

6 Linear Viscoelasticity

Chapter Outline

6.1	Introduction	310
6.2	Small Strain Linear Viscoelasticity	310
6.2.1	Stress Relaxation Behavior	313
6.2.2	Monotonic Loading Response	314
6.2.3	Cyclic Loading Response	320
6.2.4	Experimental Determination of the Storage and Loss Moduli	322
6.2.5	Representing Linear Viscoelasticity Using Spectra	328
6.2.6	Computer Implementation	329
Matlab Implementation	329	
Python Implementation	330	
6.3	Large Strain Linear Viscoelasticity	331
6.3.1	Numerical Implementation	332
6.4	Creep Compliance Behavior	335
6.4.1	Relationships Between Creep Compliance and Relaxation Modulus	336
6.5	Differential Form of Linear Viscoelasticity	337
6.5.1	Rheological Models	338
Maxwell Model	338	
Multi-Network Maxwell Model	339	
6.6	The Use of Shift Functions to Generalize Linear Viscoelasticity Theory	340
6.6.1	Time-Temperature Equivalence	341
6.6.2	Vertical Shifts	345
6.7	Use of Linear Viscoelasticity in Polymer Modeling	345
6.8	Exercises	349
	References	350

6.1 Introduction

Many polymeric materials exhibit a combination of elastic and viscous responses when subjected to external loads and displacements. The simplest way to model this combined behavior is through *linear viscoelasticity*, which is a material model framework that has been used extensively for many years and its mathematical foundation has been extensively studied [1–3].

The following sections present the basic theory of linear viscoelasticity in relative detail, more advanced concepts and models that extend linear viscoelasticity are discussed in later chapters. The theory that is presented is derived from simple arguments, and is closely tied to the linear elastic and hyperelastic models that were discussed in the previous chapter.

6.2 Small Strain Linear Viscoelasticity

This section summarizes the theory for small strain linear viscoelasticity. That is, a material model framework based on linear elasticity with linear viscoelasticity. The more general large strain viscoelasticity that is based on hyperelasticity and linear viscoelasticity is discussed in [Section 6.3](#).

The foundation of linear viscoelasticity is Boltzmann's superposition principle [4]. One way to state this linear superposition principle is through the statement:

Each loading step makes an independent contribution to the final state.

This formulation of the Boltzmann superposition principle can be used to create an integral equation representation of linear viscoelasticity. The approach is to perform a though experiment in which a step function in strain is applied: $\varepsilon(t) = \varepsilon_0 H(t)$, and the stress response $\sigma(t)$ is measured, see [Figure 6.1](#). In this equation $H(t)$ is the Heaviside step function defined by:

$$H(t) = \begin{cases} 0, & \text{if } t < 0, \\ 1/2, & \text{if } t = 0, \\ 1, & \text{if } t > 0. \end{cases} \quad (6.1)$$

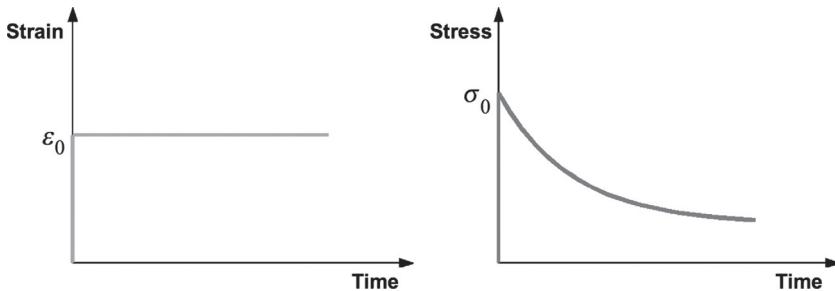


Figure 6.1 Stress relaxation experiment in which the applied strain is rapidly ramped from 0 to ε_0 and then held constant during which the stress response is monitored.

In this section we are only considering small deformations, and only load cases with one non-zero stress component (such as uniaxial loading).

The stress response from the strain jump experiment can be used to define a stress relaxation modulus:

$$E_R(t) \equiv \frac{\sigma(t)}{\varepsilon_0}. \quad (6.2)$$

Note that the applied strain jump ε_0 does not have to be infinitesimal when calculating the stress relaxation modulus due to the assumed superposition principle.

To develop a model capable of predicting the stress response due to an arbitrary applied strain history, and not only a step in strain, we will start by decomposing the strain history into a sum of infinitesimal strain steps:

$$\varepsilon(t) = \sum_{i=1}^{\infty} \Delta\varepsilon_i H(t - \tau_i), \quad (6.3)$$

where $\Delta\varepsilon_i$ is the strain increment applied at time τ_i , see [Figure 6.2](#).

The total stress response from applying this strain history can be obtained from the superposition principle:

$$\sigma(t) = \sum_{i=1}^{\infty} \Delta\varepsilon_i E_R(t - \tau_i). \quad (6.4)$$

This stress response can be written in integral form as the number of strain increments goes to infinity:

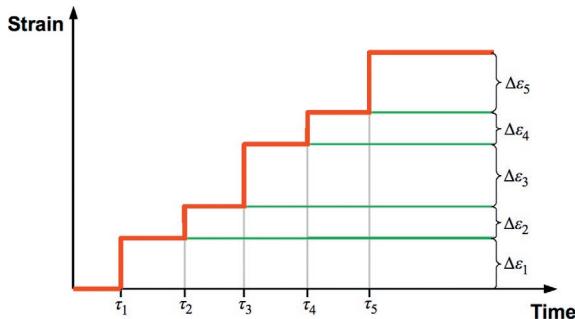


Figure 6.2 The applied strain history can be represented as number of discrete time increments.

$$\sigma(t) = \int_{-\infty}^t E_R(t - \tau) d\epsilon(\tau) = \int_{-\infty}^t E_R(t - \tau) \frac{d\epsilon(\tau)}{d\tau} d\tau. \quad (6.5)$$

Note that if the material response is purely elastic (i.e. $E(t) = E_0$), then the stress response becomes equal to Hooke's law: $\sigma(t) = E_0\epsilon(t)$. Also, once $E_R(t)$ has been determined then Equation (6.5) can be used to predict the stress response due to any imposed strain history.

In order to create a complete material model, the results presented so far need to be generalized into a three-dimensional form suitable for arbitrary deformation histories and finite element analysis. The most common way to do this is to separate the stress and strain into deviatoric and volumetric parts, similarly to what is commonly done for hyperelastic models as discussed in Chapter 5:

$$\sigma(t) = \int_0^t 2\mu_R(t - \tau) \dot{\epsilon}_{dev} d\tau + \int_0^t \kappa_R(t - \tau) \dot{\epsilon}_{vol} d\tau. \quad (6.6)$$

In this equation σ is the Cauchy stress tensor, $\mu_R(t)$ is the stress relaxation shear modulus, $\dot{\epsilon}_{dev} = \frac{d}{dt}[\text{dev}[\epsilon]]$ the time derivative of the applied deviatoric strain tensor, $\kappa_R(t)$ the stress relaxational bulk modulus, and $\dot{\epsilon}_{vol} = \frac{d}{dt}[\text{vol}[\epsilon]]$ the time derivative of the applied volumetric strains.

In this formulation only two relaxation moduli need to be determined in order to predict any arbitrary deformation: the shear and bulk relaxation moduli. For most polymeric materials, the volumetric relaxation is typically much smaller and less

influential than the deviatoric relaxation. It is therefore often possible to neglect the volumetric flow response. This assumption makes it possible to obtain the shear relaxation modulus from the uniaxial relaxation modulus by:

$$\mu_R(t) = \frac{E_R(t)}{3 - E_R(t)/(3\kappa)}, \quad (6.7)$$

which can be approximated as $\mu_R(t) = E_R(t)/3$ if $\kappa \gg E$.

The linear viscoelastic stress-strain equations in Equation (6.6) can be generalized to anisotropic materials (see also Section 5.2.2) by replacing the shear and bulk relaxation moduli with anisotropic relaxation moduli:

$$\sigma_{ij}(t) = C_{ijkl}(0)\varepsilon_{kl}(t) + \int_0^t \varepsilon_{kl}(t-\tau) \frac{dC_{ijkl}(\tau)}{d\tau} d\tau. \quad (6.8)$$

Here C_{ijkl} is the time-dependent stiffness relaxation tensor that need to be determined from experimental data.

6.2.1 Stress Relaxation Behavior

As illustrated in the previous section, a linear viscoelastic model is completely characterized by its stress relaxation moduli. This section presents a selection of commonly used functional forms of the stress relaxation moduli.

First, as an example, consider a polymer sample that is uniaxially loaded and that has a stress relaxation modulus that is exponentially decaying:

$$E_R(t) = \begin{cases} E_0 \exp(-t/\tau_0), & \text{if } t \geq 0, \\ 0, & \text{if } t < 0, \end{cases} \quad (6.9)$$

where E_0 is the instantaneous Young's modulus, and τ_0 the characteristic relaxation time, see Figure 6.3 for a graphical representation. The characteristic relaxation time is here defined as the time at which the modulus has decayed down to 36.7%¹ of its original value.

¹36.7% is an approximation of the value $1/e$.

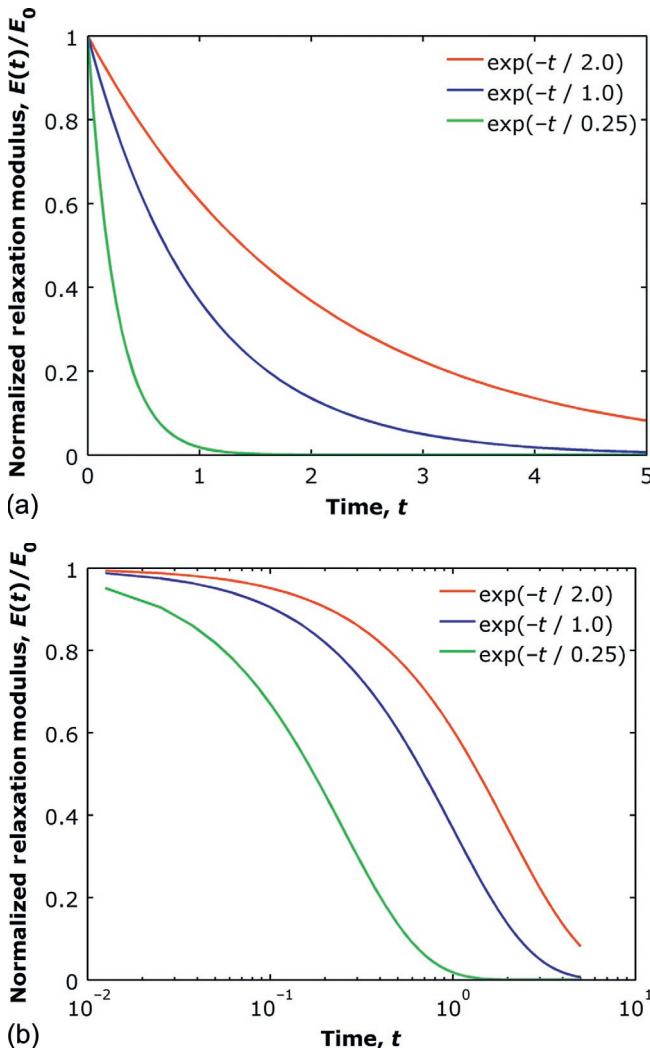


Figure 6.3 Relaxation modulus as a function of time. Figure (a) shows the relaxation modulus as a function of time on a linear scale, and figure (b) shows the relaxation modulus as a function of time on a logarithmic scale.

6.2.2 Monotonic Loading Response

Now consider a load case in which the applied strain is increasing linearly with time:

$$\varepsilon(t) = \begin{cases} 0, & \text{if } t < 0, \\ \dot{\varepsilon}_0 t, & \text{if } t \geq 0. \end{cases} \quad (6.10)$$

Inserting this strain history into Equation (6.5) gives the stress

$$\sigma(t) = \int_0^t E_0 \dot{\varepsilon}_0 \exp\left[-\frac{(t-\tau)}{\tau_0}\right] d\tau, \quad (6.11)$$

which can be simplified to:

$$\sigma(t) = E_0 \dot{\varepsilon}_0 \tau_0 \left[1 - \exp\left(\frac{-t}{\tau_0}\right) \right], \quad (6.12)$$

or when expressed in terms of applied strains:

$$\sigma(t) = E_0 \dot{\varepsilon}_0 \tau_0 \left[1 - \exp\left(\frac{-\varepsilon}{\dot{\varepsilon} \tau_0}\right) \right]. \quad (6.13)$$

This stress-strain response is plotted in Figure 6.4 illustrating that a small characteristic relaxation time τ_0 corresponds to fast relaxation and more viscous response.

From Equation (6.11) it is also clear that at a fixed time, the stress response is always predicted to be proportional to the applied strain rate; but at a fixed strain, the stress is not a linear function of the applied strain rate. Furthermore, by introducing a characteristic strain $\hat{\varepsilon} \equiv \dot{\varepsilon} \tau_0$ it is clear that for $\varepsilon \gg \hat{\varepsilon}$ the stress $\sigma \rightarrow E_0 \hat{\varepsilon} = E_0 \dot{\varepsilon} \tau_0$. Also, when the applied strain is equal to $\hat{\varepsilon}$ the stress will have reached 63% of its final value.

More commonly, the stress relaxation function is written as the following normalized series expansion:

$$g_R(t) = \frac{E_R(t)}{E_0} = 1 - \sum_{i=1}^N g_i (1 - e^{-t/\tau_i}) \quad (6.14)$$

$$= \left(1 - \sum_{i=1}^N g_i \right) + \sum_{i=1}^N g_i e^{-t/\tau_i}. \quad (6.15)$$

This relaxation function is used, for example, by Abaqus [5], and is called a *Prony series*.

Figure 6.5 shows one example of a two-term Prony series plotted on a logarithmic time scale. The main differences between this relaxation function and the simple exponential relaxation

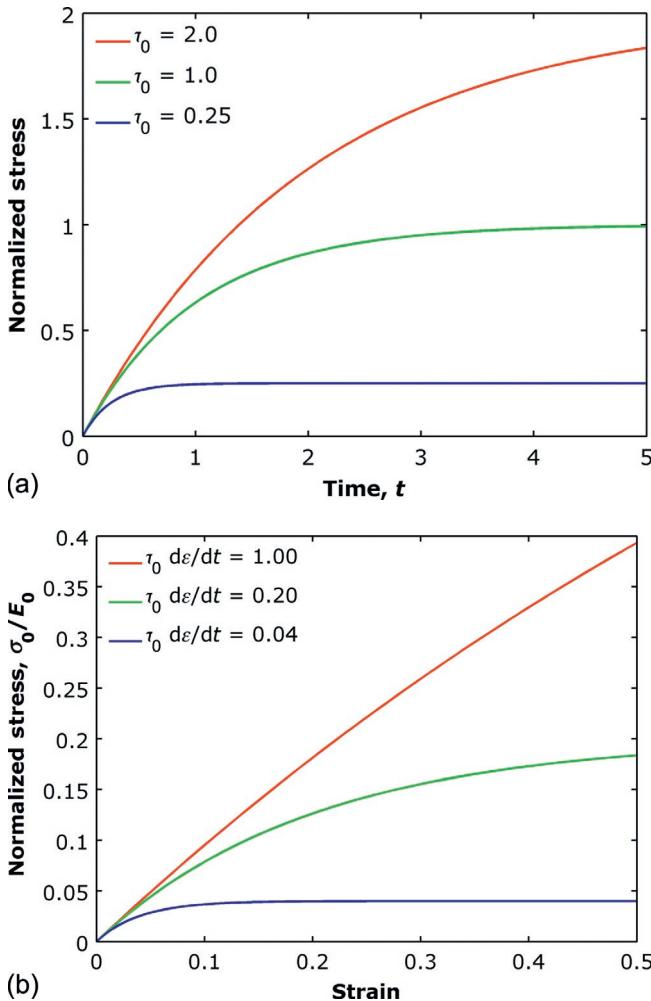


Figure 6.4 (a) Stress response as a function of time. (b) Stress response as a function of strain.

function in Equation (6.9) are that the modulus can stay finite as $t \rightarrow \infty$, and that multiple terms can be used to fit the relaxation function to experimental data.

The stress response in monotonic uniaxial loading for the stress relaxation modulus in Figure 6.5 is shown in Figure 6.6.

Another interesting but less used functional form of the relaxation modulus is the stretched exponential (often called the KWW form [6, 7]):

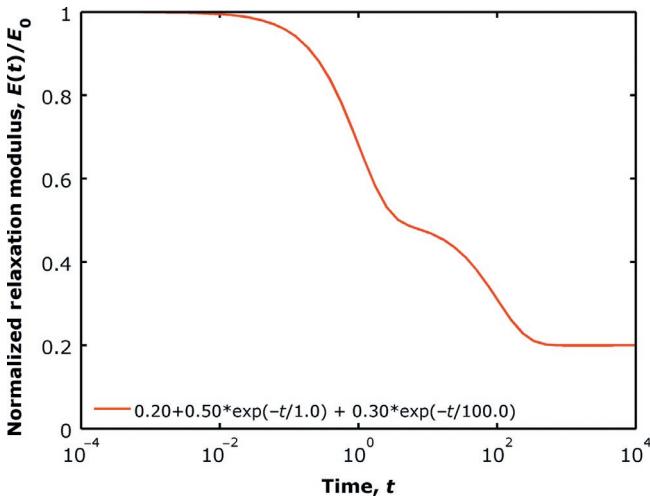


Figure 6.5 Exemplar 2-term Prony series.

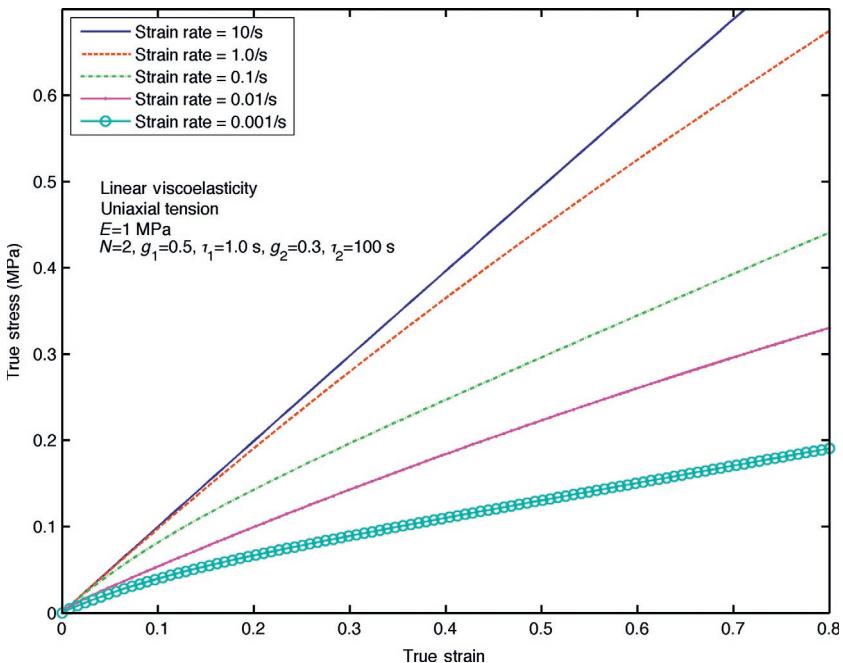


Figure 6.6 Predicted stress response from the Prony series shown in Figure 6.5.

$$E(t) = E_0 \exp \left[- \left(\frac{t}{\tau_0} \right)^\beta \right], \quad (6.16)$$

where E_0 , τ_0 , and β are material parameters, see Figure 6.7. With this representation, the relaxation modulus decreases down to 36.7% of its original value at the time $t = \tau_0$, and β specifies the shape of the relaxation function.

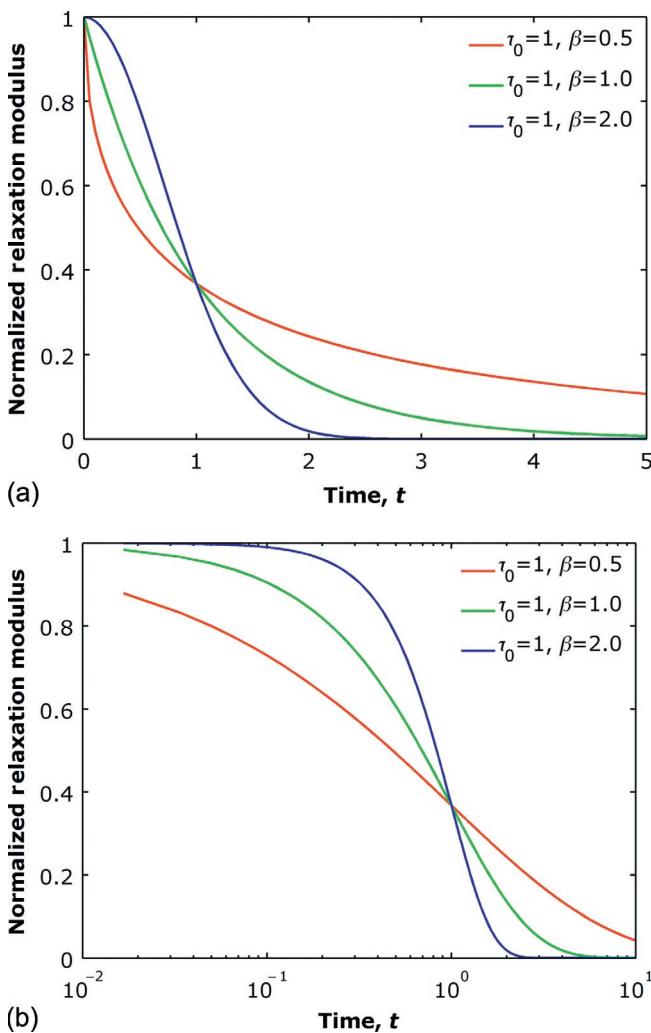


Figure 6.7 Stretched exponential stress relaxation modulus as a function of time. (a) Linear time, (b) Logarithmic time.

If we again consider a constant strain rate loading situation, the stress response becomes:

$$\sigma(t) = \int_0^t E_0 \dot{\epsilon} \exp \left[-\left(\frac{t}{\tau_0} \right)^\beta \right] dt, \quad (6.17)$$

which is not easy to solve in closed-form but can be solved numerically, see [Figure 6.8](#).

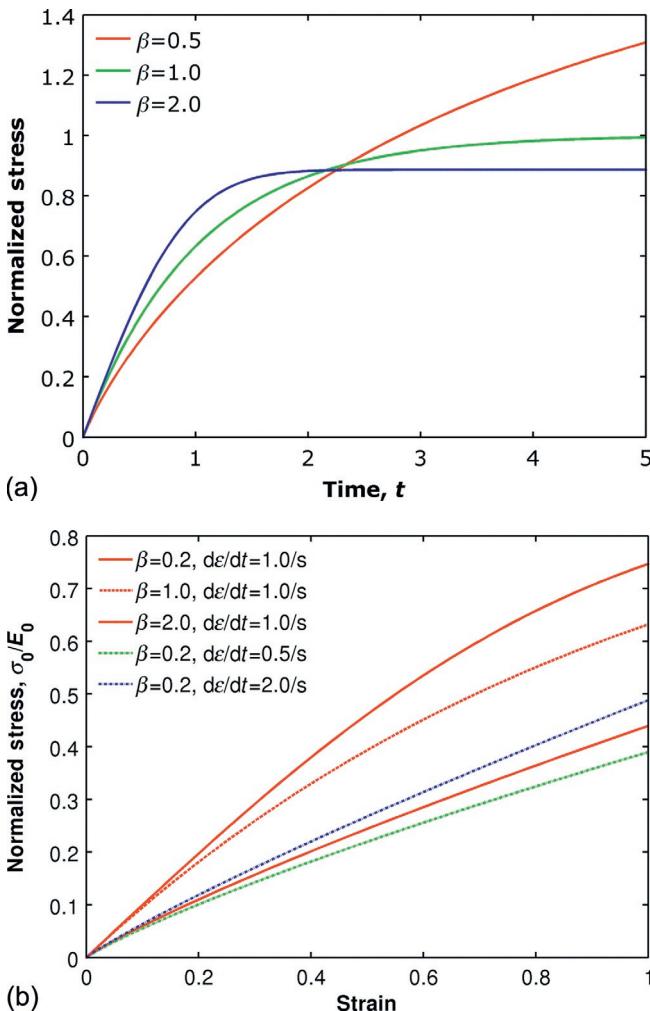


Figure 6.8 Stress response using the stretched exponential stress relaxation modulus, $\tau_0 = 1$ s.

Figure 6.8 shows that the parameter β strongly influences the shape of the stress-strain response.

6.2.3 Cyclic Loading Response

One of the more common applications of linear viscoelasticity is for predictions of the small-strain dynamic response of polymers. This section presents in more detail the response of a general linear viscoelastic model when exposed to a sinusoidal applied strain. Specifically, consider a case when the applied strain is given by:

$$\varepsilon(t) = \begin{cases} \varepsilon_0 \sin(\omega t), & \text{if } t \geq 0, \\ 0, & \text{if } t < 0. \end{cases} \quad (6.18)$$

The resulting stress response for this strain history can be obtained from Equation (6.5) giving:

$$\sigma(t) = \int_0^\infty E(s) \omega \varepsilon_0 \cos[\omega(t-s)] ds, \quad (6.19)$$

where $s \equiv t - \tau$. By using the relationship $\cos(\alpha - \beta) = \cos \alpha \cos \beta + \sin \alpha \sin \beta$, this equation can be expanded into

$$\begin{aligned} \sigma(t) = \varepsilon_0 \sin(\omega t) &\left[\omega \int_0^\infty E(s) \sin(\omega s) ds \right] \\ &+ \varepsilon_0 \cos(\omega t) \left[\omega \int_0^\infty E(s) \cos(\omega s) ds \right]. \end{aligned} \quad (6.20)$$

Note, the integrals in Equation (6.20) only converge if

$$\lim_{s \rightarrow \infty} E(s) = 0. \quad (6.21)$$

By defining two frequency-dependent functions: the *storage modulus* $E'(\omega)$ and the *loss modulus* $E''(\omega)$, the stress response can be defined by

$$\sigma(t) = \varepsilon_0 [E'(\omega) \sin(\omega t) + E''(\omega) \cos(\omega t)], \quad (6.22)$$

where

$$\begin{cases} E'(\omega) = \omega \int_0^\infty E(s) \sin(\omega s) ds, \\ E''(\omega) = \omega \int_0^\infty E(s) \cos(\omega s) ds. \end{cases} \quad (6.23)$$

The stress response can also be written

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta), \quad (6.24)$$

$$= \sigma_0 \sin(\omega t) \cos \delta + \sigma_0 \cos(\omega t) \sin \delta. \quad (6.25)$$

Hence,

$$\varepsilon_0 E'(\omega) = \sigma_0 \cos \delta, \quad (6.26)$$

$$\varepsilon_0 E''(\omega) = \sigma_0 \sin \delta, \quad (6.27)$$

giving

$$\tan \delta = \frac{E''}{E'}. \quad (6.28)$$

It is sometimes convenient to introduce a complex variable based notation for the dynamic moduli E' and E'' :

$$E^* = \frac{\sigma^*}{\varepsilon^*} = E' + iE''. \quad (6.29)$$

It is also possible to consider a stress driven oscillation giving a complex compliance:

$$J^* = \frac{\varepsilon^*}{\sigma^*} = \frac{1}{G^*} = J' - iJ''. \quad (6.30)$$

This approach is discussed in more detail in various texts [1]. It can be shown, for example, that the relationships between J' , J'' , E' , and E'' are:

$$J' = \frac{G'}{G'^2 + G''^2}, \quad (6.31)$$

$$J'' = \frac{G''}{G'^2 + G''^2}, \quad (6.32)$$

$$G' = \frac{J'}{J'^2 + J''^2}, \quad (6.33)$$

$$G'' = \frac{J''}{J'^2 + J''^2}. \quad (6.34)$$

These relations, whose derivations are left as an exercise, are not pursued in more detail in this text.

As a last example consider a shear relaxation function that is given by an exponential function:

$$G(t) = \begin{cases} G_0 \exp(-\alpha t) & \text{if } t \geq 0, \\ 0 & \text{if } t < 0 \end{cases} \quad (6.35)$$

and an applied strain that is sinusoidal:

$$\varepsilon(t) = \begin{cases} 0 & \text{if } t < 0, \\ \varepsilon \sin(\omega_0 t) & \text{if } t \geq 0. \end{cases} \quad (6.36)$$

In this case it can be shown that the stress response is given by the following equations:

$$\begin{aligned} \sigma(t) &= \int_0^t G_0 \exp(-\alpha \tau) \varepsilon \omega \cos(\omega \tau) d\tau \\ &= \frac{G_0 \varepsilon_0 \omega}{\alpha^2 + \omega^2} [\alpha \cos(\omega t) + \omega \sin(\omega t) - \alpha \exp(-\alpha t)]. \end{aligned} \quad (6.37)$$

The stress response consists of a transient term superimposed on a sinusoidal term that is out of phase with the applied strain. The response due to a sinusoidal strain history is studied in more detail in the next section.

6.2.4 Experimental Determination of the Storage and Loss Moduli

As discussed in Chapter 2, the dynamic properties of a polymer can be determined using a wide variety of loading modes and experimental techniques. This section presents the use of uniaxial sinusoidal loading to determine the storage modulus, loss modulus, $\tan(\delta)$, and the amount of hysteresis. The results presented here can easily be converted to other loading modes, for example simple or pure shear.

First, consider an experiment in which a specimen is uniaxially loaded with a sinusoidal strain history:

$$\varepsilon(t) = \varepsilon_m + \varepsilon_a \sin(\omega t), \quad (6.38)$$

where ε_m is the mean strain, ε_a is the strain amplitude, and ω is the angular frequency of the applied strain. Assume that the experimentally determined stress response is also sinusoidal with a mean stress σ_m and a stress amplitude σ_a , but is shifted with a phase angle δ :

$$\sigma(t) = \sigma_m + \sigma_a \sin(\omega t + \delta). \quad (6.39)$$

This stress response can be expanded into a term that is in-phase with the applied strain and a term that is 90° out of phase with the applied strain:

$$\sigma(t) = \sigma_m + \sigma_a \cos(\delta) \sin(\omega t) + \sigma_a \sin(\delta) \cos(\omega t). \quad (6.40)$$

The *storage modulus* (E') is defined as the stiffness of the response that is in-phase with the applied strain, and the *loss modulus* (E'') is defined as the stiffness of the response that is lagging 90° behind the applied strain. Hence, E' and E'' can be defined by²:

$$\sigma(t) \equiv \sigma_m + \varepsilon_a E' \sin(\omega t) + \varepsilon_a E'' \cos(\omega t). \quad (6.41)$$

By comparing terms between Equation (6.40) and Equation (6.41), and by defining $E^* = \sigma_a/\varepsilon_a$, the storage modulus E' and the loss modulus E'' can be determined from the following equations:

$$E' = E^* \cos(\delta), \quad (6.42)$$

$$E'' = E^* \sin(\delta). \quad (6.43)$$

The amount of energy loss (hysteresis) per unit reference volume per load cycle is given by:

$$u_{\text{loss}} = \oint_{1 \text{ cycle}} \sigma \, d\varepsilon = \int_0^{2\pi/\omega} \sigma(t) \dot{\varepsilon} \, dt. \quad (6.44)$$

Inserting (6.38) and (6.40) into (6.44) gives

$$u_{\text{loss}} = \pi \varepsilon_a \sigma_a \sin(\delta), \quad (6.45)$$

which can also be written

$$u_{\text{loss}} = \pi \varepsilon_a^2 E''. \quad (6.46)$$

The quantity $\tan(\delta)$ can therefore also be calculated from:

$$\tan(\delta) = \frac{u_{\text{loss}}}{\sqrt{(\pi \varepsilon_a \sigma_a)^2 - u_{\text{loss}}^2}}. \quad (6.47)$$

²The storage modulus and the loss modulus are secant moduli.

In summary, if the applied strain is sinusoidal with the amplitude ε_a , the resulting stress is sinusoidal with known amplitude σ_a , and the amount of hysteresis per cycle (u_{loss}) are known, then the storage modulus, loss modulus, and $\tan(\delta)$ can be calculated from:

$$E'' = \frac{u_{\text{loss}}}{\pi \varepsilon_a^2}, \quad (6.48)$$

$$E^* = \frac{\sigma_a}{\varepsilon_a}, \quad (6.49)$$

$$E' = \sqrt{(E^*)^2 - (E'')^2}, \quad (6.50)$$

$$\tan(\delta) = \frac{E''}{E'}. \quad (6.51)$$

Example

Assume that the experimentally determined stress response from a uniaxial test with a sinusoidal applied strain is given by a function $\sigma(t)$. Then, approximate $\sigma(t)$ by sum of a sine and a cosine term³:

$$\sigma(t) \approx \sigma_m + A \sin(\omega t) + B \cos(\omega t), \quad (6.52)$$

where $\sigma_m = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \sigma(t) dt$ is the mean stress. In order to determine the storage modulus (E') and the loss modulus (E'') multiply each side of (6.52) by $\sin(\omega t)$ or $\cos(\omega t)$, and then integrate⁴ from 0 to $N\pi/\omega$:

$$\begin{aligned} \int_0^{N\pi/\omega} \sigma(t) \sin(\omega t) dt &= A \int_0^{N\pi/\omega} \sin^2(\omega t) dt \\ &\quad + B \int_0^{N\pi/\omega} \sin(\omega t) \cos(\omega t) dt, \end{aligned} \quad (6.53)$$

$$\begin{aligned} \int_0^{N\pi/\omega} \sigma(t) \cos(\omega t) dt &= A \int_0^{N\pi/\omega} \sin(\omega t) \cos(\omega t) dt \\ &\quad + B \int_0^{N\pi/\omega} \cos^2(\omega t) dt. \end{aligned} \quad (6.54)$$

³This is a first order Fourier series expansion of $\sigma(t)$.

⁴The variable N is an integer larger than or equal to 1.

This set of equations is solved if

$$A = \frac{2\omega}{N\pi} \int_0^{N\pi/\omega} \sigma(t) \sin(\omega t) dt, \quad (6.55)$$

$$B = \frac{2\omega}{N\pi} \int_0^{N\pi/\omega} \sigma(t) \cos(\omega t) dt. \quad (6.56)$$

As before, the definition of E' and E'' is given by

$$\sigma(t) \equiv \sigma_m + \varepsilon_a E' \sin(\omega t) + \varepsilon_a E'' \cos(\omega t). \quad (6.57)$$

By comparing terms between (6.52), (6.55)–(6.57), the storage modulus E' and the loss modulus E'' can then be determined from the following equations:

$$E' = \frac{2\omega}{N\pi} \int_0^{N\pi/\omega} \frac{\sigma(t)}{\varepsilon_a} \sin(\omega t) dt, \quad (6.58)$$

$$E'' = \frac{2\omega}{N\pi} \int_0^{N\pi/\omega} \frac{\sigma(t)}{\varepsilon_a} \cos(\omega t) dt. \quad (6.59)$$

Example

Now consider a case in which the applied strain is not sinusoidal but instead triangular, square, or some other similar waveform specified by a function $f(\cdot)$:

$$\varepsilon(t) = \varepsilon_m + \varepsilon_a f(\omega t), \quad (6.60)$$

where as before ε_a is the applied strain amplitude. Assume that the stress response in this case is given by a term that is in-phase with the applied strain and a term that is 90° out-of phase with the applied strain:

$$\sigma(t) = Af(\omega t) + Bf\left(\omega t + \frac{\pi}{2\omega}\right). \quad (6.61)$$

Then, if $f(x)$ and $f(x + \pi/2)$ are orthogonal over the interval $[0, N\pi]$, the constants A and B can be found by multiplying (6.61) by $f(\omega t)$ or $f(\omega t + \pi/2\omega)$ and then integrating over $[0, N\pi/\omega]$. Using this approach the storage modulus and loss modulus can be calculated from:

$$E' = \frac{1}{\varepsilon_a} \frac{\int_0^{N\pi/\omega} \sigma(t)f(\omega t) dt}{\int_0^{N\pi/\omega} f^2(\omega t) dt}, \quad (6.62)$$

$$E'' = \frac{1}{\varepsilon_a} \frac{\int_0^{N\pi/\omega} \sigma(t)f\left(\omega t + \frac{\pi}{2\omega}\right) dt}{\int_0^{N\pi/\omega} f^2\left(\omega t + \frac{\pi}{2\omega}\right) dt}. \quad (6.63)$$

Example

An alternative approach to determine the storage and loss moduli from experimental time-strain-stress data is to use the Fourier transform approach [8]:

1. Take the Fourier transform of the strain and stress data. Shift the means strain to be zero if necessary.
2. Calculate the complex modulus from the ratio of the transformed stress to transformed strain, at the location where the transformed strain has the largest magnitude.
3. The storage modulus is given the real part of the complex modulus, and the loss modulus is given by the imaginary part of the complex modulus.

Python code illustrating this approach is listed below:

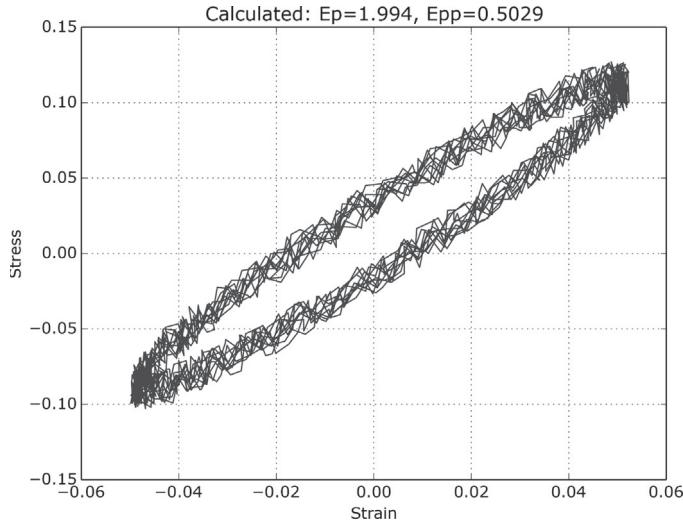
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Python Code: "analyze_data.py"
from pylab import *

### Input
freq_Hz = 1.4
strain_mean = 0.0 # subtract out the mean strain
strain_amp = 0.05
stress_mean = 0.0
nr_cycles = 10.0
nr_dpts_per_cycle = 144.0
Ep = 2.0
Epp = 0.5

### Create virtual time-strain-stress data
freq_rad = freq_Hz * 2.0 * pi
time = linspace(0.0, 1.0 * 2.0*pi*nr_cycles / freq_rad, \
nr_cycles * nr_dpts_per_cycle)
strain = strain_mean + strain_amp * sin(time * freq_rad) + \
0.05 * strain_amp * random(size(time))
stress = stress_mean + strain_amp * Ep * sin(time * freq_rad) + \
strain_amp * Epp * cos(time * freq_rad) + \
0.05 * Epp * random(size(time))

### Extract the storage and loss moduli
hanning_window = hanning(size(time))
fft_strain = fft(strain * hanning_window)
fft_stress = fft(stress * hanning_window)
fft_strain_mag = abs(fft_strain)
i = argmax(fft_strain_mag)
Gstar = fft_stress[i] / fft_strain[i]
Ep_calc = Gstar.real
Epp_calc = Gstar.imag
```

The results from running the code is shown in the following figure.



Note the following restrictions on the dynamic properties discussed in this section:

- It may or may not be possible to determine E' and E'' for a material that is *non-linear* viscoelastic, or for a case when the applied mean strain and/or strain amplitudes are large. The usefulness of E' and E'' depends on whether the resulting stress response is proportional to a scaled and shifted representation of the input strain. If the resulting stress has a different shape (e.g. due to yielding, or other non-linear behavior) then it is not appropriate to utilize E' and E'' to describe the material response.
- It is not possible to determine E' and E'' from tests using monotonic strain histories. The applied strain need to oscillate with a constant frequency, strain amplitude, and wave form.

6.2.5 Representing Linear Viscoelasticity Using Spectra

Several different means of specifying viscoelastic mechanical properties have been given in the previous section. Specifically, relaxation functions, creep functions, and complex moduli have been discussed. Another way of characterizing the material response is through *spectra*. To introduce the concept of a relaxation spectrum consider a relaxation modulus given by a series of exponential terms:

$$E(t) = \sum_{i=1}^n E_i \exp\left[\frac{-t}{\tau_i}\right]. \quad (6.64)$$

In the limit as $i \rightarrow \infty$, the summation can be replaced by an integral:

$$E(t) = \int_0^\infty f(\tau) \exp\left[\frac{-t}{\tau}\right] d\tau. \quad (6.65)$$

The function $f(\tau)$ is called the *relaxation time spectrum*. In practice it is often more convenient to use a logarithmic time scale when defining the relaxation time spectrum

$$G(t) = \int_{-\infty}^{+\infty} H(\tau) \exp\left[\frac{-t}{\tau}\right] d(\ln \tau) + G(\infty). \quad (6.66)$$

Similarly, a retardation time spectrum can be defined by

$$J(t) = \int_{-\infty}^{+\infty} L(\tau) \left[1 - \exp\left(\frac{-t}{\tau}\right)\right] d(\ln \tau) + J(\infty). \quad (6.67)$$

It is possible to solve for $H(t)$ and $L(t)$ by using Laplace transforms, see [1] for more details on the use of relaxation spectra. The theory of relaxation spectra is elegant and provides a concise way to represent linear viscoelastic behavior. It is, however, of limited use in practice since the major finite element programs specify the linear viscoelastic response using Prony series instead of relaxation spectra.

Finally, even if a relaxation spectrum is chosen, the Boltzmann's superposition principle does not allow for a sigmoidal shaped stress-strain response that is typical for polymers at intermediate to large strains.

6.2.6 Computer Implementation

To make the linear viscoelasticity theory more concrete it is useful to consider a simple one-dimensional computational implementation. This section summarizes two implementations, one using Matlab and one using Python.

Matlab Implementation

The Matlab files `mat_LVE.m` and `test_mat_LVE.m` illustrate one possible implementation of small strain linear viscoelasticity for uniaxial loading. The algorithm that is used here is directly follows the theory that was derived in previous sections, but the code is not numerically efficient.

The `mat_LVE()` function takes a time vector, a strain vector, and a vector with material parameters where the first parameter is the initial Young's modulus and the remaining parameters are the pairs of Prony series parameters $[g_i, \tau_i]$. The code is using the built-in Matlab function `quad()` to numerically integrate the integral.

```
Matlab File Name: "mat_LVE.m"
function stressVec = mat_LVE(timeVec, strainVec, params)
%mat_LVE Linear viscoelastic model
%Uniaxial loading
for i = 1 : length(timeVec)
    tmax = timeVec(i);
    F = @(t) integrand(t, tmax, timeVec, strainVec, params);
    stressVec(i) = quad(F, eps, tmax);
end
end

function res = integrand(tau, tmax, timeVec, strainVec, params)
E0 = params(1); % ABAQUS-style Prony series
g = params(2:2:end);
tauG = params(3:2:end);
for i = 1 : length(tau)
    ER = E0 * (1 - sum( g .* (1 - exp(-(tmax-tau(i))./tauG)) ));
    edot = (interp1(timeVec, strainVec, tau(i) + 1e-4, ...
        'linear', strainVec(end)) - ...
        interp1(timeVec, strainVec, tau(i))) / 1e-4;
    res(i) = ER * edot;
end
end

Matlab File Name: "test_mat_LVE.m"
time = linspace(0,2)';
strain = [linspace(0, 0.5, 50)'; linspace(0.5, 0, 50)'];
stress = mat_LVE(time, strain, [1.0 0.8 0.1]);
```

The predictions from running the `test_mat_LVE` function are shown in [Figure 6.9](#). This figure shows that the model predicts significant hysteresis during cyclic loading.

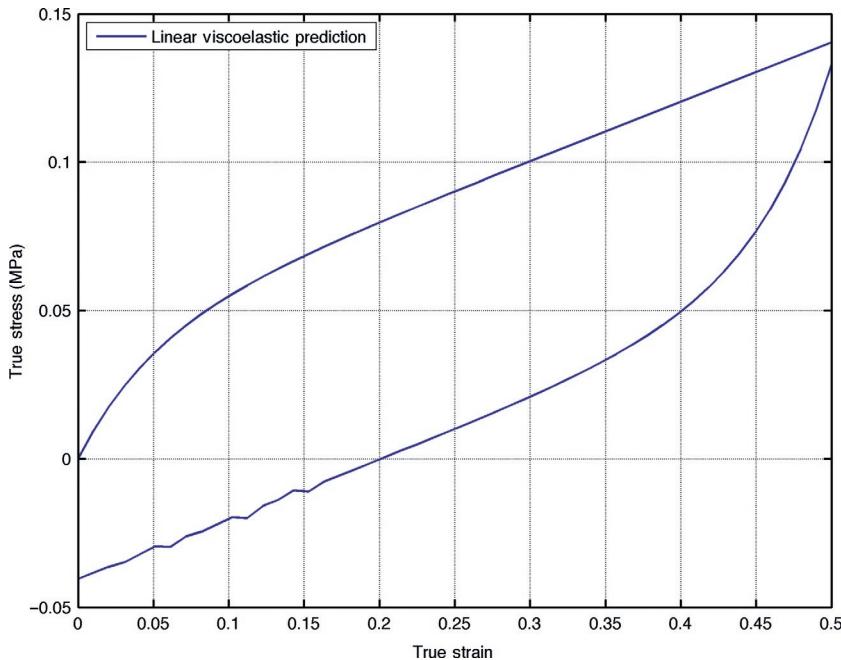


Figure 6.9 Example prediction of the linear viscoelasticity model. The prediction was created using the Matlab file `test_mat_LVE.m`.

Python Implementation

A linear elastic model with linear viscoelasticity model can also readily be implemented in Python. Similar to the Matlab example from the previous section, this implementation aims to illustrate a simple practical algorithm, and not focus on numerical efficiency.

```
Python File Name: "LVE_small_strain.py"
from pylab import *
from scipy.integrate import quad
from scipy.interpolate import interp1d

def integrand(tau, tmax, timeVec, strainVec, params):
    E0 = params[0]
    g = params[1:2]
    tauG = params[2:2]
    ER = E0 * (1.0 - sum(g * (1 - exp((-tmax+tau)/tauG) )))
    f = interp1d(timeVec, strainVec)
    edot = (f(tau+1e-5) - f(tau)) / 1e-5
    return ER * edot

def mat_LVE(timeVec, strainVec, params):
    """Linear viscoelasticity, Uniaxial loading."""
    stressVec = zeros(len(timeVec))
    for i in arange(len(timeVec)):
        tmax = timeVec[i]
        stressVec[i] = quad(integrand, 0, tmax, \
                           args=(tmax, timeVec, strainVec, params))[0]
    return stressVec

time = linspace(0, 2, 100)
strain = concatenate((linspace(0,0.5), linspace(0.5,0)))
stress = mat_LVE(time, strain, [1.0, 0.8, 0.1])
plot(strain, stress, label='LVE')
show()
```

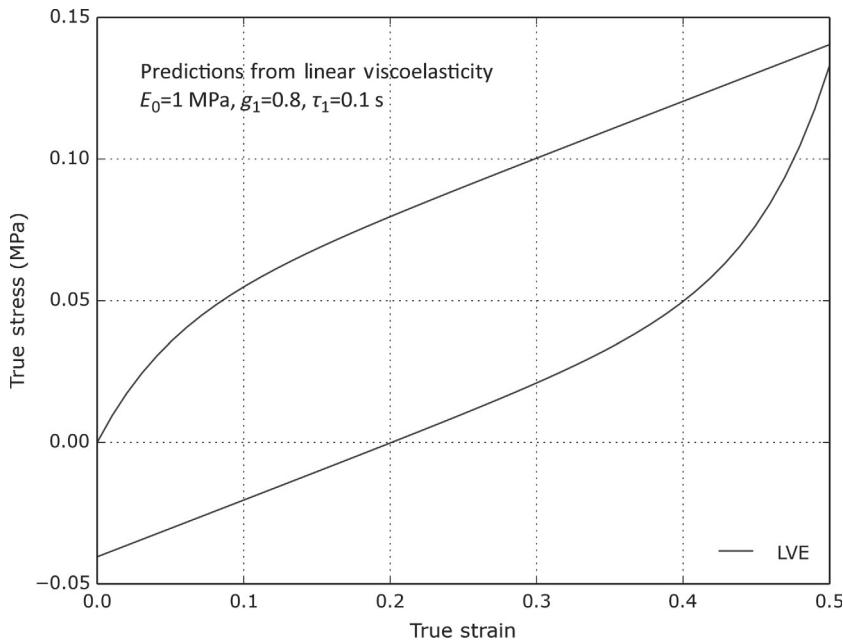


Figure 6.10 Example prediction of the linear viscoelasticity model. The prediction was created using the Python file `LVE_small_strain.py`.

The predictions from running the file `LVE_small_strain.py` are shown in Figure 6.10.

6.3 Large Strain Linear Viscoelasticity

Linear viscoelasticity is often used in large strain predictions. In order to perform these calculations it is recommended to generalize the previous derivation of linear viscoelasticity to use hyperelasticity instead of linear elasticity as the instantaneous and long-term response.

One way to illustrate this generalization (in a non-rigorous way) is to start with the basic linear viscoelasticity equation:

$$\sigma(t) = \int_{-\infty}^t E_R(t-\tau) d\varepsilon(\tau) = \int_{-\infty}^t E_R(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau. \quad (6.5\text{-repeat})$$

This equation can be integrated in parts to:

$$\sigma(t) = E_0 \varepsilon(t) - \int_0^t \dot{g}_R(t-\tau) E_0 \varepsilon(\tau) d\tau, \quad (6.68)$$

where the normalized relaxation modulus $g_R(t) = E_R(t)/E_0$ has been introduced.

We can now introduce the hyperelastic stress function:

$$\sigma_{hyp}(\varepsilon) = \sigma_{hyp}(\varepsilon(t)) \equiv E_0 \varepsilon(t), \quad (6.69)$$

which when inserted into (6.5) becomes:

$$\sigma(t) = \sigma_{hyp}(\varepsilon(t)) - \int_0^t \dot{g}_R(t-\tau) \sigma_{hyp}(\varepsilon(\tau)) d\tau. \quad (6.70)$$

This equation expresses how a stress relaxation function (expressed as a Prony series) and a hyperelastic stress function can be combined to give a complete material model capable of predicting the stress response caused by any arbitrary large uniaxial deformation strain history.

The large-strain linear viscoelasticity model is available in all major finite element programs.

6.3.1 Numerical Implementation

Consider a case of uniaxial incompressible loading. In this case the stress response at time t is given by Equation (6.5), which can also be written:

$$\sigma(t) = \sigma_{hyp}(t) - \sigma_{visc}(t), \quad (6.71)$$

where $\sigma_{visc}(t)$ is the viscoelastic stress at time t . Similarly, the stress at $t + \Delta t$ is given by:

$$\sigma(t + \Delta t) = \sigma_{hyp}(t + \Delta t) - \int_0^{t+\Delta t} \dot{g}_R(t + \Delta t - \tau) \sigma_{hyp}(\tau) d\tau \quad (6.72)$$

$$\equiv \sigma_{\text{hyp}}(t + \Delta t) - \sum_{i=1}^N \sigma_{\text{visc}}^i(t + \Delta t), \quad (6.73)$$

where σ_{visc}^i is the viscoelastic stress due to Prony series term i , which is given by:

$$\sigma_{\text{visc}}^i(t + \Delta t) = \int_0^{t+\Delta t} \frac{d}{d\tau} \left[(1 - g_i) + g_i e^{-(t+\Delta t-\tau)/\hat{\tau}_i} \right] \sigma_{\text{hyp}}(\tau) d\tau \quad (6.74)$$

$$= \int_0^t \frac{d}{d\tau} \left[(1 - g_i) + g_i e^{-(t+\Delta t-\tau)/\hat{\tau}_i} \right] \sigma_{\text{hyp}}(\tau) d\tau \quad (6.75)$$

$$+ \int_t^{t+\Delta t} \frac{d}{d\tau} \left[(1 - g_i) + g_i e^{-(t+\Delta t-\tau)/\hat{\tau}_i} \right] \sigma_{\text{hyp}}(\tau) d\tau \quad (6.76)$$

$$\equiv A_i + B_i. \quad (6.77)$$

The first integral A_i is given by:

$$A_i = \int_0^t \frac{g_i}{\hat{\tau}_i} \left[e^{-t/\hat{\tau}_i} \cdot e^{-\Delta t/\hat{\tau}_i} \cdot e^{\tau/\hat{\tau}_i} \right] \sigma_{\text{hyp}}(\tau) d\tau \quad (6.78)$$

$$= e^{-\Delta t/\hat{\tau}_i} \cdot \sigma_{\text{visc}}^i(t). \quad (6.79)$$

To evaluate the second integral B_i , assume $\sigma_{\text{hyp}}(\tau)$ varies linearly with τ in the interval $[t, t + \Delta t]$:

$$\sigma_{\text{hyp}}(\tau) = \sigma_{\text{hyp}}(t) + \Delta\sigma_{\text{hyp}} \cdot \frac{\tau - t}{\Delta t}, \quad (6.80)$$

where

$$\Delta\sigma_{\text{hyp}} = \sigma_{\text{hyp}}(\varepsilon(t + \Delta t)) - \sigma_{\text{hyp}}(\varepsilon(t)). \quad (6.81)$$

With this approximation the integral B_i can be solved in closed form. The algebra is here left as an exercise, the results become:

$$B_i = g_i \sigma_{\text{hyp}}(t) \left[1 - e^{-\Delta t/\hat{\tau}_i} \right] + g_i \frac{\Delta\sigma_{\text{hyp}}}{\Delta t} \left[(\Delta t - \hat{\tau}_i) + \hat{\tau}_i e^{-\Delta t/\hat{\tau}_i} \right]. \quad (6.82)$$

To summarize, the stress at $t + \Delta t$ can be calculated from:

$$\sigma(t + \Delta t) = \sigma_{\text{hyp}}(t + \Delta t) - \sum_{i=1}^N \sigma_{\text{visc}}^i(t + \Delta t), \quad (6.83)$$

where

$$\begin{aligned}\sigma_{\text{visc}}^i(t + \Delta t) &= e^{-\Delta t/\hat{\tau}_i} \cdot \sigma_{\text{visc}}^i(t) + g_i \sigma_{\text{hyp}}(t) \left[1 - e^{-\Delta t/\hat{\tau}_i} \right] \\ &\quad + g_i \frac{\Delta \sigma_{\text{hyp}}}{\Delta t} \left[(\Delta t - \hat{\tau}_i) + \hat{\tau}_i e^{-\Delta t/\hat{\tau}_i} \right].\end{aligned}\quad (6.84)$$

In this equation, σ_{visc}^i are internal state variables for each Prony series term. The large strain linear viscoelasticity model shown here can easily be implemented in Python, as shown below. The implementation shown here is using a Neo-Hookean hyperelastic model with a 1-term Prony series, and the implementation is numerically very efficient. A numerically efficient implementation for compressible, multiaxial deformations can also be implemented [5], but is outside the scope of this chapter.

```
Python File Name: "LVE_large_strain.py"
from pylab import *

def NH(strain, params):
    """Neo-Hookean model. Incompressible uniaxial loading."""
    mu = params[0]
    lam = exp(strain)
    return mu * (lam*lam - 1/lam)

def LVE_uniax(time, strain, params):
    """Linear viscoelasticity. [mu, g1, tau1, g2, tau2, ...]"""
    stress = zeros(len(time))
    g = params[1::2]
    tau = params[2::2]
    stressV = zeros(len(g))
    stressH0 = NH(strain[0], params)
    for i in range(1, len(time)):
        stressH1 = NH(strain[i], params)
        dstressH = stressH1 - stressH0
        dt = time[i] - time[i-1]
        stress[i] = stressH1
        for j in range(len(g)):
            stressV[j] = exp(-dt/tau[j]) * stressV[j] + \
                g[j]*stressH*(1 - exp(-dt/tau[j])) + \
                g[j]*dstressH/dt*(dt-tau[j])+tau[j]*exp(-dt/tau[j]))
        stress[i] = stress[i] - stressV[j]
    stressH0 = stressH1
    return stress

N = 100
time = linspace(0, 2, 2*N)
strain = concatenate((linspace(0,0.5,N), linspace(0.5,0,N)))

params = [1.0, 0.8, 0.1] # [mu, g, tau]
stress = LVE_uniax(time, strain, params)
plot(strain, stress, 'b.-', label='LVE')
show()
```

The predictions from running this file are shown in Figure 6.11.

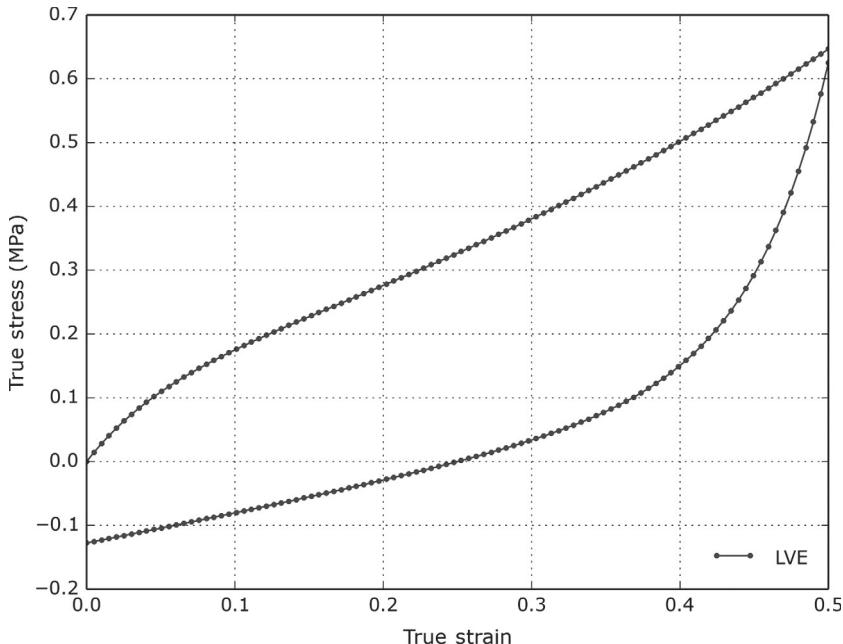


Figure 6.11 Linear viscoelastic predictions using the Python file `LVE_large_strain.py`. Material parameters: $\mu = 1 \text{ MPa}$, $g_1 = 0.8$, and $\tau_1 = 0.1 \text{ s}$.

6.4 Creep Compliance Behavior

The linear viscoelasticity theory presented in this chapter has been formulated in terms of strains as the driving quantity. It is also possible to formulate the linear viscoelasticity theory for the case when the stress is the driving quantity.

In this case the creep compliance, defined by $J(t) \equiv \varepsilon(t)/\sigma$, is the key quantity. And the resulting strain from an applied stress history can be calculated from:

$$\varepsilon(t) = \int_{-\infty}^t J(t-\tau) \frac{d\sigma(\tau)}{d\tau} d\tau. \quad (6.85)$$

Since most major FE programs are formulated in displacement form, with strain as the driving quantity, this alternative formulation of linear viscoelasticity in terms of stresses is only briefly discussed in the following, and is discussed in more detail in various references [1–3].

6.4.1 Relationships Between Creep Compliance and Relaxation Modulus

The formal relationship between the relaxation modulus $G(t)$ and the creep compliance $J(t)$ can be derived by taking the Laplace transformation:

$$\mathcal{L}\{f(t)\} = \int_0^\infty e^{-st} f(t) dt, \quad (6.86)$$

of Equations (6.5) and (6.85) giving:

$$\tilde{\sigma}(s) = s\tilde{G}(s)\tilde{\varepsilon}(s), \quad (6.87)$$

$$\tilde{\varepsilon}(s) = s\tilde{J}(s)\tilde{\sigma}(s). \quad (6.88)$$

This equation can be rewritten

$$\tilde{G}(s) = \frac{1}{s^2\tilde{J}(s)}. \quad (6.89)$$

Based on the Laplace limit theorems it can be shown [1] that:

$$\lim_{t \rightarrow 0} J(t) = \lim_{t \rightarrow 0} \frac{1}{G(t)}, \quad (6.90)$$

$$\lim_{t \rightarrow \infty} J(t) = \lim_{t \rightarrow \infty} \frac{1}{G(t)}. \quad (6.91)$$

Also since $\mathcal{L}^{-1}(1/s^2) = t$ we directly get:

$$\int_0^t G(t-\tau)J(\tau) d\tau = \int_0^t J(t-\tau)G(\tau) d\tau = t. \quad (6.92)$$

These functional relationships can be used when converting a stress relaxation function to a creep compliance function, or when converting a creep compliance function to a stress relaxation function. This type of conversion can also be achieved through direct numerical optimization of, for example, the Prony series. This may be of interest if the creep compliance is known and the corresponding Prony series is required for a finite element analysis.

One way to perform this conversion is to:

1. Select an initial guess of the Prony series parameters.
2. Calculate the creep compliance through a direct simulation

3. Use an optimization algorithm (e.g. the Nelder-Mead simplex algorithm) to modify the current value of the Prony series parameters.
4. If the predicted creep compliance is in good agreement with the experimental creep compliance stop, otherwise go to (2).

This algorithm is implemented in specialized software, e.g. MCALibration [9], and can be effectively used to determine the Prony series parameters from creep data.

6.5 Differential Form of Linear Viscoelasticity

So far the presentation of linear viscoelasticity has used an integral equation formulation:

$$\sigma(t) = \int_{-\infty}^t E(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau. \quad (6.5\text{-repeat})$$

This equation can also be written in differential form as

$$P(D)\sigma(t) = Q(D)\varepsilon(t), \quad (6.93)$$

where $P(D)$ and $Q(D)$ are polynomials of the differential operator $D \equiv d/dt$. To show this start by taking the Laplace transform of Equation (6.93):

$$\begin{aligned} P(s)\tilde{\sigma}(s) - \frac{1}{s} \sum_{k=1}^N p_k \sum_{r=1}^k s^r \sigma^{(k-r)}(0) \\ = Q(s)\tilde{\varepsilon}(s) - \sum_{k=1}^N q_k \sum_{r=1}^N s^r \varepsilon^{k-r}(0). \end{aligned} \quad (6.94)$$

The Laplace transform of (6.5) is

$$\tilde{\sigma}(s) = s\tilde{G}(s)\tilde{\varepsilon}(s), \quad (6.87\text{-rep})$$

illustrating that the two forms are equal if

$$s\tilde{G}(s) = \frac{\tilde{Q}(s)}{\tilde{P}(s)} \quad (6.95)$$

and

$$\sum_{r=k}^N p_r \sigma_{ij}^{r-k}(0) = \sum_{r=k}^N q_r \varepsilon^{r-k}(0), \quad k = 1, 2, \dots, N, \quad (6.96)$$

which is a restriction on the initial conditions. The integral equation formulation and the differential equation formulation are therefore functionally equivalent.

6.5.1 Rheological Models

One interesting way to visualize and develop differential forms of a linear viscoelastic model is to start with a one-dimensional rheological representation. This representation uses springs and dashpots to visualize the material model structure. Rheological representations can also be used to convert a linear viscoelastic model to a *non-linear* viscoelastic model. This will be discussed in detail in Chapter 8.

To initiate the discussion about rheological models we will first study two common model structures.

Maxwell Model

The Maxwell rheological model consists of a linear spring ($\sigma = E\varepsilon_1$) and a linear dashpot ($\dot{\varepsilon}_2 = \sigma/\eta$) in series, see [Figure 6.12](#). Here E is the Young's modulus, and η is the viscosity.

The rate of change in strain of the system is given by the equilibrium equation

$$\dot{\varepsilon} = \frac{d}{dt}(\varepsilon_1 + \varepsilon_2) = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\eta}, \quad (6.97)$$

which is a differential equation representation of the Maxwell model.

Now consider a stress relaxation experiment with an applied strain step: $\varepsilon(t) = \varepsilon_0 H(t)$. Inserting this into Equation (6.97) gives

$$\frac{d\sigma}{dt} + \frac{E}{\eta}\sigma = 0 \quad (\text{for } t > 0).$$

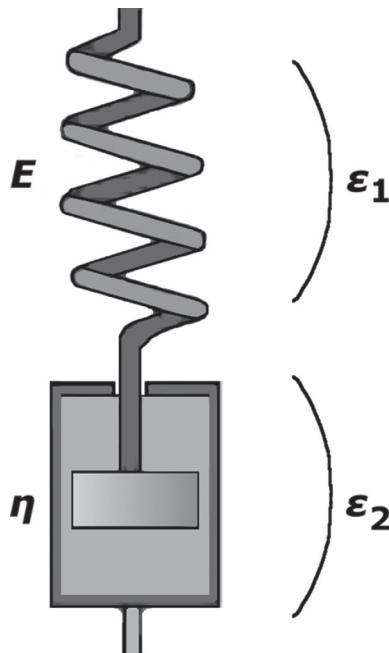


Figure 6.12 Rheological representation of the Maxwell model.

This differential equation can be solved in closed form

$$\sigma(t) = \sigma_0 \exp\left[\frac{-t}{\eta/E}\right]. \quad (6.98)$$

Hence, the stress relaxation function for the Maxwell model is given by an exponentially decaying stress relaxation modulus

$$E(t) = E_0 \exp\left[\frac{-t}{\eta/E}\right],$$

which is a single Prony series term. Or equivalently, a single Prony series term is equivalent to a Maxwell rheological model.

Multi-Network Maxwell Model

A multi-network Maxwell model consists of a number of parallel Maxwell models, see [Figure 6.13](#).

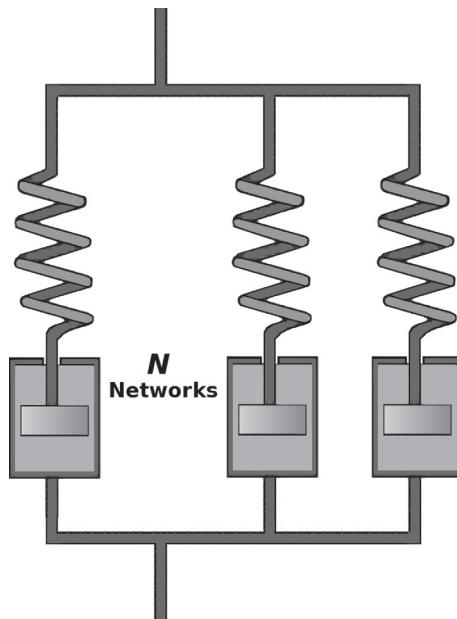


Figure 6.13 A multi-network Maxwell model is equivalent to a Prony series.

From the results in the previous section it is clear that the effective stress relaxation modulus for this multi-network model is

$$E_R(t) = E_0 + \sum_{i=1}^N E_i e^{-t/\tau_i}, \quad (6.99)$$

which is equivalent to the Prony series in Equation (6.14). Hence:

A linear viscoelastic model with a given Prony series is identical to a multi-network Maxwell model.

This equivalence can be of use when formulating strategies for solving the constitutive equations, and when developing extensions to linear viscoelasticity.

6.6 The Use of Shift Functions to Generalize Linear Viscoelasticity Theory

For many polymeric materials the domain in which linear viscoelasticity theory gives good predictions is unfortunately

relatively small. Based on experimental observations it turns out that the influence of variations in external parameters (such as temperature and aging time), which contribute to the limited applicability of the theory, can be accounted for by using a shift function approach. The reason for the success of this simple idea is that when the material functional is plotted using appropriate log-scales, changes in these external parameters do not change the shape of the plotted curve to any significant degree, only shift it.

6.6.1 Time-Temperature Equivalence

The discussion has so far been for a general viscoelastic material and can therefore be applied also to a polymer. But when considering polymers a number of complications become apparent. One of the more important issues that need to be recognized is the strong temperature dependence of polymeric materials. It has been shown experimentally that in many cases the temperature dependence can be modeled by a scaling of time using what has been termed the *time-temperature equivalence*.

The basis for this principle is shown in Figure 6.14 illustrating that if the experimentally determined stress relaxation modulus is plotted as a function of logarithmic time, the shape of the resulting curves is the same for a wide interval of temperatures.

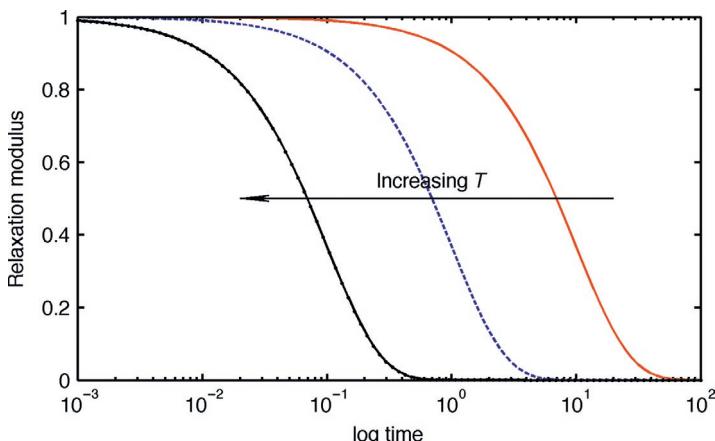


Figure 6.14 Dependence of stress relaxation modulus on time and temperature.

In fact, the only significant difference between the curves is a horizontal shift. This observation suggests that if the relaxation modulus is known at one temperature (i.e. the *master curve* is known) then the relaxation modulus at any other temperature can be obtained if the horizontal shift factor $a_T = a_T(T)$ is known. A material that has this property is called a *rheologically simple material*.

The time shifts can be defined by

$$\log t_{T_0} - \log t_T = \log a_T, \quad (6.100)$$

where t_T is the time at temperature T , and t_{T_0} the time at temperature T_0 . Equation (6.100) gives $a_T = t_{T_0}/t_T$, or $t_T = t_{T_0}/a_T$, hence the behavior at a temperature of T becomes exactly the same as the behavior at the reference temperature T_0 if the time is *accelerated* by the factor a_T .

In general, the temperature can be a function of time $T(t_{T_0})$, so instead of $t_T = t_{T_0}/a_T$ it is necessary to write

$$dt_T = \frac{dt_{T_0}}{a_T(T(t_{T_0}))} \quad (6.101)$$

giving

$$t_T = \int_0^{t_{T_0}} \frac{dt'_{T_0}}{a_T(T(t'_{T_0}))}. \quad (6.102)$$

The effective time experienced by the material, the material time, is a function of temperature and wall clock time. For a rheologically simple material, the scaling of time with temperature occurs in all viscoelastic quantities such as G , J , J' , J'' , $\tan \delta$, etc. And the scaling constant must be the same for all quantities for the material to be rheologically simple.

Another common way to use time-temperature equivalence is to use experimental data obtained at different temperatures to estimate the stress-relaxation behavior at longer times than what was experimentally tested. As an example, consider the experimental data for butyl rubber [10] shown in Figure 6.15. The data shows the stress relaxation behavior for times between 10 s and 3 hours and for temperatures between -81.7°C and

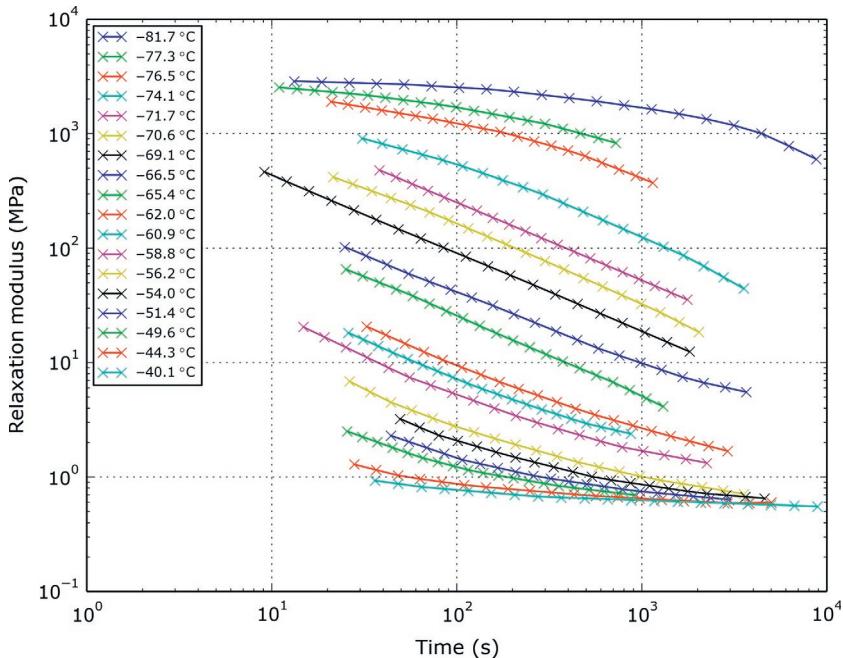


Figure 6.15 Experimental stress relaxation data at different temperatures.

$-40.1\text{ }^\circ\text{C}$. As shown in the figure the relaxation modulus is very temperature sensitive under these conditions.⁵

The stress relaxation behavior can be horizontally shifted using the William-Landel-Ferry (WLF) equation using the parameters: $C_1 = 9.71$, $C_2 = 63.1\text{ K}$, and $T_0 = -62\text{ }^\circ\text{C}$, see [Figure 6.16](#). By applying the time-temperature equivalence the experimental data now covers stress relaxation times from 10^{-4} s to 10^6 s .

Example

To exemplify this idea consider a simple Maxwell element: $G(t) = G_0 \exp(-t)$. If the material is rheologically simple the relaxation modulus becomes

$$G(t, T) = G_0 \exp[-a_T(T)t].$$

⁵The glass transition temperature is approximately $-62\text{ }^\circ\text{C}$ for butyl rubber.

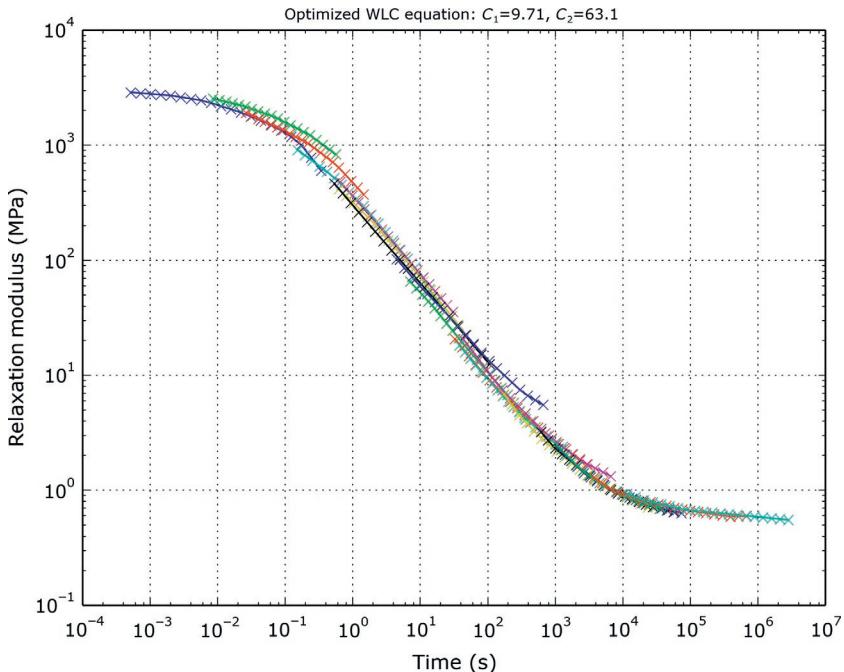


Figure 6.16 Experimental stress relaxation data after horizontal shifting using the WLF equation.

The influence of $a_T(T)$ on the stress-strain behavior was examined in [Section 6.2.1](#).

One commonly used representation of the shift factor a_T is the WLF equation [11]:

$$\log a_T(T) = \frac{C_1(T - T_0)}{C_2 + T - T_0}, \quad (6.103)$$

where $C_1 = 17.4$ and $C_2 = 51.6\text{ K}$. This relationship is often used [2] for amorphous polymers in the temperature range $T \in [T_g - 50\text{ K}, T_g + 50\text{ K}]$.

Another common equation for the shift factor a_T is the Arrhenius model:

$$\ln a_T(T) = -\frac{E_0}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right), \quad (6.104)$$

where E_0 is the apparent activation energy for viscoelastic relaxation, $R \approx 8.314 \text{ J/(mol K)}$ is the gas constant, T_0 is a reference temperature, and T is the current temperature.

6.6.2 Vertical Shifts

As will be discussed in more detail below, the stress relaxation modulus (and also the creep compliance) curves when plotted as a function of logarithmic time often turn out to have the same shape not only for different temperatures but also for variations in other parameters (such as aging time). But to create a master curve in these cases it is often necessary to also use vertical shifts (on a log-scale):

$$\log G^\alpha - \log G^{\alpha_0} = \log b \quad (6.105)$$

giving

$$b = \frac{G^\alpha}{G^{\alpha_0}}. \quad (6.106)$$

In summary, the integral formulation

$$\sigma(t) = \int_{-\infty}^t G(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau \quad (\text{6.5-rep})$$

becomes

$$\sigma(t) = \int_0^t b(t) G(\hat{t}(t) - \hat{t}(\tau)) \frac{d\varepsilon(\tau)}{d\tau} d\tau \quad (6.107)$$

when both vertical shift $b(\theta_1(t))$ and horizontal shift $\hat{t}(t) = \hat{t}(\theta_2(t))$, where θ_1 and θ_2 are external parameters such as temperature, are considered.

6.7 Use of Linear Viscoelasticity in Polymer Modeling

In this chapter the key aspects of linear viscoelasticity theory have been presented. It has been shown that to characterize the material only the instantaneous elastic (or the long-term elastic)

response and the Prony series relaxation modulus⁶ function need to be determined. The Prony series terms can be determined through one creep, stress relaxation or oscillatory experiment. Once the material dependent Prony series has been determined the response due to any arbitrary imposed deformation or loading can be directly calculated.

Linear viscoelasticity is mainly used for predicting the response of elastomer-like materials, and to a lesser degree, the very small strain response of thermoplastic materials. Since linear viscoelasticity cannot predict plastic or viscoplastic deformations, it should not be used to predict the response of glassy polymers for strains that are similar in magnitude to the yield strain, or larger.

One example of what can happen if linear viscoelasticity is attempted to be used for ultra-high molecular weight polyethylene (UHMWPE) is shown in [Figure 6.17](#). This figure shows that linear viscoelasticity is completely unable to predict the response of thermoplastics beyond yielding.

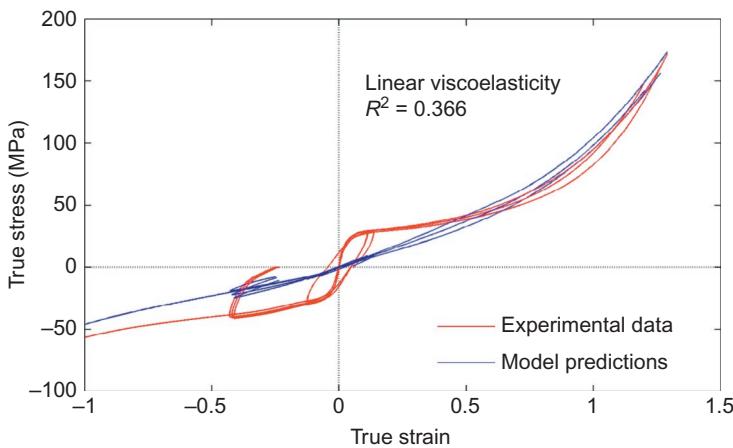


Figure 6.17 Application of LVE to the large strain behavior of UHMWPE.

⁶Only one material relaxation function is required for an incompressible isotropic material subjected to a one-dimensional loading situation. For an isotropic material subjected to a general loading situation two material functionals need to be determined, and for an anisotropic material the number of functionals are dependent on the material symmetry.

Linear viscoelasticity is also not always able to accurately predict the viscoelastic response of elastomers. Figure 6.18 shows experimental data for a chloroprene rubber tested in uniaxial compression, followed by unloading. The experiment was repeated at three different strain rates. The figure also shows the best predictions from linear viscoelasticity. In this case linear viscoelasticity does not accurately predict the material response. The reason for the poor predictions of this material behavior is that the material is not *linearly* viscoelastic. The strains in this case are large enough that the material response is non-linear viscoelastic. Better material models for predicting this data set is discussed in Section 8.2 of Chapter 8.

The strain magnitude below which linear viscoelasticity is an effective tool can be experimentally determined by running dynamic mechanical analysis (DMA) tests where the strain amplitude is gradually ramped from small to large values. Due to the Boltzmann superposition principle, the predictions from linear viscoelasticity will be independent of the strain amplitude. So, the results from this type of DMA tests can be used to determine the strain level below which the material response is *linearly* viscoelastic.

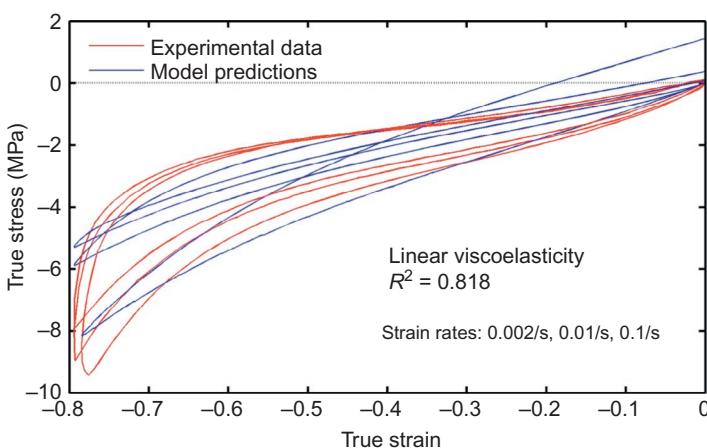


Figure 6.18 Application of LVE to the large strain behavior of elastomers.

Dynamic storage and loss modulus data for natural rubber and silicone rubber as a function of strain amplitude are shown in Figures 6.19–6.21. These figures show that response of these materials is only linear viscoelastic at very small applied strains (less than 1%).

The storage modulus as a function of strain amplitude, for many elastomers, is a decreasing function of the strain amplitude.

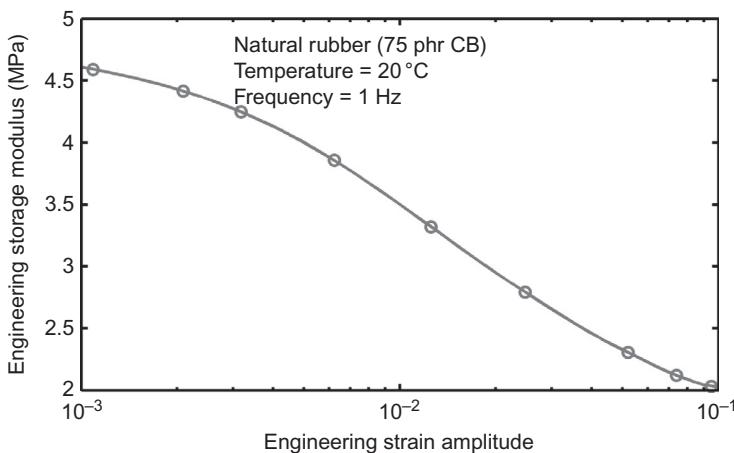


Figure 6.19 Experimentally determined storage modulus as a function of strain amplitude for a natural rubber [12].

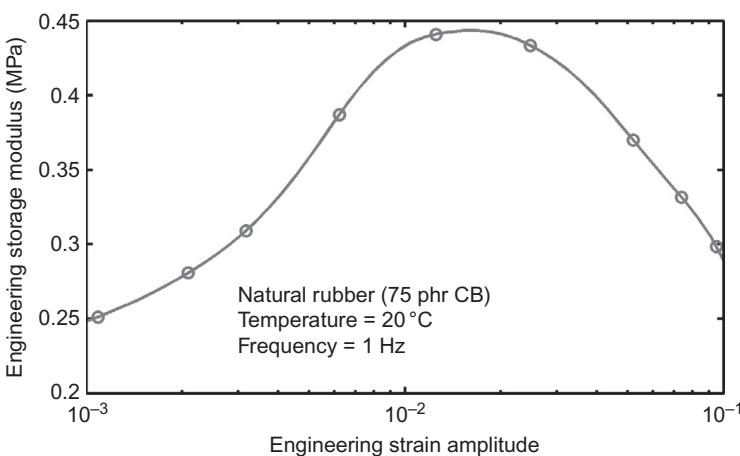


Figure 6.20 Experimentally determined loss modulus as a function of strain amplitude for a natural rubber [12].

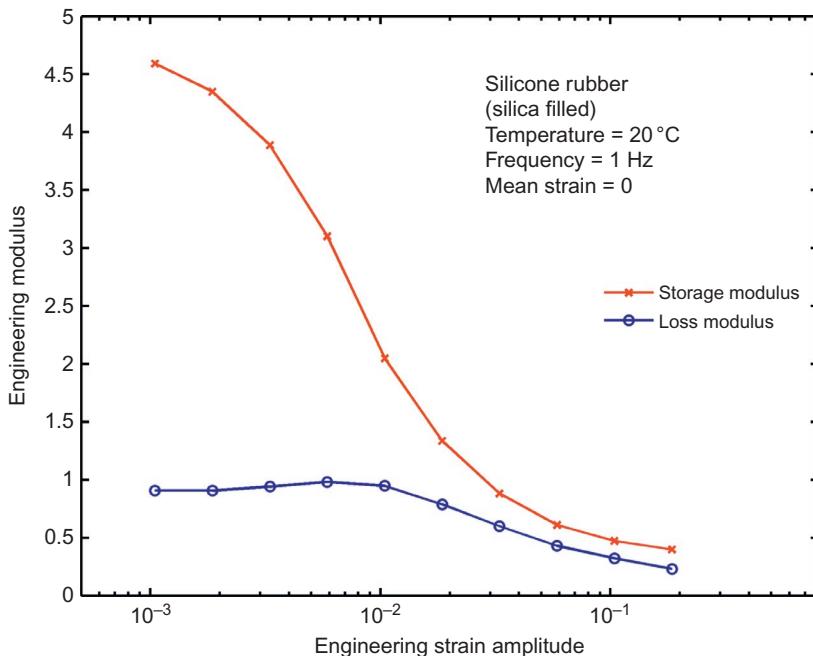


Figure 6.21 Experimentally determined loss modulus as a function of strain amplitude for a silicone rubber [12].

This effect, which is called the *Payne effect*, cannot be captured using linear viscoelasticity, but can be captured using non-linear viscoelasticity. To capture the Payne effect requires non-linear viscoelastic, a topic that will be discussed in Chapter 8.

6.8 Exercises

1. Describe the Boltzmann superposition principle.
2. Explain why linear viscoelasticity in uniaxial loading only requires an elastic modulus and the stress relaxation behavior.
3. How many Prony series terms should be experimentally determined before using linear viscoelasticity? What controls the required number of Prony series terms?
4. Which of the following sets of experimental data are *sufficient* for calibrating a linear viscoelastic model?

- stress relaxation from a given strain level
 - creep from a given stress level
 - monotonic uniaxial tension at a given strain rate
 - monotonic uniaxial tension at two different strain rates
 - a DMA temperature sweep
 - a DMA frequency sweep
5. Which of the following sets of experimental data are *recommended* for calibrating a linear viscoelastic model?
- stress relaxation from a given strain level
 - creep from a given stress level
 - monotonic uniaxial tension at a given strain rate
 - monotonic uniaxial tension at two different strain rates
 - a DMA temperature sweep
 - a DMA frequency sweep
6. Why is the Prony series written as a sum of exponentially decaying terms?
7. What is the definition of viscoelastic spectra?
8. Draw a schematic rheological model for a linear viscoelastic model with a 2-term Prony series.
9. What is a rheologically simple material?
10. What is the definition of the WLF equation?
11. What experiments would you run to determine if the response of a material is linear viscoelastic?
12. What is the graphical representation of a Maxwell element?
13. Describe the time-temperature superposition principle.

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