Polymer Rheology: Theory and Practice

Polymer Rheology: Theory and Practice

Yuri G. Yanovsky

Institute of Applied Mechanics,
Russian Academy of Sciences,
Moscow, Russia

SPRINGER-SCIENCE+BUSINESS MEDIA, B.V

First edition 1993

Originally published by Chapman & Hall in 1993
Softcover reprint of the hardcover 1st edition 1993

Typeset in 10/12pt Times by Interprint Ltd, Malta.

ISBN 978-94-010-4938-2

A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication data

Yanovsky, Yuri G.
Polymer rheology: theory and practice / Yuri G. Yanovsky.
p. cm.
Includes bibliographical references and index.
ISBN 978-94-010-4938-2 ISBN 978-94-011-2116-3 (eBook)
DOI 10.1007/978-94-011-2116-3
1. Polymers—Rheology. I. Title.
TA455.P58Y36 1993
620.1'920423—dc20 92-24454
CIP

Preface

The present book is devoted to a rapidly developing field of science which studies the behavior of viscoelastic materials under the influence of deformation—the rheology of polymers.

Rheology has long been treated as the theoretical foundation of polymer processing, and from this standpoint it is difficult to overestimate its importance in practice. Rheology plays an important role in developing our ideas on the nature of viscoelastic behavior in connection with the structural features of polymers and composites based on them. This expands the possibilities of employing rheological methods to characterize a variety of materials and greatly magnifies the interest in this field of research.

The rheological properties of polymer systems are studied experimentally, chiefly under conditions of shear and tensile strains. One explanation is that many aspects of polymer material processing are associated with the stretching of melts or a combination of shear and tensile strains.

In scientific investigations, either periodic or continuous conditions of shear deformation are employed. Each mode provides widespread information. In periodic deformation, most attention is generally given to conditions with low deformation amplitudes that do not alter the structure of the polymer system during an experiment (the region of linear deformation conditions). Here the viscoelastic parameters are generally determined with respect to the frequency. Continuous deformation involves considerable strains, and may be attended by significant reversible and irreversible changes in the structure of a polymer. Of major importance in these cases is the appraisal of the parameters characterizing both steady flow conditions in closed channels and conditions causing a loss of stability of the flow. The latter is manifest in the form of separation of the material from the channel walls, distortion of the shape of the streams flowing out of the channels, and even their disintegration into parts. A comparison of the parameters determined in low-amplitude periodic deformation and in continuous deformation enables one to compare the properties of polymer systems with changed and unchanged structures.

Analysis of the rheological properties of a system in tension can show the behavior of a polymer system within a very broad range of magnitude of the strains. The latter include regions of both linear and nonlinear deformation, and pre-ultimate values up to failure of a system. Here one can trace the relation between the viscoelastic, stress–strain, and relaxation characteristics.

The book contains sections concerning modern approaches to the theoretical, model, and experimental descriptions of the viscoelastic behavior of individual polymers, blends of polymers and copolymers, and filled compositions, and also to problems of the relation between the rheological, physicomechanical, and stress–strain properties. They are discussed, in particular, with a view to the achievements of Russian scientists during the last few years. The selected chapter topics reflect the various aspects of the scientific and applied problems of rheology.

Since the rheological behavior of individual fluid polymers has been analyzed in detail in many monographs, in the following these matters are discussed only superficially. The characteristics and properties of individual polymers and systems with a polymer matrix differing in chemical structure, molecular weight, inherent viscosity, melting point, etc., are not compared in detail where this is not required for elucidating the examples. The customary description of the specific results would be cumbersome and of only partial significance. (References to the original literature are an important source of specific information.)

I have also assumed that the reader is acquainted with the fundamentals of rheological science.

In view of the limited volume of the book, I have focused attention on the aspects that are most urgent today, namely the general laws of rheological behavior of composite systems, including blends of polymers, copolymers, and filled compositions. It is exactly the structural features of these objects that ensure their useful properties as materials intended for engineering purposes. Blends, copolymers, and composites are reinforced materials because many factors improving their resistance to failure are realized in them. Although it is difficult to describe the strengthening processes with the aid of a unified theory, one can follow the path of model ideas and construct theoretical substantiations of definite experimental facts.

The book consists of five chapters.

The first chapter is devoted mainly to discussing modern theoretical approaches and also methods for the analytical and numerical calculation of the viscoelastic characteristics of polymer systems (individual polymers, blends, filled polymers) under various deformation conditions. The appendices, which include prototypes of programs for imitation (method of Brownian dynamics) and geometric (method of finite elements) modeling and the test calculations, illustrate the possibilities of the approaches and methods being discussed and the expediency of employing them.

The second chapter deals with the deformation and relaxation behavior of flowing polymer systems within broad temperature and rate (or frequency) ranges covering various physical states of a system. Attention is given mainly to the critical parameters of deformation of fluid polymer systems. They include, on the one hand, the critical stresses and strains determining the conditions of the transitions of a polymer system from the fluid to the rubbery and leather-like states; and, on the other hand, the parameters characterizing the initial state of a system, i.e., those corresponding to the zero values of strains and rates of deformation, determined by the initial viscosity of the polymers. The relation between these two groups of limiting parameters is traced for the example of the dependence of service life on the initial viscosity of a system, its molecular weight and temperature.

The relation between the viscoelastic and relaxation properties measured in the linear and nonlinear deformation regions, on the one hand, and the stress–strain properties, on the other, is analyzed, as well as approaches to determining the relaxation characteristics in the nonlinear deformation region up to failure of a system.

The discussion of the viscoelastic properties of polymer blends and copolymers (Chapters 3 and 4) reveals the general principles of their rheological behavior. Polymer blending is in many ways similar to copolymerization as a way of achieving required properties by combining various chemical structures. The only difference is that blending reaches this goal physically, and not chemically (as for copolymerization).

The features of a number of typical blends exhibiting the properties of various classes of these compositions—compatible (miscible), limitedly compatible, and incompatible—are set out, as well as the features of random and block copolymers. The advantages of the model approach when describing the viscoelastic behavior of the above compositions within a wide range of changes in the composition of the components, their molecular weights, and the nature of the polymers, are discussed.

Copolymers are a structural form of macromolecules having a number of merits and shortcomings in comparison with mechanical mixtures. In some cases, copolymers (block copolymers in particular) exhibit unique possibilities that cannot be realized for other polymer materials. In others, they have no advantages.

The fifth chapter analyzes the rheological behavior of filled polymers using as examples both model systems, viz. filled linear flexible-chain polymers with a narrow molecular weight distribution including fillers of various activities, and samples of commercial filled polymers. The possible relation between the viscoelastic characteristics of filler polymer melts and parameters showing the physicomechanical and stress–strain properties of compositions based on them in the solid state is dealt with. Also discussed are the relaxation properties of filled polymers within a broad range of temperatures covering various physical states of a material—glassy, rubbery, fluid—and also the relaxation process due to the mobility of certain kinetic units.

In writing the book, I did everything possible to combine the individual problems instead of compiling it from separate treatises. At the same time, each chapter is relatively independent to avoid sending the reader frequently to other chapters.

Every book is intended for a definite circle of readers. I hope the present one will be helpful to specialists and scientists in the field of the mechanics of non-Newtonian liquids, and to specialists in the production and processing of polymer materials, both to those with experience and to beginners in these fields. Although the book has not been conceived as a textbook, it will nevertheless be an excellent aid for senior students and postgraduates who are interested in polymer rheology.

I wish to thank everyone who participated in discussing the separate chapters of the book. I am especially grateful to Professor Dr V.N. Pokrovsky, Dr E.K. Borisenkova, Dr V.U. Novikov and Dr Yu.K. Kokorin for their aid in working on the separate chapters, and also to G.L. Leib for his creative approach to the translation of sections of the book.

I also appreciate highly the support and collaboration by the Department of Mechanics and the Institute of Applied Mechanics of the Russian Academy of Sciences, and the aid of the technical staff.

Yuri Yanovsky

Contents