatile technique with equipment available for factory use or in a portable form suitable for on-site use. The heated platen is generally flat, but three-dimensional joint profiles can be achieved with the design of a more complex plate geometry. Hot-plate welding has the drawback of being a relatively slow process with weld times ranging from 10 s for small components to 1 h for parts with a large joint area. However, short-term weld strengths equal to that of the parent material can be achieved. Hot-plate welding can be performed on composite components, using higher welding forces, but high-temperature resins such as PEEK (**Polyether ether ketone**) have a tendency to stick to the hot plate during heating.

The most important application of hot-plate welding is in the joining of thermoplastic water, gas and effluent pipes, where it is often referred to as butt-fusion welding. It is also used by the automotive industry in the manufacture of fluid reservoirs and in the welding of PVC door and window frames.

### *Hot-bar welding*

Hot-bar welding is a technique for the sealing of films. A heated metal bar applies pressure to the films, softens the plastic at the joint and forms a weld. The equipment consists of one or two electrically heated bars, one of which is hinged for the insertion and removal of the films. The film is placed on the base bar, the upper bar is brought down and pressure is applied either mechanically by the operator, or pneumatically. After the required weld time, the bar is lifted to release the joined films. The bars are often PTFE-coated to prevent molten polymer from adhering to them.

Hot-bar welding is a rapid process. Typical weld times for a 100- $\mu\text{m}$  thick sheet are in the range from 1–3 s. A reduction in welding time can be achieved by the use of two heated bars, one on either side of the films to be joined. The necessity for the heat to conduct through the film to the joint imposes a restriction, of approximately 1 mm, on the thickness of material that may be welded.

Hot-bar welding is widely used in industry, mainly in the joining of thermoplastic films having a thickness of less than 0.5 mm. It could be used to weld thin composites and has the potential to tack prepregs. It is used extensively within the packaging industry for producing plastic bags.

### *Impulse welding*

Impulse welding is an advanced form of hot-bar welding in which both the heating and cooling regimes are controlled while the joint is still under pressure.

### *Hot-gas welding*

Hot-gas welding of thermoplastics is a manual welding technique, analogous to oxygas welding of metals. In the hot-gas gun, a stream of gas (typically air) passes over an electrically heated element and emerges from a nozzle. The stream of heated gas is directed towards the joint between two thermoplastic parts, where it melts or softens the polymer and a filler rod. A weld is formed by the fusing together of the thermoplastic

parts and the filler rod, which is composed of the same polymer type as the parts. The main advantage of hot-gas welding is that the equipment is easily portable. However, it is a slow process and the weld quality depends on the skill of the operator. Typical applications include chemical storage vessels and pipework.

### *Extrusion welding*

Extrusion welding is similar to hot-gas welding except that the filler material is separately heated in the barrel of a hand-held screw extruder. The molten material is then extruded through a PTFE die into the joint. The joint is pre-heated using a hot-gas gun mounted on the extruder barrel. It is preferable to hot-gas welding when thicker sections are to be joined. Extrusion welding could be used for composites, although the weld strength would be that of the filler rod and not the composite.

### *Flash-free welding*

Flash-free welding refers to techniques for butt joining thermoplastic parts (sheets, pipes or rods) without the generation of weld flash. The parts to be joined are butted together and fixed in place to prevent axial movement during the welding cycle. The parts are then constrained laterally using heated metal parts, which would be bars for joining sheets or a collar in the case of pipes and rod.

As the metal parts are heated to above the melting point of the thermoplastic, the material at the joint softens and melts. However, it is totally constrained and a melt pressure is built up because of thermal expansion. For pipes, the molten material is prevented from extruding into the bore by using an inflatable bladder, which is expanded at the joint line prior to welding. After a predetermined time, related to the thickness of the thermoplastic part, the heat supply is switched off and the joint is allowed to cool.

Currently, flash-free welding machines are commercially available only for joining thermoplastic pipes, where the smooth bore at the joint line is a major advantage for high-purity applications, such as in the food or pharmaceutical industries.

### *Select References*

- R. J. Wise, *Thermal Welding of Polymers*, Abington Publishing, Cambridge, 1999.  
Anon, *Handbook of Plastics Joining*, Plastics Design Library, New York, 1997.

---

## ***Welding plastics – mechanical movement***

---

A L BUXTON

### *Introduction*

There are around 20 different methods of welding plastics, which can be split into three general classifications:

- techniques employing an external heat source;
- techniques in which heat is generated by mechanical movement;
- techniques that directly employ electromagnetism.

This article provides an overview of welding processes where heat is generated by mechanical movement, and considers the factors affecting the choice of process. Examples of industrial applications are given throughout. Other related articles include **Welding plastics – electromagnetic radiation**, **Welding plastics – external heat source**, **Polymer–polymer adhesion: weld strength**, **Solvent welding** and **Wood bonding by vibration welding**.

### *Vibration welding*

Vibration welding, also known as linear friction welding, is one of a number of welding techniques in which the heat is generated by the mechanical movement of the components to be joined. It is an established industrial technique with commercially available equipment. The two parts to be joined are brought into contact under an applied load. One part is constrained while the other undergoes a rapid linear reciprocating motion in the plane of the joint. The heat generated by the friction at the two surfaces creates local melting. Subsequently, the vibration stops, the parts are aligned and the joint is cooled under pressure to consolidate the weld.

Vibration welding may be performed on almost any thermoplastic material. The joint alignment is consistently good and joint strengths approach that of the parent material. Vibration welding is feasible for composites but a higher force is required and fibre damage at the joint can be a problem. It is most suited to the welding of linear joints that are too long for the practical application of ultrasonic welding (e.g. >200 mm) and for which hotplate welding would prove too slow (vibration welding being four times faster than hotplate welding for large weld areas). The major drawbacks are the high capital cost of equipment and the difficulty in dealing with three-dimensional joints.

Vibration welding is used extensively by the automotive industry in the manufacture of components such as car bumpers, air intake manifolds, fuel pumps, instrument panels, parcel shelves, inner door panels and for the hermetic sealing of air ducting to the internal surface of the dashboard. Other applications include spectacle frames, typewriter covers, filter housings, motor saw housings and heating valves.

### *Spin welding*

Spin welding is a variation of friction welding that uses a rotational motion. Consequently, this technique is only applicable to circular joint areas. Spin welding can involve relatively simple pieces of equipment such as lathes or drilling machines. A lathe would produce a constant speed during the frictional heating stage (continuous drive friction welding), and a drilling machine would produce a reducing speed characteristic during the frictional heating stage (inertia friction welding). In practice, purpose-built machines are generally employed for spin welding in order to provide greater control, and they may be of either the continuous drive or inertia type. Spin welding has been exploited in applications as diverse as ball cocks, aerosol bottles, transmission shafts and PVC pipes and fittings.

### *Orbital welding*

In orbital welding, unlike spin welding, each point on the surface orbits a different point on the face of the stationary part. The orbit is of constant rotational speed and is identical for all points on the joint surface. This motion is stopped after sufficient material is melted and the thermoplastic then solidifies to form a weld.

### *Ultrasonic welding*

Ultrasonic welding involves the use of high-frequency mechanical sound energy to soften or melt the thermoplastic at the joint line. Parts to be joined are held together under pressure and are then subjected to ultrasonic vibrations via the welding horn, usually at a frequency of 20 or 40 kHz. The heating effect of the ultrasound varies with the degree of crystallinity of the material being welded. The ability to weld a component successfully is governed by the design of the equipment, the mechanical properties of the material to be welded and the design of the components. Ultrasonic welding is a fast process (weld times are typically less than one second) and can easily be automated. Consequently, it is ideally suited to welding components in mass production. However, the joint and horn design are critical, and there is a restriction of approximately 250 mm on the length of weld possible.

Ultrasonic welding is widely used in the automotive, appliance, medical, textile, packaging, toy and electronic markets. It is suitable for composite materials, but highly filled materials can result in weak joints. Examples of ultrasonically welded components include vacuum cleaners, automotive light fixtures, audio and videocassettes, blister packs, juice pouches and toys.

### *Friction stir welding*

Friction stir welding was invented at TWI in 1991, primarily as a means of welding aluminium alloys, but it has subsequently been found to be applicable to the welding of thermoplastics. As its name suggests, it is a friction process. However, unlike conventional friction welding processes, which rely upon relative motion between the two parts to be welded, friction stir welding involves driving a rotating or reciprocating tool along the joint line between two fixed components. Frictional contact of the moving tool with the plastic causes the material at the joint to melt and then solidify to form a weld once the tool has passed.

Since, in friction stir welding, the parts to be joined are fixed, it makes an ideal process for continuous joining of sheet or plate. Applications are anticipated in the fabrication of tanks and vessels with thick sections. Joints with good mechanical properties have been demonstrated in materials such as PMMA, polyethylene and polypropylene with weld speeds up to 200 mm min<sup>-1</sup>. This process is under continuing development at TWI.

### *Select References*

- R. J. Wise, *Thermal Welding of Polymers*, Abington Publishing, Cambridge, 1999.  
Anon, *Handbook of Plastics Joining*, Plastics Design Library, New York, 1997.

## Wetting and spreading

M E R SHANAHAN

Depending on its affinity for the solid, a liquid placed on a substrate will show a tendency either to remain as a drop with a finite area of contact or to spread out and cover the solid surface available.<sup>1</sup> In this article, it is assumed that equilibrium has been attained; considerations of **Wetting kinetics** are given in a separate entry.

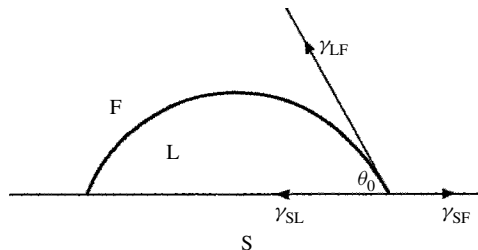
Consider a liquid drop at rest on an ideal solid surface (Fig. 1) and, in particular, the triple line of contact where solid S, liquid L and surrounding fluid F (either vapour of the liquid or a second liquid immiscible with the first) meet. To each interface solid–liquid, solid–fluid, liquid–fluid can be attributed a free interfacial energy or interfacial tension (respectively  $\gamma_{SL}$ ,  $\gamma_{SF}$ ,  $\gamma_{LF}$ ). (The equivalence of these definitions is discussed in **Surface energy**). Using the mechanical (tension) definition, a force (per unit length of triple line) acts along each interface. In order to assure equilibrium, a horizontal force balance must exist, and defining as  $\theta_0$  the equilibrium **Contact angle** measured between the solid–liquid interface and the tangent to the liquid–fluid interface at the triple line, Young’s equation<sup>1</sup> must be respected:

$$\gamma_{SF} = \gamma_{SL} + \gamma_{LF} \cos \theta_0 \quad [1]$$

This very simple demonstration of Young’s fundamental relation is sometimes questioned, but other, more rigorous, derivations based on minimizing the overall free energy of the system solid–liquid–fluid lead to precisely the same result (e.g. Ref. [2]). Consideration of the vertical force component  $\gamma \sin \theta_0$  leading to a “wetting ridge” – local deformation of the solid of dimensions of the order of  $\gamma/G$  ( $G$  = shear modulus of solid) – is only necessary for very soft solids (e.g. soft polymers, gels) and does not modify the macroscopic validity of Eqn. 1<sup>3</sup>.

The above applies to cases where  $|\gamma_{SF} - \gamma_{SL}|/\gamma_{LF} < 1$ . Under these conditions, finite **Contact angles** are obtained and the liquid is said to wet the solid. In the case where  $\gamma_{SF} \leq \gamma_{SL} - \gamma_{LF}$ ,  $\theta_0$  will be  $\pi$ . This corresponds to lack of affinity between the solid and the liquid and contact will then be assured uniquely by external force fields (e.g. gravity). There is no wetting. This situation, however, arises rarely, if ever, when the surrounding fluid is vapour, although it can occur for a two-liquid system.

At the other extreme, we consider the situation when  $\gamma_{SF} \geq \gamma_{SL} + \gamma_{LF}$ . The contact angle  $\theta_0$  is then necessarily zero, and the liquid is said to spread on the solid (some



**Fig. 1.** Wetting and spreading. Sessile drop of liquid L exhibiting an equilibrium contact angle  $\theta_0$  on solid S with surrounding fluid F, which may be vapour of the liquid L or a second liquid

authors refer to wetting and spreading respectively as partial and complete wetting). We define the quantity  $S$ , the spreading coefficient of liquid  $L$  on solid  $S$  in the presence of fluid  $F$ :

$$S = \gamma_{SF} - \gamma_{SL} - \gamma_{LF} \quad [2]$$

which may be interpreted as the net force (per unit length of triple line) provoking radial spreading of the liquid on the solid for a (hypothetical) contact angle of zero (see **Wetting and work of adhesion**). Referring to Young's equation, we see that if  $S$  is negative, we obtain a finite contact angle, whereas if  $S$  is positive, spreading ensues. If  $S$  is zero, Antonow's rule is respected. This corresponds to final equilibrium.

Each  $\gamma$  term, and as a consequence  $S$ , is both temperature and composition dependent. In general, surface tensions decrease with temperature, and several empirical expressions are known both for liquids and polymers.<sup>4</sup> Liquid surface and interfacial tensions may also be modified by altering the proportions of mixtures. Judicious changes of composition can be used to alter  $S$  for a given solid–liquid system in order to favour the wetting of the substrate by one or other of the liquids. Diagrams showing wetting propensity as defined by  $S$  as a function of components of surface tension are known as wetting envelopes. These can be of great use for such practical processes as lithographic printing.<sup>5</sup>

#### *Importance of the spreading coefficient in adhesion*

When an adhesive joint is produced, clearly intimate molecular contact between the adhesive and the substrate is desirable. Considering that at some stage in the process the adhesive will be liquid, it is clearly a good principle to choose a combination of surfaces with  $S$  positive. However, a second reason for favouring a high value of  $S$  also exists, as shown by the following simple argument. Although actual energies of adhesion may for various reasons be many factors larger than those predicted thermodynamically, it is generally accepted that high values of the latter are concomitant with good strength properties. Dupré's thermodynamic work of adhesion  $W_A$  for a liquid  $L$  (the adhesive) on a solid  $S$  (the substrate) in the presence of fluid  $F$  is given by:

$$W_A = \gamma_{SF} + \gamma_{LF} - \gamma_{SL} \quad [3]$$

( $W_A$  is sometimes differently defined: see Eqn. 4 in **Wetting and work of adhesion**).

The work of cohesion  $W_C$  of the liquid is

$$W_C = 2\gamma_{LF} \quad [4]$$

Using Eqn. 2 we have

$$S = W_A - W_C \quad [5]$$

Thus, the higher the value of  $S$ , the greater is the thermodynamic work of adhesion compared to the cohesive energy of the adhesive. Although after solidification of the adhesive these thermodynamic quantities are likely to be modified, the overall features will remain similar. Since the weak part of an adhesive bond tends to be the interface, a high value of  $S$  will favour cohesive failure within the adhesive rather than interfacial failure and in turn will tend to lead to a more reliable junction.



*N.B.* The above descriptions assume thermodynamic equilibrium to be attainable. In practice, it is common to observe the phenomenon of wetting hysteresis. Metastable rather than stable equilibrium is reached, as shown experimentally by a range of contact angles instead of a unique value. The causes are multiple: heterogeneity of the solid surface, local adsorption, Roughness of surfaces, and so on.

Related articles are **Contact angles and interfacial tension**, **Surface characterization by contact angles – polymers**, **Surface characterization by contact angles – metals**, **Surface energy** and **Wetting kinetics**.

### References

1. P. G. de Gennes, *Rev. Mod. Phys.*, **57**(3), 827 (1985).
2. R. E. Johnson, *J. Phys. Chem.*, **63**, 1655 (1959).
3. M. E. R. Shanahan, P. G. de Gennes, in *Adhesion 11*, K. W. Allen, Ed., Elsevier Applied Science Publishers, London, 1987, Chap 5.
4. S. Wu, *J. Macromol. Sci. – Rev. Macromol. Chem.*, **C10**(1), 1 (1974).
5. D. H. Kaelble, P. J. Dynes and D. Pav, in *Polymer Science and Technology*, Vol. 9B. *Adhesion Science and Technology*, L. H. Lee, Ed., Plenum Press, New York, 1975, p. 735.

## Wetting and work of adhesion

J F PADDAY\*

Adhesion, by its definition, depends on the ability of two unlike phases to hold themselves together across a common interface. Physical adhesion must first take place before any other bonding processes such as chemical reaction can occur, and such physical adhesion depends on the strength of intermolecular force interaction,<sup>1</sup> on the area of contact and on the distance separating the atoms forming the top layer of each surface (see **Dispersion forces**, **polar forces**). When both phases are undeformable, such as with two solids that are not atomically smooth, poor adhesion results because an insufficient area of each surface is in atomic contact with the other. When one phase is deformable, such as with a liquid of low viscosity, physical adhesion takes place at all parts of the surface. Physical adhesion with a liquid in contact with a solid leads to spreading and wetting: processes that now depend on the competition of adhesion forces with cohesion forces within the liquid.

Wetting is defined<sup>2</sup> as the process whereby a liquid when brought into contact with a solid displaces some of the fluid phase so that a stable triple-phase line of contact is formed, as seen in Fig. 1. Spreading, also described in Fig. 1, is the process whereby the liquid, once in contact with the solid, displaces the third phase completely from all parts of the surface and at the same time creates a new liquid–air (third phase). Finally, one describes the process of dewetting (or spontaneous dewetting) as that wherein the third phase, usually a liquid, itself spreads and displaces completely the first liquid from the solid surface.

The free energies of adhesion, wetting and spreading are expressed in terms of the free energies of each interface,  $\gamma$ , such that

$$\text{adhesion } W_{a_{123}} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad [1]$$

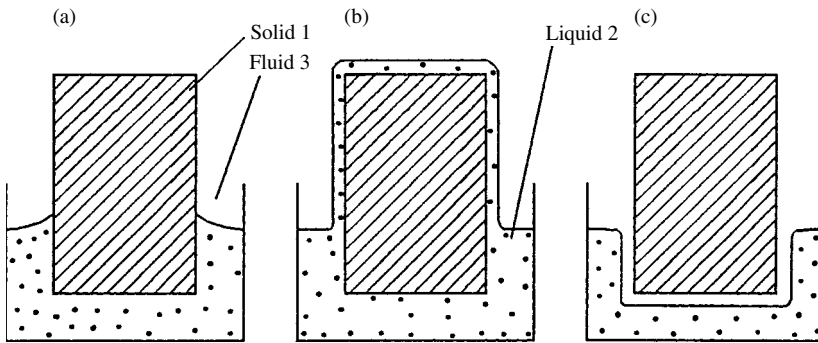


Fig. 1. A description of wetting (a), spreading (b) and spontaneous dewetting (c)

$$\text{wetting } W_{e_{123}} = \gamma_{13} - \gamma_{12} \tag{2}$$

$$\text{spreading } S_{c_{123}} = \gamma_{13} - \gamma_{12} - \gamma_{23} \tag{3}$$

The spreading energy is often termed the “spreading coefficient”,<sup>3</sup> see also **Wetting and spreading**. All these equations apply to ideally smooth surfaces: if the surface is rough, they require modification by the Wenzel roughness factor (see **Contact angle**).

It should be noted that Eqn. 1 defines work of adhesion in terms of  $\gamma_{13}$ , the surface energy of the solid 1 in contact with fluid 3, which according to the circumstances may be a second liquid, may be a gas or may be air saturated with the vapour of liquid 2. Work of adhesion is often defined in a subtly different way:

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \tag{4}$$

where  $\gamma_1$  is the surface energy of solid 1 and  $\gamma_2$  that of liquid 2, both *in vacuo*, in equilibrium with their own vapour. In Eqn. 4,  $W_a$  gives a measure of the energy required to cut cleanly along the 2–3 interface, removing the two phases into separate enclosures.

The treatment here is developed in terms of Eqns. 1–3, introducing Young’s equation,<sup>3</sup> which relates the surface energies to  $\theta$ , the **Contact angle**:<sup>4</sup>

$$\gamma_{13} - \gamma_{12} = \gamma_{23} \cos \theta \tag{5}$$

so that

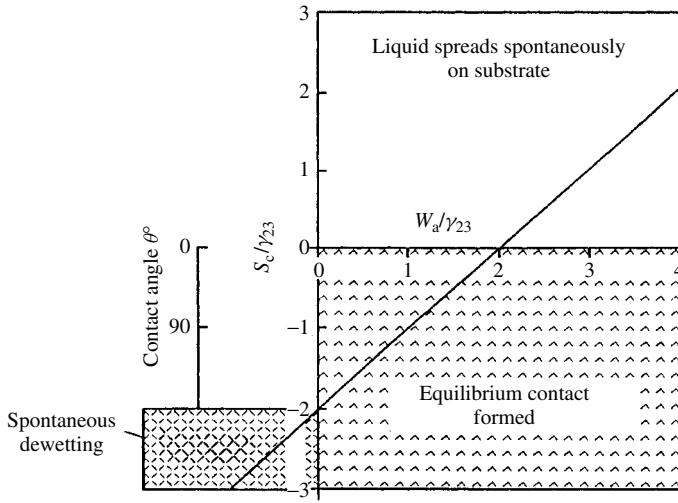
$$S_{c_{123}} = \gamma_{23}(\cos \theta - 1) \tag{6}$$

$$W_{a_{123}} = \gamma_{23}(\cos \theta + 1) \tag{7}$$

and

$$W_{e_{123}} = \gamma_{23} \cos \theta \tag{8}$$

Finally, we may divide these equations by  $\gamma_{23}$  to present them in dimensionless form and plot the reduced spreading coefficient  $S_{c_{123}}/\gamma_{23}$  as a function of the reduced work of adhesion,  $W_{a_{123}}/\gamma_{23}$  as seen in Fig. 2.



**Fig. 2.** Reduced spreading coefficient  $S_c/\gamma_{23}$  as a function of the reduced work of adhesion  $W_a/\gamma_{23}$

It is important to note that the value of the spreading coefficient is not in any way limited in magnitude or sign. In Fig. 2, the three processes of Fig. 1 are now clearly defined by

$$0 < S_{c_{123}}/\gamma_{23} < \infty$$

Liquid 2 spreads spontaneously. No contact angle is formed.

$$-2 < S_{c_{123}}/\gamma_{23} < 0$$

Liquid 2 wets and a stable contact angle is formed.

$$-\infty < S_{c_{123}}/\gamma_{23} < -2$$

Liquid 2 spontaneously recedes. No contact angle is formed.

The contact angle is thus only of significance when the reduced spreading coefficient is negative and lies between 0 and 2. The problem of measuring the spreading coefficient when there is no contact angle is overcome by measuring the disjoining pressure first described by Derjaguin.<sup>5</sup> The disjoining pressure  $\pi_{sl}$  is the pressure required to thin a spread layer by an element of thickness  $dt$ .

$$\int_{t_0}^{\infty} \pi_{12} dt = S_{c_{123}} \tag{9}$$

where  $t_0$  is the distance of closest approach of the surface atoms of the spreading liquid to those in the solid surface. The disjoining pressure is readily measured in a variety of ways and increases as the thickness of the spread layer is decreased by some external force such as gravitational drainage. Its value may also be calculated from Hamaker constants<sup>1</sup> for some systems where the physical interaction is derived principally from dispersion forces.

Thus, it is deduced that effective adhesion depends critically on the liquid adhesive displacing the third phase and spreading into all the space between the two solid surfaces to be attached to one another. The angle of contact, the liquid surface tension and the disjoining pressure are the appropriate measurable properties that enable quantitative values of the free energy of spreading to be assessed.

### References

1. J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd edn, Academic Press, 1991.
2. J. F. Padday, in *Contact Angle, Wettability and Adhesion*, K. L. Mittal, Ed., VSP, Utrecht, 1993, p. 97.
3. A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, 6th edn, Wiley, Chichester, New York, 1997.
4. K. L. Mittal, Ed., *Contact Angle, Wettability and Adhesion*, VSP, Utrecht, 1993.
5. A. D. Zimon, *Adhesion of Dust and Powder*, trans. from Russian by Morton Corn, Plenum Press, New York, 1969.

## Wetting kinetics

M E R SHANAHAN

When a liquid is put into contact with a solid surface, be it an adhesive, a paint, an ink or merely a drop of water, equilibrium will not generally be ensured immediately. **Wetting and spreading** will ensue spontaneously until either an equilibrium (stable or metastable) **Contact angle** is obtained or until the liquid has spread leaving a thin layer covering the solid surface available. Commonly observed situations usually invoke one or both of two main categories of the wetting process. If the solid is impervious, the essential phenomenon will consist of the liquid drop spreading outwards, lowering its contact angle and increasing its radius of contact until equilibrium defined by Young's equation (see **Wetting and spreading**) is obtained. However, in the case of a porous solid, penetration of the liquid within the bulk may also occur – a phenomenon similar to capillary rise. In both cases, the detailed kinetics are exceedingly complex,<sup>1-3</sup> but the following arguments may be applied in order to understand the basic underlying physical principles.

### *Spreading of a drop on a solid surface*

*Capillary regime* Consider the idealized case of a drop of liquid in the form of a spherical cap of small contact angle  $\theta(t)$  spreading radially with time  $t$  to its equilibrium configuration represented by angle  $\theta_0$  [ $\theta_0 \leq \theta(t)$ ]. The solid is taken to be smooth, flat, horizontal, isotropic and homogeneous. If the drop is small, the force causing spreading will be essentially that due to the capillary imbalance at the triple line.<sup>2</sup> Referring to the solid–liquid, solid–vapour and liquid–vapour interfacial tensions respectively as  $\gamma_{SL}$ ,  $\gamma_{SV}$  and  $\gamma$ , the force (per unit length) of the triple line at the drop periphery, directed radially outwards,  $F$ , will be

$$F = \gamma_{SV} - \gamma_{SL} - \gamma \cos \theta(t) \sim \frac{\gamma}{2} [\theta^2(t) - \theta_0^2] \quad [1]$$

where the simplified (second) expression is obtained from Young's equation and the approximate form of  $\cos \theta$  for small  $\theta$ .

If the drop spreads at radial speed  $U(t)$ , the work done (per unit time) is  $FU$ . This work will be dissipated by viscous effects due to the flow field within the liquid. Calculation of these flow fields represents a formidable task, but a useful approximation was suggested by de Gennes<sup>2</sup> in which the "lubrication approximation" is adopted. The liquid is regarded as a nearly flat wedge with a parabolic (Poiseuille) velocity profile parallel to the solid surface. (Boundary conditions of zero stress at the liquid–vapour interface and no slip at the solid–liquid interface, together with overall displacement rate  $U$ , allow the profile to be defined.) Viscous dissipation/unit volume takes the form  $\eta v_z^2$ , where  $\eta$  is viscosity and  $v_z$  the local velocity gradient. Integration of this quantity using the velocity profile leads to a dissipation term  $k\eta U^2 r/h$ , where  $k$  is a numerical constant and  $r$  and  $h$  are drop contact radius and height respectively.

Bearing in mind that  $U = dr/dt$  and taking for simplicity the case corresponding to  $\theta_0 = 0$ , we equate  $FU$  to the dissipation to obtain

$$\frac{dr}{dt} \sim \frac{2\gamma h^3}{k\eta r^3} \quad [2]$$

Ignoring henceforth numerical constants and using the expression for constant drop volume ( $V \sim \pi r^2 h/4$ ), Eqn. 2 is simply solved to obtain the scaling law for drop spreading:

$$r \sim V^{3/10} \left( \frac{\gamma t}{\eta} \right)^{1/10} \quad [3]$$

We thus see that the spreading of small drops where capillary forces dominate is proportional to  $t^{1/10}$  and the overall rate is essentially governed by the ratio  $\gamma/\eta$ .

*Gravitational regime* If a drop of liquid is sufficiently large, gravitational forces predominate over capillary effects. Defining a capillary length  $K^{-1} = (\gamma/\rho g)^{1/2}$ , where  $\rho$  is the liquid density (or more precisely the difference in densities between the liquid and the surrounding fluid) and  $g$  is the gravitational acceleration, the transition between the regimes occurs typically at  $K^{-1} \sim 1.5$  mm.<sup>4</sup>

For larger drops, we may reasonably ignore the effects of Eqn. 1 and consider that the "motive power" of spreading comes mainly from gravitational potential energy related to the height of the centre of the gravity of the drop above the solid surface.

Again using dimensional arguments, we may consider the spreading force to be of the form  $\rho g V$  and acting at a fraction  $f$  of the height  $h$  of the drop. The work done per second can then be expressed as:

$$\frac{dW}{dt} = -F \frac{d(fh)}{dt} \sim -\rho g V \frac{dh}{dt} \quad [4]$$

Equating this to the dissipation term described above (multiplied by  $2\pi r$  to take into account the entire periphery of the drop) and using the constant volume condition, we obtain:

$$\frac{dr}{dt} \sim \frac{\rho g V^3}{\eta r^7} \quad [5]$$

giving after integration:

$$r \sim V^{3/8} \left( \frac{\rho g t}{\eta} \right)^{1/8} \quad [6]$$

Thus, in the gravitational regime, contact radius increases as  $t^{1/8}$  and thus more rapidly than in the capillary regime. The overall rate is governed by the ratio  $\rho g/\eta$ . Note that, in both cases, the relative values of driving force to viscosity control the process, as may be expected intuitively.

### Capillary rise

The penetration of a liquid within a porous medium can be compared to a first approximation to the phenomenon of capillary rise. We shall derive what is commonly known as Washburn's equation.<sup>5</sup> Consider a capillary tube touching a liquid surface with its axis vertical and internal radius  $r_0$ .

Assuming a concave meniscus within the capillary, due to contact angle  $\theta$  of the liquid on the tube, the radius of curvature of the liquid surface is  $r_0/\cos\theta$ . It follows that the excess Laplace pressure across the liquid/air interface is  $2\gamma \cos\theta/r_0$  and the overall upward force is  $2\pi r_0\gamma \cos\theta$ . This force upwards is reduced by the effective weight of the column of liquid of height  $h$  in the tube,  $\pi r_0^2 \rho g h$ , and so the net force is

$$F = 2\pi r_0\gamma \cos\theta - \pi r_0^2 \rho g h \quad [7]$$

(*N.B.* No distinction is made between dynamic and static contact angles in this elementary treatment.)

Force  $F$  is equilibrated by viscous drag within the tube. A Poiseuille velocity profile is assumed to exist because of the average pressure difference  $p$  across the height  $h$  and equal to  $F/\pi r_0^2$ . Standard fluid mechanical arguments lead to the volume increase per unit time in the capillary,  $dV/dt$ :

$$\frac{dV}{dt} = \frac{\pi p r_0^4}{8\eta h} = \pi r_0^2 \frac{dh}{dt} \quad [8]$$

Substitution of Eqns. 7 into 8 leads to:

$$\frac{dh}{dt} = \frac{r_0^2}{8\eta h} \left[ \frac{2\gamma \cos\theta}{r_0} - \rho g h \right] \quad [9]$$

Although this simple equation is open to criticism on several grounds (constancy of  $\theta$ , simultaneous assumption of regular meniscus and laminar flow), it serves as a basis. In the case of porous media, the gravitational terms will generally be neglected. In this case, straightforward integration of Eqn. 9 leads to the simple scaling expression  $h \sim t^{1/2}$ . Capillary penetration then bears a remarkable similarity to Fickian diffusion!

Related articles are **Contact angles and interfacial tension**, **Surface Energy** and **Wetting and spreading**.

### References

1. C. Huh, L. E. Scriven, *J. Colloid Interface Sci.*, **35**, 85 (1971).
2. P. G. de Gennes, *Rev. Mod. Phys.*, **57**(3), 827 (1985).
3. Th. F. Tadros and A. W. Neumann, Eds., *Adv. Coll. Interface Sci.*, **39**, (1992), (Special Issue: Contact Angles and Wetting Phenomena).
4. J. Lopez, C. Miller and E. Ruckenstein, *J. Colloid Interface Sci.*, **56**, 460 (1976).
5. E. W. Washburn, *Phys. Rev.*, **17**, 374 (1921).

## Wood adhesives – aminoplastics

A PIZZI

For a general introduction, see **Wood adhesives – basics**. Aminoplastic resins are polycondensation products of the reaction of aldehydes with compounds carrying amine or amide groups. Formaldehyde is by far the primary aldehyde used. The name “aminoplastic” is traditional, but is a misnomer: these are thermosetting, irreversibly hardening resins. Two main classes of these resins exist: urea–formaldehyde (UF) resins and melamine–formaldehyde (MF) resins. Today, for wood adhesives, pure MF resins are not used anymore because of cost, and only melamine–urea–formaldehyde (MUF) adhesives are used. The main use of these resins is in composite products such as particle board, plywood, medium density fibreboard (MDF), oriented strand board (OSB), glulam/fingerjointing and furniture.

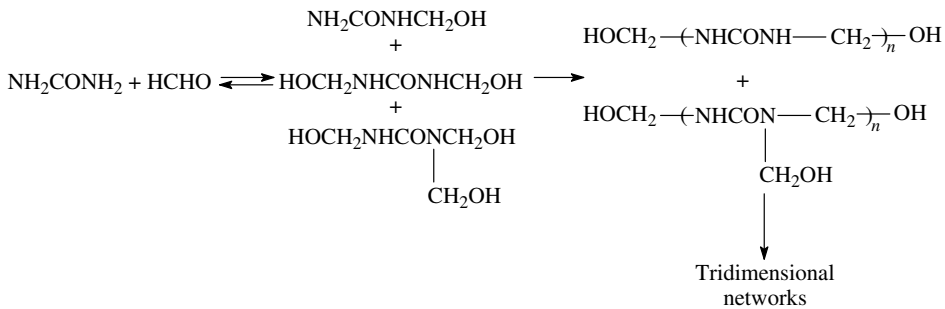
### Urea–formaldehyde (UF) adhesives

UF resins are the most important and most used class of amino resin adhesives.<sup>1–3</sup> They constitute more than 80% of all thermosetting wood adhesives in Europe, and around 50% in North America. The advantage of UF adhesives are their (1) initial water solubility (this renders them eminently suitable for bulk and relatively inexpensive production), (2) hardness, (3) non-flammability, (4) good thermal properties, (5) absence of colour in cured polymers, and (6) easy adaptability to a variety of curing conditions.

Thermosetting amino resins produced from urea are built up by condensation polymerization. Urea is reacted with formaldehyde, which results in the formation of addition products such as methylol compounds. Further reaction and the concurrent elimination of water leads to the formation of low-molecular-weight condensates, which are still soluble. Higher-molecular-weight products, which are insoluble and infusible, are obtained by further condensing the low-molecular-weight condensates.

The greatest disadvantage of UF adhesives is their bond deterioration caused by water and moisture. This is due to the hydrolysis of their aminomethylene bond. Therefore, pure UF adhesives are used exclusively for interior applications.

Resin flow is very important, which reflects viscosity under hot-pressing conditions. Resin flow is a determining factor in manufacturing good particleboard. Excessive flow causes the resin to soak into the wood particles and causes glue-line starvation; insufficient flow causes insufficient contact surface. Resins that have lost part of their flow during manufacture or storage must be corrected by the addition of a flow agent. The simplest



means is often the addition of water, mixed in well. If a resin is still capable of flowing, this procedure produces a resin with properties that are still acceptable. In cases where moisture content control is critical, it may be necessary to allow a little more time for “heating” to let the added moisture escape.

UF resins are acid-curing resins (they cure around pH 4). They need the addition of a hardener to lower the pH of the resin on heating, or at ambient temperature if the resin is wanted as a cold-setting type. Many substances have been suggested as curing agents. Ammonium sulphate is the most widely used curing agent in the wood products industry, when the resin is hardened by heat. The hardener effect can be altered by retarding the reaction of the resin. This is done by the simultaneous addition of small amounts of ammonia solution (which is eliminated during hot curing) to lengthen the pot life of the glue mix. In cold-setting UF resins for joinery, hardeners consisting of mixtures of a salt such as ammonium chloride or ammonium sulphate with an acid such as phosphoric acid, citric acid or others are used to regulate pot life and rate of curing. Both pot life and rate of curing of the resin can then be regulated by (1) varying the concentration of the hardener in the resin, (2) by changing the relative proportions of acid and salt, and (3) by changing the type of acid and/or salt composing the hardener. Acting on these three principles, ambient temperature setting times of between a few minutes and several hours can easily be obtained.

If a UF-bonded board immediately after hot-pressing is stacked at a temperature higher than 75 °C, some degradation with consequent loss of performance will occur. This is due mainly to some progressive degradation of the UF adhesive hardened network.<sup>2</sup> Conversely, if the board is just cooled down, there will not be any further curing of the resin. The predominance of the effect derived from the first of these two considerations has led to the need to limit the heat conservation of UF particle board after pressing and hence to today’s widespread practice of cooling the board after pressing. Recently, it has been shown with modern low formaldehyde content resin that degradation does not occur as readily, if at all, and that the boards can be hot-stacked with some advantages in performance.<sup>1,4</sup>

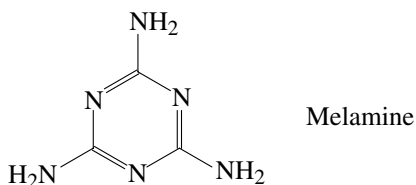
UF resins in their cured state are non-toxic. Urea itself is also harmless. High temperatures and high relative humidity can result in formaldehyde odour problems in a room containing particleboard manufactured with UF resins.<sup>1,5</sup> However, free formaldehyde and formaldehyde generated by slow hydrolysis of the aminoplastic bond may cause some inflammation of the mucous membranes of the eyes, nose and mouth.<sup>1,5</sup> Even a low concentration of formaldehyde vapour can be disagreeable. However, such irritations usually disappear in a short time without permanent damage. The problem of formaldehyde



emission from UF-bonded boards has been solved in the early 1990s with the introduction of the so-called E1 UF formulations containing a much lower proportion of formaldehyde in the resin.

### Melamine resins (MF and MUF)

Melamine–urea–formaldehyde (MUF) resins are among the most used adhesives for exterior and semi-exterior wood panels.<sup>2,3,6</sup> Their much higher resistance to water attack is their main distinguishing characteristic from urea–formaldehyde (UF) resins.



The condensation reaction of melamine with formaldehyde is similar to, but presents some differences from, the reaction of formaldehyde with urea. For example, formaldehyde addition to melamine occurs more easily and completely than does addition to urea. Each amino group in melamine accepts easily up to two molecules of formaldehyde. Thus, complete methylation of melamine is possible, which is not the case with urea. Another important difference is that MF condensation to give resins, and their curing, can occur not only under acid conditions but also under neutral or even slightly alkaline conditions. MUF resins obtained by copolymerization during the resin preparation stage are superior in performance to MUF resins prepared by mixing preformed UF and MF resins. The relative mass proportions of melamine to urea used in MUF resins is generally in the melamine:urea range 50:50 to 30:70. Today, even lower levels of melamine (3–10% of urea) are used to prepare interior UF resins whose resistance to humidity is somewhat improved.

A type of resin also used today is the so-called phenol-melamine-urea-formaldehyde (PMUF) (or MUPF according to which author is writing) adhesives. These are fundamentally MUF resins in which a minor proportion of phenol (between 3 and 10%, P:M:U by weight of 10:30:60 just as an example) has been hopefully coreacted with to further upgrade weather resistance of the bonded joint. Unfortunately, the alleged superior performance of such resins is often only wishful thinking as the phenol has frequently not been properly reacted with the other materials, and consequently the PMUF resin will have a worse performance than a comparable top-of-the-range MUF resin.

The important control parameter to take care of during and after manufacture is the water tolerance or hydrophobicity point, which marks the end of the reaction. The latter is a direct measure of the extent of condensation of the resin and indicates the percentage of water or mass of liquid on the reaction mixture that the MUF resin can tolerate before precipitating out. It is typically set for resins of higher formaldehyde/melamine ratios and lower condensation levels at around 170 to 190%, but for resins of lower formaldehyde/melamine molar ratios and higher condensation level, it is set at around 120%.

Hardeners are either acids or materials that will liberate acids on addition to the resin or on heating, exactly as in the case of UF resins.

Several effective techniques to decrease the expensive melamine content in MUF wood adhesives without any loss of performance have also been recently developed.<sup>1</sup> Among these are the addition of melamine/acid salts to UF and MUF resins,<sup>6–8</sup> the use of acetals such as ethylal and methylal<sup>6,9,10</sup> and the use of special type buffers.<sup>6,11</sup>

MUF resin can be also used as cold-setting wood laminating adhesives for glulam and fingerjointing by the use of adequate acid hardeners. In all semi-exterior and protected exterior structural laminated beam (glulam) applications where a clear/invisible glue line is preferred for aesthetic reasons, then a MUF adhesive is preferred to the classical phenol–resorcinol–formaldehyde (PRF) adhesives used for this purpose. It is then more a question of fashion cycles, but notwithstanding this, MUF resins have taken a considerable hold today in Europe (contrary to North America where PRFs are by far preferred) and confidence in them for this application has been steadily growing.

Related articles include **Wood adhesives – hot melts**, **Wood adhesives – isocyanates/urethanes**, **Wood adhesives – phenolics** and **Wood composites – adhesives**.

## References

1. A. Pizzi, Urea-formaldehyde adhesives, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003, Chap 31.
2. A. Pizzi, *Wood Adhesives: Chemistry and Technology*, Vol. 1, Dekker, New York, 1983.
3. A. Pizzi, *Advanced Wood Adhesives Technology*, Dekker, New York, 1994.
4. X. Lu and A. Pizzi, *Holz Roh Werkstoff*, **56**(5), 393–401 (1998).
5. R. Marutzky, Release of formaldehyde by wood products, in *Wood Adhesives: Chemistry and Technology*, Vol. 2, A. Pizzi, Ed., Dekker, New York, 1989, Chap 10.
6. A. Pizzi, Melamine-formaldehyde adhesives, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003. Chap 32.
7. M. Prestifilippo, A. Pizzi, H. Norback and P. Lavisci, *Holz Roh Werkstoff*, **54**(6), 393–398 (1996).
8. C. Cremonini and A. Pizzi, *Holzforschung Holzverwertung*, **49**(1), 11–15 (1997).
9. A. Pizzi, M. Beaujean, C. Zhao, M. Properzi and Z. Huang, *J. Appl. Polym. Sci.*, **84**(13), 2561–2571 (2002).
10. M. Zanetti, A. Pizzi, M. Beaujean, H. Pasch, K. Rode and P. Dalet, *J. Appl. Polym. Sci.*, **86**(8), 1855–1862 (2002).
11. M. Zanetti, A. Pizzi and C. Kamoun, *Holz Roh Werkstoff*, **61**(1), 55–65 (2003).

## Wood adhesives – basics

A PIZZI

A considerable variety of thermosetting and thermoplastic resins are used to bond a multitude of wood products. Today, at least 80% of wood products are bonded in some manner. The quality of wood bonding is determined by three main parameters: (1) the wood, especially the wood surface, including the interface between the wood surface and the bond-line; (2) the applied adhesive; (3) the working conditions and process parameters. Good-quality bonding and adequate properties of the wood-based panels can be attained only if each of these three parameters contributes to the necessary

extent to the bonding and production process. In wood adhesives, the application parameters other than those characteristic of the adhesive itself account for around 50% of performance. In this article, the types of adhesives used in the wood industry and their characteristics are covered; for a more detailed consideration see **Wood adhesives – aminoplastics**, **Wood adhesives – hot melts**, **Wood adhesives – phenolics**, **Wood adhesives – isocyanates/urethanes** and **Wood composites – adhesives**. Attention is also drawn to an article on **Wood bonding by vibration welding**.

### *Types of wood adhesives*

Condensation resins based on formaldehyde represent the biggest volume within the wood adhesives field.<sup>1–5</sup> They are prepared by the reaction of formaldehyde with various chemicals like urea, melamine, phenol or resorcinol or combinations thereof. At delivery, these adhesive resins are mainly liquid and consist of linear or branched oligomers and polymers in aqueous solution or dispersion. During hardening and gelling, they convert to three-dimensionally cross-linked and, therefore, insoluble and non-meltable networks. The hardening conditions used can be acidic (for aminoplastic resins), highly alkaline (for phenolic resins) or neutral to lightly alkaline (for resorcinol resins). Isocyanates (especially PMDI, polymeric 4,4'-diphenyl methane diisocyanate) is another important chemical group used for various applications in the wood industry, especially for water-resistant bonds. In Table 1 are reported the main wood adhesives in use today, with their main applications.

### *Requirements concerning wood adhesives*

Table 2 summarizes the general parameters of importance for wood adhesives.

Formaldehyde and other VOC emissions from wood products are one of the most important concerns in this industry. The so-called E1-emission class regulations shown in Table 3 for different panel products describe the level of formaldehyde emission that is low enough to prevent any danger, irritation or inflammation of the mucous membranes in the eyes, nose and mouth. However, it is important that not only the boards themselves, but also veneering and carpenter's adhesives, lacquers, varnishes and other sources of formaldehyde be controlled, since they also might contribute to a close environment formaldehyde steady-state concentration.

### *Application parameters*

As 50% of the success of wood adhesives is in its application parameters, these need to be carefully considered: even an excellent wood adhesive will give very poor bonding if the correct applications parameters are not respected. Foremost about these is the wood percentage moisture content. Generally, thermosetting resins for panels are used at moisture contents of 10–12% for particleboard or similar panels and at 7–9% for plywood, with some notable exception such as tannin adhesives, which can reach 25%<sup>3,5</sup>. For ambient temperature applications, standard resins such as RF and MUF cannot bond

Table 1. Fields of application for various wood adhesives

Type	V20	V100	V313	FP	MDF	PLW	HLB	MH	Ven.	Furn.
UF	x				x	x	x	x	x <sup>a</sup>	x <sup>a</sup>
MUF	x <sup>b</sup>				x					
MF/MUF		x <sup>c</sup>	x		x	x	x	x		
MUPF		x			x	x				
PF/PUF		x		x	x	x				
RF							x			
PMDI	x	x			x		x			
PVAc								x	x	x
Old nat.adhesives										x
Nat.adhesives	x	x	x		x	x				
Inorg.adhesives	x			x <sup>d</sup>						
Activation				x						

UF: urea–formaldehyde resin

MUF: melamine-fortified UF resin

MF/MUF: melamine–and melamine–urea–formaldehyde resins; MF resins are used only mixed/coreacted with UF resins

MUPF: melamine–urea–phenol–formaldehyde resin

PF/PUF: phenol–and phenol–urea–formaldehyde resin

(P)RF: resorcinol–(phenol–) formaldehyde resin

PMDI: polymethylenediisocyanate

PVAc: polyvinylacetate adhesive

Old nat.adhesives: old (historic) natural adhesives, e.g. starch, gluten, casein adhesives

Nat.adhesives: natural adhesives (tannins, lignins, carbohydrates)

Inorg.adhesives: inorganic adhesives: cement, gypsum

Activation: activation of polymeric constituents of wood to function as adhesives (i.e. lignin)

V20: particleboard according to DIN 68761 (part 1 and 4, FPY, FPO), DIN 68763 (V20) and EN 312-2 to 4 and –6

V100: particleboard according to DIN 68763 and EN 312-5 and 7, option 2 (internal bond after boil test according to EN 1087-1)

V313: particleboard according to EN 312-5 and 7, option 1 (cycle test according to EN 321)

FP: hardboard (wet process) according to EN 622-2

MDF: medium-density fiberboard according to EN 622-5

PLW: plywood according to EN 636 interior grade and water-resistant exterior of different grades

HLB: laminated beams

MH: solid wood panels according to OeNORM B 3021 to B 3023 (prEN 12775, prEN 13353 part 1 to 3, prEN 13017-1 and 2, prEN 13354)

Ven.: veneering and covering with foils

Furn.: production of furnitures

<sup>a</sup>Partly powder resins

<sup>b</sup>Boards with reduced thickness swelling, e.g. for laminate flooring

<sup>c</sup>Only possible as MUF + PMDI

<sup>d</sup>Special production method

well at moisture contents higher than 14–15%, again with the notable exception of some polyurethanes (80%) and honeymoon-type RF and MUFs (up to 30%).<sup>4,6</sup>

Other important application parameters are

- the pressing cycle length and type of cycle in panelboards, this being one of the most important parameters;<sup>1–5</sup>
- the wood species, wood extractives content and wood chemical composition;

Table 2. General parameters to be considered for wood adhesives

- 
- Composition, solids content, viscosity, purity
  - Colour and smell
  - Sufficient storage stability for given transport and storage conditions
  - Easy application
  - Low transport and application risks
  - Proper gluing quality
  - Climate resistance
  - Hardening characteristic: reactivity, hardening, cross-linking
  - Compatibility for additives
  - Cold tack behaviour
  - Ecological behaviour: LCA, waste water, disposal etc.
  - Emission of monomers, VOC, formaldehyde during production of the wood-based panels and during their use
- 

Table 3. Actual regulations concerning formaldehyde emission from wood-based panels according to European Norms for E1 emission class (the lowest emission type) panels

- 
- (a) maximum steady state concentration in a controlled climatic chamber:  
0.1 ppm (prEN 717-1; 1995)
  - (b) laboratory test methods (based on experimental correlation experiences):

PB: 6.5 mg/100 g dry board as perforator value (EN 120; 1992)

MDF: 7 mg/100 g dry board as perforator value

Plywood: 2.5 mg/hr m<sup>2</sup> with gas analysis method (EN 717-2)

PB and MDF: correction of the perforator value to 6.5% board moisture content

---

- the wood particle size and shape in panel boards;
- its wettability, porosity and surface conditions and characteristics.

### References

1. M. Dunky and A. Pizzi, Wood adhesives, in *Adhesion Science and Engineering – 2*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, Chap 23.
2. M. Dunky, Adhesives in the wood industry, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003, Chap 47.
3. A. Pizzi, *Wood Adhesives: Chemistry and Technology*, Vol. 1, Dekker, New York, 1983.
4. A. Pizzi, *Wood Adhesives: Chemistry and Technology*, Vol. 2, Dekker, New York, 1989.
5. A. Pizzi, *Advanced Wood Adhesives Technology*, Dekker, New York, 1994.
6. M. Properzi, C. Simon, A. Pizzi, B. George, L. Uzielli and G. Elbez, *Holzforschung Holzverwertung*, **54**(1), 18–20, (2002).

---

### Wood adhesives – hot melts

---

A PIZZI

An overview of wood adhesives is to be found in **Wood adhesives – basics**. Here, **Hot-melt adhesives** are considered. They are used in wood mainly for edge veneering and

vener splicing. These adhesives are 100% solid thermoplastic materials that are supplied in pellet, slug, block or irregularly shaped chip form. They require heating to melt and to be applied and excellent control of the temperature and coverage rate are strictly essential. Variations of even 1 °C can sometimes make the difference between miserable failure and a joint having good performance. As the adhesive is applied, the heat source is removed, inducing cooling and rapid setting of the thermoplastic material. It is this characteristic mechanism that renders hot-melt adhesives particularly suited for high-throughput rates of continuous bonding on automatic lines. This is why they are largely used for furniture and board edge veneering.

There are two main types of hot-melt adhesives that are used for wood. The most used are the **Ethylene–vinyl acetate copolymers (EVA)** types.

#### *Ethylene–vinyl acetate (EVA) based hot melts*

Edge veneering requires hot melts of relatively high viscosity at their characteristic temperature of application (usually around 190–200 °C). This is necessary to avoid flowing, or, even worse, dripping of the molten adhesive from vertical surfaces during application; to avoid glue-line starvation by a too deep penetration of the substrate surface. It must also be relatively easy to spread and wet the substrate surface well. To achieve all these characteristics, viscosities of approximately 50,000 mPa are needed at the temperature of application. Such viscosity level is achieved by the combination of the correct grade of EVA and the due proportion and type of reinforcing filler.<sup>1,2</sup> The softening point of the adhesive system is markedly influenced by the grade and proportion of EVA copolymer and by the type and proportion of tackifying resin contained in the system.

For optimum adhesion, the wetting capability of the hot-melt system must be good. Wetting is related to viscosity and is again largely influenced by tackifying resin selection and quantity.

Adhesive stability in the molten state is another important characteristic. In the molten state, in the applicator, the adhesive must resist/minimize oxidation, colour change (generally darkening), and thermal degradation of the various components contained in the system, which would lead to bonds of inferior performance. Extremes of degradation may give adhesive charring and applicator blockages.

EVA hot melt adhesives are fundamentally just a mix, done at higher temperature, in the resins molten state, of a variety of components. It must be made clear that, in general, there is no chemical reaction among these components: the adhesive is just a blend of different components. The components that melt must then be chosen, unless special systems are sought, with melting ranges not too different or at least showing some overlap. These adhesives are then blends of generally the following types of components:

1. EVA copolymer
2. A tackifying and adhesion promoting resin (e.g. hydrocarbons, rosin esters, coumarone-indene resins, terpene resins)
3. Fine powder fillers, usually barium sulphate (barytes) or calcium carbonate
4. Antioxidants.

The EVA copolymer is the main binder and its choice greatly influences the viscosity and rheology of the system, the cohesive strength of the joint, the flexibility of the glue-line and the adhesive strength. EVAs with a great variety of vinyl acetate (VA) contents

and viscosities (melt index) exist for the ease of the formulator. EVAs of higher VA content yield better adhesion and greater glue-line flexibility. However, the cost of the EVA increases with increasing VA contents. In general, EVA-based edge-veneering hot melts average 28% VA by weight and the adhesive system contains around 40% EVA on the total system. Often, two or three different EVA grades are mixed to achieve the correct balance of properties.

Tackifying resins generally constitute between 8 and 25% of the total adhesive system. The type of resin used influences flow, hot tack, adhesion and substrate ease of wetting. The most commonly used are hydrocarbon resins, such as different petroleum waxes, but many other types (rosin esters, coumarone-indene resins, terpene resins) imparting often some better characteristics, such as a better heat stability, are often used.

The most common fillers used are barytes, especially because of their off-white to cream and even dark brown colour, which renders them particularly suitable for wood. They are used generally in the proportion of 35 to 40% of the total adhesive system but can be used even up to 50%. The primary aim of the filler is to reduce costs, but it has also a positive effect on the cohesive strength of the adhesive, and gives to the molten adhesive some “body”.

Antioxidants in proportion of 0.2 to 0.5% of the system are added to protect the organic components, mostly the resins from oxidation/discolouration at high temperature.

### *Polyamide hot melts*

These adhesives are high-performance types, which are used selectively where better heat resistance is required. They are markedly more costly than the EVA-based hot melts. They offer high tensile strengths and high initial tack, often without the need for additional formulating. Their high melting points ensure good heat-resistance qualities and are responsible for rapid setting on cooling. The polyamide hot melts' main drawback other than cost is their tendency to char easily if kept at high temperature.

The basic polyamide resins need some modification to obtain suitable application viscosity, correct flexibility and to reduce their high cost, when this is possible. The more flexible types of polyamide resins are then often modified by the addition of up to 25% of higher viscosity and higher melt index EVAs. This type of blend can be further modified by addition of selected tackifying resins and small amounts of fillers, to optimize the balance of properties of the system. To achieve maximum adhesion, it is common for polyamide hot melts to be used in conjunction with a polyamide resin primer for edging material. The primer is generally a dilute solution of the basic polyamide resin.

Other information about bonding of wood can be found in **Wood adhesives – aminoplastics**, **Wood adhesives – isocyanates/urethanes**, **Wood adhesives – phenolics**, and **Wood composites – adhesives**.

### *References*

1. A. Pizzi, Hot-Melt adhesives, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003, Chap 37.
2. N. E. Quixley, Hotmelts for wood products, in *Wood Adhesives: Chemistry and Technology*, Vol. 2, A. Pizzi, Ed., Dekker, New York, 1989, Chap 8.

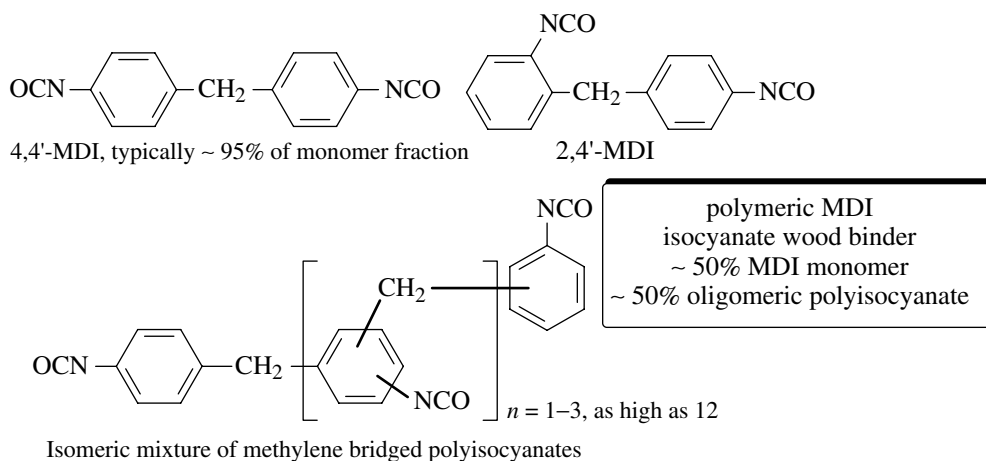
## Wood adhesives – isocyanates/urethanes

A PIZZI

A general introduction to bonding wood can be found in **Wood adhesives – basics**; here, isocyanates are considered. They are extensively used in wood panels bonding, exclusively as thermosetting adhesives for exterior-grade wood panels. For this purpose, they are the main competitors of phenolic and melamine resins (see **Wood adhesives – phenolics** and **Wood adhesives – aminoplastics**). The use of polyurethanes is much less extensive, but one-component polyurethanes are starting to be used as cold-setting structural adhesives for glulam and other exterior structural solid timber to bond when the timber is very wet.

### Isocyanates

Adhesives based on isocyanates,<sup>1-5</sup> almost exclusively polymeric 4,4' diphenylmethane diisocyanate (PMDI), have been used now for more than 25 years. Their main application is the production of exterior-grade waterproof panels and also the production of panels from raw materials that are difficult to glue like straw, bagasse, rice shells or sugar cane bagasse. They have the advantage of using smaller amounts of adhesive, but are more expensive than other resins, the two balancing out. They can be used alone as adhesives for wood-based composites, but not alone for plywood. PMDI is a specific mixture of different molecules. PMDI has an average functionality of 2.7 with a NCO content of approximately 30.5%. The HCl content is usually below 200 ppm.

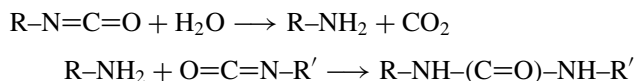


PMDI is used whenever the colour of the finished adhesive is not of concern as it imparts a relatively darker appearance to the board surface. The excellent application properties of PMDI and of the wood-based panels produced are based on its excellent wetting behaviour of the wood surface, compared to aqueous condensation resins. Even surfaces with poor wetting behaviour, like straw, can be glued. The wetting angles for PMDI on various surfaces are much lower than for other resins. The impossibility of



diluting PMDI with water was solved by the introduction of emulsified PMDI, often called EMDI, which allows a regular distribution of the adhesive during the gluing process.

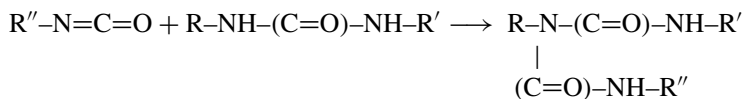
The isocyanate group in PMDI is characterized by a high reactivity towards all substances that contain active hydrogen. The main hardening reaction goes via water to the amide group. The necessary water is applied together with the PMDI or present in wood in sufficient amount. The amide group reacts further with another isocyanate group to a polyurea structure:



The reaction of an isocyanate group with a hydroxyl group leads to urethane bridges, and it is this reaction which leads finally to a hardened, cross-linked network:



Such a reaction theoretically can also occur between an isocyanate group and an OH group of the cellulose or the lignin, forming covalent bonds. These generally do not form during the very fast-curing times required industrially today for wood adhesives, and their contribution to final strength is negligible, if present at all. If an isocyanate group reacts with a hydrogen within the polyurea structure, a branching point is formed in the form of a biuret group, leading eventually to final networking:



During the hardening of PMDI urethanes, polyureas, biuretes and triuretes/polyuretes have been found.<sup>1-5</sup> The proportions of the various compounds depend on the hardening conditions. Network formation is especially influenced by the ratio between isocyanate and water.

Usually, no hardeners are added during the production of wood-based panels (PB, MDF, OSB, Engineered Wood Products). With special additives, a distinct acceleration of the hardening reaction and hence shorter press times or lower press temperatures can be achieved. Possible catalysts are the traditional ones used for the promotion of urethane formation.<sup>1</sup>

Isocyanates by themselves cannot be used to bond plywood because of the characteristic balance of rheology and rate of hardening, which are characteristic of PMDI. However, recently, they have been used as minority additives (10–30%), copolymerized during panel hot-pressing with formaldehyde-based resins such as PF and even UF to yield very strong bondlines. These combinations have been used industrially to yield excellent bonding both in plywood and in particleboard.<sup>2</sup>

### *Polyurethanes*

**Polyurethane** adhesives<sup>4,6</sup> are formed by the reaction of various types of isocyanates with polyols. Depending on the raw materials used, glue-lines with rubber-like elastic



the moisture content of the wood. This may cause some foaming of the bond line. The bond lines themselves are resistant to weather, humidity and water. Attention must be paid to the extent of creep of the glue-line. Some extent of creep is always present with a polyurethane, but it is minimal in some types while it is unacceptable in other types (the great majority). The characteristic of bonding very wet solid timber is a major advantage of these adhesives. Fig. 1 shows examples of strength growth of close contact joints prepared according to British Standard 1204, part 1 when bonded with a polyurethane at rather high (22% by weight) and standard (12% by weight) timber moisture content. They are compared with joints bonded with their main competitors namely, resorcinol (PRF) and melamine (MUF) “honeymoon”-type resins. At normal moisture content, the PRF resin gives fastest bonding, MUF is second and the PU is slower. At the higher moisture content, PU greatly outperforms the other two resins. This predominance, however, is partly illusory, because (1) the bonded joint has to dry first to normal moisture content before releasing it from clamping to avoid wood twist, and (2) PRF and MUF in doing what is indicated in (1) give equally good final strength results.<sup>6</sup>

Other articles on bonding of wood include **Wood adhesives – hot melts**, and **Wood composites – adhesives**.

### References

1. K. C. Frisch, L. P. Rumaio and A. Pizzi, Diisocyanates as wood adhesives, in *Wood Adhesives: Chemistry and Technology*, Vol. 1, Dekker, New York, 1983, Chap 6.
2. A. Pizzi, *Advanced Wood Adhesives Technology*, Dekker, New York, 1994.
3. C. E. Frazier, Isocyanate wood binders, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003, Chap 33.
4. M. Dunky and A. Pizzi, Wood adhesives, in *Adhesion Science and Engineering 2*, M. Chaudhury and A. V. Pocius, Eds., Elsevier, Amsterdam, 2002, Chap 23.
5. M. Dunky, Adhesives in the wood industry, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003, Chap 47.
6. M. Properzi, C. Simon, A. Pizzi, B. George, L. Uzielli and G. Elbez, *Holzforschung Holzverwertung*, **54**(1), 18–20 (2002).

### Wood adhesives – phenolics

A PIZZI

The fundamentals of wood adhesives are surveyed in **Wood adhesives – basics**. This article is concerned with phenolic resins, polycondensation products of the reaction of phenol with formaldehyde (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**). Phenols condense initially with formaldehyde in the presence of either acid or alkali to form a methylolphenol or phenolic alcohol, and then dimethylolphenol. The initial attack may be at the 2-, 4-, or 6-position. The second stage of the reaction involves methylol groups with other available phenol or methylolphenol, leading first to the formation of linear polymers and then to the formation of hard-cured, highly branched structures.<sup>1–3</sup>



the acetyl groups of cellulose. This leads to an enhanced emission of acetic acid. The higher the content of alkali, the higher is acetic acid emission. In European Norms (EN) EN 312-5 and 312-7, the content of alkali is limited to 2.0% for the whole board and 1.7% for the face layer.

Phenolic resins wood adhesives are used without any hardeners. Only heat sets off their hardening reaction. Their rate of hardening is strongly dependent on the resin pH. Their minimum reactivity occurs at around pH 4. They harden progressively and markedly faster as the pH increases, up to pH between 9 and 13, the maximum hardening rate pH depending on the type and age of the resin.<sup>1-3</sup>

Numerous additives to improve PF resins characteristics are added at times to the resins. Among these are condensed vegetable tannins, isocyanates and urea.<sup>1-3</sup>

Some natural phenolic-based materials, in particular, condensed flavonoid tannins, produced usually for leather making, are used in some parts of the world as exterior phenolic wood adhesives. They are different from synthetic PF resins in two aspects: (1) formaldehyde is not needed to build the linear polymer as the tannin itself is composed of flavonoid oligomers and (2) formaldehyde is only needed to be added to the glue mix as the hardener of the natural tannin extract. Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages at reactive positions on the flavonoid molecules. Tannins are however much more reactive than phenol; they are, in reality, the equivalent of natural resorcinols, and thus they can be used also to upgrade PF resins. The use of tannins as accelerators of PF resins for plywood (and much more recently for some type of particleboard) is a well-established industrial reality for the last forty years.<sup>4</sup>

### *Cold-setting resorcinol adhesives*

Resorcinol–formaldehyde (RF), and phenol–resorcinol–formaldehyde (PRF) cold-setting adhesives are used primarily in the manufacture of structural, exterior-grade glulam, finger joints and other exterior timber structures. They produce bonds of high strength and outstanding water and weather resistance when exposed to many climatic conditions.<sup>1-3</sup> PRF resins are prepared mainly by grafting resorcinol onto the low-condensation resols obtained by the reaction of phenol with formaldehyde. Resorcinol is the chemical species that gives to these adhesives their characteristic cold-setting behaviour. At ambient temperature and on addition of a hardener, it provides accelerated and improved cross-linking. Resorcinol is an expensive chemical and its high price is the determining factor in the cost of RF and PRF adhesives. It is for this reason that the history of RF and PRF resins is closely interwoven with the search for a decrease in their resorcinol content, without loss of adhesive performance.

Significant reductions in resorcinol content have been achieved: from pure resorcinol–formaldehyde resins, to today's PRF resins in which the percentage, by mass, of resorcinol on liquid resins is between 15 and 18%. A step forward has also been the development and commercialization of the "honeymoon" fast-set system,<sup>1-3</sup> which in certain countries is used to obtain PRFs of 8 to 9% resorcinol content without loss of performance.

The same chemical mechanisms and driving forces presented for phenol–formaldehyde resins apply to resorcinol resins. As regards application and hardening, PRF adhesives are always delivered as a liquid and must be blended with a liquid or powder hardener (generally paraformaldehyde and wood flour fillers) before use.

Table 1. Typical tensile strength and percentage wood failure results obtainable with synthetic PRF resins

Dry test		24-h cold water soak		6-h boil test	
Strength (N)	Wood failure (%)	Strength (N)	Wood failure (%)	Strength (N)	Wood failure (%)
3000–3500	90–100	2600–3200	75–100	2500–3000	75–100

Further discussion of bonding wood can be found in **Wood adhesives – aminoplastics**, **Wood adhesives – hot melts**, **Wood adhesives – isocyanates/urethanes** and **Wood composites – adhesives**.

### References

1. A. Pizzi, Phenolic resin adhesives, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003, Chap 26.
2. A. Pizzi, *Wood Adhesives: Chemistry and Technology*, Vol. 1, Dekker, New York, 1983.
3. A. Pizzi, *Advanced Wood Adhesives Technology*, Dekker, New York, 1994.
4. A. Pizzi, Natural phenolic adhesives 1: tannins, in *Handbook of Adhesive Technology*, 2nd edn, A. Pizzi and K. L. Mittal, Eds., Dekker, New York, 2003, Chap 27.

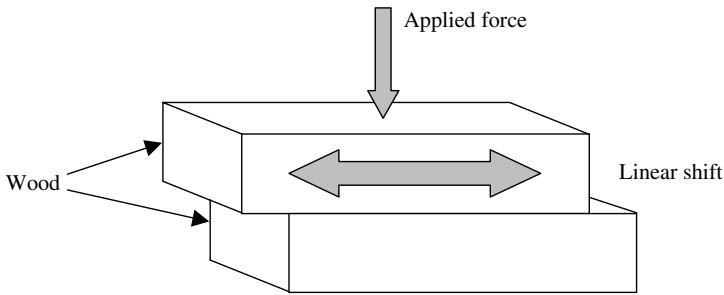
### Wood bonding by vibration welding

A PIZZI

Adhesive bonding of wood is very well established; see **Wood adhesives – basics**. A relatively novel joining technique is discussed here. Thermoplastic welding techniques, which are widely used in the plastic and car industries, have recently been applied also to joining wood, by melting a thermoplastic polymer between the two wood surfaces to be joined. A variety of techniques such as ultrasound, mechanical friction and others have been used to melt the thermoplastic polymer *in situ*.

However, the same mechanical techniques at the interface of two solid wood surfaces in the absence of any thermoplastic material, or any other binder, yields joints of considerable strength.<sup>1–3</sup> The equipment used for the mechanical vibration welding of wood in the absence of an adhesive is the same type of equipment as used for frictional welding of metals. Figure 1 shows the characteristic linear vibrational movement of the type of industrial metal welding machine used, as well as the frictional shift and force applied to the two pieces of wood during welding.

Linear welding of wood can give bonding results satisfying the relevant standards, while orbital welding gives much lower results. Some of the parameters that influence welding of metals with the same type of equipment also influence wood welding. Thus, the influence on the final bond of the vibration welding time, the contact holding time after the welding vibration had stopped, the welding pressure exerted on the surfaces, the holding pressure after the welding vibration had stopped, and the amplitude of the shift imparted to one surface relative to the other during vibrational welding are of importance.



**Fig. 1.** Direction of linear movements and pressure applied in wood welding without adhesives

Welding frequencies of 100 Hz are used. The joint tensile strength depends on vibration amplitude, showing some good bond strength for 3-mm vibrational amplitude. The joint tensile strength depends on welding pressure, values of 2 to 2.3 Mpa giving the best results. The joint tensile strength depends on welding time, but less markedly than on welding pressure. In general, combinations of 3 s welding time and 4–5 s holding time give strong joints, presenting strength in excess of 10 and sometimes of 11 MPa. The relevant European Norm for these types of joints requires strengths equal to or higher than 10 MPa.

The strong joints obtained are not capable of satisfying specifications for exterior joints as they show very poor resistance to water. These joints can then only be considered for interior applications such as for furniture and for interior grade wood joints. Furthermore, the technique at this stage is only usable for solid wood joints and perhaps joints between pre-manufactured panels presenting the same type of characteristics as solid wood, such as oriented strand board (OSB). The technique however is of considerable interest for its low cost and in the implementation of totally environment friendly wood joints in joinery and furniture manufacturing.

The mechanism of mechanically induced wood vibration welding has been shown to be due mostly to the melting and flowing of some amorphous, cells-interconnecting polymer material in the structure of wood, mainly lignin, but it may also be due to hemicelluloses. This causes partial detachment, the “ungluing” of long wood cells, wood fibres, and the formation of a fibres entanglement network in the matrix of molten cell-interconnecting material, which then solidifies. Thus, a wood cells/fibres entanglement network composite having a molten lignin polymer matrix is formed. Figure 2 shows a scanning electron micrographs with details of the type of composite formed in the bondline of a solid wood joint.

During the welding period, some of the detached wood fibres that are no longer held by the interconnecting material are pushed out of the joint as excess fibres. It has been shown, and confirmed, that cross-linking chemical reactions occur (the most likely one of these identified by NMR appears to be a cross-linking reaction of lignin with carbohydrate-derived furfural and furfural self-polymerization). These reactions, however, are relatively minor contributors during the very short welding period. Their contribution increases after welding has finished, explaining why some holding time under pressure after the end of welding contributes strongly to obtaining a good bond.



**Fig. 2.** Scanning electron micrograph of the entanglement of fibres and wood cells immersed in a matrix of molten cell interconnecting material generated by vibration-induced wood welding

### References

1. B. Gfeller, A. Pizzi, M. Zanetti, M. Properzi, F. Pichelin, M. Lehmann and L. Delmotte, *Holz-forschung*, **58**(1), 45–52 (2004).
2. B. Gfeller, M. Zanetti, M. Properzi, A. Pizzi, F. Pichelin, M. Lehmann and L. Delmotte, *J. Adhes. Sci. Techn.*, **17**(11), 1425–1590 (2003).
3. B. Gfeller, M. Lehmann, M. Properzi, F. Pichelin, M. Zanetti, A. Pizzi and L. Delmotte, *For. Prod. J.*, **54**(718), 72–79 (2003).

### Wood composites – adhesives

B H PAXTON

Adhesion between the phases is inevitably a vital aspect of all **Composite materials**. This article is concerned with adhesives in wood-based composite boards, which provide economic and effective ways of using a natural material. Other articles referring to these materials are **Wood adhesives – basics** and cross-references therein.

The range of wood-based boards, and the applications in which they are used, is large, and increasing. Examples are the use of plywood in structural situations, such as I-beams or box beams, on the one hand, to the construction of short-lived products, such as coffins from veneered particle board. Not all types of wood-based boards are suitable for all uses,



and although only a limited number of adhesives are used in their manufacture, choice of adhesive can be the most important factor governing performance in service.

British and European Standards<sup>1–6</sup> define property and durability levels for different types of boards and give recommendations for use.

### *Types of adhesive*

Adhesives of the aminoplastic (see **Step polymerization**) and phenol formaldehyde (see **Phenolic adhesives: single-stage resoles** and **Phenolic adhesives: two-stage novolacs**) types are most widely used. Although basically similar, an adhesive for plywood manufacture will require a different formulation to one for particle board, or medium-density fibre board (MDF) since methods of application and processing differ. Thus, in plywood, large sheets of veneer must be uniformly coated with adhesive, usually by a roller or curtain coater; in particle board, chips or wafers must be coated with very fine adhesive droplets, while small bundles of wet fibres must be sprayed with adhesive in the manufacture of MDF. Hence, formulation and production of resins has become a mixture of art and science, with resin manufacturers able to produce resins tailored for use in a particular board-manufacturing plant, or with a particular species of timber.

*Urea–formaldehyde* These are widely used for particle board and MDF manufacture and, to a smaller extent, for plywood. They are produced by the reaction of formaldehyde with urea, in molar ratios of between 1.2 and 1 and 2.0 and 1. Low molar ratios are preferred to minimize emission of formaldehyde in service; although low molar ratio resins have had inferior strength and water resistance and are slower curing, recent formulations have overcome these drawbacks to some extent. Curing occurs at elevated temperatures, with ammonium chloride, a common catalyst.

Typical adhesive spreads for plywood are 100–170 g m<sup>-2</sup>, with curing temperatures of 100–160 °C, and bonding pressure of 1–1.6 MPa. For particle board, the adhesive content is around 8 g of solid resin per 100 g of dry chips, and 12 g solid resin per 100 g dry fibres in the case of MDF. Curing rates are very fast, typically 8–10 s mm<sup>-1</sup> of board thickness for particle board.

Urea–formaldehyde bonded boards are suitable only for interior use because of their limited water resistance. They undergo hydrolytic degradation in the presence of moisture, particularly at temperatures above 40 °C.

*Melamine–formaldehyde* They are rarely used alone because of their high price. However, combining with urea–formaldehyde, either by mixing the two resins or preferably by producing as a co-condensate, gives a very substantial improvement in the durability of urea adhesives (see **step polymerization**). A melamine content of at least 40% is needed to satisfy a standard method of accelerated ageing for moisture-resistant grades of particle board and MDF.<sup>3,4</sup>

*Phenol–formaldehyde* This adhesive is most widely used in the manufacture of plywood. The resin is usually a “resol” type, prepared by the reaction of phenol with excess formaldehyde in the presence of an alkali catalyst. Curing occurs at elevated temperatures in the presence of an alkali. Phenolic adhesives need higher spreads, are slower curing

and are more expensive than urea–formaldehyde, but they give the most durable “weather and boil-proof” (WBP) bonding.

Although “resol” types are also used in the manufacture of wood chipboard, other forms of particle board, such as waferboard and oriented strand board (OSB) are usually made using “novolac” types. These resins are produced by reacting excess phenol with formaldehyde in the presence of an acid catalyst. The resin is converted to a fine powder, which is usually sprayed on to the large wafers along with molten wax, which helps the dry resin powder adhere to the wafers until it is cured under elevated temperatures of up to 200 °C. With this method, very small quantities of adhesive – as low as 2.5 g solid resin per 100 g dry wafers – can be used, while still achieving satisfactory bonding.

*Isocyanates* These are finding increasing use in the manufacture of particle board and MDF and avoid problems of formaldehyde release experienced with aminoplastic adhesives. They have the advantage of forming strong chemical (covalent) bonds with the wood, and so relatively low quantities of adhesive give high levels of bonding with good resistance to moisture. The high initial cost of the resins is offset by the small quantities needed, together with rapid curing rates at elevated temperature. Self-releasing isocyanates are now available, which overcome the problems of the binder adhering to metal platens and cauls characteristic of early formulations.

*Mineral binders* Cement and gypsum have limited, but increasing, use as binders. Portland cement is used in producing wood wool slabs and cement-bonded particle board. Only a limited number of species, such as spruce, can be used, since most species contain chemicals that inhibit the curing of the cement.

In the manufacture of cement-bonded particle board, wood chips are mixed with Portland cement in the ratio 60% cement, 20% wood and 20% water. Curing times are very long – about 7 h at 70–80 °C, followed by a further 2–3 weeks conditioning at ambient temperature. The boards produced have high density (1300 kg m<sup>-3</sup>, double normal particle board), but have exceptional dimensional stability, moisture and fire resistance compared to other wood-based boards.

Gypsum is used as a binder in gypsum-bonded particle boards, and in fibre boards from waste paper.

*Other binders* Adhesives based on tannins, occurring naturally in some timbers, are likely to be more widely used in future as price and availability of oil-based products becomes less favourable. Usually, small amounts of urea, phenol or isocyanate are incorporated with the tannin to improve use and performance.

Natural lignin, present in the wood, is used as the binder in most fibre building boards (hardboard), which are produced by subjecting wet wood fibres to heat and pressure.

## References

1. BS EN 636: Parts 1 to 3, 1997, *Plywood*.
2. BS 5268: Part 2: 2002, *Structural Use of Timber*.
3. BS EN 622: Parts 1 to 5: 1997, *Fibreboards*.

4. BS EN 312: Parts 1 to 7: 1997, *Particleboards*.
5. BS EN 300: 1997, *Oriented Strand Board. (O.S.B)*.
6. BS EN 634: Part 1: 1995, Part 2: 1996, *Cement Bonded Particleboard*.

#### *Select References*

- A. Pizzi, *Wood Adhesives – Chemistry and Technology*, 2 vols, Marcel Dekker, New York, 1983, 1989.
- A. Pizzi, *Advanced Wood Adhesive Technology*, Marcel Dekker, New York, 1994.

# X

---

## *X-ray photoelectron spectroscopy (XPS)*

---

D BRIGGS

X-ray photoelectron spectroscopy (XPS) is a very widely used **Surface analysis** technique, frequently referred to as ESCA (electron spectroscopy for chemical analysis).

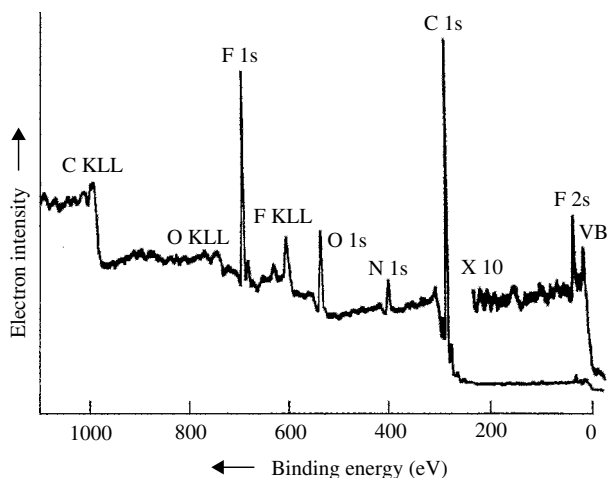
The sample, in ultra-high vacuum, is bombarded with soft X-rays (usually  $\text{MgK}\alpha$  or  $\text{AlK}\alpha$  with energies of 1253.6 and 1486.6 eV respectively). The photoelectrons emitted are energy analysed to give a spectrum of the type shown below. Three types of peaks are superimposed on a secondary electron background: core level, Auger and valence band (VB) peaks. Core level peaks are due to photoelectrons emitted from the atomic (core) levels of the atoms present, for example, C 1s designates an electron from the 1 s level of carbon. The binding energies ( $E_B$ ) of these electrons are obtained from the Einstein relation

$$E_B = h\nu - E_k - \phi$$

where  $h\nu$  is the X-ray energy,  $E_k$  is the measured kinetic energy and  $\phi$  is the sample work function. The  $E_B$  values are highly characteristic and allow identification of all elements except H. The peak intensities are proportional to the number of atoms sampled so that atomic composition can be calculated, with detection limits of typically 0.2 at%. Small variations in  $E_B$ , known as chemical shifts, occur for a given elemental core level in different chemical states. These can be determined from spectra obtained with high-energy resolution and allow some structural information to be derived.

A series of broader peaks, for example, C KLL, are due to Auger electrons. The process giving rise to these is described in the article **Auger electron spectroscopy**. Electrons emitted, with very low binding energy, from the valence shell, or bonding orbitals, appear in the valence band. These weak peaks are of very limited analytical value.

The surface sensitivity of XPS is the result of the limited depth below the surface from which electrons can escape elastically (without energy loss). This depth depends on the



**Fig. 1.** XPS survey scan of the surface of an epoxy adhesive cured in contact with PTFE. The PTFE film became detached in a peel test at very low load, but some transfer to the epoxide has taken place. Characteristic core level peaks (e.g. F 1s), Auger peaks (F KLL) and valence band peaks (VB) are all present in this spectrum

kinetic energy of the electron, but typically, the information comes from a region  $<100 \text{ \AA}$  beneath the surface. For flat surfaces, the sampling depth can be varied by changing the angle at which electrons leave the surface (the “take-off” angle). For grazing exit angles, the sampling depth can be reduced to  $\sim 10 \text{ \AA}$ .

The principal advantages of XPS are its low radiation damage rate and the lack of serious charging problems with insulators. Traditionally, spatial resolution has been very poor, but with modern instruments, microanalysis and imaging can be performed with a resolution of  $<10 \text{ \mu m}$ . Wide use of XPS is made in the study of adhesion problems, for example, in establishing failure planes (see **Stress distribution: mode of failure**), and it has contributed significantly to our understanding of pre-treatment processes (see **Pre-treatments of polymers** and **Pre-treatment of metals prior to bonding**) and the associated mechanisms of adhesion enhancement; Fig. 1 gives an example.

### Select References

- D. Briggs and M. P. Seah, Eds., *Practical Surface Analysis*, Vol. 1: *Auger and X-ray Photoelectron Spectroscopy*, John Wiley, Chichester, 1990.
- J. F. Watts, *An Introduction to Surface Analysis by Electron Spectroscopy*, Oxford University Press, Oxford, 1990.
- D. Briggs, *Surface Analysis of Polymers by XPS and Static SIMS*, Cambridge University Press, Cambridge, 1998.

## Appendix

---

### A. Literature and information sources

In days of easy Internet access with its formidable literature-searching power, it would be superfluous to provide here a selected bibliography on adhesion. The references in the articles in the body of the book give details of most, if not all, important compendia presently in print. The Adhesion Society website includes a “Publications Center”, no doubt regularly updated, with links to many important sources of information and to an extensive classified book list:

<http://www.adhesionsociety.org/pubs/index.html>

Harrington<sup>1</sup> has recently published a article on information sources in adhesion and adhesives, which includes 24 pages of comprehensive lists including journals, books, directories, trade publications, learned societies and trade associations and consulting laboratories.

### References


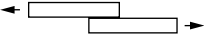
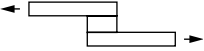
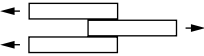

1. W. F. Harrington, Information resources, in *Handbook of Adhesive Technology*, 2nd edn, K. L. Mittal and A. Pizzi Eds., Marcel Dekker, 2003, pp. 13–51.

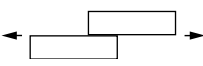
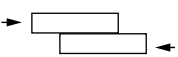

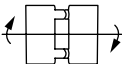

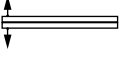
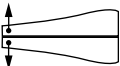
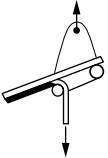
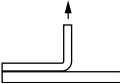


### B. Standard test methods for adhesive joints

As described in **Standards for adhesives and adhesion**, up-to-date standards lists can be obtained on line from the standards organizations of which some of the principal ones are:

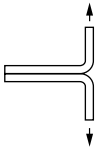


- Association Européenne des Constructeurs de Matériel Aérospatial AECMA, Brussels, at <http://www.aecma-stan.org>
- American Society for Testing and Materials, ASTM, Pennsylvania, at <http://www.astm.org>
- British Standards Institution, BSI, London, at <http://www.bsi-global.com>
- Comité Européen de Normalisation, CEN, Brussels, at <http://www.cenorm.be>
- International Organisation for Standardization, ISO, Geneva, at <http://www.iso.ch>


The table below, reproduced with permission from *Adhesion and Adhesives, Science and Technology*, by A. J. Kinloch, Chapman and Hall, 1987, is provided as a quick pictorial guide to some of the more widely used standards associated with adhesive joints.

Joint geometry	Standard	Comments
Axially loaded (tensile) butt joints		
	ASTM D 897-78	For substrates in “block” form
	ASTM D 2094-69 and D 2095-72	Specifically for bar- and rod-shaped substrates
	BS 5350: Part C3: 1979	UK version of above
	ASTM D 429-73	Rubber-to-metal bonding
	ASTM D 816-82	Specifically for rubbery adhesives
	ASTM D 1344-78	Cross-lap specimen specifically for glass substrates
Lap joints loaded in tension		
	ASTM D 1002-72	Basic metal-to-metal single-lap joint test giving the “single-lap-shear strength”
		UK version of above test
	BS 5350: Part C5: 1976	Single-lap joint test for metal-to-metal joints at elevated test temperatures
	ASTM D 2295-72	
	ASTM D 2557-72	As above, but a low temperatures
	ASTM D 3163-73	Single-lap joint for rigid plastic substrates
	ASTM D 3164-73	Single-lap joint in which a small rectangle of plastic substrate is sandwiched between metallic substrates
	ASTM D 3528-76	Basic metal-to-metal double-lap joint test giving the “double-lap-shear strength”
	BS 5350: Part C5: 1976	UK version of test
	ASTM D 3165-73	Metal-to-metal laminate test for large bonded areas but may also be used with plastic substrates
	ASTM D 906-82	Specifically for adhesives used in plywood laminate constructions
	ASTM D 2339-82	Specifically for wooden (two-ply) laminate substrates

Joint geometry	Standard	Comments
	ASTM D 3983-81	Thick substrates used in a single-lap joint; shear modulus and strength of adhesive determined
Lap joints loaded in compression		
	ASTM D 905-49	Mainly intended for wooden substrates
	ASTM D 4027-81	For measuring shear modulus and strength of adhesive: uses "rails" to maintain only shear load
Torsional shear		
	ASTM D 3658-78 ASTM E 229-70	Specifically for ultraviolet light-cured glass-to-metal joints Uses a "napkin ring" test for determining shear modulus and shear strength of structural adhesives
Cleavage		
	ASTM D 1062-78	Metal-to-metal joints
	ASTM D 3807-79	For engineering plastics substrates
	ASTM D 3433-75	Flat and contoured cantilever-beam specimens for determining the adhesive fracture energy, $G_{Ic}$
Peel joints		
	ASTM D 3167-76 BS 5350: Part C9: 1978	Floating roller test
	BS 5350: Part C10: 1976	90° peel test for flexible-to-rigid joints
	BS 5350: Part C14: 1979	90° peel test for rigid-to-rigid joints
	ASTM D 903-49. BS 5350: Part C11: 1979	180° peel test



Joint geometry	Standard	Comments
	ASTM D 1876-72 BS 5350: Part C12: 1979	T peel test
	ASTM D 1781-76  ASTM 429-73 ASTM D 2558-69	Climbing drum peel test for skin-sandwich assemblies For rubber-to-metal bonding For shoe-soling materials
Impact resistance 	ASTM 950-82	Uses a block shear joint
Disc shear strength in compression	ASTM D 2182-78	Determines adhesive shear strength on compression
Creep resistance	ASTM 1780-72.  ASTM D 2294-69 ASTM D 2293-69	Single-lap joint loaded in tension employed  Single-lap joint, having a long overlap and between “rails”, loaded in compression
	BS 5350: Part C7: 1976	Various test geometries permitted
Fatigue	ASTM D 3166-73	Single-lap joint loaded in tension employed
Environmental resistance	ASTM D 896-84  ASTM D 904-57  ASTM 1151-84	General method for assessing resistance of joints to chemicals; may use any ASTM standard test geometry General method for assessing resistance of joints to artificial and natural light; may use any ASTM standard test geometry General method for assessing resistance of joints to moisture and temperature; may use any ASTM standard test geometry

Joint geometry	Standard	Comments
	ASTM D 1183-70	General method for assessing resistance of joints to a cyclic laboratory-ageing environment (moisture and temperature): may use various ASTM standard test geometries
	ASTM D 1828-70	General method for assessing resistance of joints to natural outdoor ageing; may use any ASTM standard test geometry
	ASTM D 1879-70	General method for assessing resistance of joints to high-energy irradiation; may use any ASTM standard test geometry
	ASTM D 2918-71	Method for assessing the effect of <i>stress</i> and moisture and temperature; uses a peel joint test
	ASTM D 2919-71	As above, but uses single-lap joints loaded in tension
	ASTM D 3762-79	As above, but uses a wedge (cleavage) test
	ASTM D 3632-77	Effect of a high-pressure oxygen environment on wood-to-wood and wood-to-metal joints: uses a lap joint test
Pressure-sensitive tack	ASTM D 2979-71	Inverted probe test
	ASTM 3121-73	Rolling-ball test

## How to use the *Handbook*

The book consists of short, self-contained articles on scientific, engineering and industrial aspects of adhesion. They are arranged alphabetically. In many cases, the titles have been chosen to keep related articles together so that they can be read in sequence.

To find information on a particular topic, locate the most relevant article(s) by referring to:  
the **Alphabetical List of Articles**, p. xiii (this includes a one-line guide to the article's contents);  
the **Index**.

Further information can be obtained by following up the **cross-references**: these are indicated by referring to other articles by name in **bold**, within the text. The **Index** will also give reference to other pages in which particular terms occur.

The **Classified List of Articles** provides a list of all the articles concerned with broad topics. It is of use both in locating specific information and in providing a structured reading list. The headings are as follows:

### GENERAL

#### BACKGROUND MATERIALS SCIENCE

- secondary bonds, surface energy, interfacial tension
- polymer science
- mechanics
- other

### THEORIES OF ADHESION

#### ADHESIVE-SUBSTRATE INTERFACE

#### SURFACE CHARACTERIZATION

#### ADHESIVE TYPES

- classification
- broad categories
- specific chemical types

#### TESTING

#### PRE-TREATMENT OF SURFACES

- metals
- polymers

#### PRIMERS

#### DURABILITY – HOSTILE ENVIRONMENTS

#### ENGINEERING DESIGN

#### PROCESSING AND ASSEMBLY

#### WELDING AND AUTOHESION

#### APPLICATIONS OF ADHESIVES

#### COMPOSITE MATERIALS

#### PAINT

#### RUBBER

#### SEALANTS AND MASTICS

#### WOOD

The **Appendix** (p. 623) provides concise guidance on literature and information sources and gives a quick pictorial guide to standard test methods for adhesive joints.

Remember that **CROSS-REFERENCES** are shown by giving titles of articles in **bold**.

## Index

---

**Note:** entries in bold refer to self-contained articles.

- Abrasion treatment 1–3**
  - metals 374
  - rubber to metal bonding 421
- ABS 276
- Accelerated ageing 3–5**
  - see also* weathering
- accelerators
  - cyanoacrylate adhesives 97
  - epoxide adhesives 151, 154
- Acid–base interactions: introduction 5–7**
  - inverse gas chromatography 255–7
- Acid–base surface energy parameters 7–9**
- Acids 10–12**
- Acrylic adhesives 12–14**
  - anaerobic 44–5
  - chemistry and properties 507
  - curing 68, 397
  - polymerisation 12–13
  - toughened 26, 546–50
  - uses 13–14, 306, 364, 456
- acrylonitrile–butadiene rubbers 562
- addition cure of silicones 469–71
- addition polymerization *see* chain polymerization
- additives
  - cyanoacrylate adhesives 96
  - natural rubber adhesives 293
  - nitrile rubber 295–6
  - phenol-formaldehyde adhesives 614
  - polychloroprene rubber 332–5
  - and surface of polymers 525
  - toughened adhesives 550–2, 554, 557–8
- Adhesion 14–16**
- Adhesion –fundamental and practical 16–19**
- Adhesion in dentistry: orthodontics and prosthodontics 19–21**
- Adhesion in dentistry: restorative materials 21–3**
- Adhesion in medicine 23–5**
- adhesion promoters
  - rubber bonding agents 417–19
  - silicone adhesives 468
  - see also* silane adhesion promoters
- Adhesive classification 25–8**
- Adhesives –historical perspective 28–31**
- Adhesives for textile fibre bonding 32–6**
- Adhesives in the textile industry 36–8**
- Adsorption theory of adhesion 38–40, 536**
  - adsorption energy 255
- Aerospace applications of adhesives 40–2**
  - phenolic resins 318, 321–2
  - repair methods 402–5
- alkaline cleaners 102–3
- Alkyl-2-cyanoacrylates 42–4**
  - adsorption energy 255
- aluminium
  - adhesion promoters 387–8
  - adhesion to polyethylene 276
  - anodizing 41, 49–50, 276–7
  - Auger depth profile 56
  - bismaleimide-bonded joints 341
  - corrosion inhibiting primers 390
  - electron micrograph 128–9
  - FLP etch 196–7
  - metallizing plastic 277–8
  - pre-treatment 234, 368–71
  - surface characterization 510
  - thermal spray process 543
  - X-ray photoelectric spectrum 2
- aminoplastic wood adhesives 600–3
- Anaerobic adhesives 44–6**
  - classification 26–7
  - dispensing 106
  - and joint design 263–5
- Animal glues and technical gelatins 47–8**
  - classification 26
- Anodizing 49–50**
  - copper 371
  - quality control 135
  - surface electron micrograph 129
- antioxidants
  - nitrile rubber 296
  - polychloroprene rubber 333, 334
  - rubber-based adhesives 436
- application, methods of *see* dispensing
- aramid fibres 169, 176
- arc-plasma process 541–2, 543
- arc-wire process 541, 544
- arrowhead test piece 423–4
- Atomic force microscopy 50–2, 442**
- Auger electron spectroscopy 52–6**
  - autohesion 103–4, 353, 482, 527–8
- Automotive applications 56–7**
  - anaerobic adhesives 44–5
  - engine mounts 412
  - gears and engines 44–5, 235–6, 262–5, 318, 322
  - impact resistance 233
  - non-metallic components 236–7, 331, 358

**Automotive applications (continued)**

- rubber to metal bonding 415
- screen printing of adhesives 110
- tyre cord adhesion 427–9

**Autophoretic primers 57–8**

beam on elastic foundation 492–4

belts 33

binders, paint 308, 309, 310

bismaleimide adhesives 341

bisphenol A 148–50, 316

blast cleaning 1–3

**Blister test 59–60**

- mould adhesion 288

bolted joints 167

bonding of adhesives 39–40, 267–8

bonding agents for rubber 417–18

**Bondline thickness effects 494–6**

- and joint design 267–8

**Bonds between atoms and molecules 60–2**

boron fibres 169

BOSS coating system 541

brass-plating and rubber 419–20, 427–9

Brønsted acids 10–11, 12

butyl rubber 434, 456

cantilever beams 209–11

capillary rise

- and contact angle 83

- wetting kinetics 599

carbon black 293, 412

carbon fibres 169

- mechanical properties of composites 180–1

- surface treatment and microstructure 178–80

carpets 35, 36

cartridge dispensers 110

casein 30

cashewnut shell oil 316

catalyst *see* hardeners

**Cathodic disbondment 63–6**

cement 619

ceramics 362

- bond coatings 541–2

**Chain polymerization 66–9**

- acrylic adhesives 12–13

- alkyl-2-cyanoacrylates 43–4

- mechanisms 43–4, 66–8

- silicone cure 469–71

chlorinated rubber primer 394

chromic acid etching

- metals 196–7, 370, 374, 375, 377

- plastics 276

classification of adhesives 25–8

- epoxides 148–9

- structural adhesives 505–6

ClearWeld process 586

**Climbing drum peel test 69–71**

coefficient of expansion 532

**Coextrusion 71–3**

- tie layers 546

cold press moulding 172

collagen 47

combustion powder spray 544

combustion wire spray process 544

**Compatibility 73–6****Composite materials 76–7**

- aerospace structures 41

- and coextrusion 72

- honeycomb testing 299–302

- joining 166–7

- peel test 69–71

- repair methods 402–5

- see also* fibre composites; filler–matrix adhesion; laminating

concrete and stone 394

condensation cure of silicones 471–3

condensation polymerization *see* step polymerization

cone test piece 42

**Contact adhesives 77–9****Contact angle 79–82**

- surface characterization of metals 510–11

- surface characterization of polymers 511–14

**Contact angle measurement 82–4****Contact angles and interfacial tension 84–6**

- critical surface tension 94

contact moulding 172

contaminants, surface 113–14

**Conversion coating 86–8**

- and bond failure 120

- steel 378–9

copolymerization 68

copper

- anodized 50

- microfibrinous surface 279, 280

- pre-treatment 371–2

core-shell rubbers 558

corners 504

**Corona discharge treatment 89–90, 382, 384**

corrosion

- inhibiting primers 390

- silane pre-treatment 464, 465

coupling agents *see* silane adhesion promoters

cracks *see* fracture and fatigue

**Creep 90–3**

- rupture 114–16

- testing of adhesives 531

- and viscoelasticity 573, 575

critical energy 207

**Critical surface tension 94–6**

cryoblasting 374

CTBN rubbers 561

curing

- acrylic adhesives 13, 68

- cyanoacrylates 68, 283–4

- epoxides 68, 149–50, 150–5, 490–1

- isocyanates 284–5, 491, 610

- melamine resins 602

- nitrile rubbers 296

- novolacs 317

- polychloroprene rubber 330, 333, 334, 335

- polysulphides 491

- radiation 395–7

- reaction setting adhesives 397–9

- resoles 489–90

- rubber-based adhesives 435–6  
 sealants 447, 448, 457  
 silicone adhesives 284, 285, 469–73, 491  
 structural adhesives 506–7  
 testing 531–2  
 toughened acrylics 547  
 urea–formaldehyde adhesives 490, 601
- Cyanoacrylate adhesives 96–9**  
 acrylics and epoxies compared 14, 508  
 automotive applications 236–7  
 chemistry and properties 507  
 classification 12, 26–7  
 curing 68, 283–4  
*see also* alkyl-2-cyanoacrylates
- cylinder liner bonding 235–6  
 cylindrical component bonding 235  
 Cytec BR-127 inhibitor 390
- data analysis 485–7  
 dauber application 228  
 Debye induction forces 61, 111, 273, 328  
 degradation testing 532  
*see also* weathering
- Degreasing 101–3**  
 environmental impact 145  
 metals 374  
 rubber to metal bonding 421
- delamination 63
- dentistry  
   orthodontics and prosthodontics 19–21  
   radiation-cured adhesives 396–7  
   restorative materials 21–3
- dielectric welding 585  
 diffusion coefficient 4  
 diffusion, polymer 341–4
- Diffusion theory of adhesion 103–5, 536–7**  
 diphenyl methane diisocyanate 357  
 dipoles 111, 326–7
- Dispensing of adhesives 105–11**  
 emulsion and dispersion adhesives 137  
 hot melt adhesives 228
- Dispersion forces 61 111–13**  
 absorption theory 39  
 surface energy component 517–18, 520
- Displacement mechanisms 113–14**  
 Dupré's equation 24
- Durability 121–2**  
 selection of adhesives 455  
 underwater adhesives 567–8
- Durability: creep rupture 114–16**  
**Durability: fatigue 116–17**  
**Durability: fundamentals 119–21**  
**Durability: subcritical debonding 121–2**  
 dynamic mechanical analysis 538
- ebonite bonding 419  
 Ebonol C 371  
 EDX analysis 130  
 elastomeric adhesives 476  
*see also* rubber-based adhesives
- Electrical adhesion 123–5**  
 electro-rheological fluids 124–5
- Electrochemical pre-treatment of polymers 125–7**  
 electrochemical reactions 65
- Electron microscopy 127–9**  
*see also* scanning electron microscope
- Electron probe microanalysis 129–32**
- Electrostatic theory of adhesion 132–3, 537**
- Ellipsometry 133–5**  
 emulsifiers 334  
 emulsion cleaners 103
- Emulsion and dispersion adhesives 136–8**  
 classification 26  
 and textiles 37
- enamel, tooth 21–2  
 energy content of polymers 144  
 engine mounts 412
- Engineering design with adhesives 138–41**
- Engineering surfaces of metals 141–3**  
 enthalpy changes 538–9
- Environment and the impact of adhesive technology 143–5**
- Environmental sustainability 146–7**
- Epoxide adhesives 147–50**  
 aerospace industry 41  
 at high temperature 224, 225  
 chemistry and properties 506  
 compared with other adhesives 14, 508  
 epoxy novolacs 318  
 fibre composite joints 166–8  
 interfacial failure 120  
 matrix resins 170, 180  
 and microporous surfaces 281  
 nitrile rubber blends 297  
 transmission IR spectra 244  
 underwater 567–9  
*see also* toughened epoxide adhesives
- Epoxide adhesives: curatives 149–50, 150–5**
- ESCA 621–2
- Etch primers 156**  
 etching  
   aluminium 369–70  
   FPL etch 196–7  
   PEEK 336  
   titanium 380  
*see also* conversion coatings
- ethanol 401
- Ethylene–vinyl acetate copolymers 156–9**  
 adhesion to microfibrinous surfaces 280–1  
 extrusion 160  
 hot melt wood adhesives 607–8  
 laminating 272  
 microstructure 282  
 textiles 32, 35  
 toughened epoxides 557
- extrusion 160, 228
- Extrusion coating 160–1**  
 extrusion welding 589
- fabric *see* textiles  
 failure, mode of 496–9  
*see also* fracture and fatigue  
 fatigue *see* fracture and fatigue
- Fibre composites –introduction 163–5**  
**Fibre composites –joining 166–7**

- Fibre composites –matrices and fibres** 168–71  
**Fibre composites –processing techniques** 171–3  
**Fibre–matrix adhesion –assessment techniques** 173–6  
**Fibre–matrix adhesion –carbon fibres** 177–81  
**Fibre–matrix adhesion –glass fibres** 181–6  
 Fickian diffusion 4  
 filament winding 172  
 filled joints 445  
**Filler–Matrix adhesion** 186–9  
 fillers  
   barytes 608  
   and internal stress 251  
   and microstructure of joints 282  
   polyvinyl alcohols 360  
   rubber 296, 411–14  
   rubber-based adhesives 293, 432, 435  
   silicone adhesives 468  
 films *see* thin films  
**Finite-element analysis** 189–92  
**Finite-element analysis: rubber** 192–4  
**Flame treatment** 195–6  
 flash-free welding 589  
 flocking 33, 36  
 fluorocarbon polymers, pre-treatment of 372–3  
 Fokker bond tester 299–300  
 Fourier-transform infrared spectroscopy 242, 243  
 Fowkes' method 6  
**FPL etch** 196–7  
**Fractals** 197–9  
**Fractals and fractal dimension** 200–3  
**Fractals and surface roughness** 203–6, 409  
 fracture energy 17–18  
   fracture mechanics 207, 208  
   microfibrous surface 281  
   and polymer–polymer adhesion 347–8, 351–2  
   and wedge test 583  
 fracture and fatigue 116–19  
   cracks 118, 121, 206, 207, 234, 496–8  
   creep 92–3, 114–16  
   failure modes 119–20  
   fatigue test 4–5  
   finite-element analysis 189–92  
   joint design 269–70  
   peel tests 70, 121  
   stress distribution and failure mode 496–9  
   and surface contamination 113  
   wedge test 4, 121, 534, 582–3  
**Fracture mechanics** 206–7  
**Fracture mechanics test specimens** 208–11  
**Friction –adhesion aspects** 211–13  
 friction coefficient 212–13  
   and powders 362  
 friction force microscopy 51–2  
 friction stir welding 591  
 fundamental adhesion 15, 16–19  
  
 gaskets 45–6, 110  
 gear to shaft bonding 235, 264–5  
 gelatin 29–30, 47–8  
 glass fibres 169  
   finish 182, 183  
   interfacial adhesion 184–5  
  
   surface treatment 182–4  
   types and forms 182  
**Glass transition temperature** 215–17  
   silicone properties 474  
   thermal analysis 539–40  
 glow discharge treatment 325–6  
**Good–Girifalco interaction parameter** 217–19  
   and critical surface tension 95  
   and interfacial tension 512–13  
 gums 29, 33  
 Gutmann's acceptor and donor numbers 256–7  
 gypsum 619  
  
 hardeners (epoxide) 149–50, 150–5, 398  
 hazard labels 223  
**Health and Safety** 221–4  
   chromate treatments 376, 377  
   isocyanates 359  
   and packaging 307  
   polybenzimidazoles 329  
   rubber-based adhesives 431  
   and selecting adhesives 454  
   solvent welding 480  
   urea–formaldehyde adhesives 601, 605, 606  
   UV radiation 397  
 hexamethylene tetramine (hexamine) 316, 317  
 high-frequency welding 585  
**High-temperature adhesives** 224–6  
   polybenzimidazoles 328–9  
   polyphenylquinoxalines 355–6  
**High-temperature stability: principles** 226–7  
 high-velocity oxygen fuel spray 544  
 history of adhesives 28–31  
 honeycombs  
   repair methods 402–3, 404  
   and resoles 321  
   testing 299–302  
 hose 33  
**Hot melt adhesives** 227–9  
   classification 26  
   natural products 29, 402  
   and textiles 32, 37–8  
   wood adhesives 606–8  
 hot-bar welding 588  
 hot-gas welding 588–9  
 hot-plate welding 587–8  
**Humidity** 229–30  
**Hydrogen bonding** 62, 230–1  
 hydrosilylation addition cure 469–70  
 hyperelasticity 192–4  
  
 imide prepolymers 340–1  
**Impact resistance** 233–5  
 impulse welding 588  
 in-vulcanization bonding 417  
 induction welding 584  
**Industrial applications of adhesives** 235–7  
**Inelastic electron tunnelling spectroscopy** 238–42  
 infrared curing 395  
**Infrared spectroscopy** 242–4  
**Infrared spectroscopy: attenuated total reflection** 245–7

**Infrared spectroscopy: RAIR 247–50**

- infrared welding 586
- interdiffusion 104, 342, 354
- interdigitation 341–4
- interfaces
  - incompatible 344–7
  - primary bonding 385–9
- interfacial tension
  - acid-base interactions 8
  - contact angle 84–6, 511–12, 592
  - surface energies 219
  - wetting and spreading 592–3
  - see also* surface tension

**Internal stress 250–2**

- paint films 310

**Inverse gas chromatography 252–4****Inverse gas chromatography and acid–base interactions 255–7**

- ion beam sputtering 509
- ionic structures 61, 326
- isocyanates 357, 359, 394, 491, 604
- wood adhesives 609–10, 619

**JKR theory 259–62****Joint design –cylindrical joints 262–6****Joint design –general 266–9****Joint design: strength and fracture perspectives 269–70**

## joints

- beam on elastic foundation 492–4
- in composites 166–8
- failure 4, 17
- finite-element analysis 190–1
- flexible 208–9
- fracture mechanics 206–7, 208–11
- and impact resistance 233–5
- internal stress 250–2
- microstructure 281–3
- rigid 208–9
- rubber-metal 416
- sealant 444–51, 456–9
- shear lag model 501–3
- shear testing 460–2
- tensile tests 529–30
- thickness of bond 494–6, 534
- types of stress 266–7
- see also* joint design

Keesom forces 61, 111, 273, 328

kinetic spray process 545

Koch curve 197–9, 200–2

**Laminating 270–3**

- and coextrusion 71–3, 161
- nitrile rubbers 296–7
- polychloroprene rubber 331
- polyurethane adhesives 358
- radiation-cured adhesives 397
- repair methods 402–5
- testing 299–302
- textiles 34–5

lap joints 168

LARC-TPI polyimides 339–40

laser ablation 374

laser Raman (fluorescence) spectroscopy 175

laser welding 585

latex adhesives 32, 293, 294, 297

- cold seal 306

- polychloroprene rubber 331, 334

Lewis acids 6, 7, 11–12

Lewis bases 6, 7

**Lifshitz-van der Waals forces 5–7, 62, 273–4,**  
513, 519

London dispersion forces 39, 112, 218, 273

magnesium, anodized 50

mastic 448, 456

matrix polymers 170–1

- and carbon fibre adhesion 173–6, 177–81,  
179–80

- filler matrix adhesion 186–9

- and glass fibre adhesion 173–6, 181–6, 184–5

**Mechanical theory of adhesion 275–7, 536**

medicine 23–5, 361

medium-density fibre board 618

melamine resins 602–3, 618

metallic films

- and inelastic tunnelling spectroscopy 238–42

- vacuum deposited 133, 386–7

**Metallizing plastics 277–9**

- primary bonding at the interface 386–7

metals

- engineering surfaces 141–3

- pre-treatment prior to bonding 373–6, 463–6

- pre-treatment prior to painting 376–7

- rubber bonding 414–17

- surface characterization by contact angle 510–11

- surface contaminants 141–3, 374

methacrylates 12, 547

**Microfibrous surfaces 279–81**

microindentation test 174

**Microstructure of joints 281–3**

microwave curing 395

microwave welding 586–7

**Mode of failure: stress effects 496–9**

moisture

- and diffusion coefficient 4

- double glazing 449–50

- effect on transition temperature 217

- penetration index 450

- and sealants 458

- and urea–formaldehyde adhesives 600

- weathering 579–80

- wood bonding parameters 604–5, 612

- see also* humidity

**Moisture cure of adhesives and sealants 283–5****Mould adhesion and fouling 286–7****Mould adhesion –measurement 288–9**

moulding of rubbers 414, 418–19, 425

multiple fragmentation test 173–4

nail model 348

**Napkin ring test 291–2**

natural products 47–8



- natural products (*continued*)  
 in the body 23–5  
 and environmental impact 143  
 historical perspective 29–31  
 renewable sources of adhesives 401  
 rubber 292–4, 364  
 textile sizing 33  
*see also* animal glues
- Natural rubber-based adhesives 292–4**  
 compounding 434  
 pressure-sensitive tapes 364  
 renewable sources of adhesives 402
- Neoprene *see* polychloroprene
- Nipol® 562
- Nitrile rubber adhesives 294–8**  
 compounding 434  
 and resoles 320  
 textile use 32  
 and toughened epoxide 556
- nitrile–butadiene rubber (NBR) *see* nitrile rubber
- Non-destructive testing of adhesively bonded structures 298–302**
- non-structural bonds 119–20  
 novolac adhesives 315–18, 619  
 nylon powder 558
- open-drained joints 445
- Optical microscopy 303–4**  
 near field scanning 442–3
- orbital welding 591
- organosilanes *see* silane adhesion promoters
- orthodontics 19–20
- Packaging industry 305–7**
- Paint constitution and adhesion 308–9**  
 paint and metal pre-treatment 373–6
- Paint primers 309–10**
- Paint service properties and adhesion 310–11**
- paper and board  
 adhesives 360–1  
 laminating 272
- paraformaldehyde 316
- Paris law 117–18
- particle board 618, 619
- PEEK *see* polyether ether ketone
- peel angle 314–15  
 peel energy 312–15  
 peel force 312–14  
 time dependence 105
- peel ply 167, 381
- peel strength 71  
 and joint design 266  
 natural rubber adhesives 293–4
- Peel tests 311–15**  
 climbing drum 69–70  
 elastomeric material 534  
 and EVA 157  
 fracture mechanics 208  
 pressure-sensitive tapes 366–7  
 rubber to metal bonds 423
- phase-stepping technique 175
- Phenolic adhesives: single-stage resoles 318–22**  
 curing 489–90  
 wood composites 618–19
- Phenolic adhesives: two-stage novolacs 315–18**  
 wood composites 619
- phenolic adhesives, general  
 aerospace 41  
 chemistry and properties 506  
 fibre composites 170–1  
 high temperature 225  
 nitrile rubber blends 297  
 wood adhesives 612–15, 618
- phosphate conversion coating 86–8, 120, 370, 375, 376, 378
- photoinitiators 395, 396
- pickling 377–8
- pigment printing 35–6
- Plasma-polymerized coatings 322–5**
- Plasma treatment 325–6, 382, 385**  
*see also* corona discharge treatment
- plasticizers  
 cyanoacrylate adhesives 98  
 and glass transition temperature 217  
 natural rubber adhesives 293  
 nitrile rubber 295–6  
 paint 308  
 rubber-based adhesives 432, 435  
 silicone adhesives 472
- plywood 617, 619
- Poisson's ratio 499–511**  
 tensile tests 529
- Polar forces 61–2, 326–8**  
 surface energy component 518–19
- pollution 144–5
- polyalkenoate cements 19, 23
- polyamides 320, 608
- Polybenzimidazoles 225, 328–9**
- polybutadiene 386
- Polychloroprene rubber adhesives: applications and properties 329–32**
- Polychloroprene rubber adhesives: modifiers and additives 332–5**
- polydimethylsiloxane 399–400, 473–4, 475–7
- polyesters 170
- Polyether ether ketone 335–6**, as matrix 171
- polyetherimide 563
- polyethersulphone 563
- polyethylene  
 adhesion to aluminium 276  
 coextrusion 72  
 electrochemical pre-treatment 126–7  
 industrial uses 160  
 and infrared spectroscopy 245, 246  
 and microfibrinous surfaces 280  
 microstructure 282  
 pre-treatment of 383–5
- polyethylene terephthalate 558
- poly(ethylenevinyl alcohol) 72
- Polyimide adhesives 336–41**  
 high temperature adhesives 225, 226  
 as matrix polymers 170  
 and toughened epoxy 563
- polyisobutylene 434, 448, 449
- polyisoprene 292–3

- Polymer diffusion: reptation and interdigitation** 341–4
- Polymer–polymer adhesion: incompatible interfaces** 76, 344–7
- Polymer–polymer adhesion: models** 342, 347–50
- Polymer–polymer adhesion: molecular weight dependence** 350–2
- Polymer–polymer adhesion: weld strength** 353–5
- polymeric 4,4-diphenyl methane diisocyanate 604, 609–10
- polymerization *see* chain polymerization; step polymerization
- polymers
- glass transition temperature 215–17
  - plasma coating 322–5
  - pre-treatment 126–7, 195–6, 372–3, 381–3, 383–5
  - reactive liquid 551, 552, 555, 560, 561
  - surface characterization by contact angle 511–14
  - surface nature 524–5
  - thermal spraying 542
  - and toughened epoxides 557–8
  - viscoelasticity 571–5
- poly(methyl methacrylate), micrograph of 188
- polyolefins
- pre-treatment 195–6, 383–5
  - priming 141
  - tie layers 545
  - and toughened acrylics 548
- polyols 357
- polyphenylenesulphidesulphone 563
- Polyphenylquinoxalines** 355–7
- polypropylene
- electrochemical pre-treatment 126–7
  - industrial uses 160
  - as matrix 171
  - pre-treatment 383–5
- polystyrene 355
- metal plating 276
- polysulfide sealants 448, 449, 457, 491
- polytetrafluoroethylene, pre-treatment of 125–6, 372–3
- Polyurethane adhesives** 357–9
- chemistry and properties 506–7
  - classification 26
  - curing 491
  - laminating 33
  - sealants 448, 449, 459
  - textile use 33
  - and toughened epoxy 555–6
  - wood adhesives 610–12
- polyvinyl acetals 320
- polyvinyl acetates 136–8, 360
- and glass transition temperature 158–9
  - polyvinyl alcohol manufacture 359–60
- Polyvinyl alcohol in adhesives** 359–61
- post-vulcanizing bonding 420
- Powder adhesion** 361–3
- practical adhesion 15, 16–19
  - prepregs 172–3
  - pressure impregnation 172
- Pressure-sensitive adhesives** 363–5
- classification 26
  - electrostatic theory 132–3, 537
- Pressure-sensitive adhesives –adhesion properties** 365–8
- pressure-time dispensers 106–10
  - pre-stressing 251
- Pre-treatment of aluminium** 368–71
- see also* anodizing; conversion coating; FPL etch
- Pre-treatment of copper** 279–80, 371–2
- Pre-treatment of fluorocarbon polymers** 372–3
- Pre-treatment of metals prior to bonding** 373–6
- Pre-treatment of metals prior to painting** 376–7
- Pre-treatment of polymers** 381–3
- see also* electrochemical pre-treatment of polymers; flame treatment
- Pre-treatment of polyolefins** 383–5
- Pre-treatment of steel** 377–9
- thermal spray coatings 541
- Pre-treatment of titanium** 379–80
- pre-treatments, general
- abrasion 1–3, 381
  - aerospace structures 41
  - anodizing 41, 49–50
  - autophoretic primers 57–8
  - carbon fibres 178
  - chromium containing agents 375, 376
  - conversion coatings 86–8, 120
  - copper 279–80, 371–2
  - corona discharge 384–5
  - corrosion inhibiting primers 390
  - degreasing metal 101–3
  - electrochemical of polymers 125–7, 382
  - filler surface 187
  - flame treatment 195–6, 381, 384
  - glass fibres 182–4
  - metal with silanes 463–9
  - PEEK 336
  - plasma 382, 385
  - rubber to metal bonding 421–2
  - sealant primers 393–4
  - solvent based 381, 384
  - study methods 383
  - surface contamination 81, 113
  - surface protection primers 389
  - thermal spray processes 541–2, 542–5
  - titanium 379–80
  - underwater adhesives 566–7
- Primary bonding at the interface** 60–1, 385–9
- Primers for adhesive bonding** 389–93
- Primers for sealants** 393–4
- primers, general
- autophoretic 57–8
  - corrosion inhibiting 390
  - etch 156, 196–7
  - paint 309–10
  - sealants 393–4
  - surface protection 387
  - titanium 380
- printed circuit boards 278
- probe tack test 367
- profilometers 409–10
- prosthodontics 20–1
- protheses 24
- PTFE pre-treatment 125–6, 372–3

- pull-out test 174  
pulse-echo testers 301–2  
pultrusion 172  
push-in test 174  
PVA 136–8, 158–9
- quality control 488  
quickstick test 368
- Radiation-cured adhesives 395–7**  
radio frequency welding 585  
RAIR spectroscopy 247–50
- Reaction-setting adhesives 397–9**  
classification 26  
and textiles 38  
reactive liquid polymer 551, 552, 555, 560, 561
- Release 399–400**  
*see also* mould adhesion and fouling
- Renewable sources of adhesives 400–2**
- Repair methods 402–5**  
reptation 341–4  
resistive implant welding 584  
resole adhesives 318–22, 489–90, 618–19  
resonance testers 299–300  
resorcinol–formaldehyde adhesives 614–15
- Rheological theory 405–6**  
rheometer 288  
rolling ball test 368  
rotospray unit 110
- Roughness and adhesion 407–8**  
roughness factor 204, 205–6, 595
- Roughness of surfaces 408–11**  
scanning electron microscopy 440
- Rubber fillers 411–14**
- Rubber to metal bonding –applications 414–17**
- Rubber to metal bonding –basic techniques 417–20**
- Rubber to metal bonding –pre-treatments 421–2**
- Rubber to metal bonding: processing effects 425–7**
- Rubber to metal bonding: testing 422–5**
- Rubber: tyre cord adhesion 427–9**
- Rubber-based adhesives 430–2**
- Rubber-based adhesives: compounding 432–7**
- Rubber-based adhesives: typical characteristics 437–8**
- rubbers  
acrylonitrile–butadiene 562  
CTBN 561  
finite element analysis 192–4  
and toughened adhesives 546–8, 550–2, 558  
*see also* nitrile rubber adhesives
- S–N plots 117  
sacrificial pre-treatment 566–8  
safety *see* health and safety  
scanning Auger microscopy 53, 54  
scanning electron micrographs 54, 55, 280, 440, 441
- Scanning electron microscope 130, 339–441**
- Scanning probe microscopy 441–3**  
scanning thermal microscopy 443  
scanning tunnelling microscopy 442
- scarf joints 166, 167–8  
Schallamach waves 212
- Scratch test 444**  
screen printing of adhesives 110  
scrim cloth 495
- Sealant joint design 444–8**
- Sealants 448–9**  
primers for 393–4  
selection 456–9
- Sealants in double glazing 449–51**
- Secondary ion mass spectrometry (SIMS) 451–3**  
secondary molecular bonds 61–2  
and contact angles 84
- Selection of adhesives 453–6**
- Selection of sealants 456–9**  
self-adhesion 103–4, 353, 482, 527–8  
self-etching primer, dentistry 22  
shear  
accelerated ageing 4  
crack propagation 498  
effect of contaminant 113–14  
pressure-sensitive tape 365–6  
shear lag model 492, 501–3  
shear modulus 574, 576–7
- Shear tests 459–62**  
napkin ring 291–2, 461–2  
pressure-sensitive adhesives 365–6  
resonance tester 299–300
- shoes 294, 331  
shrinkage of adhesive 250–1
- Silane adhesion promoters 462–3**  
chemical structure 391  
dentistry 20  
double glazing 450  
glass fibres 183–4  
hydrolysis 184  
IET spectra 241  
interfacial bonding 378–9  
metal pre-treatment 375, 463–6  
non-porous surfaces 393  
paint weathering 311
- Silanes as metal pre-treatments 463–6**  
silica 413
- Silicone adhesion 467–8**
- Silicone adhesives: addition cure 469–71**
- Silicone adhesives: condensation cure 471–3, 491**
- Silicone properties 473–5**  
silicone release agents 287  
silicone sealants 457
- Silicone structures 475–7**  
SIS thermoplastic rubber 364–5  
solubility parameters 74–5
- Solvent welding 75, 477–80**
- Solvent-based adhesives 481–3**  
classification 25–6  
compatibility 75  
historical perspective 29–30  
textiles 33, 34, 35
- solvents  
cleaners 101–2  
pre-treatment 381  
rubber-based adhesives 296, 436  
for solvent welding 75, 478–9

- specific heat capacity 539  
spin welding 590  
spinodal decomposition 560  
spreading coefficient 83, 593–6  
spring ball valve application 228  
standard deviation 487  
**Standards for adhesives and adhesion 483–5,**  
623–7  
starch 30, 33, 36, 306, 401  
**Statistics 485–7**  
steel  
  Boss coating system 541  
  galvanized 379  
  pretreatment 377–9  
  stainless 378  
  surface morphology 2  
**Step polymerization 489–91**  
  novalac resins 316  
  phenolic wood adhesives 613  
  polybenzimidadoles 328–9  
  polyimides 337–8  
  polyurethane adhesives 357  
  resole resins 319  
  silicone cure 471–3  
  urea-formaldehyde adhesives 600, 601  
stepped-lap joints 166  
**Stress distribution: beam on elastic**  
**foundation 491–4**  
**Stress distribution: bond thickness 494–6**  
**Stress distribution: mode of failure 496–9**  
**Stress distribution: Poisson's ratio 499–501**  
**Stress distribution: shear lag solution 501–3**  
**Stress distribution: stress singularities 503–5**  
stress rupture tests 115–16  
**Structural adhesives 505–8**  
structural bonds 119–20  
styrene-butadiene rubber (SBR)  
  compounding 434  
  and interfacial forces 18  
  sealants 448  
  textile use 32, 36  
surface  
  fractal nature 197, 199–200, 202–3  
  microstructure 282–3  
  polymers 524–5  
  roughness and fractals 203–6  
  and surface forces apparatus 523–4  
**Surface analysis 508–9**  
**Surface characterization by contact angles**  
  –metals 510–11  
**Surface characterization by contact angles**  
  –polymers 511–14  
surface contaminants and metals 141–3  
**Surface energy 514–17**  
  acid–base interactions 5–6  
  and contact angle 81, 510  
  and corona discharge treatment 89  
  critical surface tension 95, 511–12  
  interfacial roughness 407  
  interfacial tension 219  
  inverse gas chromatography 255–7  
  parameters and components 7–9  
  polymer–polymer adhesion 348, 351–2  
**Surface energy components 517–20**  
**Surface forces apparatus 520–4**  
**Surface nature of polymers 522–5**  
surface tension  
  and contact angle 83–4, 511  
  critical 94–6, 511–12  
  and surface energy 515  
surface texture *see* roughness  
syringe dispensers 107, 110  
**Tack 527–9**  
  autohesive 527–8  
  natural rubber adhesives 293  
  polyurethane adhesives 358  
  pressure-sensitive tape 367–8  
  rubber-based adhesives 432  
  strength 104  
  and transition temperature 217  
tackifier resins 529  
  EVA wood adhesives 608  
  nitrile rubbers 295  
  polychloroprene rubber 333  
  pressure-sensitive tape 364  
  rubber-based adhesives 432, 435  
tannins 614, 619  
tapered double cantilever beam 4–5  
technical gelatins 26  
**Tensile tests 529–31**  
**Testing of adhesives 531–3**  
  blister test 59–60  
  fracture approach 269–70  
  and fracture mechanics 208–11  
  multiple fragmentation 173  
  pull-out test 174  
  pulse-echo 301–2  
  push-in test 174  
  resonance (Fokker) test 299–301  
  shear tests 173, 459–62, 533–4  
  standards 483–4, 623–7  
  tensile tests 529–31, 534  
  *see also* peel tests; wedge test  
**Tests of adhesion 533–5**  
textiles  
  adhesive applications summarised 36–8  
  carpets 35, 36, 294  
  flocking 33, 36  
  lamination 34–5, 36  
  non-woven materials 32–3  
  pigment printing 35  
  seaming 35  
  sizing 33  
  tyres, belts and hose 33  
**Theories of adhesion 535–8**  
**Thermal analysis 538–40**  
**Thermal spray coatings used for adhesion 541–2**  
**Thermal spray processes 542–5**  
thermogravimetric analysis 538  
thick-lap shear test 460  
thickness of bond 494–6, 534  
thin films  
  inelastic electron tunnelling spectroscopy 238–42  
  infrared spectroscopy 247–50  
  measurements 134

- thin films (*continued*)  
 metallizing plastics 277–9  
 nitrile rubber lamination 296–7  
 plasma-polymerized coatings 322–5  
 scratch test 444  
 vacuum deposited 133, 386–7  
*see also* thermal spray
- threadlocking 45
- Tie layers** 72, **545–6**
- titanium  
 anodized layer 374  
 bonding with PEEK 336  
 plasma spray 541  
 polyimide-bonded joints 338, 339–40  
 polyquinoxaline-bonded joints 356  
 pre-treatment 379–80
- TMS rheometer 288
- Tof-SIMS 452, 453
- toluenediisocyanate 357
- Toughened acrylic adhesives** 26, **546–50**
- Toughened adhesives** 550–2  
 automotive applications 56
- Toughened epoxide adhesives** 552–5  
 surface fracture micrograph 441, 555
- Toughened epoxide adhesives: blend synergy** 555–6
- Toughened epoxide adhesives: particle formation prior to cure** 557–9
- Toughened epoxide adhesives: precipitation during cure** 559–63
- transmission electron microscope 127–9
- triadic Koch curve 197–8, 197–9, 200–3
- triethylenetetramine 491
- true adhesion 15
- Tyre cord adhesion** 427–9
- tyres 33, 318
- ultrasonic welding 591
- ultraviolet cured adhesives 395–7
- ultraviolet degradation 458, 471, 474
- Underwater adhesives** 565–9  
 urea–formaldehyde adhesives 490, 600–2, 618
- vacuum impregnation 172
- van der Waals forces 5–6, 61, 112, 260, 273–4
- variance 487
- Vasenin's equation 104
- vector percolation model 348–9, 351, 353
- vibration welding 590  
 wood bonding 615–17
- vinyl acetate 359
- vinyl ester resins 170
- Viscoelasticity** 571–5
- Viscoelasticity –time–temperature superposition** 575–8
- vulcanization 419, 427–9, 431, 435–6
- Washburn's equation 599
- water  
 ingress 4, 310, 579–80  
 underwater adhesives 566–9  
 and urea–formaldehydes adhesives 600  
*see also* weathering
- water break test 167
- water-based adhesives 26, 30
- water-vapour transmission rate 450–1
- WDX analysis 130
- Weathering of adhesive joints** 579–81
- Weathering tests** 581–2
- Wedge test** 4, 121, 534, **582–3**
- Welding plastics –electromagnetic radiation** 583–7
- Welding plastics –external heat source** 587–9
- Welding plastics –mechanical movement** 589–91
- Wetting and spreading** 592–4  
 and contact angle 79–80  
 spreading of a drop on solid surface 597–9  
 underwater adhesion 565–7
- Wetting and work of adhesion** 594–7
- Wetting kinetics** 597–600
- wheel applicator 228
- white reinforcement 413
- WLF equation 577–8
- Wood adhesives –aminoplastics** 600–3
- Wood adhesives –basics** 603–6
- Wood adhesives –hot melts** 606–8
- Wood adhesives –isocyanates/urethanes** 609–12
- Wood adhesives –phenolics** 612–15
- Wood bonding by vibration welding** 615–17
- Wood composites –adhesives** 617–19
- work of adhesion 5–7, 17–19, 24, 85, 217–18  
 and hydrogen bonding 230  
 and JKR theory 261–2  
 and surface energy components 518  
 wetting and spreading 593, 594–7
- work of cohesion 8, 17, 218, 518
- X-ray analysis 130
- X-ray photoelectron spectroscopy (XPS)** 621–2  
 aluminium 2
- Young's equation  
 and contact angle 79, 80, 84–5, 512  
 wetting 592, 596
- Young's modulus 529, 574

*With thanks to W. F. Farrington for compilation of this index.*