NONLINEAR VISCOELASTICITY

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Contents

Summary

When a viscoelastic material is subjected to a deformation that is neither very small nor very slow, its behavior is no longer linear, and there is no universal rheological constitutive equation that can predict the response of the material to such a deformation. Equations based on continuum concepts are empirical in nature, while those based on molecular models are not yet able to make reliable predictions for polymers with broad molecular weight distributions or long-chain branching. While molecular models, in particular those based on the concept of a molecule in a tube, are not useful for quantitative predictions of polymers with complex structures, the relaxation mechanisms that are assumed to occur in these models provide a useful basis for categorizing responses to various deformations. Molecular orientation is the mechanism responsible for linear viscoelastic phenomena, but in large, rapid deformations, it is responsible for new phenomena, particularly normal stress differences in shear flow. A phenomenon that comes into play only for large, rapid deformations is chain stretch. Among shearing deformations, step strain is most effective in generating chain stretch, but extensional flows are naturally more effective in generating stretch. Extensional flow properties are particularly sensitive to the presence of long-chain branching. The other new relaxation mechanism that contributes to nonlinearity is convective constraint release, which is most prominent in steady simple shear at significant shear rates. This relaxation mechanism is responsible for the strong effect of shear rate on the viscosity and normal stress differences. Capillary and cone-plate rheometers are used for the study of nonlinear shear behavior. The former is useful for the measurement of viscosity at high shear rates, while the latter can be used to measure viscosity and normal stress differences and the responses to transient shear deformations. However, rotational rheometers are limited to use at low shear rates.

1. Introduction

Linear viscoelastic behavior is exhibited by a material that is subjected to a deformation that is either very small or very slow. Linear properties are of interest, because they are closely related to molecular structure. On the other hand, the industrial processing of viscoelastic materials always involves large, rapid deformations in which the behavior is nonlinear. Virtually all viscoelastic materials of practical importance are polymeric, and this section deals with concentrated solutions and melts in which the concentration and molecular weight are such that there are strong interactions, called entanglements, between the molecules.

We indicate components of the stress tensor as σ_{ij} where the second index indicates the direction of the force, and the first index indicates the face of a fluid element on which it acts. We adopt the standard sign convention of mechanics in which a tensile stress has a positive value. Shear stresses ($i \neq j$) always generate deformation in liquids, but an isotropic normal stress ($i = j$) generates no deformation in an incompressible material. In other words, only differences in normal stresses can generate deformation and have rheological significance.

For linear behavior, the Boltzmann superposition principle describes the response to any deformation, as long as it is very small or very slow. But the nonlinear world is a much more complex realm in which there is no such unifying principle. One approach to describing nonlinear behavior is based on continuum mechanics principles and attempts to establish a rheological constitutive equation to replace the Boltzmann principle. While continuum mechanics models sometimes contain elements inspired by molecular or thermodynamic concepts, they are basically empirical. This means that their applicability outside of the conditions under which their predictions can be tested by experiment is unreliable. Another approach is to build up a model of flow behavior starting from a picture of the material at the molecular level. This is an enormously complex undertaking, and some degree of success has been achieved only when the problem is drastically simplified by the use of a *mean field* theory, in which attention is focused on one molecule, with the influence of the surrounding molecules modeled by representing them as a tube or a series of slip-links that severely restrict the motion of the molecule of interest. Over the past twenty years great effort has been put into developing and improving such models, and considerable progress has been made. In this chapter, both the continuum and tube-model approaches to nonlinear viscoelasticity will be used to build a broad understanding of nonlinear phenomena. A more detailed treatment of all the topics included in this section can be found in the book by Dealy and Larson (2006).

2. A Continuum Mechanics Description of Nonlinear Phenomena

A thorough treatment of rheological constitutive equations is provided in *Constitutive Modeling of Viscoelastic Fluids* of this encyclopedia and by Larson (1988). We wish here only to develop a basic understanding of nonlinear phenomena. We will build a continuum description starting from the solid foundation provided by the Boltzmann superposition principle that was introduced in *Linear Viscoelasticity*. One statement of this principle is given by Eq. (1).

$$\sigma_{ij}(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}_{ij}(t')dt' \qquad (1)$$

where $\sigma_{ij}(t)$ is a typical component of the extra stress tensor at time t, $\dot{\gamma}_{ij}(t')$ is a typical component of the rate of deformation tensor evaluated at the time t', and $G(t\text{-}t')$ is the relaxation modulus evaluated at a time equal to the length of time from a past time t' up to t, the time at which the stress is to be evaluated. The extra stress is the portion of the total stress that is related to deformation and does not include an isotropic contribution to the stress that is not related to deformation in an incompressible material. Both the stress and the rate of strain tensors have nine components that are functions of time and position in space, but they are symmetrical tensors, so only six components are independent. A polymeric liquid has a fading memory, which means that as time passes, the strain that occurred at a given past time t' has less and less influence on the stress at time t as t increases. This implies that the relaxation modulus approaches zero at a sufficiently long time, *i.e.*, $G(\infty)=0$.

To begin our discussion of nonlinear constitutive equations we look at the features of Eq.

(1) that fail to describe nonlinear behavior. One basic limitation of Eq. (1) is that the product of the strain rate tensor and the time interval dt' is not able to describe large strains. In preparation for the introduction of a strain tensor describing finite strains, we first rewrite Eq. (1) in terms of the infinitesimal strain tensor, whose components are γ_{ij}. This tensor is defined on page 31 of the book by Dealy and Wissbrun (1999), and it will suffice for our purpose to say that it is totally adequate to describe very small deformations.

A strain tensor describes the shape and volume of a material element at a given time t_1 relative to its shape at some reference time t_0. In other words, strain is a measure of the amount of deformation that occurs in a material element between times t_0 and t_1. A typical component of the infinitesimal strain tensor is $\gamma_{ij}(t_o, t_1)$. If the components of the strain rate tensor at intermediate times are $\dot{\gamma}_{ij}(t'')$, the components of the strain tensor at time t_1, relative to the state of the fluid element at time t_0, are given by:

$$\gamma_{ij}(t_0,t_1) = \int_{t_0}^{t_1} \dot{\gamma}_{ij}(t'')dt'' \tag{2}$$

In dealing with large strains, it is obviously necessary to establish the reference state of a fluid element, *i.e.*, its state at time t_0. For a cured rubber, there is a unique configuration that the material will always return to when the extra stress is zero, and a time when the element was in this configuration is the obvious choice for the reference time. For a melt, there is no such unique, unstrained state, so some other reference time must be selected. In a laboratory experiment in which a sample is initially in a given, stress-free configuration, the time at which the deformation begins is an obvious reference time. For example, for a step strain experiment, the relaxation modulus $G(t)$ is measured as a function of the time from the instant of the initial strain ($t = 0$). Thus it is convenient to let $t_0 = 0$.

However, in general, as time passes, the configuration at any given time in the past will have less and less relevance to the present state of stress in the sample, which is reflected in the fact that $G(t - t_0 = \infty) = 0$. Thus, for purposes of writing a general description of viscoelastic behavior, *i.e.*, a constitutive equation, the only time during the strain history that is unique and continues to be relevant as time passes is the current time t, *i.e.*, the time at which the stress is to be evaluated. Thus, we adopt this as the reference time for use in describing large strains and consider deformations occurring at previous times, t', relative to the configuration of a fluid element at the present time t. We note that from Eq. (2) if the strain rate is always positive, then:

$\gamma_{ij}(t,t') = 0$ when $t' = t$

$\gamma_{ij}(t,t') < 0$ when $t' < t$

We can now obtain the basic principle of linear viscoelasticity, which gives the stress at time t resulting from any strain occurring over past times t', by integrating Eq. (2) by parts and recalling that $G(\infty) = 0$:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} m(t-t')\gamma_{ij}(t,t')dt' \tag{3}$$

where $m(t\text{-}t')$ is the linear memory function, which is related to $G(t\text{-}t')$ as follows:

$$m(t-t') = \frac{dG(t-t')}{dt'} = -\frac{dG(s)}{ds} \tag{4}$$

with $s \equiv t\text{-}t'$

Now we return to our objective of examining the ways in which Eq. (1) and its equivalent Eq. (3) fail to describe the behavior of polymeric liquids when the deformation is large and fast. As noted above a fundamental limitation of Eq (1) and its equivalent, Eq. (3) is that the infinitesimal strain tensor cannot describe large deformations. In fact there are many deformation tensors capable of describing large strains, but one that has proven especially useful in describing polymeric liquids is the Finger tensor, the components of which we represent as B_{ij}. This tensor is defined, for example, in the books by Dealy and Wissbrun (1999) and by Dealy and Larson (2006). In order to introduce nonlinear concepts, Lodge (1964) wrote a very simple model of nonlinear behavior by simply replacing the infinitesimal tensor $\gamma_{ij}(t,t')$ in Eq. (3) by the Finger tensor $B_{ij}(t,t')$. He called the material described by this model a *rubberlike liquid*. Its constitutive equation is shown as Eq. (5).

$$\sigma_{ij}(t) = \int_{-\infty}^{t} m(t-t')B_{ij}(t,t')dt' \tag{5}$$

The use of the Finger tensor to build a model for the response of a material to large deformations implies that the deformation is *affine*. This means that the strain at the microscopic level, *i.e.*, of the molecules, is the same as the strain in a macroscopic sample. This forces the segments of the chain to orient accordingly and may also require the chain to be stretched beyond its equilibrium contour length. Thus, the use of the Finger tensor is not adequate by itself to describe large departures of polymeric liquids from linearity.

The rubberlike liquid exhibits a few nonlinear viscoelastic phenomena. In particular, some effects arising from the finite orientation of chain segments are predicted, for example a nonzero first normal stress difference. However, it fails to describe many other nonlinear effects. For example, it predicts that the viscosity is constant with shear rate. In fact, all its predictions for the shear stress in simple shear are the same as those of the Boltzmann superposition principle. Let us see if a further modification of the Boltzmann principle can bring us closer to describing nonlinear behavior.

Wagner (1979) proposed the introduction of a nonlinear memory function to correct some of the deficiencies of the rubberlike liquid model. Inspired by the fact that the relaxation of stress following a large step strain can often be separated into time-dependent and strain-dependent factors, Wagner proposed the use of a memory function defined as the product of the linear function $m(s)$, defined by Eq. (4) and a nonlinear scalar function called the *damping function*. This function $h(I_1, I_2)$ depends on the Finger strain tensor through its *scalar invariants*. Whereas a vector has only one scalar invariant, its magnitude, a second order tensor has three. But for a material of uniform density, which we assume here, the Finger tensor has only two non-zero scalar invariants, which we represent as I_1 and I_2. Wagner's model can then be written as follows:

$$\sigma_{ij}(t) = \int_{-\infty}^{t} m(t-t')h(I_1, I_2)B_{ij}(t,t')dt' \qquad (6)$$

In this model the damping function $h(I_1, I_2)$ is an empirical function whose parameters are determined by fitting experimental data. Thus, Eq. (6) does not have general predictive capabilities, but it has been found useful in the interpretation of experimental data and has been used in simulating some flows of practical importance. As a result of the introduction of the damping function, Wagner's equation (6) predicts shear thinning, *i.e.*, the decrease of viscosity with shear rate.

3. Molecular Theories of Viscoelasticity

Our principal concern here is the relationship between rheological behavior and molecular structure in highly entangled polymers. Thus, the fast, localized molecular motions that dominate the behavior of unentangled systems, such as very dilute solutions and low molecular weight melts, are not of primary interest to us. However, the Brownian motion that every element of a molecule is constantly undergoing is ultimately the cause of all relaxation phenomena, and some key parameters that arise in the modeling of the dynamics of unentangled polymers will be found to carry through into models of entangled ones. Thus, we begin our treatment of polymer dynamics by describing a theory for unentangled polymers.

3.1. The Rouse-Bueche Model for Unentangled Polymers

It is not feasible to model the dynamics of a single long polymer molecule in a very dilute solution starting from an atomically detailed picture of the molecule because of the number of bonds involved and the limitations on the motion of the backbone bonds with respect to each other. However, it is possible to obtain useful results by means of a much simpler approach as long as we do not wish to account for the very short-range motions that govern the fast early stages of relaxation after a deformation. In this case, many useful results can be obtained by considering the molecule to be made up of a number of *submolecules*, each containing enough backbone bonds to behave like a unit in a freely-jointed, Gaussian chain. It turns out that about ten backbone bonds are required to form a submolecule that acts like a single link in a freely-jointed chain, so an entire molecule must contain many such units. For typical, flexible synthetic polymers the minimum number of such units is about 100. In other words, order that the description of an entire molecule be sufficiently detailed to model its viscoelastic behavior, it must contain many submolecules, so the submolecule must be much smaller than the macromolecule. It is important to note that this model will be unable to describe the very fast initial response to a deformation, as this involves short-range interactions between segments of the molecule that are within a submolecule, and these are not accounted for in the model.

Dealy and Larson (2006) have explained how Bueche modified a model originally proposed by Rouse for polymer solutions to treat unentangled (low-molecular weight) polymers. The resulting model predicts the relaxation modulus given by Eq. 7.

$$G(t) = \frac{\rho RT}{M}\sum_{p=1}^{N} e^{-t/\tau_p} \qquad (7)$$

The *Rouse relaxation times* τ_p play a central role in all the relaxation models discussed here, as they govern the time scales for the basic molecular motions that are involved, directly or indirectly, in all relaxation processes. The Rouse time corresponding to $p = 1$ is the *longest Rouse relaxation time* τ_{R}:

$$\tau_{\mathrm{R}} = \frac{6\eta_0 M}{\pi^2 \rho RT} \qquad (8)$$

We see that the theory predicts that the viscosity is proportional to the molecular weight.

$$\eta_0 = \frac{b^2 M\zeta \ \rho N_A}{36 M_0^2} \qquad (9)$$

where b is a characteristic segment length, M and M_0 are the molecular weights of the polymer and monomer respectively, N_{A} is Avogadro's number, and ζ is the monomeric friction coefficient.

In the *terminal zone*, when t is a long time after a step strain, the relaxation modulus approaches a single exponential obtained by noting that $p = \tau_{\mathrm{R}} / p^2$

$$G(t) = \frac{\rho RT}{M}\exp(-t/\tau_{\mathrm{R}}) \text{ (long-time limiting behavior)} \qquad (10)$$

The steady-state compliance is another property that arises from behavior in the limit of long times and is given by:

$$J_s^0 = 0.40\frac{M}{\rho RT} \qquad (11)$$

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Biographical Sketch

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