

# Contents

<b>1</b>	<b>Biodegradability of Polymers – Mechanisms and Evaluation Methods</b>	<b>1</b>
1.1	Introduction	1
1.2	Background	1
1.3	Defining Biodegradability	2
1.4	Mechanisms of Polymer Degradation	4
1.4.1	Non-biological Degradation of Polymers	4
1.4.2	Biological Degradation of Polymers	5
1.5	Measuring Biodegradation of Polymers	11
1.5.1	Enzyme Assays	13
1.5.2	Plate Tests	14
1.5.3	Respiration Tests	15
1.5.4	Gas (CO <sub>2</sub> or CH <sub>4</sub> ) Evolution Tests	16
1.5.5	Radioactively Labelled Polymers	18
1.5.6	Laboratory-scale Simulated Accelerating Environments	18
1.5.7	Natural Environments – Field Trials	20
1.6	Factors Affecting Biodegradability	20
1.7	Conclusions	22
	References	22
<b>2</b>	<b>Biodegradation Behaviour of Polymers in Liquid Environments</b>	<b>33</b>
2.1	Introduction	33
2.2	Degradation in Real Liquid Environments	34
2.2.1	Degradation in Sweet Water and Marine Environment	35
2.3	Degradation in Laboratory Tests Simulating Real Aquatic Environments	37
2.3.1	Aerobic Liquid Environments	37

2.3.2 Anaerobic Liquid Environments .....	40
2.4 Degradation in Laboratory Tests with Optimised and Defined Liquid Media.....	43
2.5 Standard Tests for Biodegradable Polymers Using Liquid Media .....	46
2.6 Summary .....	51
References .....	51
<b>3 Biodegradation Behaviour of Polymers in the Soil .....</b>	<b>57</b>
3.1 Introduction .....	57
3.1.1 Biodegradable Polymers and the Environment.....	57
3.1.2 Biodegradable Polymers and Soil.....	57
3.2 How Polymers Reach Soil .....	58
3.2.1 Intentional Delivery .....	58
3.2.2 Unintentional Delivery: Littering.....	60
3.3 The Soil Environment .....	60
3.3.1 Surface Factors.....	62
3.3.2 Underground Factors .....	65
3.4 Degradability of Polymers in Soil .....	71
3.4.1 The Standardisation Approach .....	71
3.4.2 Test Methods and Criteria .....	73
3.5 Effects of Biodegradable Polymers on Soil Living Organisms .....	81
3.5.1 Performing the Assessment: Transient and Permanent Effects .....	81
3.5.2 Test Material Concentration.....	82
3.5.3 Preparation of the Soil Sample Ready for Ecotoxicity Testing.....	82
3.5.4 Test Methods.....	83
3.6 Biodegradability of Materials in Soil: A Survey of the Literature.....	83
Acknowledgements.....	84

References .....	94
<b>4 Ecotoxicological Aspects in the Biodegradation Process of Polymers .....</b>	<b>103</b>
4.1 The Need of Ecotoxicity Analysis for Biodegradable Materials .....	103
4.1.1 Standards and Regulations for Testing of Biodegradable Polymers .....	104
4.1.2 Detection of the Influences on an Ecosystem Caused by the Biodegradation of Polymers.....	106
4.1.3 Potential Influences of Polymers After Composting .....	108
4.1.4 Potential Influences of Polymers During and After Biodegradation in Soil and Sediment .....	109
4.2 A Short Introduction to Ecotoxicology .....	111
4.2.1 Theory of Dose-Response Relationships.....	111
4.2.2 Test Design in Ecotoxicology.....	111
4.2.3 Toxicity Tests and Bioassays.....	113
4.2.4 Ecotoxicity Profile Analysis .....	114
4.3 Recommendations and Standard Procedures for Biotests.....	114
4.3.1 Bioassays with Higher Plants.....	115
4.3.2 Bioassays with Earthworms ( <i>Eisenia foetida</i> ).....	119
4.3.3 Preparation of Elutriates for Aquatic Ecotoxicity Tests .....	119
4.3.4 Bioassays with Algae .....	120
4.3.5 Bioassays with Luminescent Bacteria.....	122
4.3.6 Bioassays with <i>Daphnia</i> .....	123
4.3.7 Evaluation of Bioassay Results Obtained from Samples of Complex Composition.....	123
4.3.8 Testing of Sediments.....	124
4.4 Special Prerequisites to be Considered when Applying Bioassays for Biodegradable Polymers.....	125
4.4.1 Nutrients in the Sample .....	125
4.4.2 Biodegradation Intermediates .....	127
4.4.3 Diversity of the Microorganism Population.....	128

4.4.4	Humic Substances .....	128
4.4.5	Evaluation of Test Results and Limits of Bioassays.....	129
4.5	Research Results for Ecotoxicity Testing of Biodegradable Polymers..	130
4.5.1	The Relationship Between Chemical Structure, Biodegradation Pathways and Formation of Potentially Ecotoxic Metabolites .....	130
4.5.2	Ecotoxicity of the Polymers .....	131
4.5.3	Ecotoxic Effects Appearing After Degradation in Compost or After Anaerobic Digestion .....	132
4.5.4	Ecotoxic Effects Appearing During Degradation in Soil .....	132
4.6	Conclusion .....	133
4.6.1	Consequences for Test Schemes for Investigations on Biodegradable Polymers .....	135
4.6.2	Conclusion .....	136
	References .....	137
5	<b>International and National Norms on Biodegradability and Certification Procedures .....</b>	<b>145</b>
5.1	Introduction .....	145
5.2	Organisations for Standardisation .....	147
5.3	Norms .....	149
5.3.1	Aquatic, Aerobic Biodegradation Tests .....	151
5.3.2	Compost Biodegradation Tests .....	154
5.3.3	Compostability Norms .....	158
5.3.4	Compost Disintegration Tests .....	163
5.3.5	Soil Biodegradation Tests .....	164
5.3.6	Aquatic, Anaerobic Biodegradation Tests .....	166
5.3.7	High-Solids, Anaerobic Biodegradation Tests .....	167
5.3.8	Marine Biodegradation Tests .....	168
5.3.9	Other Biodegradation Tests .....	168
5.4	Certification .....	169

5.4.1	Introduction .....	169
5.4.2	Different Certification Systems .....	170
	References .....	175
<b>6</b>	<b>General Characteristics, Processability, Industrial Applications and Market Evolution of Biodegradable Polymers .....</b>	<b>183</b>
6.1	General Characteristics.....	183
6.1.1	Polymer Biodegradation Mechanisms.....	184
6.1.2	Polymer Molecular Size, Structure and Chemical Composition.....	185
6.1.3	Biodegradable Polymer Classes.....	185
6.1.4	Naturally Biodegradable Polymers .....	186
6.1.5	Synthetic Biodegradable Polymers .....	191
6.1.6	Modified Naturally Biodegradable Polymers .....	199
6.2	Processability.....	200
6.2.1	Extrusion .....	202
6.2.2	Film Blowing and Casting .....	204
6.2.3	Moulding .....	205
6.2.4	Fibre Spinning.....	206
6.3	Industrial Applications .....	206
6.3.1	Loose-Fill Packaging.....	206
6.3.2	Compost Bags .....	207
6.3.3	Other Applications.....	208
6.4	Market Evolution .....	209
	References .....	212
<b>7</b>	<b>Polyhydroxyalkanoates .....</b>	<b>219</b>
7.1	Introduction .....	219
7.2	The Various Types of PHA .....	220
7.2.1	Poly[R-3-hydroxybutyrate] (P[3HB]).....	220

7.2.2	Poly[3-hydroxybutyrate- <i>co</i> -3-hydroxyvalerate] (P[3HB- <i>co</i> -3HV]) .....	222
7.2.3	Poly[3-hydroxybutyrate- <i>co</i> -4-hydroxybutyrate] (P[3HB- <i>co</i> -4HB]).....	224
7.2.4	Other PHA Copolymers with Interesting Physical Properties.....	225
7.2.5	Uncommon PHA Constituents .....	227
7.3	Mechanisms of PHA Biosynthesis.....	228
7.3.1	Conditions that Promote the Biosynthesis and Accumulation of PHA in Microorganisms.....	229
7.3.2	Carbon Sources for the Production of PHA.....	229
7.3.3	Biochemical Pathways Involved in the Metabolism of PHA....	231
7.3.4	The Key Enzyme of PHA Biosynthesis, PHA Synthase.....	234
7.4	Genetically Modified Systems and Other Methods for the Production of PHA.....	235
7.4.1	Recombinant <i>Escherichia coli</i> .....	235
7.4.2	Transgenic Plants.....	236
7.4.3	<i>In vitro</i> Production of PHA.....	237
7.5	Biodegradation of PHA .....	237
7.6	Applications of PHA .....	238
7.7	Conclusions and Outlook.....	240
	References .....	241
8	Starch-Based Technology .....	257
8.1	Introduction .....	257
8.2	Starch Polymer .....	258
8.3	Starch-filled Plastics.....	260
8.4	Thermoplastic Starch.....	261
8.5	Starch-Based Materials on the Market.....	271
8.6	Conclusions.....	274

References .....	275
<b>9 Poly(Lactic Acid) and Copolyesters .....</b>	<b>287</b>
9.1 Introduction .....	287
9.2 Synthesis.....	287
9.2.1 Homopolymers.....	287
9.2.2 Copolymers.....	289
9.2.3 Functionalised Polymers.....	290
9.3 Structure, Properties, Degradation, and Applications .....	291
9.3.1 Physical Properties.....	291
9.3.2 Chemical Properties.....	292
9.3.3 Applications .....	294
9.4 Conclusions.....	294
References .....	294
<b>10 Aliphatic-Aromatic Polyesters .....</b>	<b>303</b>
10.1 Introduction .....	303
10.2 Development of Biodegradable Aliphatic-Aromatic Copolyesters.....	304
10.3 Degradability and Degradation Mechanism .....	307
10.3.1 General Mechanism/Definition.....	307
10.3.2 Degradation of Pure Aromatic Polyesters .....	310
10.3.3 Degradation of Aliphatic-Aromatic Copolyesters .....	311
10.4 Commercial Products and Characteristic Material Data.....	324
10.4.1 Ecoflex .....	325
10.4.2 Eastar Bio.....	326
10.4.3 Biomax.....	327
10.4.4 EnPol .....	328
10.4.5 Characteristic Material Data .....	328
References .....	330

<b>11</b>	<b>Material Formed from Proteins</b>	<b>339</b>
11.1	Introduction	339
11.2	Structure of Material Proteins	341
11.3	Protein-Based Materials	347
11.4	Formation of Protein-Based Materials	352
11.4.1	'Solvent Process'	352
11.4.2	'Thermoplastic Process'	356
11.5	Properties of Protein-Based Materials	362
11.6	Applications	370
	References	372
<b>12</b>	<b>Enzyme Catalysis in the Synthesis of Biodegradable Polymers</b>	<b>385</b>
12.1	Introduction	385
12.2	Polyester Synthesis	386
12.2.1	Polycondensation of Hydroxyacids and Esters	386
12.2.2	Polymerisation of Dicarboxylic Acids or Their Activated Derivatives with Glycols	388
12.2.3	Ring Opening Polymerisation of Carbonates and Other Cyclic Monomers	396
12.2.4	Ring Opening Polymerisation and Copolymerisation of Lactones	402
12.3	Oxidative Polymerisation of Phenol and Derivatives of Phenol	408
12.4	Enzymic Polymerisation of Polysaccharides	417
12.5	Conclusions	419
	References	420
<b>13</b>	<b>Environmental Life Cycle Comparisons of Biodegradable Plastics</b>	<b>431</b>
13.1	Introduction	431
13.2	Methodology of LCA	431



13.3	Presentation of Comparative Data.....	433
13.3.1	Starch Polymers.....	434
13.3.2	Polyhydroxyalkanoates .....	448
13.3.3	Polylactides (PLA) .....	451
13.3.4	Other Biodegradable Polymers .....	452
13.4	Summarising Comparison .....	452
13.5	Discussion .....	457
13.6	Conclusions.....	459
	Acknowledgements.....	462
	References .....	462
	Appendix 13.1 Overview of environmental life cycle comparisons for biodegradable polymers included in this review .....	467
	Appendix 13.2 Checklist for the preparation of an LCA for biodegradable plastics.....	477
<b>14</b>	<b>Biodegradable Polymers and the Optimisation of Models for Source Separation and Composting of Municipal Solid Waste .....</b>	<b>485</b>
14.1	Introduction .....	485
14.1.1	The Development of Composting and Schemes for Source Separation of Biowaste in Europe: A Matter of Quality.....	486
14.2	The Driving Forces for Composting in the EU.....	488
14.2.1	The Directive on the Landfill of Waste .....	488
14.2.2	The Proposed Directive on Biological Treatment of Biodegradable Waste .....	488
14.3	Source Separation of Organic Waste in Mediterranean Countries: An Overview.....	490
14.4	‘Biowaste’, ‘VGF’ and ‘Food Waste’: Relevance of a Definition on Performances of the Waste Management System.....	494
14.5	The Importance of Biobags.....	497

14.5.1 Features of 'Biobags': The Importance of Biodegradability and its Cost-Efficiency .....	498
14.6 Cost Assessment of Optimised Schemes.....	499
14.6.1 Tools to Optimise the Schemes and their Suitability in Different Situations.....	502
14.7 Conclusions.....	504
References .....	505
<b>Abbreviations .....</b>	<b>507</b>
<b>Contributors .....</b>	<b>515</b>
<b>Index .....</b>	<b>517</b>