Polymer Interface and Adhesion

SOUHENG WU

E. I. du Pont de Nemours & Company
Wilmington, Delaware

MARCEL DEKKER, INC. New York and Basel

Contents

Preface
Acknowledgments

1. INTERFACIAL THERMODYNAMICS 1

1.1 Formulation of Interfacial Thermodynamics 1
1.2 Work of Adhesion and Work of Cohesion 4
1.3 Interfacial and Hydrostatic Equilibrium 5
1.4 Effect of Curvature on Vapor Pressure and Surface Tension 7
1.5 Spreading Pressure and Spreading Coefficient 8
1.6 Contact Angle Equilibrium: Young Equation 11
1.7 Contact Angle Hysteresis 15
References 26

2. MOLECULAR INTERPRETATIONS 29

2.1 Microscopic Theories of van der Waals Forces 30
2.2 Additivity and Fractional Contributions of Various Types of Molecular Forces 40
2.3 Approximations for Unlike Molecules 42
2.4 Lennard-Jones Potential Energy Function 44
2.5 Attraction Between Macroscopic Bodies 47
2.6 Macroscopic Theory of van der Waals Forces: The Lifshitz Theory 54
References 62

3. INTERFACIAL AND SURFACE TENSIONS OF POLYMER MELTS AND LIQUIDS 67

3.1 Surface Tensions of Polymer Melts and Liquids 67
3.2 Interfacial Tensions Between Polymers 96
References 129

4. CONTACT ANGLES OF LIQUIDS ON SOLID POLYMERS 133

4.1 Equilibrium Spreading Pressure 133
4.2 Spreading Coefficient 139
4.3 Effect of Temperature on Contact Angle 139
4.4 Effect of Primary and Secondary Transitions 147
4.5 Contact Angle and Heat of Wetting 148
4.6 Polarity of Liquids 148
4.7 Prediction of Contact Angles 152
4.8 Effect of Solute Adsorption on Contact Angle 152
4.9 Tabulation of Equilibrium Contact Angle 157
4.10 Distortion of Liquid Surfaces: Marangoni Effect 161
4.11 Spreading of Partially Submerged Drops 164
References 165

5. SURFACE TENSION AND POLARITY OF SOLID POLYMERS 169

5.1 Determination of Surface Tension and Polarity 169
5.2 Surface Tension and Polarity of Organic Pigments 198
5.3 Constitutive Effect on Surface Tension 201
5.4 Morphological Effect on Surface Tension 201
5.5 Effects of Additives, Polymer Blends, Copolymers, Conformation, and Tacticity on Surface Tension 209
References 211

6. WETTING OF HIGH-ENERGY SURFACES 215

6.1 Introduction 215
6.2 Spreading on High-Energy Surfaces 219
6.3 Effect of Water and Organic Contaminations 222
6.4 Kinetics of Surface-Energy Variation 229
References 231

7. DYNAMIC CONTACT ANGLES AND WETTING KINETICS 235

7.1 Introduction 235
7.2 Kinetics of Spontaneous Motion 236
7.3 Kinetics of Forced Motion 247
References 254

8. EXPERIMENTAL METHODS FOR CONTACT ANGLES AND INTERFACIAL TENSIONS 257

8.1 Measurements of Contact Angles 257
8.2 Measurements of Interfacial and Surface Tensions of Polymer Liquids and Melts 266
References 274

9. MODIFICATIONS OF POLYMER SURFACES: MECHANISMS OF WETTABILITY AND BONDABILITY IMPROVEMENTS 279

9.1 Chemical Treatments 280
9.2 Flame and Thermal Treatments 296
9.3 Plasma Treatments 298
9.4 Photochemical Treatments 322
9.5 Crystalline Modifications of Polymer Surfaces 323
9.6 Miscellaneous Modifications 327
References 328

10. ADHESION: BASIC CONCEPT AND LOCUS OF FAILURE 337

10.1 Definitions 337
10.2 Basic Concept of Adhesive Bond Strength 338
10.3 Locus of Failure 344
References 354

11. FORMATION OF ADHESIVE BOND 359

11.1 Elementary Processes in Adhesive Bond Formation 359
11.2 Wetting and Adhesion 360
11.3 Diffusion and Adhesion 380
11.4 Chemical Adhesion 406
11.5 Mechanical Adhesion 434
References

12. WEAK BOUNDARY LAYERS 449

12.1 Weak-Boundary-Layer Theory 449
12.2 Examples of Weak Boundary Layers 450
12.3 Critique of Weak-Boundary-Layer Theory 456
References 460

13. EFFECT OF INTERNAL STRESS ON BOND STRENGTH 465

13.1 Shrinkage of a Coating Adhering to a Substrate 467
13.2 Free Thickness Contraction in a Butt Joint 470
13.3 No Thickness Contraction in a Sandwich Structure 472
13.4 No Thickness Contraction in a Long, Narrow Adhesive Layer in an Annulus 472
References 473

14. FRACTURE OF ADHESIVE BOND 475

Part I. Fundamentals of Fracture Mechanics 475

14.1 Linear Elastic Fracture Mechanics 476
14.2 Local Plastic Flow 484
14.3 Generalization of Flaw Theory to Viscoelastic Materials: Rivlin and Thomas Theory 486
14.4 Properties of Fracture Energy 488

Part II. Analysis and Testing of Adhesive Bonds 497

14.5 Tensile Tests (Butt Joints) 497
14.6 Shear Tests (Lap Joints) 510
14.7 Peel Tests (Peel Joints) 530
14.8 Cantilever Beam Tests 555
14.9 Other Fracture Energy Tests 560
References 563

15. CREEP, FATIGUE, AND ENVIRONMENTAL EFFECTS 571

Part I. Creep and Fatigue of Adhesive Joints 571

15.1 Creep Fracture 572
15.2 Fatigue Fracture 579

Part II. Environmental Effects 586

15.3 Spontaneous Separation 589
15.4 Effect of Interfacial Chemical Bonds 593
15.5 Stress Corrosion Cracking and Fatigue in Wet Environment 603
References 609

Appendix I: Calculation of Surface Tension and Its Nonpolar and Polar Components from Contact Angles by the Harmonic-Mean and the Geometric-Mean Methods 613

Appendix II: Unit Conversion Tables 619

Index 621