

Volume 4

Handbook of Engineering and Specialty Thermoplastics

Nylons

Edited by

Sabu Thomas and Visakh P.M.

Handbook of Engineering and Specialty Thermoplastics

Volume 4
Nylons

Edited by
Sabu Thomas and Visakh P.M.



Scrivener

 **WILEY**

Copyright © 2012 by Scrivener Publishing LLC. All rights reserved.

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

For more information about Scrivener products please visit www.scrivenerpublishing.com.

Cover design by Russell Richardson

Library of Congress Cataloging-in-Publication Data:

ISBN 978-0-470-63925-2

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Handbook of Engineering and Specialty Thermoplastics

Scrivener Publishing
3 Winter Street, Suite 3
Salem, MA 01970

Scrivener Publishing Collections Editors

James E. R. Couper	Ken Dragoon
Richard Erdlac	Rafiq Islam
Norman Lieberman	Peter Martin
W. Kent Muhlbauer	Andrew Y. C. Nee
S. A. Sherif	James G. Speight

Publishers at Scrivener

Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

List of Contributors

Zulkifli Ahmad graduated with his doctoral degree from University of Reading, UK in 2005. His main research interest is the synthesis of high performance polymers with application in opto-electronic devices. He has published 50 papers in refereed journals and presented talks in several international conferences as well as authored a monograph on crystal structure of high performance polymers. At present he is at Universiti Sains Malaysia as an Associate Professor.

Carlos Alemán earned his PhD in Sciences at the Technical University of Catalonia in 1994 and is currently a full professor there. He has received several awards including the Distinction of the Generalitat de Catalunya to the University Research (2003), the I3 Research Award of MICINN (2006), and the ICREA-ACADEMIA from ICREA Foundation (2007). He is group leader of the "Innovation in Materials and Molecular Engineering" (Chemical Engineering Department) and "Nanochemistry/Conducting" (CRNE) laboratories.

Sabrina Carroccio is a researcher at the Institute of Chemistry and Technology of Polymers of the National Research Council (CNR), Catania, Italy. Her research interests on degradation of polymers include molecular characterization of macromolecules by advances mass spectrometry techniques, polymer pyrolysis, polymer thermo and photo oxidation mechanisms.

F.C. García is a professor in the Department of Chemistry at the University of Burgos, Spain. He received his PhD at the University of Burgos, Spain in 2001. His research interest is in polymers with sensing capabilities in water environments.

J.M. García is a professor in the Department of Chemistry at the University of Burgos, Spain. He received his PhD in Chemistry at the Complutense University of Madrid, Spain, in 1995. Prof. Garcia is a co-author of more than 50 peer reviewed scientific publications, books and book chapters, and has a number of patents. His principal areas of research are high performance materials, functional polymers, and sensory polymers as sensing materials for water environments.

Ghobad Azizi Ghahfarrokhi received his MS degree in 2008 in organic chemistry from Isfahan University of Technology, Isfahan, Iran. He is pursuing his PhD degree in organic chemistry and his research interests are organic synthesis in ionic liquid media, MW assisted reactions and organometallic catalyzed reactions.

Annarosa Gugliuzza is a senior researcher at the Institute on Membrane Technology, ITM-CNR, Italy. She has a degree with honours in Chemistry and a PhD in Chemical Science. She is a membrane technologist with solid expertise in advanced materials and development of highly structured membranes with specific functions at molecular scale by sophisticated nanotechnologies, including self-assembly and layer-by-layer techniques.

Abdolreza Hajipour received his MS degree in 1983 from Shiraz University, Iran and his PhD degree in organic chemistry from Wollongong University, Australia in 1994. He is a Professor of Organic Chemistry at Isfahan University of Technology. His research interests cover the synthesis of novel optically active polymers, microwave-assisted organic and polymerization reactions, solid-state reactions, new reagents for oxidation and reduction of organic compounds.

José I. Iribarren received his PhD in Sciences from the Technical University of Catalonia (Spain) in 1996. After many years developing his research activity in the structural characterization of chiral polyamides, in 2003 he joined the "Innovation in Materials and Molecular Engineering" group at the Technical University of Catalonia. His current research interests concern the protection against corrosion using conducting polymers.

Melek Kiristi is a PhD candidate with research interests in the synthesis and application of conducting and biopolymers. She holds a BS degree from Suleyman Demirel University in Isparta, Turkey and a MS degree from Suleyman Demirel University in Isparta, Turkey.

Giorgio Montaudo is a Professor in the Department of Chemistry, University of Catania, Italy. He has been the Director of ICTMP-Catania of the CNR of Italy. Dr. Montaudo received a PhD in chemistry from the University of Catania and has been active in the field of the synthesis, degradation, and characterization of polymeric

materials by mass spectrometry. He is the author of more than 300 publications in international journals and chapters in books.

J.L. de la Peña is a Professor in the Department of Chemistry at the University of Burgos, Spain. He carried out his doctoral studies at the Institute of Polymer Science & Technology, Spanish National Research Council (CSIC), receiving his PhD in Chemistry at the Complutense University of Madrid, Spain, in 1972. His research interests cover all fields of polymer preparation and applications.

Concetto Puglisi is a Research Manager in the Institute of Chemistry and Technology of Polymers of the Italian National Research Council (CNR). He received his degree in Industrial Chemistry at the University of Catania in 1978. His research activity include thermal degradation and oxidation mechanisms of polymers, mechanisms of chemical exchange of polymer blends in the molten state and application of advanced mass spectrometry techniques to the analysis of polymers.

Jordi Puiggalí earned his PhD in Industrial Engineering at the Technical University of Catalonia (UPC) in 1987 and is currently full professor at the same University. His research activity is mainly focused in the development of biodegradable polymers for biomedical applications and in the structural studies of polyamides and polyesters. He is group leader of the "Synthetic Polymers: Structure and Properties" (<http://psep.upc.edu>), "Macromolecular Chemistry" and "Nanotechnology" (<http://www.upc.edu/crne>) laboratories of the Chemical Engineering Department of the UPC.

Fatemeh Rafiee received her MS degree in 2007 in organic chemistry from Isfahan University of Technology, Iran, She is pursuing her PhD degree in organic chemistry at the Isfahan University of Technology, Iran. Her research interests are organic synthesis in ionic liquid media, MW assisted reactions and organometallic catalyzed reactions.

F. Serna is Associate Professor in the Department of Chemistry at the University of Burgos, Spain. He carried out his doctoral studies at the Institute of Polymer Science & Technology, Spanish National Research Council (CSIC), receiving his PhD in Chemistry at the Complutense University of Madrid, Spain, in 1985. His research interest is related with polymers for advanced technologies.

Aysegul Uygun is a Professor of Chemistry at the Department of Chemistry in the Middle East Technical University, Turkey with expertise in polymer chemistry. Her research interests include conducting polymers. Prof.Uygun has more than 50 publications in scientific journals. She received her PhD degree from Suleyman Demirel University in Isparta, Turkey. She is the recipient of DFG and Fulbright Scholarships.

Contents

List of Contributors	xi
1. Engineering and Specialty Thermoplastics: Nylons	1
<i>Visakh. P. M and Sabu Thomas</i>	
1.1 Polyamide-imides	1
1.2 Polyetherimide (PEI)	2
1.3 Poly(Ether-Block-Amide)	2
1.4 Aromatic Polyamides:	3
1.5 Polyaniline	5
1.6 Polyimides	6
1.7 New Challenges and Opportunities	8
References	9
2. Polyamide Imide	11
<i>Zulkifli Ahmad</i>	
2.1 Introduction and History	11
2.2 Polymerization	13
2.3 Properties	19
2.3.1 Solubility	19
2.3.2 Crystallinity	19
2.3.3 Thermal	22
2.3.4 Mechanical	24
2.3.5 Opto-electronic	25
2.3.6 Hydrogen bonding	26
2.4 Processing	27
2.5 Applications	30
2.5.1 Membrane Material	30
2.5.2 Coatings	31
2.5.3 Electronic	32
2.5.4 Optical	33
2.6 Recent Developments on Blends and Composites	33
2.6.1 Blends	33
2.6.2 Composites	34
2.7 Conclusions	38
References	38

3. Polyphthalamides	43
<i>J. I. Iribarren, C. Alemán, J. Puiggali</i>	
3.1 Introduction and History	43
3.2 Polymerization and Fabrication	47
3.3 Properties	53
3.4 Chemical Stability	61
3.5 Processing	66
3.6 Applications	68
3.7 Developments in Polyphthalamide Based Blends and Composites and their Applications	71
References	75
4. Polyetherimide	79
<i>Sabrina Carroccio, Concetto Puglisi, and Giorgio Montaudo</i>	
4.1 Introduction and History	79
4.2 Polymerization	82
4.2.1 Two Step Polymerization Reaction	82
4.2.2 One Step Processes	82
4.2.3 Synthesis Via Nucleophilic Substitution Reaction	85
4.2.4 Synthesis Via Exchange Reactions	87
4.3 Properties	88
4.3.1 Thermal Properties	89
4.3.2 Electrical Properties	89
4.3.3 Mechanical Properties	92
4.4 Stability	92
4.4.1 Hydrolytic Stability	92
4.4.2 Thermal Stability	95
4.4.3 Thermo and Photo Oxidative Stability	96
4.5 Special Additives	99
4.6 Processing	99
4.7 Applications	101
4.8 Environmental Impact and Recycling	102
4.9 Recent Developments In Polyetherimides Based Blends and Composites	102
References	105
5. Poly(ether-block-amide) Copolymers Synthesis, Properties and Applications	111
<i>Annarosa Gugliuzza</i>	
5.1 Introduction	111

5.2	Synthesis and Micro-phase Separated Morphology	113
5.3	Nomenclature, Properties and Relevant Area Applications	117
5.4	Compounding and Special Additives	122
5.5	Environmental Impact and Recycling	123
5.6	Poly ether-block-amides Membrane in Separation Processes	124
5.6.1	Treatment of Gaseous Streams	126
5.6.2	Water Permeable Poly(ether-block-amide) Membranes	130
5.6.3	Separation of Organic Compounds from Organic and Aqueous Streams	131
5.7	Poly(ether-block-amide) Membranes in Food	133
5.8	Concluding Remarks	135
	References	136
6.	Aromatic Polyamides (Aramids)	141
	<i>José M. García, Félix C. García, Felipe Serna, and José L. de la Peña</i>	
6.1	Introduction and History	142
6.2	Polymerization and Fabrication	145
6.2.1	Polymerization	145
6.2.2	Fabrication	149
6.3	Properties	149
6.4	Chemical Stability	154
6.5	Special Additives	154
6.6	Processing	157
6.6.1	Processing PMPI and ODA/PPPT	157
6.6.2	Processing of PPPT	157
6.7	Applications	158
6.8	Environmental Impact and Recycling	161
6.9	Recent Developments in Aromatic Polyamides and their Applications	162
6.9.1	Forthcoming and Future Application of Aramids	163
6.9.2	Polyamides with Improved Solubility	171
	Acknowledgments	174
	References	174
7.	Polyaniline	183
	<i>Melek Kiristi and Aysegul Uygun</i>	
7.1	Introduction and History	183

7.2	Polymerization and Fabrication	184
7.3	Properties	186
7.3.1	Electrical Properties of Polyaniline	186
7.3.2	Chemical Properties of Polyaniline	186
7.3.3	Mechanical Properties of Polyaniline	187
7.3.4	Optical Properties of Polyanilines	188
7.4	Chemical Stability	188
7.5	Compounding and Special Additives	189
7.6	Processing	195
7.7	Applications	197
7.8	Environmental Impact and Recycling	202
7.9	Recent Developments in Polyaniline Based Blends and Composites and their Applications	203
	References	205
8.	Polyimides: Synthesis Properties, Characterization and Applications	211
	<i>Abdolreza Hajipour, Fatemeh Rafiee, Ghobad Azizi</i>	
8.1	Introduction	211
8.2	Synthesis and Properties of Polyimides	213
8.2.1	Two-step Poly(amic acid) Process	213
8.2.2	Bulky Substituent in Polymer Backbone	215
8.2.3	Polyimides with Flexible Ether Links	217
8.2.4	Polyimides Containing Trifluoromethyl Group	221
8.2.5	Polyimides Containing Pyridine	228
8.2.6	Polyimides Containing Silicon	233
8.2.7	Polyimides Containing Phosphine Oxide Group	233
8.2.8	Synthesis of Polyimides via Dithioanhydride and Diamine	235
8.2.9	Synthesis of Polyimides via Polyamic Acid Alkyl Esters	236
8.2.10	Synthesis of Polyimides via Polyamic Acid Trimethylsilyl Esters	238
8.2.11	Polyimides Containing Six Membered Rings	239
8.2.12	Synthesis of Polyimides via Dianhydride and Diisocyanate	241

8.2.13	Preparation of Polyimides via Imide Exchange	243
8.2.14	Synthesis of Polyimides via Mitsunobu Reaction	244
8.2.15	Synthesis of Polyimides via Coupling by using Metals	245
8.2.16	Green Media for Preparation of Polyimides	246
8.2.17	Copolymers of Polyimides	251
8.3	Characterization and Analysis of Polyimides	258
8.4	Applications	261
8.4.1	Polyimides for Electronic Applications	262
8.4.2	Application of Polyimides in Membranes	270
8.4.3	Application of Polyimides in Fuel Cells	273
8.4.4	Polyimide Foams	275
8.4.5	Adhesives	276
	References	277
	Index	289

Engineering and Specialty Thermoplastics: Nylons

State of Art, New Challenges and Opportunities

Visakh. P. M¹ and Sabu Thomas²

^{1,2}*School of Chemical Sciences, Mahatma Gandhi University,
Kerala, INDIA*

²*Centre for Nanoscience and nanotechnology, Mahatma Gandhi University,
Kerala, INDIA*

Abstract

This chapter discusses a brief account on various types of nitrogen containing engineering polymers. Synthesis, morphology, structure, properties and applications of all different types of nitrogen containing engineering polymers are summarized in a concise manner. The new challenges and opportunities are also discussed.

1.1 Polyamide-imides

Polyamide-imides are thermoplastic amorphous polymers that have exceptional mechanical, thermal and chemical resistant properties. These properties put polyamide-imides at the top of the price and performance pyramid. Polyamide-imides are produced by Solvay Advanced Polymers under the trademark Torlon. Other high-performance polymers in this same realm are polyetheretherketones and polyimides. Polyamide-imides hold, as the name suggests, a positive synergy of properties from both polyamides and polyimides, such as high strength, melt processibility, exceptional high heat capability, and broad chemical resistance.

Polyamide-imide polymers can be processed into a wide variety of forms – from injection or compression molded parts and ingots – to coatings, films, fibers and adhesives. Generally these articles reach their maximum properties with a subsequent thermal cure process.

1.2 Polyetherimide (PEI)

Polyetherimide (PEI) is an amorphous, amber-to-transparent thermoplastic with characteristics similar to the related plastic PEEK. Relative to PEEK, PEI is cheaper, but less temperature-resistant and lower in impact strength. Polyetherimide combines high temperature resistance, rigidity, impact strength, and creep resistance. Glass-fiber-reinforced PEI plastic grades are available for general-purpose molding and extrusion; carbon-fiber-reinforced and other specialty grades also are produced for high-strength applications and PEI itself can be made into a high-performance thermoplastic fiber. PEI has found use in medical applications because of its heat and radiation resistance, hydrolytic stability, and transparency; in the electronics field, it is used to make burn-in sockets, bobbins, and printed circuit substrates; automotive uses include lamp sockets and under-hood temperature sensors; and PEI plastic sheeting is used in aircraft interiors. The PEI's history started in 1970, when USSR researchers (1) introduced the concept that the insertion of a flexible linkage into the polyimide chains considerably decreased glass transition temperatures without significantly lowering of thermal stability. Due to the wide range of PEI's applications, scientists continuously report studies concerning PEI synthesis from new monomers (2–4).

1.3 Poly(ether-block-amide)

Polyether block amide or PEBA is a thermoplastic elastomer (TPE). It is also known under the tradename of PEBAX® (Arkema). It is a block copolymer obtained by polycondensation of a carboxylic acid polyamide (PA6, PA11, PA12) with an alcohol termination polyether (PTMG, PEG). PEBA is a high performance thermoplastic elastomer. It is used to replace common elastomers – thermoplastic polyurethanes, polyester elastomers, and silicones - for these characteristics: lower density among TPE, superior mechanical

and dynamic properties (flexibility, impact resistance, energy return, fatigue resistance) and keeping these properties at low temperature (lower than $-40\text{ }^{\circ}\text{C}$), and good resistance against a wide range of chemicals. It is sensitive to UV degradation. Challenging high-performance polymeric materials are in high demand and poly(ether-block-amide) copolymers meet the requirements of advanced applications in various marketplaces. Thermoplastic elastomers with desired final properties can be tailored through addressed interplay of polymer segments having different chemical nature, length, and weight. Insightful investigations have suggested that the micro-phase separated morphology as the major factor for the outstanding properties of these copolymers that are not usually observed for each individual component. Excellent mechanical resistance enhanced chemical inertia and powerful perm-selective transport properties can be regarded as the result of the intricate interplay of the various constituents of these segmented copolymers. Excellent chemical, mechanical and transport properties of these polymers render them challenging systems for a broad range of applications, including high-performance waterproof breathable clothing, barrier films, engineered packaging, membrane separation processes. It is important to add that these materials are being used for many advanced industrial applications, including textile, packaging and medical devices. The latter appears to be a key issue to meet the requirements of advanced applications in textile, construction, food and waste processing, packaging and medical fields.

1.4 Aromatic Polyamides

Poly(amide)s, most commonly called polyamides, are polymers incorporating the amide group in their repeating unit ($-\text{CO}-\text{NH}-$) (5). Aromatic polyamides, wholly aromatic polyamides, or aramids, are considered to be high-performance materials owing to their outstanding thermal and mechanical resistance. The high performance properties of these materials can be attributed to their fully aromatic structure and amide linkages, which give rise to stiff rod-like macromolecular chains that interact with each other via strong and highly directional hydrogen bonds. These physical links deeply favor the development of effective crystalline micro-regions or domains, resulting in a compact intermolecular packing and cohesive energy. The better-known