



INTRODUCTION TO

POLYMER VISCOELASTICITY

FOURTH EDITION

MONTGOMERY T. SHAW
WILLIAM J. MACKNIGHT

with website



WILEY

Introduction to Polymer Viscoelasticity

Introduction to Polymer Viscoelasticity

Fourth Edition

Montgomery T. Shaw
William J. MacKnight

WILEY

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*To A. V. Tobolsky, who first introduced us to the
mysteries of polymer viscoelasticity and to the art of
scientific research.*

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Preface to the Fourth Edition

For the last dozen years, the 3rd Edition of *Introduction to Polymer Viscoelasticity* has served well. During this time, the authors have received many constructive suggestions from students and instructors, including conflicting ones such as “simplify; it’s a bit too complicated” paired with “expand the theoretical parts.” In response to these and other comments, rather modest goals were set for the 4th Edition, namely

- *Correct all known errors reported by many kind readers.* Errors fall into two categories: (1) the usual grammatical slips and (2) serious mistakes such as equations with missing parts and poorly posed problems. Indeed, one problem was found that we could not solve, and obviously didn’t belong in an introductory text. It has been removed.
- *Provide more unanswered problems.* Since the birth of this text in the early 1970s, answers have been provided for many of the chapter-end problems. The reason for this is these problems typically review fundamental concepts, serving as additional solved examples. Some introduce new concepts. However, most instructors want unsolved problems that can be assigned as homework, adapted for active learning exercises and short projects, or used for tests or quizzes.
- *Introduce the fields of microrheology and large-amplitude oscillatory strain (LAOS).* The former attempts to examine dynamics around very tiny particles, including molecules, to gain information about the local environment, while the latter pushes the material hard enough to cause structural changes. LAOS is particularly important for complex materials where the concepts of structural strength and healing are of significant practical importance. Professors Eric Furst and Randy Ewoldt provided valuable advice on these sections, respectively.

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- *Open the very large topic of biopolymer viscoelasticity.* There is no end to the examples that could be chosen, so we settled on some very different polymers: wood at the high-modulus extreme and hydrogels for the low-modulus extreme. Guidance for this section from Professor Kelly Burke is gratefully acknowledged.
- *Provide an Instructor's Guide with detailed answers to problems presented in the text.* The answers are much more than a key for grading homework, in that they provide guidance for what to say to the students who are having trouble approaching a problem solution. Nearly 80 new problems were added, including a selection of problems that do not appear in the text.

Items we have resisted including in this introductory text are tensorial representation of stress and strain, viscoelastic properties and analysis of composite materials (with wood being an exception), self-structured materials such as liquid crystals and block copolymers with long-range order, and the more baffling characterization methods and analyses such as transform, multiwave, and sonic methods. As the general level of student training and understanding increases, such topics may become more appropriate for an introductory text.

This book is about polymers. We assume some knowledge of polymer structure and behavior, but hope to add to that knowledge by viewing familiar behavior from a different angle. No attempt is made to explore admittedly important areas of suspension and colloid rheology, two-phase flow, particulate flow, foams, etc. All are good topics for advanced texts.

Finally, a word about the authors. Because of advancing age, Prof. MacKnight has become a nonparticipating author, but is included in the author list in recognition of his significant contributions to the original versions and to the entire field of polymer properties and structure. Thanks to advancing technology, I have only myself to blame for errors and shortcomings. Please mail notice of such, along with general comments and advice, to montgomery.shaw@uconn.edu. (This will, I am told, be my e-mail address in perpetuity, a somewhat daunting thought.) Granddaughter Katherine Shaw diligently checked Web links, for which the authors are grateful. Finally, I wish to thank my wife, Maripaz N. Shaw, for once again coping with the issues created by any large writing project.

MONTGOMERY T. SHAW

*Storrs, Connecticut
November 2017*

Preface to the Third Edition

More than 20 years have passed since the publication of the 2nd Edition of *Introduction to Polymer Viscoelasticity*. Although many of the fundamental aspects of the field remain unchanged, there have been a number of significant developments. Many have to do with instrumentation and the revolution in data collection and analysis, which in no small part has been due to the advent of the personal computer and the associated progression of instrumentation of all types.

In recognition of these changes, we have included descriptions of newer techniques for studying molecular motion along with updated descriptions of the classical experimental methods. An example of the latter is a new appendix that describes in more detail the advantages and disadvantages of the various geometries commonly used for measuring mechanical response. Included are tables with the working equations for these geometries. Those familiar with the earlier editions will also notice an increased emphasis on shear properties, which is an understandable response to the wide availability of instruments that can measure viscoelastic properties in simple shear. We have also, where possible, changed nomenclature to follow the recommendations of the Society of Rheology, and updated all the figures to increase readability and consistency.

Inexpensive computation hardware along with accessible software has impacted not only the acquisition of viscoelastic data, but also its interpretation. In the spirit of these changes, the 3rd Edition features many examples and problems that involve numerical modeling and analysis. To

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relieve the student of the drudgery of data entry, a CD with data files for most numerical problems has been included.

The authors' experience has shown that by far the most effective way to master the material in the text is to work as many problems as possible, hence the increased emphasis on this aspect in the 3rd Edition. The problems range from relatively straightforward use of an equation included in the book, to far more challenging problems requiring detailed analysis and/or numerical methods. Some of these would even be suitable for term projects. Problems requiring the use of the computer are clearly marked, as are open-ended problems that have no one "correct" answer. This type of problem, which is required in many undergraduate curricula, provides the student with an opportunity to search, assume, approximate and innovate. As in past editions, answers to many of the problems are provided in an appendix. These answers form an important part of the book, and contain in some cases more details concerning the subject phenomena.

New topics have been introduced such as interfacial polarization, thermally stimulated currents (TSC), impedance spectroscopy for highly conducting polymers, nuclear magnetic resonance (NMR) relaxation techniques, and the physical relaxation of elastomers. Because impedance spectroscopy has not been used extensively as a tool for examining polymer motion, this short section is included more to explain the similarities and differences between this spectroscopy and the related dielectric spectroscopy. On the other hand, NMR techniques have undergone rapid development in the last few decades, not only in fields such as imaging and high-resolution studies of the structures of biological macromolecules, but also as a tool for studying the relaxation behavior of polymers, particularly in identifying the molecular motions responsible for a given relaxation process. While the new section describing NMR techniques is necessarily introductory, we have attempted to compare its capabilities with dielectric and mechanical spectroscopy in a direct fashion.

As for other changes, we have with considerable trepidation moved the description of deformation in materials from one to three dimensions. Perhaps the main impetus for doing this was to simplify the rather complex explanation in previous editions of the relationship between tensile and shear properties. As an admitted expense, we now have double-subscripted variables in several sections. However, we have refrained from including nonlinear strain theory, which should properly be left for more advanced courses.

It is always a difficult task to select material appropriate for inclusion and exclusion in an introductory text of modest size and cost. Because of the discussion of the topics mentioned above and a somewhat expanded treatment of the phenomenology of viscoelasticity, it was felt appropriate to eliminate the chapter on chemical stress relaxation. In its place, a discussion of this topic

has been included in the chapter entitled Transitions and Relaxations in Polymers; and, of course, in several problems at the end of this chapter.

Professor Aklonis did not participate in the preparation of the 3rd Edition, but, as was the case with Professor Shen in the 2nd Edition, his influence is clearly present and it is a pleasure for us to acknowledge it.

Many individuals and organizations have been involved with the assembly of the 3rd edition. We wish to thank Ms. Jennifer Chudy and Mr. Alvin A. Altamirano for help with data entry and equation editing; Dr. Mark Poliks, Dr. Lou Madsen and Prof. Marcel Utz for critically reviewing the NMR section, Mr. Antonio Senador for checking several problem solutions and Mr. Gerald Ling who provided assistance with the challenging task of finding authors of classical publications for courtesy permission to reproduce figures. We especially want to acknowledge the patience displayed by our spouses, Maripaz N. Shaw and Carol B. MacKnight, as they endured through this lengthy project.

Errors in the text are, of course, the sole responsibility of the authors. It is to be hoped that we have recognized and corrected at least some of the errors in the 2nd Edition, (many of which were pointed out to us by friends and colleagues) and have refrained from introducing a significant number of new ones in the 3rd Edition.

M. T. SHAW
W. J. MACKNIGHT

*Storrs, Connecticut
Amherst, Massachusetts
December 2004*

Preface to the Second Edition

In the decade since the 1st of *Introduction to Polymer Viscoelasticity* appeared, we have noted a number of significant scientific developments. We also suffered a personal tragedy with the passing of Professor M. C. Shen.

Among the major developments are a new approach to long-range relaxational motions known as the theory of reptation and the further elucidation of the kinetic theory of rubber elasticity. In this 2nd edition, we have attempted to take account of some of these developments on a level consistent with the introductory nature of the text. We have also added an entirely new chapter on dielectric relaxation, a technique now widely used to investigate molecular motions in polar polymers. Finally, we have tried to strengthen and clarify several other sections as well as eliminate errors or inconsistencies in the 1st edition that have been pointed out to us by colleagues and students.

Both of us felt very deeply the untimely death of Professor Shen, as did many others who valued his friendship and respected his scientific prowess. He made important and lasting contributions to such diverse areas as rubber elasticity theory, the understanding of mechanical properties of block copolymers, and plasma polymerization, to name but a few. His collaboration in the preparation of the 2nd Edition was sorely missed, but we feel that his influence remains clear and we are proud to acknowledge it.

We wish to thank Dr. Richard M. Neumann, who read the manuscript critically, and Ms. Teresa M. Wilder, who drew many of the figures. We are also indebted to Dr. Neumann and Professor L. L. Chapoy for furnishing some of the new problems contained in this edition.

Once again we accept sole responsibility for any errors in the text, be they old ones remaining from the 1st Edition or new ones that may appear in the second.

J. J. AKLONIS
W. J. MACKNIGHT

Los Angeles, California
Amherst, Massachusetts
December 1982

Preface to the First Edition

The viscoelastic response of polymeric materials is a subject that has undergone extensive development over the past 20 years and still accounts for a major portion of the research effort expended. It is not difficult to understand the reason for this emphasis in view of the vast quantities of polymeric substances that find applications as engineering plastics and the still greater volume that are utilized as elastomers. The central importance of the time and temperature dependence of the mechanical properties of polymers lies in the large magnitudes of these dependencies when compared to other structural materials such as metals. Thus, an understanding of viscoelastic behavior is fundamental for the proper utilization of polymers.

Viscoelasticity is a subject of great complexity fraught with conceptual difficulties. It is possible to distinguish two basic approaches to the subject which we shall designate as the continuum mechanical approach and the molecular approach. The former attempts to describe the viscoelastic behavior of a body by means of a mathematical schema, which is not concerned with the molecular structure of the body, while the latter attempts to deduce bulk viscoelastic properties from molecular architecture. The continuum mechanical approach has proven to be very successful in treating a large number of problems and is of very great importance. However, it is not our intention to treat this approach rigorously in this text. Rather, we shall be concerned with the molecular approach and attempt to present a basic foundation upon which the reader can build. The fundamental difficulty encountered with the molecular approach lies in the fact that polymeric

materials are large molecules of very complex structures. These structures are too complex, even if they were known in sufficient detail, which, in general, they are not, to lend themselves to mathematical analysis. It is therefore necessary to resort to simplified structural models, and the results deduced from these are limited by the validity of the models adopted.

Several excellent treatments of molecular viscoelasticity are available. (See the references of Chapter 1.) The book by Professor Ferry, in particular, is an exhaustive and complete exposition. The question may then be asked, why the necessity for still another text and one restricted to bulk amorphous polymers, at that? Such a question must send each of the authors scurrying in quest of an “apologia pro vita sua.” The answer to the question lies in the use of the word “introduction” in the title. What we have attempted to do is to provide a detailed grounding in the fundamental concepts. This means, for example, that all derivations have been presented in great detail, concepts and models have been presented with particular attention to assumptions, simplifications, and limitations, and problems have been provided at the end of each chapter to illustrate points in the text. The level of mathematical difficulty is such that the average baccalaureate chemist should be able to readily grasp it. Where more advanced mathematical techniques are required, such as transform techniques, the necessary methods are developed in the text.

Having attempted to delineate what this book is, it may be well to remind the reader what it is not. First of all, it is not a complete treatment, lacking among other topics discussions of crystalline polymers, solution behavior, melt rheology, and ultimate properties. It is also not written from the continuum mechanics approach and thus is not mathematically sophisticated. Finally, it is not a primer of polymer science. Familiarity with the basic concepts of the field is presumed.

The authors' first acquaintance with the literature of viscoelastic behavior in polymers evoked a response much like that experienced by neophytes in the literary arts on a first reading of *Finnegan's Wake*, by James Joyce. It is immediately apparent that one is in the presence of a great work, but somehow it will be necessary to master the language before appreciation, let alone understanding, may be achieved. Recognizing the nature of the problem, Joycean scholars came to the rescue with works of analysis to provide a skeleton key to *Finnegan's Wake*. Proper utilization of this skeleton key will open the door to an understanding of that forbidding masterwork. It was thus our intent to provide a similar skeleton key to the literature of molecular viscoelasticity. How well we have succeeded must be left to the judgment of our readers.

We are grateful to the students at our respective institutions who have suffered our attempts to present the material in this text in coherent form at

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various stages of development. Their criticisms and suggestions have led to significant improvements. We are also grateful to Mrs. William Jackson, who translated many rough sketches into finished drawings. It is hardly to be expected that a work of this nature could be free from errors. We have attempted to eliminate as many as possible but, of course, bear full responsibility for those remaining.

JOHN J. AKLONIS
WILLIAM J.
MACKNIGHT
MITCHEL SHEN

Los Angeles, California

About the Companion Website

This book is accompanied by a companion website:

www.wiley.com/go/Shaw/Intro_to_polyviscoelasticity



Available on the Wiley website is the *Instructor's Guide* for the 4th edition of the textbook *Introduction to Polymer Viscoelasticity*. Intended for legitimate instructors using the text in courses they are teaching, the Guide offers advice on using the text along with scores of unpublished problems of all sorts, many of which are suitable for homework, exams, or small projects. The answers are not just answers but an explanation of how the problem can be approached and solved. Thus, the solutions can be used almost directly for lecture examples.

1

Introduction

The subject matter of this book is the response that polymers exhibit when they are subjected to external forces of various kinds. Almost without exception, polymers belong to a class of substances known as “viscoelastic bodies.” As the name implies, these materials respond to external forces in a manner intermediate between the behavior of an elastic solid and a viscous liquid. To set the stage for what follows, it is necessary to describe in very general terms the types of forces to which the viscoelastic bodies might be subjected for characterization purposes.

Consider first the motion of a rigid body in space. This motion can be thought of as consisting of translational and rotational components. If no forces act on the body, it will maintain its original state of motion indefinitely in accordance with Newton’s first law of motion. However, if a single force or a set of forces whose vector sum is nonzero act on the body, it will experience acceleration or a change in its state of motion. Consider, however, the case where the vector sum of forces acting on the body is zero and the body experiences no change in either its translational or rotational component of motion. In such a condition, the body is said to be stressed. If the requirement of rigidity is removed, the body will in general undergo a deformation as a result of the application of these balanced forces. If this occurs, the body is said to be strained. It is the relationship between stress and strain that is our main concern. Depending on the types of stress and strain applied to a body, we can use these quantities to define new quantities—material properties—that ultimately relate to the chemical and physical structure of the body. These material properties are referred to using the terms “modulus” and

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Montgomery T Shaw and William J MacKnight.

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Companion Website: www.wiley.com/go/Shaw/Intro_to_polyviscoelasticity

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“compliance.” To understand in rough terms the physical meaning of the modulus of a solid, consider the following simple experiment.

Suppose we have a piece of rubber (e.g., natural rubber), $\frac{1}{2} \text{ cm} \times \frac{1}{2} \text{ cm} \times 4 \text{ cm}$, and a piece of plastic (e.g., polystyrene) of the same dimensions. The experiment to be performed consists of suspending a weight (applying a force) of, say 1 kg, from each sample as shown in Figure 1-1.

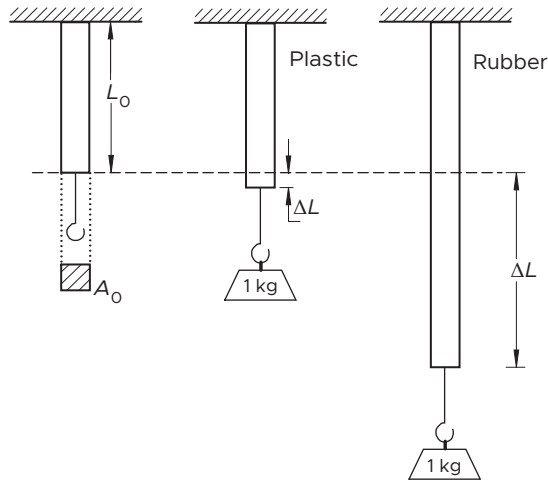


Figure 1-1. Deformation of samples made from plastic vs. rubber. As a reference, the undeformed shape for both samples is shown on the left side. A_0 refers to the cross-sectional area of the undeformed sample.

As is obvious, the deformation of the rubber will be much greater than that of the plastic. Using this experiment, we might define a spring constant k as the applied force f divided by the change in length ΔL

$$k = F / \Delta L \quad (1-1)$$

and use this number to compare the samples. However, to obtain a measure that is independent of the sample size, that is, a material property, as opposed to a sample property, we must divide the applied force by the initial cross-sectional area A_0 and divide the ΔL by the initial sample length L_0 . Then, the modulus M is

$$M = \frac{F / A_0}{\Delta L / L_0} \quad (1-2)$$

Because ΔL is much larger for the rubber than for the plastic, from equation (1-2) it is clear that the modulus of the rubber is much lower than the modulus of the plastic. Thus, the particular modulus defined in equation (1-2) specifies the

resistance of a material to elongation at small deformations and is called the Young's modulus. It is normally given the symbol E . (See www.rheology.org for suggestions on standard nomenclature for viscoelastic quantities.)

Further experimentation, however, reveals that the situation is more complicated than is initially apparent. If, for example, one were to carry out the test on the rubber at liquid nitrogen temperature, one would find that this "rubber" undergoes a much smaller elongation than with the same force at room temperature. In fact, the extension would be so small as to be comparable to the extension exhibited by the plastic at room temperature. A more dramatic demonstration of this effect is obtained by immersing a rubber ball in liquid nitrogen for several minutes. The cold ball, when bounced, no longer has the characteristic properties of a rubbery object but, instead, is indistinguishable from a hard sphere made of plastic.

On the other hand, if the piece of plastic is heated in an oven to 130 °C and then subjected to the modulus measurement, it is found that a much larger elongation, comparable to the elongation of the rubber at room temperature, results.

These simple experiments indicate that the modulus of a polymeric material is not invariant, but is a function of temperature T , that is, $M = M(T)$.

An investigation of the temperature dependence of the modulus of our two samples is now possible. At temperature T_1 , we measure the modulus as before, and then increase the temperature to T_2 , and so on. Schematic data from such an experiment are plotted in Figure 1-2. The temperature dependence of the modulus is so great that it must be plotted using a logarithmic scale. (This large variation in modulus presents experimental problems that will be treated subsequently.) The region between the vertical dashed lines represents normal-use temperatures and, consistent with the opening experiment, we find that in this range the plastic has a high modulus while the rubber has a relatively low modulus. Upon cooling, the modulus of the rubber rises markedly, by as much as four orders of magnitude, indicating that the rubber at lower temperatures behaves like a plastic. The nearly constant modulus for the rubber is evidenced at higher temperatures. This behavior is discussed in detail in Chapter 6. At low temperatures, the modulus-temperature behavior for the plastic is seen to be quite similar in shape to that of the rubber except that the large drop, called the glass transition, occurs at higher temperatures, resulting in the high modulus observed at room temperature. At ~100 °C it is clear that the modulus of the plastic is close to that of a rubber, agreeing with the results of one of the earlier "experiments" in this discussion. At yet higher temperatures, the

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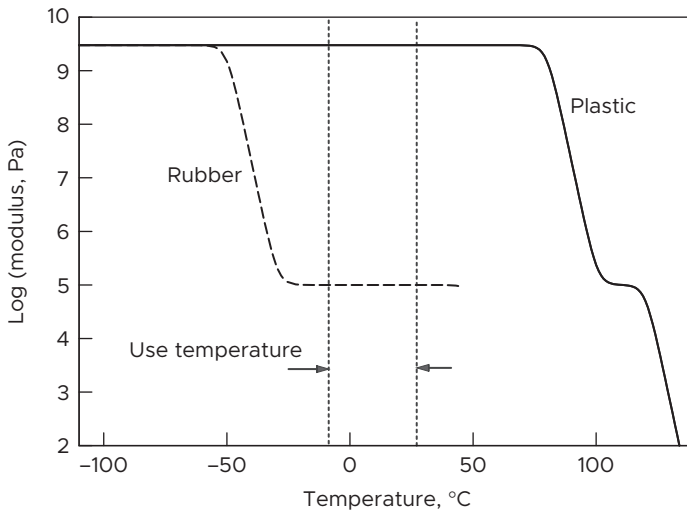


Figure 1-2. Schematics of the modulus vs. temperature behavior for a rubber and a plastic over a broad temperature range.

plastic's modulus drops once again; this is the region where the material can be easily molded.

One more type of deformational experiment remains to be discussed. Consider a material like pitch or tar, which is used as a roof coating and is applied at elevated temperatures. Our test is similar to the standard experiment done above, utilizing the same size sample at room temperature. First, we suspend the 1-kg weight from the sample and observe the small resultant extension; the modulus calculated according to equation (1-2) is high. However, if the sample is left suspended in this vertical position for several hours, the result is a considerable elongation of the sample. Now application of equation (1-2) gives a very low value for the modulus. Thus, the modulus measurement on the short timescale of a few seconds resulted in a high value while the modulus measurement on the longer time scale of hours resulted in a low modulus. This apparent discrepancy is accounted for by realizing that the modulus is a function of time as well as temperature; this has been found to be the case generally for polymeric materials. Strictly then, the measurements spoken of earlier in this chapter and depicted schematically in Figure 1-2 should have some time associated with each modulus value. (Time represents the duration between the application of the force and the measurement of the extension.) It is convenient to pick the same constant time for all measurements, so one might consider the constant time in Figure 1-2 to be 10 seconds.