

SECOND EDITION

Radiation Technology for Polymers



Jiri George Drobny

 CRC Press
Taylor & Francis Group

SECOND EDITION

Radiation Technology for Polymers



CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **Informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2010 by Taylor and Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number: 978-1-4200-9404-6 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

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

Library of Congress Cataloging-in-Publication Data

Drobny, Jiri George.

Radiation technology for polymers / Jiri George Drobny. -- 2nd ed.
p. cm.

Includes bibliographical references and index.

ISBN 978-1-4200-9404-6 (hardcover : alk. paper)

1. Radiation curing. 2. Radiation--Industrial applications. 3. Ultraviolet radiation--Industrial applications. 4. Plastic coating. I. Title.

TP156.C8D76 2010

668.9--dc22

2010005447

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

SECOND EDITION

**Radiation
Technology
for
Polymers**

To Betty Anne

Preface to the First Edition

The industrial use of ultraviolet (UV) and electron beam (EB) radiation is growing at a fast pace and is penetrating many areas, such as electronics, automotive, printing, adhesives and coatings, packaging, etc., which traditionally have had their own well-established processes. Information on this topic useful to a professional can be found in many places, such as encyclopedias (*Encyclopedia of Polymer Science and Engineering*, *Ullmann's Encyclopedia of Industrial Chemistry*), professional publications (*PCI, Paint and Coating Industry, Paint & Powder, FLEXO, Converting, Modern Plastics, Rubber Chemistry and Technology, Modern Plastics, Wire and Cable, Radiation Physics and Chemistry, Journal of Applied Polymer Science*), and others. RadTech News, a publication of RadTech North America, covers applications, new technology, and industry news. During the past few years, several very informative books have been published by SITA Technology Ltd. in the UK that cover different aspects of UV/EB radiation technology in great detail. However, seeking specific information may be prohibitively time-consuming and a need for a quick reference book is obvious.

Radiation Technology for Polymers is designed to meet this need by providing systematic fundamental information about practical aspects of UV/EB radiation to professionals in many different fields. The intended audiences are mainly chemists or chemical engineers new to UV/EB radiation technology. Another reader of this book may be a product or process designer looking for specifics about the effects of UV/EB on a specific polymeric material or for a potential technological tool. This book may also be a useful resource for recent college and university graduates or for graduate or undergraduate students in polymer science and engineering and for corporate training. Because of the breadth of the field and the multitude of applications, the book does not go into details; this is left to publications of a much larger size and scope and to professional periodicals. Rather, it covers the essentials and points the reader toward sources of more specific and/or detailed information. *Radiation Technology for Polymers* is not a competition to other books on the subject, it merely complements them. With this in mind, this book is divided into eleven separate chapters, covering the principles of generating UV and EB energy, equipment, processes, applications, dosimetry, safety, and hygiene. The last chapter covers the newest developments and trends.

This book began as lectures and seminars at the Plastics Engineering Department of the University of Massachusetts at Lowell and to varied professional groups and companies in the United States and abroad. It draws from the author's more than 40 years of experience as an R&D and manufacturing professional in the polymer processing industry and more recently as an independent international consultant.

My thanks are due to the team from the CRC Press, Susan Farmer, Helena Redshaw, and Sylvia Wood, for helping to bring this work to fruition; to my family for continuing support; and Dr. Ewa Andrzejewska, John Chrusciel, Dr. Joseph Koleske, and Richard W. Stowe for valuable comments and recommendations.

*Merrimack, New Hampshire
April 2002*

Preface to Second Edition

The first edition of *Radiation Technology for Polymers* had the main goal of providing systematic fundamental information to professionals entering the industrial practice of radiation technology as it applies to processing of polymers or already working in this field. Since its publication in 2003 the industry has changed markedly. Many technological developments have taken place, new applications and products have been developed and commercialized, and some already established ones were discontinued. Companies were sold and bought, reorganized, or renamed. UV/EB technology is becoming increasingly more important in a variety of issues, such as its continuing quest for further reduction of volatile organic compounds and toxic substances in the environment, development of alternative sources of energy, and more. Thus, it was time to update the publication to include these changes, developments, and issues. As the first edition, the second edition still stresses the practical aspects of UV/EB technology and its industrial applications. Few illustrations were added, and one of the major features is the addition of processing and engineering data of some commercial products. In addition, the feedback from colleagues, students, clients, and attendants of various seminars and training sessions was helpful in preparing the manuscript of this updated and expanded edition.

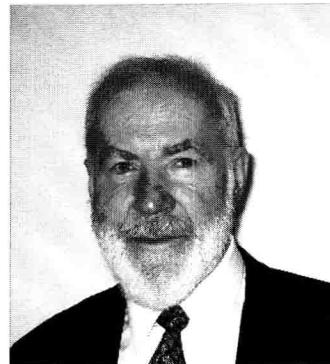
Special thanks go to Anthony J. Berejka, Dr. Marshall R. Cleland, and Richard W. Stowe for editing parts of the manuscript and providing helpful comments and recommendations.

Allison Shatkin, who was very helpful and encouraging from the beginning until the end of the preparation of the manuscript, deserves many thanks. A special credit is due to the team from CRC Press, particularly to Andrea Dale, Jennifer Ahringer, and Amy Rodriguez, for bringing this work to fruition.

Jiri George Drobny
Merrimack, New Hampshire, and Prague, Czech Republic
June 2009

About the Author

Jiri George Drobny was educated at the Technical University in Prague in chemical engineering, specializing in processing of plastics and elastomers, and at the Institute of Polymer Science of the University of Akron (Ohio) in physics and engineering of polymers. He also earned an MBA in finance and management at Shippensburg State University in Shippensburg, Pennsylvania. His career spans over 40 years in the rubber and plastics processing industries in Europe, the United States, and Canada, mainly in R&D with senior and executive responsibilities. Currently, he is president of Drobny Polymer Associates, an international consulting firm specializing in fluoropolymer science and technology, radiation processing, and elastomer technology. Drobny is also active as an educator, author, and technical and scientific translator. He is a member of the Society of Plastic Engineers, American Chemical Society, and RadTech International North America, and is listed in *Who's Who in America*, *Who's Who in Science and Engineering*, *Who's Who in Plastics and Engineering*, and *Who's Who in the East*. He resides in New Hampshire.



Contents

List of Illustrations	xiii
List of Tables	xvii
Preface to the First Edition.....	xix
Preface to Second Edition	xxi
About the Author	xxiii
1. Introduction	1
1.1 Basic Concepts	2
References	4
2. Review of Radiation Science and Technology	5
2.1 UV and Visible Radiation	5
2.1.1 Light Emission from Mercury Gas Discharge.....	6
2.1.2 Light Emission from a Microwave-Excited Discharge.....	7
2.1.3 Generation of Monochromatic UV Radiation.....	7
2.2 Ionizing Radiation	11
2.2.1 Electron Beam Energy.....	11
2.2.2 Gamma Rays.....	15
2.2.3 X-Rays	16
2.2.4 Other Types of Ionizing Radiation.....	17
2.3 Comparison of UV and EB Processes	18
References	19
3. UV and EB Curing Equipment	21
3.1 UV Curing Equipment	21
3.1.1 Lamps	22
3.1.1.1 Medium-Pressure Lamps.....	23
3.1.1.2 Electrodeless Lamps	24
3.1.1.3 Low-Pressure Mercury Lamps.....	25
3.1.1.4 High-Pressure Mercury Lamps	25
3.1.1.5 Excimer Lamps	26
3.1.1.6 Xenon Lamps	29
3.1.2 Lamp Housing.....	29
3.1.3 Power Supply and Controls.....	33
3.1.3.1 Power Supply Systems.....	33
3.1.3.2 Control Systems.....	35

3.2	Electron Beam Curing Equipment	36
3.2.1	Particle Accelerators	39
3.2.1.1	Direct Accelerators	40
3.2.1.2	Indirect Accelerators	44
3.2.1.3	Low-Energy Electron Accelerators	48
3.2.2	Recent Trends in Development of EB Curing Equipment and Technology	54
	References	58
4.	UV Radiation Processes	63
4.1	Basic Concepts	63
4.2	Photoinitiators and Photosensitizers	65
4.2.1	Free Radical Photoinitiators	66
4.2.1.1	Type I Photoinitiators	67
4.2.1.2	Type II Photoinitiators	67
4.2.2	Cationic Photoinitiators	68
4.2.3	Anionic Photoinitiators	68
4.2.4	Oxygen Inhibition of Cure	68
4.2.5	Initiation of UV Hybrid Curing	68
4.3	Kinetics of Photoinitiated Reactions	70
4.3.1	Kinetics of Free Radical Photopolymerization	70
4.3.2	Kinetics of Cationic Photopolymerization	72
4.4	Chemical Systems in UV Processing	73
4.4.1	Free-Radical-Initiated Systems	74
4.4.1.1	Acrylate/Methacrylate Systems	74
4.4.1.2	Styrene/Unsaturated Polyesters	76
4.4.1.3	Vinyl Ether/Unsaturated Esters	76
4.4.1.4	Thiol-ene Systems	77
4.4.1.5	Donor-Acceptor Complexes	77
4.4.2	Cationic Systems	78
4.5	Photo-Cross-Linking of Polymers	79
	References	80
5.	Electron Beam Processes	85
5.1	Introduction	85
5.2	Radiation Cross-Link Promoters	91
5.2.1	Indirect Cross-Link Promoters	91
5.2.1.1	Halogenated Compounds	91
5.2.1.2	Nitrous Oxide	91
5.2.1.3	Sulfur Monochloride	91
5.2.1.4	Bases	92

5.2.2	Direct Cross-Link Promoters	92
5.2.2.1	Maleimides.....	92
5.2.2.2	Thiols (Polymercaptans).....	92
5.2.2.3	Acrylic and Allylic Compounds	93
5.3	Retardants of Radiation Cross-Linking.....	94
5.4	Electron Beam Processing of Plastics.....	94
5.4.1	Polyolefins	94
5.4.1.1	Polyethylene	95
5.4.1.2	Polypropylene	97
5.4.2	Polystyrene.....	98
5.4.3	Polyvinylchloride.....	98
5.4.4	Polymethacrylates and Polyacrylates.....	98
5.4.5	Polyamides.....	98
5.4.6	Polyesters.....	99
5.4.7	Fluoroplastics.....	99
5.4.7.1	Polytetrafluoroethylene	99
5.4.7.2	FEP.....	99
5.4.7.3	Other Fluoroplastics.....	99
5.5	Electron Beam Processing of Elastomers.....	100
5.5.1	Physical Properties of Radiation Cross-Linked Elastomers.....	103
5.5.2	Effects of Radiation on Individual Elastomers	104
5.5.2.1	Natural Rubber (NR) and Synthetic Polyisoprene.....	104
5.5.2.2	Polybutadiene and Its Copolymers.....	108
5.5.2.3	Polyisobutylene and Its Copolymers.....	111
5.5.2.4	Ethylene-Propylene Copolymers and Terpolymers.....	112
5.5.2.5	Polychloroprene.....	113
5.5.2.6	Silicone Elastomers	114
5.5.2.7	Fluorocarbon Elastomers	114
5.5.2.8	Fluorosilicone Elastomers	115
5.5.2.9	Thermoplastic Elastomers.....	116
5.6	Electron Beam Processing of Liquid Systems.....	118
5.7	Grafting and Other Polymer Modifications	120
5.7.1	Grafting	120
5.7.2	Other Polymer Modifications.....	123
	References	123
6.	Coating Methods Used in UV/EB Technology	133
6.1	Roll Coating	133
6.1.1	Direct Roll Coating	133
6.1.2	Reverse Roll Coating	134

6.2	Curtain Coating.....	135
6.3	Spray Application.....	135
6.3.1	Compressed Air Gun Spraying	137
6.3.2	Airless Gun Spraying	137
6.4	Dip Coating	137
6.5	Flow Coating.....	137
6.6	Spin Coating	137
6.7	Rod Coating	138
6.8	Vacuum Coating.....	138
	References	139
7.	Applications of UV Radiation	141
7.1	UV Curing of Coatings and Paints.....	143
7.1.1	Functional and Decorative Coatings.....	143
7.1.1.1	Coatings on Flat, Rigid Substrates.....	143
7.1.1.2	UV Curing of Coatings on Flexible Substrates.....	144
7.1.2	UV Curing of Lacquers, Varnishes, and Paints	145
7.1.3	Three-Dimensional Curing	146
7.1.4	UV Curing of Coatings and Inks on Cylindrical-Shaped Parts.....	146
7.1.5	UV Matting of Coatings.....	146
7.2	UV Curing of Adhesives	147
7.2.1	Energy Curable Laminating Adhesives	147
7.2.2	Energy Curable Pressure-Sensitive Adhesives.....	148
7.2.3	Energy Curable Assembly Adhesives.....	152
7.3	UV Cured Silicone Release Coatings	152
7.4	Spot Curing.....	153
7.5	UV Curing in Printing and Graphic Arts.....	156
7.5.1	Screen Printing.....	157
7.5.2	Flexography	158
7.5.3	Letterpress and Offset Letterpress (Dry Offset)	160
7.5.4	Lithography	161
7.5.5	Rotogravure Printing	162
7.6	Rapid Prototyping.....	163
7.7	UV Powder Coatings	164
7.7.1	The Chemistry of UV Curable Powders	165
7.7.2	Material and Substrate Preparation	166
7.7.3	Powder Coating Application	167
7.7.4	Substrates Suitable for UV Powder Coating	168
7.7.5	Industrial Applications	170
7.8	Other Applications for UV Curing.....	170
7.8.1	Electronics.....	170

7.8.2	Optical Components and Optoelectronic Applications.....	171
7.8.2.1	Optical Fibers.....	171
7.8.2.2	Other Optical and Optoelectronic Applications	171
7.9	Automotive Applications	172
7.9.1	OEM Applications.....	172
7.9.2	Automotive Refinish Applications	173
7.10	Production of Composites by UV Radiation.....	174
7.10.1	Dental Applications.....	174
7.10.2	Other Composite Applications	175
7.11	Hydrogels	175
	References	176
8.	Applications of Electron Beam Radiation	181
8.1	Electron Beam Process in Wire and Cable Technology.....	181
8.1.1	Equipment and Process.....	185
8.1.2	Materials.....	187
8.1.3	Recent Developments and Trends	188
8.2	Electron Beam Process in Tire Technology	189
8.3	Electron Beam Process in the Manufacture of Polyolefin Foams.....	193
8.3.1	Foam Expansion and Its Control	194
8.3.2	Manufacturing Processes	194
8.3.3	Comparison of Chemical and Radiation Processes	196
8.4	Electron Beam Process in the Production of Heat-Shrinkable Materials	196
8.4.1	Heat-Shrinkable Tubing	197
8.4.2	Heat-Shrinkable Sheets and Films	200
8.5	Electron Beam Process in Coatings, Adhesives, Paints, and Printing Inks	202
8.5.1	Magnetic Media	202
8.5.2	Coatings.....	203
8.5.3	Printing and Graphic Arts.....	204
8.5.4	Adhesives.....	205
8.5.4.1	Pressure-Sensitive Adhesives (PSAs)	205
8.5.4.2	Laminating Adhesives	206
8.5.5	Polymeric Fiber-Reinforced Composites	207
8.5.6	Hydrogels.....	208
	References	209
9.	Dosimetry and Radiometry.....	215
9.1	EB Dosimetry.....	215
9.2	UV Radiometry	220
9.2.1	Actinometers	221

9.2.2 Radiometers	221
9.2.3 Radiochromic Films	224
References	230
10. Safety and Hygiene	233
10.1 UV Equipment Health and Safety	233
10.2 EB Equipment Health and Safety	235
10.3 Chemical Hazards	236
References	237
11. Recent Developments and Trends.....	239
11.1 Current Trends in Equipment and Chemistry	239
11.1.1 UV/EB Equipment	240
11.1.2 Chemistry	240
11.2 Emerging Technologies and Applications	241
11.2.1 Composite Processing and Repairs.....	241
11.2.2 UV Curable Concrete Coatings.....	242
11.2.3 Wood Finishing.....	242
11.2.4 Other	244
References	246
Glossary	249
Appendix I: Bibliography.....	261
Appendix II: Major Equipment Manufacturers	263
Appendix III: Standard Dosimetry Tests	265
Appendix IV: Major Suppliers of Raw Materials for UV/EB Curing	267
Appendix V: The Twelve Principles of Green Chemistry.....	269
Index	271

List of Illustrations

Figure 2.1	Spectral outputs of some typical metal halide lamps compared to that of the standard mercury lamp mercury barrier discharge lamp: (a) mercury barrier discharge lamp, (b) iron additive lamp, and (c) gallium additive lamp.....	8
Figure 2.2	Spectral output of commercial microwave-driven lamps	10
Figure 2.3	The process of generation of reactive species by high-energy electrons	15
Figure 2.4	Schematic of a cyclotron	17
Figure 2.5	Comparison of UV and EB radiations (r_0 = substrate thickness)	18
Figure 3.1	Medium-pressure mercury lamp	23
Figure 3.2	Electrodeless lamp	23
Figure 3.3	Barrier discharge excimer lamp	27
Figure 3.4	UV curing system with a barrier discharge excimer lamp	28
Figure 3.5	Spectral dependence of a xenon lamp on electrical operating parameters	30
Figure 3.6	Spiral xenon lamp used for DVD bonding	30
Figure 3.7	Two basic designs of reflectors	31
Figure 3.8	Example of a cold mirror reflector	32
Figure 3.9	Manual shutter open	33
Figure 3.10	Power supply for mercury lamps	34
Figure 3.11	Example of a control system for a mercury lamp	35
Figure 3.12	Traditional design of a high-energy EB unit	37
Figure 3.13	Schematic of a particle accelerator	39
Figure 3.14	Schematic of the Van de Graaff accelerator.....	41
Figure 3.15	Schematic of a direct accelerator (Dynamitron) accelerator	43
Figure 3.16	Schematic of an indirect accelerator (microwave linac).....	44
Figure 3.17	Schematic of a Rhodotron accelerator	46
Figure 3.18	An example of a Rhodotron system with a scanning horn	47
Figure 3.19	Common designs of industrial low-energy accelerators	49
Figure 3.20	Single-stage scanned beam accelerator with a range of accelerating voltages from 80 to 300 kV	50
Figure 3.21	Self-shielding EB processor with the accelerating voltages of 800 kV	51
Figure 3.22	Schematic of the processor EBOGEN	52
Figure 3.23	EBOGEN processing unit	52

Figure 3.24	BROADBEAM processor.....	53
Figure 3.25	Low-energy self-shielding electron beam processor.....	53
Figure 3.26	Miniature electron beam processor (gun and power supply)	55
Figure 3.27	(a) Schematic of a low-voltage electron beam emitter (U.S. Patent 6,545,398). (b) Low-voltage 10-in. emitter	56
Figure 4.1	Primary processes occurring in the excited state of a UV radical photoinitiator.....	64
Figure 5.1	Depth dose distribution for electron energies 100–200 keV.....	87
Figure 5.2	Electron penetration range in g/m ² as the function of electron energy.....	88
Figure 5.3	Elastomeric material: (a) un-cross-linked and (b) cross-linked.....	101
Figure 5.4	Effect of cross-link density on selected properties of an elastomeric material	102
Figure 5.5	Tensile strength of radiation cured purified natural rubber. o, gum; •, compound (50 phr N330 carbon black)	106
Figure 5.6	Tensile strength of radiation cured purified natural rubber. o, sulfur; Δ, peroxide; •, EB irradiation in nitrogen at 2.5 kGy/s	106
Figure 6.1	The arrangement for direct roll coating	134
Figure 6.2	Different types of cells on the surface of a gravure roll: (a) pyramidal, (b) quadrangular, (c) trihelical	134
Figure 6.3	Reverse roll coating	135
Figure 6.4	Different roll coating methods and roll arrangements: S = steel roll, R = rubber-covered roll, E = engraved roll.....	136
Figure 6.5	Diagram of vacuum coating system	139
Figure 7.1	3D UV curing using robotics	143
Figure 7.2	Example of UV curing of wood coatings	145
Figure 7.3	Curing section of a modern coating line with four UV lamps.....	146
Figure 7.4	Spot curing lamp	153
Figure 7.5	Mercury-xenon lamp for small area curing.....	154
Figure 7.6	Flood curing lamp	155
Figure 7.7	LED curing lamp	155
Figure 7.8	Floor cure LED equipment.....	156
Figure 7.9	Flexographic printing deck	159
Figure 7.10	Modern flexographic folding carton press with three UV processors.....	160
Figure 7.11	Offset letterpress (dry offset)	161
Figure 7.12	Lithographic printing station.....	162
Figure 7.13	Rotogravure printing station	163
Figure 7.14	Printing line with UV curing lamps. PS, printing station; UV, UV curing lamps.....	163