

Introduction to Polymer Viscoelasticity

Third Edition

This Page Intentionally Left Blank

Introduction to Polymer Viscoelasticity

This Page Intentionally Left Blank

Introduction to Polymer Viscoelasticity

Third Edition

Montgomery T. Shaw

William J. MacKnight



A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2005 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic format. For information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data is available.

ISBN 13: 978-0-471-74045-2

ISBN 10: 0-471-74045-4

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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

This Page Intentionally Left Blank

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 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 the endured though 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*

This Page Intentionally Left Blank

Preface to the Second Edition

In the decade since the first edition of *Introduction to Polymer Viscoelasticity* appeared, we have noted a number of significant scientific developments. We also suffered a personal tragedy with the death 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 second 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 first 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 second 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

xii PREFACE

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 first 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 which has undergone extensive development over the past twenty 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 which find applications as engineering plastics and the still greater volume which 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, that concepts and models have been presented with particular attention to assumptions, simplifications, and limitations, and that 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 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

This Page Intentionally Left Blank

Contents

1. Introduction	1
Suggested Reading, 6	
2. Phenomenological Treatment of Viscoelasticity	7
A. Elastic Modulus, 7	
B. Transient Experiments, 19	
C. Dynamic Experiments, 23	
D. Boltzmann Superposition Principle, 27	
E. Relationship Between the Creep Compliance and the Stress Relaxation Modulus, 32	
F. Relationship Between Static and Dynamic Properties, 33	
Appendix 1. Connecting Creep Compliance and Stress Relaxation Modulus Using Laplace Transforms, 35	
Appendix 2. Borel's Theorem, 38	
Appendix 3. Geometries for the Measurement of Viscoelastic Functions, 38	
1. Axial Geometries, 38	
2. Rotational Geometries, 42	
Problems, 46	
References, 50	
3. Viscoelastic Models	51

A. Mechanical Elements, 51	
1. Maxwell Model, 53	
2. Voigt Model, 59	
3. Generalized Maxwell Model, 61	
4. Voigt-Kelvin Model, 64	
B. Distributions of Relaxation and Retardation Times, 66	
C. Molecular Theories, 69	
D. Application of Flexible-Chain Models to Solutions, 78	
E. The Zimm Modification, 79	
F. Extension to Bulk Polymer, 82	
G. Reptation, 93	
Appendix: Manipulation of the Rouse Matrix, 97	
Problems, 102	
References, 105	
4. Time–Temperature Correspondence	107
A. Four Regions of Viscoelastic Behavior, 107	
B. Time–Temperature Superposition, 114	
C. Master Curves, 117	
D. The WLF Equation, 119	
E. Molecular Interpretation of Viscoelastic Response, 124	
Problems, 125	
References, 128	
5. Transitions and Relaxation in Polymers	129
A. Phenomenology of the Glass Transition, 129	
B. Theories of the Glass Transition, 132	
1. Free-Volume Theory, 133	
2. Thermodynamic Theory, 137	
3. Kinetic Theories, 141	
C. Structural Parameters Affecting the Glass Transition, 145	
D. Relaxations in the Glassy State, 151	
E. Relaxation Processes in Networks, 154	
1. Physical Relaxation, 154	
2. Chemical Processes, 156	
Problems, 159	
References, 163	

6. Elasticity of Rubbery Networks	165
A. Thermodynamic Treatment, 166	
B. Statistical Treatment, 172	
1. Derivation, 172	
2. Energy Contribution, 183	
C. Phenomenological Treatment, 187	
D. Factors Affecting Rubber Elasticity, 190	
1. Effect of Degree of Crosslinking, 190	
2. Effect of Swelling, 192	
3. Effect of Fillers, 195	
4. Effect of Strain-Induced Crystallization, 198	
Appendix 1. Statistics of a Polymer Chain, 199	
Appendix 2. Equation of State for a Polymer Chain, 206	
Problems, 208	
References, 211	
7. Dielectric and NMR Methods	213
A. Dielectric Methods, 213	
1. Phenomenology, 214	
2. Molecular Interpretation of Dielectric Constant, 220	
3. Interfacial Polarization, 227	
4. Application to Polymers, 229	
5. Experimental Methods, 231	
6. Application of Dielectric Relaxation to Polymethyl Methacrylate, 235	
7. Comparisons Between Mechanical and Dielectric Relaxation for Polymers, 236	
B. Nuclear Magnetic Resonance Methods, 237	
Problems, 243	
References, 244	
Answers to Problems	247
List of Major Symbols	293
List of Files on CD	301
Author Index	305
Subject Index	308

This Page Intentionally Left Blank

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 force to which the viscoelastic bodies are subjected.

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, it is possible to 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 called moduli. To understand the physical meaning of the modulus of a solid, consider the following simple experiment.

2 INTRODUCTION

Suppose we have a piece of rubber (e.g., polyisobutylene), $\frac{1}{2}$ cm $\frac{1}{2}$ cm \times 4 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.

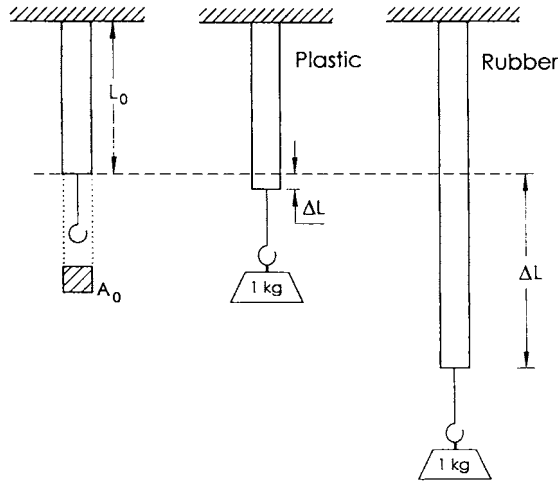


Figure 1-1. Deformation of samples made from plastic vs. rubber. As a reference, the undeformed shape for both samples is shown on the left.

As is obvious, the deformation of the rubber will be much greater than that of the plastic. Using this experiment we can 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, i.e., 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:

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

Since 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, that is, $M=M(T)$.

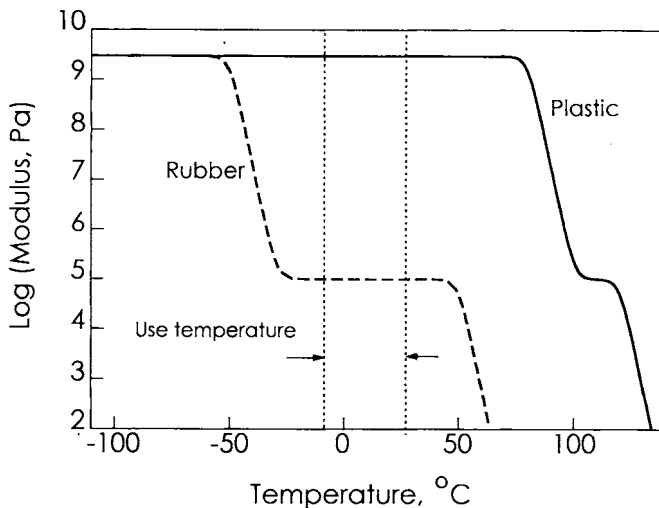


Figure 1-2. Schematic of the modulus vs. temperature behavior for a rubber and a plastic over a broad temperature range.

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, 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 on 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

4 INTRODUCTION

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. Another drastic change in modulus for the rubber is evidenced at higher temperatures; here the material is becoming softer, as indicated by further decreases in modulus. This behavior is discussed in detail in Chapter 4. The modulus-temperature behavior for the plastic is seen to be quite similar to that of the rubber except that the changes occur at higher temperatures, resulting in the high modulus observed at room temperature. At 135°C it is clear that the modulus of this material is that of a rubber, agreeing with the results of one of the earlier "experiments" in this discussion.

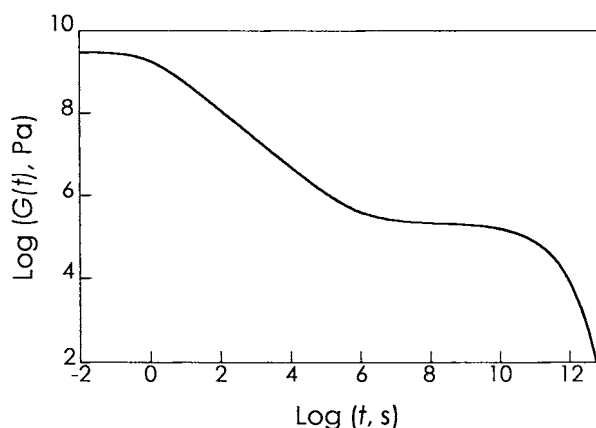


Figure 1-3. Schematic modulus-time curve for a polymer at constant temperature.

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. According to equation (1-2), the modulus calculated 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 time-scale 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 systems. 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-factor in Figure 1-2 to be 10 seconds.

As is evident from the above discussion, it should be possible to measure the behavior of a material as a function of time at constant temperature. A schematic modulus-time behavior is shown in Figure 1-3. The modulus is seen to fall from its initial high value by about three orders of magnitude to a modulus indicative of a rubber and, after evidencing a plateau, fall again. The ordinate here is $\log t$; at the chosen temperature an experiment lasting for 1 to 30 minutes would characterize this material as a plastic. However, in an experiment lasting 10^8 minutes (200 years), the material would "look like" an elastomer. Longer measurements would correspond to still softer materials. Methods for obtaining curves of the type shown in Figure 1-3 are discussed in Chapter 4, as well as methods of converting from modulus-time behavior to modulus-temperature behavior and vice versa.

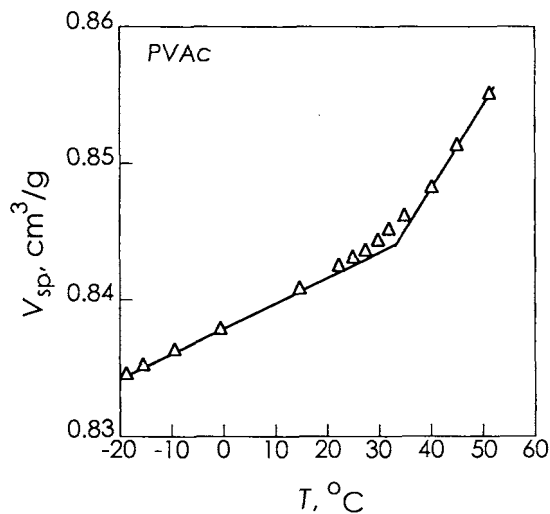


Figure 1-4. Specific-volume data for poly(vinyl acetate) used to determine its T_g .

Another experiment is often carried out in laboratories dealing with the physical properties of polymers. This is the determination of the temperature at which the material properties change from those of a plastic to those of a rubber. This temperature is known as the glass transition temperature and is a characteristic property of each substance. In Figure 1-2, for example, it is clear that at about 100°C , the modulus of the plastic exhibits a steep decrease. Careful analysis of the curve in this region, however, indicates no abrupt change in modulus but rather a smoothly varying change. From this experiment, it would seem that the glass transition occurs over a range of

6 INTRODUCTION

temperatures rather than at a single temperature. Experimentally, it has been found that the coefficient of expansion of a substance undergoes a more abrupt change in the region of the glass transition. The temperature at this change, in fact, is defined as the glass transition temperature T_g . An example of the data obtained in the determination of a glass transition temperature by this method is presented in Figure 1-4. The volume of a sample is measured as a function of temperature using a dilatometer, care being taken to change the temperature slowly and at an essentially constant rate. The temperature where there is a change in slope (due to a discontinuity in the coefficient of expansion) is taken as T_g . In the example shown in Figure 1-4, T_g is about 34 °C.

SUGGESTED READING

- Alfrey, T.**, *Mechanical Behavior of High Polymers*, Interscience, New York, 1948.
- Bueche, F.**, *Physical Properties of Polymers*, Interscience, New York, 1962.
- Christensen, R. M.**, *Theory of Viscoelasticity, an Introduction*, Academic Press, New York, 1971.
- Eirich, F. R., Ed.**, *Rheology, Theory and Applications*, Vol. 1, Academic Press, New York, 1956.
- Ferry, J. D.**, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1990.
- Findley, W. N.**, *Creep and Relaxation of Nonlinear Viscoelastic Materials with Introduction to Linear Viscoelasticity*, North-Holland Publishing Co., Amsterdam, 1976.
- McCrum, N. G., B. E. Read, and G. Williams**, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.
- Middleman, S.**, *The Flow of High Polymers*, Interscience, New York, 1968.
- Nielsen, L. E. and R. F. Landel**, *Mechanical Properties of Polymers and Composites*, Marcel-Dekker, New York, 1994.
- Pipkin, A. C.**, *Lectures on Viscoelasticity Theory*, Applied Mathematical Sciences, Vol. 7, Springer-Verlag, New York, 1972.
- Schwarzl, F. R.**, "Viscoelasticity," in *Encyclopedia of Polymer Science and Engineering*, Vol. 17, (H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz, eds.) Wiley-Interscience, New York, 1989, pp. 587-665.
- Timoshenko, S., and J. N. Goodier**, *Theory of Elasticity*, McGraw-Hill, New York, 1951.
- Tobolsky, A. V.**, *Properties and Structure of Polymers*, Wiley, New York, 1960.
- Tobolsky, A. V., and H. F. Mark, Eds.** *Polymer Science and Materials*, Wiley, New York, 1971.
- Treloar, L. R. G.**, *The Physics of Rubber Elasticity*,arendon Press, Oxford, 1975.
- Tschoegl, N.**, *The Phenomenological Theory of Linear Viscoelastic Behavior: An Introduction*, Springer-Verlag, New York, 1989.
- Ward, I. M.**, *Mechanical Properties of Solid Polymers*, Wiley, New York, 1971.
- www.rheology.org is the web site of the Society of Rheology. It gives current information on many aspects of the deformation and flow of materials.

2

Phenomenological Treatment of Viscoelasticity

To place the concepts discussed in the Introduction on a more quantitative basis, and to understand better some of the added complications that arise from the time dependence of the modulus, several methods commonly used to make physical measurements on polymeric systems are described in this chapter. First, however, it is necessary to define rigorously the parameters to be derived from the experimental data in terms of the type of deformation applied to the sample.*

A. ELASTIC MODULUS

Perhaps the simplest deformation that can be applied to a sample is uniaxial tension or compression, shown in Figure 2-1a. This is the type of deformation mentioned in the Introduction. However, our previous concept of force is

* In this context, both stress and strain are defined considering very small deformations. Under these conditions, the properties of the material are strictly constant and second-order effects (nonlinearities) are negligible. For example, to effect large shear strains, it is necessary to apply stresses to the material other than the obvious shear stress. While nonlinear effects are important, they are beyond the scope of this book, and the reader is advised to consult more advanced texts.

8 PHENOMENOLOGICAL TREATMENT OF VISCOELASTICITY

modified slightly in this more quantitative discussion to become the stress defined as

$$\sigma_E = \frac{F}{A} = \frac{F}{YZ} \quad (2-1)$$

where the subscript E represents uniaxial extension and the other symbols are defined in the figure. Stress, denoted in general by the symbol σ , has the units of dynes/cm² (dynes per square centimeter), lb_f/in.² (psi), or N/m² (Newtons per square meter). Current international convention prescribes the latter, which is named the Pascal (after Blaise Pascal, 1623–1662). Pa is the abbreviation for the Pascal. Note that static definitions are being considered here, that is, the parameters do not vary with time. These initial considerations will shortly be generalized to time-dependent functions.

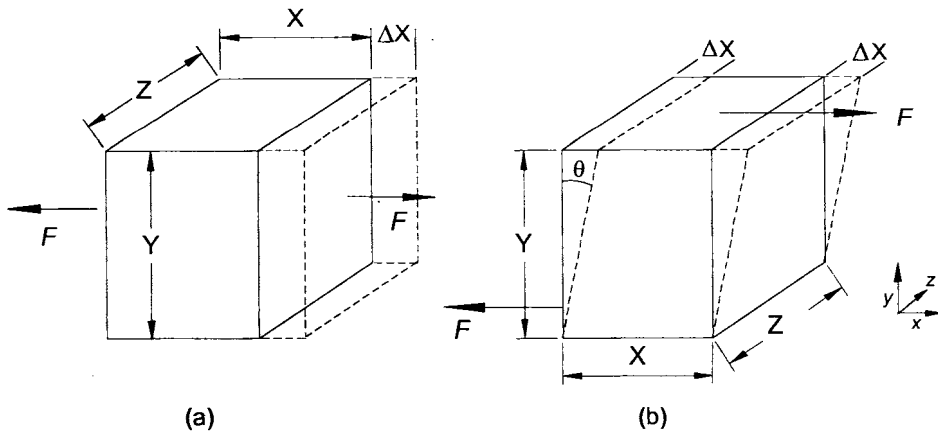


Figure 2-1. Tension (a) and shear (b) of a three-dimensional sample subjected to very small deformations.

The application of a tensile stress to a real body will result in a corresponding extensional deformation as illustrated in Figure 2-1a. The fractional extension is defined as the tensile strain. Thus, ε , the tensile strain resulting from the application of a uniaxial stress, is given as

$$\varepsilon = \frac{\Delta X}{X} \quad (2-2)$$

and it is clear from this expression that ε is dimensionless. For the static situation, the tensile modulus E and the tensile compliance D are defined by equation (2-3)