

Edited by Ray Smith



<u>WP</u>

Biodegradable polymers for industrial applications

Related titles from Woodhead's materials engineering list:

Green composites – polymer composites and the environment (ISBN 1 85573 739 6)
Life cycle assessment is of paramount importance at every stage of a product's life, from initial synthesis through to final disposal, and a sustainable society needs environmentally safe materials and processing methods. With an internationally recognised team of authors, Green composites examines polymer composite production and explains how environmental footprints can be diminished at every stage of the life cycle. Green composites is an essential guide for agricultural crop producers, government agricultural departments, automotive companies, composites producers and material scientists all dedicated to the promotion and practice of eco-friendly materials and production methods.

Recent advances in environmentally compatible polymers (ISBN 1 85573 545 8) Based on the proceedings of the eleventh international Cellucon conference held in Tsukuba, Japan, this book offers a comprehensive overview of recent research undertaken into all aspects of environmentally compatible polymers. It deals with natural and synthetic polymer materials such as gels, fibres, pulp and paper, films, foams, blends and composites and shows how environmental compatibility such as biodegradability and recyclability can de developed by utilising natural polymers such as polysaccharides and polyphenols.

Environmental impact of textiles (ISBN 1 85573 541 5)

This comprehensive book examines the effects that textile production and use have on the environment. It looks at the physical environment affected by these processes, including resource depletion, pollution and energy use and the biological environment, by considering what happens as a result of manufacture. It also considers the degradation suffered by textile materials within the environment whether by air pollution, wind, water and other agents. The most recent solutions adopted by the industry are considered and an analysis offered of the likely effectiveness of these strategies. It is an essential reference for anyone concerned with the environmental footprint of the global textile industry.

Bast and other plant fibres (ISBN 1 85573 684 5)

Environmental concerns have regenerated interest in the use of natural fibres for a much wider variety of products, including high-tech applications such as geotextiles, and in composite materials for automotive and light industry use. This new study covers: the chemical and physical structure of these natural fibres; fibre, yarn and fabric production; dyeing; handle and wear characteristics; economics; environmental and health and safety issues.

Details of these books and a complete list of Woodhead's materials engineering and textile technology titles can be obtained by:

- visiting our web site at www.woodheadpublishing.com
- contacting Customer Services (e-mail: sales@woodhead-publishing.com; fax: +44 (0) 1223 893694; tel.: +44 (0) 1223 891358 ext. 30; address: Woodhead Publishing Limited, Abington Hall, Abington, Cambridge CB1 6AH, England)

If you would like to receive information on forthcoming titles in this area, please send your address details to: Francis Dodds (address, tel. and fax as above; e-mail: francisd@woodhead-publishing.com). Please confirm which subject areas you are interested in.

Biodegradable polymers for industrial applications

Edited by Ray Smith



CRC Press Boca Raton Boston New York Washington, DC

WOODHEAD PUBLISHING LIMITED

Cambridge England

Published by Woodhead Publishing Limited Abington Hall, Abington Cambridge CB1 6AH England www.woodheadpublishing.com

Published in North America by CRC Press LLC 2000 Corporate Blvd, NW Boca Raton FL 33431 USA

First published 2005, Woodhead Publishing Limited and CRC Press LLC © 2005, Woodhead Publishing Limited
The authors have asserted their moral rights.

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. Reasonable efforts have been made to publish reliable data and information, but the authors and the publishers cannot assume responsibility for the validity of all materials. Neither the authors nor the publishers, nor anyone else associated with this publication, shall be liable for any loss, damage or liability directly or indirectly caused or alleged to be caused by this book.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming and recording, or by any information storage or retrieval system, without permission in writing from the publishers.

The consent of Woodhead Publishing Limited and CRC Press LLC does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific permission must be obtained in writing from Woodhead Publishing Limited or CRC Press LLC for such copying.

Trademark notice: product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation, without intent to infringe.

British Library Cataloguing in Publication Data A catalogue record for this book is available from the British Library.

Library of Congress Cataloging-in-Publication Data A catalog record for this book is available from the Library of Congress:

Woodhead Publishing Limited ISBN 1 85573 934 8 CRC Press ISBN 0-8493-3466-7

CRC Press order number: WP3466

The publishers' policy is to use permanent paper from mills that operate a sustainable forestry policy, and which has been manufactured from pulp which is processed using acid-free and elementary chlorine-free practices. Furthermore, the publishers ensure that the text paper and cover board used have met acceptable environmental accreditation standards.

Project managed by Macfarlane Production Services, Markyate, Hertfordshire (macfarl@aol.com)
Typeset by Godiva Publishing Services Ltd, Coventry, West Midlands
Printed by TJ International Limited, Padstow, Cornwall, England

Contents

	Contributor contact details	xiii
Part I	Classification and development	
1	Classification of biodegradable polymers A-M CLARINVAL and J HALLEUX, CRIF, Belgium	3
1.1	Introduction	3
1.2	Biopolymers from natural origins	4
1.3	Biopolymers from mineral origins	21
1.4	Conclusions	29
1.5	References	29
2	Polyhydroxyalkanoates G G-Q CHEN, Tsinghua University, China	32
2.1	Introduction	32
2.2	Mechanical and thermal properties of PHA	37
2.3	Process development and scale up for microbial PHA production	42
2.4	Applications of PHA	48
2.5	Future developments	50
2.6	References	50
3	Oxo-biodegradable polyolefins D M WILES, Plastichem Consulting, Canada	57
3.1	Introduction	57
3.2	Polyolefin peroxidation	58
3.3	Control of polyolefin lifetimes	62
3.4	Oxidative degradation after use	63
3.5	Aerobic biodegradation	66

vi	Contents
V I	COLICIIO

3.6	Applications of oxo-biodegradable polyolefins	66
3.7	Environmental impact	69
3.8	Future developments	73
3.9	References	74
4	New developments in the synthesis of aliphatic	
	polyesters by ring-opening polymerisation	77
	R JEROME and P LECOMTE, University of Liège, Belgium	
4.1	Introduction	77
4.2	Synthesis of aliphatic polyesters by ring-opening	
	polymerisation	77
4.3	Reactive extrusion	87
4.4	Supercritical carbon dioxide as a medium for the ring-opening polymerisation of lactones and lactides and a processing aid	
	for aliphatic polyesters	91
4.5	Future developments	101
4.6	Acknowledgements	102
4.7	Bibliography	102
5	Biodegradable polyesteramides	107
	PAMLIPS and PJDIJKSTRA, University of Twente,	
	The Netherlands	
5.1	Introduction	107
5.2	Poly(ester amide)s synthesis	107
5.3	Polydepsipeptides	124
5.4	Concluding comments	132
5.5	Further information	132
5.6	References	132
6	Thermoplastic starch biodegradable polymers	140
	P J HALLEY, The University of Queensland, Australia	
6.1	Introduction	140
6.2	Properties of starch	141
6.3	Thermoplastic starch and their blends	149
6.4	Modified thermoplastic starch polymers	153
6.5	Commercial applications and products for thermoplastic	
	starch polymers	155
6.6	Thermoplastic starch polymers – looking beyond traditional	
	polymer applications	156
6.7	Future developments	157
6.8	Further information	158

	Contents	Vİİ
6.9 6.10	Acknowledgements References	159 159
Part II	Materials for production of biodegradable polymers	
7	Biodegradable polymers from sugars A J VARMA, National Chemical Laboratory, India	165
7.1	Introduction	165
7.2	Biodegradable polymers obtained from monosaccharides and disaccharides	166
7.3	Biodegradable polymers obtained from synthetic	172
7.4 7.5	polysaccharides Biodegradable polymers obtained from natural polysaccharides Future developments – 'biodegradable' polymers obtained	173 178
7.5	from hemicelluloses	180
7.6	References	184
8	Biodegradable polymer composites from natural fibres DPLACKETT, Risø National Laboratory, Denmark	189
8.1	Introduction	189
8.2	Natural fibres as polymer reinforcement	190
8.3	Natural fibre-polyhydroxyalkanoate (PHA) composites	191
8.4	Natural fibre-polylactide (PLA) composites	198
8.5	Natural fibre-starch composites	203
8.6	Natural fibre-soy resin composites	208
8.7	Natural fibres in combination with synthetic biodegradable	210
8.8	polymers Commonial developments	210 211
8.9	Commercial developments Conclusion	211
8.10	Further information	213
8.11	References	214
0	Die de mediale en el mane forma en en el la format	
9	Biodegradable polymers from renewable forest	210
	resources	219
	T M KEENAN, S W TANENBAUM and J P NAKAS, College of Environmental Science and Forestry Syracuse, USA	
9.1	Lignocellulosic biomass as a renewable and value-added	
	feedstock for biodegradable polymer production	219
9.2	Cellulose: as a platform substrate for degradable polymer	222
	synthesis	223

viii Contents

9.3	Hemicellulose and its application as a feedstock for	
	biodegradable polymers	226
9.4	Sources of further information	244
9.5	Conclusions and future developments	246
9.6	References	246
10	Poly(lactic acid)-based bioplastics	251
	J-F ZHANG and X SUN, Kansas State University, USA	
10.1	Introduction	251
10.2	Properties of PLA	252
10.3	Blends of PLA	261
10.4	Plasticization of PLA-based bioplastics	270
10.5	Aging and biodegradation	275
10.6	Applications of PLA based bioplastics	280
10.7	References	281
11	Biodegradable protein-nanoparticle composites	289
	K DEAN and L YU, CSIRO – Manufacturing and Infrastructure Technology, Australia	
	illitastructure Technology, Australia	
11.1	Introduction	289
11.2	Delaminating clay using ultrasonics	293
11.3 11.4	Processing protein-nanoparticle composites using extrusion Microstructure and mechanical properties of protein-	298
	nanoparticle composites	298
11.5	Conclusion	306
11.6	References	307
Part III	Properties and mechanisms of degradation	
12	Standards for environmentally biodegradable plastics G S C O T T, Aston University, UK	313
12.1	Why standards are necessary	313
12.2	Bio-based polymers	316
12.3	The post-use treatment of plastics for the recovery of value	317
12.4	Mechanisms of polymer biodegradation	319
12.5	Laboratory studies	322
12.6	The development of national and international standards for	
	biodegradable plastics	323
12.7	Lessons from the past and future developments	329

	Conter	nts ix
12.8	Acknowledgements	331
12.9	References	332
13	Material properties of biodegradable polymers M BHATTACHARYA, University of Minnesota, USA, R L REIS, V CORRELO and L BOESEL, University of Minho, Portugal	336
13.1	Introduction	336
13.2	Biodegradation	337
13.3	Natural polymers	340
13.4	Microbial polyesters	341
13.5	Synthetic polyesters	343
13.6	Poly-lactic acid	343
13.7	Poly(glycolic) acid	345
13.8	Polycaprolactone	345
13.9	Poly(alkene succinate)	345
13.10	Aliphatic-aromatic copolyesters	346
13.11	Poly(orthoesters)	346
13.12	Polyanhydrides	347
13.13	Polycarbonates/polyiminocarbonates	347
13.14	Blends	347
13.15	Water-soluble polymers	348
13.16	Future developments	349
13.17	Acknowledgements	352
13.18	References	352
14	Mechanism of biodegradation	357
	S MATSUMURA, Keio University, Japan	
14.1	Introduction	357
14.2	Biodegradation mechanism: overview	359
14.3	Biodegradation mechanism of naturally occurring polymers	s 362
14.4	Biodegradation mechanism of polyesters	365
14.5	Biodegradation mechanism of polycarbonates and polyethe	ers 372
14.6	Biodegradation mechanism of poly(vinyl alcohol)	376
14.7	Biodegradation mechanism of polyurethanes	382
14.8	Biodegradation mechanism of poly(amino acid)	384
14.9	Biodegradation mechanism of miscellaneous polymers	389
14.10	Future trends	393
14.11	Bibliography	394
14.12	References	395