Rheology and Processing of Polymeric Materials

VOLUME I POLYMER RHEOLOGY

Chang Dae Han
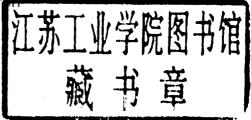
RHEOLOGY AND PROCESSING OF POLYMERIC MATERIALS

Volume 1
Polymer Rheology

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Remarks on Volume 1

This volume consists of two parts. Part I describes the fundamental principles of the rheology of polymeric fluids: (1) the kinematics and stresses of deformable bodies, (2) the continuum theories for the viscoelasticity of flexible homogeneous polymeric liquids, (3) the molecular theories for the viscoelasticity of flexible homogeneous polymeric liquids, and (4) experimental methods for measurement of the rheological properties of polymeric liquids. Part I is 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. Part II describes the rheology of various polymeric materials, ranging from flexible ordinary thermoplastic homopolymers to thermosets, namely, (1) homopolymers, (2) miscible polymer blends, (3) block copolymers, (4) liquid-crystalline polymers, (5) thermoplastic polyurethanes, (6) immiscible polymer blends, (7) particulate-filled polymers, organoclay nanocomposites, and fiber-reinforced thermoplastic composites, (8) molten polymers with solubilized gaseous component, and (9) thermosets. In presenting the materials in Part II, I have pointed out an urgent need for further experimental and theoretical investigations. I sincerely hope that the materials presented in Part II will not only encourage further experimental investigations, but also stimulate future development of theory.

C.D.H.

In Memory of My Parents

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 homogeneous 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 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, and (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 was not to provide the recipes that necessarily guarantee better product quality. Rather, I put emphasis on presenting fundamental approach 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 have presented the fundamental aspects of several processing operations (plasticating single-screw extrusion, wire coating extrusion, fiber spinning, tubular 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 presenting Volume 2, I have used some materials presented in Volume 1.

In the preparation of this monograph, 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 presented in this monograph will not

only encourage further experimental investigations but also stimulate future develop-
ment of theory. I wish 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
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and highly professional. Such a long collaboration was made possible by mutual respect
and admiration.

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