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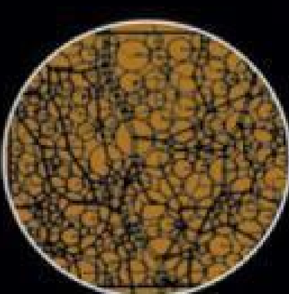

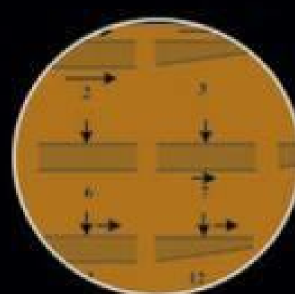

PRINCIPLES OF

POLYMER PROCESSING

SECOND EDITION

ZEHEV TADMOR • COSTAS G. GOGOS

PRINCIPLES OF POLYMER PROCESSING

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Second Edition

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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).

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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.

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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 machines, 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 7.7, 9, and 10. *For a two-semester course: in the first semester*, Chapters 1, 5, and 6; 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, $\boldsymbol{\pi} = P\boldsymbol{\delta} + \boldsymbol{\tau}$, where $\boldsymbol{\pi}$ is the total stress tensor, P is the pressure, and $\boldsymbol{\tau}$ is that part of the stress tensor that vanishes when no flow occurs; both P and τ_{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 η_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.

*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.

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