

Contents

Preface *XIII*

List of Contributors *XVII*

1	Glass-Transition Phenomena in Polymer Blends	1
	<i>Ioannis M. Kalogeras</i>	
1.1	Introduction	1
1.2	Phenomenology and Theories of the Glass Transition	4
1.2.1	Thermodynamic Phase Transitions	4
1.2.2	Structural, Kinetic, and Thermodynamic Aspects	7
1.2.3	Relaxation Dynamics and Fragility	11
1.2.3.1	Relaxations in Glass-Forming Materials	12
1.2.3.2	The Concept of Fragility	17
1.2.4	Theoretical Approaches to the Glass Transition	20
1.2.4.1	General Overview	20
1.2.4.2	Energy Landscapes and Many-Molecule Relaxation Dynamics	21
1.2.4.3	Approaches with an Underlying Avoided Dynamical Transition	24
1.2.4.4	Models Showing a Thermodynamic (or Static) Critical Point	26
1.2.4.5	Percolative Phenomena in Glass Formation	34
1.3	Manipulating the Glass Transition	36
1.3.1	Effects of Chemical Structure	37
1.3.2	Externally Controlled Processes or Treatments	40
1.3.2.1	Pressure Effects	40
1.3.2.2	Crystallization Effects	42
1.3.2.3	Plasticizer Effects	43
1.3.2.4	Filler Effects	44
1.3.2.5	Cross-linker Effects	45
1.3.2.6	Geometric Confinement Effects	47
1.4	Experimental Means of Determination	50
1.4.1	Calorimetric Techniques	52
1.4.2	Thermomechanical Analysis (TMA)	57
1.4.3	Dynamic Mechanical Analysis (DMA)	60

1.4.4	Dielectric Analysis (DEA)	63
1.5	Blend Morphology and Glass Transitions	66
1.5.1	Miscibility and Phase Boundaries in Polymer Blends	67
1.5.2	State of Dispersion and the Glass Transition	71
1.6	Analyzing Glass Transitions in Single-Phase Systems	78
1.6.1	Shape Characteristics and Strength of the Transition	78
1.6.2	Description and Interpretation of T_g versus Composition Behaviors	81
1.6.2.1	Specific Volumes or Flexible Bonds Additivity Models	81
1.6.2.2	Additivity of Free Volumes	82
1.6.2.3	Predictions Based on Thermodynamic Considerations	85
1.6.2.4	Empirical Concentration Power T_g (w) Equations and Systems' Complexity	89
1.6.2.5	Dynamically Heterogeneous Miscible Blends	94
1.7	Case Studies	99
1.7.1	Miscibility Achievement via Chemical Modification	99
1.7.2	Microstructure of the Amorphous Phase in Semicrystalline Blends	108
1.7.3	Ternary Polymer Blends: Phase Behavior and Glass Transitions	111
1.8	Concluding Remarks	115
	Abbreviations	117
	Symbols	119
	Greek Symbols	121
	References	122
2	Crystallization and Melting Behavior in Polymer Blends	135
	<i>Saleh A. Jabarin, Kazem Majdzadeh-Ardakani, and Elizabeth A. Lofgren</i>	
2.1	Introduction	135
2.2	Miscibility of Polymer Blends	136
2.3	Miscible Blends	138
2.3.1	Crystalline/Amorphous Polymer Blends	139
2.3.2	Glass Transition and Melting Behavior	139
2.3.2.1	Melting Point Depression	140
2.3.3	Crystallization	142
2.3.4	Spherulite Growth Rate of the Crystallizable Component	144
2.3.5	Overall Crystallization Kinetics	147
2.3.5.1	Isothermal Kinetics	147
2.3.5.2	Nonisothermal Kinetics	150
2.3.6	Crystalline/Crystalline Polymer Blends	152
2.4	Immiscible Blends	158
2.4.1	Blends with an Amorphous Dispersed Phase in a Crystallizable Matrix	158
2.4.1.1	Nucleation of the Crystalline Phase	158
2.4.1.2	Spherulite Growth Rate of the Crystalline Phase	159
2.4.1.3	Overall Crystallization Kinetics	161
2.4.1.4	Glass Transition of the Amorphous Component and Melting Behavior of the Crystalline Matrix in Immiscible Polymer Blends	163

2.4.2	Blends with a Crystallizable Dispersed Phase in an Amorphous Matrix	164
2.4.2.1	Fractionated Crystallization	164
2.4.2.2	Determination of the Number Density of Heterogeneities	165
2.4.3	Effect of the Fillers on the Crystallization of Immiscible Polymer Blends	166
2.5	Compatibilized Polymer Blends	167
2.5.1	Addition of Blocks or Graft Copolymers	167
2.5.2	Reactive Compatibilization	168
2.5.2.1	Reactive Compatibilization in Bio-based Polymer Blends	169
2.5.3	Crystallization of Compatibilized Blends	170
2.5.3.1	Differences Between the Crystallization Behaviors of Polymer Blends and Copolymers	171
2.5.4	The role of Transesterification on the Miscibility and Morphology of Polyester Blends	172
2.6	Summary and Conclusions	173
2.7	Nomenclature	175
2.7.1	Abbreviations	175
2.7.2	Notations	177
2.7.3	Symbols	177
2.7.3.1	Roman Letters	177
2.7.3.2	Greek Letters	179
	References	179

3 Morphology and Structure of Crystalline/Crystalline Polymer Blends

191

Zhaobin Qiu and Shouke Yan

3.1	Introduction	192
3.2	Systems with Small Melting Point Difference	193
3.2.1	Preliminary Study on Morphology and Structure of PES/PEO Blends	193
3.2.2	Effect of Blend Composition on the Formation of Interpenetrating Spherulites of PES/PEO Blends	195
3.2.3	Effect of Crystallization Temperature on the Crystalline Morphologies of PES/PEO Blends	198
3.3	Systems with Large Melting Point Difference	201
3.3.1	Crystallization Behavior of the High- T_m Component in Miscible Polymer Blends	201
3.3.2	Crystallization Behavior of Low- T_m Component in Miscible Polymer Blends	209
3.3.3	Morphology and Structure of Blend Systems with Large Melting Point Difference	213
3.4	Concluding Remarks	225
	Acknowledgment	226
	References	226

4	Rubber–Plastic Blends: Structure–Property Relationship	229
	<i>Sudhin Datta</i>	
4.1	Introduction: Key Challenges	229
4.2	Rubber Toughening of Thermoplastics	233
4.2.1	Mechanism	233
4.2.2	Morphology	235
4.2.3	Failure Process	236
4.3	Models for Rubber Toughening of Plastics	240
4.3.1	Crazing Model	241
4.3.2	Interparticle Distance Model	242
4.3.3	Percolation Models	243
4.4	Characterization of Rubber–Plastic Blends	243
4.4.1	Glass Transition	243
4.4.2	Dynamic Mechanical Characterization	244
4.4.3	Calorimetric Methods	245
4.4.4	Dielectric Characterization	246
4.4.5	Morphology/Microscopy	246
4.4.6	Optical Microscopy	247
4.4.7	Transmission Electron Microscopy	248
4.4.8	Scanning Electron Microscopy	249
4.4.9	Atomic Force Microscopy	250
4.4.10	Scanning Tunneling Microscopy	250
4.4.11	X-Ray Microscopy	251
4.4.12	Scattering Methods: Light, X-Ray, and Neutron	251
4.4.13	X-Ray Scattering	251
4.4.14	Neutron Scattering	252
4.4.15	Neutron Reflectivity	253
4.4.16	Neutron Spin Echo Spectroscopy	253
4.4.17	Nuclear Magnetic Resonance	253
4.4.18	Spectroscopic Methods	254
4.4.19	Infrared Spectroscopy	254
4.4.20	UV–Visible Spectroscopy	254
4.4.21	Raman Spectroscopy	254
4.4.22	Fluorescence Spectroscopy: Nonradiative Energy Transfer and Excimer Fluorescence	255
4.4.23	X-Ray Photoelectron Spectroscopy and Secondary Ion Mass Spectroscopy	255
4.4.24	Vapor Sorption and Solvent Probe Techniques	255
4.4.25	Characterization of Interfacial Properties	256
4.5	Experimental Rubber–Plastic Blends	257
4.5.1	Early Work	257
4.5.2	Blends of Polyvinyl Chloride	257
4.5.3	Blends of Polystyrene and Styrene Copolymers	260
4.5.4	Blends of Polyamides	265
4.5.5	Blends of Isotactic Polypropylene	269

4.5.5.1	With Ethylene–Propylene Copolymer Rubber	270
4.5.5.2	With Ethylene–Isotactic Propylene Copolymers	272
4.5.5.3	With Higher α -Olefin Rubber	272
4.5.5.4	With Ethylene–Butene-1 Copolymer	273
4.5.5.5	With Ethylene–Hexene-1 Copolymer	274
4.5.5.6	With Ethylene–Octene-1 Copolymer	275
4.5.6	Tensile Properties	275
4.5.7	Structure in Injection-Molded Specimens	276
4.5.8	Impact Performance	277
4.5.9	Poly(butene-1) as Semicrystalline Rubber	278
4.5.10	Styrene Block Polymer Rubber	278
4.6	Thermoplastic Vulcanizates	279
4.6.1	Nonpolar Rubber with Nonpolar Thermoplastic	282
4.6.1.1	EPDM Elastomer with iPP Thermoplastic	282
4.6.1.2	Natural Rubber Elastomer with PE Thermoplastic	282
4.6.1.3	Natural Rubber Elastomer with Polypropylene Thermoplastic	283
4.6.1.4	Butyl Rubber Elastomer with Polypropylene Thermoplastic	283
4.6.2	Polar Rubber with Nonpolar Plastic	283
4.6.2.1	NBR Elastomer with iPP Thermoplastic	283
4.6.2.2	Acrylate Rubber with iPP Thermoplastic	283
4.6.3	Nonpolar Rubber with Polar Thermoplastic	284
4.6.3.1	EPDM Rubber with PA6 Thermoplastic	284
4.6.3.2	EPDM Rubber with PBT Thermoplastic	284
4.6.3.3	EPDM Rubber with iPP + PA6 Thermoplastic	284
4.6.4	Polar Rubber with Polar Thermoplastic	284
4.6.4.1	Acrylate Elastomer with Polyester Thermoplastic	284
4.7	Blends Made during Polymerization	285
4.7.1	Gum Elastomers	285
4.7.1.1	Diene Rubbers	285
4.7.1.2	Ethylene-Based Elastomers	286
4.7.1.3	Ethylene Copolymers	287
4.7.1.4	Ionomers	287
4.7.2	Emulsion Rubbers	287
4.7.3	Core–Shell Graft Polymers	287
4.7.4	Block Polymers	288
4.7.4.1	Butadiene–Styrene Block Copolymers	288
4.8	Conclusions	288
	References	289
5	Morphology of Rubber/Rubber Blends	299
	<i>Avraam I. Isayev and Tian Liang</i>	
5.1	Introduction	299
5.2	Characterization Techniques for Rubber Blends	300
5.2.1	Optical Microscopy	300

5.2.2	Transmission Electron Microscopy	300
5.2.3	Scanning Electron Microscopy	301
5.2.4	Atomic Force Microscopy	301
5.2.5	Dynamic Testing	301
5.2.6	Thermal Analysis	302
5.3	Effect of Material Parameters and Processing on Structure and Morphology of Rubber Blends	303
5.4	Distribution of Fillers and Cure Balance in Rubber Blends	308
5.4.1	Distribution of Fillers in Rubber Blends	308
5.4.2	Migration of Curatives in Rubber Blends	310
5.5	Morphology and Properties of Different Rubber Blends	311
5.5.1	Blends Containing NR	311
5.5.2	Blends Containing BR	318
5.5.3	Blends Containing SBR	319
5.5.4	Blends Containing EPDM	322
5.5.5	Blends Containing Butyl Rubber	323
5.5.6	Blends Containing NBR	324
5.5.7	Blends Containing CR	325
5.5.8	Blends Containing Silicone Rubber	326
5.5.9	Blends Containing Hydrogenated Nitrile Butadiene Rubber (HNBR)	327
5.6	Conclusions	328
	References	329
6	Phase Morphology and Properties of Ternary Polymer Blends	335
	<i>V.N. Kuleznev and Yu. P. Miroshnikov</i>	
6.1	Introduction	335
6.2	Miscibility of Polymers in Ternary Polymer Blends	336
6.3	Formation of Phase Morphology	345
6.3.1	Prediction of Phase Morphologies of Polymer Blends	346
6.3.1.1	Binary Blends	347
6.3.2	Ternary Polymer Blends	348
6.3.3	Encapsulated Morphologies: Influence of Different Factors	358
6.3.3.1	Blend Composition	358
6.3.3.2	Kinetic Factors	363
6.3.3.3	Morphological Types	369
6.3.3.4	Multiple Percolated Structures	372
6.3.3.5	Partial Wetting Morphology	375
6.3.4	Ternary Blends with Separated Dispersed Phases	379
6.3.4.1	Effects of Interaction between Dispersed Phases	379
6.3.4.2	Ternary Systems with One Solid Phase – Proof of the Mechanism of Phase Interaction	384
6.4	Properties of Ternary Polymer Blends	389
6.5	Conclusions and Future Development	393
	References	395

7	Morphology and Structure of Polymer Blends Containing Nanofillers	401
	<i>Hossein Nazockdast</i>	
7.1	Introduction	401
7.2	Type of Nanofiller Used in Polymer Nanocomposite	402
7.2.1	Structure and Characteristic of Layered Silicate	402
7.2.1.1	Surface Modification of Layered Silicates	403
7.2.1.2	The Structure of Polymer-Silicate Nanocomposites	405
7.2.2	Structure and Characteristic of Carbon Nanotube	405
7.2.2.1	Surface Modification of Carbon Nanotube	407
7.2.3	Structure and Characteristics of Silica Nanoparticles	408
7.3	Nanostructural Characterization	409
7.3.1	X-Ray Diffraction	409
7.3.2	Transition Electron Microscopy (TEM)	410
7.3.3	Differential Scanning Calorimetry	411
7.3.4	The Linear Rheological Measurements	412
7.4	Partially Miscible Polymer Blends Containing Nanoparticle	414
7.4.1	The Effect of Nanoparticles on Phase Separation of Partially Miscible Polymer Blends	415
7.4.2	The Effect of Silica Nanoparticles on Phase Separation of PMMA/Polyvinyl Acetate	417
7.4.3	Effect of Nanosilica on Phase-separation Behavior of PMMA/SAN Blends	418
7.4.4	Effect of Addition of Nanoparticles on Phase-separation Behavior of PS/PVME	428
7.5	Immiscible Polymer Blends Containing Nanoparticle	433
7.5.1	Introduction	433
7.5.2	Parameters Determining Localization of Nanoparticles	433
7.5.2.1	Thermodynamic Parameters (Wetting Parameters)	434
7.5.2.2	Kinetic Parameters (Dynamic Processes)	437
7.5.2.3	Effect of Feeding Sequence	437
7.5.2.4	Effect of Viscosity	441
7.5.3	Rheology of Immiscible Polymer Blends Containing Nanoparticle	446
7.5.3.1	Polymer Blends Containing Nanosilica	447
7.5.3.2	Polymer Blends Containing Nanoclay	450
7.5.3.3	Polymer Blends Containing Carbon Nanotubes	459
7.5.4	The Role of Nanoparticles on the Morphology Evolution of Nanofilled Polymer Blends	462
7.5.4.1	Nanoparticle Migration (Dynamic and Transfer of Nanoparticles)	462
7.5.4.2	The Compatibilizing Effect of Nanoparticles	464
	References	473
	Index	483