







# PRINCIPLES OF POLYMER PROCESSING



SECOND EDITION



ZEHEV TADMOR • COSTAS G. GOGOS

### PRINCIPLES OF POLYMER PROCESSING

## PRINCIPLES OF POLYMER PROCESSING

## **Second Edition**

ZEHEV TADMOR

The Wolfson Department of Chemical Engineering Technion-Israel Institute of Technology Haifa, Israel

COSTAS G. GOGOS

Otto H. York Department of Chemical Engineering Polymer Processing Institute New Jersey Institute of Technology Newark, New Jersey



An SPE Technical Volume



A John Wiley & Sons, Inc., Publication

Regarding the cover: The five bubbles contain images that represent the five elementary steps of polymer processing. The bottom image is a picture of the Thomas Hancock masticator, the first documented processing machine, developed in 1820. This image was originally published in the book *Thomas Hancock: Personal Narrative of the Origin and Progress of the Caoutchouc or India-Rubber Manufacture in England* (London: Longman, Brown, Green, Longmans, & Roberts, 1857).

Copyright © 2006 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada

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

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

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

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

#### Library of Congress Cataloging-in-Publication Data:

Tadmor, Zehev, 1937-Principles of polymer processing / Zehev Tadmor, Costas G. Gogos. – 2nd ed. p. cm. Includes index.
ISBN 0-471-38770-3 (cloth)
1. Polymers. 2. Polymerization. I. Gogos, Costas G. II. Title. TP1087.T32 2006
668.9–dc22

2006009306

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

## **Series Preface**

The Society of Plastics Engineers is pleased to sponsor and endorse the second edition of *Principles of Polymer Processing* by Zehev Tadmor and Costas Gogos. This volume is an excellent source and reference guide for practicing engineers and scientists as well as students involved in plastics processing and engineering. The authors' writing style and knowledge of the subject matter have resulted in an enjoyable and thoughtful presentation, allowing the reader to gain meaningful insights into the subject.

SPE, through its Technical Volumes Committee, has long sponsored books on various aspects of plastics. Its involvement has ranged from identification of needed volumes and recruitment of authors to peer review and approval of new books. Technical competence pervades all SPE activities, from sponsoring new technical volumes to producing technical conferences and educational seminars. In addition, the Society publishes periodicals, including *Plastics Engineering, Polymer Engineering and Science*, and *The Journal of Vinyl and Additive Technology*.

The resourcefulness of some 20,000 practicing engineers, scientists, and technologists has made SPE the largest organization of its type worldwide. Further information is available from the Society of Plastics Engineers, 14 Fairfield Drive, Brookfield, Connecticut 06804 or at *www.4spe.org*.

Susan E. Oderwald

Executive Director Society of Plastics Engineers

## **Preface to the Second Edition**

Tremendous science and engineering progress has been made in polymer processing since the publication of the First Edition in 1979. Evolution in the field reflects the formidable contributions of both industrial and academic investigators, and the groundbreaking developments in rheology, polymer chemistry, polymer physics, life sciences and nanomaterials, in instrumentation and improved machinery. The emerging disciplines of computational fluid mechanics and molecular modeling, aided by exponentially expanding computing power are also part of this evolution.

As discussed in Chapter 1 of this Second Edition, polymer processing is rapidly evolving into a *multidisciplinary* field. The aim is not only to analyze the complex thermomechanical phenomena taking place in polymer processing equipment, *per se*, but to quantitatively account for the *consequences*, on the fabricated polymer products. Thus, the focus of future polymer processing science will shift away from the machine, and more on the product, although the intimate material-machine interactions in the former are needed for the latter.

Consequently, this edition contains not only updated material but also a significant restructuring of the original treatment of polymer processing. First, we deleted Part I which discussed polymer structure and properties, since the subject is thoroughly covered in many classic and other texts. Second, in light of the important technological developments in polymer blends and reactive processing, new chapters on Devolatilization, Compounding and Reactive Processing, and Twin Screw and Twin Rotor-based Processing Equipment are introduced. These processes are widely used because of their unique abilities to affect rapid and efficient solid deformation melting and chaotic mixing.

However, the basic philosophy we advocated in the First Edition, which was to analyze polymer processing operations in terms of *elementary* and *shaping* steps, which are common to all such processing operations, and thereby unifying the field is retained. We have continued our attempt to answer not only "how" the machines and processes work, but also "why" they are best carried out using a specific machine or a particular process. In fact, we believe that this approach has contributed to the fundamental understanding and development of polymer processing in the last quarter-century, and to the change of focus from the machine to the quantitative prediction of product properties.

As with the First Edition, this volume is written both as a textbook for graduate and undergraduate students, as well as resource for practicing engineers and scientists. Normally, a two-semester course in needed to cover the material in the text. However for students who are familiar with fluid mechanics, heat transfer and rheology, it is possible to cover the material in one semester. To enhance the usefulness of the Second Edition for both students and practitioners of the field, an extensive Appendix of rheological and thermo-mechanical properties of commercial polymers, prepared and assembled by Dr. Victor Tan, and for teachers, a complete problem Solution Manual, prepared by Dr. Dongyun Ren are included. For all it is hoped that this Second Edition, like the First, proves to be a useful professional "companion".

We would like to acknowledge, with gratitude, the role and help of many: foremost, the invaluable assistance of Dr. Dongyun Ren, who spent almost three years with us at the Technion and NJIT/PPI, assisting with many aspects of the text preparation, as well as the Solution Manual; and Dr. Victor Tan, whose expert and meticulous work in measuring and gathering rheological and thermo-mechanical polymer properties provides the data needed to work out real problems. In addition, we wish to thank our colleagures, and students, who have influenced this book with their advice, criticism, comments, and conversations. Among them are David Todd, Marino Xanthos, Ica Manas-Zloczower, Donald Sebastian, Kun Hyun, Han Meijer, Jean-Francois Agassant, Dan Edie, John Vlachopoulos, Musa Kamal, Phil Coates, Mort Denn, Gerhard Fritz, Chris Macosko, Mike Jaffe, Bob Westover, Tom McLeish, Greg Rutledge, Brian Qian, Myung-Ho Kim, Subir Dey, Jason Guo, Linjie Zhu and Ming Wan Young. Special thanks are due to R. Byron Bird for his advice and whose classic approach to Transport Phenomena, inspired our approach to polymer processing as manifested in this book.

There are others we wish to mention and recall. While they are no longer with us, their work, ideas, and scientific legacy resurface on the pages of this book. Among them: Joe Biesenberger, Luigi Pollara, Peter Hold, Ally Kaufmann, Arthur Lodge, Don Marshall, Imrich Klein, Bruce Maddock, and Lew Erwin.

We wish to thank our editor, Amy Byers, our production editor, Kristen Parrish, the copy editor Trumbull Rogers, and the cover designer Mike Rutkowski. We give special thanks to Abbie Rosner for her excellent editing of our book and to Mariann Pappagallo and Rebecca Best for their administrative support.

Finally, we thank our families, who in many respects paid the price of our lengthy preoccupation with this book at the expense of time that justly belonged to them.

ZEHEV TADMOR COSTAS G. GOGOS

Haifa, Israel Newark, New Jersey May 2006

## **Preface to the First Edition**

This book deals with polymer processing, which is the manufacturing activity of converting raw polymeric materials into finished products of desirable shape and properties.

Our goal is to define and formulate a coherent, comprehensive, and functionally useful engineering analysis of polymer processing, one that examines the field in an integral, not a fragmented fashion. Traditionally, polymer processing has been analysed in terms of specific processing methods such as extrusion, injection molding calendering, and so on. Our approach is to claim that what is happening to the polymer in a certain type of machine is *not unique*: polymers go through similar experiences in other processing methods, and these experiences can be described by a set of *elementary processing steps* that prepare the polymer for any of the *shaping* methods available to these materials. On the other hand, we emphasize the *unique* features of particular polymer processing methods or machines, which consist of the particular elementary step and shaping *mechanisms* and *geometrical solutions* utilized.

Because with the approach just described we attempt to answer questions not only of "how" a particular machine works but also "why" a particular design solution is the "best" among those conceptually available, we hope that besides being useful for students and practicing polymer engineers and scientists, this book can also serve as a tool in the process of creative design.

The introductory chapter highlights the technological aspects of the important polymer processing methods as well as the essential features of our analysis of the subject. Parts I and II deal with the fundamentals of polymer science and engineering that are necessary for the engineering analysis of polymer processing. Special emphasis is given to the "structuring" effects of processing on polymer morphology and properties, which constitute the "meeting ground" between polymer engineering and polymer science. In all the chapters of these two parts, the presentation is utilitarian; that is, it is limited to what is necessary to understand the material that follows.

Part III deals with the elementary processing steps. These "steps" taken together make up the total thermomechanical experience that a polymer may have in any polymer processing machine prior to shaping. Examining these steps separately, free from any particular processing method, enables us to discuss and understand the range of the mechanisms and geometries (design solutions) that are available. Part III concludes with a chapter on the modeling of the single-screw extruder, demonstrating the *analysis* of a complete processor in terms of the elementary steps. We also deal with a new polymer processing device to demonstrate that *synthesis* (invention) is also facilitated by the elementary-step approach.

We conclude the text with the discussion of the classes of shaping methods available to polymers. Again, each of these shaping methods is essentially treated independently of any particular processing method. In addition to classifying the shaping methods in a logical fashion, we discuss the "structuring" effects of processing that arise because the macromolecular orientation occurring during shaping is fixed by rapid solidification.

The last chapter, a guide to the reader for the analysis of any of the major processing methods in terms of the elementary steps, is necessary because of the unconventional approach we adopt in this book.

For engineering and polymer science students, the book should be useful as a text in either one-semester or two-semester courses in polymer processing. The selection and sequence of material would of course be very much up to the instructor, but the following syllabi are suggested: *For a one-semester course*: Chapter 1; Sections 5.2, 4, and 5; Chapter 6; Sections 7.1, 2, 7, 9, and 10; Sections 9.1, 2, 3, 7, and 8; Chapter 10; Section 12.1; Sections 13.1, 2, 4, and 5; Section 14.1; Section 15.2; and Chapter 17—students should be asked to review Chapters 2, 3, and 4, and for polymer science students the course content would need to be modified by expanding the discussion on transport phenomena, solving the transport methodology problems, and deleting Sections 7.1, 2, and 7 to 13; Sections 8.1 to 4, and 7 to 13; Chapters 9 and 10; and Sections 11.1 to 4, 6, 8, and 10—students should be asked to review Chapters 2, 3, and 4; and *in the second semester*, Chapters 12 and 13; Section 14.1, and Chapters 15, 16, and 17.

The problems included at the end of Chapters 5 to 16 provide exercises for the material discussed in the text and demonstrate the applicability of the concepts presented in solving problems not discussed in the book.

The symbols used follow the recent recommendations of the Society of Rheology; SI units are used. We follow the stress tensor convention used by Bird et al.,\* namely,  $\pi = P\delta + \tau$ , where  $\pi$  is the total stress tensor, *P* is the pressure, and  $\tau$  is that part of the stress tensor that vanishes when no flow occurs; both *P* and  $\tau_{ii}$  are positive under compression.

We acknowledge with pleasure the colleagues who helped us in our efforts. Foremost, we thank Professor J. L. White of the University of Tennessee, who reviewed the entire manuscript and provided invaluable help and advice on both the content and the structure of the book. We further acknowledge the constructive discussions and suggestions offered by Professors R. B. Bird and A. S. Lodge (University of Wisconsin), J. Vlachopoulos (McMaster University), A. Rudin (University of Waterloo), W. W. Graessley (Northwestern University), C. W. Macosko (University of Minnesota), R. Shinnar (CUNY), R. D. Andrews and J. A. Biesenberger (Stevens Institute), W. Resnick, A. Nir, A. Ram, and M. Narkis (Technion), Mr. S. J. Jakopin (Werner-Pfleiderer Co.), and Mr. W. L. Krueger (3M Co.). Special thanks go to Dr. P. Hold (Farrel Co.), for the numerous constructive discussions and the many valuable comments and suggestions. We also thank Mr. W. Rahim (Stevens), who measured the rheological and thermophysical properties that appear in Appendix A, and Dr. K. F. Wissbrun (Celanese Co.), who helped us with the rheological data and measured  $\eta_0$ . Our graduate students of the Technion and Stevens Chemical Engineering Departments deserve special mention, because their response and comments affected the form of the book in many ways.

<sup>\*</sup>R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960; and R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, Wiley, New York, 1977.

We express our thanks to Ms. D. Higgins and Ms. L. Sasso (Stevens) and Ms. N. Jacobs (Technion) for typing and retyping the lengthy manuscript, as well as to Ms. R. Prizgintas who prepared many of the figures. We also thanks Brenda B. Griffing for her thorough editing of the manuscript, which contributed greatly to the final quality of the book.

This book would not have been possible without the help and support of Professor J. A. Biesenberger and Provost L. Z. Pollara (Stevens) and Professors W. Resnick, S. Sideman, and A. Ram (Technion).

Finally, we thank our families, whose understanding, support, and patience helped us throughout this work.

ZEHEV TADMOR COSTAS G. GOGOS

Haifa, Israel Hoboken, New Jersey March 1978

## Contents

#### 1 History, Structural Formulation of the Field Through Elementary Steps, and Future Perspectives, 1

- **1.1** Historical Notes, 1
- 1.2 Current Polymer Processing Practice, 7
- **1.3** Analysis of Polymer Processing in Terms of Elementary Steps and Shaping Methods, 14
- **1.4** Future Perspectives: From Polymer Processing to Macromolecular Engineering, 18

#### 2 The Balance Equations and Newtonian Fluid Dynamics, 25

- 2.1 Introduction, 25
- **2.2** The Balance Equations, 26
- 2.3 Reynolds Transport Theorem, 26
- 2.4 The Macroscopic Mass Balance and the Equation of Continuity, 28
- **2.5** The Macroscopic Linear Momentum Balance and the Equation of Motion, 32
- 2.6 The Stress Tensor, 37
- 2.7 The Rate of Strain Tensor, 40
- 2.8 Newtonian Fluids, 43
- **2.9** The Macroscopic Energy Balance and the Bernoulli and Thermal Energy Equations, 54
- 2.10 Mass Transport in Binary Mixtures and the Diffusion Equation, 60
- 2.11 Mathematical Modeling, Common Boundary Conditions, Common Simplifying Assumptions, and the Lubrication Approximation, 60

#### 3 Polymer Rheology and Non-Newtonian Fluid Mechanics, 79

- **3.1** Rheological Behavior, Rheometry, and Rheological Material Functions of Polymer Melts, 80
- **3.2** Experimental Determination of the Viscosity and Normal Stress Difference Coefficients, 94
- 3.3 Polymer Melt Constitutive Equations Based on Continuum Mechanics, 100
- 3.4 Polymer Melt Constitutive Equations Based on Molecular Theories, 122

- 4 The Handling and Transporting of Polymer Particulate Solids, 144
  - 4.1 Some Unique Properties of Particulate Solids, 145
  - 4.2 Agglomeration, 150
  - **4.3** Pressure Distribution in Bins and Hoppers, 150
  - 4.4 Flow and Flow Instabilities in Hoppers, 152
  - 4.5 Compaction, 154
  - 4.6 Flow in Closed Conduits, 157
  - 4.7 Mechanical Displacement Flow, 157
  - 4.8 Steady Mechanical Displacement Flow Aided by Drag, 159
  - 4.9 Steady Drag-induced Flow in Straight Channels, 162
  - 4.10 The Discrete Element Method, 165

#### 5 Melting, 178

- 5.1 Classification and Discussion of Melting Mechanisms, 179
- 5.2 Geometry, Boundary Conditions, and Physical Properties in Melting, 184
- **5.3** Conduction Melting without Melt Removal, 186
- 5.4 Moving Heat Sources, 193
- 5.5 Sintering, 199
- 5.6 Conduction Melting with Forced Melt Removal, 201
- **5.7** Drag-induced Melt Removal, 202
- 5.8 Pressure-induced Melt Removal, 216
- 5.9 Deformation Melting, 219

#### 6 Pressurization and Pumping, 235

- 6.1 Classification of Pressurization Methods, 236
- 6.2 Synthesis of Pumping Machines from Basic Principles, 237
- 6.3 The Single Screw Extruder Pump, 247
- 6.4 Knife and Roll Coating, Calenders, and Roll Mills, 259
- 6.5 The Normal Stress Pump, 272
- 6.6 The Co-rotating Disk Pump, 278
- 6.7 Positive Displacement Pumps, 285
- **6.8** Twin Screw Extruder Pumps, 298

#### 7 Mixing, 322

- 7.1 Basic Concepts and Mixing Mechanisms, 322
- **7.2** Mixing Equipment and Operations of Multicomponent and Multiphase Systems, 354
- 7.3 Distribution Functions, 357
- 7.4 Characterization of Mixtures, 378
- 7.5 Computational Analysis, 391

#### 8 Devolatilization, 409

- 8.1 Introduction, 409
- **8.2** Devolatilization Equipment, 411
- 8.3 Devolatilization Mechanisms, 413

- 8.4 Thermodynamic Considerations of Devolatilization, 416
- 8.5 Diffusivity of Low Molecular Weight Components in Molten Polymers, 420
- **8.6** Boiling Phenomena: Nucleation, 422
- 8.7 Boiling–Foaming Mechanisms of Polymeric Melts, 424
- 8.8 Ultrasound-enhanced Devolatilization, 427
- 8.9 Bubble Growth, 428
- 8.10 Bubble Dynamics and Mass Transfer in Shear Flow, 430
- **8.11** Scanning Electron Microscopy Studies of Polymer Melt Devolatilization, 433

#### 9 Single Rotor Machines, 447

- 9.1 Modeling of Processing Machines Using Elementary Steps, 447
- 9.2 The Single Screw Melt Extrusion Process, 448
- 9.3 The Single Screw Plasticating Extrusion Process, 473
- 9.4 The Co-rotating Disk Plasticating Processor, 506

#### 10 Twin Screw and Twin Rotor Processing Equipment, 523

- 10.1 Types of Twin Screw and Twin Rotor–based Machines, 525
- 10.2 Counterrotating Twin Screw and Twin Rotor Machines, 533
- 10.3 Co-rotating, Fully Intermeshing Twin Screw Extruders, 572

#### 11 Reactive Polymer Processing and Compounding, 603

- **11.1** Classes of Polymer Chain Modification Reactions, Carried out in Reactive Polymer Processing Equipment, 604
- **11.2** Reactor Classification, 611
- **11.3** Mixing Considerations in Multicomponent Miscible Reactive Polymer Processing Systems, 623
- **11.4** Reactive Processing of Multicomponent Immiscible and Compatibilized Immiscible Polymer Systems, 632
- 11.5 Polymer Compounding, 635

#### 12 Die Forming, 677

- 12.1 Capillary Flow, 680
- 12.2 Elastic Effects in Capillary Flows, 689
- **12.3** Sheet Forming and Film Casting, 705
- 12.4 Tube, Blown Film, and Parison Forming, 720
- 12.5 Wire Coating, 727
- 12.6 Profile Extrusion, 731

#### 13 Molding, 753

- 13.1 Injection Molding, 753
- 13.2 Reactive Injection Molding, 798
- 13.3 Compression Molding, 811

#### xvi CONTENTS

#### 14 Stretch Shaping, 824

- 14.1 Fiber Spinning, 824
- **14.2** Film Blowing, 836
- **14.3** Blow Molding, 841

#### 15 Calendering, 865

- **15.1** The Calendering Process, 865
- 15.2 Mathematical Modeling of Calendering, 867
- **15.3** Analysis of Calendering Using FEM, 873

## Appendix ARheological and Thermophysical Properties of Polymers, 887Appendix BConversion Tables to the International System of Units (SI), 914

Appendix C Notation, 918

Author Index, 929 Subject Index, 944