POLYMER AND COMPOSITE RHEOLOGY

Second Edition, Revised and Expanded

RAKESH K. GUPTA

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MARCEL DEKKER

MARCEL DEKKER, INC. NEW YORK • BASEL

The first edition of this book was published as *Polymer Rheology*, by L. E. Nielsen, 1977.

ISBN: 0-8247-9922-4

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.

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

PRINTED IN THE UNITED STATES OF AMERICA

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To my wife, Gunjan

BHARYA MOOLAM GRIHASTHASYA
BHARYA MOOLAM SUKHASYA CHA
BHARYA DHARMA FALA VAPTYAI
BHARYA SANTAN BRIDHYAYE

A wife is the quintessence of a home. She is the source of happiness and of everything that is good in life and the future of children.

Skanda Puran (Hindu scripture)

Preface

Several outstanding books on rheology have appeared since *Polymer Rheology* was published in 1977. This book remains unique in the simple and straightforward manner in which it introduces the concepts of rheology and the observed flow behavior of polymers to the student as well as to the practicing engineer. The first edition emphasized general principles and their practical implications rather than theoretical constructs. This practical, industrial orientation has been maintained in the second edition, and the book has been updated to include developments of the past quarter century. The book has also been expanded to give essentially equal coverage to single-phase and multiphase systems. A knowledge of chemorheology is often essential for understanding the processing of (thermosetting) polymer-matrix composites; discussion of reactive polymers has been included for this reason. Few, if any, of the currently available rheology books treat as wide a range of topics as are covered in the second edition.

The specific aims of the second edition are: (i) to present the general behavior of polymer melts, polymer solutions, suspensions, emulsions, foams, granular powders, and polymer composites during flow, together with physical explanations of the observations; (ii) to provide information on the effects of the different factors that influence flow behavior, (iii) to describe and recommend methods of measuring, calculating, or theoretically estimating flow properties of polymers and polymeric composites; and (iv) to direct readers to the appropriate technical literature for further study and consideration of current research issues. All this is done using the minimum amount of mathematics—not an easy undertaking given the universally accepted complexity of the subject.

In pursuit of these goals and after an introductory chapter, standard techniques for making rheological measurements are presented in Chapter 2. Thereafter, each chapter begins with an explanation of the practical and theoretical importance of the topic being examined. This is followed by a presentation of typical data and how these data might be represented in graphical form and also by means of empirical equations. The body of each chapter considers the use of any specialized instruments, data reduction when employing the most relevant rheological techniques, and the influence of the various material, geometrical, and processing variables on the property of interest, and it provides physical explanations for the observations. There is discussion, with minimum mathematics, of available theoretical models and their ability to both predict observed behavior and quantitatively represent the data. Each chapter also elaborates on work in progress and research needs for the future. Finally, there is a listing of complete citations to the technical literature. The book concludes with a short chapter on the enigma of melt fracture, an annoying instability of rheological origin, that limits production rates during polymer processing operations.

This is a practical book aimed at both practicing engineers and graduate students. It is a storehouse of information but with an emphasis on science rather than on technology. No specific background has been assumed of the reader, and it is hoped that the book will be as useful to a chemist or an engineer who wants to learn about rheology owing to the requirements of a new assignment as it will be to a student engaged in advanced research. The choice of topics and the depth of coverage have been dictated as much by my own research interests as by my perception of the importance of the subject at hand. Time will tell whether these choices have been judicious ones or not.

I would like to thank Professor Hota V. S. GangaRao, my colleague at West Virginia University, for having introduced me to the fascinating field of polymer composites and also for involving me in research on a variety of topics related to the processing and use of composite materials. Professor Raj Chhabra of the Indian Institute of Technology at Kanpur read the entire manuscript, as did Dr. Deepak Doraiswamy of the DuPont Company (also an Adjunct Professor in the Department of Chemical Engineering at West Virginia University); both of them corrected errors, made suggestions for improvement, and directed me to appropriate work in the literature. Deepak, in addition, coauthored Chapter 10 on solid-in-liquid suspensions. I am grateful to them both for their constant help and encouragement. The book also benefited from the several suggestions of Professor Jan Mewis and Dr. Kurt Wissbrun, who helped with and read Chapter 8 on the rheology of liquid crystalline polymers. Parts of the book were written during 1998/99 while I was on sabbatical leave as a Visiting Research Scientist at DuPont's Washington Works in Parkersburg, West Virginia; I thank Dr. Robert Cook for making my stay there possible, and I thank all my DuPont associates for their hospitality. In the course of the three years that it took me to complete

the writing of this book, I badgered innumerable friends and professional colleagues for reprints, preprints, and thesis copies. Their courtesy in acceding to my frantic requests made my work and the work of the ever-helpful interlibrary loan personnel in our Evansdale Library so much easier. I also wish to thank Ms. Linda Rogers, who typed all the equations for me and helped me incorporate all the revisions in the manuscript.

I did not know the late Larry Nielsen personally even though I worked briefly for the Monsanto Company. I feel honored to have been asked to revise and expand *Polymer Rheology*. I have made a sincere effort to maintain the character of the first edition, and I have attempted to retain as much as possible of the material that appeared in that edition. I hope that the readers will recognize this book to be as much Nielsen's as mine.

Rakesh K. Gupta

Contents

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Introduction to Polymer Rheology

I. RHEOLOGY

Rheology can be defined as the science of the flow and deformation of matter. For low-molecular-weight fluids, the study of rheology involves the measurement of viscosity. For such fluids, the viscosity depends primarily upon the temperature and hydrostatic pressure. However, the rheology of high-molecular-weight liquids, whether neat or filled, is much more complex because polymeric fluids show nonideal behavior. In addition to having complex shear viscosity behavior, polymeric liquids show elastic properties, such as unequal normal stresses in shear and a prominent tensile viscosity in extension. All these rheological properties depend upon the rate of deformation, the molecular weight and structure of the polymer, and the concentration of various additives and fillers, as well as upon the temperature. In addition, even at a constant rate of deformation, stresses are found to depend on time.

The subject of rheology is very important for both polymers and polymeric composites. This is true for two reasons. Firstly, flow is involved in the processing and fabrication of such materials in order to make useful objects. Thus, fluid rheology is relevant to polymer processing and determines stress levels in operations such as extrusion, calendering, fiber spinning, and film blowing. Similarly, rheology influences residual stresses, cycle times, and void content in composite processing operations such as bag molding, compression molding, and injection molding. Clearly, a quantitative description of polymer and composite rheology is essential for developing models of the various polymer processing operations; these models can be employed for process optimization and for predicting the onset of flow instabilities. In the use of polymers, though, it is generally the