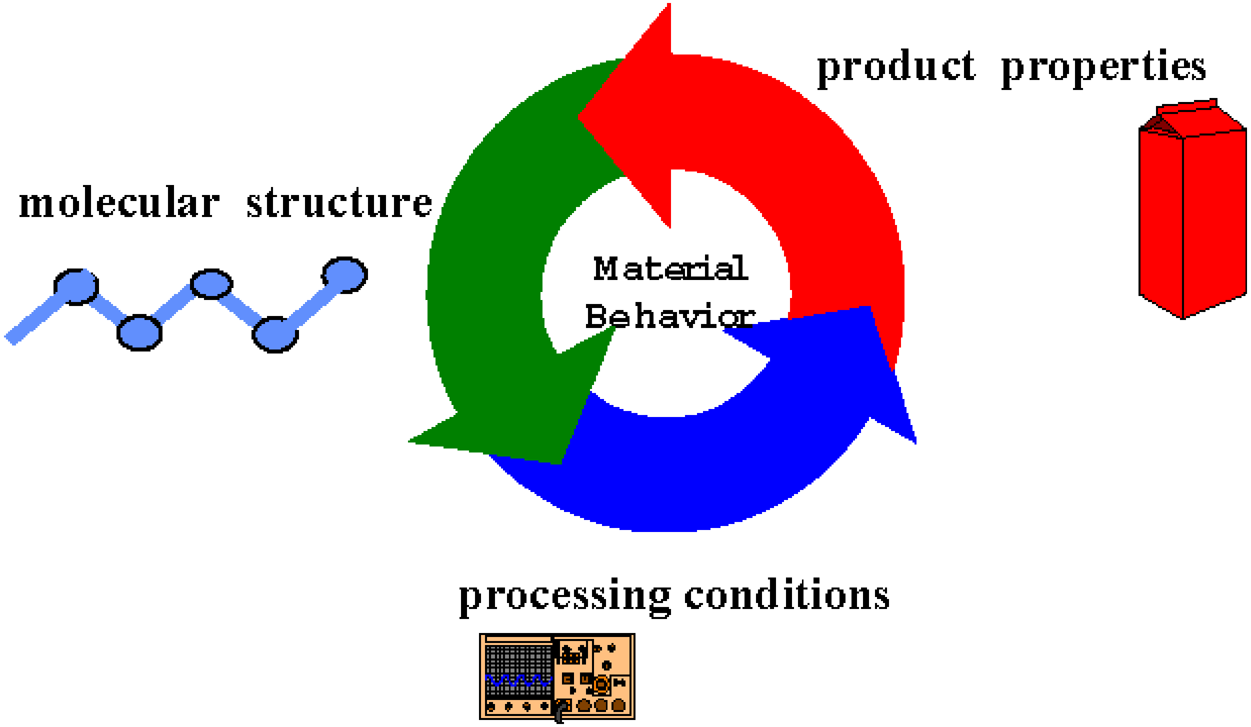
Course: Physical Chemistry of Polymeric Materials

Polymer Viscoelasticity

and

Rheology

Introduction



molecular structure

Material Behavior

product properties

processing conditions

Introduction

Molecular Weight Dependence of the Steady Flow Viscosity

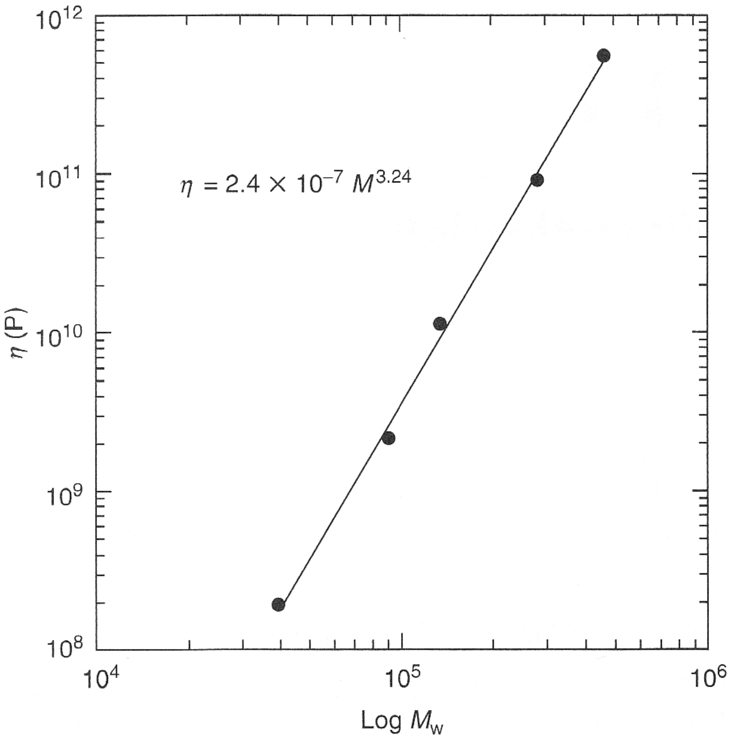


Figure 11.1 Viscosity versus molecular weight for molten poly(α-methyl styrene) at 186°C. (Data taken from Fujimoto, T., Ozaki, N., and Nagasawa, M., *J. Polym. Sci. Part A-2*, 6, 129, 1968.)

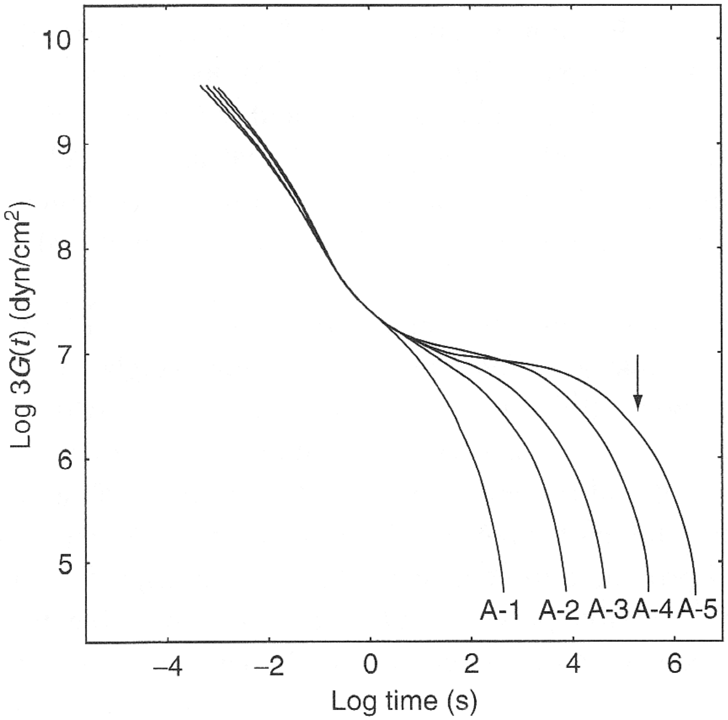


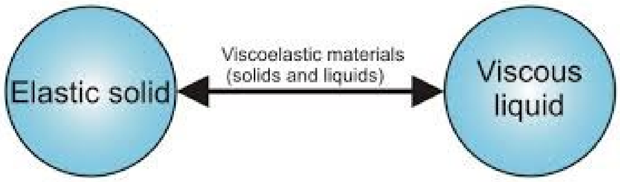
Figure 11.2 Stress relaxation modulus, $G(t)$, versus time for molten poly(α-methyl styrene) at 186°C; samples A-1 through A-5 correspond to the five samples in Figure 11.1. The arrow locates the longest relaxation time for sample A-5, as discussed in Example 11.1. (Data taken from Fujimoto, T., Ozaki, N., and Nagasawa, M., *J. Polym. Sci. Part A-2*, 6, 129, 1968. With permission.)

Outline

- Mechanical Models of Viscoelasticity
- Boltzmann Superposition Principle and Master Curves
- Bead – Spring – Model of Rouse and Zimm
- Entanglements
- Reptation Model of de Gennes
- Polymer Melt Viscosity
- Rheometers

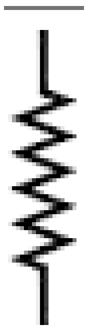
Viscoelasticity - Responses of Materials to Stress

Two limiting cases:



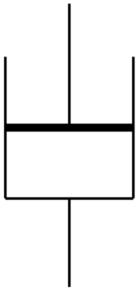
Hookean solids

$\sigma = E\,\varepsilon$



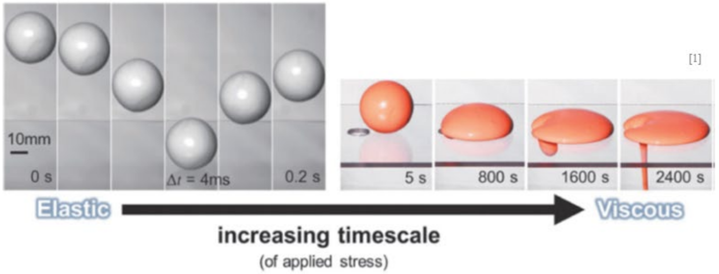
Newtonian liquids

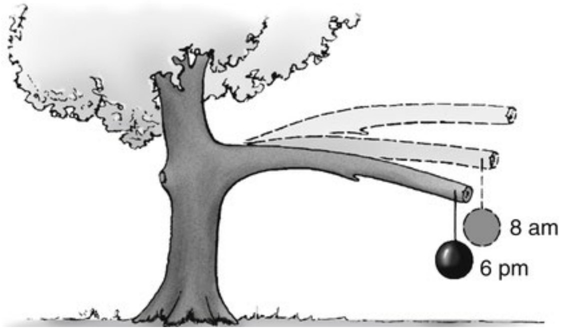
$\tau = \eta\,\dot{\gamma}$



spring and dashpot as models

Time

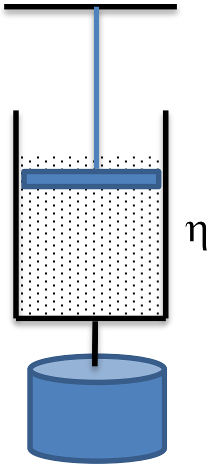


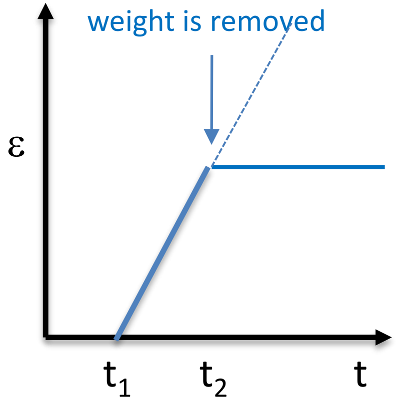


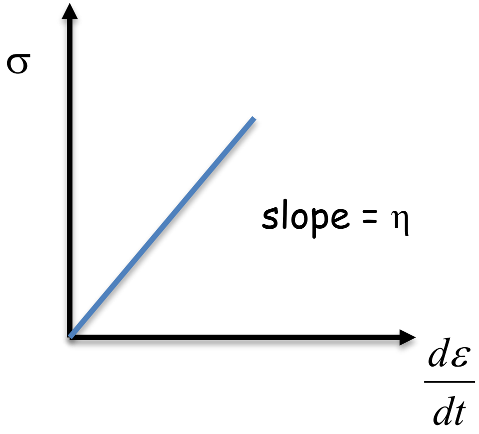
Most „real“ materials combine elastic and viscous behaviour (i.e. are viscoelastic)

Purely Viscous Element: The Dashpot

The dashpot is a purely viscous element characterized by a viscosity η. The rate at which the dashpot moves depends on the strain rate. The viscous response is **non-reversible**.



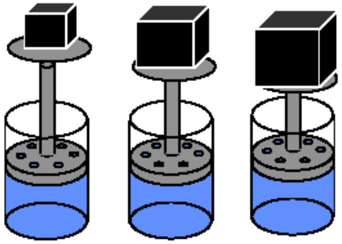




$$\tau = \eta\left(\frac{d\varepsilon}{dt}\right)$$

$$\varepsilon = \frac{\tau}{\eta}t + c$$ (integrated form)

time dependence of the strain $$\boxed{\frac{d\varepsilon}{dt} = \frac{\tau}{\eta}}$$



The speed at which the fluid flows through the holes (the strain rate) increases with stress!!!

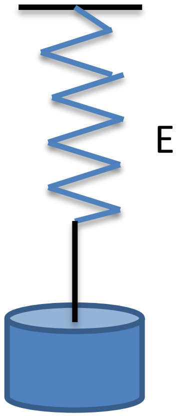
Purely Elastic Element: The Spring

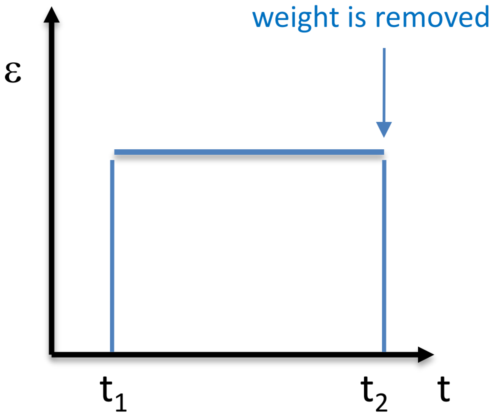
The spring is a purely elastic element which obeys Hooke's law and is characterized by an E-modulus:

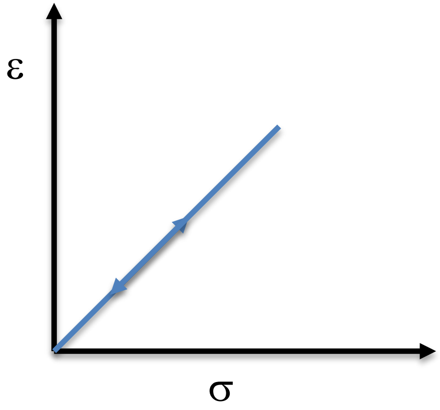
$$\sigma = E\varepsilon$$ tensile deformation

$$\tau = G\gamma$$ shear deformation

The elastic response is characterized as being **reversible** (time independent elastic properties).





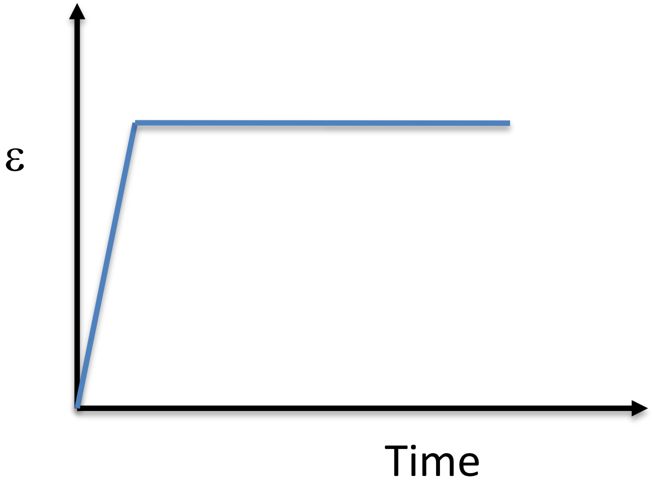


time dependence of the strain

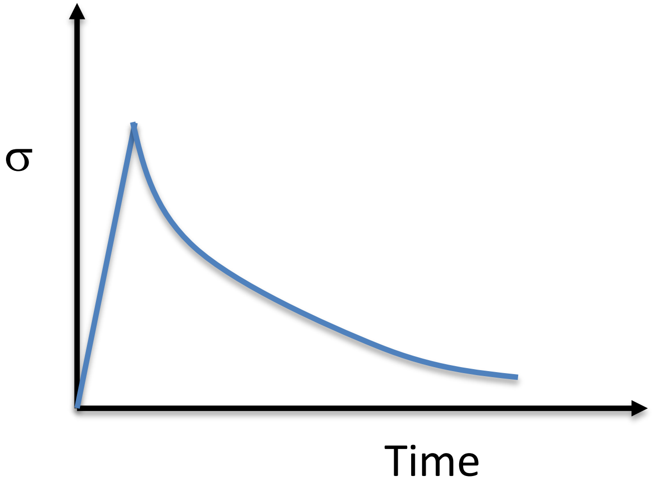
$$\boxed{\frac{d\varepsilon}{dt} = \frac{1}{E}\left(\frac{d\sigma}{dt}\right)}$$

Stress Relaxation

This is what we impose on the sample



This is what we measure



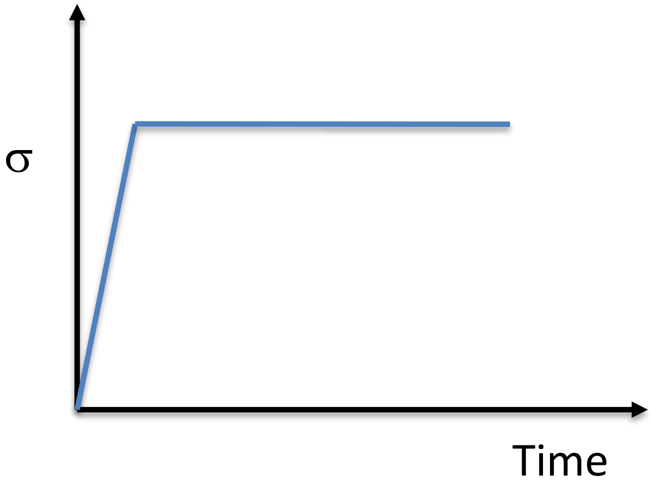
In stress relaxation experiments, a chosen strain is applied to the sample and maintained.

The stress is then measured as a function of time. This value decreases because the polymer chains reorganize (relax)

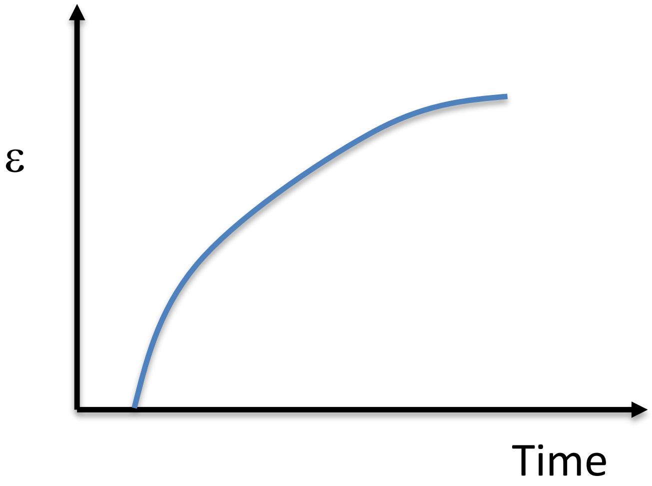
This experiment is equivalent to stretching a rubber band to twice its length, holding it there, and measuring how much its pulls on your fingers over time.

Creep

This is what we impose on the sample



This is what we measure



In creep experiments, a chosen stress is applied to the sample and maintained.

The strain (length of the sample) is then measured as a function of time. This value increases because the polymer chains reorganize (relax)

This experiment is equivalent to putting a weight on a rubber band and seeing how its length changes over time.

Molecular Basis of Stress Relaxation and Creep

1. **Chain scission**: mainly oxidative degradation and hydrolysis

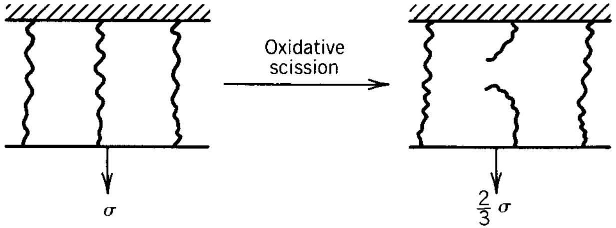
2. **Bond interchange**: Polysiloxanes, polyesters

3. **Viscous flow**: caused by linear chains slipping past one another

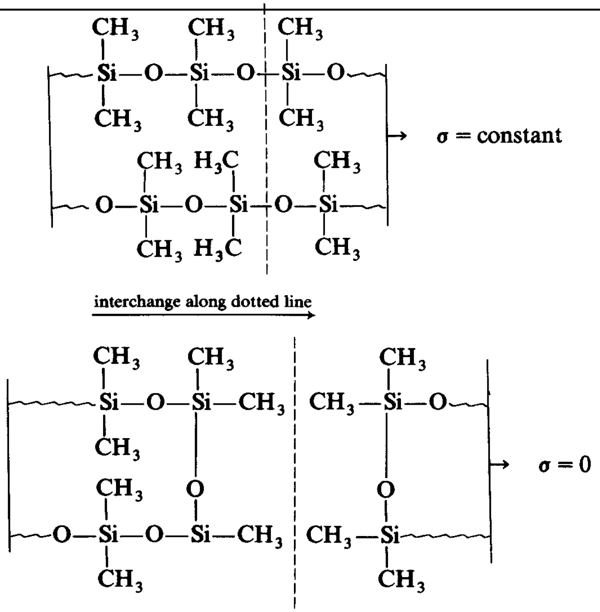
4. **Thirion relaxation**: reversible relaxation of the physical crosslinks or trapped entanglements in elastomeric networks

5. **Molecular relaxation**: especially near T_g. In this range the chains relax at about the same rate as the time frame of the experiment

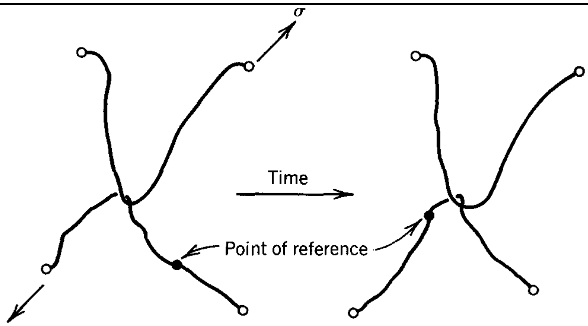
Ad 1.



Ad 2.



Ad 4.



An illustration of reversible motion in a trapped entanglement under stress. The marked point of reference moves with time. When the stress is released, entropic forces return the chains to near their original positions.

Models for Stress Relaxation and Creep

Stress relaxation and creep experiments allow us to measure the viscoelastic properties of polymers.

There exist several mechanical models for interpreting the stress relaxation and creep behavior of polymers.

A) Purely elastic element → spring
B) Purely viscous element → dashpot
C) Maxwell → for fluid polymers
D) Voigt/Kelvin → for solid polymers
E) 4 element model

The last three models combine both purely elastic and purely viscous elements.

Maxwell Element

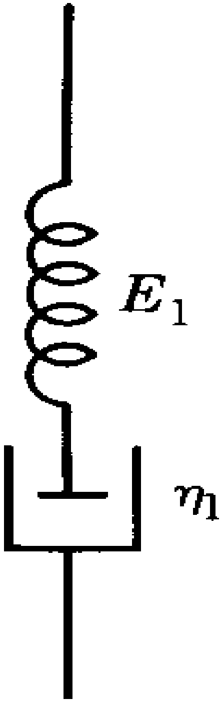
Model for Viscoelastic Liquid

- Spring and dashpot in series

- Both spring and dashpot are subjected to the same stress, but are permitted independent strains (total strain is the sum of the strains of dashpot and spring)

- Spring responds instantaneously. Reponse defined by: $\varepsilon = \sigma / E$

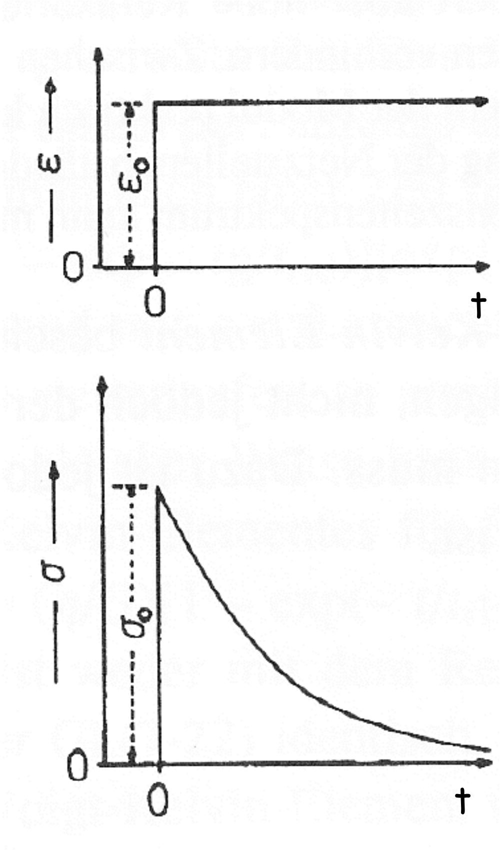
- Spring remains extended as the dashpot gradually moves out



Stress Relaxation Experiment (Maxwell Element)

$$\frac{d\varepsilon}{dt} = \left(\frac{1}{\eta}\right)\sigma + \frac{1}{E}\left(\frac{d\sigma}{dt}\right)$$

Integrated form: $\boxed{\sigma(t) = \sigma_0 \exp\left(\frac{-t}{\tau_1}\right)}$ with relaxation time $\boxed{\tau_1 = \eta/E}$

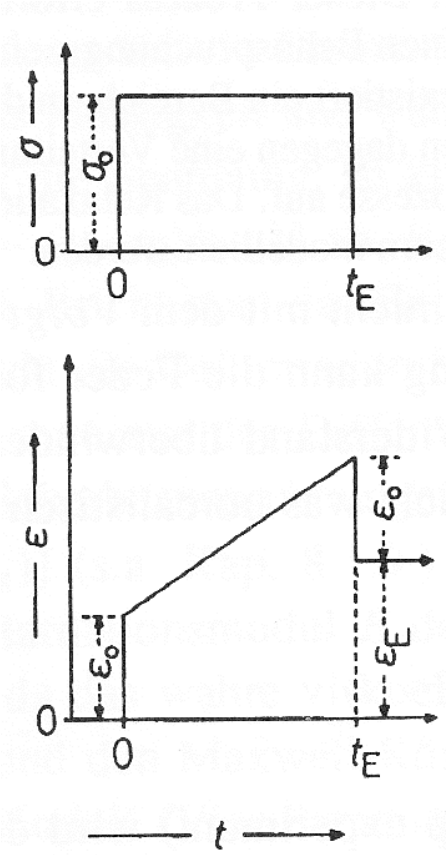


Relaxation time is a measure of the time required for a system to return to equilibrium after any kind of disturbance. It is the time in which the stress is decreased to 1/e-part = 0.368 of the original value

Relaxation time $\tau_1 = \eta/E$; indicates the order of magnitude of time required for a certain proportion of the polymer chains to relax, i.e. to respond to the external stress by thermal motion

Creep Experiment on Maxwell Element

At time t = 0 a stress σ_0 is applied. Because of the series of spring and dashpot the Maxwell element has directly a strain at t = 0 of $\varepsilon_0 = \sigma_0/E$ (spring).
With uniform loading (σ = const, $d\sigma/dt = 0$) the Maxwell element expands because of the dashpot with the velocity σ_0/η . It results a creep, which is a retardation process.



The strain at time t is given as (condition $\sigma = \sigma_0$ = const.)

$$\varepsilon(t) = \left(\frac{\sigma_0}{E}\right) + \left(\frac{\sigma_0}{\eta}\right)t = \varepsilon_0 + \left(\frac{\sigma_0}{\eta}\right)t$$

At t = t_E the stress is removed and the body retracts with $\varepsilon_0 = \sigma_0/E$, but it rests an permanent set of $\varepsilon_E = (\sigma_0/\eta)t_E$

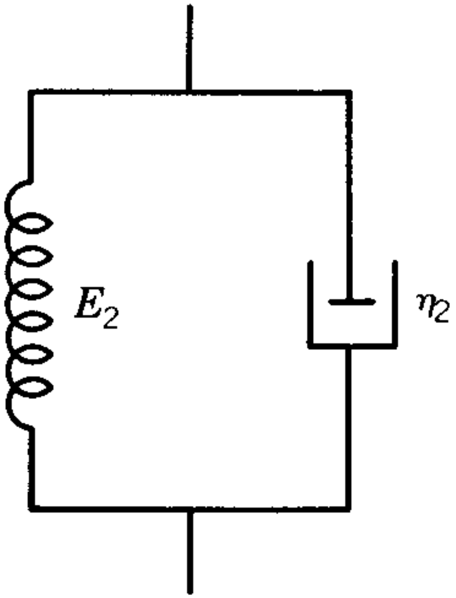
This means on the beginning t = 0, the Maxwell element behaves like a elastic solid, but during the experiment it becomes a viscous liquid.

For polymers the strain at constant stress is not linear with the time
→ Maxwell model is unrealistic

Kelvin/Voigt Element

Model for Viscoelastic Solid

- Parallel arrangement
- Both elements are subjected to the same strain, but experience a different stress
- Spring and dashpot undergo concerted motion as they are constrained to remain parallel
- The dashpot responds slowly to stress, bearing all of it initially and gradually transferring it to the spring as the latter becomes extended
- When the spring bears all the stress, both the spring and dashpot stop deforming and creep stops => asymptotic behaviour.

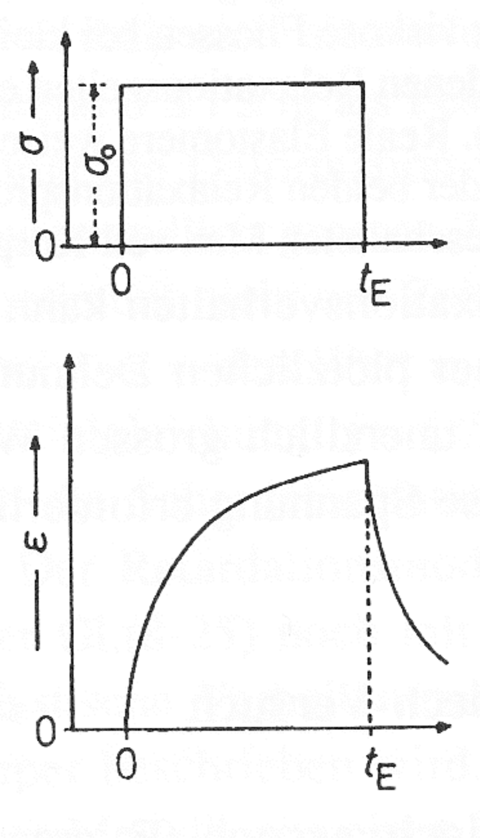


The relaxation behavior cannot described by the Kelvin/Voigt element. Because upon deformation (imposed strain) the spring can immediately follow but the dashpot cannot. The dashpot must be overcome a very high resistance for which an infinite high stress is necessary.

Creep Experiment on Kelvin/Voigt Element

The Voigt-Kelvin Element describes the time dependent increase of the strain

$$\varepsilon(t) = \left(\frac{\sigma_0}{E}\right)\left[1 - exp\left(-\left(\frac{E}{\eta}\right)t\right)\right] = \left(\frac{\sigma_0}{E}\right)\left[1 - exp\left(-\frac{t}{\tau_2}\right)\right]$$



At t = 0 the strain ε = 0, but increases rapidly with the time like a liquid with a slope of σ_0/η. Later the increase will be much less.
The retardation time τ_2 is the time required for E_2 and η_2 in the Kelvin element to deform to 1 – 1/e or 63,21% of the total expected creep.

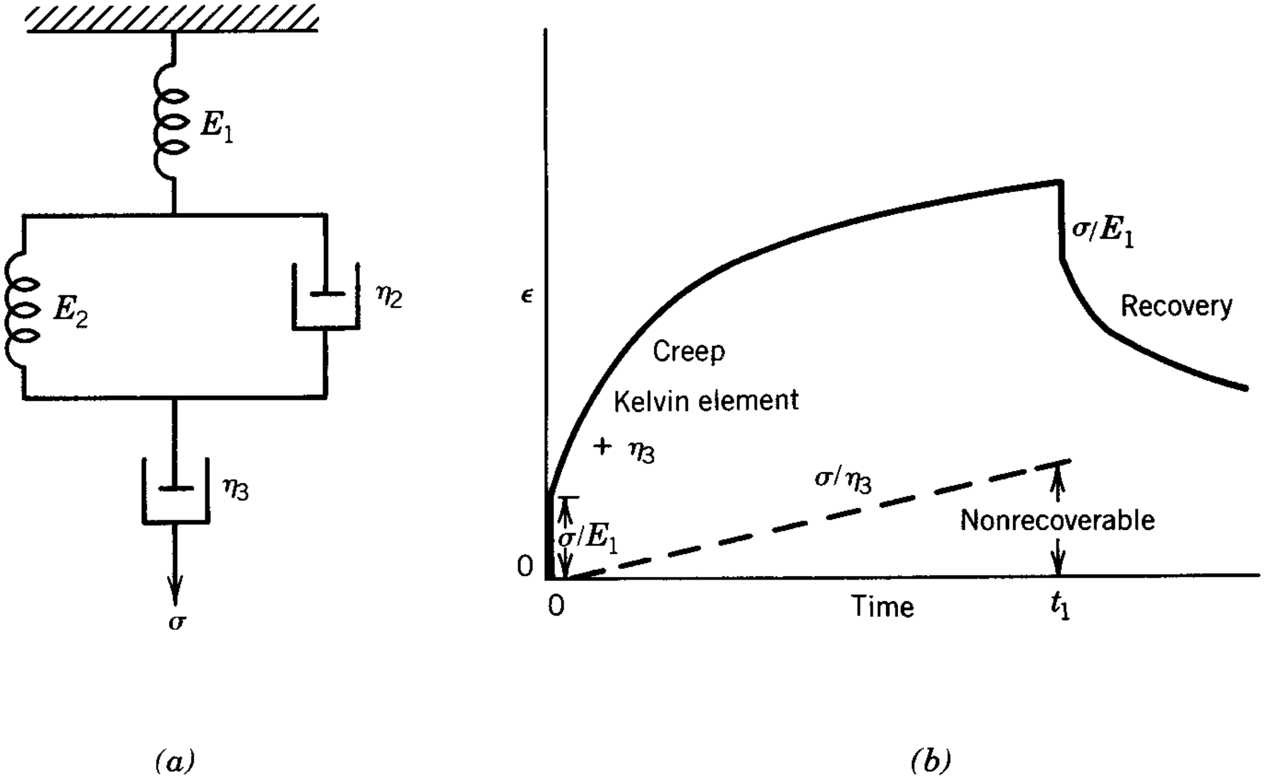
Model for viscoelastic solid: on the beginning the Kelvin element behaves like a liquid, but during $0 \leq t \leq t_E$ as a solid.

If we have not normal stress but shear stress the resulting shear strain is given as

$$\gamma(t) = \left(\frac{\sigma_0}{G}\right)\left[1 - exp\left(-\left(\frac{G}{\eta}\right)t\right)\right] = \left(\frac{\sigma_0}{G}\right)\left[1 - exp\left(-\frac{t}{\tau_2}\right)\right]$$

4 Element Model

Maxwell and Kelvin/Voigt elements can be combined in more complex arrangements:



(*a*) The four-element model. (*b*) Creep behavior as predicted by this model. At t_1, the stress is relaxed, and the model makes a partial recovery.

Exp.: Stretching a rubber band around a book

Dynamic Mechanical Analysis: Complex Modulus and Loss Tangent

Applying a sinusoidally time-varying strain $\gamma(t) = \gamma_0 \sin\omega t$ (or stress) and measure the sinusoidally time-varying stress (or strain)

→ the viscous and elastic character of the response can be resolved concurrently.

$$\boxed{G^*(\omega) = G' + iG''}$$

G* is the **complex modulus** with its real part G' (storage modulus) because it is in-phase with the applied strain and with its imaginary G'' part (loss modulus) because it is 90° out-of-phase with the applied strain.

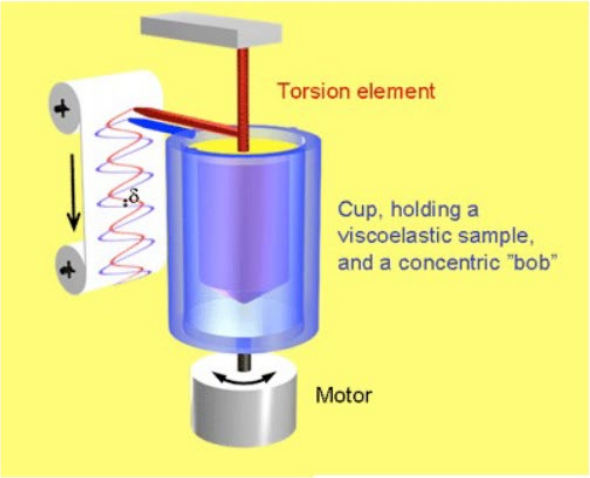
The phase angle δ is often given in terms of the

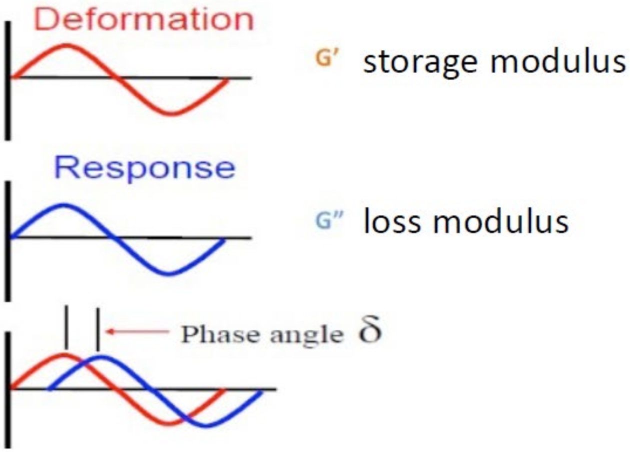
$$\boxed{\text{loss tangent}\quad tan\delta = \frac{G''}{G'}}$$

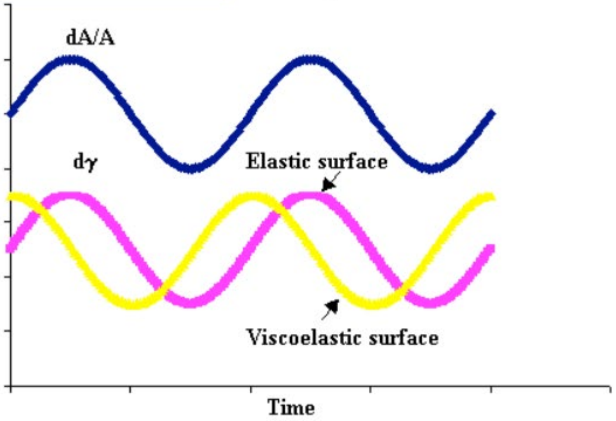
because it is the direct ratio of the viscous and elastic part.

→ $\tan\delta >> 1$	the material behaves like a liquid
→ $\tan\delta << 1$	the material is a solid
→ at $\tan\delta \sim 1$	the crossover occurs

Determination of storage and loss Modulus

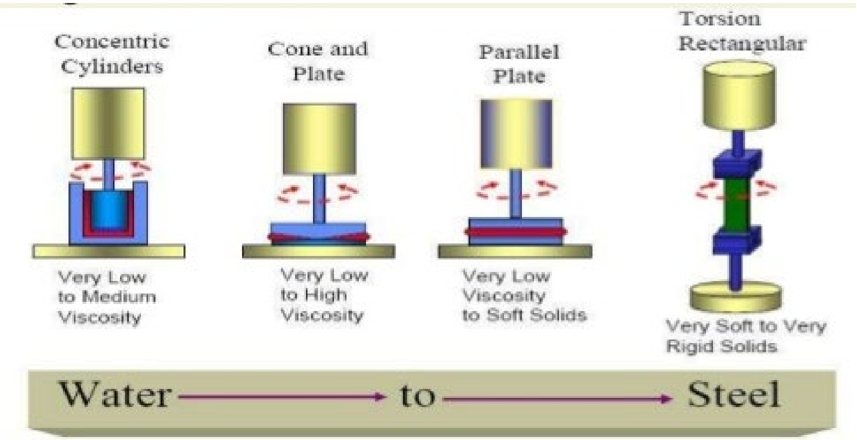


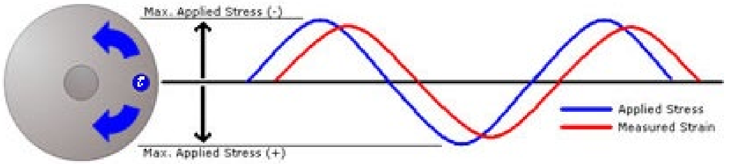


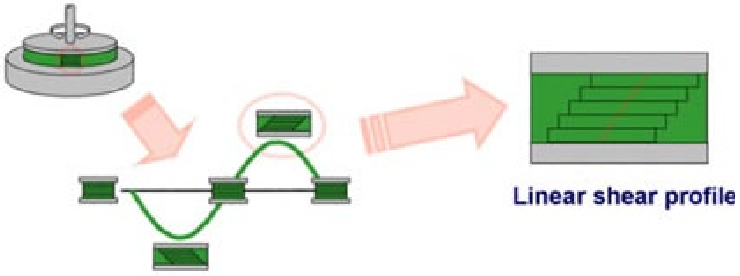


6

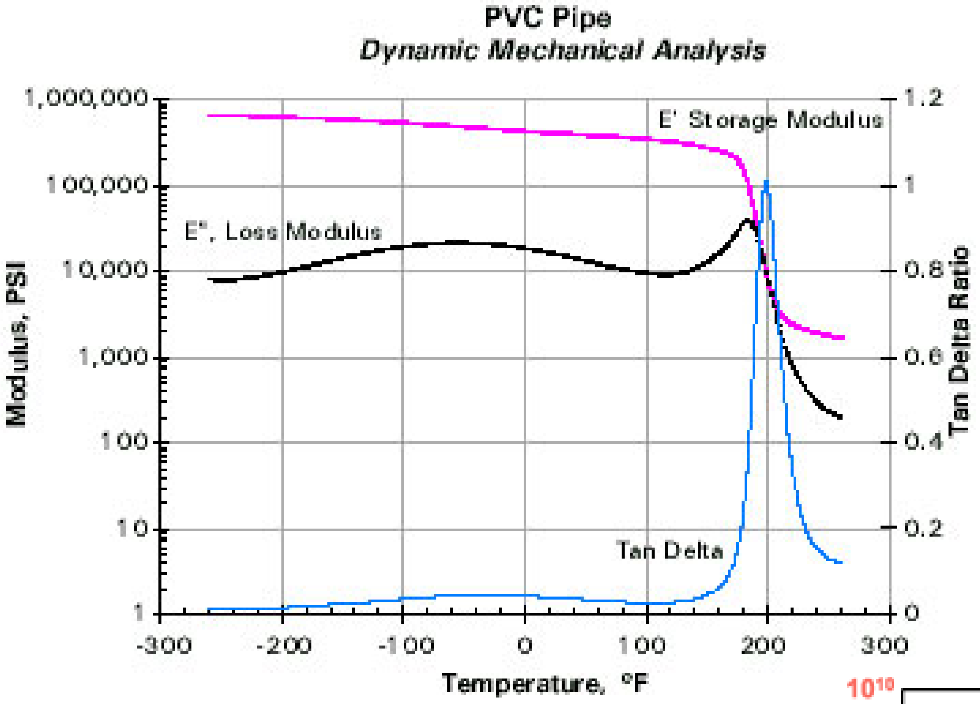
Types of Rheometers





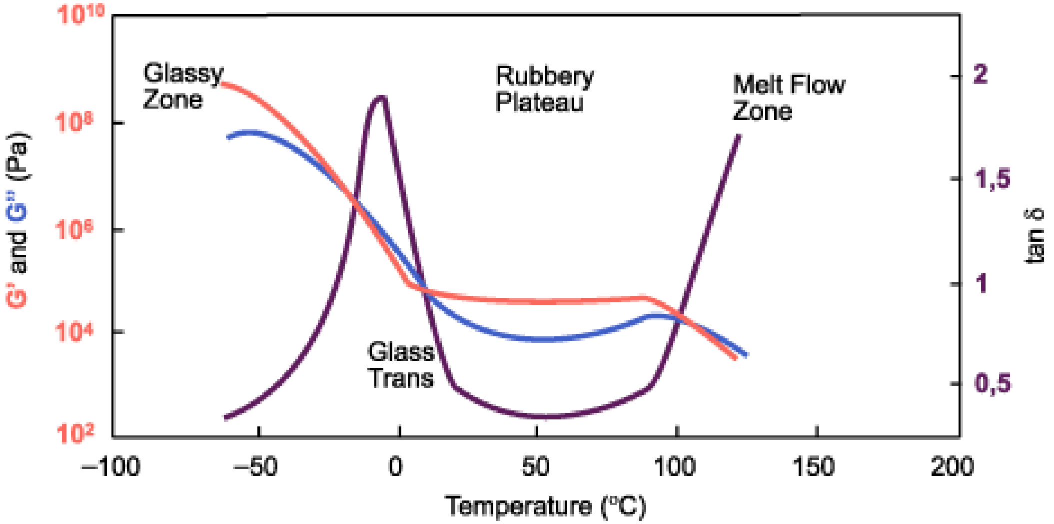


Example of DMA



200 °F = 93 °C

styrene isoprene styrene



The Boltzmann Superposition Principle

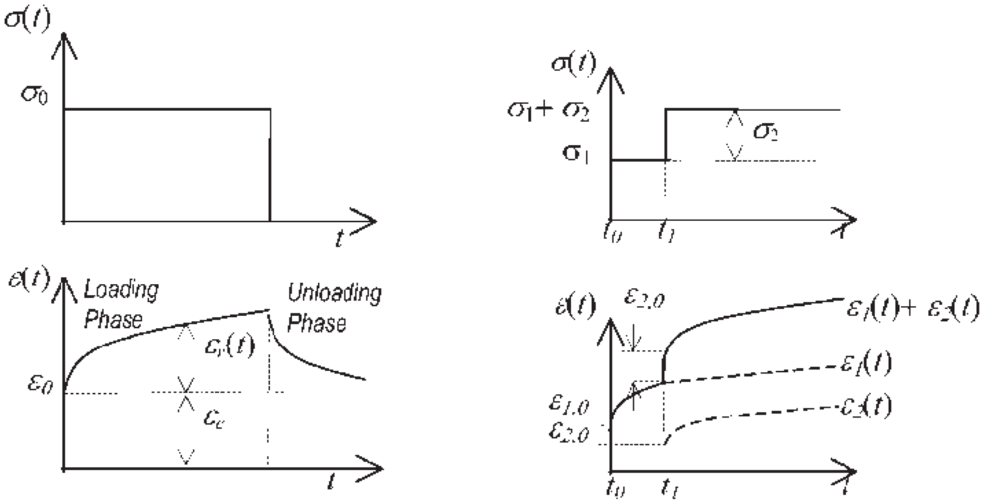
The stress from any combination of small step strains is simply the linear combination of the stresses resulting from each individual step $\delta\gamma_i$ applied at time t_i.

$$\sigma(t) = \sum_i G(t - t_i)\delta\gamma_i$$

γ_i shear strain

$\delta\gamma_i = \dot{\gamma}_i \delta t_i$

The stress relaxation modulus tells how much stress remains at time t from each past deformation $\delta\gamma_i$ through the elapsed time $t - t_i$ that has passed since that deformation was applied at time t_i. The stress from any smooth strain history can be written as an integral by replacing the above summation with



$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')dt'$$

Time – Temperature Equivalence – Master Curve

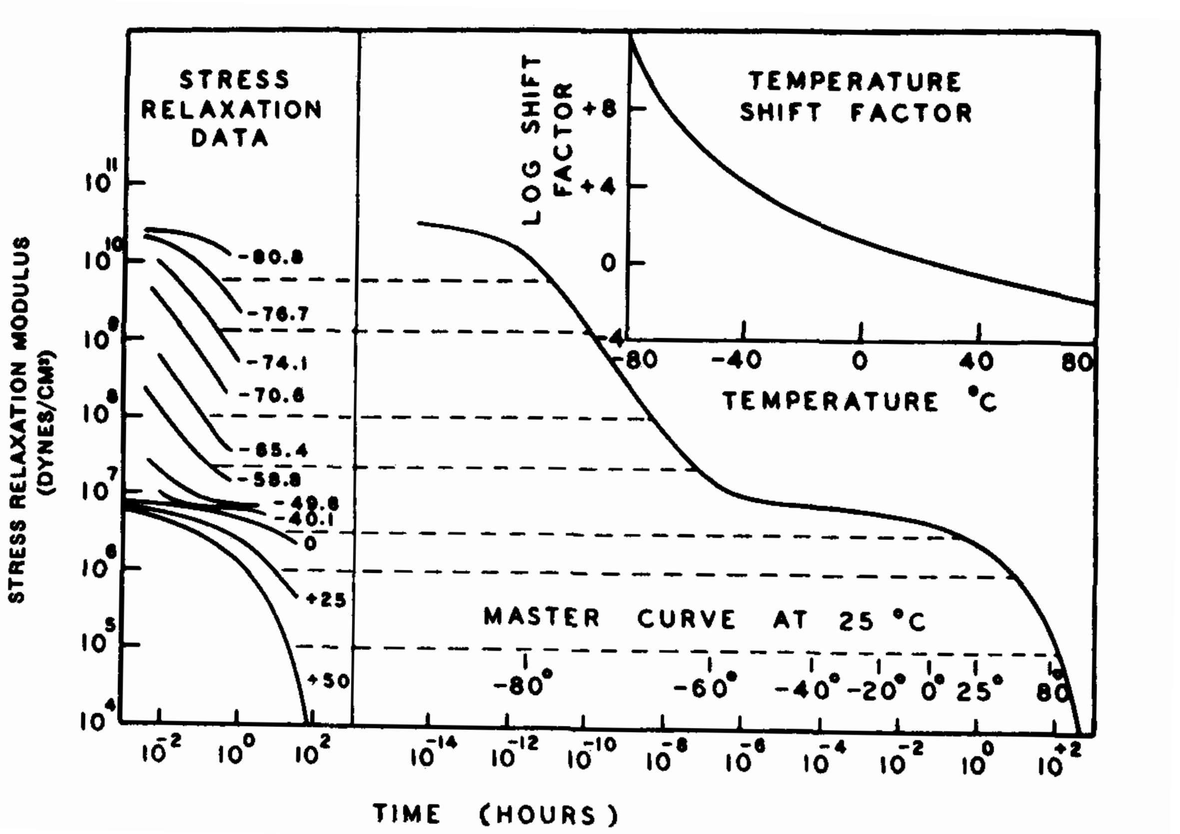
For viscoelastic materials, time and temperature are equivalent to the extent that data at one temperature can be superimposed upon data at another temperature by shifting along the log time axis.

→ data (e.g. moduli) can be measured conveniently over a narrow time scale, ~ 1 – 10^5 sec

$$\log A_T = \log\frac{\tau}{\tau_0} = \log\frac{\eta_T}{\eta_{T_g}} = \frac{-17.44(T-T_0)}{51.6+(T-T_0)}$$

A_T is a scaling factor which allows us to "assemble" the isothermal curves into a "master curve"

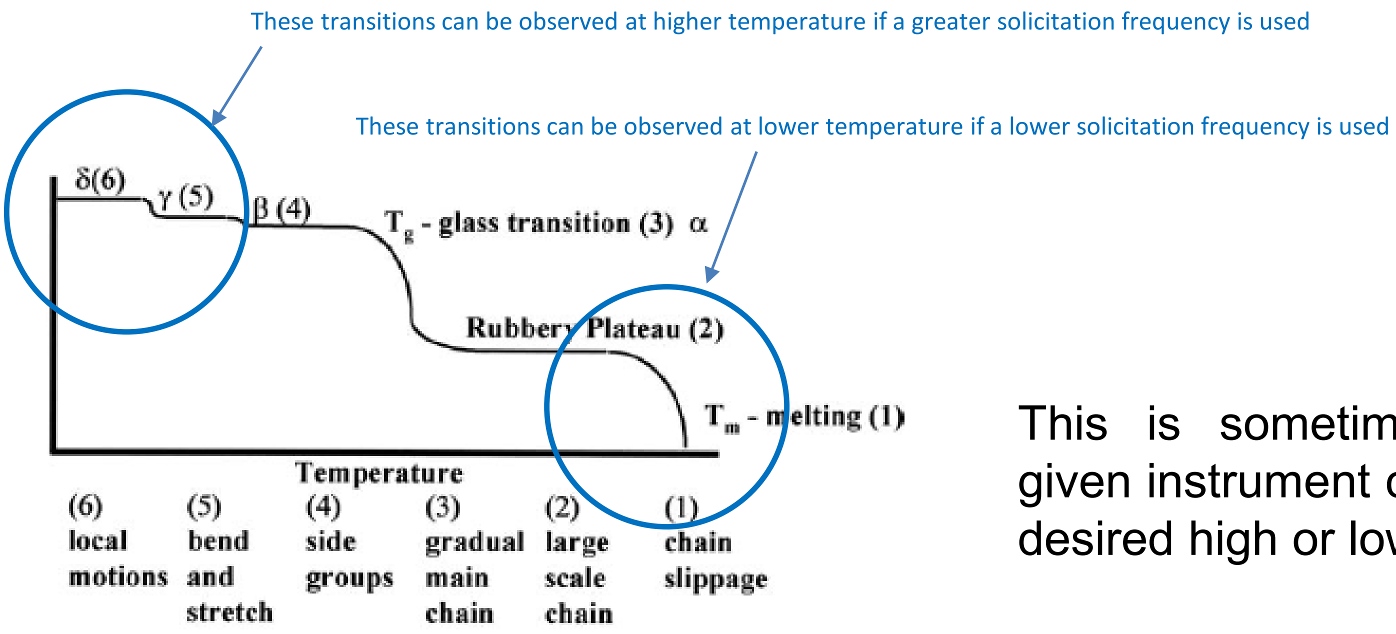
Master Curve of polyisobutylene
The classical T_g at 10 seconds is at – 70°C



What is the use of Generating Master Curves?

Varying frequency and temperature gives access to a much broader range of frequencies and/or temperatures.

Some molecular movements occur at very low frequency (<<< 1Hz). This can significantly increase the time required to examine a sample. This data can be accessed at a higher frequency if we simply lower the temperature.


These transitions can be observed at higher temperature if a greater solicitation frequency is used

These transitions can be observed at lower temperature if a lower solicitation frequency is used

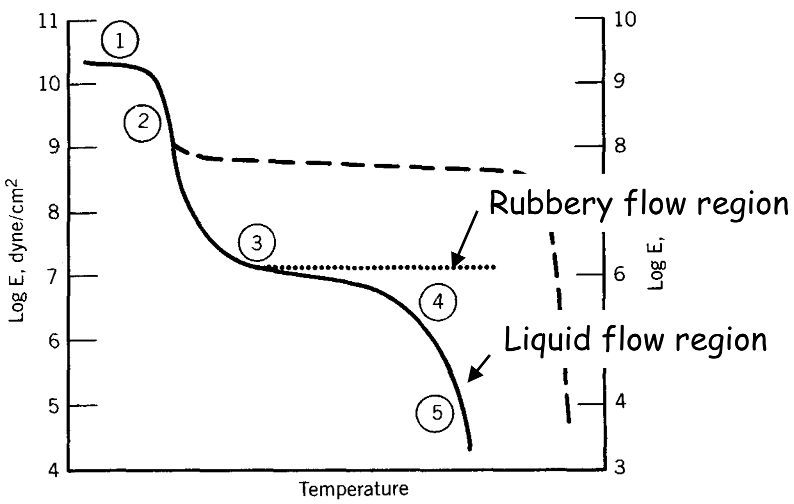
This is sometimes useful if a given instrument cannot reach the desired high or low temperatures.

Polymer Melt Viscosity

Williams-Landel-Ferry (WLF) equation:

$$\log\left(\frac{\eta}{\eta_{T_g}}\right) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}$$

- C_1/C_2: Constants. If unknown, C_1 = 17.44 and C_2 = 51.6 may be used
- η_{Tg} = melt viscosity at T_g (frequently $\eta_{Tg} = 1 \times 10^{13}$ poises is used)
- Can be used to estimate melt viscosities if T_g is known



Five regions of viscoelastic behavior for a linear, amorphous polymer. Also illustrated are effects of crystallinity (dashed line) and cross-linking (dotted line).

WLF Parameters

Polymer	C_1	C_2	T_g, °K
Polyisobutylene	16.6	104	202
Natural rubber (Hevea)	16.7	53.6	200
Polyurethane elastomer	15.6	32.6	238
Polystyrene	14.5	50.4	373
Poly(ethyl methacrylate)	17.6	65.5	335
"Universal constants"	17.4	51.6	

Source: J. J. Aklonis and W. J. MacKnight, *Introduction to Polymer Viscoelasticity*, Wiley-Interscience, New York, 1983, Table 3-2, p. 48.

Molecular Weight Dependence of the Melt Viscosity

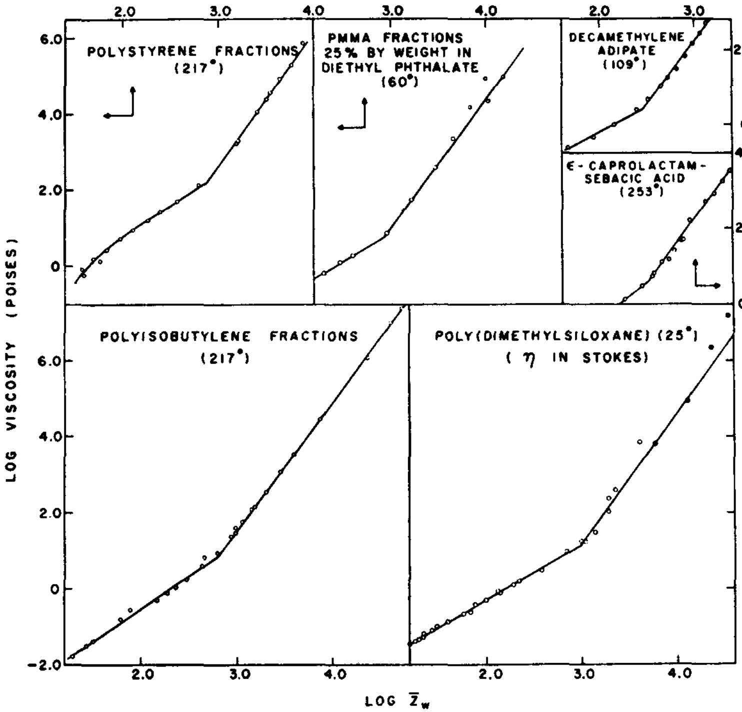
Polymer melt viscosity is determined by the number of atoms that constitute the polymer backbone (Z). Two regimes:

$Z < Z_{c,w}$: $\eta = K_L \, DP_w^{1.0}$

$Z > Z_{c,w}$: $\eta = K_H \, DP_w^{3.4}$

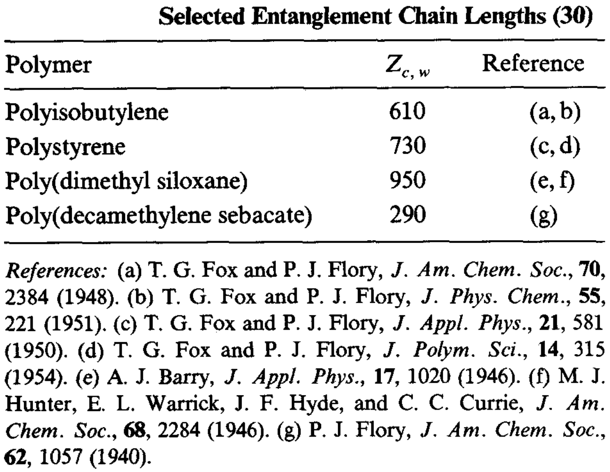
K_L, K_H: constants for low and high molecular weight
DP_w: weight average DP. Viscosity is related to M_w!!
$Z_{c,w}$: critical entanglement chain length

For vinyl polymers: Z = 2 DP
For diene polymers: Z = 4 DP



A plot of log η versus log Z_w for several polymers of importance. Below about $Z_w = 600$, the melt viscosity goes as the first power of Z_w; above 600, the melt viscosity depends on the 3.4 power of Z_w

$Z < Z_{c,w}$: flow behaviour represents the increase in viscosity with increasing chain length; 1.0 power dependence
$Z > Z_{c,w}$: flow behaviour dictated by entanglement and diffusion considerations; 3.4 power dependence



Selected Entanglement Chain Lengths (30)

Polymer	$Z_{c,w}$	Reference
Polyisobutylene	610	(a, b)
Polystyrene	730	(c, d)
Poly(dimethyl siloxane)	950	(e, f)
Poly(decamethylene sebacate)	290	(g)

References: (a) T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.*, **70**, 2384 (1948). (b) T. G. Fox and P. J. Flory, *J. Phys. Chem.*, **55**, 221 (1951). (c) T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950). (d) T. G. Fox and P. J. Flory, *J. Polym. Sci.*, **14**, 315 (1954). (e) A. J. Barry, *J. Appl. Phys.*, **17**, 1020 (1946). (f) M. J. Hunter, E. L. Warrick, J. F. Hyde, and C. C. Currie, *J. Am. Chem. Soc.*, **68**, 2284 (1946). (g) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1057 (1940).

Summary

1. Polymer liquids show generally viscoelastic behavior = a response to an imposed deformation that is between the viscous flow of liquids and the elastic deformation of solids, characterized by material function such as steady flow viscosity and dynamic modulus.

2. Using simple mechanical models – Maxwell and Kelvin/Voigt.
   A polymer liquid behaves more like an elastic solid at short times (or high frequencies) and more like a viscous liquid at long times.

3. In the limit of linear response, i.e. sufficiently small strain amplitudes and strain rates such that the material functions do not depend on the strain amplitude or rate, the Boltzmann superposition principles provides a direct route to calculate the viscosity, dynamic moduli from the stress relaxation modulus.