

## Contents

**Preface** XV

**List of Contributors** XVII

<b>1</b>	<b>Introduction</b>	<b>1</b>
	<i>Raju Thomas, Christophe Sinturel, Sabu Thomas, and Elham Mostafa Sadek El Akiaby</i>	
1.1	Epoxy Resin – Introduction	1
1.2	Cure Reactions	1
1.3	Curing Agents	2
1.3.1	Catalytic Cure	3
1.3.2	Co-reactive Cure	3
1.3.2.1	Primary and Secondary Amines	3
1.3.2.2	Mercaptans	5
1.3.2.3	Isocyanates	5
1.3.2.4	Carboxylic Acids	5
1.3.2.5	Acid Anhydrides	5
1.4	Different Curing Methods	7
1.4.1	Thermal Curing	7
1.4.2	Microwave Curing	8
1.4.3	Radiation Curing	10
1.4.3.1	Electron Beam Curing	10
1.4.3.2	Gamma Ray Irradiation	11
1.5	Curing of Epoxy Resins: Structure–Property Relationship	12
1.6	Toughening of Epoxy Resin	13
1.6.1	Different Toughening Agents	13
1.6.1.1	Liquid Elastomers for Toughening Epoxy Matrices	13
1.6.1.2	Rigid Crystalline Polymers	14
1.6.1.3	Hygrothermal Toughening Agents	14
1.6.1.4	Core–Shell Particles	14
1.6.1.5	Nanoparticles for Epoxy Toughening	15
1.6.1.6	Thermoplastic Modification of Epoxy Resin	15
1.6.1.7	Block Copolymers as Modifiers for Epoxy Resin	16
1.7	Rubber-Modified Epoxy Resin: Factors Influencing Toughening	16

1.7.1	Concentration Effects	16
1.7.2	Particle Size and Distribution of Rubber	16
1.7.3	Effect of Temperature	17
1.7.4	Effect of Rubber	17
1.7.5	Interfacial Adhesion	18
1.8	Toughening Mechanisms in Elastomer-Modified Epoxy Resins	18
1.8.1	Particle Deformation	18
1.8.2	Shear Yielding	19
1.8.3	Crazing	20
1.8.4	Simultaneous Shear Yielding and Crazing	21
1.8.5	Crack Pinning	22
1.8.6	Cavitation and Rumples	22
1.9	Quantitative Assessment of Toughening Mechanisms	23
1.10	Introduction of Chapters	24
	References	25
<b>2</b>	<b>Liquid Rubbers as Toughening Agents</b>	<b>31</b>
	<i>Hanieh Kargarzadeh, Ishak Ahmad, and Ibrahim Abdullah</i>	
2.1	Introduction	31
2.2	Toughening of Thermoset Resins	31
2.3	Fracture Behavior of Rubber-Toughened Thermosets	32
2.4	Natural Rubbers	35
2.4.1	Preparation Method of LNR	36
2.4.1.1	Oxidation in the Presence of Redox System	36
2.4.1.2	Oxidation by Photochemical Method	37
2.4.1.3	Oxidation at High Temperatures and High Pressures	38
2.4.1.4	Oxidation by Cleavage Reagent Specific to Double Bonds	38
2.4.1.5	Metathesis Degradation	40
2.5	Liquid-Toughening Rubber in Thermoset Resins	43
2.6	Concluding Remarks	49
	References	50
<b>3</b>	<b>Nanostructured Epoxy Composites</b>	<b>53</b>
	<i>Yuan Meng and Xinghong Zhang</i>	
3.1	Introduction	53
3.2	Preparation Methods of the Nanostructured Epoxy Thermoset	54
3.3	Morphology of the Nanostructured Epoxy Thermoset	56
3.3.1	Parameters Controlling the Morphologies	56
3.3.1.1	Blends Composition	56
3.3.1.2	The Choice of Curing Agent	58
3.3.1.3	Topological Architecture of the Copolymer	59
3.4	Microphase Separation Mechanism	60
3.4.1	Self-Assembly Mechanism	61
3.4.2	Reaction-Induced Microphase Separation Mechanism	63
3.5	Mechanical and Thermal Properties	65

3.5.1	Fracture Toughness	65
3.5.2	Glass Transition Temperature	67
3.6	Conclusions and Outlooks	67
	References	68
<b>4</b>	<b>Manufacture of Epoxy Resin/Liquid Rubber Blends</b>	<b>73</b>
	<i>Sahrim Bin Hj Ahmad, Mimi Azlina Abu Bakar, Ying Yi, and Qi Qin</i>	
4.1	Introduction	73
4.2	Comparison of Hardeners	74
4.3	Rubber-Toughened Epoxy Resins	77
4.4	Cure Reaction Analysis	79
4.5	Conclusions	79
	References	80
<b>5</b>	<b>Cure and Cure Kinetics of Epoxy-Rubber Systems</b>	<b>83</b>
	<i>Humberto Vázquez-Torres</i>	
5.1	Introduction	83
5.2	Cure Analysis	83
5.3	Curing Kinetics	84
5.3.1	Kinetics Analysis	85
5.3.2	Autocatalytic Model	85
5.3.3	Activation Energies	86
5.3.3.1	Dynamic Kinetics Methods	86
5.3.3.2	Isothermal Methods	87
5.4	Diffusion Factor	88
5.5	Differential Scanning Calorimetry	88
5.5.1	Dynamic DSC	89
5.5.2	Isothermal DSC	90
5.6	FTIR Spectroscopy	92
5.7	Dielectric Spectroscopy Thermal Method	94
5.8	Pressure–Volume–Temperature (PVT) Method	96
5.9	Dynamic Mechanical Analysis (DMA) and Rheological Methods	97
5.10	Conclusions	101
	Acknowledgments	101
	References	101
<b>6</b>	<b>Theoretical Modeling of the Curing Process</b>	<b>105</b>
	<i>Nicolas Boyard, Vincent Sobotka, and Didier Delaunay</i>	
6.1	Introduction	105
6.2	Modeling of the Curing Kinetics	106
6.2.1	Mechanistic Approach	107
6.2.2	Phenomenological Models Describing the Reaction	109
6.2.2.1	<i>n</i> th-Order Model	109
6.2.2.2	Autocatalytic Model	113
6.2.2.3	Kamal and Sourour Model	115
6.2.2.4	Bailleul Model	117

- 6.2.3 Rheological Models 118
- 6.2.3.1 Gel Time Model 118
- 6.2.3.2 Viscosity Model 118
- 6.2.4 Effect of Vitrification ( $T_g$ ) on the Reaction Rate 119
- 6.3 Applications of the Empirical Models 120
- 6.4 Conclusion 122
- References 123
  
- 7 Phase-Separation Mechanism in Epoxy Resin/Rubber Blends 127**  
*Vattikuti Lakshmana Rao and Bejoy Francis*
- 7.1 Introduction 127
- 7.2 Thermodynamics of Phase Separation 128
- 7.2.1 Nucleation and Growth Mechanism 130
- 7.2.2 Spinodal Decomposition 130
- 7.3 Phase Separation in Uncured Epoxy Resin/Liquid Rubber Blends 131
- 7.4 Phase-Separation Mechanism in Cured Blends 133
- 7.5 Conclusion 144
- References 144
  
- 8 Morphology Analysis by Microscopy Techniques and Light Scattering 147**  
*Daohong Zhang, Junheng Zhang, and Aiqing Zhang*
- 8.1 Introduction 147
- 8.2 Developments of Morphology Analysis in Rubber-Modified Epoxies 147
- 8.2.1 Optical Microscopy (OM) 148
- 8.2.2 Scanning Electron Microscopy (SEM) 150
- 8.2.3 Atomic Force Microscopy (AFM) 153
- 8.2.4 Transmission Electron Microscopy (TEM) 155
- 8.2.5 Small-Angle Light Scattering (SALS) 159
- 8.3 Different Types of Morphologies 160
- 8.3.1 Phase-Separation Morphology of Epoxy/Rubbers Blends 160
- 8.3.2 Morphology of Hybrids 161
- 8.3.3 Homogeneous Morphology 163
- 8.4 Morphology of Toughening and Reinforcing Effects 165
- 8.4.1 Conventional Additives 165
- 8.4.2 Hyperbranched Polymers 167
- 8.5 Conclusions 171
- Acknowledgments 172
- References 172
  
- 9 Pressure–Volume–Temperature (PVT) Analysis 179**  
*Didier Delaunay, Nicolas Boyard, and Vincent Sobotka*
- 9.1 Introduction 179

9.2	Generalities on the Behavior of the Polymers	180
9.3	Measurement Techniques	184
9.4	PvT Measures on Epoxies	187
	References	190
<b>10</b>	<b>Rheology of Rubber-Toughened Structural Epoxy Resin Systems</b>	<b>193</b>
	<i>Richard A. Pethrick</i>	
10.1	Introduction	193
10.2	Epoxy Resin Chemistry	194
10.2.1	Basic Epoxy Chemical Reactions	195
10.2.2	Kinetics of Cure	196
10.2.3	Epoxy Reactivity	198
10.3	Modeling of the Cure Process	198
10.4	Rheological Implication of Differences in Reactivity	201
10.4.1	Modeling Rheological Behavior	202
10.4.2	Connection between Rheology and Cure	203
10.5	Rheological Studies of Cure	206
10.6	Toughened Epoxy Resins	209
10.6.1	Carboxy-Terminated Butadiene Acrylonitrile (CTBN)	210
10.6.2	Polyethersulfone (PES)	211
10.6.3	Nano Clay Toughening of Epoxy Resins	213
10.6.4	Toughening with Nano Carbon and Silica Nano Particles	213
10.6.5	Plasticization	213
10.7	Concluding Comments	214
	Acknowledgments	214
	References	214
<b>11</b>	<b>Viscoelastic Measurements and Properties of Rubber-Modified Epoxies</b>	<b>219</b>
	<i>Yingfeng Yu</i>	
11.1	Introduction	219
11.1.1	State Transitions from Liquid to Solid	220
11.1.2	Viscoelasticity of Cured Materials	222
11.2	Viscoelastic Behavior Below and Near Gel Point	224
11.2.1	Liquid-Rubber-Modified Epoxies	224
11.2.2	Core-Shell Rubber-Modified Epoxies	224
11.2.3	Ternary Systems with Fillers	228
11.3	Viscoelasticity of Cured Materials	228
11.3.1	Dynamic Mechanical Study	228
11.3.2	Dielectric Measurement	231
11.4	Other Remarks	233
11.5	Conclusion	234
	References	234

<b>12</b>	<b>Light, X-ray, and Neutron Scattering Techniques for Miscibility and Phase Behavior Studies in Polymer Blends</b>	<b>239</b>
	<i>Chikkakuntappa Ranganathaiah</i>	
12.1	Introduction	239
12.2	Brief Theoretical Considerations of Scattering	240
12.3	Light Scattering Experiment	242
12.4	X-ray Scattering	251
12.5	Neutron Scattering	261
12.5.1	Small-Angle Neutron Scattering (SANS)	261
12.6	Conclusions and Future Outlook	267
	Acknowledgments	267
	References	267
<b>13</b>	<b>Mechanical Properties</b>	<b>271</b>
	<i>Shinu Koshy</i>	
13.1	Introduction	271
13.2	Morphology and Mechanical Properties of Rubber-Modified Epoxies	272
13.2.1	Influence of Rubber Concentration	273
13.2.2	Influence of Initial Cure Temperature	276
13.2.3	Influence of Curing Agent	278
13.2.4	Influence of Acrylonitrile Content	279
13.2.5	Influence of Strain Rate	280
13.2.6	Kerner Equation	281
13.3	Fracture Toughness	281
13.3.1	Effect of Concentration on Fracture Toughness	282
13.3.2	Effect of Strain Rate on Fracture Toughness	284
13.3.3	Effect of Curing Agent on Fracture Toughness	285
13.4	Conclusion	285
	References	286
<b>14</b>	<b>Thermal Properties</b>	<b>289</b>
	<i>Vincent Sobotka, Didier Delaunay, Nicolas Boyard, Sabu Thomas, and Poornima Vijayan P.</i>	
14.1	Specific Heat	289
14.2	Thermal Conductivity	292
14.2.1	Main Methods of Characterization	292
14.2.1.1	Thermal Steady-State Methods	292
14.2.1.2	Thermal Transient Methods	293
14.2.2	Classical Model to Describe Thermal Conductivity as a Function of Temperature and Degree of Cure	296
14.3	Thermogravimetric Analysis of Rubber/Epoxy Systems	297
14.4	Kinetic Study from TGA	300
	References	301

- 15 Dielectric Properties of Elastomeric Modified Epoxies 305**  
*Yerrapragada Venkata Lakshmi Ravi Kumar, Swayampakula Kalyani, and Nidamarthy Vasantha Kumar Dutt*
- 15.1 Introduction 305
- 15.2 Dielectric Study in Rubber/Epoxy Systems 306
- 15.2.1 Dielectric Constant ( $\epsilon$ ) 306
- 15.2.2 Volume Resistivity (VR) 308
- 15.2.3 Conductivity ( $\sigma$ ) 310
- 15.2.4 Combined Studies on Dielectric Constant, Volume Resistivity, and Conductivity 311
- 15.3 Summary 312
- References 312
- 16 Spectroscopy Analysis of Micro/Nanostructured Epoxy/Rubber Blends 315**  
*Xiaojiang Wang and Mark D. Soucek*
- 16.1 Introduction 315
- 16.2 Fourier Transform Infrared (FTIR) and Raman Spectroscopy 316
- 16.2.1 DGEBA Epoxy/Rubber Blends 316
- 16.2.2 Other Epoxy/Rubber Blends 320
- 16.2.3 FTIR Image and Raman Spectroscopy 322
- 16.3 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) 323
- 16.3.1 Acid-Terminated Rubber/DGEBA Epoxy Blends 323
- 16.3.2 Hydroxyl-Terminated Rubber/DGEBA Epoxy Blends 326
- 16.3.3 Neutral Rubber/DGEBA Epoxy Blends 329
- 16.3.4 Other Type Epoxy/Rubber Blends 331
- 16.4 Other Spectroscopy 333
- 16.5 Summary 333
- Abbreviations 334
- References 334
- 17 Applications 339**
- 17.1 **Applications of Toughened Epoxy Resins 339**  
*Richard A. Pethrick*
- 17.1.1 Introduction 339
- 17.1.2 Aerospace Adhesive Applications 339
- 17.1.3 Rubber-Modified Resins 340
- 17.1.4 Composites 341
- 17.1.5 Epoxy Resin Modification 342
- 17.1.6 Thermoplastic Modification 343
- 17.1.7 Nanoparticle Modification 343
- 17.1.8 Other Areas of Application 343

17.2	<b>Thermoset-Based Materials for Optical Applications Containing Azobenzene Chromophores</b> 344
	<i>Luciana M. Sáiz, Antonela B. Orofino, María José Galante, and Patricia A. Oyanguren</i>
17.2.1	Introduction 344
17.2.2	Synthesis and Optical Properties of Cross-linked Azo Polymers 345
17.2.2.1	Epoxy-Based Networks 345
17.2.2.2	Urethane-Based Networks 349
17.2.3	Photoaddressable Networks Containing Alkyl Compounds 354
17.2.4	Conclusions 358
	References 360
<b>18</b>	<b>Comparison of Epoxy/Rubber Blends with Other Toughening Strategies: Thermoplastic and Hyperbranched Modifiers</b> 363
	<i>Gianluca Cicala</i>
18.1	Epoxy/Thermoplastic Blends: Development and Properties 363
18.2	Epoxy/Hyperbranched Polymer Blends: Development and Properties 375
18.3	Novel Toughening Approaches for Liquid Molding Technologies 378
18.4	Rubbers as Tougheners: Comparison with Thermoplastics and Hyperbranched Modifiers 383
18.5	Conclusions 387
	References 388
<b>19</b>	<b>Reliability Testing</b> 391
	<i>Marius Băzu and Titu Băjenescu</i>
19.1	Introduction 391
19.2	Reliability Tests Used in Micro/Nanotechnologies 392
19.3	Behavior in Real Applications and Aging Studies of Epoxy/Rubber Blends 394
19.3.1	Epoxy/Rubber Blends Used in Packaging of Active Electronic Components 394
19.3.1.1	Molding Material 396
19.3.1.2	Adhesives 398
19.3.2	Epoxy Matrix Used in Nanocomposites 399
19.4	Conclusions 402
	References 402
<b>20</b>	<b>Failure Analysis</b> 405
	<i>Marius Băzu and Titu Băjenescu</i>
20.1	Introduction 405
20.2	Methods for Failure Analysis of Epoxy/Rubber Blends 405
20.3	Typical Failure Modes and Failure Mechanisms of Epoxy/Rubber Blends Used in Micro and Nanotechnologies 405
20.3.1	Mechanical Damages 409



20.3.1.1	Fracture	409
20.3.1.2	Creep	413
20.3.2	Ion Contamination	414
20.4	Self Healing	416
20.5	Conclusions	417
	References	418
<b>21</b>	<b>Life Cycle Assessment (LCA) of Epoxy-Based Materials</b>	<b>421</b>
	<i>Jyotishkumar Parameswaranpillai and Dhanya Vijayan</i>	
21.1	Introduction to Life Cycle Assessment (LCA)	421
21.2	Significance of Life Cycle Assessment (LCA)	422
21.2.1	Goal and Scope Definition	422
21.2.2	Life Cycle Inventory Analysis	423
21.2.3	Life Cycle Impact Assessment	423
21.2.4	Life Cycle Result Interpretation	424
21.3	Life Cycle Analysis of Epoxy Systems	424
21.3.1	Life Cycle Analysis of Epoxy Resins Produced Based on Propylene and Glycerin	424
21.3.2	Life Cycle Analysis of Epoxy Resin Containing Carbon Nanotubes	426
21.3.3	Life Cycle Assessment of Wind Turbine Blade Materials	426
21.3.4	Life Cycle Assessment in Automotive Application	428
21.3.5	Life Cycle Assessment in Aerospace Application	429
21.3.6	Life Cycle Assessment of a Novel Hybrid Glass-Hemp/Thermoset Composite	429
21.3.7	Natural Fiber-Reinforced Epoxy Composites	430
21.4	Conclusion	430
	References	431
	<b>Index</b>	<b>433</b>

