Rheology and Processing of Polymeric Materials

VOLUME 2 POLYMER PROCESSING

Chang Dae Han

RHEOLOGY AND PROCESSING OF POLYMERIC MATERIALS

Volume 2
Polymer Processing

Chang Dae Han

Department of Polymer Engineering
The University of Akron

江苏工业学院图书馆
藏书章

OXFORD
UNIVERSITY PRESS

2007

OXFORD
UNIVERSITY PRESS

Oxford University Press, Inc., publishes works that further
Oxford University's objective of excellence in research, scholarship,
and education.

Oxford New York
Auckland Cape Town Dar es Salaam Delhi Hong Kong Karachi
Kuala Lumpur Madrid Melbourne Mexico City Nairobi
New Delhi Shanghai Taipei Toronto

With offices in
Argentina Austria Brazil Chile Czech Republic France Greece
Guatemala Hungary Italy Japan Poland Portugal Singapore
South Korea Switzerland Thailand Turkey Ukraine Vietnam

Copyright © 2007 by Oxford University Press, Inc.

Published by Oxford University Press, Inc.
198 Madison Avenue, New York, New York 10016
www.oup.com

Oxford is a registered trademark of Oxford University Press

All rights reserved. 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, or otherwise,
without the prior permission of Oxford University Press.

Library of Congress Cataloging-in-Publication Data
Han, Chang Dae.
Rheology and processing of polymeric materials/Chang Dae Han.
v. cm.
Contents: v. 1 Polymer rheology—; v. 2 Polymer processing—
Includes bibliographical references and index.
ISBN: 978-0-19-518782-3 (vol. 1); 978-0-19-518783-0 (vol. 2)
1. Polymers–Rheology. 1. Title.

QC189.5.H36 2006
620.1′920423—dc22 2005036608

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

Preface

In the past, a number of textbooks and research monographs dealing with polymer rheology and polymer processing have been published. In the books that dealt with rheology, the authors, with a few exceptions, put emphasis on the continuum description of homogeneous polymeric fluids, while many industrially important polymeric fluids are heterogeneous, multicomponent, and/or multiphase in nature. The continuum theory, though very useful in many instances, cannot describe the effects of molecular parameters on the rheological behavior of polymeric fluids. On the other hand, the currently held molecular theory deals almost exclusively with homogenous polymeric fluids, while there are many industrially important polymeric fluids (e.g., block copolymers, liquid-crystalline polymers, and thermoplastic polyurethanes) that are composed of more than one component exhibiting complex morphologies during flow.

In the books that dealt with polymer processing, most of the authors placed emphasis on showing how to solve the equations of momentum and heat transport during the flow of homogeneous thermoplastic polymers in a relatively simple flow geometry. In industrial polymer processing operations, more often than not, multicomponent and/or multiphase heterogeneous polymeric materials are used. Such materials include microphase-separated block copolymers, liquid-crystalline polymers having mesophase, immiscible polymer blends, highly filled polymers, organoclay nanocomposites, and thermoplastic foams. Thus an understanding of the rheology of homogeneous (neat) thermoplastic polymers is of little help to control various processing operations of heterogeneous polymeric materials. For this, one must understand the rheological behavior of each of those heterogeneous polymeric materials.

There is another very important class of polymeric materials, which are referred to as thermosets. Such materials have been used for the past several decades for the fabrication of various products. Processing of thermosets requires an understanding of the rheological behavior during processing, during which low-molecular-weight oligomers (e.g., unsaturated polyester, urethanes, epoxy resins) having the molecular

weight of the order of a few thousands undergo chemical reactions ultimately giving rise to cross-linked networks. Thus, a better understanding of chemorheology is vitally important to control the processing of thermosets. There are some books that dealt with the chemorheology of thermosets, or processing of some thermosets. But, very few, if any, dealt with the processing of thermosets with chemorheology in a systematic fashion.

The preceding observations have motivated me to prepare this two-volume research monograph. Volume 1 aims to present the recent developments in polymer rheology placing emphasis on the rheological behavior of structured polymeric fluids. In so doing, I first present the fundamental principles of the rheology of polymeric fluids: (1) the kinematics and stresses of deformable bodies, (2) the continuum theory for the viscoelasticity of flexible homogeneous polymeric liquids, (3) the molecular theory for the viscoelasticity of flexible homogeneous polymeric liquids, and (4) experimental methods for measurement of the rheological properties of polymeric liquids. The materials presented are intended to set a stage for the subsequent chapters by introducing the basic concepts and principles of rheology, from both phenomenological and molecular perspectives, of structurally simple flexible and homogeneous polymeric liquids.

Next, I present the rheological behavior of various polymeric materials. Since there are so many polymeric materials, I had to make a conscious, though somewhat arbitrary, decision on the selection of the polymeric materials to be covered in this volume. Admittedly, the selection has been made on the basis of my research activities during the past three decades, since I am quite familiar with the subjects covered. Specifically, the various polymeric materials considered in Volume 1 range from rheologically simple, flexible thermoplastic homopolymers to rheologically complex polymeric materials including (1) block copolymers, (2) liquid-crystalline polymers, (3) thermoplastic polyurethanes, (4) immiscible polymer blends, (5) particulate-filled polymers, organoclay nanocomposites, and fiber-reinforced thermoplastic composites, (6) molten polymers with solubilized gaseous component. Also, chemorheology is included in Volume 1.

Volume 2 aims to present the fundamental principles related to polymer processing operations. In presenting the materials in this volume, again, the objective is not to provide the recipes that necessarily guarantee better product quality. Rather, I put emphasis on presenting fundamental approaches to effectively analyze processing problems. Polymer processing operations require combined knowledge of polymer rheology, polymer solution thermodynamics, mass transfer, heat transfer, and equipment design. Specifically, in Volume 2, I present the fundamental aspects of several processing operations (plasticating single-screw extrusion, wire-coating extrusion, fiber spinning, tabular film blowing, injection molding, coextrusion, and foam extrusion) of thermoplastic polymers and three processing operations (reaction injection molding, pultrusion, and compression molding) of thermosets. In Volume 2, I have reused some materials presented in Volume 1.

In the preparation of these volumes I have tried to present the fundamental concepts and/or principles associated with the rheology and processing of the various polymeric materials selected and I have tried to avoid presenting technological recipes. In so doing, I have pointed out an urgent need for further experimental and theoretical investigations. I sincerely hope that the materials in this monograph will not only encourage further experimental investigations but also stimulate future development of theory. I wish

试读结束：需要全本请在线购买： www.ertongbook.com

to point out that I have tried not to cite articles appearing in conference proceedings and patents unless absolutely essential, because they did not go through rigorous peer review processes.

Much of the material presented in this monograph is based on my research activities with very capable graduate students at Polytechnic University from 1967 to 1992 and at the University of Akron from 1993 to 2005. Without their participation and dedication to the various research projects that I initiated, the completion of this monograph would not have been possible. I would like to acknowledge with gratitude that Professor Jin Kon Kim at Pohang University of Science and Technology in the Republic of Korea read the draft of Chapters 4, 6, 7, and 8 of Volume 1 and made very valuable comments and suggestions for improvement. Professor Ralph H. Colby at Pennsylvania State University read the draft of Chapter 7 of Volume 1 and made helpful comments and suggestions, for which I am very grateful. Professor Anthony J. McHugh at Lehigh University read the draft of Chapter 6 of Volume 2 and made many useful comments, for which I am very grateful. It is my special privilege to acknowledge wonderful collaboration I had with Professor Takeji Hashimoto at Kyoto University in Japan for the past 18 years on phase transitions and phase behavior of block copolymers. The collaboration has enabled me to add luster to Chapter 8 of Volume 1. The collaboration was very genuine and highly professional. Such a long collaboration was made possible by mutual respect and admiration.

Chang Dae Han
The University of Akron

Akron, Ohio
June, 2006

Contents

Remarks on Volume 2, xvii

Part I

Processing of Thermoplastic Polymers

1 Flow of Polymeric Liquid in Complex Geometry, 3

1.1 Introduction, 3
1.2 Flow through a Rectangular Channel, 4
1.2.1 Flow Patterns in a Rectangular Channel, 4
1.2.2 Extrudate Swell from a Rectangular Channel, 6
1.2.3 Analysis of Flow through a Rectangular Channel, 6
1.3 Flow in the Entrance Region of a Slit Die, 20
1.4 Flow through a Converging or Tapered Channel, 25
1.5 Exit Region Flow, 32
1.6 Flow through a Channel Having Small Side Holes or Slots, 35
1.7 Analysis of Flow in a Coat-Hanger Die, 40
1.7.1 Analysis of Flow in the Manifold, 42
1.7.2 Analysis of Flow in the Coat-Hanger Section, 45
1.8 Summary, 48
Problems, 49
Notes, 53
References, 54

Remarks on Volume 2

This volume consists of two parts. Part I has ten chapters presenting fundamental principles associated with the processing of thermoplastic polymers. A thermoplastic polymer, when heated, is transformed into a liquid, which can then readily be transported through a shaping device (e.g., extrusion die or mold cavity), and then cooled down to a solid, rendering specific mechanical/physical properties. Barring thermal degradation and/or chemical reaction, a thermoplastic polymer can be regenerated by heating and cooling repeatedly. Since the processing of thermoplastic polymers in the molten state invariably involves flow, a successful processing operation requires a good understanding of their rheological behavior, which we have discussed in Part II of Volume 1. Since there are so many different polymer processing operations practiced in industry, I had to make a conscious, though somewhat arbitrary, decision on the selection of the polymer processing operations to be covered in this volume. Admittedly, the selection has been made on the basis of my research activities during the past three decades.

Specifically, Chapter 1 presents the flow of polymeric liquids in complex geometries. In this chapter, we consider the flow of a viscoelastic fluid through a rectangular channel, through a converging channel (entrance flow), and through a channel having small side holes. Chapter 2 presents plasticating single-screw extrusion. This chapter describes the principles associated with the design of screws for single-screw extruders. Chapter 3 presents the morphology evolution in immiscible polymer blends during compounding. Chapter 4 presents the compatibilization of two immiscible homopolymers, in which the principles associated with the selection of a block copolymer to compatibilize a pair of immiscible homopolymers are presented. Chapter 5 presents wire coating extrusion, placing emphasis on the principles of die design. Chapter 6 presents fiber spinning, with a detailed discussion of high-speed melt spinning as reported in the 1980s and 1990s. Chapter 7 presents tubular film blowing, in which an analysis of tubular film blowing including extrudate swell region is discussed.

3.4 Stability of Co-Continuous Morphology during Compounding, 169
3.5 Summary, 174
Appendix: Theoretical Interpretation of Figure 3.34, 177
Notes, 179
References, 179

4 Compatibilization of Two Immiscible Homopolymers, 181

4.1 Introduction, 181
4.2 Experimental Observations of Compatibilization of Two Immiscible Homopolymers Using a Block Copolymer, 186
4.2.1 A/B/(A-*block*-B) Ternary Blends, 187
4.2.2 A/B/(A-*block*-C) Ternary Blends, 194
4.2.3 A/B/(C-*block*-D) Ternary Blends, 210
4.3 Reactive Compatibilization of Two Immiscible Polymers, 224
4.4 Summary, 229
Notes, 231
References, 232

5 Wire-Coating Extrusion, 235

5.1 Introduction, 235
5.2 Analysis of Wire-Coating Extrusion, 236
5.3 Experimental Observations, 245
5.4 Summary, 253
Problems, 255
Notes, 256
References, 256

6 Fiber Spinning, 257

6.1 Introduction, 257
6.2 Fiber Spinning Processes, 258
6.2.1 Melt Spinning Process, 258
6.2.2 Wet Spinning Process, 260
6.2.3 Dry Spinning Process, 262
6.2.4 Other Fiber Spinning Processes, 263
6.3 High-Speed Melt Spinning, 268
6.3.1 Experimental Observations of High-Speed Melt Spinning, 269
6.3.2 Modeling of High-Speed Melt Spinning, 273
6.3.3 Model Prediction and Comparison with Experiment, 284
6.4 Spinnability, 294
6.5 Summary, 296
Problems, 297
Notes, 300
References, 302

7 Tubular Film Blowing, 305

7.1 Introduction, 305
7.2 Processing Characteristics of Tubular Film Blowing, 307
7.2.1 Kinematics and Stress Field in Tubular Film Blowing, 308
7.2.2 Tensile Stresses at the Freeze Line and Processing–Property Relationships in Tubular Film Blowing, 311
7.3 Analysis of Tubular Film Blowing Including Extrudate Swell, 317
7.3.1 Force Balance Equation, 319
7.3.2 Energy Balance Equation, 322
7.3.3 Viscoelastic Constitutive Equation, 323
7.3.4 Analysis of Tubular Film Blowing in the Extrudate Swell Region, 326
7.3.5 Analysis of Tubular Film Blowing in the Stretching Region, 329
7.3.6 Model Predictions and Comparison with Experiment, 330
7.4 Tubular Film Blowability, 341
7.5 Summary, 346
Problems, 348
Notes, 348
References, 349

8 Injection Molding, 351

8.1 Introduction, 351
8.2 Flow of Molten Polymer through a Runner, 354
8.3 Injection Molding of Amorphous Polymers, 358
8.3.1 Flow Patterns during Mold Filling, 358
8.3.2 Governing System Equations for Mold Filling of Amorphous Polymers, 363
8.3.3 Molecular Orientation during Mold Filling and Residual Stress in Injection Molded Articles, 366
8.4 Injection Molding of Semicrystalline Polymers, 370
8.4.1 Crystallization during Injection Molding, 370
8.4.2 Governing System Equations for Injection Molding of Semicrystalline Polymers, 372
8.4.3 Morphology of Injected-Molded Semicrystalline Polymers, 373
8.5 Summary, 375
Notes, 376
References, 376

9 Coextrusion, 379

9.1 Introduction, 379
9.2 Coextrusion Die Systems, 382
9.2.1 Feedblock Die System for Flat-Film or Sheet Coextrusion, 382
9.2.2 Multimanifold Die System for Flat-Film or Sheet Coextrusion, 383

9.2.3 Feedblock Die System for Blown-Film Coextrusion, 384
9.2.4 Rotating-Mandrel Die System for Blown-Film Coextrusion, 386
9.3 Polymer–Polymer Interdiffusion across the Initially Sharp and Flat Interface, 388
9.3.1 Polymer–Polymer Interdiffusion under Static Conditions, 389
9.3.2 Polymer–Polymer Interdiffusion in the Shear Flow Field, 400
9.4 Nonisothermal Coextrusion, 407
9.5 Summary, 417
Appendix: Derivation of Equation (9.36), 418
Problems, 419
Notes, 421
References, 421

10 Foam Extrusion, 424

10.1 Introduction, 424
10.2 Solubility and Diffusivity of Gases in a Molten Polymer, 425
10.2.1 Solubility of Gases in a Molten Polymer, 425
10.2.2 Diffusivity of Gases in a Molten Polymer, 433
10.3 Bubble Nucleation in Polymeric Liquids, 443
10.3.1 Experimental Observations of Bubble Nucleation, 446
10.3.2 Theoretical Considerations of Bubble Nucleation in Polymer Solutions, 462
10.4 Foam Extrusion, 468
10.4.1 Processing–Property–Morphology Relationships in Profile Foam Extrusion, 469
10.4.2 Processing–Property Relationships in Sheet Foam Extrusion, 482
10.5 Summary, 487
Problems, 488
Notes, 489
References, 489

Part II

Processing of Thermosets

11 Reaction Injection Molding, 495

11.1 Introduction, 495
11.2 Analysis of Reaction Injection Molding, 497
11.2.1 Main Flow, 498
11.2.2 Front Flow, 501

试读结束：需要全本请在线购买： www.ertongbook.com

11.2.3 Cure Stage, 502
11.2.4 Chemorheological Model, 503
11.3 Conversion and Temperature Profiles during Mold Filling, 503
11.4 Summary, 512
Problems, 513
Notes, 514
References, 515

12 Pultrusion of Thermoset/Fiber Composites, 517

12.1 Introduction, 517
12.2 Effect of Mixed Initiators on the Cure Kinetics of Unsaturated Polyester, 519
12.3 Cure Kinetics of Unsaturated Polyester/Fiber Composite, 525
12.4 Analysis of the Pultrusion of Thermoset/Fiber Composite, 528
12.4.1 General System Equations, 528
12.4.2 System Equations with an Empirical Kinetic Model, 530
12.4.3 System Equations with a Mechanistic Kinetic Model, 531
12.5 Conversion and Temperature Profiles in a Pultrusion Die, 531
12.6 Summary, 540
Problems, 541
References, 542

13 Compression Molding of Thermoset/Fiber Composites, 544

13.1 Introduction, 544
13.2 Thickening Behavior of Unsaturated Polyester, 547
13.3 Effect of Pressure on the Curing of Unsaturated Polyester, 552
13.4 Analysis of Compression Molding of Unsaturated Polyester/Glass Fiber Composite, 561
13.5 Time Evolution of Temperature during Compression Molding of Unsaturated Polyester/Glass Fiber Composite, 564
13.6 Summary, 568
References, 569

Author Index, 571

Subject Index, 578

Part I

Processing of Thermoplastic Polymers

1

Flow of Polymeric Liquid in Complex Geometry

1.1 Introduction

The flow geometry encountered in many polymer processing operations of industrial importance is often far more complex than that in cylindrical or slit dies. As will be shown in the following chapters, the industry manufactures polymeric products using very complex flow geometries. For instance, the fiber industry produces "shaped fibers," which have cross sections that are noncircular. What is most intriguing in the production of shaped fibers is that a desired fiber shape is often produced by spinneret holes whose cross-sectional shape is quite different from that of the final fiber produced. Hence, an important question may be raised as to how one can determine, from a sound theoretical basis, the cross-sectional shape of spinneret holes that will produce a fiber with a desired cross-sectional shape. In extrusion and injection molding, a polymeric liquid invariably passes through a large cross section before entering into a small cross section, and such a flow is referred to as "entrance flow." The entrance flow of polymeric liquids, due to their viscoelastic nature, is quite different from that of Newtonian liquids. Similarly, the flow behavior of viscoelastic polymeric liquids near the exit of a die, commonly referred to as "exit flow," is quite different from that of Newtonian liquids. A better understanding of the unique characteristics of both entrance and exit flows of viscoelastic polymeric fluids is essential for successful design of extrusion dies and molds, as well as to solve difficult technical problems related to a particular processing operation.

Before presenting specific polymer processing operations in following chapters, in this chapter we consider the flow of polymeric liquids through complex geometry: (1) fully developed flow through a rectangular channel with uniform channel depth; (2) fully developed flow through a rectangular channel with a moving channel wall; (3) flow through a rectangular channel with varying channel depth; (4) flow in the entrance region of a rectangular die having constant cross section; (5) flow through

a tapered die; (6) flow in the exit region of a cylindrical or slit die; (7) flow through a slit die having side holes; and (8) flow through a coat-hanger die. These flow geometries are encountered in many polymer processing operations. The primary objective of this chapter is to present the unique flow characteristics of viscoelastic polymeric liquids in complex geometries of practical industrial importance.

1.2 Flow through a Rectangular Channel

The flow of polymeric liquids through a rectangular channel having constant cross section or varying cross section is much more complex than the flow through a capillary or slit die considered in Chapter 5 of Volume 1. The complexity arises from both the viscoelastic nature of polymeric fluids and the two-dimensional nature of a rectangular channel. In this section, we present some unique features of flow of polymeric liquids through a rectangular channel.

1.2.1 Flow Patterns in a Rectangular Channel

In the past, using perturbation methods, some investigators (Ericksen 1956; Green and Rivlin 1956; Langlois and Rivlin 1963; Rivlin 1964; Wheeler and Wissler 1966) predicted transverse circulating (secondary) flow patterns in each of the four quadrants of the rectangle, as schematically shown in Figure 1.1, when a viscoelastic fluid flows through a rectangular channel. For instance, using the Rivlin–Ericksen constitutive equation[1] (Rivlin and Ericksen 1964), Langlois and Rivlin (1963) found that it required a fourth-order fluid to yield secondary flow, with the second-order fluid only affecting the pressure field and the third-order fluid only distorting the normal Newtonian velocity profile. To obtain a streamline pattern of secondary flow in a rectangular channel, one must solve all three components of the equations of motion, whereas in the absence of secondary flow, only the axial component of the equations of motion must

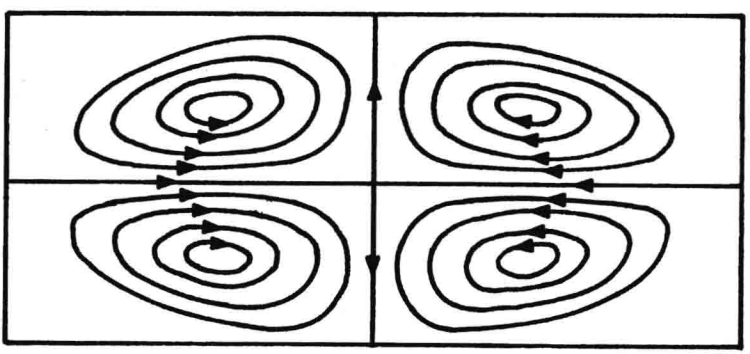

Figure 1.1 Schematic showing secondary flow of viscoelastic fluids in a duct of rectangular cross section.

be solved. The usually complex form of the constitutive equations for viscoelastic fluids complicates the solution of the equations of motion when secondary flow is to be considered. Wheeler and Wissler (1966) solved the equations of motion numerically for flow through a square duct by considering the Reiner–Rivlin constitutive equation (Reiner 1945; Rivlin 1948), and obtained the streamlines for the secondary flow. They found that the transverse components of velocity are about 1% of the axial component of velocity when the Reynolds number is as large as 100, and that the axial velocity profiles computed for a Reynolds number of 26.38 are virtually indistinguishable from those computed when secondary flow was neglected. It should be mentioned that typical values of the Reynolds number in polymer melt flow, owing to very high viscosities, lie below 0.001.

The experimental evidence is mixed. Some investigators (Giesekus 1965; Semjonow 1965) report that secondary flows have been observed, and others (Han 1976; Wheeler and Wissler 1965) report that they have not seen evidence of secondary flows. Figure 1.2 gives a micrograph of the cross section of an extrudate, which was obtained in the flow of a blend of polypropylene (PP) and polystyrene (PS) through a rectangular channel having an aspect ratio of 2. In this figure, the dark areas represent the PS phase and the bright areas represent the PP phase, obtained by etching out the PS phase with the aid of xylene as solvent before the photograph was taken using an optical microscope (Han 1976). Well-characterized rectilinear flow patterns are observed in Figure 1.2, which is at variance with some of the theoretical predictions depicted schematically in Figure 1.1. We can thus conclude that the occurrence of secondary flow is not a general phenomenon that would occur in the flow of every viscoelastic fluid in a rectangular channel. The apparent absence of secondary flow patterns in the rectangular channel having an aspect ratio of 2, shown in Figure 1.2, may be attributable to the extremely slow motion that is characteristic of polymer melt flow having a very low Reynolds number (i.e., below 0.001). Figure 1.3 gives a micrograph of the cross section of an extrudate, which was obtained in the flow of a blend of PP and PS through a rectangular channel having an aspect ratio of 6. It is of interest to observe in this figure that the flow patterns are only rectilinear at the region that corresponds to an aspect ratio of about 4, and different flow patterns set in at a region near the edge of the long side of the cross section. At present, the physical origin of the flow patterns given in Figure 1.3 is not clear.

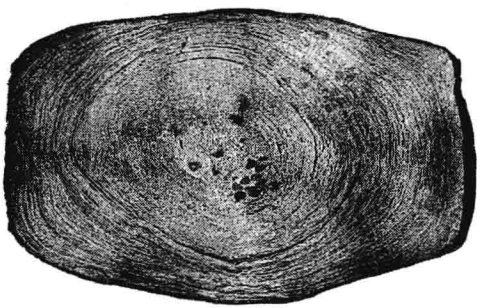

Figure 1.2 Micrograph of the extrudate cross section showing the flow patterns of a blend of polypropylene (the bright areas) and polystyrene (the dark areas) that was extruded through a rectangular channel having an aspect ratio of 2. (Reprinted from Han, *Rheology in Polymer Processing*, Chapter 6. Copyright © 1976, with permission from Elsevier.)

试读结束：需要全本请在线购买： www.ertongbook.com