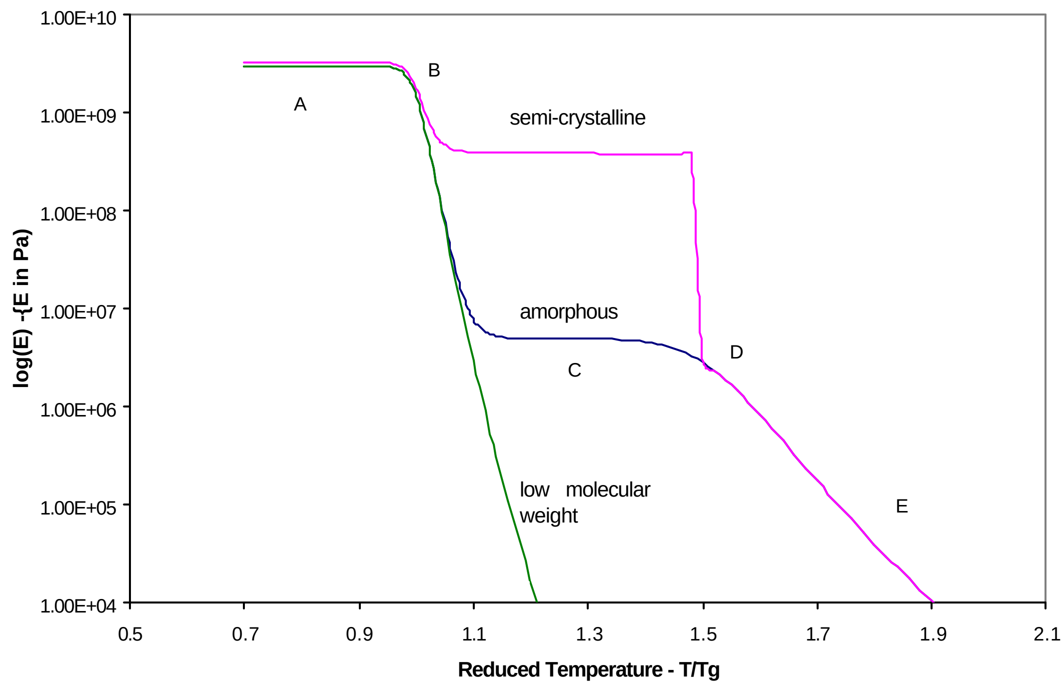
Introduction to Viscoelasticity

The viscoelastic curve represents the relationship between a sample's temperature and its modulus. The modulus is a measure of the sample's resistance to being deformed by an imposed stress. The viscoelastic curve is divided into five distinct regions (labeled A – E).



A - <u>Glass</u>. The material is rigid, yet brittle if not reinforced by chemical cross-links or crystallites. Polystyrene and plexiglass are amorphous glasses at room temperature.

B - <u>Glass Transition Zone</u>. The material starts to become compliant over time (at constant temperature), or in a narrow temperature range. The glass transition temperature, T_g, identifies this zone.

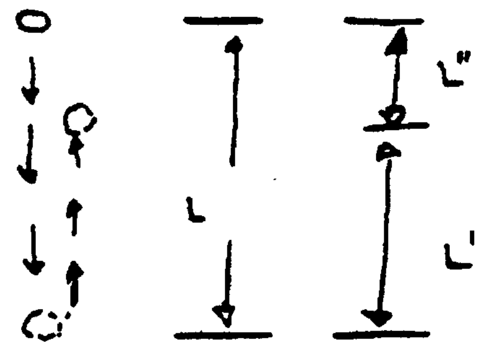
C - <u>Rubber</u>. The material is very flexible, capable of being stretched to several times its original dimensions without breaking. Commercial rubbers are chemically crosslinked to keep them from softening at elevated temperatures.

D - <u>Rubbery Flow Zone</u>. The material becomes tacky, and will spread like a liquid if pressure is applied. Pressure-sensitive adhesives are designed to exhibit this behavior at room temperature.

E - <u>Polymer Melt</u>. As the polymeric material is heated beyond the rubbery flow zone its viscosity steadily decreases. As the viscosity (resistance to flow) decreases, so does the materials modulus. This is the processing region of the viscoelastic curve.

Viscoelasticity: The response of a polymeric material to an imposed stress can be divided up into an elastic component and a viscous component.

Example:



Elastic response is proportional to L'
viscous response is proportional to L''

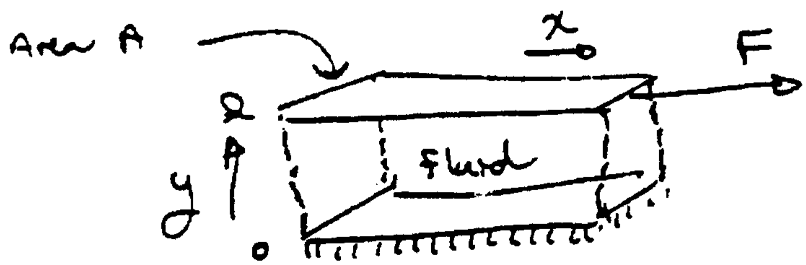
$$\text{Loss tangent} \equiv \tan\delta = \frac{L''}{L'} = \frac{E''}{E'}$$

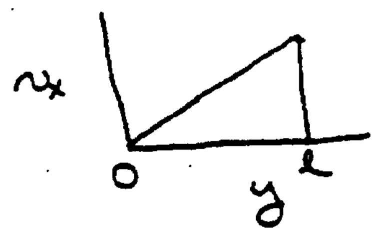
E'' loss modulus (viscous damping)
E' - storage modulus (elastic recovery)

Definition: An elastic response conserves the energy of the system. $\propto E'$ or G'

A viscous response dissipates the energy of the system. $\propto E''$ or G''

Flow of Viscous Fluids





Newton's Law of Viscosity $\frac{F}{A} = +\eta \frac{dv_x}{dy}$

$$\frac{\text{force}}{\text{area}} = \text{stress} \equiv \sigma_s = +\eta \frac{dv_x}{dy}$$

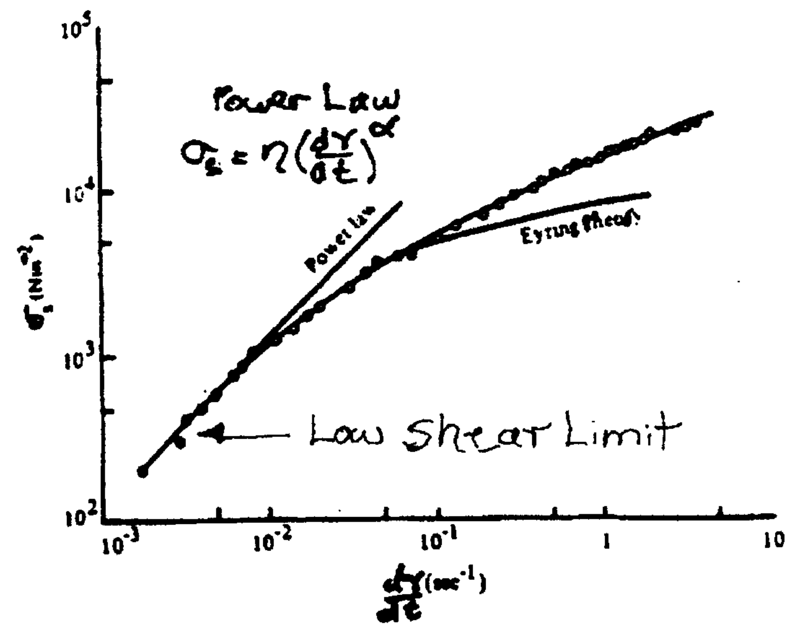
g/cm·sec = centipoise

however: $\frac{\Delta x}{\Delta y} \equiv$ shear strain γ

Recall $\sigma_s = G\gamma$

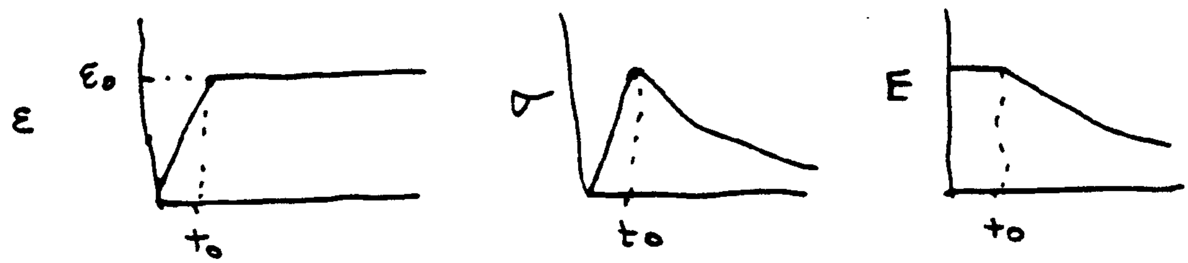
and $\frac{dv_x}{dy} = d\gamma/dt$

Therefore $\sigma_s = +\eta\, d\gamma/dt = \eta\dot{\gamma}$



Viscoelastic Experiments.

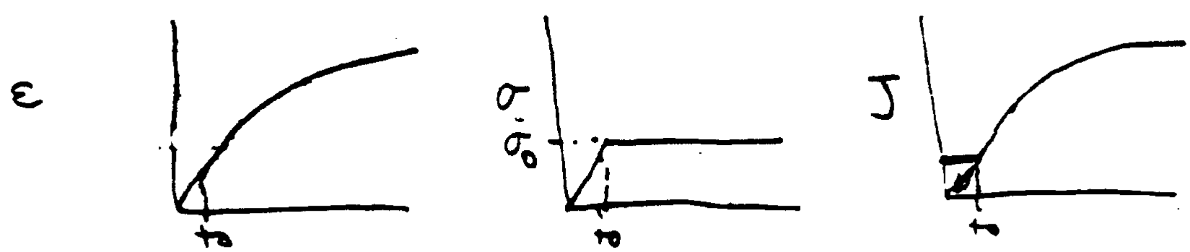
Stress Relaxation: constant strain → measure the time variation of the stress



$$\sigma_c(t) = E(t)\,\varepsilon_0$$

constant

Creep: constant stress → measure the time variation of the strain



$$\varepsilon(t) = \sigma_0 J(t) \neq \sigma_0 / E(t)$$

put another way $\quad \varepsilon(t) = \sigma_0 J_0' + J''(t)\sigma_0$

elastic ↗ viscous

A second look at a <u>creep</u> <u>experiment</u>:

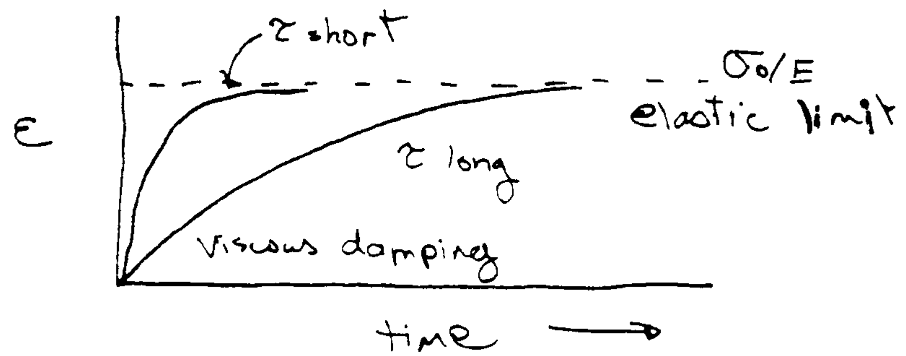
$$\sigma_0 = E\varepsilon + \eta_t \frac{d\varepsilon}{dt}$$

elastic   viscous

$$\frac{\sigma_0}{E} = \varepsilon + \frac{\eta_t}{E}\frac{d\varepsilon}{dt} \qquad \text{Let} \quad \frac{\eta_t}{E} = \tau$$

then $$\frac{\sigma_0}{E} = \varepsilon + \tau\frac{d\varepsilon}{dt}$$

solving $$\varepsilon = \frac{\sigma_0}{E}\left(1 - e^{-t/\tau}\right)$$



τ is known as a relaxation time for the mechanical system exposed to a controlled stress.

The Deborah number $\equiv De = \frac{\lambda_c}{t_s}$

λ_c = material relaxation time

t_s = Measurement time

Gives a measure of viscous vs elastic response.

$De \ll 1$ Elastic Limit

$De \gg 1$ Viscous Limit.

Viscoelastic Models:

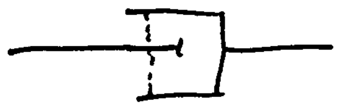
Pure Elastic

Spring

Hooke's Law

$\sigma_0 = E\varepsilon_0$

Pure Viscous



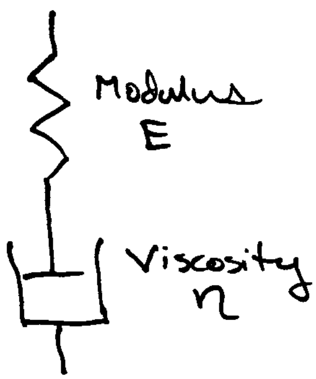
Dashpot

$\sigma = \eta \frac{\partial \varepsilon}{\partial t}$

Newton's Law

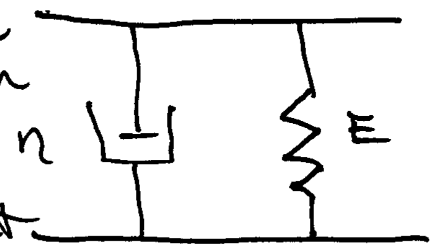
Maxwell Element

Same stress in each element



Voigt Element

Same strain in each element



$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

$$\sigma(t) = E \cdot \varepsilon(t) + \eta \frac{d\varepsilon}{dt}$$

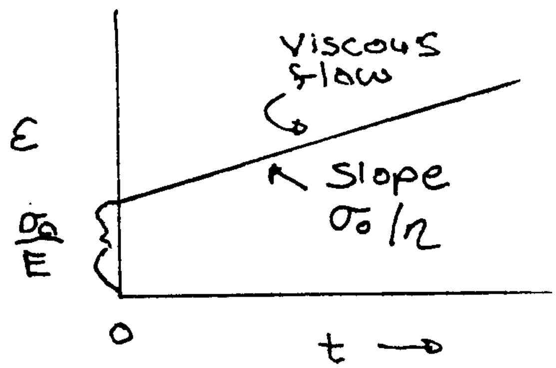
Relaxation Time $\tau = \frac{\eta}{E}$

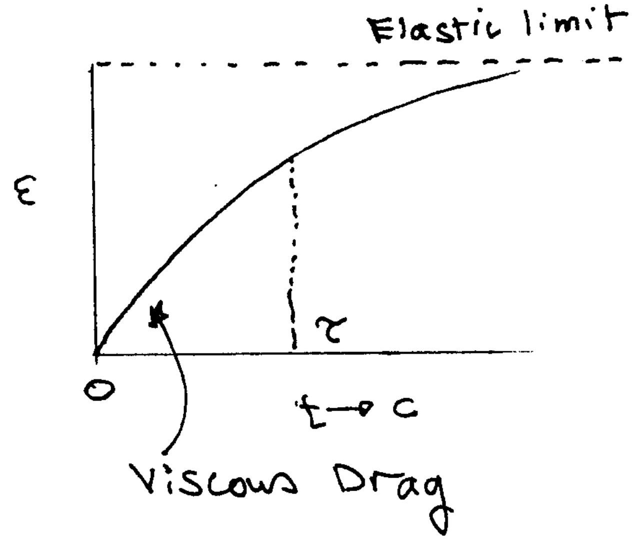
Each mechanical element has an associated relaxation time that is temperature dependent.

Under what circumstances are these models good approximations for the behavior of a viscoelastic solid? liquid?

Creep and Stress Relaxation in the Elements

Creep: Time varying strain at constant stress





Maxwell
(Bingham Plastic)

Voigt
(Solid)

from $\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$

$$d\varepsilon = \frac{1}{\eta}\sigma_0 dt$$

$$\varepsilon - \varepsilon_0 = \frac{1}{\eta}\sigma_0 t$$

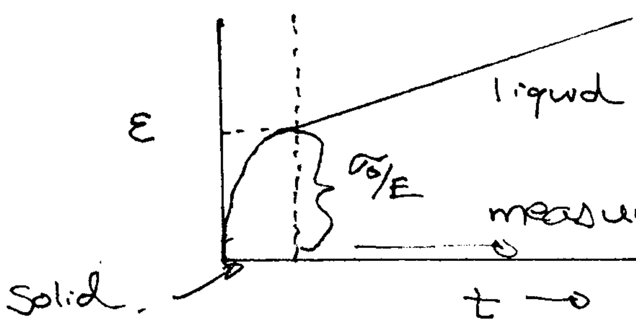
$$\varepsilon = \frac{\sigma_0}{E}\left(1 - e^{-t/\tau}\right)$$

from pg. 14.13

For constant Modulus

$\frac{1}{E} = J_t$ tensile compliance

If the relaxation time is very short, then during the measurement time the elastic limit has been reached.



Bingham Plastic behavior

$$\varepsilon = \sigma_0 J_t\left(1 - e^{-t/\tau}\right) + \frac{1}{\eta}\sigma_0 t$$

<u>Stress</u> - <u>Relaxation</u>: Time varying stress at constant strain.

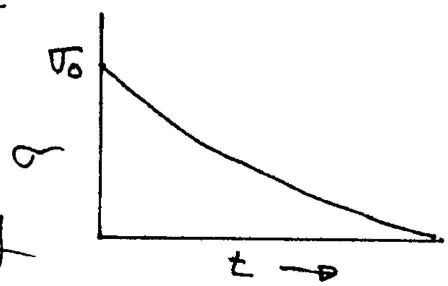
<u>Maxwell</u>:

$$\cancelto{0}{\frac{d\varepsilon}{dt}} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

$$\frac{d\sigma}{dt} = -\sigma\frac{E}{\eta}$$

$$\frac{d\sigma}{\sigma} = -\frac{1}{\tau}\,dt$$

$$\sigma = \sigma_0\, e^{-t/\tau}$$

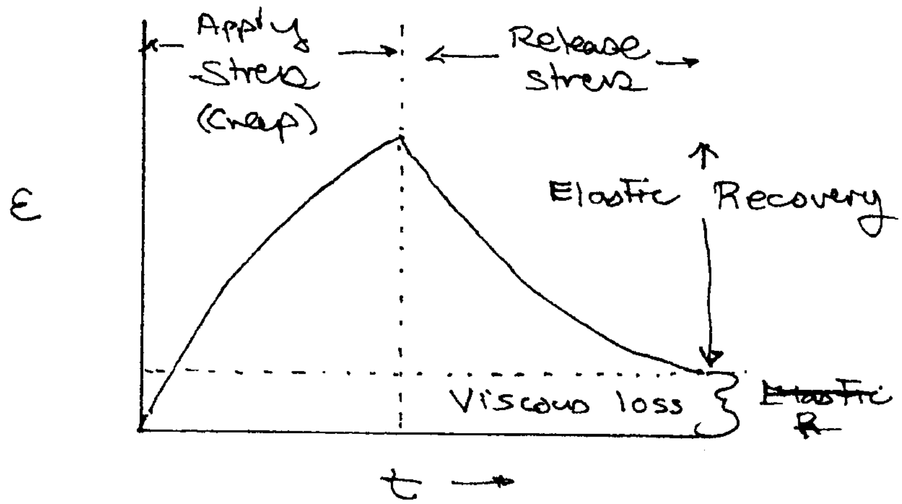


Elastic Recovery

<u>Voigt</u>:

$$\sigma = E\varepsilon + \eta\cancelto{0}{\frac{d\varepsilon}{dt}}$$

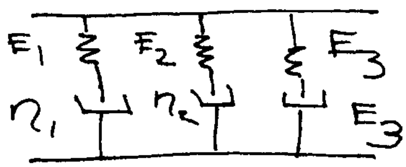
$$\sigma = E\varepsilon_0 = \sigma_0 \qquad \text{Rigid spring}$$



<u>Need to combine Maxwell and Voigt</u>

Combination Models

Maxwell-Weichert Model



Each element has constant stress.

Assembly maintains constant strain

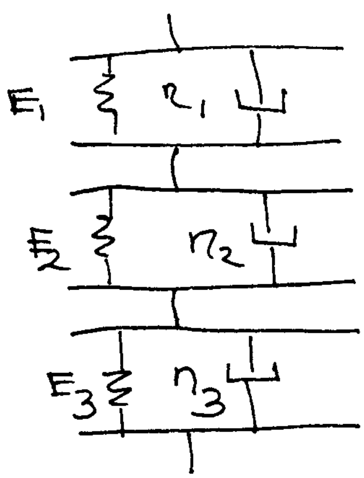
For stress-relaxation - controlled strain

$$\sigma = \Sigma \sigma_i = \varepsilon_0 \Sigma E_i \, e^{-t/\tau_i}$$

where $\tau_i = \eta_i / E_i$

A time dependent stress can be interpreted as a time dependent modulus $E(t) = \dfrac{\sigma(t)}{\varepsilon_0}$.

Voigt-Kelvin Model - controlled stress



Each element has constant strain

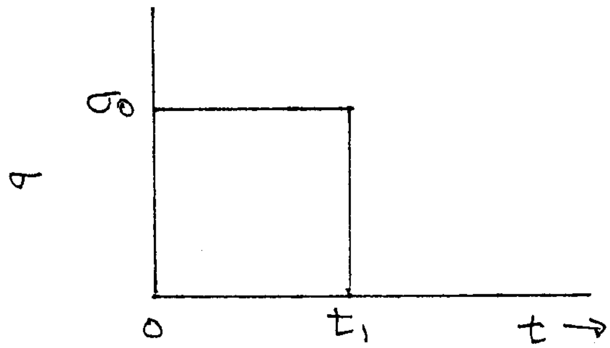
Assembly maintains constant stress

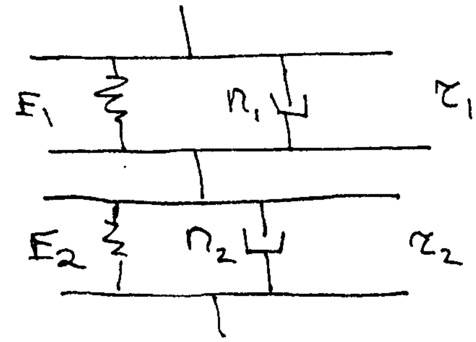
For Creep

$$\varepsilon = \Sigma \varepsilon_i = \sigma_0 \Sigma J_i \left(1 - e^{-t/\tau_i}\right)$$

A time dependent stress can be interpreted as a time dependent compliance $J(t) = \dfrac{\varepsilon(t)}{\sigma_0}$

Example: Creep recovery based on a 2-component Voigt-Kelvin model.





Let $E_2 << E_1$ to account for recovery loss.

[Time Interval $0 \le t < t_1$]

$$\varepsilon(t) = \sigma_0 J_1 \left(1 - e^{-t/J_1\eta_1}\right) + \sigma_0 J_2 \left(1 - e^{-t/J_2\eta_2}\right)$$

If E_2 is very small, then J_2 is large

$$\therefore \; \sigma_0 J_2 \left(1 - e^{-t/J_2\eta_2}\right) \approx \sigma_0 J_2 \left(t/J_2\eta_2\right)$$

therefore, at t_1 $\quad \varepsilon(t_1) = \sigma_0 \left[J_1 \left(1 - e^{-t_1/\tau_1}\right) + t_1/\eta_2 \right]$

[Time Interval $t_1 \le t$]

For each element $\quad \overset{0}{\cancel{\sigma(t)}} = E\varepsilon(t) + \eta \frac{d\varepsilon}{dt}$

$$\varepsilon(t) = \varepsilon_0 e^{-t/\tau}$$

where t now starts at t_1

Therefore $\quad \varepsilon(t) = \varepsilon_1 + \varepsilon_2 = \sigma_0 J_1 \left(1 - e^{-t_1/\tau_1}\right) e^{-(t-t_1)/\tau_1}$

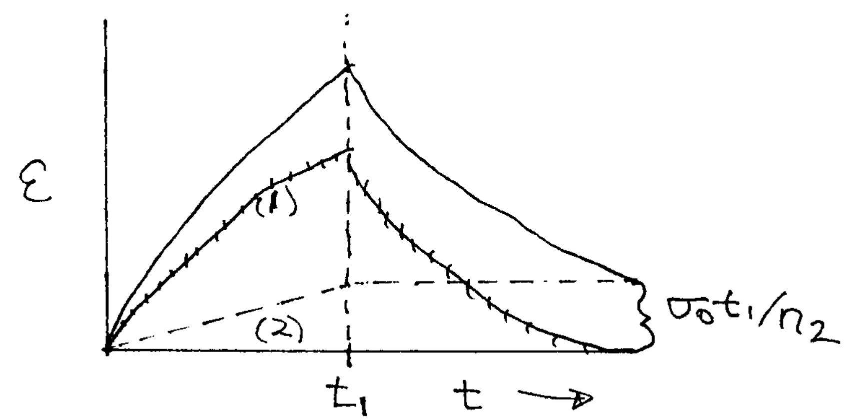
$$+ \sigma_0 \frac{t_1}{\eta_2} e^{-(t-t_1)/\tau_2}$$

Since τ_2 is large, the second term becomes

$$\frac{\sigma_0 t_1}{\eta_2} e^{-(t-t_1)/\tau_2} \approx \frac{\sigma_0}{\eta_2} t_1 \left(1 - \frac{(t-t_1)}{\tau_2}\right) \approx \frac{\sigma_0}{\eta_2} t_1$$

combining gives

$$\varepsilon(t) = \sigma_0 \left[J_1 e^{-t/\tau_1} \left(e^{t_1/\tau_1} - 1 \right) + \frac{t_1}{\eta_2} \right]$$



As we mentioned before, for a constant stress, the curve of ε vs. time can be interpreted as a curve for a time-dependent compliance.

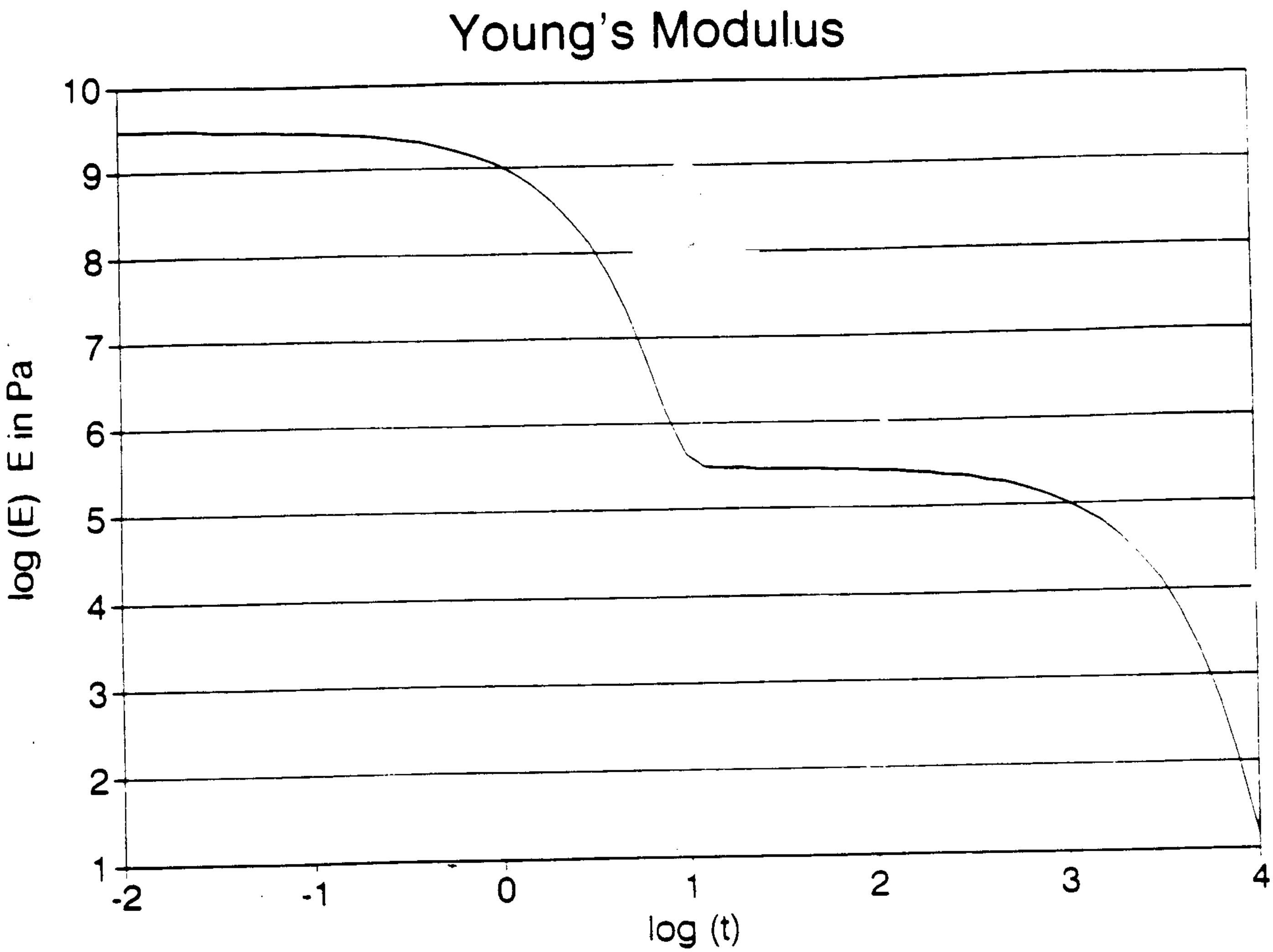
Similarly, at constant strain (or shear rate) a curve of stress vs. time is essentially a curve of a time-dependent modulus (viscosity). These curves are referred to as <u>master curves</u>.

Viscoelastic Curve: Modulus vs. Temperature
constant time

Master Curve: Modulus vs. Time
constant Temperature

The constant strain, stress relaxation experiment is modelled by the following Master Curve.

use two-element Maxwell-Weichert model.



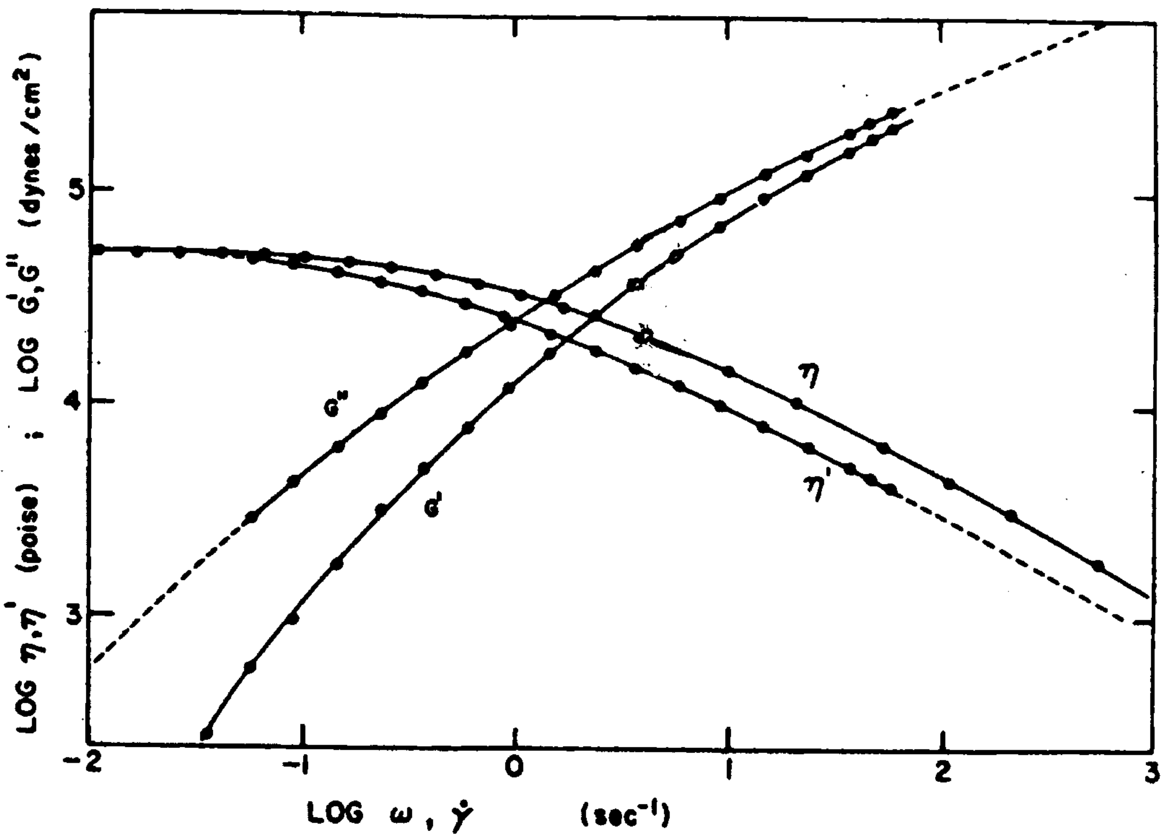
stress relaxation for

$\tau_1 = 1$ sec $\quad E_1 = 3 \times 10^9$ Pa

$\tau_2 = 1000$ sec $\quad E_2 = 3 \times 10^5$ Pa

Constant Temperature

Viscous Solid or Elastic Fluid?



The apparent viscosity η, the dynamic viscosity η', the elastic shear modulus G', and the dynamic loss factor G'' as a function of either the angular frequency ω or the shear rate $\dot{\gamma}$. The absolute value of the complex viscosity η^* would be nearly identical to η. [Reprinted from Shroff, Trans. Soc. Rheol., 15, 163 (1971).]

Solid $\qquad G = G' - iG''$

$$|G| = \sqrt{G'^2 + G''^2}$$

Fluid $\qquad \eta = \eta' + i\eta''$

$$|\eta| = \sqrt{\eta'^2 + \eta''^2}$$

$$\tau = \frac{\eta'}{G'} = \text{Relaxation Time}$$

$$\omega\eta = \dot{\gamma}\eta = \omega\eta' + i\omega\eta''$$

angular frequency $\omega = 2\pi f$

where $\omega\eta' = G''$ $\quad \omega\eta'' = G'$

Polymer Flow at High Shear Rates

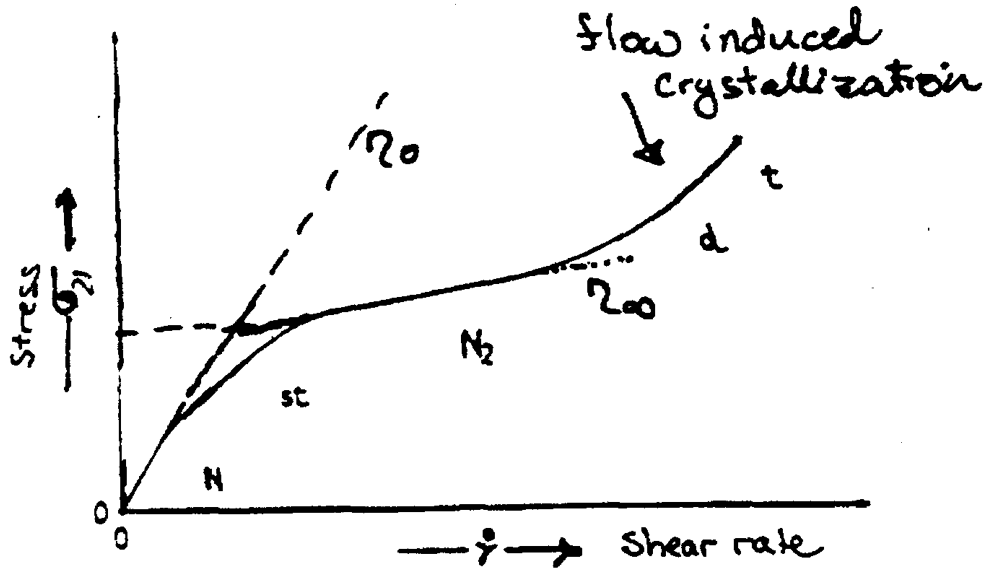


Figure 7-5. Generalized flow curve with the first Newtonian region (N), pseudoplastic region (st), second Newtonian region (N_2), dilatant region (d), and onset of turbulence or melt break (t).

η_0 — zero shear viscosity. This viscosity is determined by extrapolating the slope of the flow curve in the first Newtonian region to the $\dot{\gamma} = 0$ limit.

η_∞ — is the slope of the tangent to the flow curve in the second Newtonian region. The second Newtonian region is a transition region between pseudoplastic behavior and dilatant behavior.