



# Contents

<b>Series Preface</b>	<b>xiii</b>
<b>Preface</b>	<b>xv</b>
<b>List of Contributors</b>	<b>xvii</b>
<b>1 Bio-Based Plastics – Introduction</b>	<b>1</b>
<i>Stephan Kabasci</i>	
1.1 Definition of Bio-Based Plastics	2
1.2 A Brief History of Bio-Based Plastics	3
1.3 Market for Bio-Based Plastics	5
1.4 Scope of the Book	6
<b>2 Starch</b>	<b>9</b>
<i>Catia Bastioli, Paolo Magistrali, and Sebastià Gestí Garcia</i>	
2.1 Introduction	9
2.2 Starch	10
2.3 Starch-Filled Plastics	13
2.4 Structural Starch Modifications	14
2.4.1 Starch Gelatinization and Retrogradation	14
2.4.2 Starch Jet-Cooking	16
2.4.3 Starch Extrusion Cooking	16
2.4.4 Starch Destructurization in Absence of Synthetic Polymers	17
2.4.5 Starch Destructurization in Presence of Synthetic Polymers	19
2.4.6 Additional Information on Starch Complexation	23
2.5 Starch-Based Materials on the Market	27
2.6 Conclusions	28
References	28
<b>3 Cellulose and Cellulose Acetate</b>	<b>35</b>
<i>Johannes Ganster and Hans-Peter Fink</i>	
3.1 Introduction	35
3.2 Raw Materials	36



3.3	Structure	37
3.3.1	Cellulose	37
3.3.2	Cellulose Derivatives	40
3.4	Principles of Cellulose Technology	42
3.4.1	Regenerated Cellulose	43
3.4.2	Organic Cellulose Esters – Cellulose Acetate	46
3.5	Properties and Applications of Cellulose-Based Plastics	52
3.5.1	Fibres	53
3.5.2	Films	54
3.5.3	Moulded Articles	56
3.6	Some Recent Developments	57
3.6.1	Cellulose	57
3.6.2	Cellulose Acetate and Mixed Esters	58
3.7	Conclusion	59
	References	59
<b>4</b>	<b>Materials Based on Chitin and Chitosan</b>	<b>63</b>
	<i>Marguerite Rinaudo</i>	
4.1	Introduction	63
4.2	Preparation and Characterization of Chitin and Chitosan	64
4.2.1	Chitin: Characteristics and Characterization	64
4.2.2	Chitosan: Preparation and Characterization	66
4.3	Processing of Chitin to Materials and Applications	69
4.3.1	Processing of Chitin and Physical Properties of Materials	69
4.3.2	Applications of Chitin-Based Materials	70
4.4	Chitosan Processing to Materials and Applications	71
4.4.1	Processing of Chitosan	71
4.4.2	Application of Chitosan-Based Materials	74
4.5	Conclusion	77
	References	77
<b>5</b>	<b>Lignin Matrix Composites from Natural Resources – ARBOFORM®</b>	<b>89</b>
	<i>Helmut Nägele, Jürgen Pfitzer, Lars Ziegler, Emilia Regina Inone-Kauffmann, Wilhelm Eckl, and Norbert Eisenreich</i>	
5.1	Introduction	89
5.2	Approaches for Plastics Completely Made from Natural Resources	90
5.3	Formulation of Lignin Matrix Composites (ARBOFORM)	92
5.3.1	Lignin	92
5.3.2	Basic Formulations and Processing of ARBOFORM	95
5.3.3	The Influence of the Fibre Content	97
5.4	Chemical Free Lignin from High Pressure Thermo-Hydrolysis (Aquasolv)	100
5.4.1	Near Infrared Spectroscopy of Lignin Types	100
5.4.2	Lignin Extraction by High-Pressure Hydrothermolysis (HPH)	101
5.4.3	Thermoplastic Processing of Aquasolv Lignin	104
5.5	Functionalizing Lignin Matrix Composites	105
5.5.1	Impact Strength	106



5.5.2	Flame Retardancy	106
5.5.3	Electrical Conductivity with Nanoparticles	106
5.5.4	Pyrolysis to Porous Carbonaceous Structures	108
5.6	Injection Moulding of Parts – Case Studies	109
5.6.1	Loudspeaker Boxes	110
5.6.2	Precision Parts	110
5.6.3	Thin Walled and Decorative Gift Boxes and Toys	111
	Acknowledgements	112
	References	112
<b>6</b>	<b>Bioplastics from Lipids</b>	<b>117</b>
	<i>Stuart Coles</i>	
6.1	Introduction	117
6.2	Definition and Structure of Lipids	117
6.2.1	Fatty Acids	117
6.2.2	Mono-, Di- and Tri-Substituted Glycerols	118
6.2.3	Phospholipids	118
6.2.4	Other Compounds	119
6.3	Sources and Biosynthesis of Lipids	119
6.3.1	Sources of Lipids	119
6.3.2	Biosynthesis of Lipids	120
6.3.3	Composition of Triglycerides	120
6.4	Extraction of Plant Oils, Triglycerides and Their Associated Compounds	120
6.4.1	Seed Cleaning and Preparation	121
6.4.2	Seed Pressing	121
6.4.3	Liquid Extraction	121
6.4.4	Post Extraction Processing	122
6.5	Biopolymers from Plant Oils, Triglycerides and Their Associated Compounds	122
6.5.1	Generic Triglycerides	122
6.5.2	Common Manipulations of Triglycerides	123
6.5.3	Soybean Oil-Based Bioplastics	125
6.5.4	Castor Oil-Based Bioplastics	126
6.5.5	Linseed Oil-Based Bioplastics	127
6.5.6	Other Plant Oil-Based Bioplastics	127
6.5.7	Biological Synthesis of Polymers	128
6.6	Applications	128
6.6.1	Mimicking to Reduce R&D Risk	128
6.6.2	Composites	129
6.6.3	Coatings	129
6.6.4	Packaging Materials	130
6.6.5	Foams	130
6.6.6	Biomedical Applications	130
6.6.7	Other Applications	131
6.7	Conclusions	131
	References	131



<b>7 Polyhydroxyalkanoates: Basics, Production and Applications of Microbial Biopolyesters</b>	<b>137</b>
<i>Martin Koller, Anna Salerno, and Gerhart Braunegg</i>	
7.1 Microbial PHA Production, Metabolism, and Structure	137
7.1.1 Occurrence of PHAs	137
7.1.2 <i>In Vivo</i> Characteristics and Biological Role of PHAs	139
7.1.3 Structure and Composition of PHAs	140
7.1.4 Metabolic Aspects	141
7.2 Available Raw Materials for PHA Production	143
7.3 Recovery of PHA from Biomass	144
7.3.1 General Aspects of PHA Recovery	144
7.3.2 Direct Extraction of PHA from Biomass	146
7.3.3 Digestion of the non-PHA Cellular Material	147
7.3.4 Disruption of Cells of Osmophilic Microbes in Hypotonic Medium	148
7.4 Different Types of PHA	149
7.4.1 Short Chain Length vs. Medium Chain Length PHAs	149
7.4.2 Enzymatic Background: PHA Synthases	149
7.5 Global PHA Production	151
7.6 Applications of PHAs	152
7.6.1 General	152
7.6.2 Packaging and Commodity Items	152
7.6.3 Medical Applications	154
7.6.4 Application of the Monomeric Building Blocks	155
7.6.5 Smart Materials	156
7.6.6 Controlled Release of Active Agents	156
7.7 Economic Challenges in the Production of PHAs and Attempts to Overcome Them	156
7.7.1 PHA Production as a Holistic Process	156
7.7.2 Substrates as Economic Factor	156
7.7.3 Downstream Processing	157
7.7.4 Process Design	157
7.7.5 Contemporary Attempts to Enhance PHA Production in Terms of Economics and Product Quality	158
7.8 Process Design	160
7.9 Conclusion	162
References	163
<b>8 Poly(Lactic Acid)</b>	<b>171</b>
<i>Hideto Tsuji</i>	
8.1 Introduction	171
8.2 Historical Outline	173
8.3 Synthesis of Monomer	174
8.4 Synthesis of Poly(Lactic Acid)	176
8.4.1 Homopolymers	176
8.4.2 Linear Copolymers	176
8.5 Processing	178



8.6	Crystallization	178
8.6.1	Crystal Structures	178
8.6.2	Crystalline Morphology	181
8.6.3	Crystallization Behaviour	182
8.7	Physical Properties	182
8.7.1	Mechanical Properties	182
8.7.2	Thermal Properties	186
8.7.3	Permeability	188
8.7.4	Surface Properties	188
8.7.5	Electrical Properties	189
8.7.6	Optical Properties	189
8.8	Hydrolytic Degradation	191
8.8.1	Degradation Mechanism	192
8.8.2	Effects of Surrounding Media	195
8.8.3	Effects of Material Parameters	196
8.9	Thermal Degradation	200
8.10	Biodegradation	204
8.11	Photodegradation	205
8.12	High-Performance Poly(Lactic Acid)-Based Materials	207
8.12.1	Nucleating or Crystallization-Accelerating Fillers	207
8.12.2	Composites and Nanocomposites	208
8.12.3	Fibre-Reinforced Plastics (FRPs)	211
8.12.4	Stereocomplexation	212
8.13	Applications	213
8.13.1	Alternatives to Petro-Based Polymers	213
8.13.2	Biomedical	214
8.13.3	Environmental Applications	216
8.14	Recycling	217
8.15	Conclusions	219
	References	219
<b>9</b>	<b>Other Polyesters from Biomass Derived Monomers</b>	<b>241</b>
	<i>Daan S. van Es, Frits van der Klis, Rutger J. I. Knoop, Karin Molenveld, Lolke Sijtsma, and Jacco van Haveren</i>	
9.1	Introduction	241
9.2	Isohexide Polyesters	242
9.2.1	Introduction	242
9.2.2	Semi-Aromatic Homo-Polyesters	244
9.2.3	Semi-Aromatic Co-Polyesters	247
9.2.4	Aliphatic Polyesters	248
9.2.5	Modified Isohexides	250
9.3	Furan-Based Polyesters	251
9.3.1	Introduction	251
9.3.2	2,5-Dihydroxymethylfuran (DHMF)-Based Polyesters	253
9.3.3	5-Hydroxymethylfuroic Acid (HMFA) Based Polyesters	254
9.3.4	Furan-2,5-Dicarboxylic Acid (FDCA) Based Polyesters	254
9.3.5	Future Outlook	256



9.4	Poly(Butylene Succinate) (PBS) and Its Copolymers	257
9.4.1	Succinic Acid	257
9.4.2	1,4-Butanediol (BDO)	258
9.4.3	Poly(Butylene Succinate) (PBS)	259
9.4.4	PBS Copolymers	259
9.4.5	PBS Biodegradability	260
9.4.6	PBS Processability	260
9.4.7	PBS Blends	260
9.4.8	PBS Markets and Applications	260
9.4.9	Future Outlook	261
9.5	Bio-Based Terephthalates	261
9.5.1	Introduction	261
9.5.2	Bio-Based Diols: Ethylene Glycol, 1,3-Propanediol, 1,4-Butanediol	262
9.5.3	Bio-Based Xylenes, Isophthalic and Terephthalic Acid	263
9.6	Conclusions	267
	References	267
<b>10</b>	<b>Polyamides from Biomass Derived Monomers</b>	<b>275</b>
	<i>Benjamin Brehmer</i>	
10.1	Introduction	275
10.1.1	What are Polyamides?	275
10.1.2	What is the Polymer Pyramid?	276
10.1.3	Where do Polyamides from Biomass Derived Monomers Fit?	277
10.2	Technical Performance of Polyamides	277
10.2.1	How to Differentiate Performance	277
10.2.2	Overview of Current Applications	279
10.2.3	Typical Association of Biopolymers	280
10.3	Chemical Synthesis	281
10.3.1	Castor Bean to Intermediates	281
10.3.2	Undecenoic Acid Route	283
10.3.3	Sebacic Acid Route	283
10.3.4	Decamethylene Diamine Route	284
10.4	Monomer Feedstock Supply Chain	284
10.4.1	Description of Supply Chain	284
10.4.2	Pricing Situation	285
10.5	Producers	287
10.6	Sustainability Aspects	287
10.6.1	Biosourcing	287
10.6.2	Lifecycle Assessments	288
10.6.3	Labelling and Certification	291
10.7	Improvement and Outlook	292
	References	293
<b>11</b>	<b>Polyolefin-Based Plastics from Biomass-Derived Monomers</b>	<b>295</b>
	<i>R.J. Koopmans</i>	
11.1	Introduction	295



11.2	Polyolefin-Based Plastics	296
11.3	Biomass	299
11.4	Chemicals from Biomass	300
11.5	Chemicals from Biotechnology	302
11.6	Plastics from Biomass	303
11.7	Polyolefin Plastics from Biomass and Petrochemical Technology	303
11.7.1	One-Carbon Building Blocks	304
11.7.2	Two-Carbon Building Blocks	305
11.7.3	Three-Carbon Building Blocks	305
11.8	Polyolefin Plastics from Biomass and Biotechnology	305
11.9	Bio-Polyethylene and Bio-Polypropylene	306
11.10	Perspective and Outlook	307
	References	308
<b>12</b>	<b>Future Trends for Recombinant Protein-Based Polymers: The Case Study of Development and Application of Silk-Elastin-Like Polymers</b>	<b>311</b>
	<i>Margarida Casal, António M. Cunha, and Raul Machado</i>	
12.1	Introduction	311
12.2	Production of Recombinant Protein-Based Polymers (rPBPs)	312
12.3	The Silk-Elastin-Like Polymers (SELPs)	314
12.3.1	SELPs for Biomedical Applications: Hydrogels for Localized Delivery	317
12.3.2	Mechanical Properties of SELP Hydrogels	319
12.3.3	Spun Fibres	320
12.3.4	Solvent Cast Films	323
12.4	Final Considerations	324
	References	325
<b>13</b>	<b>Renewable Raw Materials and Feedstock for Bioplastics</b>	<b>331</b>
	<i>Achim Raschka, Michael Carus, and Stephan Piotrowski</i>	
13.1	Introduction	331
13.2	First- and Second-Generation Crops: Advantages and Disadvantages	331
13.3	The Amount of Land Needed to Grow Feedstock for Bio-Based Plastics	333
13.4	Productivity and Availability of Arable Land	336
13.5	Research on Feedstock Optimization	338
13.6	Advanced Breeding Technologies and Green Biotechnology	339
13.7	Some Facts about Food Prices and Recent Food Price Increases	341
13.8	Is there Enough Land for Food, Animal Feed, Bioenergy and Industrial Material Use, Including Bio-Based Plastics?	343
	References	345
<b>14</b>	<b>The Promise of Bioplastics – Bio-Based and Biodegradable-Compostable Plastics</b>	<b>347</b>
	<i>Ramani Narayan</i>	
14.1	Value Proposition for Bio-Based Plastics	348
14.2	Exemplars of Zero or Reduced Material Carbon Footprint – Bio-PE, Bio-PET and PLA	349



14.3	Process Carbon Footprint and LCA	351
14.4	Determination of Bio-Based Carbon Content	352
14.5	End-of-Life Options for Bioplastics – Biodegradability-Compostability	353
14.6	Summary	356
	References	356
<b>Index</b>		<b>359</b>