

Brydson's Plastics Materials

Eighth Edition

Edited by

Marianne Gilbert



AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD • PARIS
SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Butterworth-Heinemann is an imprint of Elsevier



Butterworth-Heinemann is an imprint of Elsevier
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

Copyright © 2017 Elsevier Ltd. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN: 978-0-323-35824-8

For information on all Butterworth-Heinemann publications
visit our website at <https://www.elsevier.com/>



Publisher: Matthew Deans

Acquisition Editor: David Jackson

Editorial Project Manager: Edward Payne

Production Project Manager: Lisa Jones

Designer: Victoria Pearson

Typeset by TNQ Books and Journals

Contents

About the Authors	xvii	2.4 Molar Mass and Molar Mass Distribution	23
Preface to the Eighth Edition	xix	2.4.1 General Information	23
Acknowledgments	xxi	2.4.2 Measurement of Molar Mass and Molar Mass Distribution	25
Abbreviations for Plastics	xxiii	2.5 The Chemistry of Chain Reaction Polymerization	26
Standard Test Methods	xxix	2.5.1 Free-Radical Polymerization	26
		2.5.2 Basic Kinetics of Free-Radical Addition Polymerization	29
		2.5.3 Controlled Radical Polymerization	32
		2.5.4 Ionic Polymerization	33
		2.5.5 Ziegler–Natta and Metallocene Polymerization	35
		2.6 Step Reaction Polymerization	36
		References	37
1. Plastics Materials: Introduction and Historical Development	1	3. States of Aggregation in Polymers	39
<i>Marianne Gilbert</i>		<i>Marianne Gilbert</i>	
1.1 Introduction	1	3.1 Introduction	39
1.2 The First Plastics	1	3.2 Amorphous Polymers	39
1.3 Pre-1900	3	3.2.1 Physical States in Amorphous Polymers	39
1.4 1900–1930	4	3.2.2 The Glass Transition Temperature	41
1.4.1 Casein	4	3.2.3 Sub- T_g Transitions	42
1.4.2 Formaldehyde Resins	4	3.2.4 Physical Aging	42
1.4.3 Cellulose Acetate	5	3.2.5 Orientation in Amorphous Polymers	43
1.5 1930–1940	5	3.3 Crystalline Polymers	44
1.6 1940–1950	6	3.3.1 Introduction	44
1.7 1950–1960	6	3.3.2 Crystallinity in Polymers	45
1.8 1960–2000	7	3.3.3 Physical States in Crystalline Polymers	48
1.9 Raw Materials for Plastics	7	3.3.4 Temperature Dependence of Crystallization Rate	49
1.10 Plastics Now	9	3.3.5 Orientation in Crystalline Polymers	51
1.10.1 Health and Safety and the Environment	14	3.3.6 Liquid Crystal Polymers	52
1.10.2 Sustainability	15	3.4 Cross-Linked Structures	52
References	17	3.5 Impact Modification of Plastics	54
Bibliography	18	3.5.1 Copolymers	54
		3.5.2 Plasticizers	55
		3.5.3 Polymer Blends	55
		3.5.4 Hard Fillers, Pigments, and Foams	55
		3.5.5 Core–Shell Elastomer Impact Modifier Particles	55
2. The Chemical Nature of Plastics Polymerization	19		
<i>Steve Edmondson, Marianne Gilbert</i>			
2.1 Introduction	19		
2.2 Linear and Cross-Linked Molecules	19		
2.3 Copolymers and Blends	22		
2.3.1 Random Copolymers	22		
2.3.2 Block Copolymers	22		
2.3.3 Alternating Copolymers	23		
2.3.4 Graft Copolymers	23		
2.3.5 Other Methods of Combining Polymers	23		

3.6 Summary	56	5.8 Fire and Plastics	97
References	56	5.8.1 Introduction	97
Bibliography	57	5.8.2 Fire Testing	98
		References	101
		Bibliography	102
4. Relation of Structure to Thermal and Mechanical Properties	59	6. Relation of Structure to Electrical and Optical Properties	103
<i>Marianne Gilbert</i>		<i>Carole Raymond, Sara Ronca</i>	
4.1 Introduction	59	6.1 Electrical Properties	103
4.2 Factors Affecting the Glass Transition Temperature	59	6.1.1 Introduction	103
4.2.1 General Considerations	59	6.1.2 Dielectric Constant, Power Factor, and Structure	103
4.2.2 Effect of Molar Mass	62	6.1.3 Some Quantitative Relationships for Dielectrics	109
4.2.3 Effect of Copolymerization	62	6.1.4 Electronic Applications of Polymers	111
4.2.4 Effect of Cross-Linking	63	6.1.5 Electrically Conductive Polymers	111
4.2.5 Effect of Liquids	64	6.2 Optical Properties	115
4.3 Factors Affecting the Ability to Crystallize	64	6.2.1 Refractive Index	115
4.4 Factors Affecting the Crystalline Melting Point	68	6.2.2 Birefringence	116
4.5 Transition Temperatures in Copolymers	68	6.2.3 Transparency, Haze, and Clarity	118
4.6 Thermodynamic Treatment of Melting Temperature	70	6.2.4 Surface Appearance: Gloss and Reflectance	121
4.7 Some Individual Properties	71	6.2.5 Color	123
4.7.1 Melt Viscosity	72	References	125
4.7.2 Yield Strength and Modulus	72	Bibliography	125
4.7.3 Density	72		
4.7.4 Toughness	72	7. Additives for Plastics	127
References	73	<i>Sahar Al-Malaika, Frederick Axtell, Roger Rothon, Marianne Gilbert</i>	
Bibliography	73		
5. Relation of Structure to Chemical Properties	75	7.1 Introduction	127
<i>Marianne Gilbert</i>		7.2 Antioxidants	128
5.1 Introduction	75	7.2.1 Oxidation of Hydrocarbon Polymers	129
5.2 Chemical Bonds	75	7.2.2 Antioxidant Classes and Mechanisms of Action	132
5.3 Polymer Solubility	78	7.2.3 Antioxidants—Thermal Stabilizers	135
5.3.1 Solubility Parameters	78	7.2.4 Antioxidants—Photostabilizers and Photoactivators	137
5.3.2 Plasticizers	84	7.2.5 Antioxidants—Metal Deactivators	140
5.3.3 Other Additives	86	7.2.6 Biological Antioxidants	141
5.3.4 Determination of Solubility Parameter	86	7.2.7 High Molar Mass and Reactive Antioxidants	141
5.3.5 Thermodynamics and Solubility	89	7.2.8 Antioxidant Mixtures—Synergism and Antagonism	142
5.4 Chemical Reactivity	90	7.2.9 Stabilizers against Dehydrochlorination	143
5.5 Effects of Thermal, Photochemical, and High-Energy Radiation	91	7.3 Colorants	143
5.6 Aging and Weathering	93	7.3.1 Introduction	143
5.7 Diffusion and Permeability	94	7.3.2 Production of Color	143
5.7.1 Introduction	94	7.3.3 Additives for Coloration	145
5.7.2 Diffusion through a Film	95	7.4 Plasticizers and Softeners	150
5.7.3 Effect of Polymer and Diffusant Structure	96		

7.5 Lubricants and Flow Promoters	150	8.5.3 Coating Level	184
7.6 Impact Modifiers	151	8.5.4 Identification and Characterization of Surface Modifiers	185
7.6.1 Types of Impact Modifiers	151	8.5.5 Surface Modifier Types	185
7.6.2 Addition of Impact Modifiers	151	8.6 Examples of Filler Use in Plastics	188
7.7 Fire Retardant Additives	154	8.6.1 Principal Differences Affecting Polymer Response to Fillers	188
7.7.1 Terminology	154	8.6.2 Applications	190
7.7.2 Fire and Flammability Testing	155	8.6.3 Processing	190
7.7.3 Flame Retardant Mechanisms	155	8.6.4 Effects on Composite Properties	191
7.7.4 Main Flame Retardant Additives	155	8.7 Sustainability and Recycling Issues Affecting Fillers and Composites	201
7.8 Blowing Agents	158	8.7.1 Sustainability and Fillers	201
7.8.1 Physical Blowing Agents	159	References	203
7.8.2 Chemical Blowing Agents	159		
7.9 Other Additives	160	9. Processing, Design, and Performance of Plastics Products	205
7.9.1 Cross-Linking Additives	160	<i>António S. Pouzada</i>	
7.9.2 Surface Modifiers	163	9.1 Introduction	205
7.9.3 Compatibilizers for Polymer Blends	163	9.1.1 Plastics Products	206
7.9.4 Viscosity Modifiers	164	9.1.2 Processing Route of Thermoplastics	207
7.9.5 Biocides	164	9.1.3 Relevant Factors in Processing	207
7.9.6 Nucleating and Clarifying Agents	164	9.1.4 Design and Processing	208
References	165	9.2 Main Processing Techniques	208
Bibliography	168	9.2.1 Melt Processing of Thermoplastics	210
8. Fillers (Including Fiber Reinforcements)	169	9.2.2 Screw Extrusion	214
<i>Roger Rethon, Christopher DeArmitt</i>		9.2.3 Production of Continuous Articles	215
8.1 Introduction	169	9.2.4 Molding Techniques	215
8.2 Reasons for Using Fillers	169	9.2.5 Injection Molding	216
8.3 Important Characteristics of Particulate Fillers for Plastics Applications	171	9.2.6 Rotational Molding	222
8.3.1 Cost	171	9.3 Morphology and Processing	223
8.3.2 Chemical Composition	171	9.3.1 Orientation and Anisotropy	225
8.3.3 Specific Gravity (Density)	171	9.3.2 Shrinkage	227
8.3.4 Hardness	171	9.3.3 Distortion	227
8.3.5 Morphology (Particle Size and Shape)	172	9.3.4 Weld Lines	228
8.3.6 Thermal Properties	175	9.3.5 Residual Stresses	230
8.3.7 Electrical Properties	176	9.3.6 Voids	230
8.3.8 Optical Properties	176	9.4 Time-Dependent Properties	230
8.4 Principal Filler Types Used in Thermoplastics and Thermosets	176	9.4.1 Stress—Strain—Time Behavior	230
8.4.1 Calcium Carbonate Minerals	176	9.4.2 Creep Curves	231
8.4.2 Talc	177	9.4.3 Recovery from Deformation	233
8.4.3 Wood Flour	177	9.5 Stiffness	233
8.4.4 Aluminum Hydroxide	178	9.5.1 Practical Assessment of Long-Term Behavior	234
8.4.5 Wollastonite	178	9.5.2 Assessing Stiffness	235
8.4.6 Mica	179	9.5.3 Stiffness of Large Area Plastics Parts	236
8.4.7 Glass Fibers	179	9.6 Toughness	238
8.4.8 Nanofillers	180	9.6.1 Assessment of Impact Resistance	239
8.5 The Use of Surface Modifiers	183	9.6.2 Morphology and Impact Resistance	239
8.5.1 General Principles	184	9.7 Friction	240
8.5.2 Methods of Using Surface Modifiers	184	9.7.1 Solid Friction	240
		9.7.2 Friction in Injection Molds	240

9.8 Concluding Remarks	244
References	244
Bibliography	246

10. Polyethylene 247

Sara Ronca

10.1 Introduction	247
10.2 Preparation of Monomer	248
10.3 Polymerization	249
10.3.1 High-Pressure Polymerization	249
10.3.2 Ziegler Processes	250
10.3.3 The Phillips Process	250
10.3.4 Standard Oil Company (Indiana) Process	251
10.3.5 Processes for Making LLDPE and Metallocene PE	251
10.4 Structure and Properties of PE	252
10.5 Properties of PE	255
10.5.1 Mechanical Properties	255
10.5.2 Thermal Properties	258
10.5.3 Chemical Properties	260
10.5.4 Electrical Properties	261
10.5.5 Properties of LLDPE and VLDPE	262
10.5.6 Properties of Metallocene-Catalyzed PEs	262
10.6 Additives	263
10.7 Processing	265
10.8 PEs of Low and High Molar Mass	269
10.9 Cross-Linked PE	270
10.10 Oriented PE	271
10.11 Other Copolymers of Ethylene	273
10.11.1 Ethylene-Vinyl Acetate Copolymers	273
10.11.2 Ethylene-Ethyl Acrylate Copolymers	273
10.11.3 Ionomers	273
10.11.4 Ethylene-Carbon Monoxide Copolymer (Polyketone)	274
10.12 Applications	274
10.12.1 LDPE Applications	275
10.12.2 LLDPE Applications	275
10.12.3 HDPE Applications	275
10.12.4 HMWPE and UHMWPE Applications	276
10.12.5 PE for Molding Applications	277
10.12.6 PE as Dielectric Material	277
References	277

11. Polypropylene and Other Polyolefins 279

Markus Gahleitner, Christian Paulik

11.1 Polypropylene	279
11.1.1 Monomer Sources and Preparation	280
11.1.2 Polymerization—Catalysts and Processes	281
11.1.3 General Structure and Properties	286
11.1.4 Product Types and Compositions	290
11.1.5 Modifications	292
11.1.6 Additives for PP	294
11.1.7 Processing and Applications	297
11.1.8 Future Developments	303
11.2 Poly(but-1-ene)	304
11.2.1 Introduction	304
11.2.2 Structure and Properties	304
11.2.3 Processing	305
11.2.4 Applications	305
11.3 Poly(4-methylpentene-1)	306
11.3.1 Introduction	306
11.3.2 Structure and Properties	306
11.3.3 Processing	307
11.3.4 Applications	307
References	307

12. Plastics Based on Styrene 311

Kerry Satterthwaite

12.1 Introduction	311
12.2 Preparation/Source of Monomer	311
12.2.1 Preparation of Ethylbenzene	312
12.2.2 Dehydrogenation	312
12.2.3 Styrene Purification	313
12.3 Polymerization	313
12.3.1 Mass Polymerization	314
12.3.2 Solution Polymerization	314
12.3.3 Suspension Polymerization	314
12.4 Properties and Structure of Polystyrene	314
12.5 General Properties	315
12.6 General-Purpose High-Impact Polystyrene	316
12.6.1 Applications for GP—HI PS	318
12.7 Styrene-Acrylonitrile Copolymers	318
12.8 Acrylonitrile Butadiene Styrene	318
12.8.1 Processing of ABS	319
12.8.2 Applications of ABS	319

12.9 Rubber-Modified SAN and Related Copolymers	319	13.8.6 Pigments	361
12.10 SMA Copolymers	320	13.8.7 Polymeric Processing Aids and Impact Modifiers	362
12.11 Other Styrenic Polymers	320	13.8.8 Other Additives	363
12.12 Stereoregular Polystyrene	321	13.9 Formulations	364
12.12.1 Syndiotactic Polystyrene	321	13.9.1 Introduction	364
12.13 Processing of Plastics Based on Styrene	322	13.9.2 Sample Formulations	364
12.14 Expanded Polystyrene	322	13.9.3 Comments on Formulations	366
12.14.1 Structural Foams	324	13.10 Properties of PVC Compounds	367
12.15 Oriented Polystyrene	324	13.10.1 Rigid PVC	367
12.16 Polystyrene Blends With Polyphenylene Oxide	325	13.10.2 Flexible PVC	367
12.16.1 Introduction	325	13.11 Processing	369
12.16.2 Properties of PPO/PS Blends	326	13.11.1 Mixing	369
12.16.3 Processing of Styrenic PPOs	327	13.11.2 Unplasticized PVC	370
12.17 Future Developments for Plastics Based on Styrene	327	13.11.3 Plasticized PVC	371
References	327	13.11.4 Paste PVC	372
Bibliography	328	13.11.5 PVC Latices and Solutions	374
13. Poly(Vinyl Chloride)	329	13.12 Fusion of PVC	375
<i>Marianne Gilbert, Stuart Patrick</i>		13.12.1 Gelation and Fusion in Paste PVC	379
13.1 Introduction	329	13.13 Applications of PVC	380
13.2 Sustainability of PVC	330	13.13.1 Building and Construction	380
13.2.1 UK Developments	330	13.13.2 Health Sector	380
13.2.2 EU Responses	330	13.13.3 Film and Sheet	380
13.2.3 Sustainability Worldwide	331	13.13.4 Molded Products	381
13.3 Preparation of VC	331	13.13.5 Flexible Tubing and Profiles	382
13.4 Polymerization	332	13.14 PVC Copolymers and Chlorinated PVC	382
13.4.1 Suspension Polymerization	332	13.14.1 Copolymers	382
13.4.2 Bulk Polymerization	333	13.14.2 Chlorinated PVC	382
13.4.3 Emulsion and Microsuspension Polymerization	333	13.15 Modification of PVC Structure	383
13.5 Structure of PVC	333	13.15.1 Oriented PVC	383
13.5.1 Molar Mass	333	13.15.2 Cross-Linked PVC	385
13.5.2 Chemical Defect Structures	335	References	386
13.5.3 Tacticity	335	Bibliography	388
13.5.4 Crystallinity and Transition Temperatures in PVC	336	14. Fluorine-Containing Polymers	389
13.5.5 Polarity of PVC	339	<i>Jiri G. Drobny</i>	
13.6 Morphology of PVC	339	14.1 Introduction	389
13.6.1 Suspension/Mass PVC	339	14.2 Preparation and Properties of Fluoropolymers	391
13.6.2 Emulsion and Microsuspension PVC	341	14.2.1 Polytetrafluoroethylene	391
13.7 PVC Degradation	342	14.2.2 Perfluoroalkoxy Resins	398
13.8 Compounding Ingredients	342	14.2.3 Polychlorotrifluoroethylene	399
13.8.1 Heat Stabilizers	343	14.2.4 Copolymer of CTFE and Ethylene	400
13.8.2 Antioxidants and UV Stabilizers	346	14.2.5 Polyvinylidene Fluoride	400
13.8.3 Plasticizers	347	14.2.6 Poly(Vinyl Fluoride)	402
13.8.4 Lubricants	359	14.2.7 Terpolymers of TFE, HFP, and VDF	402
13.8.5 Fillers	360	14.2.8 Fluorinated Thermoplastic Elastomers	403
		14.2.9 Miscellaneous Fluoropolymers	404

14.3 Processing of Fluoropolymers	405	15.4 Poly(vinyl alcohol)	433
14.3.1 Processing of Polytetrafluoroethylene	405	15.4.1 Structure and Properties	434
14.3.2 Processing of Melt-Processable Fluoropolymers	411	15.4.2 Applications	435
14.3.3 Processing of Polyvinyl Fluoride	413	15.5 Poly(vinyl acetals)	435
14.3.4 Processing of Amorphous Perfluoropolymers	413	15.5.1 Poly(vinyl formal)	435
14.4 Applications of Fluoropolymers	413	15.5.2 Poly(vinyl butyral)	436
14.4.1 Applications of PTFE	413	15.6 Ethylene Vinyl Alcohol Copolymers	437
14.4.2 Applications of FEP	415	15.6.1 Structure and Properties	437
14.4.3 Applications of Perfluoroalkoxy Resins	415	15.6.2 Applications	438
14.4.4 Applications of ETFE	416	15.7 Other Vinyl Polymers	438
14.4.5 Applications of PCTFE	417	15.7.1 Poly(vinyl cinnamate)	438
14.4.6 Applications of ECTFE	417	15.7.2 Poly(vinyl carbazole)	439
14.4.7 Applications of Polyvinylidene Fluoride	418	References	440
14.4.8 Applications of Polyvinyl Fluoride	418	Bibliography	440
14.4.9 Applications of THV Fluoroplastics	419	16. Acrylic Plastics	441
14.4.10 Application of Fluorinated Thermoplastic Elastomers	419	<i>Adam P. Mosley</i>	
14.4.11 Application of Miscellaneous Fluoropolymers	420	16.1 Introduction	441
14.5 Safety and Hygiene	420	16.2 Poly(Methyl Methacrylate)	442
14.5.1 Thermal Behavior of Fluoroplastics	420	16.2.1 Preparation of Monomer	442
14.6 Recycling of Fluoropolymers	421	16.2.2 Polymerization	444
14.7 Recent Trends	422	16.2.3 Structures and Properties	446
Appendix 14.1: Typical Applications for Fluoroplastics	422	16.2.4 General Properties of Poly(Methyl Methacrylate)	447
References	422	16.2.5 Additives	449
15. Miscellaneous Vinyl Thermoplastics	427	16.2.6 Processing	449
<i>Marianne Gilbert</i>		16.2.7 Recycling	451
15.1 Introduction	427	16.2.8 Applications	451
15.2 Vinylidene Chloride Polymers and Copolymers	427	16.3 Methyl Methacrylate Polymers With Enhanced Impact Resistance and Softening Point	453
15.2.1 Production of Monomer	428	16.4 Acrylic Adhesives	454
15.2.2 Production of PVDC	428	16.5 Hydrophilic Polymers	454
15.2.3 Additives for PVDC Copolymers	429	16.6 Poly(methacrylimide)	455
15.2.4 Properties of Vinylidene Chloride Copolymers	430	16.7 Other Acrylic Polymers	455
15.2.5 Applications of Vinylidene Chloride Copolymers	431	References	456
15.3 Poly(vinyl acetate)	432	17. Polycarbonates	457
15.3.1 Preparation of Vinyl Acetate Monomer	433	<i>Deny Kyriacos</i>	
15.3.2 Polymerization	433	17.1 Introduction	457
15.3.3 Properties and Applications	433	17.1.1 General Introduction	457
		17.1.2 Health Issues	458
		17.2 Formation of Reactants for Polycarbonate Production	458
		17.3 Polycarbonate Production	459
		17.3.1 Production	459
		17.4 Chemical Modifications	461
		17.4.1 End Groups	461
		17.4.2 Branching	461
		17.4.3 Copolymerization	461
		17.4.4 Biodegradable Polycarbonates	462

17.5 Basic Properties of the Polymer	463	18.3.1 Polyamides 46, 66, 610, and 612	492
17.5.1 Introduction	463	18.3.2 Polyamide 6	492
17.5.2 Molar Mass	463	18.3.3 Polyamide 11	492
17.5.3 Structure of Polycarbonate	464	18.3.4 Polyamide 12	492
17.5.4 Transition Temperatures	464	18.3.5 Copolymers	493
17.5.5 Structure—Property Relationships	466	18.4 Structure of Aliphatic Polyamides	493
17.6 Compounding	466	18.5 Properties of Aliphatic Polyamides	495
17.6.1 Compounding Techniques	467	18.5.1 Introduction	495
17.6.2 Compounding Ingredients	467	18.5.2 Transition Temperatures and Crystallinity	495
17.6.3 Reinforcing Fillers	469	18.5.3 Chemical Resistance	496
17.7 Comparison of Properties With Engineering Thermoplastics	469	18.5.4 General Properties	496
17.7.1 Physical Properties	469	18.5.5 Frictional Properties	499
17.7.2 Mechanical Properties	470	18.5.6 Electrical Properties	500
17.7.3 Thermal Properties	473	18.5.7 Effect of Weathering	500
17.7.4 Chemical Properties	473	18.6 Additives	501
17.7.5 Electrical Properties	475	18.7 Fiber-Filled Polyamides	502
17.7.6 Optical Properties	476	18.7.1 Glass-Filled Polyamides	502
17.8 Processing	476	18.7.2 Aramid-Fiber-Filled Polyamides	504
17.8.1 Injection Molding	476	18.7.3 Carbon-Fiber-Filled Polyamides and Related Products	504
17.8.2 Extrusion	477	18.7.4 Available Grades	505
17.8.3 Blow Molding	477	18.8 Processing of Polyamides	505
17.8.4 Thermoforming	478	18.9 Applications of Polyamides	506
17.9 Applications	478	18.9.1 Automotive Applications	507
17.9.1 Optical/Lighting	478	18.9.2 Electrical and Electronic Applications	507
17.10 Polycarbonate Blends	480	18.9.3 Consumer Goods and Appliances	508
17.10.1 Polycarbonate/Acrylonitrile—Butadiene—Styrene	480	18.9.4 Films and Coating	508
17.10.2 Polycarbonate/Polybutylene Terephthalate	480	18.9.5 Fibers and Filaments	508
17.10.3 Polycarbonate/Polyethylene Terephthalate	483	18.9.6 Extruded Products	508
17.10.4 Polycarbonate/Polymethyl Methacrylate	483	18.9.7 Cast Polyamides	509
References	483	18.9.8 Polyamide Reaction Injection Molding	509
Bibliography	485	18.9.9 Recycling	509
Resources	485	18.10 Polyamides of Enhanced Solubility	509
18. Aliphatic Polyamides	487	18.11 Other Aliphatic Polyamides	510
<i>Marianne Gilbert</i>		18.12 Polyamide Blends	510
18.1 Introduction	487	References	510
18.2 Intermediates for Aliphatic Polyamides	489	Bibliography	511
18.2.1 Adipic Acid	489	19. Polyacetals	513
18.2.2 Hexamethylenediamine	489	<i>Daniel L. Jarvis</i>	
18.2.3 Sebacic Acid and Azelaic Acid	489	19.1 Introduction	513
18.2.4 Caprolactam	490	19.2 Preparation of Formaldehyde	513
18.2.5 ω -Aminoundecanoic Acid	490	19.3 Acetal Resins	514
18.2.6 Lauryl Lactam (Lauro lactam, Dodecanolactam)	491	19.3.1 Polymerization of Formaldehyde	514
18.3 Polymerization of Aliphatic Polyamides	491	19.3.2 Structure and Properties of Acetal Resins	516
		19.3.3 Properties of Acetal Resins	518

19.3.4 Processing	521	21.3.5 Processing	557
19.3.5 Additives	522	21.3.6 Applications	558
19.3.6 Applications of the Acetal Polymers and Copolymers	522	21.4 Polyphenylene Sulfide	558
19.3.7 Future Developments	524	21.4.1 Synthesis	559
19.3.8 Acetal—Polyurethane Alloys	524	21.4.2 Manufacture	559
19.4 Polyethers from Glycols and Alkylene Oxides	524	21.4.3 Structure	561
References	525	21.4.4 Properties	562
Bibliography	525	21.4.5 Additives	564
Reviews	526	21.4.6 Processing	564
		21.4.7 Applications	564
20. Thermoplastic Polyesters	527	21.5 Imide Polymers	565
<i>Henry C.A. Lim</i>		21.5.1 Thermoplastic Imide Polymers	566
20.1 Introduction	527	21.5.2 Polyamide-imides	569
20.2 Production of Thermoplastic Polyesters	528	21.5.3 Polyetherimides	572
20.3 Poly(Ethylene Terephthalate)	528	21.5.4 Properties	574
20.3.1 Introduction	528	21.5.5 Additives	579
20.3.2 Structure of PET	529	21.5.6 Processing	581
20.3.3 Processing of PET	530	21.5.7 Applications	582
20.3.4 Applications	531	21.6 Polyaryletherketones	583
20.4 Poly(Butylene Terephthalate)	532	21.6.1 Synthesis	583
20.4.1 Introduction	532	21.6.2 Structure—Property Relationships	584
20.4.2 Structure of PBT	532	21.6.3 Chemical Modifications	585
20.4.3 Properties of PBT	533	21.6.4 Properties	586
20.5 Other Thermoplastic Polyesters	536	21.6.5 Additives	586
20.5.1 Poly(1,4-Cyclohexylenedi- methylene Terephthalate)	536	21.6.6 Processing	589
20.5.2 Poly(Ethylene Naphthalate)	537	21.6.7 Applications	592
20.6 Copolyesters	537	21.7 Polybenzimidazole	593
20.7 New-Generation Copolyesters	538	21.7.1 Synthesis	594
20.7.1 Introduction	538	21.7.2 Production	595
20.7.2 Properties of Tritan™	539	21.7.3 Chemical Modifications	596
20.7.3 Applications	540	21.7.4 Structure	598
References	542	21.7.5 Properties	598
		21.7.6 Additives	600
21. High-Temperature Engineering Thermoplastics	545	21.7.7 Processing	601
<i>Deny Kyriacos</i>		21.7.8 Applications	602
21.1 Introduction	545	21.8 Liquid Crystal Polymers	603
21.1.1 Chemical Structure of High-Temperature Thermoplastics	545	21.8.1 Liquid Crystals	603
21.1.2 General Comparison of High- Temperature Thermoplastics	547	21.8.2 Liquid Crystal Polymers	603
21.2 Polyphthalamides	547	21.8.3 Synthesis	608
21.3 Sulfones	550	21.8.4 Properties	609
21.3.1 General Synthetic Methods	550	21.8.5 Additives	611
21.3.2 Structure—Property Relationships	551	21.8.6 Processing	611
21.3.3 Properties	552	21.8.7 Applications	611
21.3.4 Additives	556	References	612
		Bibliography	615
21.3.5 Processing	557		
21.3.6 Applications	558	22. Cellulose Plastics	617
21.4 Polyphenylene Sulfide	558	<i>Marianne Gilbert</i>	
21.4.1 Synthesis	559	22.1 Nature and Occurrence of Cellulose	617
21.4.2 Manufacture	559	22.2 Cellulose Esters	619
21.4.3 Structure	561	22.2.1 Cellulose Nitrate	619
21.4.4 Properties	562	22.2.2 Cellulose Acetate	620
21.4.5 Additives	564		
21.4.6 Processing	564		
21.4.7 Applications	564		
21.5 Imide Polymers	565		
21.5.1 Thermoplastic Imide Polymers	566		
21.5.2 Polyamide-imides	569		
21.5.3 Polyetherimides	572		
21.5.4 Properties	574		
21.5.5 Additives	579		
21.5.6 Processing	581		
21.5.7 Applications	582		
21.6 Polyaryletherketones	583		
21.6.1 Synthesis	583		
21.6.2 Structure—Property Relationships	584		
21.6.3 Chemical Modifications	585		
21.6.4 Properties	586		
21.6.5 Additives	586		
21.6.6 Processing	589		
21.6.7 Applications	592		
21.7 Polybenzimidazole	593		
21.7.1 Synthesis	594		
21.7.2 Production	595		
21.7.3 Chemical Modifications	596		
21.7.4 Structure	598		
21.7.5 Properties	598		
21.7.6 Additives	600		
21.7.7 Processing	601		
21.7.8 Applications	602		
21.8 Liquid Crystal Polymers	603		
21.8.1 Liquid Crystals	603		
21.8.2 Liquid Crystal Polymers	603		
21.8.3 Synthesis	608		
21.8.4 Properties	609		
21.8.5 Additives	611		
21.8.6 Processing	611		
21.8.7 Applications	611		
References	612		
Bibliography	615		

22.2.3 Other Cellulose Esters	624	24.5.5 Polyether Block Amides	695
22.3 Cellulose Ethers	626	24.5.6 Melt Processable Rubber	696
22.3.1 Ethyl Cellulose	626	24.6 Markets, Applications, and Suppliers of TPE Materials	698
22.3.2 Miscellaneous Ethers	628	24.6.1 Markets	698
22.4 Regenerated Cellulose	628	24.6.2 Applications	699
References	629	24.6.3 Manufacturers/Suppliers	701
Bibliography	629	References	701
23. Bioplastics: New Routes, New Products	631	25. Aldehyde Polymers: Phenolics and Aminoplastics	705
<i>Gareth Ross, Sukunya Ross, Brian J. Tighe</i>		<i>Richard Heath</i>	
23.1 Introduction: Definitions and Classification	631	25.1 Introduction	705
23.2 Bioplastics Development: Generic Considerations	631	25.2 Monomers for Common Aldehyde Polymers	706
23.2.1 Recycling and Life-Cycle Analysis	631	25.2.1 Phenol	706
23.2.2 Blends and Composites: The Importance of Polysaccharides	632	25.2.2 Urea	708
23.3 Biodegradable and Compostable Plastics	634	25.2.3 Melamine	709
23.3.1 Polylactic Acid (PLA)	634	25.2.4 Formaldehyde	710
23.3.2 Polyhydroxyalkanoates	640	25.3 Oligomerization or Resinification of Aldehyde Systems	710
23.3.3 Poly(Butylene Succinate)	642	25.3.1 Formaldehyde-Based Polymers	711
23.4 Bio-Based Intermediates in Conventional Plastics Production	644	25.3.2 UF Resin Manufacture and Cross-Linking	715
23.5 Biodegradation and Compostability Principles and Testing Procedures	647	25.3.3 MF Resin Manufacture and Cross-Linking	716
23.6 Conclusions	648	25.4 Molding Materials	717
References	649	25.4.1 Formaldehyde-Based Polymers	717
24. Thermoplastic Elastomers	653	25.4.2 Urea-Formaldehyde Resins	719
<i>Declan Whelan</i>		25.4.3 Melamine-Formaldehyde Resins	720
24.1 History	653	25.4.4 Molding and Processing Characteristics	720
24.2 General Definition of Thermoplastic Elastomer	653	25.4.5 Shaping and Cure of Molding Compositions	721
24.3 General Definition of Thermoplastic Elastomer	654	25.4.6 Properties and Applications of Molded Aldehyde Polymers	723
24.4 Comparison of Thermoplastic Elastomers	654	25.5 Laminates	728
24.4.1 Basic TPE Chemistry and Synthesis Routes	654	25.6 Adhesive Applications	732
24.4.2 Polymer Miscibility	665	25.6.1 Urea-Formaldehyde Resins	732
24.4.3 Morphology of Thermoplastic Elastomers	668	25.6.2 MF Adhesives	733
24.4.4 Rheology of TPE	674	25.7 Other Applications	733
24.4.5 Structure-Property Relationships	677	25.7.1 Formaldehyde-Based Polymers	733
24.5 Processing of TPE Materials	689	25.7.2 Urea-Formaldehyde Resins	735
24.5.1 Processing Santoprene™ TPV	691	25.7.3 Melamine-Formaldehyde Resins	736
24.5.2 Copolyester-Based TPE	692	25.7.4 Molecular Structure Property Relationships of PF, UF, and MF Polymers	736
24.5.3 Thermoplastic Polyurethane Elastomers	692	25.8 Other Aldehyde-Based and -Related Polymers	737
24.5.4 Styrenic-Based TPEs	694	25.8.1 Resorcinol-Formaldehyde Polymers	737
		25.8.2 Friedel-Crafts and Related Polymers	737
		25.8.3 Phenolic Resin Fibers	739
		3M Innovative Properties Co. - IPR2023-00243	

25.8.4 Polybenzoxazines	740	27.5 Diluents, Flexibilizers, and Other Additives	789
25.8.5 Aniline—Formaldehyde Polymers	740	27.6 Epoxy Vinyl Ester Resins	791
25.8.6 Thiourea-Based Polymers	741	27.7 Toughened Epoxy Resins	791
References	741	27.8 Fire Resistance	792
Bibliography	742	27.9 Epoxy Nanocomposites	793
Reviews	742	27.10 Applications	794
26. Unsaturated Polyester Resins	743	27.10.1 Paints and Surface Coatings	794
<i>Frank R. Jones</i>		27.10.2 Electrical and Electronic	794
26.1 Introduction	743	27.10.3 Composite Materials	795
26.2 Polyester Polymers and Resins	743	27.10.4 Wind Energy	796
26.3 Unsaturated Polyesters Resins for Lamination	745	27.10.5 Construction	796
26.3.1 The Choice of Components for Synthesis of the UPE	745	27.10.6 Adhesives	796
26.3.2 Synthesis of the Unsaturated Polyester	745	27.10.7 Other Applications	796
26.3.3 Unsaturated Polyester Ester Resins	748	References	797
26.3.4 Curing of Polyester Resins	750	Bibliography	797
26.3.5 Resin Microstructure	755	Reviews	797
26.3.6 Mechanical Properties of Cast Resins	756	28. Isocyanate-Based Polymers: Polyurethanes, Polyureas, Polyisocyanurates, and their Copolymers	799
26.4 Glass Fiber Polyester Composites	757	<i>Richard Heath</i>	
26.4.1 Fiber Type	758	28.1 Introduction	799
26.4.2 Fiber Surface Finish	759	28.2 Market Statistics	800
26.4.3 Glass Fiber Composite Manufacture	763	28.3 Isocyanates and their Common Coreactants: Synthesis, Reactions, and Kinetics	801
26.4.4 Low-Profile Additives	766	28.3.1 Isocyanates	801
26.4.5 Gel Coat Resins	766	28.4 Polyalcohols—Polyols	806
26.4.6 Related Resins	766	28.4.1 Polyether Polyols or Polyetherols	806
26.4.7 Water-Extended Resins	768	28.4.2 Polyester Polyols or Polyesterols	807
26.4.8 Allyl Resins	769	28.4.3 Polycarbonate Polyols	808
26.4.9 Alkyds	770	28.4.4 General Properties of Polyols	808
26.5 Conclusions	771	28.5 Other Reactants and Additives	808
Acknowledgment	771	28.5.1 Chain Extenders	808
References	771	28.5.2 Cross-linking Agents	808
Bibliography	772	28.5.3 Catalysts	809
27. Epoxy Resins	773	28.5.4 Blowing Agents and Other Cell-Forming Additives	809
<i>Geoff Gibson</i>		28.5.5 Surfactants or Emulsifiers	810
27.1 Introduction	773	28.5.6 Pigments and Coatings	810
27.2 Preparation of Resins from Bisphenol A	774	28.5.7 Fillers and Fiber Reinforcements	810
27.3 Curing of Epoxy Resins	776	28.5.8 Fire Retardants	810
27.3.1 Amine Hardeners	778	28.5.9 Release Agents	811
27.3.2 Acid Anhydride Hardeners	781	28.6 Reaction Kinetics, Structure/Properties Relationships	811
27.3.3 Miscellaneous Hardener Systems	784	28.7 Conversion of Isocyanates Into Polymeric Products	813
27.4 Miscellaneous Epoxy Resins	785	28.7.1 The Effect of Varying Reaction Conditions	813
27.4.1 Miscellaneous Glycidyl Ether Resins	785		

28.7.2 One-Shot versus Two-Shot Synthesis/Processing	813	28.7.10 Polyisocyanurates and Copolymers	832
28.7.3 Isocyanate Polymer Processes	816	28.7.11 Elastomers	833
28.7.4 Dual-Component Processing	817	28.7.12 Polycarbodiimide Resins	834
28.7.5 Foamed Isocyanate-Based Polymers	817	28.7.13 Polyurethane—Acrylic Blends	834
28.7.6 Rigid, Semirigid PU Foams and Production	824	28.7.14 Miscellaneous Isocyanate-Based Materials	834
28.7.7 Integral-Skinned Foams; the RIM Process	826	References	834
28.7.8 Fibers and Crystalline Materials	830	Bibliography	835
28.7.9 Coatings and Adhesives	831	Technical Reviews	835
		Index	837

Chapter 20

Thermoplastic Polyesters

Dr. Henry C.A. Lim

20.1 INTRODUCTION

Thermoplastics polyesters (TP polyesters), also known as linear polyesters or saturated polyesters, are condensation polymers characterized by the presence of ester ($-\text{COO}-$) functional groups along their main chains. Even though this ester link often only comprises a small part of the polymer molecule, it may influence the properties of the polymer in the following ways (Brydson, 1999):

1. It is, chemically, a point of weakness, being susceptible to hydrolysis, ammonolysis, and ester interchange, the first two reactions leading to chain scission. In some cases, the reactivity is influenced by the nature of the adjacent groupings.
2. As a polar group it can adversely affect high-frequency electrical insulation properties. Its influence is generally lower below T_g unless the portion of the polymer containing the ester group has some mobility below the main T_g .
3. The polar ester group may act as a proton acceptor, allowing interactions with other groupings either of an inter- or an intramolecular nature.
4. The ester link appears to enhance chain flexibility of an otherwise polymethylenic chain. At the same time it generally increases interchain attraction and in terms of the effects on melting points and rigidity, the effects appear largely self-canceling.

Linear polyesters can be classified into three main classes: aliphatic, partly aromatic, and aromatic polyesters. Aliphatic polyesters are produced from aliphatic dicarboxylic acids (or esters) and aliphatic diols. Due to high flexibility of the C—O bond, linear aliphatic polyesters are characterized by their low melting points and are prone to hydrolysis. Partly aromatic polyesters are obtained from aromatic dicarboxylic acids (or esters) and aliphatic diols as shown in Figure 20.1. TP

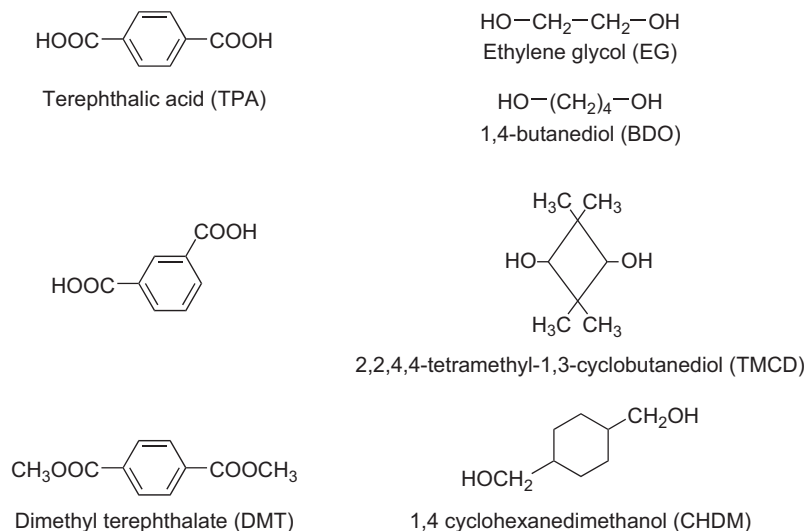
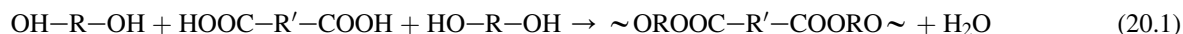


FIGURE 20.1 Some examples of monomers and comonomers used for the production of partially aromatic homo- and copolyesters.

polyesters are also available in liquid crystalline forms and these are aromatic polyesters having all ester linkages attached to aromatic rings.

20.2 PRODUCTION OF THERMOPLASTIC POLYESTERS

Major industrial consumption of TP polyesters comes from partially aromatic polyesters, which can be further classified as homo- and copolyesters. The two workhorse poly(alkylene terephthalates) homopolyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate), are produced from terephthalic acid or terephthalic acid dimethylester and ethylene glycol or 1,4-butanediol, respectively, via condensation reaction represented by the following general reaction Scheme 20.1:



They shared very similar poly(alkylene terephthalate) chemical structure and are differentiated by their methylene groups within the repeat unit structures as shown in Figure 20.2. Other common homopolyesters include polycyclohexylenedimethylene terephthalate (PCT), poly(ethylene naphthalate) (PEN), and poly(trimethylene) terephthalate (PTT).

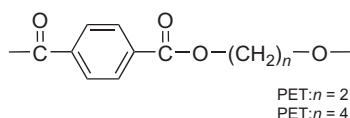


FIGURE 20.2 Repeat unit structure of poly(alkylene terephthalates).

Copolyesters such as PETG (CHDM-modified PET), PCTG (glycol-modified PCT), and PCTA (dibasic-acid-modified PCT) can be produced by the incorporation of more than one glycol and/or more than one dibasic acid during the condensation polymerization process.

Over the past decades, substantial amount of research have been focused on both material (monomer chemistry) and application development of these linear polyesters beyond the traditional fiber and film applications. TP polyesters have long proven track records in electrical and electronic appliances, and in automotive, medical, and packaging (both commodity and premium packaging) sectors. The TP polyester is a family of polymers with great versatility for modification during both polymerization and compounding stages. New advances in monomer chemistries allow greater options in the modification of crystallization behavior of the polyester resin leading to improvements in optical, thermal, mechanical properties, and reduced environmental footprint. In recent years, the ability to convert natural plant sugars into monoethylene glycol opens up the opportunities in replacing conventional petrochemical-derived PET with more environmental-friendly PET having exactly same properties and performances. The ever-growing demand for enhanced food safety packaging material leads to the replacement of conventional to bisphenol-A (BPA)-based polycarbonate (PC) resins with new improved clarity and high heat-resistant copolyesters due to health concerns of BPA monomer, which is a synthetic estrogen classified as an endocrine disruptor that causes birth defects in mice.

New advancements in additive technologies including chain extenders, impact modifiers, nucleating agents, stabilizers, halogen-free retardants, and liquid color have resulted in improvements of molar mass control/repair, impact toughness, speed of crystallization, hydrolysis resistance, flame retardancy (environmental friendly), and esthetic properties of the linear polyesters. To bridge the gaps in performances, most of the polyester resins are compounded with fillers and reinforcements for further enhancements of physical and mechanical properties.

20.3 POLY(ETHYLENE TEREPHTHALATE)

20.3.1 Introduction

PET is also commonly abbreviated as PETP and PETE. The amorphous form is abbreviated as APET and the crystalline form as CPET. PET can be produced from the polycondensation reaction of ethylene glycol (EG) with either terephthalic acid (TPA) or dimethyl terephthalate (DMT) in the presence of a catalyst and stabilizer. The molar mass of PET is generally represented by the intrinsic viscosity (IV). Commercial PET has a wide range of IV that varies from 0.4 to 1.0 dl g⁻¹ (4–10 kg m⁻³), which corresponds to number average molar masses of 10 to 40 kg mol⁻¹ (Gupta and Bashir, 2002). Different grades of PET are produced with different IV values. For PET bottle grade resins, high IV in the range of 0.7–0.85 dl g⁻¹ is required. Film grade PET requires the IV to be 0.6–1.00 dl g⁻¹.

The polymerization of bottle grade PET is normally carried out in two stages starting from a melt-phase polymerization process whereby amorphous pellets are produced through rapid quenching of the high viscosity polymer melt followed by a solid-state polymerization process just below the melting temperature. The lower temperature (typically 200–220 °C) solid-state process yields polymers with much lower acetaldehyde (AA) content. AA is a colorless, volatile substance with a fruity smell formed when PET degrades. High processing temperatures, long barrel residence time, and excessive shear flow can contribute to the production of AA. The presence of AA in PET packaging material can impart objectionable tastes to its beverages content. The current industry standard for AA in bottle grade PET resin is <1 ppm (Gupta and Bashir, 2002).

20.3.2 Structure of PET

PET is a semicrystalline polymer containing the amorphous and crystalline regions and has a glass transition temperature of around 75 °C and a melting temperature of around 250 °C. The amorphous and crystalline phases exhibit differences in heat capacity and/or enthalpy of fusion which are detectable using differential scanning calorimetry (DSC). Figure 20.3 shows a typical DSC first heating trace of a quenched cooled PET resin with a distinct glass transition temperature, cold crystallization, and melting peaks. The glass transition exhibits enthalpy relaxation as shown by the overlapping endotherm peak suggesting that the sample has been aged at temperature below the glass transition. Cold crystallization peaks are detected during first heating scans when samples are quenched rapidly from the melt with insufficient time to crystallize during the cooling phase. The final products of PET can be obtained by transforming it into a semicrystalline state, or by quenching it to a glassy state as an amorphous product. These amorphous products can be subsequently transformed into a semicrystalline state through drawing and annealing.

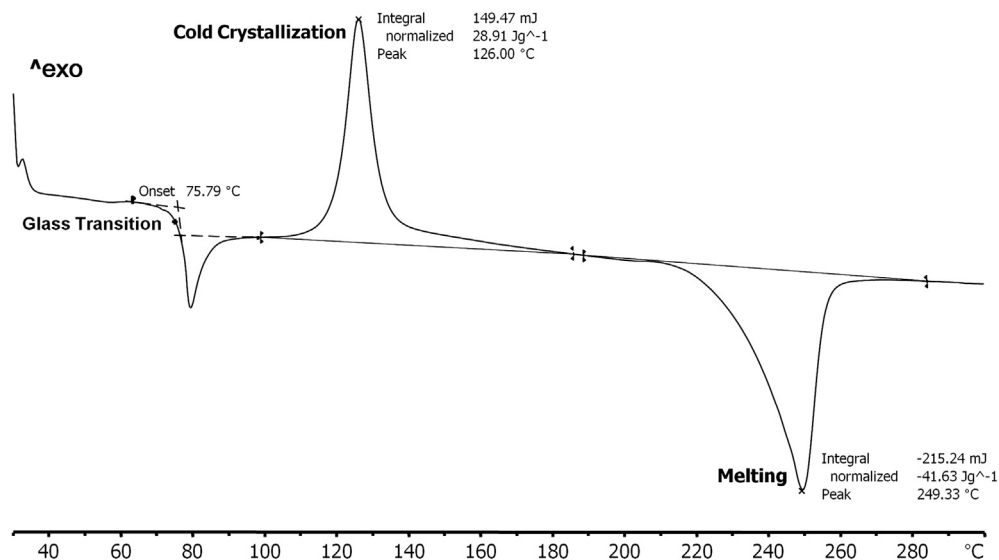


FIGURE 20.3 A typical differential scanning calorimetry heating curve of a quenched cooled poly(ethylene terephthalate) resin.

PET is known to have very slow crystallization rate compared with PBT without the addition of nucleating agents as the latter contains longer sections of aliphatic units, which would be expected to lead to more flexible chains and to crystallize more readily (Gilbert and Hybart, 1972). On the other hand, the presence of the *p*-phenylene group and the short ethylene group leads to low flexibility of the PET chains.

Due to its slow crystallizing nature, cooling PET rapidly from the melt to a temperature below T_g can produce amorphous transparent PET. Therefore, by changing the crystallization conditions of the PET, several microstructures can be developed.

As a consequence of slow crystallization rate, long cycle times are required to provide crystallinity in injection-molded PET parts. Thus, in an economical sense, unmodified PET is not suitable for injection molding applications. As a result of this limitation, there is a need for increasing the rate of crystallization through the use of *nucleating agents*. Effective organic nucleating agents for PET include low molar mass ethylene-acrylic acid sodium ionomers and sodium salt of long-chain aliphatic carboxylic acid (sodium-neutralized salts of montanic acid). Licomont NaV101 from Clariant Corporation is an example of a multifunctional montanic lubricant, which is suitable for the high processing temperatures of engineering resins due to its high thermal stability and is also an effective nucleating agent for polyesters at 0.1–0.4 wt%.

The effectiveness of a nucleating agent can be studied by evaluating the peak crystallization temperatures (T_c) of a polymer using DSC. Crystal formation is an exothermic reaction (heat given off), as crystalline order represents a state of lower energy (entropy), and thus crystallization occurs at a lower temperature than melting. When the temperature of crystallization is close to the melting temperature of a semicrystalline polymer, nucleation rate is slow but growth rate is fast. Thus in homogeneous nucleation (without the presence of an added nucleating agent), nuclei appear throughout the crystallization process leading to a broad distribution of spherulitic sizes. This is due to the fact that when a polymer melt is cooled below its equilibrium melting point, the rate of nuclei formation is extremely slow as the new phase disappears (dissolves) in the polymer melt before crystal growth can occur. The rate of nuclei formation increases only upon further cooling and declines when reaching the glass transition temperature of the polymer as the viscosity starts to increase. As the rate of nucleation is strongly dependent on temperature, crystallization of the polymer will be much controlled by the processing conditions, such as the melt and mold temperatures as well as cycle time control during injection molding processes.

On the other hand, in heterogeneous nucleation (with added nucleating agent), all nuclei are present at the start of crystallization and the nucleant controls the crystallization process. An upward shift of T_c of a polymer that contains a nucleating agent from that of the same neat polymer is an indication of nucleation. Therefore, T_c of a non-nucleated polymer is usually taken as the lower limit reference when evaluating the effectiveness of potential nucleating agents. The effectiveness of Licomont NaV101 as the nucleating agent in PET is evident through the observation of upward shifts of T_c with increased dosage of the additives as shown in Figure 20.4. The T_c of a neat PET was detected at 187.5 °C while the addition of the montanic nucleating agent at 0.1 wt% shifted the T_c to 200 °C and to 204.9 °C when the dosage was further increased to 0.4 wt%. The observation of a broader crystallization peak of the unnucleated PET in Figure 20.4 suggests broader spherulitic size distribution due to homogenous nucleation compared with the nucleated ones as discussed earlier.

The heat of crystallization obtained from the DSC curves were 36.9, 37.9, 39.5, and 41.5 J g⁻¹ for neat PET resin and increasing dosage of nucleating agent from 0.1 to 0.4 wt%, respectively. This translates to only about 1–3% increase in crystallinity based on assumption that the heat of fusion of a 100% crystallized PET is 140 J g⁻¹ (Wunderlich, 1990).

The use of nucleating agents not only helps in reducing cycle time but also encourages uniform crystallization that lowers the molded-in stresses. The use of montanic acid type nucleating agent imparts additional lubricating and mold-release effects to the molded parts. Inorganic additives such as talc can also be used as nucleating agents for PET though they are not as effective as the organics.

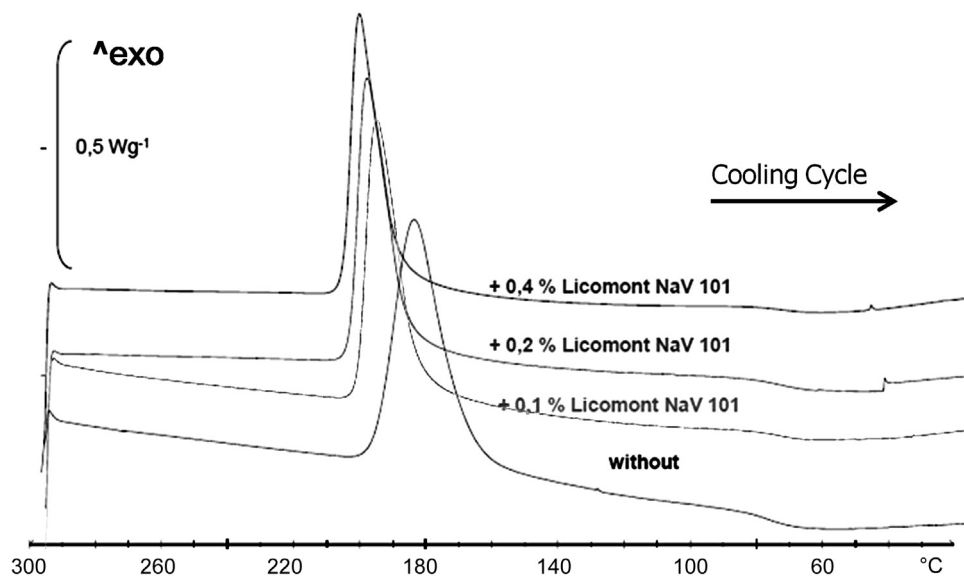


FIGURE 20.4 Nucleating effect of Licomont Nav 101 on poly(ethylene terephthalate) resin. Differential scanning calorimetry curves provided by courtesy of Clariant Corporation.

20.3.3 Processing of PET

Due to the inherent low melt strength of PET resins arising from their low molar mass, extrusion blow molding that is commonly employed for the production of PVC, PE, PP, and PC bottles cannot be applied in PET bottle productions.

Therefore, the production of PET bottles generally involves two separate operations. An amorphous transparent preform has to be injection molded first. It is then reheated from room temperature to above the glass transition temperature and then stretch-blown into the final articles. It is important to maintain the preform clarity during the injection molding process as the haze developed during injection molding process can impart haziness to the bottles. The presence of even a very small amount of crystallinity developed thermally during injection of preforms could dramatically reduce the clarity of the final bottles due to the light scattering effects of large spherulitic structures (Jabarin, 1982). In order to delay the crystallization of PET preforms during injection molding processes, a small amount of isophthalic acid (IPA) (<5 mol%) can be added during the PET polymerization process as the presence of this monomer disrupts the regularity of the main chain structure thus delaying crystallization during molding. This helps in production of bottles with better clarity without affecting the ability of the material to be strain-crystallized during the stretching process, thus preserving its gas barrier properties. During the stretch-blow process, very small crystallites are formed through strain-induced crystallization. The final biaxially oriented bottles remained highly transparent as the crystallites formed during strain-induced crystallization are much smaller than the wavelength of light, thus minimizing light scattering effects. When bottles are stretch-blow molded within the optimum window above the glass transition and below the cold crystallization temperatures, optically clear bottles are obtained even with a final crystallinity of 20–25% (Gupta and Bashir, 2002). Stretching done too near to glass transition temperature could cause pearlescence or a stress-whitening effect due to microvoiding. Strain-induced crystallization results in much improved barrier properties, impact resistance, and dimensional stability.

During the processing of PET, the presence of moisture at elevated temperature can result in hydrolysis of the polyester leading to dramatic reduction in IV. Carbodiimide (HN-C-NH)-based additives can be added to suppress hydrolysis during melt processing acting as moisture and acid scavengers. Stabaxol P, an aromatic polycarbodiimide, is a commercial hydrolysis stabilizer from Rhein Chemie (a business unit of Lanxess) commonly used at 0.5–2.5 wt% in thermoplastic polyesters. Desiccant additives such as treated calcium oxide are also known to be effective antihydrolysis agents.

During recycling of PET, the IV of the recycled products is expected to be significantly reduced due to hydrolysis and thermal degradation of the polymer. Another option for the rebuilding of the molar mass and physical properties of degraded TP is through the bridging of their functionally terminated chains, using difunctional or multifunctional chemical compounds thus recoupling them. These chemical compounds with reactive groups that are capable of reactions with the terminal hydroxyl (OH) or carboxyl (COOH) groups of the polyester resins are commonly known as chain extenders and are typically added during recycling of PET to reattach the broken chains thereby increasing the molar mass or IV of the recycled products. The use of bifunctional chain extenders promotes linear chain extension, while the tri- and tetra-functional chain extenders promote chain branching.

Traditional chain extenders for polyesters are bifunctional molecules such as diepoxides, diisocyanates, dianhydrides, and bis(oxazoline)s (Scheirs, 2003). At low concentrations and high reaction temperatures, diepoxides react rapidly with the hydroxyl and carboxyl end groups of PET leading to branched and crosslinked polymers with improved tensile and impact properties. However, the melt viscosities of PET are generally observed to increase dramatically due to the chain branching and crosslinking reactions when diepoxides are added.

In recent years, multifunctional styrene–acrylic polymers with low molar mass and high epoxy functionality (>4) developed by BASF and marketed as Joncryl chain extenders have seen commercial success in PET and other polyesters. The combination of low molar masses with low epoxy equivalent weight (EEW) values, the chain extenders are able to achieve a high degree of chain binding without inducing gelation at low dosage levels (Blasius et al., 2006). The chain extension reactions can be carried out effectively in the melt phase in single- or twin-screw extruders without the need of predrying, or without the use of high vacuum or catalysts.

20.3.4 Applications

Traditionally, PET has been used for the production of fiber for textile products and food packaging films. Biaxially oriented films have been used for X-ray and other photographic films for many years while unoriented amorphous PET films and sheets are currently used in blister packaging and drinking cups.

Over the past decades, PET has gained major share as bottle packaging material in carbonated beverages. This is due to the exceptionally good barrier properties in terms of low carbon dioxide and water transmission rates of the strain-crystallized PET bottles. The advances in liquid colorant technology allow the bottles to be colored homogeneously. The use of conventional solid color concentrates results in two major issues. Due to low dosage of color concentrates (typically 1 wt% or lower), visually defective bottles are produced with streaks of poorly distributed color, a consequence of poor melt mixing between the color concentrate pellets and the PET resin. As the liquid carriers of liquid colorant dissolves quickly into the polymer melt when introduced via a liquid pump into the injection molding machines, the bottles

can be colored homogeneously even at very low colorant dosages. Another common problem faced with using solid color concentrates is the need to precrystallize the colored pellets in a continuously agitated crystallizer before the molding process as the pellets are normally amorphous in nature due to rapid quenching of the strands during the compounding process. These amorphous color pellets would stick and form agglomerates during the drying process above their glass transition temperature leading to hopper bridging and mixing issues. The precrystallization process ensures that the pellets are fully crystallized and will not be softened when heated above the glass transition temperature. The use of liquid colorant eliminates the need for precrystallization and drying of solid color concentrates.

In recent years, with the strong drive in environmental-focused initiatives from major brand owners, plant-based PET has been developed for use in a variety of products especially in packaging applications. Coca-Cola company's PlantBottle technology converts natural sugars found in plants into monoethylene glycol component for the production of these PET PlantBottles. Such packaging material which is about 30% plant-based is chemically identical to conventional petrochemical-derived PET in appearance, functions, and recyclability but offers better sustainability through a reduced environmental footprint.

20.4 POLY(BUTYLENE TEREPHTHALATE)

20.4.1 Introduction

Polybutylene terephthalate (PBT) or (PBTP), which is also known as polytetramethylene terephthalate (PTMT), can be produced by polycondensation of 1,4-butanediol with either terephthalic acid or dimethyl terephthalate in the presence of a polyesterification catalyst such as tetraalkyl titanate.

Due to the presence of longer sequence of methyl groups in the repeating unit, the main chains of PBT are more flexible but less polar than those of PET. Thus PBT has lower melting temperature and a much faster crystallization rate than PET (Gilbert and Hybart, 1972). The characteristics of quicker crystallization rates and lower processing temperatures allow crystalline products (of about 40% crystallinity) to be obtained directly at conventional mold temperatures, and thus PBT has found major applications in injection molding when compared with PET. The melting temperature of PBT obtained from DSC ranges from 222 to 232 °C (Iroh, 2009) and the heat of fusion of 100% crystalline PBT is reported to be 145 J g⁻¹ (Wunderlich, 1990).

20.4.2 Structure of PBT

Figure 20.5 shows a typical DSC first heating trace of a PBT resin with two distinct melting peaks. The observation of multiple melting in PBT due to the influence of heating and cooling rates during DSC scans has been reported by Hobbs and Pratt (1975). The small melting endotherm observed before the main melting peak is associated with its crystallization

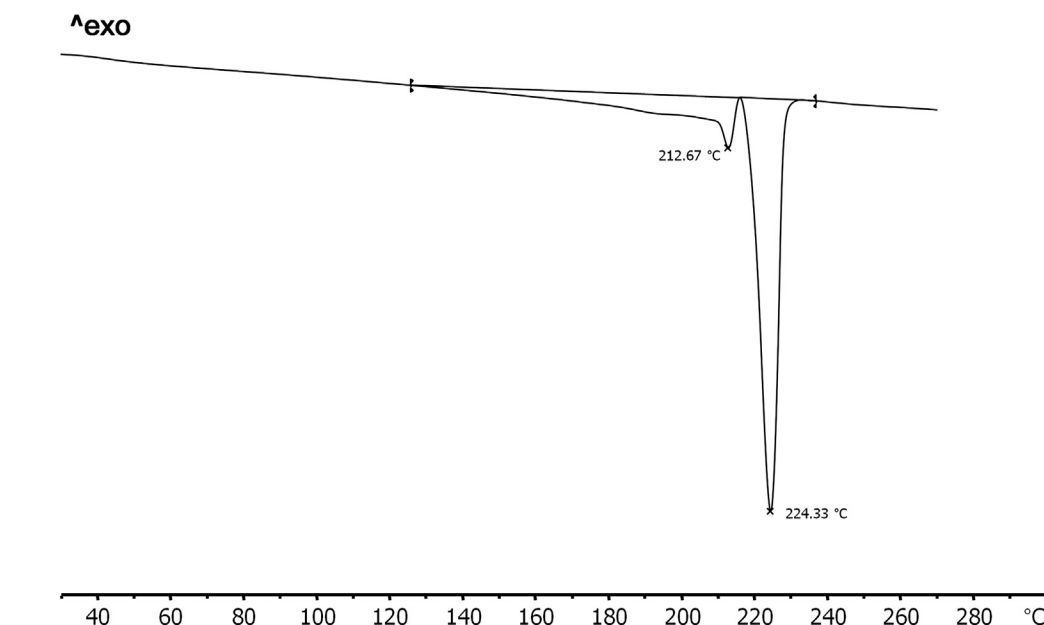


FIGURE 20.5 A typical nonisothermal differential scanning calorimetry heating scan of a poly(butylene terephthalate) resin.

conditions. Crystals that are formed at high cooling rate are inherently unstable and will anneal on heating which leads to a single endotherm centered at around 220 °C. Thus this high melting peak develops as a result of reorganization processes during heating and is not the characteristic of the material in its room temperature state. Crystals that are formed by slow cooling are more perfect and resistant to reorganization and therefore only the lower temperature peak can be identified as crystals formed during the original cooling.

The glass transition temperature of PBT is in the range of 30–60 °C (Iroh, 2009) depending on the degree of crystallinity, annealing, content and type of fillers, and methods of measurement. A “quasistatic” glass transition temperature of 15 °C has been reported for completely amorphous PBT, which enables quenched PBT to undergo cold crystallization at 20 °C (Illers, 1980).

20.4.3 Properties of PBT

PBT exhibits the following characteristic properties:

1. Low moisture absorption.
2. Good dimensional stabilities (low coefficient of thermal expansion and low moisture absorption).
3. Excellent electrical insulation properties.
4. High resistance to fuels, oil, fats, and many industrial solvents.
5. Good inherent lubricity and wear resistance.
6. High strength and modulus.
7. Good moldability.
8. Special grades for low outgassing, low warpage, better hydrolysis resistance, high tougher and halogen-free retardant grades.

As with many crystalline polymers, unreinforced PBT has a low heat deflection temperature (HDT) of about 60 °C at 1.82 MPa as the glass transition temperature of the amorphous phase dominates the load-bearing capability. While the incorporation of glass fibers has a minimal effect on the HDT of most amorphous polymers such as polystyrene, polycarbonate, polysulphone, and so on (Schweizer and Winterman, 1989), the addition of glass fiber brings the HDT of PBT to 210 °C, which is near to the melting temperature of a neat resin as shown in Figure 20.6. In glass fiber-reinforced PBT, the glass fibers and melting of spherulites are more significant than the amorphous phase in the control of deflection temperatures. Thus the vast majority of PBT compounds are glass reinforced for load-bearing applications up to temperatures close to the resin melting temperature.

In addition to improvements in HDT, the glass fibers have a profound effect on the strength and stiffness of PBT, and thus glass-reinforced PBT represents one of the major product groups within the PBT field of applications. The relationships between strength and glass fiber concentrations are shown in Figure 20.7. It is observed that the strength levels off at higher concentrations of 40 wt%, which is the consequence of the reduction of the elongation at break below yield point thus leading to premature failure before stress buildup is completed. The maximum concentration range of fiber in most glass-reinforced PBT grades lies between 40 and 50 wt% as the strength levels off and also difficulties in processing at higher fiber concentrations could contribute to poor fiber mixing and fiber breakages.

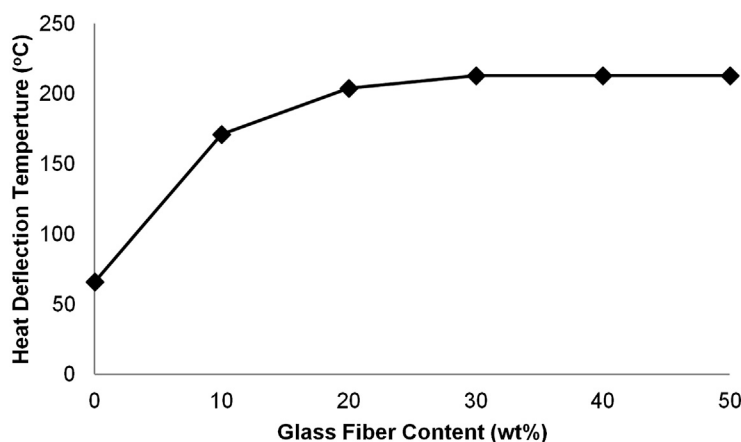


FIGURE 20.6 Effect of glass fiber on heat deflection temperature of poly(butylene terephthalate).

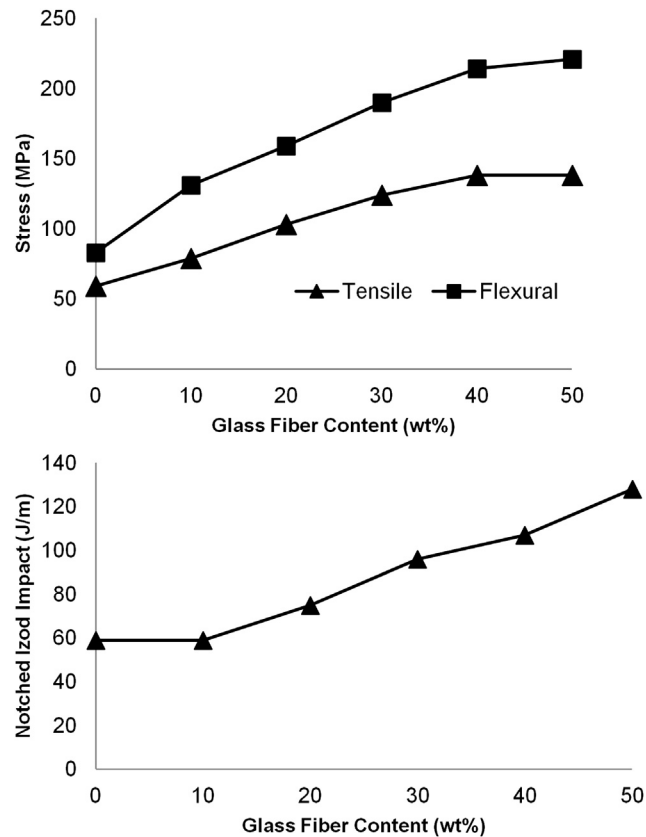


FIGURE 20.7 Effect of glass fiber on strength and toughness of poly(butylene terephthalate).

In addition to increased density and melt flow rate reduction, the incorporation of glass fiber imparts anisotropy as a result of high filler-aspect ratio and fiber orientation in the flow direction. The large differential shrinkage in flow and transverse directions would generally lead to serious part distortion or warpage. The addition of low-aspect ratio mineral fillers or spherical glass beads generally helps in improving the dimensional stability of glass-reinforced PBT compounds.

In general, the unnotched impact strength of PBT is lowered by glass fibers, but the notched impact strength is raised by the energy absorbing fiber pull-out mechanism as shown in Figure 20.7.

Although in the unnotched state PBT is a tough and ductile material, it has one major disadvantage of being highly notch sensitive leading to brittleness behavior under standard notched Izod impact testing conditions. This has led to the development of a number of impact-modified grades, which are commonly used as unfilled super tough materials or as matrix for filler-reinforced or flame retardant compounds. The notched impact strength of unmodified PBT is about 60 J m^{-1} and below, while the addition of impact modifiers could bring the impact toughness to greater than 850 J m^{-1} in the so-called “supertough” region.

In order to shift the notched impact fracture from brittle into ductile mode, a large quantity of rubber (usually up to 20 wt% or above) is required in rubber-toughened PBT. Core-shell impact modifiers that are commonly used for PVC impact modifications can also be effectively used for impact modification of PBT, as described by Farnham and Goldman (1978). The cores are usually butadiene- or acrylate-based rubber whereas the shells are typically TP, either styrenics or methyl methacrylate, which are responsible for interfacial compatibility of the modifiers with the PBT matrix. It is also possible to have at least one interlayer of polymer, to serve as a transition layer between the inner core and the outer shell. As such core-shell impact modifiers do not contain reactive moieties in the outer shell, so they generally do not have significant effects in increasing the melt viscosity of the PBT. This is often a desire by processors in injection molding of PBT.

Brady et al. (1994) reported that small amounts of polycarbonate (less than 10 wt%) could facilitate the dispersion of core-shell modifier particles and significantly improve the mechanical properties of the ternary blends. The fact that PC phase was found to be located preferentially between the PBT matrix and the PMMA shell of the modifier suggests that PC

wets PBT and PMMA better than PBT and PMMA wet each other, thus allowing PC to act as a dispersing agent for the impact modifier particles in the PBT matrix (Hobbs et al., 1988).

PBT contains both hydroxyl and carboxylic acid end groups and is thus capable of further reactions during compounding and molding processes. In recent years, more studies are being conducted on epoxide-containing elastomers that are known to be effective in the toughening of PBT due to possible reactions between the epoxide moieties and both hydroxyl and carboxyl chain ends of the PBT molecules. The interfacial bonding between the PBT and elastomers is improved through the formation of covalent bonding (in situ formed copolymer) between the two immiscible phases.

Among the epoxide containing modifiers, ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) has received much attention as impact modifier and also as compatibilizer for polyester-related blends. The use of E-MA-GMA alone may lead to possible chain branching of the PBT and also crosslinking of the dispersed rubber phase, which could result in undesirable reduction in the melt flow rate of the final blends.

Lacroix and Bouilloux (2006) reported the observation of a dramatic reduction in melt flow index of PBT containing 20 wt% of E-MA-GMA from 20 g/10 min to 0.63 g/10 min tested at 250 °C/2.16 kg. By reducing the E-MA-GMA composition to 18 wt% E-MA-GMA with the addition of 2 wt% of an MBS (methylmethacrylate-butadiene styrene) core-shell modifier, the melt flow index was increased to 3 g/10 min, and the notched Charpy impact strength at -40 °C was improved by more than 120% of the original blends containing 20 wt% E-MA-GMA.

It has been found that adding a nonreactive rubbery modifier such as ethylene-methyl acrylate (EMA) copolymer to the E-MA-GMA system results in fine blend morphologies leading to enhanced impact performance of PBT. E-MA-GMA is frequently used in combination with nonreactive ethylene-acrylate-based copolymer for adjustment of processability, impact performance, and cost during impact modifications of polyester especially in PET and PBT materials. Typically, such combination leads to the in situ formation of a core-shell morphology whereby the nonreactive rubbery modifiers are being encapsulated by the reactive E-MA-GMA, which is responsible for the interfacial reaction with the carboxyl or hydroxyl end-groups of the polyester resins. The presence of E-MA-GMA at the blend interfaces helps in prevention of coalescence of the rubber phase thus controlling the size and polydispersity of the rubber particles. The dispersed rubber particles absorb impact energy and stop craze propagation through the formation of shear bands around the particles and cavitation inside the particles. Martin et al. (2003) reported the observation of fine blend morphologies with number average diameter of rubber particles close to 0.15 µm in PBT/(EMA/E-MA-GMA) (80/20, w/w) blends containing 25–100% of E-MA-GMA component. This opens up new opportunities for tailoring the final morphology and mechanical properties of toughened PBT blends.

PBT has properties that are comparable to polyamide 6 (PA6) and both resins have somewhat similar melting points. Owing to its low water absorption characteristics, PBT is normally used for replacement of PA6 in applications where dimensional stability is critical. The typical water absorption at saturation of PA6 is about 10% whereas that of PBT is only about 0.4%. The absorbed water in PA6 acts as plasticizer thereby lowering its T_g and causes a dramatic reduction in flexural modulus and improves toughness. However, the polyamide chains are more resistant to cleavage by water under most conditions with the recovery of original properties upon removal of the water through normal drying processes. Compared to polyamide, the properties of PBT are not significantly affected by water at ambient conditions. However, PBT is sensitive to moisture during melt processing as chain cleavage occurs through hydrolysis of the polyester chains. Continuous exposure of PBT parts to water at high temperatures will result in decomposition of the PBT especially under acidic or basic conditions.

As both polymers have very similar melting and processing temperatures on top of similar shrinkage rates (PBT about 1.2%, PA6 about 1.3%), PBT is an ideal candidate for the replacement of PA6 for dimensionally stable molded parts.

Due to rapid crystallization of PBT, most end products are formed by injection molding. Applications include:

1. Electrical and Electronics

Connectors, IC sockets, bobbins, switches, relays, computer keyboard key caps, and so on.

2. Automotive

Parts for both exterior and under-the-hood-like bumper, door handles, structural brackets, lamp socket inserts, ignition system parts, coupler, and so on.

3. Household appliances

Iron skirt and handle, toaster housings, hair dryer parts, food processor blades, and so on.

20.5 OTHER THERMOPLASTIC POLYESTERS

20.5.1 Poly(1,4-Cyclohexylenedimethylene Terephthalate)

PCT is a high melting and highly crystalline polyester prepared from cyclohexanedimethanol (CHDM) and DMT or TPA.

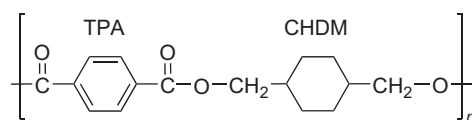


FIGURE 20.8 Chemical structure of polycyclohexylenedimethylene terephthalate.

The bulky in-chain CHDM moiety as shown in Figure 20.8 results in several other important differences between PCT and other crystallizable polyesters such as PET and PBT.

As shown in Figure 20.9, PCT has a typical melting temperature of about 285 °C, which is more than 60 °C and 30 °C higher than PBT and PET, respectively. Besides having higher T_m than these conventional polyesters, PCT exhibits superior HDT of about 260 °C when compounded with 30 wt% glass fiber. Such excellent thermal properties make PCT useful for electrical devices requiring reflow soldering of surface mount electronic components to printed circuit boards (PCB). Therefore, PCT bridges the gap between PET and liquid crystalline polymers (LCPs) in terms of short-term thermal performance.

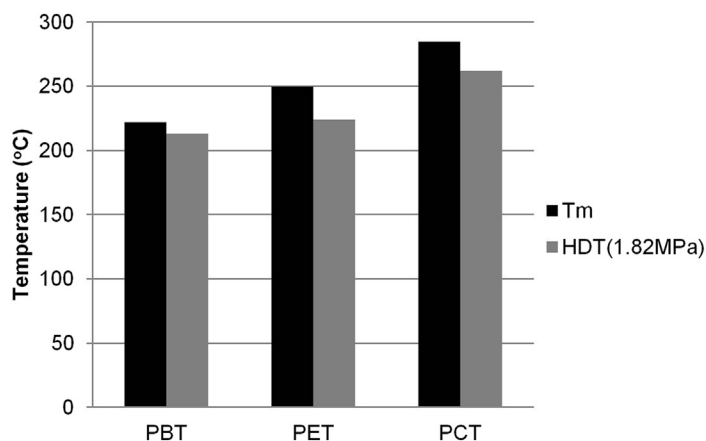


FIGURE 20.9 Typical melting point and heat deflection temperature comparison of polyesters with 30 wt% glass fiber.

The repeat unit with the presence of the cyclohexane dimethanol group makes it a more hydrocarbon polymer than PET with somewhat lower moisture absorption and better hydrolytic stability. However, the major disadvantage of PCT is the need for processing at temperatures greater than 300 °C (near decomposition temperature) due to its high melting temperature, and thus the narrow processing window between the melting temperature and decomposition temperature becomes significant. Low levels (<10 mol%) of isophthalate acid can be incorporated to widen the processing window by lowering the melting temperature of PCT while retaining its crystallinity and toughness. However, amorphous copolyesters are formed at higher levels (≥ 35 mol%) of IPA due to restrictions in crystallization.

A combination of approaches in selection of stabilizer systems, lubricants in lowering viscosities, blending with other polymers, and addition of crosslinking agents may help in minimizing the impact due to degradation during processing (Auerbach and Sell, 1990). PCT is commonly alloyed with other engineering TP such as PC (e.g., to form the blend marketed as Xenoy) that provides a good combination of clarity, chemical resistance, processability, and heat resistance.

20.5.2 Poly(Ethylene Naphthalate)

PEN is a semicrystalline polyester that is polymerized in the same way as PET but with 2,6 naphthalene dicarboxylic acid (NDA) in place of the terephthalic acid used in the production of standard PET resins. PEN with chemical structure as shown in Figure 20.10 is produced through condensation reaction between NDA and ethylene glycol. Teijin produces PEN resins under the brand name of Teonex[®].

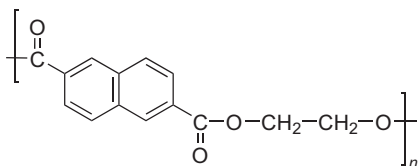


FIGURE 20.10 Chemical structure of poly(ethylene naphthalate).

The presence of a double naphthenic ring in PEN leads to chain stiffening, which results in higher T_g (about 124 °C) and T_m (about 270–273 °C) compared to PET with a single aromatic ring in the main structure (Brydson, 1999). With the gap of almost 50 °C in glass transition temperatures between PEN and PET, HDTs of more than 40 °C higher than PET can be expected from that of PEN.

The presence of bulkier double aromatic ring also leads to a slower crystallization rate of PEN than PET. This allows the production of thicker PEN bottle preforms and also the ease of obtaining transparent molded parts. The higher T_g of PEN leads to shorter cycle time as parts can be demolded sooner. As with PET, PEN is strain crystallizable through biaxial orientation but with much better gas barrier properties (both oxygen and carbon dioxide) than PET. Apart from having superior thermal and barrier properties, PEN also exhibits the following characteristic properties against PET:

1. greater chemical resistance,
2. better hydrolysis resistance in alkaline or very hot aqueous conditions,
3. better UV resistance,
4. higher tensile and flexural strength.

As with PET, PEN finds its main applications in bottles, films, and fibers.

The improved thermal properties of PEN enable the opportunities for hot fillable bottles that require up to 100 °C hot fill temperature and sterilizable applications such as medical packaging. The combination of improved thermal properties with a greater chemical resistance also opens up new opportunities for returnable and refillable containers/bottles as they are capable of withstanding high temperature washing without shrinkage or distortion. The superior oxygen barrier properties make PEN well suited for bottling beverages that are susceptible to oxidation, such as beer, which is currently not achievable with PET. The UV resistance of PEN also offers an advantage for packaging vitamin-rich drinks, milk, and juices.

Biaxially oriented PEN films having superior heat-, chemical-, and hydrolysis-resistance properties are potential candidates for filling the performance gap between durable PET films and high-performance polyimide films. These films can be used in flexible printed circuits, labels and laminates etc.

With its unique chemical structure, PEN is also well suited for the manufacturing of high-performance fibers having modulus that is 2.5 times that of PET fibers and 5 times that of polyamide fibers. Major PEN fiber uses include high-performance sailcloth, narrow- and broad-woven fabrics, and tire cord.

20.6 COPOLYESTERS

Copolyesters are produced when more than one glycol and/or more than one dibasic acid are used during the synthesis of polyesters. Due to the presence of these comonomers, the chains of copolyesters tend to be less regular than those of the homopolyesters and thus have a lower tendency to crystallize. As a result, copolyesters can be amorphous or crystalline depending on the types and concentration of comonomers used. For example, the addition of a small amount of IPA (typically <5 mol%) as comonomers during the production of PET introduces some irregularities to the chain structure thus slowing down the rate of crystallization. The retardation of the rate of thermal crystallization allows completely amorphous bottle preforms to be injection molded. The ultimate level of crystallinity is subsequently achieved through strain-induced crystallization during the biaxial stretching process into final product. In this way, containers with better clarity and equivalent level of crystallinity to that of a PET homopolymer can be produced.

TABLE 20.1 Some Common Copolyesters and Their Monomer Components

Copolyester	Diacid(s)	Diol(s)	Remarks
PETG	TPA	CHDM + EG	≤50% CHDM modification
PCTG	TPA	CHDM + EG	<50% EG modification
PCTA	TPA + IPA	CHDM	>35% isophthalic acid modification

Isophthalic acid (IPA), ethylene glycol (EG), and cyclohexanedimethanol (CHDM) are being used traditionally as comonomers in the production of copolyesters. CHDM is an important glycol used for the production of amorphous copolyesters such as PETG, PCTG, and PCTA as shown in [Table 20.1](#).

Amorphous copolyesters are typically produced using approximately 20–30 mol% of CHDM that is the so-called amorphous window for the production of amorphous polymers as no detectable crystallization peaks are expected from these polymers during DSC scans ([Turner, 2004](#)).

The first commercial amorphous copolyester, Kodar PETG 6763, was introduced by Eastman in 1977 for extrusion blow molding applications which require high clarity and melt strength. PETG can be made by combination of two glycols, CHDM and EG, and TPA. This copolyester contains ≤50 mol% of a mixture of 30/70 *cis/trans*-CHDM monomers. PETG that is resistant to crystallization can be injection molded, extrusion blow molded, and thermoformed while retaining the properties of an amorphous PET.

So far, PETG has found great success in extruded sheet for specialty packaging applications with its clarity, chemical resistance, and toughness competing with PET, PC, and other transparent TP commonly used in the packaging industries. Its ability for sterilization with gamma rays makes it a popular candidate for blister packaging for medical devices.

Glycol-modified PCT copolyester, PCTG, can be produced when more than 50 mol% of CHDM is introduced with EG during the manufacturing process of PCT. Compared with PETG, PCTG has better flowability and ductility. PCTG has found commercial success in injection-molded parts for medical applications due to its enhanced resistance to gamma radiation (good elongation at break retention) and chemical resistance. PCTG is commonly alloyed with other TP such as PC, which improves the thermal properties of PCTG while retaining its chemical resistance and clarity.

Apart from using diols, the crystallinity of PCT can also be modified with diacids, and the resulting copolyesters are commonly known as acid-modified PCTs or PCTA. As discussed in earlier section, an amorphous copolyester can be obtained by the incorporation of IPA at >35 mol% during the production of PCT using CHDM as the sole diol component. PCTA has a much improved resistance to hydrolysis during melt processing as a result of the more hydrophobic backbone due to the absence of EG and the slower hydrolysis of the CHDM ester linkage versus the EG ester linkage ([Turner, 2004](#)). Thus PCTA can be processed with less severe predrying conditions. PCTA offers lower extractables, greater heat resistance, better low-temperature impact, and improved hydrolytic stability when compared with PET. It is primarily used for extruded film and sheets for packaging especially in food contact applications.

20.7 NEW-GENERATION COPOLYESTERS

20.7.1 Introduction

Developed by Eastman Chemical Company and launched at K 2007 show in Dusseldorf Germany ([Esposit, 2007](#)), Eastman Tritan™ is a new-generation copolyester that retains the versatility of a copolyester but also offers additional advantages including easier processing, higher temperature resistance, and significantly higher impact resistance.

Tritan™ copolyesters are prepared by the melt phase copolymerization of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) and 1,4 cyclohexanedimethanol (CHDM) with dimethyl terephthalate (DMT) shown in [Figure 20.1](#). Important material variables include the mol% of TMCD present in the copolyester and the inherent viscosity (IV) of the copolyester.

The unique properties of Tritan™ copolyesters are achieved by modifying poly(1,4-cyclohexylenedimethylene terephthalate), or PCT, with TMCD. The incorporation of TMCD, resulted in higher glass transition temperatures (T_g) of the new copolyesters than previous copolyester compositions due to its rigid characteristics. The T_g of most traditional copolyesters is limited to around 80 °C while the T_g of Tritan™ TX2001, a typical grade designed for houseware

application, is about 120 °C. Tritan™ copolyesters crystallize very slowly relative to polyesters such as PET, and are easy to mold into amorphous parts that are transparent even in thick sections and have mold shrinkage of only 0.5–0.7%.

20.7.2 Properties of Tritan™

Due to their low heat resistance and low impact performance, conventional copolyesters have limited opportunities in applications that require exposure to high levels of heat, such as in the dishwasher. Comparing with Eastman's heritage copolyesters of PETG, PCTG, and PCTA, Tritan™ has lower specific gravity, and marked improvements in HDT and notched Izod impact strength as shown in Table 20.2.

Compared with many commercial transparent TP, Tritan™ copolyesters have excellent clarity and transparency with water-like, neutral color. As shown in Figure 20.11, Tritan™ exhibits much higher level of light transmission than multiphase transparent ABS and impact-modified acrylic.

By having lower glass transition temperatures than PC, copolyesters generally experience lower residual stress introduced to a product during molding. It is well known that the presence of high residual stresses in a part can have a significant impact on the mechanical performance and chemical resistance of a molded object. Molded-in stresses can be the cause of part warpage, shrinkage, distortion during fabrication (e.g., drilling, welding) as well as the driving force for environmental stress cracking (ESC), and poor chemical resistance. While some residual stresses (of a compressive nature) occasionally improve ESC, it is unrealistic to control the nature of the stress on all surfaces of an actual part. Consequently, it is paramount to minimize the stress magnitude of molded parts, to ensure it is robust against ESC.

A layer removal technique and chemical solvent testing can be employed for stress evaluation. Both methods show that molded-in stress levels of Tritan™-based materials are generally 0.2–0.5 times lower than levels measured in PC-based products. The layer-removal technique is a well-utilized method for assessing the stress distribution in a flat, molded object as shown by the data in Figure 20.12. The procedure is carried out by carefully machining away layers of a tensile

TABLE 20.2 Properties of Tritan™ and Conventional Copolyesters

Properties	Tritan™		PETG	PCTG	PCTA
	(TX 1001)	(TX2001)	(GN007)	(DN011)	(DS1010)
Specific gravity	1.18	1.17	1.27	1.23	1.20
Clarity transmittance (%)	90	92	90	92	91
HDT @0.455 MPa (°C)	99	109	70	73	75
HDT @1.82 MPa (°C)	85	92	62	64	65
Notched Izod impact (J m ⁻¹)	980 (NB ^a)	850 (NB ^a)	105	NB ^a	80

^aNonbreak as defined by ASTM D256 using 3.2 mm specimens.

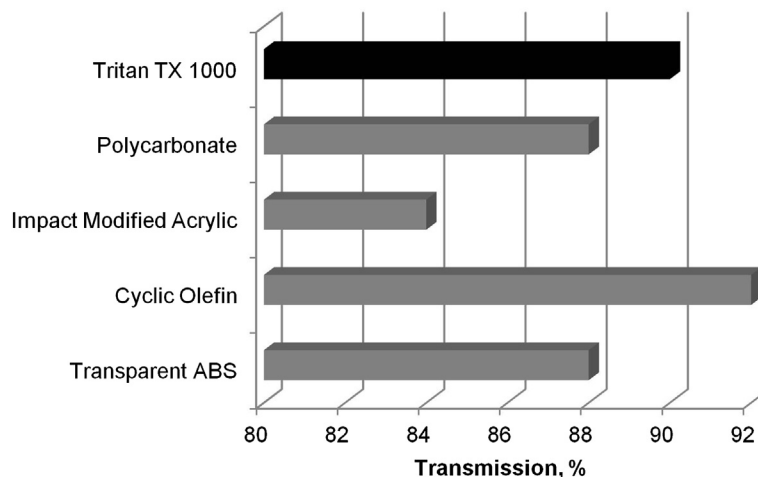


FIGURE 20.11 Clarity comparison of transparent thermoplastics.

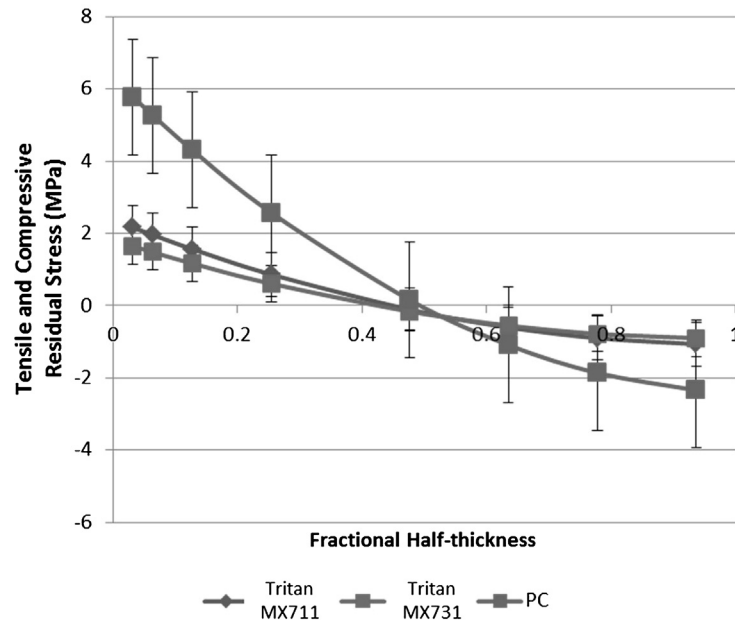


FIGURE 20.12 As-molded residual stress profile of Tritan™ copolyesters and polycarbonate.

bar (depths of 0.05, 0.10, 0.20, 0.41, 0.76, 1.02, 1.24, 1.50 mm). To ensure that no stresses or unwanted deformations are introduced during machining, a gentle end-mill is used, the surface is cooled with air, and a vacuum plate is employed to hold the tensile bar in place. Following layer removal, the deflection of the tensile bar is measured using an optical device. Using simple beam theories, established by [Treuting and Read \(1951\)](#), the residual stress as a function of part thickness can be calculated by the following expression:

$$\sigma(Z) = \left[\frac{-4E}{3(1-\nu^2)L^2} \right] \times \left[(Z_0 + Z_1)^2 \frac{df(Z_1)}{dZ} + 4(Z_0 + Z_1)f(Z_1) - 2 \int_{Z_1}^{Z_0} f(Z) dz \right] \quad (20.2)$$

The variables are defined as follows: $\sigma(Z)$ is the residual stress as a function of part thickness (or depth), E is Young's Modulus, ν is Poisson's Ratio (assumed as 0.4), L is the bar length, f is the deflection distance as a function of depth ($Z_0 - Z_1$) is the thickness removed by cutting, and Z_0 is the half-thickness of the bar.

20.7.3 Applications

In the consumer goods market, there are many applications for transparent TP such as copolyesters, acrylic, SAN, amorphous nylon, and polycarbonate. However, the growing demands for materials that can deliver durability, design flexibility, and easy processing in new applications limits the use of many existing clear TP, especially those from the commodity families in these areas. Eastman Tritan™ copolyesters are new amorphous TP aimed at filling this gap.

The unique properties of Tritan™ copolyesters allow them to be used in applications in a variety of markets from housewares to medical devices. The rapid market success of Tritan™ copolyesters in replacing polycarbonate owes much to their similarity in toughness with additional dishwasher durability and freedom from consumer concerns related to BPA.

Dishwasher durability is a very important attribute for housewares applications. The hot and caustic environment of the dishwasher renders it one of the most demanding tests for plastics. Temperatures in residential dishwashers can reach up to 75 °C, while those in commercial dishwashers can reach up to 90 °C. A pH level of 11.8 has been recorded in residential dishwashers, and detergents used in commercial dishwashers may be more aggressive. While the commercial dishwasher cycle usually lasts only a few minutes, residential dishwashing cycles can last 1.5–2 h.

Beer mugs molded from acrylic (AC), methacrylate styrene (MS) copolymer, polycarbonate (PC), SAN copolymer, and Tritan™ were dishwashed in a residential dishwasher using a powder detergent for 30, 50, 75, 100, and 125 cycles, followed by drop testing. A maximum of 25 drops was conducted with the mugs filled nearly full of water and dropped on their bottom from a height of 1.2 m. Both the acrylic and styrenics (MS & SAN) failed after a single drop and had inferior

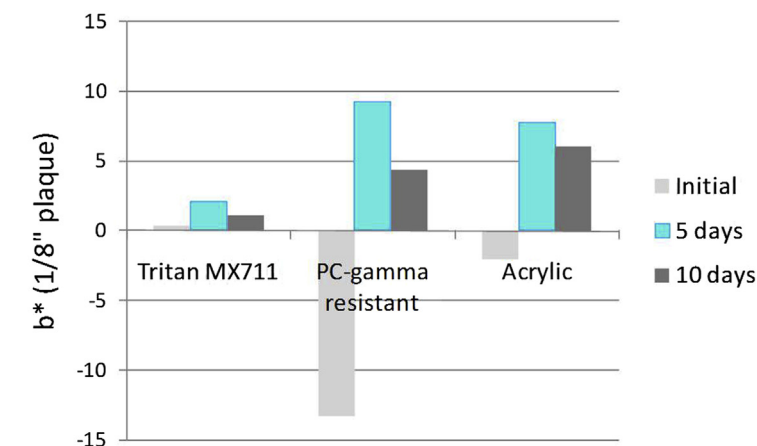
toughness compared to Tritan™. PC failed due to cracking in the dishwasher and subsequently was not drop tested. Figure 20.13 shows photographs of drop-tested beer mugs after a given number of cycles in a residential dishwasher.



FIGURE 20.13 Photos of dishwashed mugs after respective number of residential dishwasher (DW) cycles, molded from (a) acrylic after 75 DW cycles and drop test, (b) methacrylate styrene after 50 DW cycles and drop test, (c) polycarbonate after 125 DW cycles and no drop test, (d) styrene acrylonitrile (SAN) after 30 DW cycles and drop test, (e) SAN after 125 DW cycles and no drop test, and (f) Tritan™ after 125 DW cycles and drop test. *Photographs provided by courtesy of Eastman Chemical Company.*

Tritan™ copolyesters are well suited for medical applications due to their general properties of clarity, toughness, and chemical resistance. However, more specific advantages include the lack of color change after radiation sterilization, no annealing required due to low residual stresses after molding, and chemical resistance to medical disinfectants and oncology drugs. Less color shift eliminates the need for addition of stabilizers or colorants for masking of color changes during sterilization thus mitigating biocompatibility concerns of the healthcare industry.

Sterilization by autoclave, radiation, and ethylene oxide (EtO) gas is also clearly important for patient safety and comfort. Polypropylene can be repeatedly autoclaved, despite not having a high HDT but may suffer from odor and chain scission. Like most acrylic and styrenic polymers, Tritan is not autoclavable and will deform under high temperatures and pressures (>121 °C and 0.1 MPa). It is however capable of radiation sterilization and EtO sterilization without loss in properties and with minimal color shift. Figure 20.14 shows that at high radiation levels of 50 kGy, there is little color shift for Tritan™ copolyester as compared to PC and acrylic resins.



Color shift during sterilization

Less color shift — better aesthetics and patient confidence



FIGURE 20.14 Color shift measured using CIELAB color (b^*) and visual color assessment of Tritan™ MX711, gamma-resistant polycarbonate (PC) and standard grade PC and acrylic after 50 kGy of e-beam radiation. Positive and negative b^* values correspond to a yellow (light gray in print versions) and blue (gray in print versions) hue, respectively. Photographs provided by courtesy of Eastman Chemical Company.

REFERENCES

- Auerbach, A.B., Sell, J.W., 1990. Evaluation of poly(1,4-cyclohexylene dimethylene terephthalate) blends for improved processability. *Polymer Engineering & Science* 30, 1041–1050.
- Blasius Jr., W.G., Deeter, G.A., Villalobos, M.A., 2006. Oligomeric Chain Extenders for Processing, Post-Processing and Recycling of Condensation Polymers, Synthesis, Compositions and Applications. US Patent 6,984,694.
- Brady, A.J., Keskkula, H., Paul, D.R., 1994. Toughening of poly(butylene terephthalate) with core-shell impact modifiers dispersed with the aid of polycarbonate. *Polymer* 35, 3665–3672.
- Brydson, A.J., 1999. *Plastics Materials*, seventh ed. Butterworth-Heinemann, Oxford.
- Esposit, F., 2007. Eastman touts Tritan as PC Competitor. *Plastics News*, Crain Communications Inc. Available at: <http://www.plasticsnews.com/article/20071105/NEWS/311059992/eastman-touts-tritan-as-pc-competitor> (accessed 27.03.16.).
- Farnham, S.B., Goldman, T.D., 1978. Impact Modified Poly(Alkylene Terephthalates). US Patent 4,096,202.
- Gilbert, M., Hybart, F.J., 1972. Effect of chemical structure on crystallization rates and melting of polymers. 1. Aromatic polyesters. *Polymer* 13, 327–332.
- Gupta, V.B., Bashir, Z., 2002. PET fibers, films, and bottles. In: Fakirov, S. (Ed.), *Handbook of Thermoplastic Polyesters: Homopolymers, Copolymers, Blends, and Composites*. Wiley-VCH, Weinheim, pp. 317–388.

- Hobbs, S.Y., Pratt, C.F., 1975. Multiple melting in poly(butylene terephthalate). *Polymer* 16, 462–464.
- Hobbs, S.Y., Dekkers, M.E.J., Watkins, V.H., 1988. Effect of interfacial forces on polymer blend morphologies. *Polymer* 29, 1598–1602.
- Illers, K.H., 1980. Heat of fusion and specific volume of poly(ethylene terephthalate) and poly(butylene terephthalate). *Colloid and Polymer Science* 258, 117–124.
- Iroh, J.O., 2009. Poly(butylenes terephthalate). In: Mark, J.E. (Ed.), *Polymer Data Handbook*, second ed. Oxford University Press, Oxford, pp. 463–466.
- Jabarin, S.A., 1982. Optical properties of thermally crystallized poly(ethylene terephthalate). *Polymer Engineering & Science* 22, 815–820.
- Lacroix, C., Bouilloux, A., 2006. Thermoplastic Polyester Compositions Having Improved Impact Properties. US Patent 7,119,152.
- Martin, P., Gallez, C., Dexvaux, J., Legras, R., Leemans, L., Gurp, M., Duin, M., 2003. Reactive compatibilization of blends of polybutylene terephthalate with epoxide-containing rubber. The effect of the concentrations in reactive functions. *Polymer* 44, 5251–5262.
- Scheirs, J., 2003. Additives for the modification of poly(ethylene terephthalate) to produce engineering-grade polymers. In: Scheirs, J., Long, T.E. (Eds.), *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*. John Wiley & Sons, England, pp. 495–540.
- Schweizer, R.A., Winterman, A.W., 1989. Reinforcing fibers and fillers. In: Lutz, J.T. (Ed.), *Thermoplastic Polymer Additives*. Marcel Dekker, New York, pp. 417–436.
- Treuting, R.G., Read Jr., W.T., 1951. A mechanical determination of biaxial residual stress in sheet materials. *Journal of Applied Physics* 22, 130–134.
- Turner, S.R., 2004. Development of amorphous copolyesters based on 1,4-cyclohexanedimethanol. *Journal of Polymer Science Part A: Polymer Chemistry* 42, 5847–5852.
- Wunderlich, B., 1990. *Thermal Analysis*. Academic Press, London, p. 426.