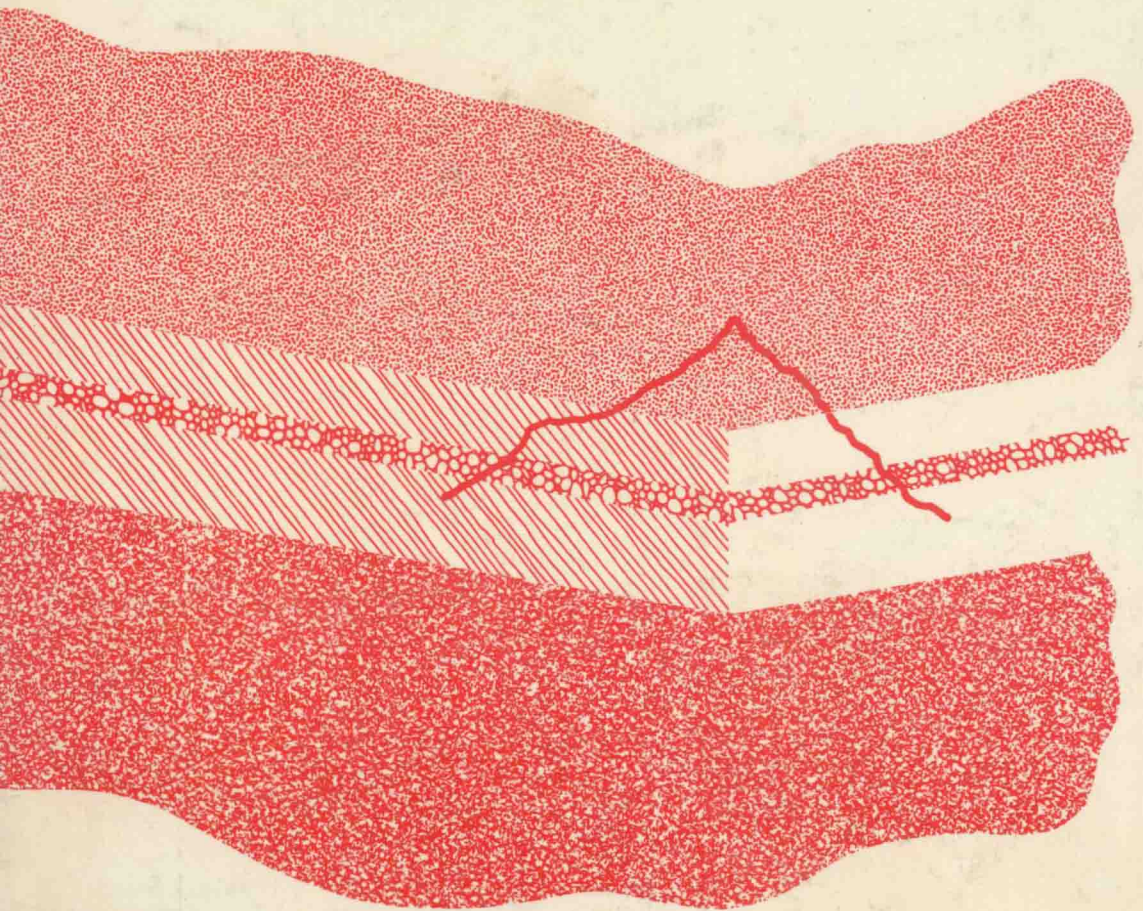

Adhesive Bonding



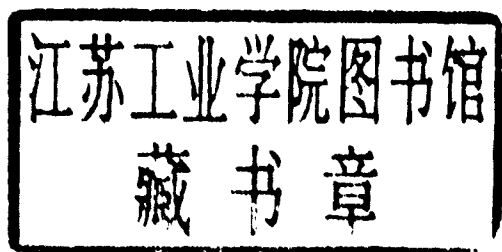
Edited by
Lieng-Huang Lee

Adhesive Bonding

Edited by

Lieng-Huang Lee

*Xerox Corporation
Webster, New York*



Plenum Press • New York and London

Library of Congress Cataloging-in-Publication Data

Adhesive bonding / edited by Lieng-Huang Lee.

p. cm.

Includes bibliographical references and indexes.

ISBN 0-306-43471-7

1. Adhesives. I. Lee, Lieng-Huang, date.

TP968.A27 1991

668'.3--dc20

90-15510

CIP

ISBN 0-306-43471-7

© 1991 Plenum Press, New York
A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher

Printed in the United States of America

Contributors

E. H. Andrews • Department of Materials, Queen Mary and Westfield College, University of London, London E1 4NS, England

Sung Gun Chu • Hercules Incorporated, Research Center, Wilmington, Delaware 19894

H. M. Clearfield • IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

Guy D. Davis • Martin Marietta Laboratories, Baltimore, Maryland 21227-3898

J. Thomas Dickinson • Department of Physics, Washington State University, Pullman, Washington 99164-2814

Jennifer A. Filbey • Finish Group, Hoechst Celanese, Charlotte, North Carolina 28232-2414.

Robert J. Good • Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

Rakesh K. Gupta • Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

Irvin M. Krieger • Center for Adhesives, Sealants, and Coatings, Case Western Reserve University, Cleveland, Ohio 44106

Raymond B. Krieger, Jr. • Engineering Materials Department, American Cyanamid Company, Havre de Grace, Maryland 21075

Lieng-Huang Lee • Webster Research Center, Xerox Corporation, Webster, New York 14580

Daniel Maugis • Laboratoire des Matériaux et Structures (UMR 113), CNRS-LCPC, 75732 Paris Cédex 15, France

D. K. McNamara • Martin Marietta Laboratories, Baltimore, Maryland 21227-3898

J. Dean Minford • Consultant, Hilton Head Island, South Carolina 29918

J. N. Reddy • The Center for Adhesive and Sealant Science and Department of Engineering Science and Mechanics, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Joseph L. Rose • Department of Mechanical Engineering, Drexel University, Philadelphia, Pennsylvania 19104

S. Roy • Engineering Materials Division, Southwest Research Institute, San Antonio, Texas 78228-0510

James P. Wightman • Center for Adhesive and Sealant Science and Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Preface

For several years, I have been responsible for organizing and teaching in the fall a short course on “Fundamentals of Adhesion: Theory, Practice, and Applications” at the State University of New York at New Paltz. Every spring I would try to assemble the most pertinent subjects and line up several capable lecturers for the course. However, there has always been one thing missing—an authoritative book that covers most aspects of adhesion and adhesive bonding. Such a book would be used by the participants as a main reference throughout the course and kept as a sourcebook after the course had been completed. On the other hand, this book could not be one of those “All you want to know about” volumes, simply because adhesion is an interdisciplinary and ever-growing field.

For the same reason, it would be very difficult for a single individual, especially me, to undertake the task of writing such a book. Thus, I relied on the principle that one leaves the truly monumental jobs to experts, and I finally succeeded in asking several leading scientists in the field of adhesion to write separate chapters for this collection. Some chapters emphasize theoretical concepts and others experimental techniques. In the humble beginning, we planned to include only twelve chapters. However, we soon realized that such a plan would leave too much ground uncovered, and we resolved to increase the coverage. After the book had evolved into thirty chapters, we started to feel that perhaps our mission had been accomplished. Originally we had thought to publish the entire project under the title *Fundamentals of Adhesion*; then it was deemed necessary to split a portion of it off into this, the second volume, *Adhesive Bonding*. Since these two volumes include chapters by many authors, some overlap is inevitable.

In the first volume, we focused on adhesion with or without the use of an adhesive, and we were chiefly concerned with mechanisms of bond formation. In this volume, we are interested in both bond-forming and bond-breaking processes. Since polymeric adhesives will be at the center of our discussions, we need to know their physical properties as well as their related measurements. After we apply an adhesive to an adherend, we must understand how to determine bond strengths. With data on hand, we should also learn how to analyze the test results and make certain predictions about the durability of adhesive bonds. Though the entire process sounds rather difficult, we hope that readers will find this volume of benefit.

Thus in this volume we shall concentrate on the fundamentals of bonding with the aid of adhesives. Chapter 1 reviews the mechanisms of polymer adhesion and summarizes significant findings from the first volume. This introduction should serve as a bridge between the two volumes. Chapters 2 and 3 introduce rheological aspects of adhesives and adhesion. They are followed by Chapters 4 and 5, discussing measurements of rheological and dynamic properties of adhesives and sealants. Chapters 6 and 7 focus our attention on adherends by showing us new methods of characterizing them and related interfaces. Then Chapter 8 delineates various methods of surface preparation for adherends. Chapter 9 reviews various ways to prepare and determine durable adhesive joints. Chapter 10 serves to introduce new methods in measuring

structural adhesive bonds and durability. The following chapters are more theoretical. Chapters 11 and 12 describe somewhat different views on the application of fracture mechanics to adhesive bonding. Chapter 13 is intended to treat some basic concepts about finite-element analysis and its applications to adhesive joints. Chapter 14 illustrates the physics of fracture in terms of fracto-emission. Finally, the last chapter leads us to applications of nondestructive testing (NDT) to adhesive joints. NDT is one of the important test methods for future adhesive and composite technology.

A book of this format can still fail in not covering the subject broadly and deeply enough. Regarding the breadth of the book, we deliberately omitted most of the organic chemistry and formulations of adhesives and sealants because there are other available books dealing with those subjects; two related books edited by me have been published in the last several years: *Adhesive Chemistry: Developments and Trends* (Plenum Press, 1984) and *Adhesives, Sealants, and Coatings for Space and Harsh Environments* (Plenum Press, 1988). Regarding the depth of the book, one may still object that none of the subjects has been treated sufficiently thoroughly. Yet, since this is only an introductory text, it is not our intention to discuss each subject at length. In fact, each chapter could have readily been expanded into a separate book, had that been the goal.

For better readability, all of the chapters have been refereed and separate nomenclature lists are included at the end of most of the chapters. I should like to take this opportunity to thank the many referees for their efforts. I also wish to thank all of the authors for their fine cooperation and patience. Finally, I sincerely appreciate the support of the Webster Research Center of Xerox Corporation in helping me to complete this task, and the assistance of Mr. F. G. Belli and Ms. E. Jonas of the Technical Information Center in preparing the indexes.

Lieng-Huang Lee

Adhesive Bonding

Contents

1. Recent Studies in Polymer Adhesion Mechanisms

Lieng-Huang Lee

1. Introduction	1
2. Diffusion Mechanism	2
2.1. Viscoelastic Properties of Polymers	2
2.2. Theories of Self-Diffusion	2
2.3. Interdiffusion, Healing, and Welding	4
2.4. Tack and Green Strength	8
2.5. Fractals at an Interface	8
3. Lifshitz–van der Waals Interactions	9
3.1. Partial Wetting of Liquid ($\theta_e > 0$)	9
3.2. Complete Wetting of Liquid ($\theta_e \rightarrow 0$)	11
3.3. Complete Wetting of Polymer Melt	14
3.4. Dry Spreading of Polymer Solution	14
4. Molecular Interactions	15
4.1. Enthalpy of the Acid–Base Interaction	15
4.2. Work of Adhesion (The Acid–Base Component)	15
4.3. Total Work of Adhesion	16
4.4. Extension of the Hard–Soft Acid–Base (HSAB) Principle to Solid Adhesion	16
5. Adsorption Mechanism—A Polymer at an Interface	17
5.1. Adsorption Profile	17
5.2. Loops, Trains, and Tails	18
5.3. Surface Energetics of Adsorption	18
5.4. Mean Field versus Scaling Theories	19
5.5. Role of Adsorption in Adhesion	19
6. Mechanical Interlocking Mechanism	19
7. Chemical Bonding Mechanism	20
8. Electrostatic Mechanism	20
8.1. Direct Evidence of the Electrical Double Layer	20
8.2. Work of Electrical Double Layer versus Peel Work	21
8.3. Elimination of the Electrical Double Layer by Surface Modification	21
8.4. Electrostatic Adhesion Between Anion and Cation Pairs	21
8.5. Particle Adhesion	22

9. Summary	23
Nomenclature	24
References	26
2. Flow Properties of Adhesives	
<i>Irvin M. Krieger</i>	
1. Introduction	31
2. Rheometry	32
2.1. Steady-State Rheometry	34
2.2. Thixotropy	36
3. Linear Viscoelasticity	36
3.1. Oscillatory Measurements	36
3.2. Transient Analysis	37
3.3. Comparison of Transient and Dynamic Moduli	38
4. Rheology of Colloids	38
4.1. Intrinsic Viscosity	38
4.2. Viscosity versus Concentration	39
4.3. Non-Newtonian Effects	40
4.4. Dimensional Analysis	41
5. Polymer Systems	43
Nomenclature	44
References	45
3. The Coupling of Interfacial, Rheological, and Thermal Control Mechanisms in Polymer Adhesion	
<i>Robert J. Good and Rakesh K. Gupta</i>	
1. Introduction	47
2. General Model for Separation of Thermoplastic Polymers from Solids	52
2.1. Elongational Work	53
2.2. Surface Work in a Real Separation Process	54
2.3. The Processes as Alternatives	56
3. Application of the Isothermal Theory	61
4. Thermal Control Mechanisms in Adhesion: Adiabatic Theory	64
4.1. Pressure-Sensitive Adhesives	64
4.2. Fracture of Polymers with High T_g Values	65
5. Application to Adhesion of High- T_g Polymers to Solids	66
6. Discussion and Summary	70
Acknowledgment	71
Nomenclature	71
References	72

4. Extensional Rheometry of Polymer Melts

Rakesh K. Gupta

1. Introduction	75
2. Kinematics of Extensional Flows	76
3. The Stress Tensor in Uniaxial Extension	78
4. The Extensional Viscosity	79
5. Uniform Stretching of Polymer Melts	80
5.1. Sample Length Variable During the Test, Constant Stretch Rate	81
5.2. Sample Length Variable During the Test, Constant Stress	82
5.3. Constant Sample Length Experiments	83
5.4. Experimental Results	84
6. Nonuniform Stretching of Polymer Melts	86
6.1. Melt Spinning of Fibers	86
6.2. Converging Flow into a Capillary	87
6.3. Other Methods of Stretching Polymer Melts	88
7. Constitutive Equations	88
8. Conclusions	91
Acknowledgment	92
Nomenclature	92
References	93

5. Dynamic Mechanical Properties of Pressure-Sensitive Adhesives

Sung Gun Chu

1. Introduction	97
2. Dynamic Mechanical Testing	98
3. Dynamic Mechanical Properties of Elastomers	102
3.1. Natural Rubber	103
3.2. Styrene-Butadiene Rubber (SBR)	104
3.3. Block Copolymers	106
4. Dynamic Mechanical Properties of Tackifying Resins	108
5. Dynamic Mechanical Properties of Commercial PSA	108
6. Elastomer-Resin Blends	115
6.1. Natural Rubber and SBR	115
6.2. Block Copolymers	117
7. Pressure-Sensitive Adhesive Testing Methods	122
8. Relation Between the Dynamic Mechanical Properties and PSA Performance	124
9. Conclusions	137
Acknowledgments	137
Nomenclature	137
References	137

6. Characterization of Surfaces

Guy D. Davis

1. Introduction	139
2. Surface-Sensitive Techniques	141
2.1. X-ray Photoelectron Spectroscopy	141
2.2. Auger Electron Spectroscopy/Scanning Auger Microscopy ...	144
2.3. Comparison of Techniques	148
3. Data Analysis	148
3.1. Quantification	148
3.2. Chemical-State Information	153
3.3. Depth-Distribution Information	155
3.4. Surface-Behavior Diagrams	161
4. Applications to Adhesive Bonding	162
4.1. Failure Analysis	162
4.2. Hydration of Phosphoric-Acid-Anodized Aluminum	165
4.3. Adsorption of Hydration Inhibitors	167
5. Conclusions	169
Acknowledgments	169
Nomenclature	169
References	170

7. Surface Characterization in Polymer/Metal Adhesion

Jennifer A. Filbey and James P. Wightman

1. Introduction	175
2. Scanning Electron Microscopy (SEM)	176
3. Scanning Transmission Electron Microscopy (STEM)	184
4. Surface Reflectance Infrared Spectroscopy (SRIRS)	185
5. Inelastic Electron Tunneling Spectroscopy (IETS)	190
6. Auger Electron Spectroscopy (AES)	190
7. Ion Scattering Spectroscopy (ISS)	192
8. Secondary Ion Mass Spectroscopy (SIMS)	195
9. X-ray Photoelectron Spectroscopy (XPS)	196
10. Summary	199
Acknowledgments	200
Nomenclature	200
References	201

8. Adherend Surface Preparation for Structural Adhesive Bonding

H. M. Clearfield, D. K. McNamara, and Guy D. Davis

1. Introduction	203
1.1. High-Resolution Scanning Electron Microscopy	203
1.2. Surface Analysis	205

2. Aluminum Adherends	205
2.1. Processing	205
2.2. Oxide Morphology and Chemistry	206
2.3. Oxide Growth	212
2.4. Durability	213
3. Titanium Adherends	217
3.1. Processing	218
3.2. Oxide Morphology and Chemistry	219
3.3. Durability	221
4. Steel Adherends	226
4.1. Cleaning as a Pretreatment for Steel	226
4.2. Chemical Etches	227
4.3. Conversion Coating Treatments	231
4.4. Bonding of Steel: An Epilogue	233
5. Summary	234
Acknowledgments	234
Nomenclature	234
References	235

9. Durability Evaluation of Adhesive Bonded Structures

J. Dean Minford

1. Introduction	239
2. Chemical and Physical Attributes of Adhesion and Durability	240
3. Failure Site Variabilities	241
4. Bondline Characteristics Affecting Bond Performance	242
4.1. Modulus of Elasticity and Coefficient of Thermal Expansion	242
4.2. Interfacial Imperfections	243
4.3. Heat Curing	244
4.4. Pressure	244
4.5. Mechanical Energy	245
4.6. Cohesive versus Adhesive Failure Observations	245
5. Characteristics of Metal Adherend Surfaces	248
6. Effect of Water on Adhesive-Bonded Structures	251
7. Bond-Joint Durability as a Function of Surface Pretreatment	254
7.1. General Relationships	254
7.2. Effect of Specific Surface Pretreatments	254
8. Test Environments for Determining the Durability of Bonded Structures	267
8.1. Static Heat Aging or Cryogenic Exposures	269
8.2. Immersion Exposures in Water	270
8.3. Varying Humidity Exposures	272
8.4. Wet, Freeze, and Thaw Cyclic Exposures	272
8.5. Continuous or Intermittent Saltwater Immersion or Spray Exposure	274

8.6. Natural Atmospheric Exposures	275
8.7. Simultaneous Stress and Environmental Exposures	276
8.8. Crack Initiation and Propagation with Environmental Exposures	279
9. Durability of Structural Joints Assembled with Combinations of Joining Procedures	281
10. Durability of Dissimilar Materials Structures	282
11. Conclusions	283
References	284

10. Testing Structural Adhesives for Properties Necessary for Stress Analysis

Raymond B. Krieger, Jr.

1. Introduction	291
2. Early Tests for Adhesive Strength	291
3. A Fundamental Stress Analysis for Bonded Metal Structure	292
4. KGR-1, An Extensometer for Measuring Adhesive Shear Strain versus Stress	294
4.1. Linear Limit (LL)	296
4.2. Knee (KN)	297
4.3. Ultimate Strength (UL)	297
5. KGR-2, An Extensometer for Measuring Adhesive Shear Strain in Bonded Structure	297
6. The Relationship Between Adhesive Shear Strain Properties and Adhesive Performance in an Actual Structure	298
7. A Specimen Configuration for Testing Adhesives in Fatigue and Creep	301
References	302

11. Adherence and Fracture Mechanics

Daniel Maugis

1. Introduction	303
2. Adherence of Two Elastic Solids in Contact	303
2.1. The Griffith Criterion for Equilibrium Contacts	304
2.2. Stability of Equilibrium and Adherence Force	306
2.3. The Griffith, Barenblatt, and Dugdale Models of Crack	307
2.4. Adherence of Punches as an Example	309
2.5. Influence of Prestresses	314
3. Adherence due to Liquid Bridges	315
4. Adherence of Viscoelastic Solids	317
4.1. Tackiness	319
4.2. Viscoelastic Losses and Negative Resistance Branch	319

4.3. Velocity Jumps and Stick–Slip	320
5. Viscous Drag and Limited Rate of Transport	324
6. Dwell-Time Effects	325
7. The Problem of the Threshold Value G_0	327
Nomenclature	331
References	332

12. Generalized Fracture Mechanics Approach to Adhesion

E. H. Andrews

1. Introduction	337
2. Fracture Mechanics	337
3. Nonlinear, Finite-Strain Fracture Mechanics	339
4. Shortcomings of Conventional Fracture Mechanics	341
5. Generalized Fracture Mechanics	342
6. Putting Generalized Fracture Mechanics to Work	344
7. Adhesion of Crosslinked Elastomers	345
8. Structural Adhesives	348
9. Moisture Attack on Interfaces	349
10. Soft-Machine Peel Testing	352
11. Conclusion	355
Nomenclature	356
References	357

13. Finite-Element Analysis of Adhesive Joints

J. N. Reddy and S. Roy

1. Introduction	359
1.1. General Comments	359
1.2. Background	360
2. Kinematic Description	366
2.1. Introduction	366
2.2. Incremental Equations of Motion	366
2.3. Finite-Element Model	369
3. Viscoelastic Formulation	370
3.1. Introduction	370
3.2. One-Dimensional Model	370
3.3. Two-Dimensional Formulation	373
3.4. Finite-Element Model	374
3.5. Diffusion Model	375
4. Sample Problems	376
4.1. Preliminary Comments	376
4.2. Geometric Nonlinear Analysis	377
4.3. Linear Viscoelastic Analysis	377
4.4. Analysis of a Thick Adherend Specimen	379

4.5. Nonlinear Viscoelastic Analysis	381
4.6. Nonlinear Viscoelastic Analysis of a Model Joint	385
4.7. Analysis of a Single Lap Laminated Composite Joint	385
4.8. Moisture Diffusion in a Butt Joint	386
4.9. Analysis of a Bonded Cantilever Beam	388
5. Summary	390
Acknowledgments	391
Nomenclature	391
References	392
14. Fracto-Emission from Adhesive Failure	
<i>J. Thomas Dickinson</i>	
1. Introduction	395
2. Experimental	397
3. Results and Discussion	398
3.1. Filled versus Unfilled Epoxy	398
3.2. Chaotic/Fractal Nature of phE and Fracture Surface of Epoxy	400
3.3. NE from Epoxy	404
3.4. phE from Embedded Interfaces	408
3.5. phE from Peeling Pressure-Sensitive Adhesives	411
4. Conclusions	419
Acknowledgments	419
Nomenclature	419
References	420
15. Ultrasonic Nondestructive Evaluation Technology for Adhesive Bond and Composite Material Inspection	
<i>Joseph L. Rose</i>	
1. Introduction	425
2. Background	426
2.1. NDT Techniques in General	426
2.2. Literature Survey	426
2.3. Physical Model Considerations	428
3. Ultrasonic Physics	432
3.1. Introduction	432
3.2. Ultrasonic Wave Generation and Wave Velocity	432
3.3. Dispersion	433
3.4. Reflection Factor	434
3.5. Wave Refraction	435
3.6. Absorption	435
3.7. Ultrasonic Field Analysis	436

3.8. Resolution	437
3.9. On the Signal-to-Noise Ratio	438
4. Feature-Based Systems and Advanced Analysis	438
References	447
About the Contributors	449
Author Index	453
Subject Index	465