

Contents

Preface *xv*

Acknowledgments *xvii*

List of Most Important Symbols and Abbreviations *xix*

1	Introduction	1
1.1	Scope	1
1.2	The Importance of Polymer Coatings	2
1.3	The General Constitution of Polymer Coatings	5
	1.3.1 Binders and Crosslinkers	6
	1.3.2 Pigments and Fillers	8
	1.3.3 Additives	12
	1.3.4 Solvents	12
1.4	Coating Requirements	14
1.5	Outline and Approach	15
	References	16
	Further Reading	16
2	Polymers and Network Characteristics	19
2.1	Polymers	19
	2.1.1 Polymer Conformations	22
	2.1.2 Entanglements	23
	2.1.3 Crystallinity	24
	2.1.4 Amorphous Polymers	26
2.2	Polymer Formation	30
	2.2.1 Step-growth Polymerization	31
	2.2.2 Branching and Gelation	33
	2.2.3 Limits to the Preparation of Branched Polymers	36
	2.2.4 Chain-growth Polymerization	38
2.3	Polymer Networks	41
2.4	Final Remarks	45
	References	45
	Further Reading	46

3	Thermoset Resins	47
3.1	Petro-based Thermoset Resins	47
3.2	Epoxy Systems	47
3.3	Acrylates and Acrylics	51
3.4	Isocyanates	53
3.5	Polyurethanes	55
3.6	Polyesters	56
3.7	Renewable Raw Materials	57
3.8	Drying Oils	63
3.9	Alkyds	65
	References	68
	Further Reading	69
4	Basic Coating Formulations	71
4.1	Coating Compositions in General	71
4.2	Solventborne Formulations	72
4.2.1	Solventborne High Solids Formulations	75
4.2.2	Chemistries of Solventborne High Solids Formulations	80
4.3	Waterborne Formulations	85
4.3.1	Chemistries of Waterborne Formulations	90
4.3.2	Challenges and Applications of Waterborne Formulations	93
4.4	Radiation Curing Formulations	96
4.4.1	Photoinitiators	97
4.4.2	Chemistries of Radiation Curing Formulations	99
4.4.3	Chemistries of Powder Coating Formulations	103
4.4.4	Pros and Cons of Radiation Curing	105
4.5	Final Remarks	106
	References	108
	Further Reading	108
5	Additives and Particulates	109
5.1	Types of Additives	109
5.2	Thickeners	110
5.2.1	Inorganic Thickeners	110
5.2.2	Organic Thickeners	112
5.3	Surface Active Agents	116
5.3.1	Wetting and Dispersing Agents	117
5.3.2	Antifoaming Agents	117
5.3.3	Adhesion Promoters	118
5.4	Surface Modifiers	120
5.5	Leveling and Coalescing Agents	120
5.6	Catalytically Active Additives	121
5.6.1	Dryers	122
5.6.2	Other Catalysts	123
5.7	Special Effect Additives	128
5.8	Particulates	130

References 133
Further Reading 134

6 Application Methods 135

- 6.1 Conventional Deposition Techniques 135
 - 6.1.1 Brushing and Rolling 135
 - 6.1.2 Spraying 136
- 6.2 Laboratory and Industrial Methods 138
 - 6.2.1 Doctor Blade Coating 138
 - 6.2.2 Spin Coating 139
 - 6.2.3 Dip Coating 141
- 6.3 Powder Coating 142
- 6.4 An Example: Automotive Coatings 147
 - 6.4.1 Electrodeposition 147
 - 6.4.2 The Automotive Coating Buildup 150
- 6.5 Network Formation Assessment 151
 - References 152
 - Further Reading 152

7 Physical–Chemical Aspects 155

- 7.1 Intermolecular and Mesoscopic Interactions 155
 - 7.1.1 Intermolecular Interactions 155
 - 7.1.2 Mesoscopic Interactions: Continuum Aspects 159
 - 7.1.3 Lifshitz Theory 164
 - 7.1.4 The Derjaguin Approximation 166
 - 7.1.5 Mesoscopic Interactions: Molecular Aspects 167
- 7.2 Polymer Solubility 170
- 7.3 Interfacial Aspects 173
 - 7.3.1 Surface Thermodynamics 173
 - 7.3.2 Representative Behavior 178
 - 7.3.3 Wetting of Ideal Surfaces 181
 - 7.3.4 Estimating Surface Helmholtz Energy 184
 - 7.3.5 Wetting of Real Surfaces 189
- 7.4 Dispersions 193
- 7.5 Emulsions 196
 - 7.5.1 Basic Types of Emulsions 196
 - 7.5.2 The HLB Concept 198
- 7.6 Coagulation Kinetics 202
 - 7.6.1 Unhindered Coagulation 202
 - 7.6.2 Hindered Coagulation 204
- 7.7 Self-assembly 207
 - 7.7.1 SCF Computations 207
 - 7.7.2 An Example: Surfactant Modeling 209
 - 7.7.3 Another Example: Fluorine Segregation 212
- 7.8 Final Remarks 213
 - References 213
 - Further Reading 219

8	Chemical and Morphological Characterization	221
8.1	The Need for Characterization	221
8.2	IR and Raman Spectroscopy	222
8.3	NMR	227
8.4	Functional Group Analysis	236
8.5	XPS, SIMS, and LEIS	239
8.6	SEC	241
8.7	MALDI-MS	242
8.8	XRD	245
8.9	Optical Microscopy	250
8.9.1	Phase Contrast Microscopy	253
8.9.2	Fluorescence Microscopy	254
8.9.3	Confocal Scanning Microscopy	254
8.9.4	Polarized Light Microscopy	255
8.10	Electron Microscopy	256
8.10.1	TEM	256
8.10.2	SEM	259
8.10.3	STEM	260
8.10.4	Sample Preparation and Related Issues	260
8.11	Surface Probe Microscopy	262
8.12	Thickness and Beyond	265
8.13	Final Remarks	266
	References	266
	Further Reading	271
9	Thermal and Mechanical Characterization	273
9.1	Thermal Characterization	273
9.1.1	DSC	273
9.1.2	TGA	277
9.2	Permeability-Diffusivity-Solubility Analysis	278
9.3	Mechanical Constitutive Behavior	285
9.3.1	Analogous Models	288
9.3.2	Generalization: The Boltzmann Superposition Principle	291
9.3.3	Dynamic Response	293
9.3.4	The Time-Temperature Equivalence	296
9.3.5	The Free Volume and Other Approaches	297
9.4	A Brief Review of Experimental Data	300
9.4.1	Local and Cooperative Processes	301
9.4.2	Chain Motion	303
9.4.3	Mechanisms in Partially Crystalline Materials	306
9.5	Mechanical Characterization	307
9.5.1	DMTA	307
9.6	Hardness	312
9.6.1	Vickers, Knoop, Berkovich, and Brinell Hardness	312
9.6.2	Nanoindentation	314
9.6.3	Estimating the Stress-Strain Curve	315
9.6.4	Empirical Hardness Tests	316

9.7	Internal Stress Analysis	317
9.8	Adherence	319
9.8.1	Thermodynamic Considerations	319
9.8.2	Thermomechanical Considerations: Monoliths	323
9.8.3	Thermomechanical Considerations: Bimaterials	330
9.8.4	Coating Adherence	334
9.8.5	Testing Coating Adherence	337
9.8.6	Practical Tests	341
9.9	Final Remarks	342
	References	342
	Further Reading	345
10	Rheological Aspects	347
10.1	The Importance of Rheology	347
10.2	Rheological Characterization	348
10.2.1	Hydrodynamic Interactions	352
10.2.2	Dissolvable Polymers	359
10.3	Rheological Control of Paints	362
10.3.1	Powder Coatings	362
10.3.2	Thickening in Waterborne Paints	363
10.4	Viscosity of Paints During Curing	366
	References	368
	Further Reading	370
11	Appearance	371
11.1	Defects	371
11.2	The Characterization of Color	379
11.2.1	Light Sources	380
11.2.2	Color Sensing, Perception, and Quantification	381
11.2.3	Scattering, Absorption, and Color	384
11.2.4	Addition and Subtraction Systems	387
11.2.5	Color Tolerancing	391
11.3	The Characterization of <i>Feel</i> or Haptic Property	393
11.3.1	QDA of Haptic Coatings: An Example	394
	References	397
	Further Reading	398
12	Electrically Conductive Coatings	399
12.1	Typical Applications	399
12.2	Electrical Conductivity Measurements	401
12.3	Intrinsically Conductive Polymers	403
12.3.1	Some Conductivity Theory	406
12.3.2	Simple Band Theory	407
12.3.3	Doping	413
12.3.4	Hopping	416
12.4	An Example: P3HT/PCBM Photovoltaics	418
12.5	Conductive Composites	423

12.5.1	A Glimpse of Percolation Theory	423
12.5.2	Other Approaches	428
12.5.3	The Influence of Aspect Ratio	430
12.5.4	Conductive Particles	431
12.6	Some Examples of Conductive Composite Coatings	434
	References	438
	Further Reading	441
13	Marine Anti-fouling Coatings	443
13.1	Marine Biofouling	443
13.2	Evolution of Marine Coatings toward Green Anti-fouling Approaches	445
13.3	Principles for Preventing Adhesion or Promoting Detachment of Biofoulants	448
13.4	Nontoxic, Non-biocide-release Anti-fouling Coatings	451
13.4.1	Detachment of Biofoulants	451
13.4.1.1	Silicone-based Materials	453
13.4.1.2	Fluorine-based Materials	458
13.4.1.3	Combined Fluorine–Silicone-based Materials	461
13.4.2	Preventing Attachment of Biofoulants	462
13.4.2.1	PEG-based Materials	463
13.4.2.2	Self-assembled Monolayers	465
13.4.2.3	Other Approaches	466
13.5	Recent and Future Approaches	469
13.5.1	Amphiphilic Approach	469
13.5.2	Topographic Approach	472
13.6	Final Remarks	475
	References	475
	Further Reading	479
14	Self-replenishing and Self-healing Coatings	481
14.1	Self-healing and Self-replenishing: Scope and Limitations	481
14.2	Damage Recovery on Different Length Scales: Preemptive Healing	482
14.3	Approaches to Self-healing Coatings	486
14.3.1	Encapsulated Liquid Binders and Particles	487
14.3.2	Deformation and Recovery in Networks	489
14.3.3	Stress Relaxation in Reversible Networks	493
14.3.4	Reversible Covalent Networks	498
14.4	Industrial Practice	502
14.5	Approaches to Self-replenishing Coatings	504
14.5.1	Barrier and Corrosion Protection	505
14.5.2	Interfacial Bonding Between Dissimilar Materials	506
14.6	Self-replenishing Low Surface Energy Coatings	508
14.6.1	Low Surface Energy (Hydrophobic) Polymeric Coatings	509
14.6.2	Time Recovery of the Surface Self-replenishing	514

14.6.3	Surface-structured Superhydrophobic Polymeric Coatings	515
14.6.4	Further Remarks	521
14.7	Scenarios for Further Options	522
14.7.1	Residual Network Reactivity	522
14.7.2	Segregation of Interactive Chain Ends	523
14.7.3	Multilayer and Graded Coatings	524
14.8	Final Remarks	524
	References	525
	Further Reading	531
15	What's Next	533
15.1	Generic Problems and Challenges	533
15.2	What Else?	535
15.3	What's Next?	537
	References	538
Appendix A: Units, Physical Constants, and Conversion Factors		541
	Basic and Derived SI Units	541
	Physical Constants	541
	Conversion Factors for Non-SI Units	542
	Prefixes	542
	Greek Alphabet	542
	Standard Values	543
Appendix B: Data		545
	Index	549