

Contents

Preface	v
About the Editors	xv
List of Contributors	xvii
Contents of Volumes in This Set	xix

CHAPTER 1. Nano Reinforcements of Renewable Plastics: To Create the Next Generation of Value-Added Novel Eco-Friendly Nanocomposites

Suprakas Sinha Ray, Mosto Bousmina

1. Introduction	2
2. Synthesis, Structure and Properties of Renewable Plastics	3
2.1. Polylactide	3
2.2. Poly(3-hydroxybutyrate)	3
2.3. Thermoplastic Starch	3
2.4. Plant Oils-Based Polymers	5
2.5. Cellulose	5
2.6. Gelatin	6
2.7. Chitosan	6
3. Polymer/Layered Silicate (PLS) Nanocomposite Technology	7
4. Structure and Properties of Layered Silicates	8
5. Techniques Used for Nanocomposite Characterizations	10
6. Preparative Techniques	10
6.1. Solution Intercalation	10
6.2. <i>In Situ</i> Intercalative Polymerization	15
6.3. Melt Intercalation	17
7. Properties	26
7.1. Mechanical Properties	26
7.2. Heat Distortion Temperature	32
7.3. Thermal Stability	33
7.4. Gas Barrier Properties	35
8. Biodegradability	37
8.1. PLA and its Nanocomposites	37
8.2. PHB and its Nanocomposites	39
9. Crystallization Behavior and Morphology	40
10. Melt Rheology and Structure Property Relationships	42
10.1. Dynamic Oscillatory Shear Measurements	42
10.2. Steady Shear Measurements	44
10.3. Elongation Viscosity	47
11. Foam Processing	47
12. Conclusions: Present Status and Future Prospects	49
References	50

CHAPTER 2. Biodegradable Foams

*Salvatore Cotugno, Ernesto Di Maio, Giuseppe Mensitieri,
Luigi Nicolais, Salvatore Iannace*

1. Introduction	56
1.1. Biodegradable Foams: Applications, Primary Required Features, and Examples in Nature	56
1.2. Basic Aspects of the Foaming Process	57
1.3. Relevant Material Properties and Processability	59
1.4. Issues Related to Biodegradable Polymers	59
2. Basic Aspects and Properties	64
2.1. Properties of Polymer-Gas Mixtures	64
2.2. Properties of Foams	70
2.3. Foaming Agents	76
3. Foaming Processes	77
3.1. Batch Foaming	77
3.2. Extrusion Foaming	81
3.3. Other Foaming Techniques	88
4. Foams from Biodegradable Polymers	91
4.1. Natural Polymers	91
4.2. Synthetic Polymers	97
References	103

CHAPTER 3. Biodegradations and Physical Properties of ϵ -Caprolactone and Lactide Copolymers

Hajime Yasuda, Hiroyuki Shirahama, Yuushou Nakayama

1. Introduction	108
2. Copolymerizations of Lactones with MOHEL	109
2.1. Synthesis of Copolymers of (<i>R</i>)-MOHEL with Lactones	109
2.2. Biodegradation by Activated Sludge	111
2.3. Biodegradation with Sea Water	112
2.4. Biodegradation with Enzymes	114
2.5. Analysis of Degraded Products	115
3. Copolymerizations of CL with Depsipeptides	115
3.1. Synthesis of Depsipeptides and their Copolymerization	115
3.2. Enzymatic Degradation of DMO/CL Copolymers	116
4. Random Copolymerizations of CL with Cyclic Carbonates	118
4.1. Synthesis of poly[(<i>R</i>)-1-methyltrimethylene carbonate- <i>ran</i> -CL] or poly[(<i>S</i>)-1-methyltrimethylene carbonate- <i>ran</i> -CL]	118
4.2. Preparation of poly[(<i>R,R</i>)-1,3-DTC- <i>ran</i> -CL]	120
4.3. Biodegradation of poly[(<i>R</i>)-1-MTC- <i>ran</i> -CL] or poly[(<i>S</i>)-1-MTC- <i>ran</i> -CL]	122
4.4. Biodegradation of poly[(<i>R,R</i>)-1,3-DTC- <i>ran</i> -CL] or poly[(<i>S,S</i>)-1,3-DTC- <i>ran</i> -CL]	123
4.5. Biodegradability of Blended Polymers	124
4.6. Change in Properties of Copolymers Before and after Enzymatic Degradation	125
4.7. Analysis of Degraded Products	127
5. Copolymerizations and Degradations of Block Copolymers Composed of CL or VL and DXO ..	127
6. Copolymerizations of LA with CL	128
6.1. Preparation of Random and Block Copolymers between L-LA or D-LA and CL, and Stereocomplexes between Them	128
6.2. Biodegradability of Random and Block Copolymers of L-LA and CL	129
6.3. Biodegradation of Stereocomplexes with Proteinase K	130
6.4. Mechanical Properties of Stereocomplexes	131

7.	Copolymerizations of LA with MOHEL	131
7.1.	Syntheses of Random Copolymers of L-LA or D,L-LA with MOHEL	131
7.2.	Biodegradation of Random Copolymers of LA with MOHEL	132
7.3.	Changes in Polymer Properties after Enzymatic Degradation	134
8.	Copolymerizations of LA with Depsipeptides	134
8.1.	Synthesis of Random Copolymers between L-LA with Depsipeptides	134
8.2.	Degradation of Copolymers with Compost	135
8.3.	Decomposition of Copolymers with Proteinase K	136
8.4.	Analysis of Degraded Products from poly(L,L-DMO-ran-L-LA) (16/84)	137
9.	Copolymerizations of LA with Cyclic Carbonates	137
9.1.	Random Copolymerization of L-LA with Six-Membered Cyclic Carbonates	137
9.2.	Degradation of poly(L-LA-ran-Cyclic Carbonate)s	139
9.3.	Mechanical Properties of poly(L-LA-ran-Cyclic Carbonate)s	141
9.4.	Changes in Copolymer Properties after Enzymatic Degradation	141
9.5.	Random Copolymerization of D,L-LA with Six-Membered Cyclic Carbonates	142
9.6.	Degradation of poly(D,L-LA-ran-Cyclic Carbonate)s	142
9.7.	Mechanical Properties of poly(D,L-LA-ran-Cyclic Carbonate)s	143
9.8.	Block Copolymerization of L- and D,L-LA with Six-Membered Cyclic Carbonates	143
10.	Conclusion	150
	References	150

CHAPTER 4. Biodegradable Polymer/Layered Silicate Nanocomposites

Masami Okamoto

1.	Introduction	154
2.	History of PLS Nanocomposites	155
3.	Structure of LS and its Modification with Surfactants	156
4.	Preparation Methods and Structure of PLS Nanocomposites	157
4.1.	Intercalation of Polymers or Prepolymers from Solution	157
4.2.	The <i>In Situ</i> Intercalative Polymerization Method	157
4.3.	The Melt Intercalation Method	158
4.4.	Structure of PLS Nanocomposites	158
5.	Characterization of PLS Nanocomposites	159
6.	Biodegradable Polymer/LS Nanocomposites	160
6.1.	PCL/LS Nanocomposites	161
6.2.	PVA/LS Nanocomposites	162
6.3.	PLA/LS Nanocomposites	162
6.4.	PBS/LS Nanocomposites	165
6.5.	PHB/LS Nanocomposites	166
6.6.	Starch/LS Nanocomposites	167
6.7.	Plant Oil/LS Nanocomposites	167
6.8.	Chitosan/LS Nanocomposites	169
7.	Materials Properties of Biodegradable Polymer/LS Nanocomposites	170
7.1.	Mechanical Properties	171
8.	Crystallization of Biodegradable Polymer/LS Nanocomposites	183
9.	Melt Rheology of Biodegradable Polymer/LS Nanocomposites	186
9.1.	Dynamic Oscillatory Shear Measurement	186
9.2.	Steady Shear Flow	189
9.3.	Elongational Flow and Strain-Induced Hardening	190
10.	Processing Operations	191
11.	Creating Porous Ceramic Materials Via PLA/LS Nanocomposites	193
12.	Current Status and Future Prospects of Biodegradable Nanocomposites	195
	References	195

CHAPTER 5. Biodegradable Edible Films and Coatings Based on Protein Resources: Physical Properties and Applications in Food Quality Management

Ioannis S. Arvanitoyannis

1. Introduction	200
2. Wheat Gluten Films	201
2.1. Thermal Properties	201
2.2. Mechanical Properties	203
2.3. Gas Permeability (GP) and Water Vapor Permeability (WVP)	206
3. Corn Zein Films	208
3.1. Thermal Properties	208
3.2. Mechanical Properties	209
3.3. Gas Permeability (GP) and Water Vapor Permeability (WVP)	211
4. Casein/Caseinate Films	211
4.1. Thermal Properties	212
4.2. Mechanical Properties	212
4.3. Gas Permeability (GP) and Water Vapor Permeability (WVP)	214
5. Whey Protein Isolate (WPI) Films	217
5.1. Thermal Properties	217
5.2. Mechanical Properties	220
5.3. Gas Permeability (GP) and Water Vapor Permeability (WVP)	221
6. Soy Protein Isolate (SPI) Films	221
6.1. Thermal Properties	224
6.2. Mechanical Properties	224
6.3. Gas Permeability (GP) and Water Vapor Permeability (WVP)	227
7. Gelatin Films	227
7.1. Thermal Properties	228
7.2. Mechanical Properties	228
7.3. Gas Permeability (GP) and Water Vapor Permeability (WVP)	230
8. Additional Research	231
8.1. Fish-Based Films	231
8.2. Pea Protein Films	231
8.3. Rapeseed Protein Films	232
8.4. Egg Albumin, White/Starch Films	232
8.5. Peanut Protein Film	232
8.6. Pickle Fermentation Brine Protein Films	232
8.7. Fruit Puree Edible Films	233
9. Conclusions	233
References	235

CHAPTER 6. Enzymatic Synthesis and Chemical Recycling of Green Polymers

*Shuichi Matsumura, Yasushi Osanai, Yasuyuki Soeda, Yoichi Suzuki,
Kazunobu Toshima*

1. Introduction	240
2. Polyester Synthesis Using PHB Synthase and Depolymerase	242
2.1. <i>In Vitro</i> Polyester Synthesis with PHB Synthase	242
2.2. <i>In Vitro</i> Polyester Synthesis with PHB-Depolymerases	244
3. Polyesters by Condensation Polymerization	245
3.1. Polycondensation of Hydroxy Acids	245

3.2.	Polycondensation of Dicarboxylic Acids and Diols	245
3.3.	Lactonization and Macrocyclization	246
3.4.	Regioselective Polycondensation	247
3.5.	Stereoselective Oligomerization	248
3.6.	Functional Polyesters	249
3.7.	Polymerization of Cyclic Diacids Anhydride with Diols or Oxiranes	250
3.8.	Polymerization of Polyanhydrides with Diols	250
3.9.	Transesterification of Polycaprolactone and Poly(alkylene dicarboxylate)s	251
3.10.	Polycondensation Mechanism of Dicarboxylic Acid with Diols	251
4.	Polyesters by Ring-Opening Polymerization of Lactones	251
4.1.	Ring-Opening Polymerization of Lactones	252
4.2.	Poly lactide and its Copolymer	253
4.3.	Macrocyclization	253
4.4.	Stereoselective Ring-Opening Polymerization of Lactones	254
4.5.	Regioselective Lactone Ring-Opening Reaction with Nucleophiles	254
4.6.	Branched Polymers and Block Copolymer	256
4.7.	Preparation of Polymalate by the Ring-Opening Polymerization of Malolactonate	257
4.8.	Polymerization Mechanism of Lactones	257
5.	A New Route to Sustainable Chemical Recycling of Polyesters Using an Enzyme	258
5.1.	Batch Procedure for the Degradation of Polyesters into Repolymerizable Oligomers	258
5.2.	Continuous Flow System for the Degradation of Polyesters	260
6.	Enzymatic Synthesis of Polycarbonate	261
6.1.	Enzymatic Synthesis of Cyclic Trimethylene Carbonate with/without Methyl Substituents	261
6.2.	Lipase-Catalyzed Ring-Opening Polymerization of Cyclic Carbonates	261
6.3.	Lipase-Catalyzed Ring-Opening Copolymerization of Cyclic Carbonates and Lactones	262
6.4.	Polycondensation of Carbonate Diesters and Diols	263
6.5.	Chemical Recycling of Polycarbonates using an Enzyme	264
6.6.	Poly(carbonate-urethane)	264
7.	Enzymatic Synthesis of Polythioesters, Polyphosphates, and Polysiloxane	265
7.1.	Polythioesters	265
7.2.	Polyphosphates	266
7.3.	Polysiloxane	266
8.	Enzymatic Synthesis of Poly(Amino Acid)	266
8.1.	Amino Acid Oligomers	267
8.2.	Poly(γ -glutamic acid) and Poly(ϵ -lysine)	267
8.3.	Poly(aspartic acid)	267
9.	Green Solvents for Polymer Production and Recycling	268
10.	Trends in Green Polymer Production Using an Enzyme	269
10.1.	Versatile Applications of Enzyme-Catalyzed Polymerization	269
10.2.	Increasing the Molecular Weight	270
10.3.	Biodegradable Crosslinkage that Allows Chemical Recycling	270
10.4.	Toward Establishment of a Sustainable Biochemical Complex	270
	References	270

CHAPTER 7. Polyphosphazenes as Novel Biomaterials

Lakshmi S. Nair, Duron Lee, Cato T. Laurencin

1.	Introduction	277
2.	Polyphosphazene Synthesis	278
3.	Structure-Property Relationships in Polyphosphazenes	281
3.1.	Crystallinity	281

3.2. Glass Transition Temperature.....	281
3.3. Solubility.....	285
3.4. Hydrophobicity/Hydrophilicity.....	285
3.5. Hydrolytic Stability/Instability.....	285
4. Biomedical Applications of Polyphosphazenes.....	286
4.1. Biostable and Bioactive Polyphosphazenes.....	286
4.2. Biodegradable Polyphosphazenes.....	289
5. Conclusions.....	303
References.....	304

CHAPTER 8. Chemical Modification of Chitin and Chitosan and Their Biodegradation

Hitoshi Sashiwa, Sei-ichi Aiba

1. Introduction.....	307
2. Dissolution of Chitosan in Organic Solvents.....	308
3. Sugar-Modified Chitosan.....	310
4. Chitosan-Dendrimer Hybrids.....	313
5. Biodegradation of Modified Chitosans.....	315
6. Enzymatic Production of <i>N</i> -Acetyl-D-Glucosamine from Chitin.....	318
7. Cyclodextrin-Linked Chitosan.....	319
8. Crown Ether-Bound Chitosan.....	321
9. Chemical Grafting of Chitosan.....	322
10. Enzymatic Modification of Chitosan.....	323
11. Other Modifications.....	325
12. Conclusions.....	326
References.....	326

CHAPTER 9. The Synthesis of Polyanhydrides

Brandon M. Vogel, Surya K. Mallapragada

1. Introduction.....	329
2. Early Polyanhydrides.....	330
3. Erosion and Degradation.....	330
4. High-Molecular-Weight Polyanhydrides: Melt Condensation.....	331
5. Coordination Catalysts.....	335
6. Solution Polymerization.....	336
7. Poly(ethylene glycol) Containing Polyanhydrides.....	337
8. Polyanhydride Networks.....	339
9. Block Copolymer Synthesis.....	339
9.1. Tin(II) Octoate.....	340
9.2. Living Polymerization.....	342
9.3. Synthesis of Anhydride Rings.....	342
9.4. Covalent Coupling of Blocks.....	343
10. Microwave Polymerization.....	344
11. Conclusions and Future Directions.....	345
References.....	345

CHAPTER 10. Micro- and Nano-Fabrication of Biodegradable Polymers

S. C. Chen, Y. Lu

1. Introduction	349
2. Laser Micromachining	350
2.1. Lasers for Micropatterning	351
2.2. Laser Micropatterning of Polymers	353
3. Nanosphere Lithography	353
3.1. Sample Preparation and Processing	354
3.2. Nanostructure Formation	355
4. Replication Techniques	356
4.1. Microimprinting Lithography	357
4.2. Soft Lithography	357
5. Rapid Prototyping Techniques	359
5.1. Direct Deposition Methods	359
5.2. Three-Dimensional Printing	360
5.3. Laser Stereolithography	361
6. Summary and Future Prospects	363
References	364
Index	367

BookFun@