

**Polymer Science 2025/26**

**Course Notes of Chapter 4.2 (Part 1)**

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**1. Introduction**

**1.1 What is Viscoelasticity?**

At small deformations and at temperatures far from phase transitions, elastic solids (such as glasses or crystals) obey **Hooke's law**:

$$\sigma = E\varepsilon \quad (1)$$

where the elastic modulus  $E$  is approximately independent of the time  $t$  and strain rate  $d\varepsilon/dt$ . Polymers, in contrast, often exhibit **viscoelastic behavior**, meaning that their mechanical response depends not only on the applied deformation but also on how long it is applied and at what temperature. This becomes particularly evident near thermal transitions such as the glass transition  $T_g$ , where the material gradually changes from glassy to rubbery.

The diagram on Slide 244 illustrates how **Young's modulus** changes with temperature for different types of polymers:

- **semi-crystalline polymers:** the modulus drops near  $T_g$  as the amorphous regions soften, while the crystalline domains remain solid up to the melting temperature  $T_m$ , where a further drop occurs. A rubbery plateau develops only if the molar mass is sufficiently high.
- **elastomers:** with effectively infinite molar mass, the rubbery plateau extends up to the degradation temperature.
- **amorphous polymers:** exhibit a pronounced decrease in modulus in the glass-transition region and strong rate-dependent behavior in the emerging rubbery regime.

Hence, the mechanical behavior of polymers near  $T_g$  or in the rubbery plateau cannot be captured by simple elasticity alone. It reflects the combined, time- and temperature-dependent nature of viscoelasticity.

## 1.2 Importance of Viscoelasticity

The time and frequency dependence of polymer properties must be considered in virtually all applications (Slides 247):

- **engineering applications:** long-term performance (creep, fatigue, dimensional stability) determines service lifetime.
- **dynamic applications:** high-frequency or impact response is crucial in vibration damping, alternating electric fields, or shock absorption.
- **processing:** polymer shaping operations such as fiber spinning, extrusion, or blow molding are governed by viscoelastic flow behavior.
- **energy dissipation:** viscoelastic losses may cause internal heating and material failure.

## 2. Linear Viscoelasticity

### 2.1 Basic Viscoelastic Functions

Slide 251 illustrates the stress and strain evolution under different test conditions:

- **creep** (constant stress),
- **relaxation** (constant strain),
- and **tension at constant strain rate**.

From these tests, the main **viscoelastic functions** are defined as:

$$E(t) = \frac{\sigma(t)}{\varepsilon_0}, \quad G(t) = \frac{\sigma(t)}{\gamma_0}, \quad D(t) = \frac{\varepsilon(t)}{\sigma_0}, \quad J(t) = \frac{\gamma(t)}{\sigma_0}, \quad (2)$$

where  $E(t)$  and  $G(t)$  are **relaxation moduli**, and  $D(t)$  and  $J(t)$  are **creep compliances**. In the **linear viscoelastic (LVE) regime**, these functions depend only on time  $t$ , not on the magnitude of the applied strain or stress. In general,  $E(t) \neq D(t)$ .

At large deformations, this assumption breaks down: moduli and compliances become stress- or strain-dependent (e.g.  $E(t, \varepsilon_0)$ ), and the Boltzmann superposition principle (see below) no longer holds. Such nonlinear effects arise when large deformations alter the material's internal structure, for example, through chain stretching or orientation. Although nonlinear phenomenological models exist, their physical interpretation is often difficult. Therefore, DMA and rheological tests are often confined to the linear viscoelastic regime.

## 2.2 The Boltzmann Superposition Principle

In a linear elastic solid, stress and strain are instantaneously related. In a viscoelastic material, however, the response depends on the **entire loading history**. According to **Boltzmann's superposition principle**, the total strain (or stress) is the sum of the effects of all previous stress (or strain) increments (Slide 261).

For example, in a tensile creep test where stress changes stepwise ( $\Delta\sigma_0, \Delta\sigma_1, \dots$ ), the total strain at time  $t$  is:

$$\varepsilon(t) = \sum_{n=0} D(t - t_n) \Delta\sigma_n \quad , \quad (3)$$

and in the continuous limit:

$$\varepsilon(t) = \int_{-\infty}^t D(t - \xi) \frac{d\sigma}{d\xi} d\xi \quad , \quad (4)$$

where  $-\infty$  indicates the entire mechanical history of the sample. In practice, the lower limit is often set to 0, assuming that the sample is undeformed at the start of the experiment. Similarly, for stress relaxation:

$$\sigma(t) = \int_{-\infty}^t E(t - \xi) \frac{d\varepsilon}{d\xi} d\xi \quad . \quad (5)$$

These relations express the **memory effect**: the present response depends on the entire deformation or stress history.

## 2.3 Dynamic Measurement Techniques

In **Dynamic Mechanical Analysis** (DMA), the sample is subjected to sinusoidal stress or strain of angular frequency  $\omega$  [rad/s]. Deformation can be applied in tension, bending, or shear.

For a strain-controlled test:

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t) \quad , \quad (6)$$

The corresponding stress response is:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad , \quad (7)$$

where  $\delta$  is the **phase lag** between stress and strain (Slide 255). Expanding using the trigonometric identity gives:

$$\sigma(t) = \sigma_0[\sin(\omega t) \cos \delta + \cos(\omega t) \sin \delta] = G' \sin(\omega t) + G'' \cos(\omega t) \quad . \quad (8)$$

Here,  $G'$  is the storage modulus (**elastic energy storage**, in-phase (i.e. immediate) with the strain), while  $G''$  is the loss modulus (**energy dissipation**, out-of-phase with strain).

The **loss factor** (or damping factor) is:

$$\tan \delta = \frac{G''}{G'} \quad . \quad (9)$$

In a Hookean solid,  $G'' = 0$ , in a Newtonian liquid,  $G' = 0$ .

It is often convenient to use the complex modulus:

$$G^* = G' + iG'' \quad , \quad (10)$$

This complex representation simplifies analysis and is widely used in DMA and rheology.

## 2.4 Simple Phenomenological Models

Linear viscoelastic behavior bridges the response of a Newtonian liquid and a Hookean solid. It **can be modeled by linear combinations of "Hookean springs" and "Newtonian dashpots"** (Slide 260).

A **Maxwell element** (Slides 263–267) combines a spring (with modulus  $E$ ) and a dashpot (with viscosity  $\eta$ ) in series. For a sudden strain  $\varepsilon_0$ , applied at  $t = 0$ :

$$\sigma = \sigma_0 e^{-t/\tau} \quad . \quad (11)$$

$\tau = \eta/E$  is the relaxation time. This exponential decay resembles experimental stress relaxation near  $T_g$ .

Under oscillatory loading, using the Boltzmann superposition principle, the model yields:

$$E' = E \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} \quad , \quad E'' = E \frac{\omega\tau}{1 + (\omega\tau)^2} \quad . \quad (12)$$

At low frequencies ( $\omega\tau \ll 1$ ), the model behaves viscously and characterizes **the terminal regime** ( $E' \sim \omega^2, E'' \sim \omega$ ). At high frequencies ( $\omega\tau \gg 1$ ), it behaves elastically ( $E' \rightarrow E$ ).

By comparison, the **Zener model** (or "standard linear solid") adds an extra spring (with modulus  $E_B$ ) in parallel with **the Voigt model** (Slide 269). It reproduces a finite rubbery plateau at low frequencies ( $E' \rightarrow E_B$ ) and a peak in  $E''$  near  $\omega\tau \approx 1$ .

**Real polymers exhibit, however, broad relaxation spectra.** The generalized Maxwell model sums multiple relaxation processes:

$$E(t) = E_{\infty} + \sum_1^n E_i e^{-\frac{t}{\tau_i}} , \quad (13)$$

or, continuously:

$$E(t) = E_{\infty} + \int_0^{\infty} H(\tau) e^{-\frac{t}{\tau}} d \ln \tau , \quad (14)$$

where  $H(\tau)$  is a **relaxation time spectrum**. These models can fit experimental data but have limited physical interpretation.

### 3. Time-Temperature Equivalence

The principle of **time-temperature equivalence** expresses the empirical observation that the temperature dependence of viscoelastic behavior is equivalent to a horizontal shift along the time or frequency axis.

Using short-term tests at different temperatures, one can reconstruct viscoelastic functions (e.g.  $E'(\omega)$ ,  $E''(\omega)$ , or  $J(t)$ ) over very wide ranges of frequency or time by shifting the data horizontally by a factor  $a_T(T, T_{\text{ref}})$ . This process is called **time-temperature superposition (TTS)**, and the resulting “**master curve**” represents the behavior at a reference temperature  $T_{\text{ref}}$ .

The success of TTS indicates that all relevant molecular relaxation processes share the same temperature dependence. In practice, this occurs when one type of motion dominates the viscoelastic response. Near the glass transition, this dominant process is **segmental relaxation**, corresponding to cooperative rearrangements of short chain segments.

The horizontal shift factors  $a_T$  follow the empirical **Williams-Landel-Ferry (WLF) equation**:

$$\log a_T = - \frac{C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}} , \quad (15)$$

where  $C_1$  and  $C_2$  are empirical constants.

Taking  $T_{\text{ref}} = T_g$  gives approximately “universal” constants  $C_1 = 17.44$  and  $C_2 = 51.6$  K, which describe many amorphous polymers near their glass transition. Although empirical in origin, the WLF equation can be justified by **free volume theory** and connected to physical quantities such as the hypothetical equilibrium glass transition temperature  $T_0$  (see Reader on WLF Equation for details). It thus captures the essential physics of segmental mobility governed by free volume and forms the basis for time-temperature superposition in polymer viscoelasticity.

#### 4. Summary

- Polymers are viscoelastic materials whose mechanical response depends strongly on both time and temperature.
- In the linear viscoelastic regime, stress and strain are related through time-dependent functions that can be modeled using linear combinations of springs and dashpots.
- The time-temperature equivalence principle provides a framework for predicting polymer behavior across wide frequency or time ranges.
- The WLF equation quantitatively describes this equivalence near the glass transition, linking molecular mobility to changes in free volume.