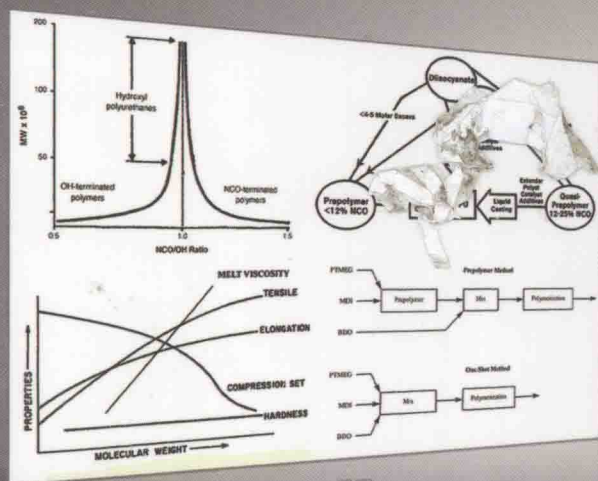


# SZYCHER'S HANDBOOK OF POLYURETHANES

Second Edition



Michael Szycher, Ph.D.



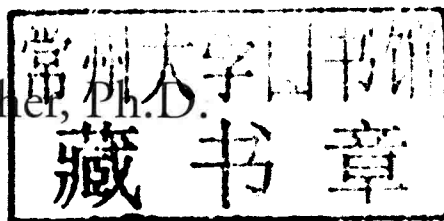
CRC Press  
Taylor & Francis Group

# SZYCHER'S HANDBOOK OF POLYURETHANES

---

Second Edition

Michael Szycher, Ph.D.



**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

© 2013 by Taylor & 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  
Version Date: 20120312

International Standard Book Number: 978-1-4398-3958-4 (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) (<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

---

Szycher's handbook of polyurethanes / edited by Michael Szycher. -- 2nd ed.  
p. cm.

Summary: "Written as a reference for polyurethane technologists and end users, raw materials suppliers, and students in the field, this second edition covers the technical advances in the field over the past 10 years. Filled with tables, charts, and photographs, it includes new data on green polyurethanes, automotive applications, new coatings, new manufacturing equipment, new health-care uses, and other topics. Individuals from all major polyurethane intermediate suppliers and equipment manufacturers contributed to this updated handbook, and discuss current products and provide a comprehensive list of product portfolios"-- Provided by publisher.

Includes bibliographical references and index.

ISBN 978-1-4398-3958-4 (hardback)

1. Polyurethanes--Handbooks, manuals, etc. I. Szycher, M. (Michael)

TP1180.P8S98 2012  
668.4'239--dc23

2012007366

---

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

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

# SZYCHER'S HANDBOOK OF POLYURETHANES

---

Second Edition

*This handbook is dedicated to my wife, Laurie,  
whose unwavering support and  
dedication made this work possible.*

---

## *Preface*

---

A handbook is a compilation of data from many sources presented in a logical and easy-to-follow sequence. The data must be compiled from disparate sources; the sources may be strictly academic, commercial, or promotional. It may come from technical publications, seminars, or the patent literature.

The U.S. patent literature is one of the most comprehensive sources of technical information. The technical information provided in patents is exhaustive, current, and represents the most valuable technology discovered by corporations, universities, and independent inventors. Because of the wealth of information contained in patents, this handbook features many full-text patents. These patents have been carefully selected by the authors to best illustrate the complex principles involved in polyurethane chemistry and technology.

This handbook is not composed of original articles; instead, it is based on hundreds of published references. The authors have tried to credit original sources by providing an extensive bibliography. The reader is encouraged to refer to the original sources for more complete information and insight.

Polyurethanes are arguably the most complex family of polymers. Polyurethanes range from soft elastomeric polymers to hard elastoplastics that rival metals. Polyurethanes are used as structural materials, coatings, adhesives, and sealants. Polyurethanes can be synthesized as thermoplastics, thermosets, and curable compositions by either heat or UV energy—and all by molecular design, as opposed to compounding by the addition of plasticizers or other modifiers.

**Dr. Michael Szycher**

---

## *Acknowledgment*

---

This handbook summarizes the published work of many polyurethane chemists, lecturers, researchers, and technologists. The contributions of these outstanding authors grace the pages of this handbook.

---

## Editor

---

**Michael Szycher**, PhD, is chairman and chief executive officer of CardioTech International, Inc., a manufacturer of medical products based on specialized polyurethanes. He holds a PhD from Boston University School of Medicine and an MBA from Suffolk University.

He is a recognized international authority on polyurethanes and blood-compatible polymers. Author of more than 100 research articles and a pivotal force in the creation of the Medical Plastics Division of the Society of Plastics Engineers (SPE), he is the editor of several other books:

- *Biocompatible Polymers, Metals and Composites*
- *Synthetic Biomedical Polymers*
- *Blood Compatible Materials and Devices: Perspectives towards the 21st Century*
- *High Performance Biomaterials: A Comprehensive Guide to Medical/Pharmaceutical Applications*
- *Szycher's Dictionary of Biomaterials and Medical Devices*
- *Szycher's Dictionary of Medical Devices*

He is also founding editor of the quarterly *Journal of Biomaterials Applications*.



---

## ***Contributors***

---

**Hugh A. Benhardt**

Department of Biomedical Engineering  
Texas A&M University  
College Station, Texas

**Elizabeth M. Cosgriff-Hernandez**

Department of Biomedical Engineering  
Texas A&M University  
College Station, Texas

**David K. Dempsey**

Department of Biomedical Engineering  
Texas A&M University  
College Station, Texas

**John Iannone**

Toxikon Corporation  
Bedford, Massachusetts

**Laurence Lister**

Toxikon Corporation  
Bedford, Massachusetts

**Charlie Martin**

Leistritz  
Nuremburg, Germany

**Jay R. Powell**

Analytical Answers, Inc.  
Woburn, Massachusetts

**Michael Szycher**

Sterling Biomedical, Inc.  
Lynnfield, Massachusetts

---

# Contents

---

Preface.....	xi
Acknowledgment.....	xiii
Editor.....	xv
Contributors.....	xvii
<b>1. Introduction .....</b>	<b>1</b>
<i>Michael Szycher</i>	
<b>2. Basic Concepts in Polyurethane Chemistry and Technology .....</b>	<b>13</b>
<i>Michael Szycher</i>	
<b>3. Structure–Property Relations in Polyurethanes.....</b>	<b>37</b>
<i>Michael Szycher</i>	
<b>4. Isocyanate Chemistry .....</b>	<b>87</b>
<i>Michael Szycher</i>	
<b>5. Polyols.....</b>	<b>135</b>
<i>Michael Szycher</i>	
<b>6. Chain Extenders.....</b>	<b>155</b>
<i>Michael Szycher</i>	
<b>7. Flexible and Semiflexible Foams.....</b>	<b>181</b>
<i>Michael Szycher</i>	
<b>8. Rigid Polyurethane Foams .....</b>	<b>257</b>
<i>Michael Szycher</i>	
<b>9. Polyurethane Foam Surfactants .....</b>	<b>309</b>
<i>Michael Szycher</i>	
<b>10. Catalysis of Isocyanate Reactions .....</b>	<b>319</b>
<i>Michael Szycher</i>	
<b>11. Elastomers .....</b>	<b>345</b>
<i>Michael Szycher</i>	
<b>12. Reaction Injection Molding.....</b>	<b>373</b>
<i>Michael Szycher</i>	
<b>13. Polyurethane Adhesives .....</b>	<b>393</b>
<i>Michael Szycher</i>	

<b>14. Waterborne Polyurethanes .....</b>	<b>417</b>
<i>Michael Szycher</i>	
<b>15. Health and Safety .....</b>	<b>449</b>
<i>Michael Szycher</i>	
<b>16. Radiation-Curable Adhesives and Coatings.....</b>	<b>495</b>
<i>Michael Szycher</i>	
<b>17. Processing Methods .....</b>	<b>523</b>
<i>Michael Szycher</i>	
<b>18. Compounding Ingredients .....</b>	<b>547</b>
<i>Michael Szycher</i>	
<b>19. Copolymers and Polyblends.....</b>	<b>587</b>
<i>Michael Szycher</i>	
<b>20. Polyurethane Coatings .....</b>	<b>597</b>
<i>Michael Szycher</i>	
<b>21. Castables, Sealants, and Caulking Compounds .....</b>	<b>613</b>
<i>Michael Szycher</i>	
<b>22. Medical Applications.....</b>	<b>633</b>
<i>Michael Szycher</i>	
<b>23. Resorbable Polyurethanes .....</b>	<b>671</b>
<i>David K. Dempsey, Hugh A. Benhardt, and Elizabeth M. Cosgriff-Hernandez</i>	
<b>24. Biodurable Polyurethanes.....</b>	<b>711</b>
<i>Michael Szycher</i>	
<b>25. Antimicrobial Polyurethanes.....</b>	<b>739</b>
<i>Michael Szycher</i>	
<b>26. Hydrophilic Polyurethanes .....</b>	<b>771</b>
<i>Michael Szycher</i>	
<b>27. Biocompatibility Testing.....</b>	<b>805</b>
<i>Michael Szycher, Laurence Lister, and John Iannone</i>	
<b>28. Eco-Friendly Polyurethanes .....</b>	<b>835</b>
<i>Michael Szycher</i>	
<b>29. Processing Thermoplastics Urethanes via Twin Screw Extrusion.....</b>	<b>873</b>
<i>Charlie Martin</i>	

**30. Infrared Analysis of Medical-Grade Polyurethane Elastomers:  
Can Durometer Hardness Be Determined by IR Analysis?** ..... 897  
*Michael Szycher and Jay R. Powell*

**Appendix A: Polyurethane Suppliers and Manufacturers** ..... 905

**Appendix B: Urethane Processing Systems** ..... 1041

**Appendix C: Glossary**..... 1057

**Appendix D: Conversions and Formulas**..... 1087

**Index** ..... 1093

# 1

---

## *Introduction*

---

Michael Szycher

### CONTENTS

1.1	Historical.....	1
1.2	Polyurethanes.....	2
1.3	Overview of Polyurethane Markets.....	6
1.4	Flexible Foams.....	7
1.5	Rigid Foams.....	8
1.6	Elastomers.....	9
	References.....	12

---

### 1.1 Historical

The year 1987 marked the 50th anniversary of the introduction of polyurethanes. Professor Otto Bayer was synthesizing polymer fibers to compete with nylon when he developed the first fiber-forming polyurethane in 1937. His invention ranks among the major breakthroughs in polymer chemistry, but the polymer was dismissed as impractical by his superiors at I.G. Farbenindustrie. For more than 20 years, Germany had been at the forefront of synthetic fiber technology, beginning with the introduction of polyvinyl chloride (PVC) fibers in 1913.

Germany remained preeminent in the fiber field until 1935, when Carothers in the United States discovered the nylons; E. I. DuPont in America introduced and began marketing nylon fibers, protected by a barrage of patents that proved impossible to overcome. Nothing as versatile and practical as the polyamides was available, prompting Bayer to investigate similar polymers not covered by the impenetrable DuPont patents.

At the end of January 1938, Rinke and collaborators were successful in reacting an aliphatic 1,8-octane diisocyanate with 1,4-butanediol to form a low-viscosity melt from which they were able to draw fibers. These early efforts resulted in what are now known as polyurethanes: the esters of carbamic acid. These polyurethanes could be spun from the melt; yarns and monofilaments that could be made from their new polymer were of high quality. Rinke and Associates were awarded the first U.S. patent on polyurethanes in 1938.<sup>1</sup>

Like many other developments, polymer chemistry, which began as a small specialized branch of organic chemistry, began to grow rapidly and adopted a new nomenclature, much as biochemistry had done before. Table 1.1 presents the recognized names of two important linkages found in polymers, comparing classical organic chemistry nomenclature to that used in polymer chemistry and biochemistry.

The first I.G. Farbenindustrie polyurethane had a melting point of 185°C and became available under the trade names Igamid U for synthetic fabrics, and Perlon U for producing artificial silk or bristles. A softer version was also available under the trade name Igamid

TABLE 1.1

Names of Some Important Nitrogen-Containing Polymer Linkages

Linkage	Organic Chemistry	Polymer Chemistry	Biochemistry
–NHCO–	Amide	Nylon	Peptide
–NHCOO–	Carbamate	Urethane	Not applicable

UL. Foams were also produced by adding water to isocyanates in the presence of hydroxyl-terminated polyesters to form carbonamides and release carbon dioxide as the blowing agent. These foams, named Tropicor M, were used to produce aircraft propeller blades and rigid, foam-filled landing flaps and skis.

DuPont<sup>2</sup> and ICI<sup>3</sup> recognized the elastomeric properties of the polyurethanes which led to production on an industrial scale in the 1940s.<sup>4</sup> Water was used as the chain extender, and the diisocyanate was naphthalene-1,5-diisocyanate (NDI).

DuPont surged to the forefront of polyurethane technology in the United States, receiving patents in 1942 covering the far-reaching reactions of diisocyanates with glycol, diamines, polyesters, and certain other active hydrogen-containing chemicals. From these humble beginnings emerged the polyurethanes, one of the most versatile polymers in the modern plastics armamentarium.

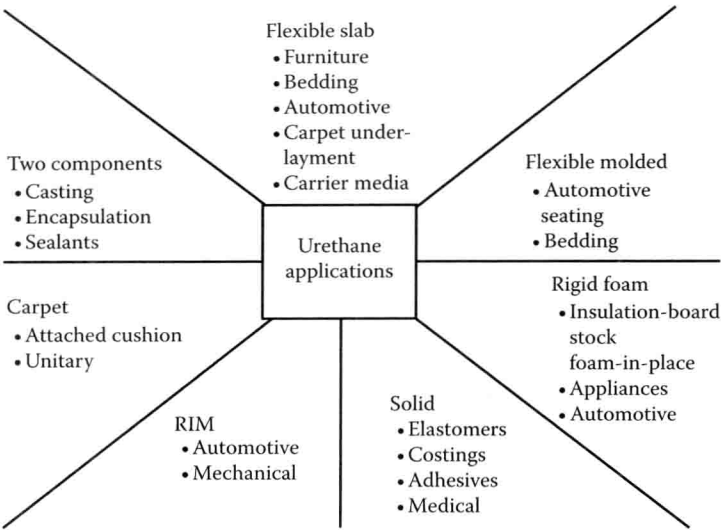
## 1.2 Polyurethanes

Polyurethanes are among the most important class of specialty polymers. But, ironically, the term *polyurethane* leads to a great deal of confusion. The term is more of convenience than of accuracy because polyurethanes are not derived from polymerizing a *methane* monomer, nor are they polymers containing primarily urethane groups. The polyurethanes include those polymers containing a plurality of urethane groups in the molecular backbone, regardless of the chemical composition of the rest of the chain. Thus, a typical polyurethane may contain, in addition to the urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, and isocyanurate groups.

Polyurethanes are used in a surprising array of commercial applications. Figure 1.1 presents the universe of polyurethane applications. For convenience, we have divided the applications into seven major groups: flexible slab, flexible molded foams, rigid foams, solid elastomers, reaction injection molding (RIM), carpet backing, and two-component formulations.

The chemistry of urethanes makes use of the reactions of organic isocyanates with compounds containing active hydrogens. When polyfunctional isocyanates and intermediates containing at least two active hydrogens per mole are reacted at proper ratios, a polymer results that can produce rigid or flexible foams, elastomers, coatings, adhesives, and sealants. An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkage, as shown in Reaction 1.1.

The isocyanates also react with amines to form substituted urea linkages; they will react with water to form carbamic acid, which is an unstable intermediate, and it decomposes readily to evolve carbon dioxide and an amine. This amine, in turn, reacts with additional isocyanate to form disubstituted urea. In addition, a number of cross-linking reactions may take place, depending on the reaction conditions such as temperature, the presence of catalysts, and the structure of the isocyanate, alcohols, and amines involved. These



**FIGURE 1.1**  
The polyurethane universe.

reactions form linkages of allophanate (reaction between urethane and isocyanate), biuret (reaction between substituted urea and isocyanate), and isocyanurate (trimerization of isocyanate groups). Isocyanates can also be polymerized to form dimers (uretidine diones), carbodiimide, and 1-nylon.

**REACTION 1.1**

Classical Urethane Linkage Reaction

N=C=O	+	H-O→NHCOO	
Isocyanate group		Hydroxyl group	Urethane linkage
<b>Trade Names (Medical Grade)</b>		<b>Manufacturer</b>	
Bionate		The Polymer Technology Group (now DSM Inc.)	
ChronoFlex		AdvanceSource Biomaterials	
ChronoThane		AdvanceSource Biomaterials	
Estane		Lubrizol, Inc.	
Isoplast		Lubrizol, Inc.	
Pellethane		Lubrizol, Inc.	
Tecoflex		Lubrizol, Inc.	
Tecothane		Lubrizol, Inc.	
Texin		Bayer Inc.	

**General Description**

Polyurethanes are produced by the condensation reaction of an isocyanate and a material with a hydroxyl functionality, such as a polyol. Polyurethane can have the chemical structure of either a thermoplastic or thermoset and can have the physical structure of a rigid solid, a soft elastomer, or a foam. The chemical composition of polyurethane can also vary widely, depending on the specific polyol- and isocyanate-bearing species which are reacted to form the polyurethane. The many different chemical structures and physical forms possible for polyurethane make it a versatile, widely used polymer. Specialty grades available include flame retardant, clay, silica, and glass-filled. In 1994, the price of polyurethane ranged approximately from \$2.50 to \$6.50 per pound at truckload quantities.

REACTION 1.1 (continued)

Classical Urethane Linkage Reaction

General Properties

The major benefits offered by polyurethane are that it retains its high impact strength at low temperatures, it is readily foamable, and it is resistant to abrasion, tear propagation, ozone, oxidation, fungus, and humidity. Although thermoplastic polyurethane is attacked by steam, fuels, ketones, esters, and strong acids and bases, it is resistant to aliphatic hydrocarbons and dilute acids and bases. The highest recommended use temperature of thermoplastic polyurethane is approximately 220°F (104°C), rendering it inappropriate for most high-temperature applications. Aromatic thermoplastic polyurethane has poor weatherability stemming from its poor resistance to UV degradation. Since polyurethane can be painted with flexible polyurethane paints without pretreatment, it has found use in many automotive exterior parts.

Typical Properties of Polyurethane

	American Engineering	SI
Processing temperature	385–450°F	196–232°C
Linear mold shrinkage	0.004–0.014 in/in	0.004–0.014 cm/cm
Mailing point	400–450°F	204–232°C
Density	69.9–77.4 lb/ft <sup>3</sup>	1.12–1.24 g/cm <sup>3</sup>
Tensile strength, yield	4.9–35.0 lb/in <sup>2</sup> × 10 <sup>3</sup>	3.4–24.6 kg/cm <sup>3</sup> × 10 <sup>3</sup>
Tensile strength, break	4.9–35.0 lb/in <sup>2</sup> × 10 <sup>5</sup>	3.4–24.6 kg/cm <sup>3</sup> × 10 <sup>2</sup>
Elongation, break	100.0–500.0%	100.0–500.0%
Tensile modulus	0.6–45.0 lb/in <sup>2</sup> × 10 <sup>5</sup>	0.4–31.6 kg/cm <sup>3</sup> × 10 <sup>4</sup>
Flexural strength, yield	6.0–60.0 lb/in <sup>2</sup> × 10 <sup>3</sup>	4.2–42.2 kg/cm <sup>3</sup> × 10 <sup>2</sup>
Flexural modulus	0.1–0.4 lb/in <sup>2</sup> × 10 <sup>5</sup>	0.0–0.2 kg/cm <sup>3</sup> × 10 <sup>4</sup>
Compressive strength	1.2–29.5 lb/in <sup>2</sup> × 10 <sup>3</sup>	0.8–20.7 kg/cm <sup>2</sup> × 10 <sup>2</sup>
Izod notched, R.T.	1.5 ft-lb/in-no break	8.1 kg/cm/cm
Hardness	A55–A95 Rockwell	A55–A95 Rockwell
Thermal conductivity	1.7–2.3 BTU-in/h-ft <sup>2</sup> -°F	0.25–0.33 W/m <sup>2</sup> -K
Linear thermal expansion	1.8–8.4 in/in-°F × 10 <sup>3</sup>	3.2–15.1 cm/cm-°C × 10 <sup>5</sup>
Deflection temperature at 264 psi	100–330°F	38–166°C
Deflation temperature at 66 psi	115–370°F	46–188°C
Continuous service temperature	180–220°F	82–104°C
Dielectric strength	430–730 V/10 <sup>-3</sup> in	1.7–2.9 V/mm × 10 <sup>4</sup>
Dielectric constant at 1 MHz	4.4–5.1	4.4–51
Dissipation factor at 1 MHz	0.060–0.100	0.060–0.100
Water absorption, 24 h	0.10–0.60%	0.10–0.60%

Typical Applications

• Automotive	Facias, padding, seats, gaskets, body panels, bumpers
• Medical	Implantable devices, catheters, blood bags, dialysis membranes, heart-assist devices
• Machinery	Bearings, nuts, wheels, seals, tubing
• Consumer	Furniture padding, mattress goods, roller skate wheels, athletic shoes
• Apparel	Fine polyurethane treads, combined with nylon monofilaments produce stretchable, lightweight, and comfortable fabrics (Lycra)



The repeating urethane linkage is the basis for the generic name *polyurethane*. However, the use of the generic term *polyurethane* is deceiving in that all useful polyurethane polymers contain a minority of urethane functional groups. Thus, polyurethane is more a term of convenience rather than accuracy, since these polymers are not derived by polymerizing a monomeric urethane reactant, nor are they polymers containing primarily urethane linkages. In fact, other groups such as ethers, amides, biurets, and allophanates are the majority linkages in the molecular chain. Urethane linkages represent the minority of functional groups as long as the polymers contain a significant number of urethane linkages. The name *polyurethane* may be correctly ascribed to these polymers.

Polyurethanes and the closely related polyureas are the products of the reaction of isocyanates ( $-N=C=O$ ) with the active hydrogen compounds ( $R-OH$ ) or ( $R-NH_2$ ). An alternative chemistry to the isocyanate reactions was explored by Hoff and Wicker<sup>5</sup> as they developed the chemistry to prepare polyurea from bis chloroformate and diamines.

The polyurethanes are a heterogeneous family of polymers unlike PVC, polyethylene, or polystyrene. The polyurethanes comprise an array of different products, ranging from rigid foams to soft, millable gums.

Figure 1.2 presents a summary of the structure–property relationship for polyurethanes; branching/cross-linking is plotted on the ordinate and intermolecular forces on the abscissa. Under these conditions, we can encompass all the commercially available polyurethanes and define which elastomeric products are of the greatest importance in current commercial applications. At the right corner, representing extreme branching and chain stiffness, are the rigid urethane foams. Therefore, at this extreme, the thermoset rigid foams occupy the highest rank of cross-linking and chain stiffness.

Table 1.2 summarizes some of the most important events in the historical development of the polyurethanes.

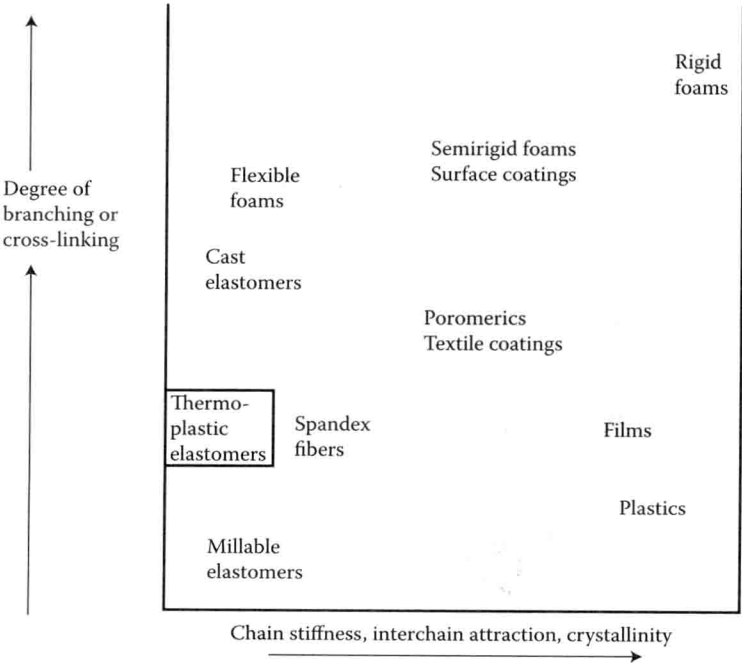


FIGURE 1.2  
Structure–property relationships in polyurethanes.