Physics of Solid Polymers – Pt. 8
Viscoelasticity

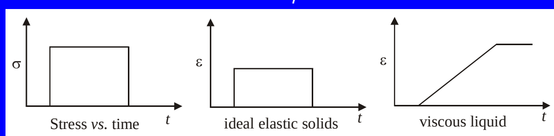
Stress-strain (σ-ε) relationship

- Perfectly elastic solids
  metals and ceramics at low strains

Hooke's law: $\sigma = E\,\varepsilon$

- Viscous liquid

Newton's law: $\sigma = \eta\, \mathrm{d}\varepsilon/\mathrm{d}t$



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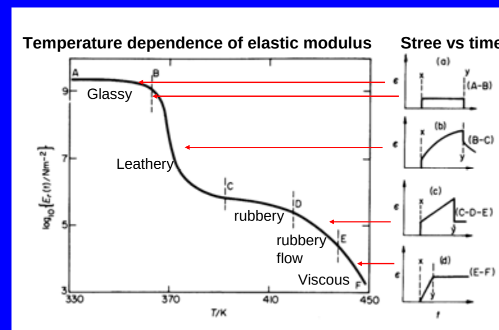
Temperature Dependence for Polymers



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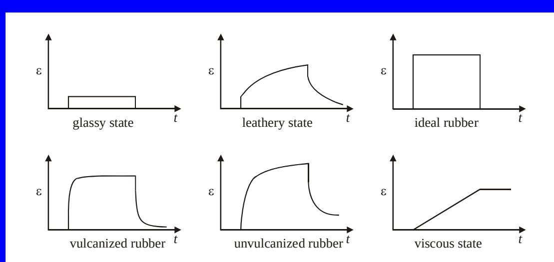
Viscoelastic Behaviour of Polymers
Deformation *vs.* Time



Polymers are ***viscoelastic***
- behaviour both **viscous** and **elastic**.

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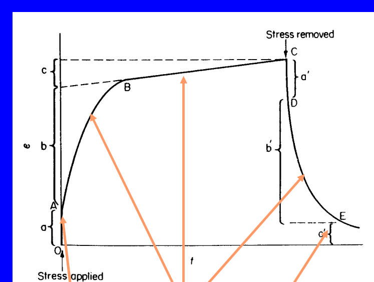
Creep
– strain vs. time



a, initial elastic response; b, creep; c, irrecoverable viscous flow.

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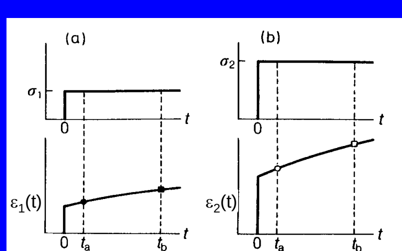
Creep

Creep = progressive increase in strain over time at constant stress.



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Linear Viscoelastic Creep

Deformation (strain): ε or γ

$$\frac{\gamma_1(t)}{\sigma_1} = \frac{\gamma_2(t)}{\sigma_2}$$

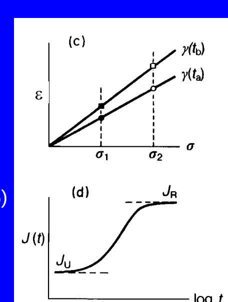
Creep compliance ***J(t)***

$$J(t) = \frac{\gamma(t)}{\sigma}$$ (inverse modulus)

linear for strains below ~0.005 (0.5%)

J_U: unrelaxed compliance

J_R: relaxed compliance



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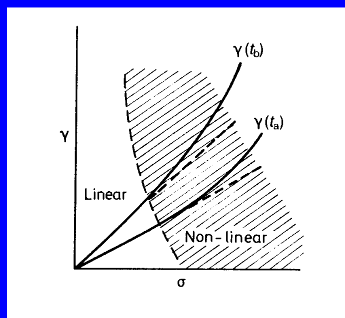
Linear and Non-linear Viscoelasticity



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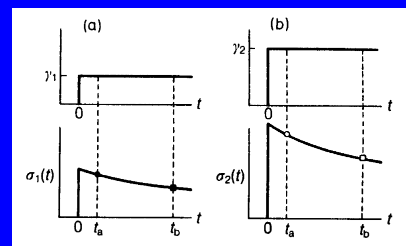
Stress-Relaxation

constant strain (γ) is applied at $t = 0$

→ measure stress $\sigma(t)$ required to maintain constant γ



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Linear Viscoelastic Stress-Relaxation

$$\frac{\sigma_1(t)}{\gamma_1} = \frac{\sigma_2(t)}{\gamma_2}$$

Stress-relaxation modulus

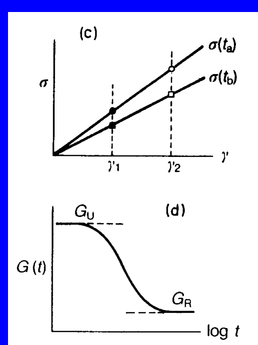
$$G(t) = \frac{\sigma(t)}{\gamma}$$

G_U: Unrelaxed modulus

$G_U = J_U^{-1}$

G_R: Relaxed modulus

$G_R = J_R^{-1}$



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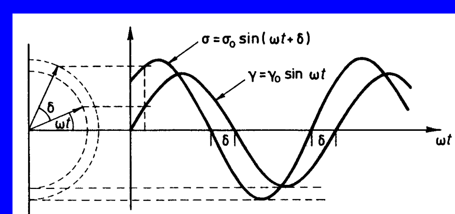
Dynamic Mechanical Analysis (DMA, DMTA)

Oscillatory sinusoidal strain of angular frequency ω

$$\gamma = \gamma_0 \sin \omega t$$

For a **linear** viscoelastic material the stress is also sinusoidal

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



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Stress-Strain Relationship for a Dynamic Analysis

$$\gamma = \gamma_0 \sin \omega t$$

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

$$\sigma = (\sigma_0 \cos \delta) \sin \omega t + (\sigma_0 \sin \delta) \cos \omega t$$

$\sigma = G^* \gamma$
G^* = complex modulus

$$\sigma = \gamma_0 [G' \sin \omega t + G'' \cos \omega t]$$

Storage modulus $G' = \frac{\sigma_0}{\gamma_0} \cos \delta$

Loss modulus $G'' = \frac{\sigma_0}{\gamma_0} \sin \delta$

Loss tangent $\tan \delta = G''/G'$

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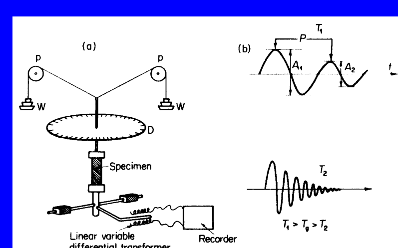
Torsion Pendulum for Dynamic Mechanical Analysis



Logarithmic decrement: $\Lambda = \ln \frac{A_n}{A_{n+1}} = \pi \tan \delta$

Storage modulus: $G' = KM\omega^2$

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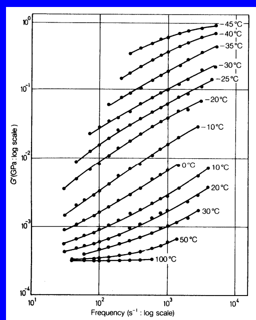
Forced Oscillation Technique



polyisobutylene

An oscillatory force is applied and the phase angle δ can be directly determined.

- a reliable technique for high values of δ
- very easy to change frequency.

Effect of timescale on glass-rubber relaxation

t ~ 10^2 s, T ~ -66 ºC
t ~ 10^{-2} s, T ~ -10 ºC

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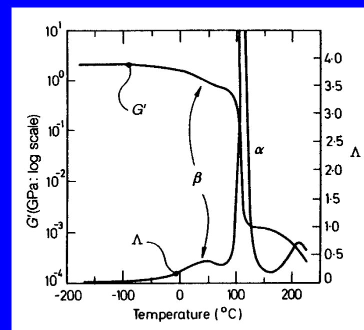
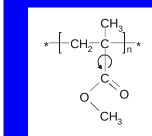
Dynamic Mechanical Properties of PMMA





Constant frequency ~ 1Hz

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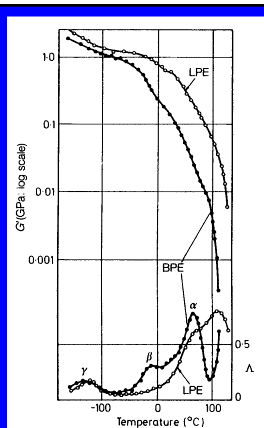
Linear and branched polyethylene



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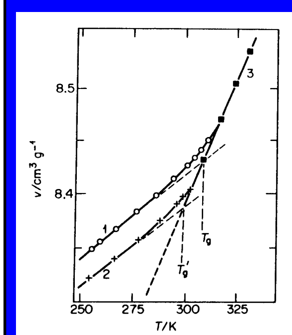
Measurement of T_g from V-T Curve



T_g is defined as the point where the thermal expansion coefficient:

$$\alpha = \frac{1}{V}\frac{dV}{dT}$$

undergoes a discontinuity.

Effect of equilibrating time
Curve 1: 0.02 hours
Curve 2: 100 hours

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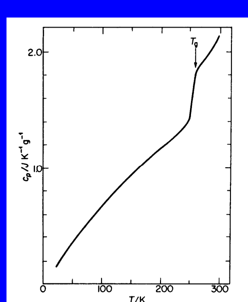
Measurment of T_g



- Heat Capacity
- Dilatometry (volume)
- DMA
- Dielectric Spectroscopy
- NMR
- Gas permeability

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Free Volume Theory of Glass Transition

The free volume, V_f, is defined as the unoccupied space in a sample, arising from the inefficient packing of disordered chains in the amorphous regions of a polymer sample.

$$V = V_o + V_f$$

V: total volume
V_o: volume actually occupied by molecules
V_f: free volume

The free volume V_f is a measure of the space available for the polymer to undergo rotation and translation.

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Temperature Dependence of the Volume

Occupied volume V_o

- Linear function of temperature (thermal vibration)
- Irrespective of whether the polymer is glassy or rubbery

Free volume V_f

- Linear (*vs* T) in the rubbery state (above T_g)
- Free volume contracts with decreasing T, and reaches a critical value at T_g that there is insufficient free space for large scale chain movement
- V_f is essentially constant below T_g because molecular chains are immobilized.

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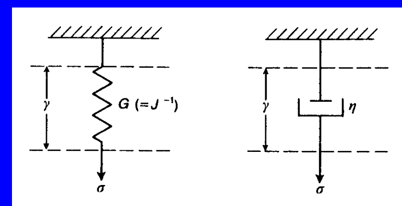
Mechanical Models of Viscoelasticity: Spring and Dashpot



$$\gamma = \frac{\sigma}{G} = \sigma J \qquad \sigma = \eta \frac{d\gamma}{dt}$$

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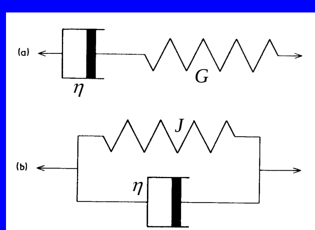
Maxwell and Voigt-Kelvin Models



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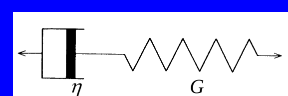
Maxwell Model: Creep



Strain: $\gamma = \gamma_1 + \gamma_2$ Stress: $\sigma = \sigma_1 = \sigma_2$

Dashpot: $d\gamma_1/dt = \sigma/\eta$ Spring: $\gamma_2 = \sigma/G$

Creep: $\sigma = \sigma_0$ is constant

$\gamma_1 = \sigma_0/\eta\, t$ $\gamma_2 = \sigma_0/G$

$\gamma = \sigma_0/\eta\, t + \sigma_0/G$

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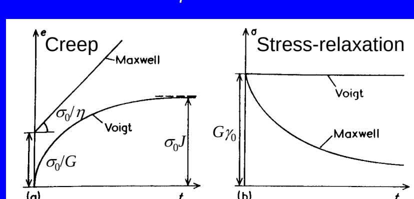
Stress relaxation behaviour of Maxwell model

$$\sigma = \sigma_0 \exp\left(-\frac{Gt}{\eta}\right) = \sigma_0 \exp(-t/\tau)$$

Creep behaviour of Voigt-Kelvin model

$$\gamma = \sigma_0 J[1-\exp(-\frac{t}{\eta J})] = \sigma_0 J[1-\exp(-t/\tau_R)]$$



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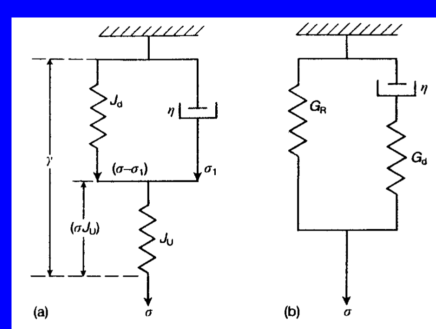
Zener Model (Standard Linear Solid)



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