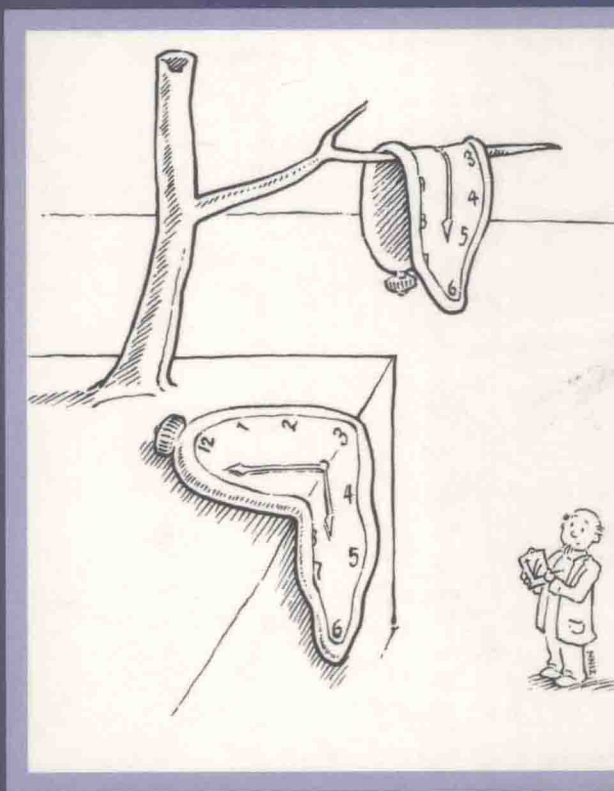


MECHANICAL RESPONSE OF POLYMERS

AN INTRODUCTION



ALAN S. WINEMAN
and K. R. RAJAGOPAL

Mechanical Response of Polymers

AN INTRODUCTION

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CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS

The Edinburgh Building, Cambridge CB2 2RU, UK <http://www.cup.cam.ac.uk>
40 West 20th Street, New York, NY 10011-4211, USA <http://www.cup.org>
10 Stamford Road, Oakleigh, Melbourne 3166, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain

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First published 2000

Printed in the United States of America

Typeface Sabon 10/13pt System 3B2 [KWP]

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

Library of Congress Cataloging-in-Publication Data

Wineman, A. S.

Mechanical response of polymers : an introduction / Alan S.
Wineman, K. R. Rajagopal.

p. cm.

ISBN 0-521-64337-6 (hb). – ISBN 0-521-64409-7 (pb)

1. Polymers – Mechanical properties. I. Rajagopal, K. R.
(Kumbakonam Ramamani) II. Title.

TA455.P58w55 2000

620.1'9292–DC21

ISBN 0 521 64337 6 hardback

ISBN 0 521 64409 7 paperback

Mechanical Response of Polymers

The use of polymers has become so commonplace that it would be nearly impossible to pass a day without coming into contact with polymer-based products. For example, automobiles, household appliances, and electronic devices all make use of polymeric materials. As polymers are used increasingly in sophisticated industrial applications, it has become essential that mechanical engineers, who have traditionally focused on the behavior of metals, become as capable and adept with polymers.

This text provides a thorough introduction to the subject of polymers from a mechanical engineering perspective, treating stresses and deformations in structural components made of polymers. Three themes are developed. First, the authors discuss the time-dependent response of polymers and its implications for mechanical response. Secondly, descriptions of mechanical response are presented for both time-dependent and frequency-dependent material properties. Finally, the stress-strain-time relation is applied to determine stresses and deformations in structures.

With numerous examples and extensive illustrations, this book will help advanced undergraduate and graduate students, as well as practicing mechanical engineers, make optimal and effective use of polymeric materials.

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Preface

During the past several decades, the use of polymers has become so commonplace that it would be nearly impossible to pass a day without coming into contact with a polymer-based product. The automobile, aerospace, appliance, and electronics industries use more polymers, by weight, than all the metals put together. Despite the increased use of polymers in engineering products, the stresses and deformations that these polymers undergo are generally determined as if the behavior is that of a classical elastic material. This is in part due to the traditional mechanical engineering education that has emphasized the behavior of metals rather than polymers. Polymeric materials have been studied more within the context of understanding their material properties by chemists, chemical engineers, and material scientists, rather than with a view toward understanding the stresses and deformations in structural components. However, rapid changes are occurring in current engineering practices involving polymers from the perspective of mechanical engineering. Polymers are being considered for increasingly sophisticated industrial applications. The effective and efficient use of these materials requires an understanding of their time-dependent response and energy dissipation properties. Thus, it is essential that the mechanical engineering education be expanded so that students become as capable and adept with polymers as they are with metals in determining stresses and deformations.

The authors have spent many years teaching engineering students about stresses and deformations in metallic structural components, on the one hand, and carrying out research in the mechanical response of polymers, on the other. They have also taught graduate courses in the viscoelastic response of polymers. In recognition of the increasing need that mechanical engineers be educated in the mechanics of polymers, we have used our teaching and research expertise to develop a book which is intended to serve as both a textbook and an engineering reference.

This book was prepared with several purposes in mind. The first is to instill a solid grasp of the phenomena of stress relaxation and creep in polymers, and their consequences for mechanical response. This is achieved by developing the stress-strain-time relation for the response of polymers, and then using it to explore characteristic material and process times, energy dissipation, and the effects of fading memory. The second purpose has to do with the mechanical properties of polymers. An engineer should be familiar with descriptions of mechanical response in terms of both time-dependent and frequency-dependent material properties. Thus, we develop the background necessary for this purpose. In particular, we use the stress-strain-time

relation to interpret the response in fundamental experiments, and then to develop relations between material properties in their creep, stress relaxation, time- and frequency-based forms.

Our third purpose is to show how the stress-strain-time relation is used to determine stresses and deformations in structures. We begin with a thorough treatment of polymeric beams and bars under torsion. Examples are presented which not only illustrate different aspects of the consequences of creep and stress relaxation, but also illustrate different methods for analyzing structural problems. In effect, given a textbook for an introductory solid mechanics course in the mechanical engineering curriculum, it is shown that each example can be defined for polymeric materials, and can be treated by the methods presented here. The same approach is then used to determine stresses and deformations in bodies with more complicated shapes and loadings. Instead of examples of beams and torsion bars, examples are drawn from the classical linear theory of elasticity.

To come to grips with viscoelasticity it is helpful to have a clear grasp of the response of elastic solids and viscous fluids. Here, we shall concentrate our efforts on describing the linear response of viscoelastic materials that stems from the material responding both as a linear elastic solid and a linear viscous fluid. While the linear viscous fluid is a proper model in its own right, the linear elastic solid model (linearized elastic solid to be more precise) is an approximation that has served as an indispensable model in virtue of its usefulness and applicability. The same can be said of the linear viscoelastic model; while it is not frame-invariant, its ease of use and the conformity of the predictions of the model with available experimental data have rendered it an essential tool to the practicing engineer.

It is our goal that the treatment of material modeling, formulation of the basic issues in mechanics, and methods for the calculation and solution of engineering problems presented here will enable the student or practicing engineer to make optimal and effective use of polymeric materials.

A word of caution to the reader about our notation: we follow the style of Timoshenko. While the equations are numbered sequentially during the development of the theory in each chapter, we assign equation numbers independently for the solution of the special problems that are treated in each chapter.

Alan S. Wineman
K. R. Rajagopal

Contents

<i>Preface</i>	<i>page</i>	ix
1 Discussion of Response of a Viscoelastic Material		1
1.1 Comparison with the Response of Classical Elastic and Classical Viscous Materials		1
1.2 Response of a Classical Elastic Solid		1
1.3 Response of a Classical Viscous Fluid		3
1.4 Comments on Material Microstructure		6
1.5 Response of a Viscoelastic Material		7
1.6 Typical Experimental Results		10
1.7 Material Properties		15
1.8 Linearity of Response		17
1.9 Aging Materials		21
PROBLEMS		24
2 Constitutive Equations for One-Dimensional Response of Viscoelastic Materials: Mechanical Analogs		28
2.1 Maxwell Model		28
2.2 Kelvin–Voigt Model		35
2.3 Three-Parameter Solid or Standard Linear Solid		40
2.4 N Maxwell Elements in Parallel		45
2.5 N Kelvin–Voigt Elements in Series		50
2.6 Relaxation and Creep Spectra		51
PROBLEMS		52
3 Constitutive Equations for One-Dimensional Linear Response of a Viscoelastic Material		54
3.1 General Restrictions on the Constitutive Equation		54
3.2 Linearity of Response: Superposition of Step Increments		58
3.3 Linearity of Response: Superposition of Pulses		62
3.4 Creep Forms of the Constitutive Equation		64
3.5 Summary of Forms of the Constitutive Equation		64
PROBLEMS		65

4	Some Features of the Linear Response of Viscoelastic Materials	67
4.1	Relation Between Relaxation and Creep Functions	67
4.2	Characteristic Creep and Relaxation Times	72
4.3	Characteristic Relaxation, Creep, and Process Times	75
4.4	Some Examples Illustrating Implications of Fading Memory	80
	PROBLEMS	83
5	Histories with Constant Strain or Stress Rates	88
5.1	Constant Strain Rate Deformation	88
5.2	Constant Strain Rate Deformation and Recovery	92
5.3	Influence of Rise Time T^* or Strain Rate α	97
5.4	Work Done in a Constant Strain Rate Deformation and Recovery Test	98
5.5	Repeated Cycles	100
5.6	Step Strain and Recovery	100
5.7	Ramp Strain Approximation to a Step Strain History	103
5.8	Constant Stress Rate Loading and Unloading History	105
	PROBLEMS	109
6	Sinusoidal Oscillations	115
6.1	Sinusoidal Strain Histories	115
6.2	Sinusoidal Stress Histories	120
6.3	Relation Between $G^*(\omega)$ and $J^*(\omega)$	123
6.4	Work per Cycle During Sinusoidal Oscillations	124
6.5	Complex Viscosity	125
6.6	Examples of Calculation of $G^*(\omega)$ and $J^*(\omega)$	125
6.7	Low and High Frequency Limits of $G^*(\omega)$ and $J^*(\omega)$	130
6.8	Fourier Integral Theorem, Fourier Transform	135
6.9	Expressions for $G(t)$ and $J(t)$ in Terms of $G^*(\omega)$ and $J^*(\omega)$	137
6.10	Work Done During a General Deformation History	140
	PROBLEMS	142
7	Constitutive Equation for Three-Dimensional Response of Linear Isotropic Viscoelastic Materials	148
7.1	Introduction	148
7.2	Linearity	149
7.3	Uniaxial Extension, Poisson's Ratio, Isotropy	150
7.4	Uniaxial Extension Along the x_2 and x_3 Directions	153
7.5	Shear Response	153
7.6	Constitutive Equation for Three-Dimensional Response	154
7.7	A Relation Between Poisson's Ratio and the Extensional and Shear Material Properties	155

7.8	Volumetric and Pure Shear Response	157
7.9	Stress in Terms of Strain History	160
7.10	Sinusoidal Oscillations	160
7.11	Laplace Transformation of the Constitutive Equations	163
7.12	Effect of Viscoelasticity on Principal Directions of Stress and Strain	164
7.13	Summary of Constitutive Relations	166
7.14	Relations for Special Cases of Volumetric Response	168
	PROBLEMS	168
8	Axial Load, Bending, and Torsion	172
8.1	Introduction	172
8.2	Structural Components Under Axial Load	172
8.3	Pure Bending of Viscoelastic Beams	176
8.4	Kinematics of Deformation	177
8.5	Constitutive Equation	179
8.6	Force Analysis	180
8.7	Stress, Bending Moment, and Curvature Relations	181
8.8	Deformation of Beams Subjected to Transverse Loads	182
8.9	Beams on Hard Supports, Correspondence Principle	185
8.10	Delayed Contact, Direct Method of Solution	190
8.11	Interaction of Polymeric Structural Components, a Viscoelastic Beam on a Viscoelastic Support	195
8.12	Extrusion of a Bar, Tracking the History of a Material Element	199
8.13	Traveling Concentrated Load on a Beam	202
8.14	Torsion of Circular Bars	207
8.15	Analysis of Viscoelastic Structures	212
	PROBLEMS	212
9	Dynamics of Bodies with Viscoelastic Support	219
9.1	Introduction	219
9.2	Comparison of Spring–Damper and Viscoelastic Supports	219
9.3	Forced Oscillations	221
9.4	Free Oscillations	228
	PROBLEM	231
10	Boundary Value Problems for Linear Isotropic Viscoelastic Materials	232
10.1	Introduction	232
10.2	Governing Equations	232
10.3	Correspondence Theorem for Quasi-Static Motion	234
10.4	Breakdown of the Correspondence Principle	237
10.5	Application of the Correspondence Principle: Pressure Loading of a Viscoelastic Cylinder	238

10.6	Application of the Correspondence Principle: Torsion of Bars of Non-Circular Cross-Section	240
10.7	Direct Solution Methods	243
	PROBLEM	246
11	Influence of Temperature	247
11.1	Introduction	247
11.2	Thermally Induced Dimensional Changes	247
11.3	Mechanical Response at Different Temperatures	248
11.4	Time-Temperature Superposition	251
11.5	Experimental Support for Time-Temperature Superposition	253
11.6	General Comments	254
11.7	Effect of Temperature on Characteristic Stress Relaxation Time	256
11.8	Other Material Property Functions	257
11.9	Implications of Time-Temperature Superposition for Processes	258
11.10	Rate of Work	259
11.11	An Experimental Study	260
11.12	Extension to Time-Varying Temperature Histories	262
11.13	Constitutive Equation for Time-Varying Temperature Histories	268
11.14	Thermo-Viscoelastic Response of a Three Bar Structure: Formulation	269
11.15	Thermo-Viscoelastic Response of a Three Bar Structure: Development of Frozen-in Deformation	271
11.16	Thermo-Viscoelastic Response of a Three Bar Structure: Frozen-in Forces	276
11.17	Thermo-Viscoelastic Response of a Three Bar Structure: Cooling Induced Warping	285
11.18	Thermo-Viscoelastic Response of a Three Bar Structure: Comments	292
Appendix A	Operator Notation for Time Derivatives	293
Appendix B	Laplace Transform	295
Appendix C	Volterra Integral Equations	299
Appendix D	Formal Manipulation Methods	305
Appendix E	Field Equations in Cartesian and Cylindrical Coordinates	308
	<i>References</i>	311
	<i>Index</i>	313

Discussion of Response of a Viscoelastic Material

1.1 Comparison with the Response of Classical Elastic and Classical Viscous Materials

As the word “viscoelasticity” suggests, the kind of mechanical response under consideration involves aspects of familiar types of material response – those of elastic solids and viscous fluids. In order to compare viscoelastic response with that of elastic solids and viscous fluids it is necessary to account for time as an explicit physical parameter. This approach is introduced by first discussing the response of linear elastic solids and linear viscous (Newtonian) fluids using time as an explicit parameter. This will set the stage for a similar discussion for viscoelastic materials.

Consider one-dimensional stress–strain states, the material being either in uniaxial extension or in simple shear. The material is in an undeformed state for times $t < 0$. As Figure 1.1 shows, σ denotes either a normal or a shear stress and ε denotes a normal strain or a shear strain. Figure 1.1 shows an extension state and a shear state at a typical time t . The mechanical response is discussed by considering variations of stress and strain with time, by means of plots of stress versus time and strain versus time. It is then possible to determine the conditions under which it is reasonable to eliminate time as an explicit parameter and plot stress versus strain. Attention will be confined to materials which are initially undeformed and unstressed, that is, $\sigma(t) = 0$ and $\varepsilon(t) = 0$ for $t < 0$.

1.2 Response of a Classical Elastic Solid

The one-dimensional mechanical response of a linear elastic solid is often represented by a mechanical analog – a linear spring, as shown in Figure 1.2. The response of the spring is characterized by the force–deformation relation $F = k\Delta$, in which F is the force, Δ is the elongation, and k is the spring constant. This relation is assumed to be valid under all conditions. The purpose of the mechanical analog is as an aid in visualizing the material response described below. The mechanical analog is also used in developing a stress–strain relation. This is done by associating force F with the stress σ and elongation Δ with the strain ε .

A number of stress–time and strain–time experiments are now considered which lead to the conclusion that $\sigma(t) = E\varepsilon(t)$, where E is the Young’s modulus. In the following discussion, it is assumed that the specimen has no mass, so that there are no inertial effects.

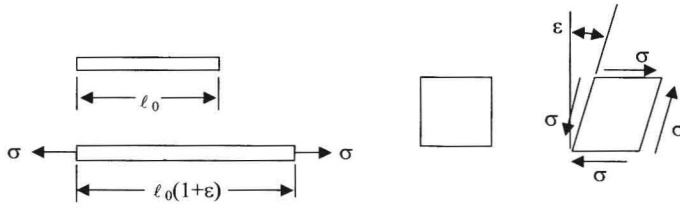


Figure 1.1. One-dimensional stress-strain states. Left: uniaxial extension. Right: simple shear.

STRESS CONTROL TEST, RESPONSE TO STEP STRESS

If the stress is instantaneously increased to σ_0 at $t = 0$ and then held constant, an elastic solid instantaneously deforms to a fixed state at some strain ϵ_0 which does not vary with t . This is shown in curves (a) of Figure 1.3.

RELEASE OF STRESS

If the stress is instantaneously removed at time t_2 , the strain instantaneously returns to zero. That is, the material instantaneously and completely recovers its original shape (springiness).

STRAIN CONTROL TEST, RESPONSE TO STEP STRAIN

If the strain is suddenly increased to ϵ_0 at $t = 0$ and then held constant, the stress instantaneously increases to σ_0 and stays constant.

EFFECT OF DIFFERENT HISTORIES

If strain ϵ_0 is reached at time t_1 by distinct strain histories (b) and (c) as well as (a), as shown in Figure 1.3, the same stress is required at time t_1 and is independent of the strain rate or how the value at time t_1 is reached. The same statements would hold if stress σ_0 were reached at time t_1 by different stress histories.

The above behavior suggests that for each value of strain ϵ there corresponds a unique value of stress σ . Whenever the strain is ϵ_0 , the corresponding stress at that instant is always σ_0 . It is then possible to eliminate t between the $\epsilon-t$ and the $\sigma-t$ plots and produce the unique stress-strain plot shown in Figure 1.4. The stress-strain relation becomes $\sigma(t) = E\epsilon(t)$.

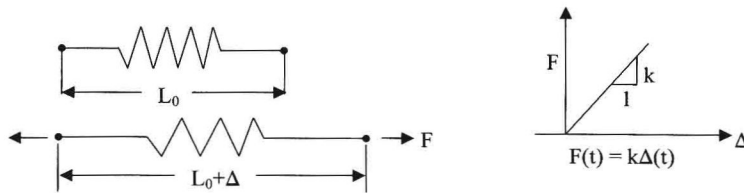


Figure 1.2. Linear elastic solid. Left: mechanical analog – linear spring. Right: force–elongation relation for the spring.

ENERGY DISSIPATION

If an elastic specimen is deformed and then returned to its original shape, the work done is zero. No energy is dissipated.

EFFECT OF SINUSOIDAL OSCILLATIONS

If $\varepsilon(t) = \varepsilon_0 \sin \omega t$ then $\sigma(t) = \sigma_0 \sin \omega t$. Stress and strain are in phase and their amplitude ratio does not vary with ω , as shown in Figure 1.5.

1.3 Response of a Classical Viscous Fluid

The one-dimensional mechanical response of a linear viscous fluid is often represented by a mechanical analog, the viscous damper (a piston in an oil bath in a cylinder) shown in Figure 1.6. The response of the viscous damper is characterized by a relation between force F and elongation rate, denoted by $d\Delta/dt = \dot{\Delta}$. The force–elongation rate relation for a linear viscous damper is then $F = c\dot{\Delta}$, where c is the viscosity. This relation is assumed to be valid under all conditions. This suggests that the linear viscous fluid is described by a relation between stress and strain rate of the form $\sigma = \mu \dot{\varepsilon}$, in which μ represents a fluid material property, its viscosity. We now consider a number of stress–time and strain–time experiments which enable us to see the implications of this relation.

STRESS CONTROL TEST, RESPONSE TO STEP STRESS

If the stress is increased to σ_0 at time zero and then held constant, a linear viscous fluid does not reach a fixed deformed state. There is continued straining in time, that is, the material flows. At constant stress σ_0 the strain rate $\dot{\varepsilon}$ becomes constant, as shown in curves (a) of Figure 1.7.

RELEASE OF STRESS

If the stress σ is released at time t_2 , the strain ε does not change. No strain is recovered. The strain stays constant, and the strain rate reduces instantaneously to zero. There is no tendency for the material to return to a previous shape.

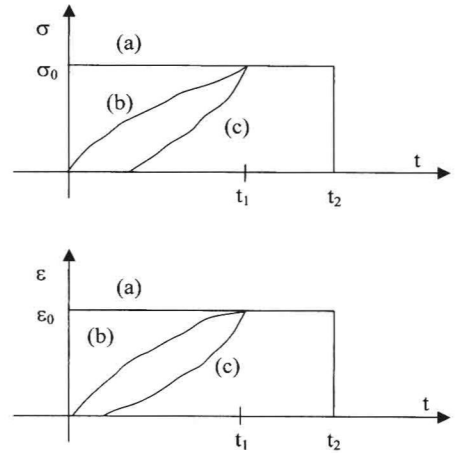
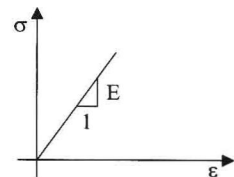


Figure 1.3. Mechanical response of a linear elastic solid. Top: several stress histories. Bottom: corresponding strain histories.

Figure 1.4. Stress–strain plot for a linear elastic solid.



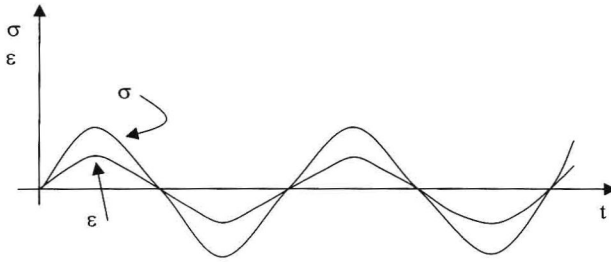


Figure 1.5. Sinusoidal stress and strain histories for a linear elastic solid.

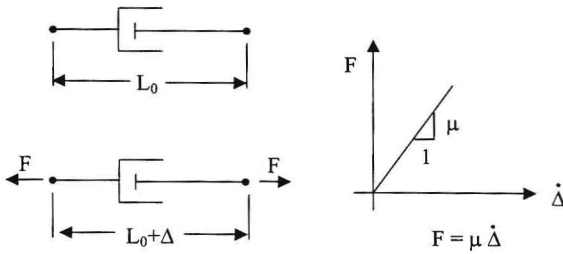


Figure 1.6. Linear viscous damper. Left: mechanical analog – linear viscous damper. Right: force–elongation rate relation.

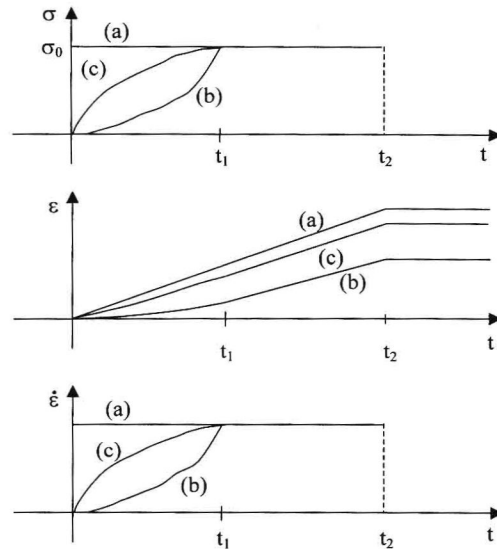
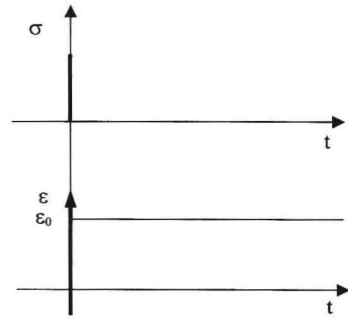


Figure 1.7. Mechanical response of a linear viscous fluid. Stress histories (top). Corresponding strain (middle) and strain rate (bottom) histories.

Figure 1.8. Linear viscous fluid: response to a step strain test.



STRAIN CONTROL TEST, RESPONSE TO STEP STRAIN

Suppose the strain is increased instantaneously to ε_0 and then held fixed. A very large stress is needed to produce the sudden shape change. If the strain is held constant for $t > 0$, the stress required to maintain this strain reduces immediately to zero. The stress is then zero for all times $t > 0$. This is shown in Figure 1.8.

EFFECT OF DIFFERENT STRAIN HISTORIES

Suppose that the strain rate $\dot{\varepsilon}$ is reached at time t_1 by strain sequences (b), (c) as well as (a), as shown in Figure 1.7. The same stress is required for each sequence at time t_1 . Note that for each strain sequence, there is a different amount of strain at time t_1 . In general, there can be any value of strain at time t_1 corresponding to the stress at time t_1 . On the other hand, there appears to be only one value of strain rate at time t_1 which corresponds to this stress. We conclude that the stress at time t_1 depends neither on the strain at time t_1 nor on the previous sequence of strain values. It depends only on the strain rate at time t_1 .

If time t is eliminated between the σ - t and the ε - t graphs, the single graph in Figure 1.9 is produced which is described by the relation $\sigma(t) = \mu \dot{\varepsilon}(t)$.

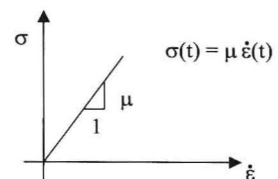
ENERGY DISSIPATION

If the specimen is deformed from its original shape and then restored to that shape, the work is completely converted to thermal energy.

EFFECT OF SINUSOIDAL OSCILLATION

If $\varepsilon(t) = \varepsilon_0 \sin \omega t$ then $\sigma(t) = \mu \varepsilon_0 \omega \sin(\omega t + \pi/2)$. The stress and strain are 90° out of phase and their amplitude ratio varies with frequency (see Figure 1.10).

Figure 1.9. Stress-strain rate plot for a linear viscous fluid.



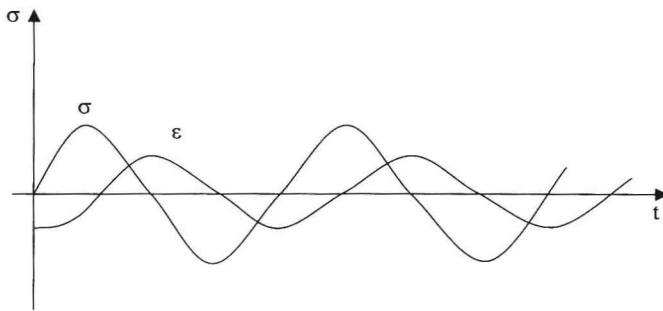


Figure 1.10. Sinusoidal stress and strain histories for a linear viscous fluid.

1.4 Comments on Material Microstructure

When an external force is applied to a piece of material, internal forces are produced. The material develops the ability to produce this internal force by distortion of its underlying physical structure. For example, metals have an atomic crystalline structure, with strong interatomic forces. Elastic response is due to large cohesive interatomic forces brought into play by small deformation of the crystalline structure. Fluids such as air and water are composed of molecules which exert weak attractive forces on each other. Internal forces are built up by the continuous movement of particles with respect to each other, which is seen as fluid flow.

Viscoelastic behavior involves qualities of both elastic solid and viscous fluid like response. This is due to the nature of the material microstructure. Viscoelastic response occurs in a variety of materials, such as soils, concrete, cartilage, biological tissue, and polymers. Soils and cartilage can be thought of as materials consisting of a porous solid material filled with fluid. Time-dependent response is due to the flow of the fluid in the pores as well as the distortion of the porous solid.

Viscoelastic phenomena in polymers and biological materials appear to be related to the movement of flexible thread-like long chain molecules, called macromolecules. They span an average volume which is much greater than atomic dimensions. In order to develop internal forces, these macromolecules must undergo changes in configuration. These shape changes involve molecular rearrangements on various scales (Figure 1.11):

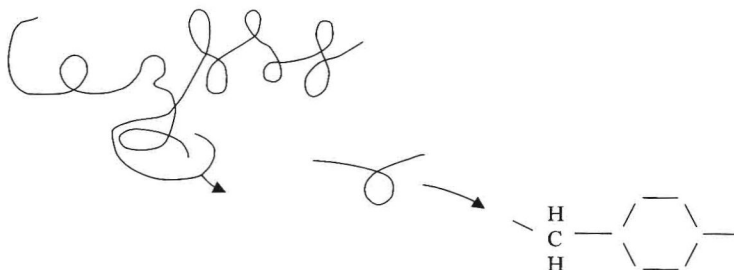


Figure 1.11. Scales of structure of macromolecules.

1. gross long-range contour rearrangements which are slowly achieved,
2. rearrangements on a more local level, which are more rapidly achieved,
3. reorientation of bonds on the chain backbone on the atomic scale.

In other words, rearrangements occur on a broad range of time scales.

The distinction between solid and fluid response is related to the cross-linking of macromolecules (see Figure 1.12). If macromolecules are cross-linked, that is, attached to one other, they form a network in which there is a maximum possible amount of deformation. If the stress is removed, the intermolecular force caused by cross-linking causes the network to return to its original configuration. If the macromolecules are not cross-linked, they can slide over one another. Under constant stress, they continue to slid over one another and flow. If the stress is removed, there are no intermolecular forces to cause the macromolecules to return to their original arrangement.

1.5 Response of a Viscoelastic Material

STRESS CONTROL TEST, RESPONSE TO STEP STRESS

Let the stress be instantaneously increased to σ_0 at $t = 0$ and then be held fixed. The typical response, as shown in Figure 1.13, consists of:

1. an instantaneous increase in strain OA ,
2. continued straining in time at a non-constant rate, ABC .

The strain OA is thought of as an instantaneous elastic response. The strain sequence ABC is a combination of elastic and viscous effects. If the material is solid-like, the strain asymptotically approaches a constant value ε_0 . If the material is fluid-like, the strain rate $\dot{\varepsilon}$ asymptotically approaches a constant value.

RELEASE OF STRESS

If the stress is reduced to zero at time t_1 , there is typically:

1. some instantaneous strain recovery CD ,
2. delayed recovery DEF .

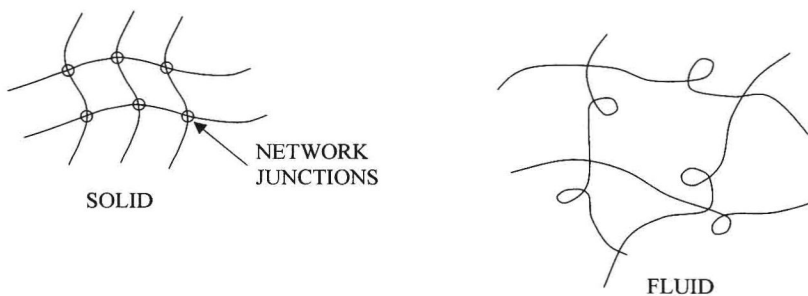


Figure 1.12. Solid: macromolecular network with junctions. Fluid: macromolecular network with no junctions.