# THERMOSETTING POLYMERS

# JEAN-PIERRE PASCAULT HENRY SAUTEREAU

Institut National des Sciences Appliquées Villeurbanne, France

# **JACQUES VERDU**

Ecole Nationale Supérieure d'Arts et Métiers Paris, France

# ROBERTO J. J. WILLIAMS

University of Mar del Plata and National Research Council (CONICET) Mar del Plata, Argentina ISBN: 0-8247-0670-6

This book is printed on acid-free paper.

### Headquarters

Marcel Dekker, Inc. 270 Madison Avenue, New York, NY 10016 tel: 212-696-9000; fax: 212-685-4540

### **Eastern Hemisphere Distribution**

Marcel Dekker AG Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland tel: 41-61-261-8482; fax: 41-61-261-8896

### World Wide Web

http://www.dekker.com

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.

### Copyright © 2002 by Marcel Dekker, Inc. All Rights Reserved.

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

Current printing (last digit): 10 9 8 7 6 5 4 3 2 1

### PRINTED IN THE UNITED STATES OF AMERICA

### PLASTICS ENGINEERING

Founding Editor

Tài liệu chỉ xem được một số trạng đầu. Vui lộng download file gốc để xem toàn bộ các trang **Donald E. Hudgin** 

Professor Clemson University Clemson, South Carolina

- 1. Plastics Waste: Recovery of Economic Value, Jacob Leidner
- 2. Polyester Molding Compounds, Robert Burns
- 3. Carbon Black-Polymer Composites: The Physics of Electrically Conducting Composites, *edited by Enid Keil Sichel*
- 4. The Strength and Stiffness of Polymers, edited by Anagnostis E. Zachariades and Roger S. Porter
- Selecting Thermoplastics for Engineering Applications, Charles P. Mac-Dermott
- Engineering with Rigid PVC: Processability and Applications, edited by I. Luis Gomez
- 7. Computer-Aided Design of Polymers and Composites, D. H. Kaelble
- 8. Engineering Thermoplastics: Properties and Applications, *edited by James M. Margolis*
- 9. Structural Foam: A Purchasing and Design Guide, Bruce C. Wendle
- Plastics in Architecture: A Guide to Acrylic and Polycarbonate, Ralph Montella
- Metal-Filled Polymers: Properties and Applications, edited by Swapan K. Bhattacharya
- 12. Plastics Technology Handbook, Manas Chanda and Salil K. Roy
- 13. Reaction Injection Molding Machinery and Processes, F. Melvin Sweeney
- 14. Practical Thermoforming: Principles and Applications, John Florian
- 15. Injection and Compression Molding Fundamentals, edited by Avraam I. Isayev
- 16. Polymer Mixing and Extrusion Technology, *Nicholas P. Cheremisinoff*
- 17. High Modulus Polymers: Approaches to Design and Development, edited by Anagnostis E. Zachariades and Roger S. Porter
- Corrosion-Resistant Plastic Composites in Chemical Plant Design, John H. Mallinson
- 19. Handbook of Elastomers: New Developments and Technology, edited by Anil K. Bhowmick and Howard L. Stephens
- 20. Rubber Compounding: Principles, Materials, and Techniques, Fred W. Barlow
- 21. Thermoplastic Polymer Additives: Theory and Practice, edited by John T. Lutz. Jr.
- 22. Emulsion Polymer Technology, Robert D. Athey, Jr.
- 23. Mixing in Polymer Processing, edited by Chris Rauwendaal
- 24. Handbook of Polymer Synthesis, Parts A and B, edited by Hans R. Kricheldorf

- 25. Computational Modeling of Polymers, edited by Jozef Bicerano
- 26. Plastics Technology Handbook: Second Edition, Revised and Expanded, Manas Chanda and Salil K. Roy
- 27. Prediction of Polymer Properties, Jozef Bicerano
- 28. Ferroelectric Polymers: Chemistry, Physics, and Applications, edited by Hari Singh Nalwa
- 29. Degradable Polymers, Recycling, and Plastics Waste Management, *edited by Ann-Christine Albertsson and Samuel J. Huang*
- 30. Polymer Toughening, edited by Charles B. Arends
- 31. Handbook of Applied Polymer Processing Technology, *edited by Nicholas P. Cheremisinoff and Paul N. Cheremisinoff*
- 32. Diffusion in Polymers, edited by P. Neogi
- 33. Polymer Devolatilization, edited by Ramon J. Albalak
- 34. Anionic Polymerization: Principles and Practical Applications, *Henry L. Hsieh and Roderic P. Quirk*
- 35. Cationic Polymerizations: Mechanisms, Synthesis, and Applications, *edited* by Krzysztof Matyjaszewski
- 36. Polyimides: Fundamentals and Applications, edited by Malay K. Ghosh and K. L. Mittal
- 37. Thermoplastic Melt Rheology and Processing, A. V. Shenoy and D. R. Saini
- 38. Prediction of Polymer Properties: Second Edition, Revised and Expanded, Jozef Bicerano
- 39. Practical Thermoforming: Principles and Applications, Second Edition, Revised and Expanded, *John Florian*
- 40. Macromolecular Design of Polymeric Materials, edited by Koichi Hatada, Tatsuki Kitayama, and Otto Voql
- 41. Handbook of Thermoplastics, edited by Olagoke Olabisi
- 42. Selecting Thermoplastics for Engineering Applications: Second Edition, Revised and Expanded, Charles P. MacDermott and Aroon V. Shenoy
- 43. Metallized Plastics: Fundamentals and Applications, edited by K. L. Mittal
- 44. Oligomer Technology and Applications, Constantin V. Uglea
- 45. Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications, edited by Donald L. Wise, Gary E. Wnek, Debra J. Trantolo, Thomas M. Cooper, and Joseph D. Gresser
- 46. Structure and Properties of Multiphase Polymeric Materials, edited by Takeo Araki, Qui Tran-Cong, and Mitsuhiro Shibayama
- 47. Plastics Technology Handbook: Third Edition, Revised and Expanded, *Manas Chanda and Salil K. Roy*
- 48. Handbook of Radical Vinyl Polymerization, *Munmaya K. Mishra and Yusuf Yaqci*
- 49. Photonic Polymer Systems: Fundamentals, Methods, and Applications, edited by Donald L. Wise, Gary E. Wnek, Debra J. Trantolo, Thomas M. Cooper, and Joseph D. Gresser
- 50. Handbook of Polymer Testing: Physical Methods, edited by Roger Brown
- 51. Handbook of Polypropylene and Polypropylene Composites, edited by Harutun G. Karian
- Polymer Blends and Alloys, edited by Gabriel O. Shonaike and George P. Simon
- 53. Star and Hyperbranched Polymers, edited by Munmaya K. Mishra and Shiro Kobayashi
- 54. Practical Extrusion Blow Molding, edited by Samuel L. Belcher

- 55. Polymer Viscoelasticity: Stress and Strain in Practice, Evaristo Riande, Ricardo Díaz-Calleja, Margarita G. Prolongo, Rosa M. Masegosa, and Catalina Salom
- 56. Handbook of Polycarbonate Science and Technology, edited by Donald G. LeGrand and John T. Bendler Villong download file good exemition by cactering
- 57. Handbook of Polyethylene: Structures, Properties, and Applications, *Andrew J. Peacock*
- 58. Polymer and Composite Rheology: Second Edition, Revised and Expanded, Rakesh K. Gupta
- Handbook of Polyolefins: Second Edition, Revised and Expanded, edited by Cornelia Vasile
- 60. Polymer Modification: Principles, Techniques, and Applications, *edited by John J. Meister*
- 61. Handbook of Elastomers: Second Edition, Revised and Expanded, edited by Anil K. Bhowmick and Howard L. Stephens
- 62. Polymer Modifiers and Additives, edited by John T. Lutz, Jr., and Richard F. Grossman
- 63. Practical Injection Molding, Bernie A. Olmsted and Martin E. Davis
- 64. Thermosetting Polymers, Jean-Pierre Pascault, Henry Sautereau, Jacques Verdu, and Roberto J. J. Williams
- 65. Prediction of Polymer Properties: Third Edition, Revised and Expanded, *Jozef Bicerano*
- 66. Fundamentals of Polymer Engineering: Second Edition, Revised and Expanded, *Anil Kumar and Rakesh K. Gupta*

### **Additional Volumes in Preparation**

Handbook of Plastics Analysis, edited by Hubert Lobo and Jose Bonilla

Metallocene Catalysts in Plastics Technology, Anand Kumar Kulshreshtha

## **Preface**

The subject of thermosetting polymers receives very brief consideration in most books covering the fundamentals of polymer science. Usually the chemistry is represented by the structure of a phenolic network of the resol type, and some statistical calculations based on Flory's derivations are presented. Therefore, anyone trying to get a first approach to the subject finds only books with chapters written by different authors and aimed at specialists in the field.

The aim of this book is to present a unified coverage of the field of thermosetting polymers, written for readers who are making their first contact with this area. The analysis, however, is carried out to a derivation of concepts and equations useful for practical purposes. The book will be of value for undergraduate and graduate students as well as for people involved in R&D activities in the industrial sector. Some of the material has been used in undergraduate and graduate courses given at ENSAM (Paris), INSA (Lyon), and INTEMA (Mar del Plata, Argentina).

The scientific basis of different aspects of thermosetting polymers was well established in the 1980s and '90s. It was a period of great excitement for people working in the field (the Gordon Conferences were devoted to this subject; a Polymer Network Group was created; several symposia were organized by different research groups; and new, specific journals were launched). Most of the developments during this period are now well settled and constitute the heart of the book. Among the subjects that may be

considered firmly established are mean-field theories of network formation; transformation diagrams used to follow the evolution of the material along polymerization; the interpretation of experimental data obtained by differential scanning calorimetry; rheology and dielectrical spectroscopy; ways to synthesize rubber-modified thermosets and thermoplastic-thermoset blends; the influence of crosslinks on physical, elastic, and viscoelastic properties of polymer networks, and factors affecting the yielding and fracture of neat and modified thermosetting polymers. Subjects that are still controversial or less established, such as the inhomogeneity of some thermosetting polymers and aspects related to their durability, are also discussed in the book. Topics related to processing and to composite materials are analyzed only in the contexts of temperature and conversion profiles developed during the cure.

The core of research activities in the field has evolved to a more sophisticated level. The development of advanced materials based on thermosetting polymers is a very active field. It includes nano-structured materials, organic—inorganic hybrid materials, multicomponent blends, polymer-dispersed liquid crystals and networks with liquid crystalline behavior, and materials with a very low dielectric constant, etc. New analytical techniques are available such as microcalorimetry and atomic-force microscopy. Sophisticated computer simulations give a more realistic approach to modeling the build-up of the polymer network or following the evolution of temperature and conversion during the cure in a complex mold. Most of these subjects are outside the scope of this book. A list of selected references, suggested to complement and expand on the material presented in the book, is available at the end of many chapters.

This book is the result of almost two decades of scientific cooperation among the authors that resulted in a significant number of joint publications. In spite of the official grant codes, we always designated our joint research activities as the Asado (typical Argentine meat) – Beaujolais (typical French wine) Program. And some of the more fruitful discussions took place in the course of a Beaujolais tour or during the ritual of preparing the asado.

Over all these years we have learned much from discussions with many colleagues working in this field. The list would be so large—and the possibility of forgetting someone so great—that we prefer to present a general acknowledgment to many friends who contributed significantly to the ideas and concepts developed in this book.

Jean-Pierre Pascault Henry Sautereau Jacques Verdu Roberto J. J. Williams