Chapter 3

Properties and Testing

mechanical

electrical

optical

thermal

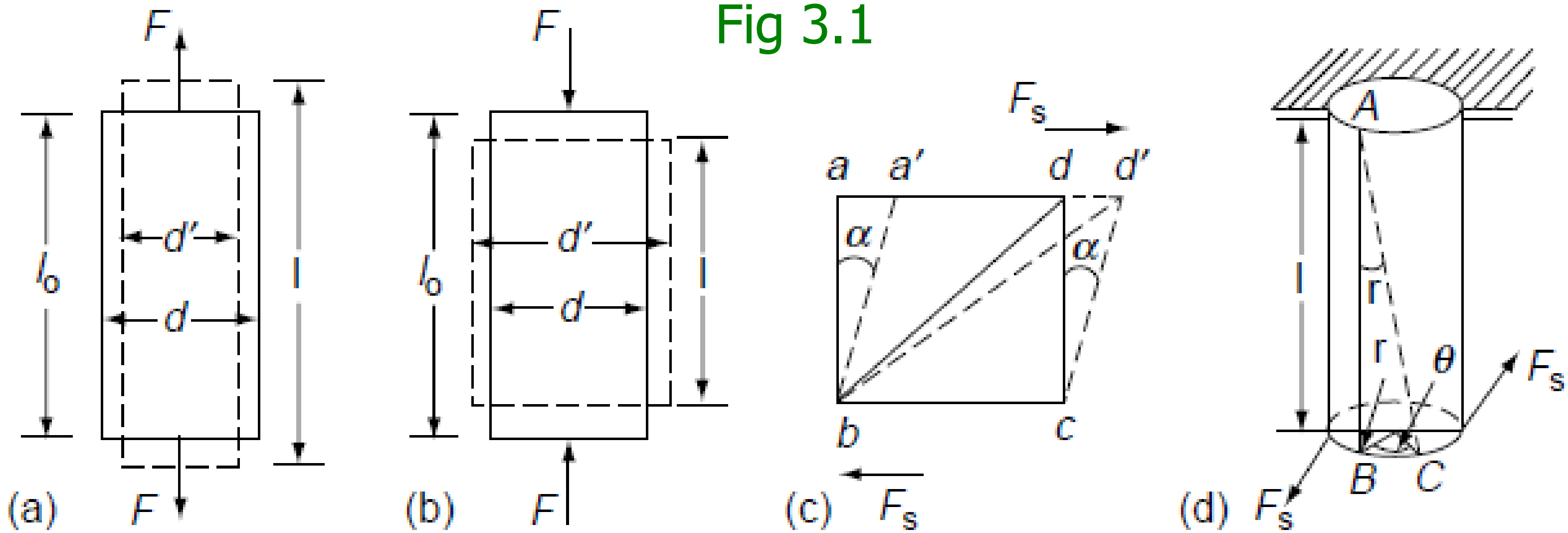
Properties of polymers

- comparison of materials
  - metal ~ strong, conducting; weak to corrosion, fatigue
  - ceramics ~ stiff, hard, heat-resistant; brittle
  - polymer ~ resilient, easy to process; weak to heat
    - light, cheap, high strength/wt, tough, corrosion-resistant, insulating, low friction, ---
- Compared to other materials, (mechanical) properties of polymers depend much on time and temperature.
  - data of time-, temp-dependency needed
  - in addition to MW, X_c, orientation, ---

Stress/strain/elasticity

- tensile and shear deformation

Fig 3.1

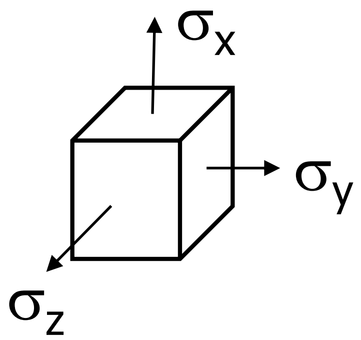


UTT | UCT | simple shear | torsion

		Tensile (Figure 3.1a) 인장	전단 비틀림 Shear (Figure 3.1c)
Stress	응력	$\sigma = F/A$	$\tau = F/A$
Strain	변형	$\varepsilon = (\ell - \ell_0)/\ell$	$\gamma = \tan\,\alpha$
Modulus	탄성률	$E = \sigma/\varepsilon$	$G = \tau/\gamma$
Compliance	순응도	$D = \varepsilon/\sigma$	$J = \gamma/\tau$

volume deformation

σ_m = mean normal stress
σ_h = $-P$

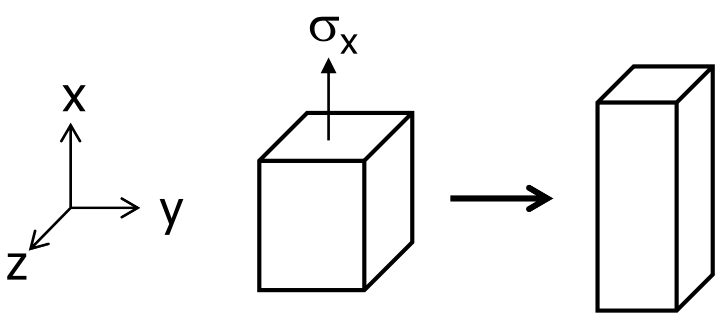


$$\frac{(\sigma_x + \sigma_y + \sigma_z)}{3} = \sigma_m = \sigma_h$$

$$K = \frac{\sigma_h}{\Delta V / V_0} = \frac{1}{\beta}$$

K = B = bulk modulus

Poisson's ratio, ν



$$\nu = -\varepsilon_y / \varepsilon_x$$

rubbers, ν = 0.5 ~ no vol change
polymers, ν ≈ 0.4
metals, ν ≈ 0.33
ceramics, ν ≈ 0.25

- relation between elastic constants (E, G, K, ν)

$$G = \frac{E}{2(1+\nu)}$$

$$\frac{1}{E} = \frac{1}{9K} + \frac{1}{3G}$$

$$K = \frac{E}{3(1-2\nu)}$$

  - Only 2 of 4 are independent.
  - for rubbers, E = 3G

s-s curve

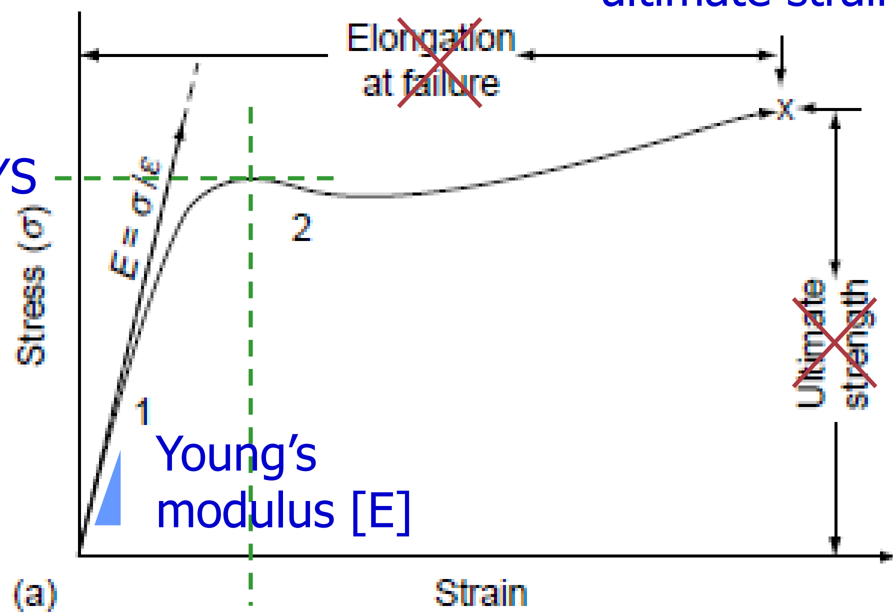
- (uniaxial) tensile test [UTT]

elongation at break [EB]
= ultimate strain [ε_u]

인장강도
tensile strength [TS]
= ultimate stress [σ_u]

항복강도
yield strength [YS]
= yield stress [σ_y]

YS

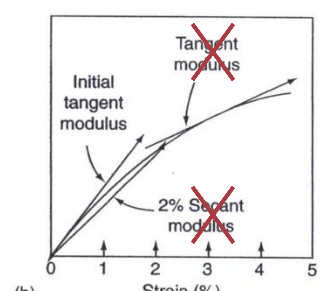


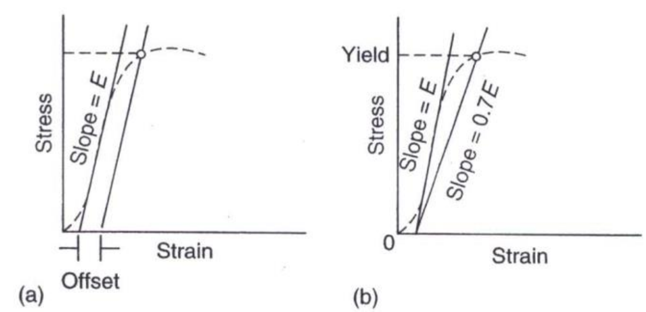
Young's modulus [E]

Fig 3.2(a)

ε_y

yield strength [ε_y]





- ignore Fig 3.2(b) and 3.3

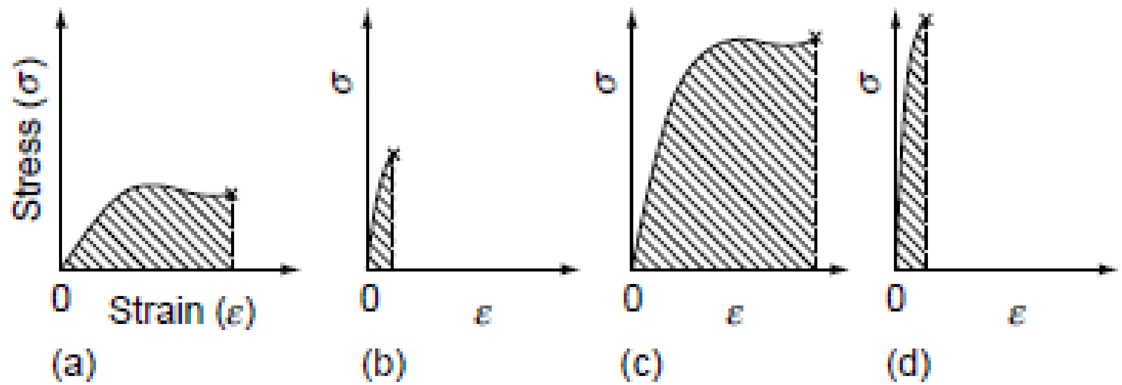


FIGURE 3.5 Classification of plastics on the basis of stress–strain diagram. (a) Soft and weak. (b) Weak and brittle. (c) Strong and tough. (d) Hard and strong.

- stiff/flexible ~ E (or G)
- strong/weak ~ TS (or FS sl 51)
- ductile/brittle ~ yield or not
- tough/fragile ~ K_{Ic} (or G_{Ic}) ~ resistance to crack propagation
- hard/soft ~ (surface) hardness

*tensile toughness

- s-s behavior depends on time and temp.

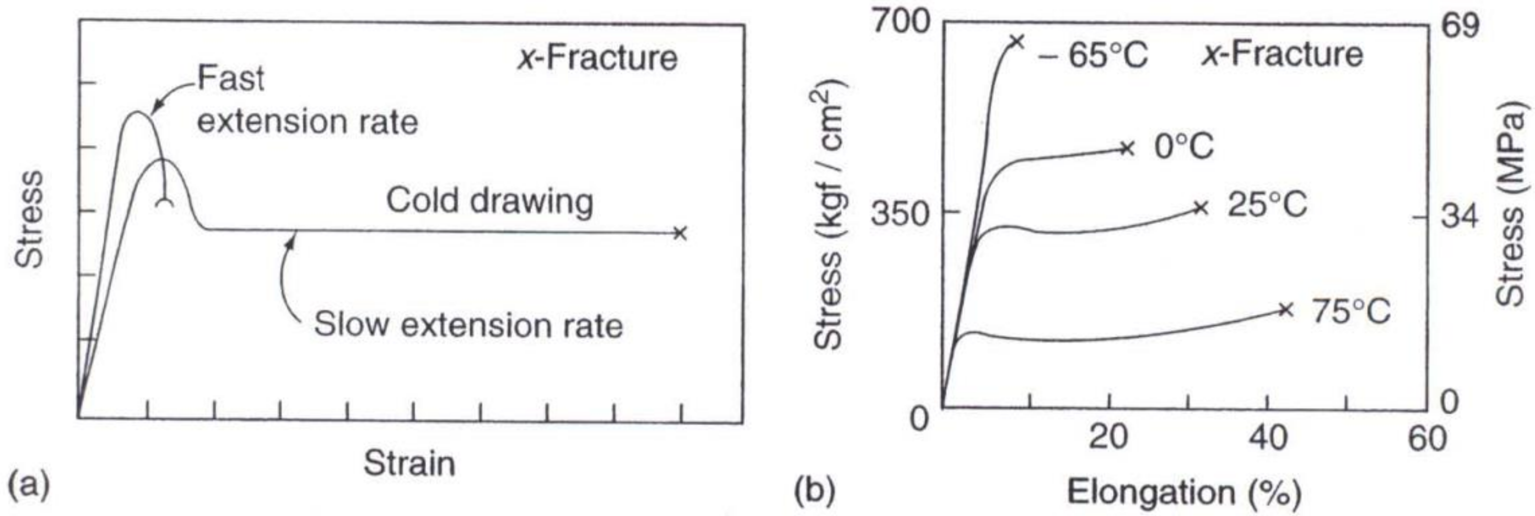


Fig 3.6

Viscoelastic behavior

- time-dependent s-s behavior
  - (linear) elastic ~ $\sigma = E\,\varepsilon$
  - viscous ~ $\tau = \eta\,(d\gamma/dt)$
  - linear VE ~ $\sigma = E(t)\,\varepsilon(t)$
  - nonlinear VE ~ $\sigma = E(t,\varepsilon)\,\varepsilon(t)$

$$\varepsilon = \varepsilon_{oe} + \varepsilon_{he} + \varepsilon_{v}$$

- for explanation
- not real

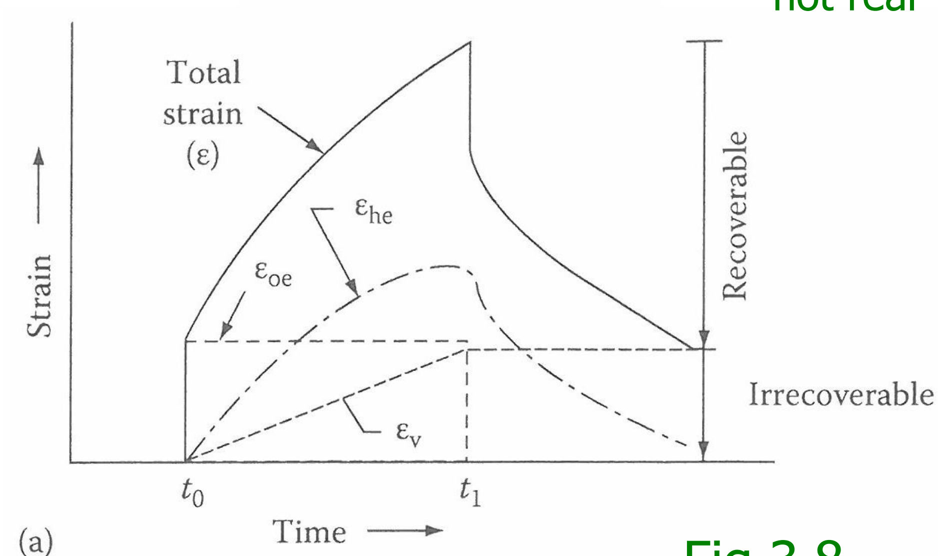
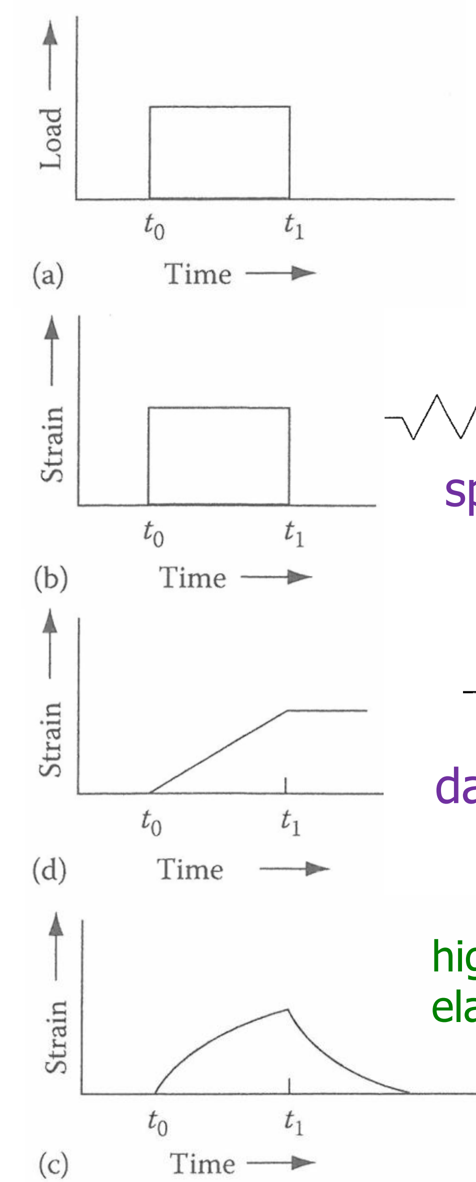
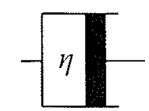


Fig 3.8



spring



dashpot

highly elastic?

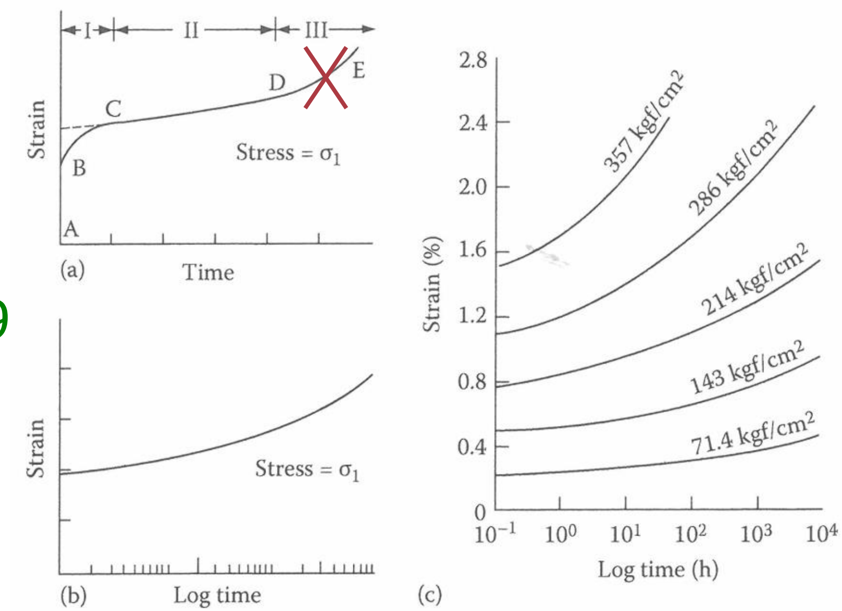
Fig 3.7

- creep vs stress relaxation
  - creep ~ constant stress
    - creep compliance

$$D(t) = \varepsilon(t)/\sigma_0$$

$$J(t) = \gamma(t)/\tau_0$$

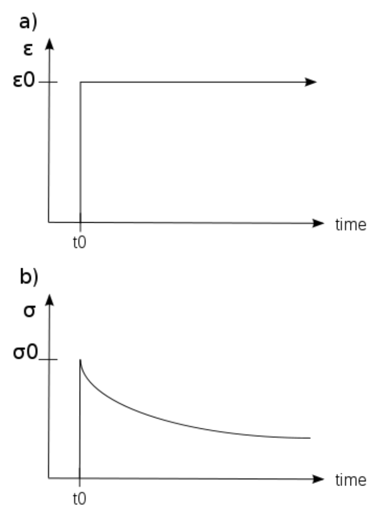
Fig 3.9

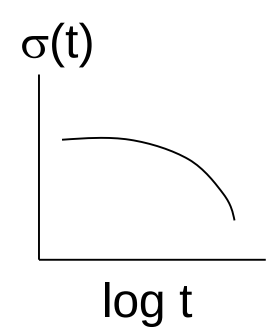


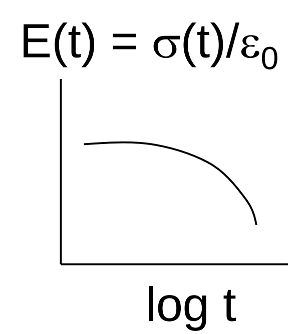
  - SR ~ constant strain
    - SR modulus

$$E(t) = \sigma(t)/\varepsilon_0$$

$$G(t) = \tau(t)/\gamma_0$$

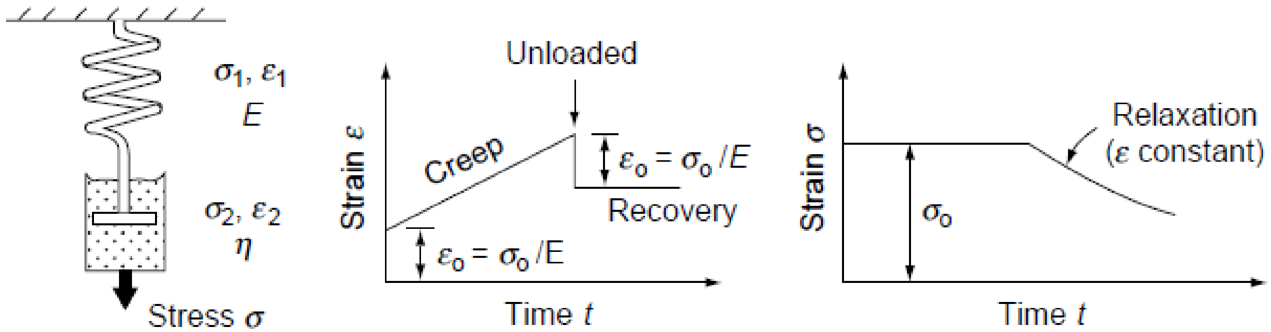






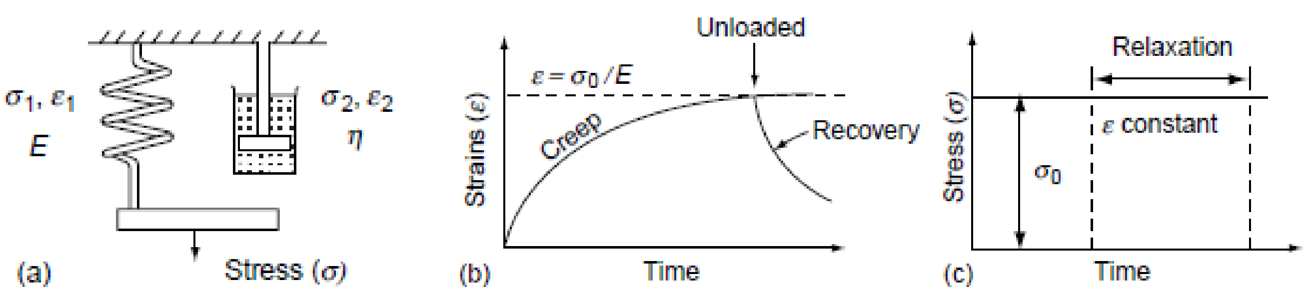
Mechanical models

- elements ~ spring and dashpot
- Maxwell model ~ serial



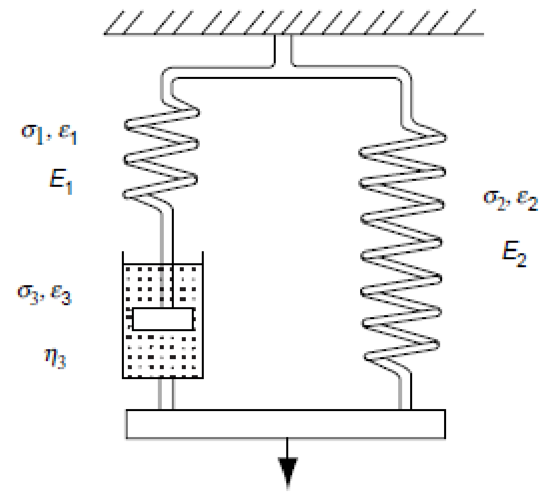
  - elastic creep; relaxation with one $\lambda = \eta/E$

- Kelvin [Voigt] model ~ parallel

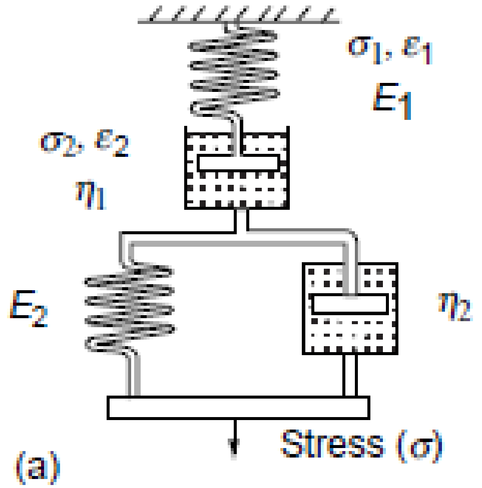


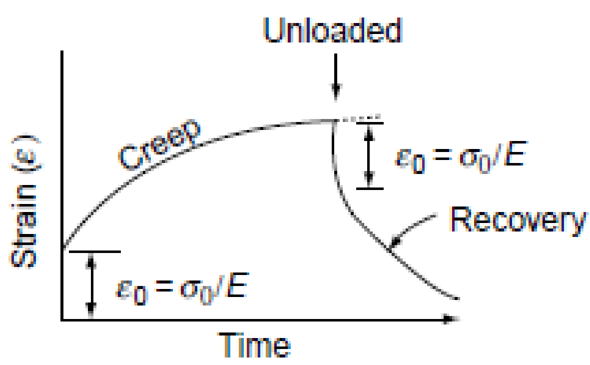
  - viscous (no) relaxation; creep with one λ

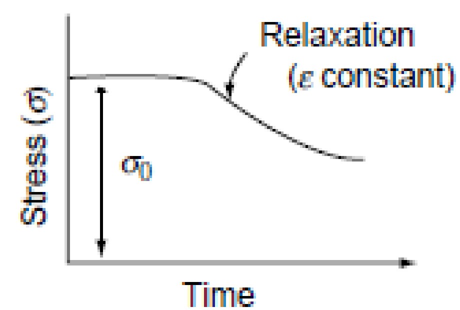
- Zener model ~ 3-elements
    - standard linear solid [SLS] model



- 4-element model







- generalized Maxwell model

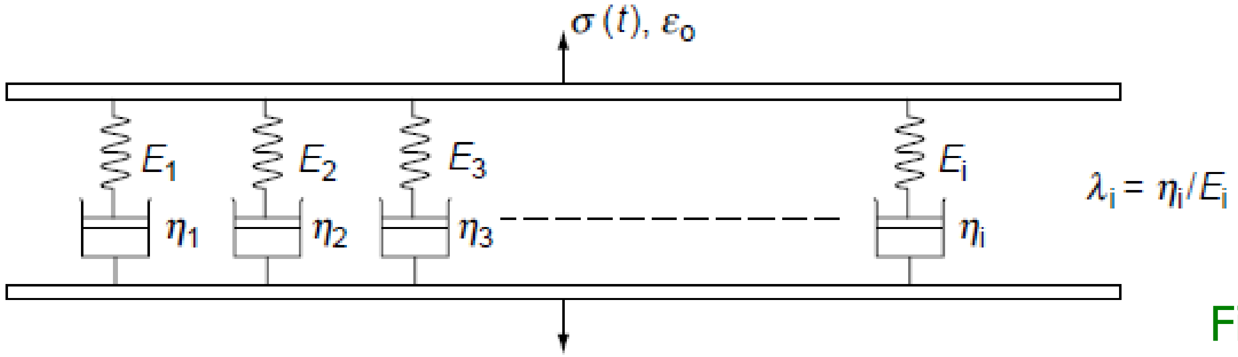
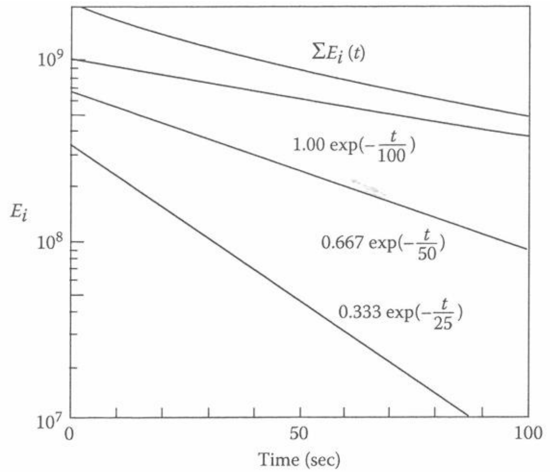


Fig 3.11,12

- distribution of relaxation time (λ)

$$E(t) = \int_{-\infty}^{+\infty} H(\ln \lambda) e^{-t/\lambda} \, d(\ln \lambda)$$



- generalized Kelvin model
- All mechanical models are mathematical models.

Superposition principle

- Boltzmann superposition principle [BSP]
  - Linear strains (and stresses) are additive.

$$\varepsilon(t) = \frac{1}{E(t)}\sigma_0 + \frac{1}{E(t-u)}\sigma_1$$

$$\varepsilon(t) = \sum_{u=-\infty}^{u=t} \sigma_i \frac{1}{E(t-u)}$$

$$\varepsilon(t) = \int_{-\infty}^{t} \frac{1}{E(t-u)} \frac{\mathrm{d}\sigma(u)}{\mathrm{d}u}\,\mathrm{d}u$$

$$\sigma(t) = \int_{-\infty}^{t} E(t-u) \frac{\mathrm{d}\varepsilon(u)}{\mathrm{d}u}\,\mathrm{d}u$$

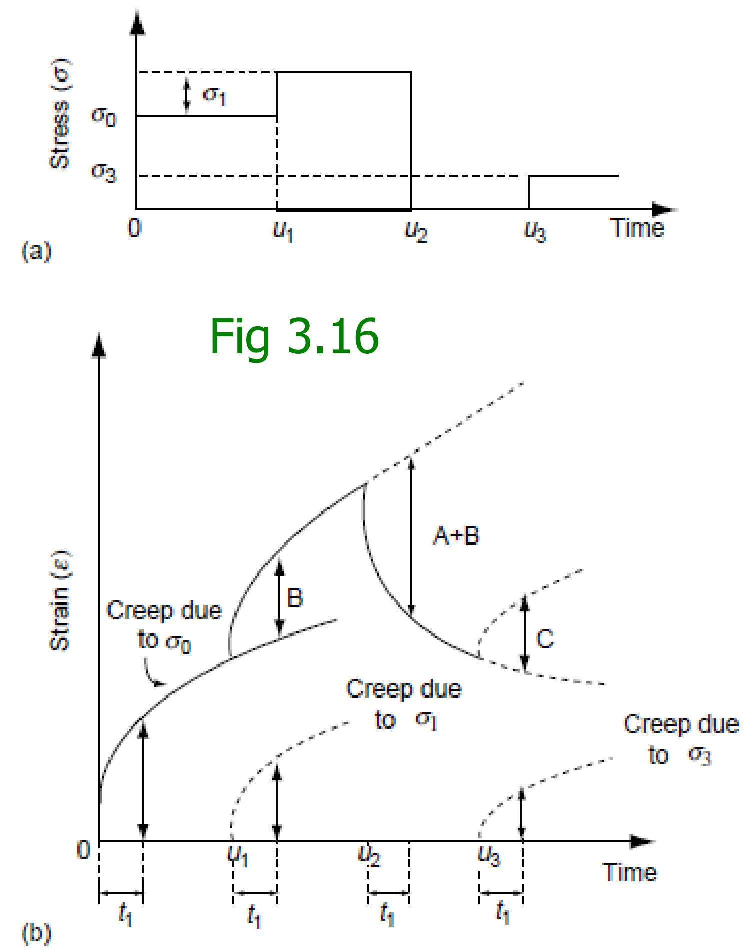
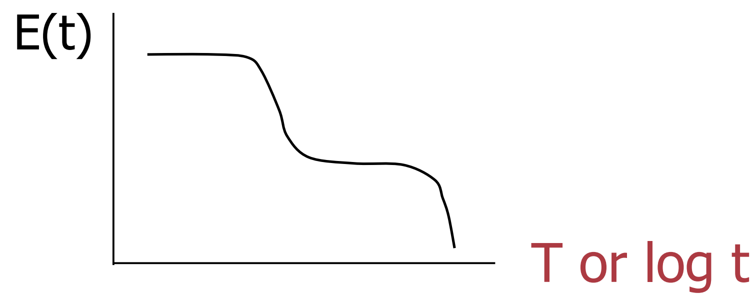


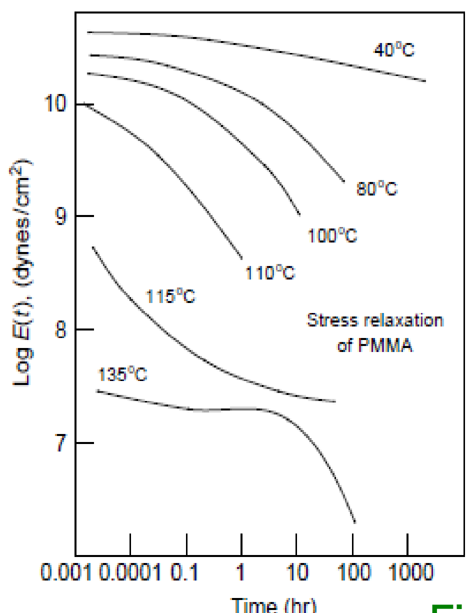
Fig 3.16

Time-temp superposition

- time-Temp equivalence



- t-T (graphical) superposition Section 3.2.14



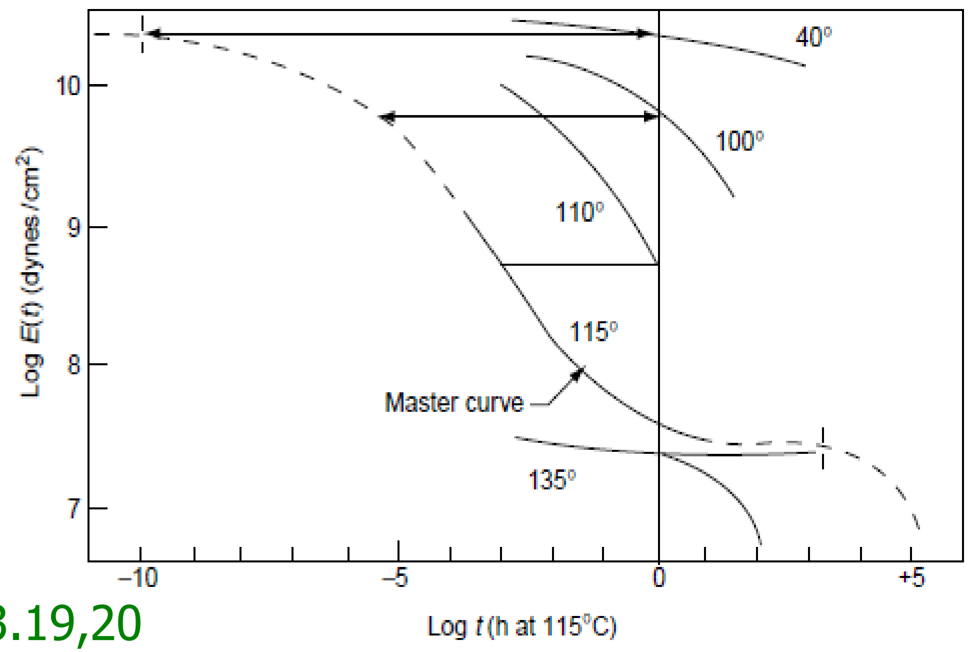


Fig 3.19,20

- t-T superposition (cont'd)

$$E(T_1, t) = E(T_2, t/a_T)$$

a_T = (time) shift factor

$$\log_{10} a_T = \log \frac{t(T)}{t(T_g)} = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}$$

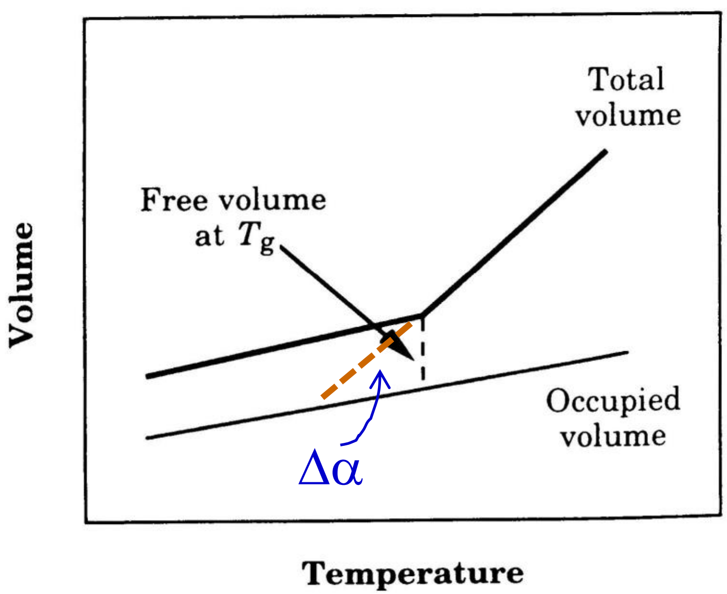
eqn 3.75

- WLF eqn Section 3.2.4.1
  - free volume theory

$$f = f_g + (\alpha_a - \alpha_b)(T - T_g)$$
$$= f_g + \Delta\alpha(T - T_g)$$

  - Doolittle eqn

$$\frac{1}{\eta_T} = Ke^{-A/f} \qquad \frac{1}{\eta_{T_R}} = Ke^{-A/f_g}$$



- WLF eqn (cont'd)

$$a_T = \frac{\tau_0(T)}{\tau_0(T_g)} = \frac{\eta(T)}{\eta(T_g)}$$

$$\log_e\left(\frac{\eta_T}{\eta_{T_g}}\right) = \frac{1}{f} - \frac{1}{f_g} \quad \text{x A}$$

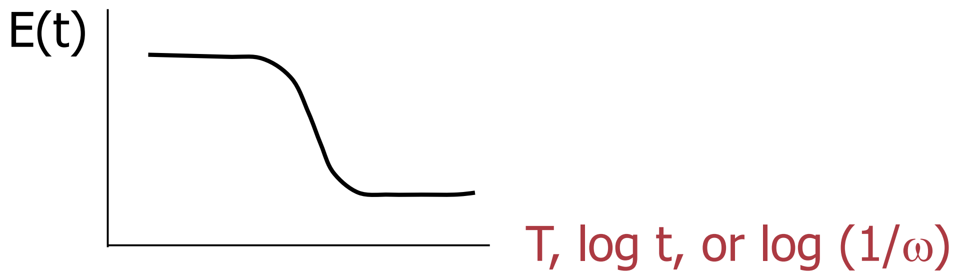
$$\log_{10}\left(\frac{\eta_T}{\eta_{T_g}}\right) = \frac{-(T - T_g) \text{ x A}}{2.303 f_g[(f_g[(f_g/\Delta\alpha) + (T - T_g)]}$$

$$\log_{10}\left(\frac{\eta_T}{\eta_{T_g}}\right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}$$

eqn 3.27

$f_g = 0.025$ and $\Delta\alpha = 4.8 \times 10^{-4}$ deg^{-1} when A=1

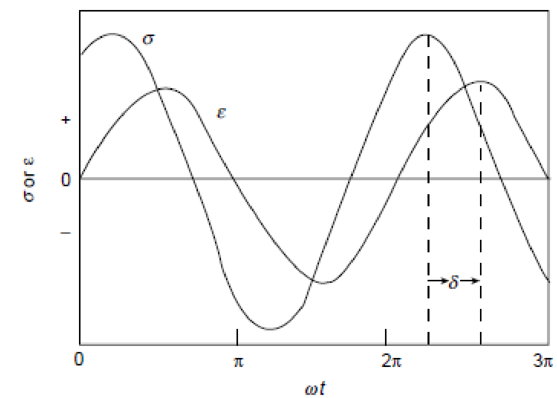
Dynamic mechanical test



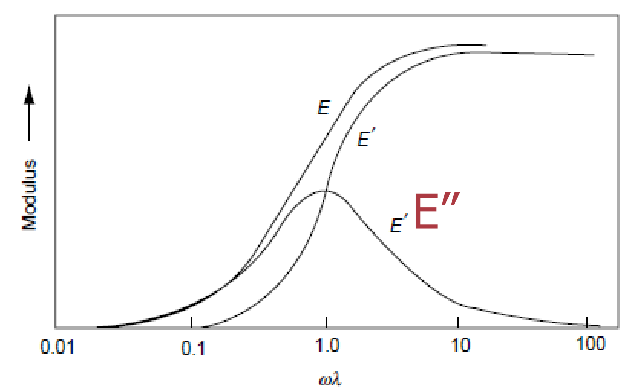
- sinusoidal (linear) stress and strain

$$\varepsilon = \varepsilon_o \sin\omega t$$

$$\begin{aligned}\sigma &= \sigma_0 \sin(\omega t+\delta)\\ &= \sigma_0 \sin\omega t \cos\delta + \sigma_0 \cos\omega t \sin\delta\\ &= \varepsilon_0 \underbrace{\sigma_0/\varepsilon_0 \cos\delta}_{\substack{E' \\ \text{storage modulus}}} \sin\omega t + \varepsilon_0 \underbrace{\sigma_0/\varepsilon_0 \sin\delta}_{\substack{E'' \\ \text{loss modulus}}} \cos\omega t\end{aligned}$$



$$= \underbrace{\varepsilon_o E' \sin\omega t}_{\substack{\text{in-phase with } \varepsilon \\ \text{elastic} \\ \text{energy stored}}} + \underbrace{\varepsilon_o E'' \cos\omega t}_{\substack{\pi/2 \text{ out-of-phase with } \varepsilon \\ \text{viscous} \\ \text{energy dissipated}}}$$



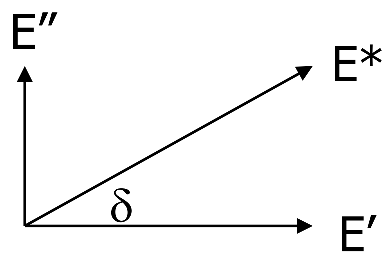
- σ and ε in complex expression

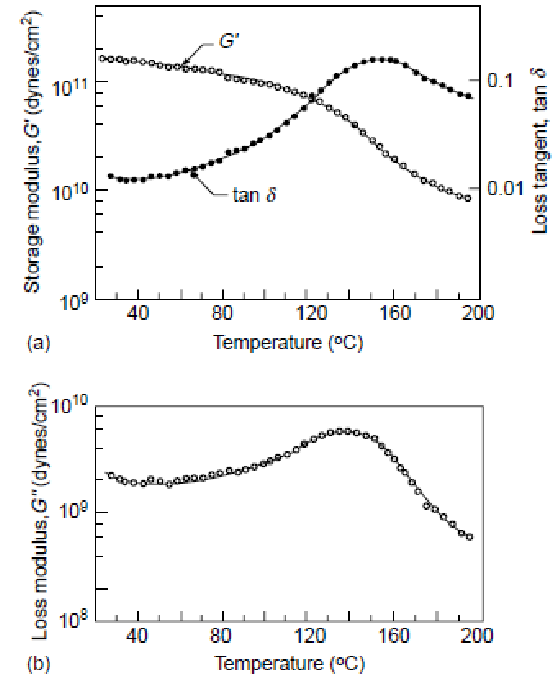
$$\varepsilon = \varepsilon_0 \exp[i\omega t]$$

$$\sigma = \sigma_0 \exp[i(\omega t+\delta)]$$

$$E = \sigma/\varepsilon = E^* = (\sigma_0/\varepsilon_0) \exp[i\delta]$$
$$= (\sigma_0/\varepsilon_0) \cos\delta + (\sigma_0/\varepsilon_0)\, i \sin\delta = E' + i\,E''$$

$$\tan\delta = E''/E'$$



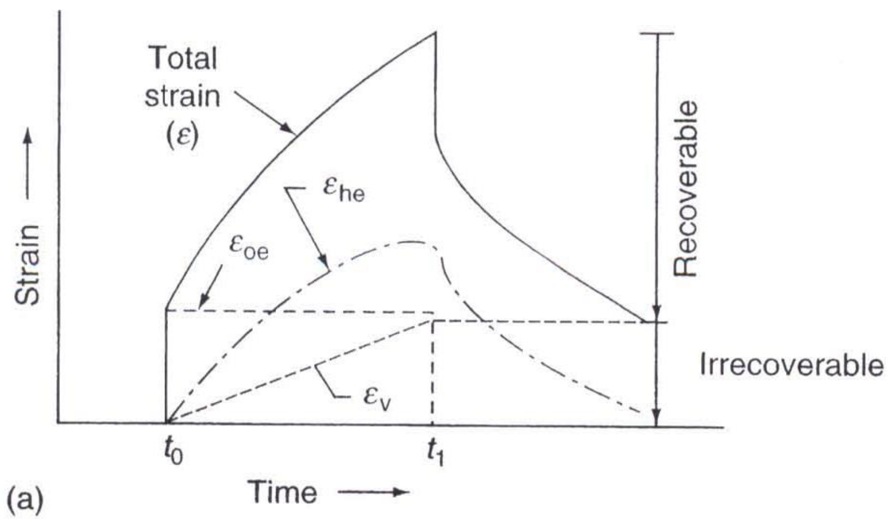


- Actually, $\tan\delta$ is small (0.1 at T_g) → $E \approx E^* \approx E'$ (in magnitude)

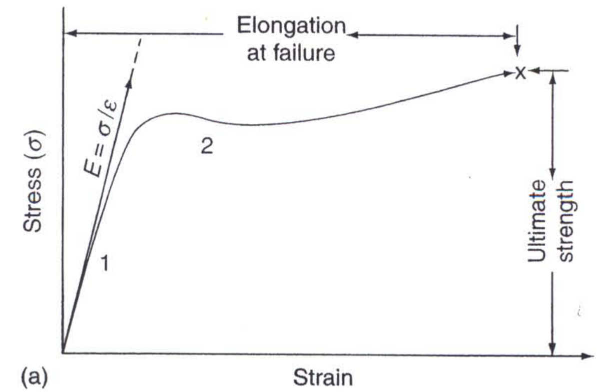
Non-linear VE

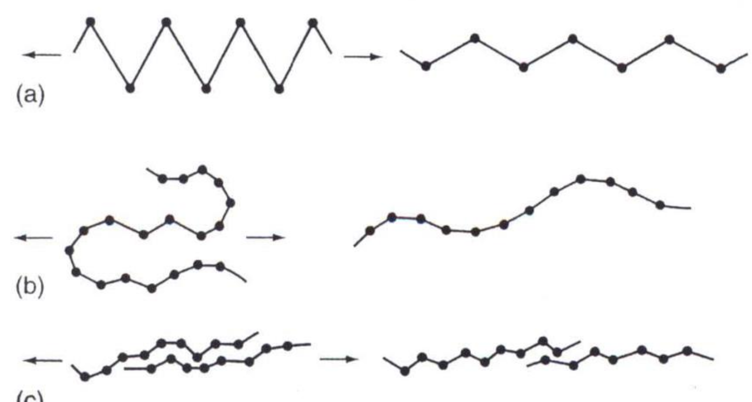
- linearity ~ stress ∝ strain
- At long t, high T, or large ε, nonlinearity evolves.
  - time-temp-strain equivalence

Fig 3.8 p315



$$\varepsilon = \varepsilon_{oe} + \varepsilon_{he} + \varepsilon_{v}$$





Isometric and isochronous curves

- from creep curves
  - at different σ
- isometric curve
  - at a ε
  - SR behavior
- isochronous curve
  - at a t
  - s-s behavior

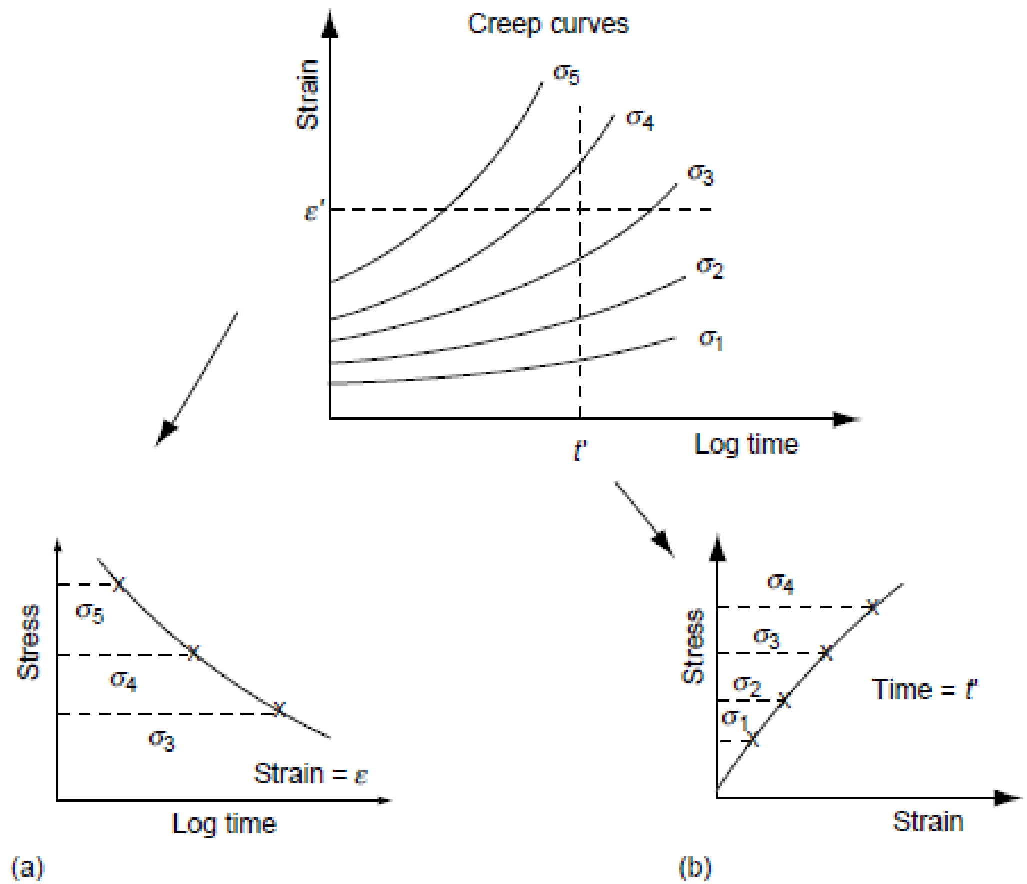
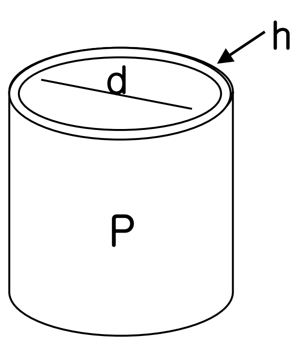


Fig 3.17

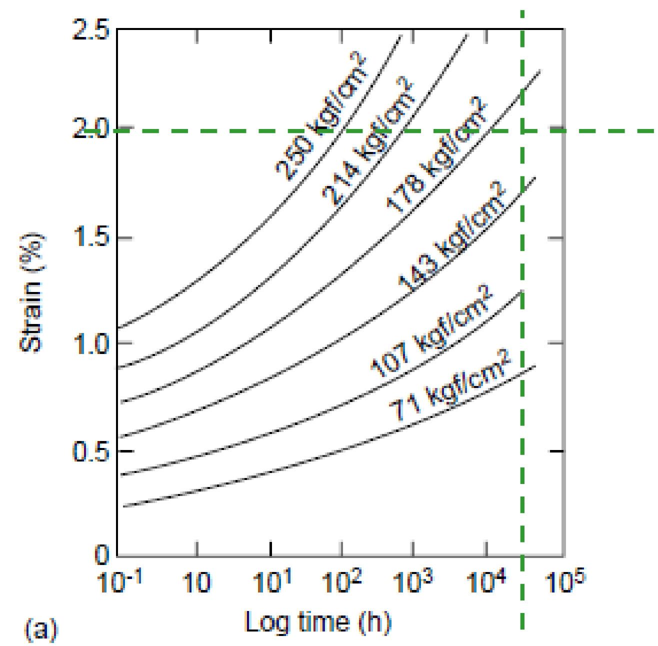
Pseudoelasticity

- For (nonlinear) VE materials, equations based on linear elasticity cannot be used.
  - $\varepsilon = \sigma/E$ (LE); $\varepsilon(t) = \sigma/E(\varepsilon,t)$ (NLVE)
- Pseudoelasticity let you can,
  - when you use long-term data
  - taken from creep, SR, isometric, or isochronous curve.
- Example 3.3 p25
  - 2% strain permitted at 20000 h
    for d = 150 mm and P = 8 kgf/cm^2



$$\sigma = \frac{Pd}{2h} \quad \text{so} \quad h = \frac{Pd}{2\sigma}$$

$$h = \frac{8 \times 150}{2 \times 167.7} = 3.58 \text{ mm}$$



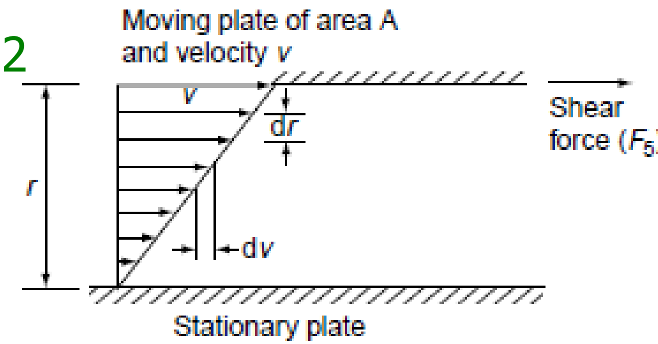
Rheology [= study on flow (of fluid)]

- viscosity, η

  $$\tau = \eta(dv/dr) = \eta\dot{\gamma} = \eta(d\gamma/dt)$$

  - constant η ~ Newtonian fluid
  - non-Newtonian ~ $\eta = f(\dot{\gamma}, T, t, P, c, \ldots\ldots)$

Fig 3.22



- η vs shear rate $d\gamma/dt$
  - pseudoplastic = shear-thinning
    - polymer melts
  - dilatant = shear-thickening
    - colloids, paste
  - Bingham plastic ~ yielding
    - plaster

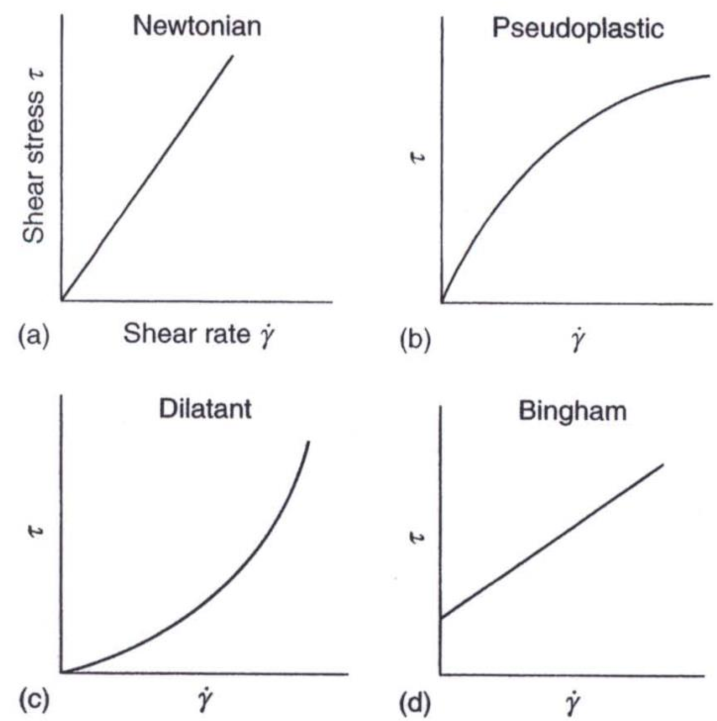
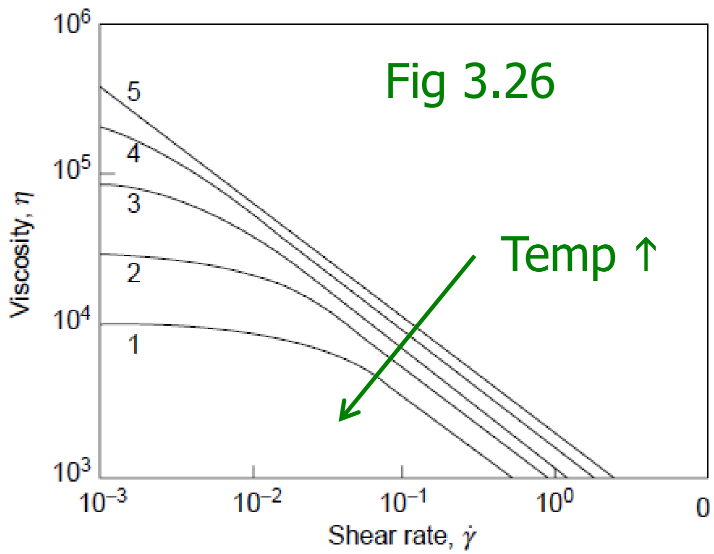


Fig 3.23

η vs shear rate dγ/dt (cont'd)



- Newtonian region at low dγ/dt
  - zero-shear viscosity, η_N or η_0

$\eta_T = 3\ \eta_N$ T = Troutonian

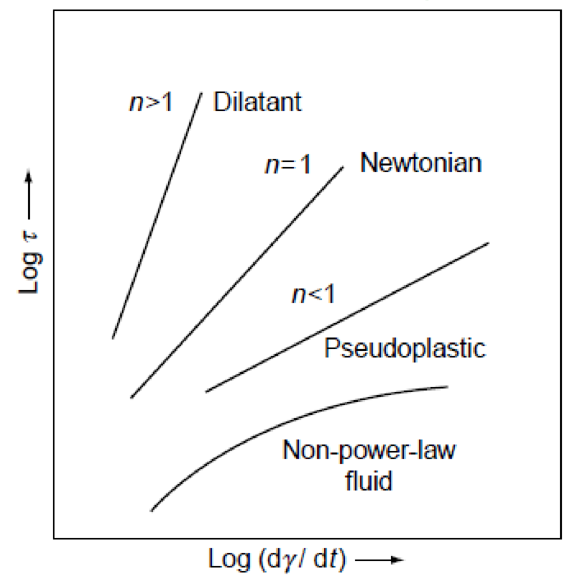
$\eta_N = \eta_{(S)}$ at dγ/dt = 0

$\eta_T = \eta_E$ at dε/dt = 0

- power-law eqn

$$\tau = \eta_N \dot{\gamma}^n$$

Fig 3.24



  - power-law fluid? only in small range

- effect of MW on η

$$\eta = K_1 M_w \quad \text{for} \quad M_w < M_c$$

$$\eta = K_2 M_w^{3.5} \quad \text{for} \quad M_w > M_c$$

- effect of Temp on η

$$\eta = Ae^{E/RT}$$

  - for small ΔT or at high T

$$\log\left(\frac{\eta_T}{\eta_{T_g}}\right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}$$

  - for large ΔT or at T near T_g

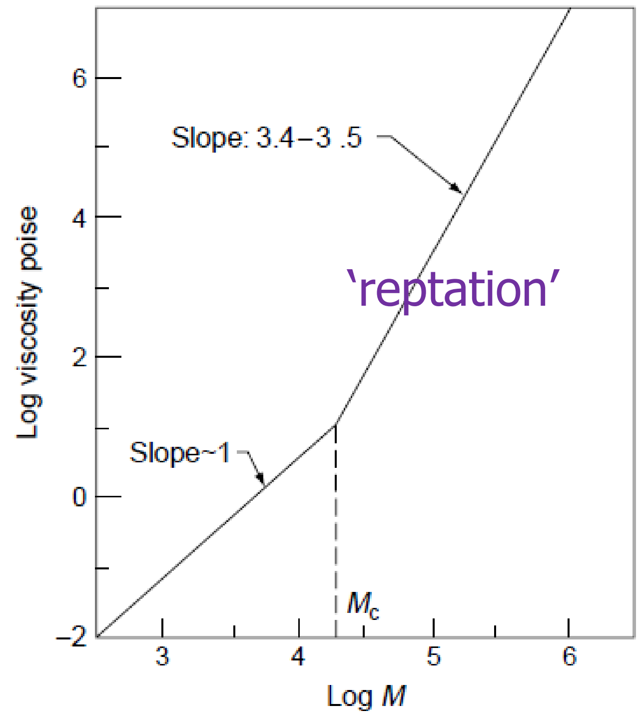


Fig 3.27

- effect of pressure on η

$$\left(\frac{\partial \eta}{\partial T}\right)_v = 0$$

  - increasing P and decreasing T the same effect
    - 100 atm is equiv to 30-50 K

- normal stress difference or normal force
  - Weisenberg effect
  - die-swell

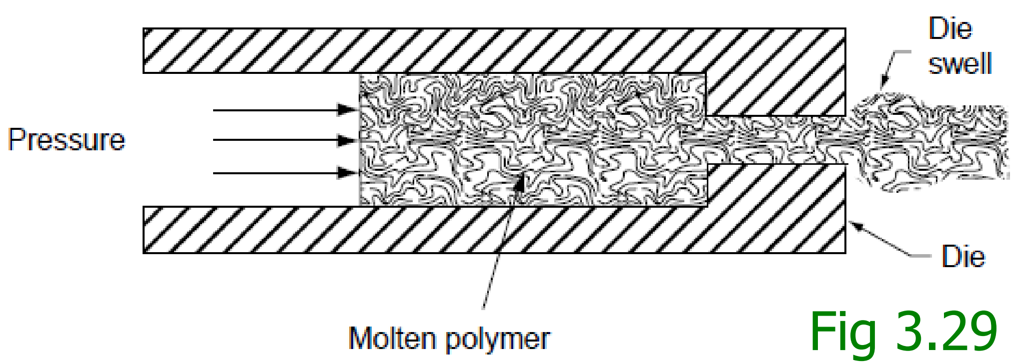


Fig 3.29

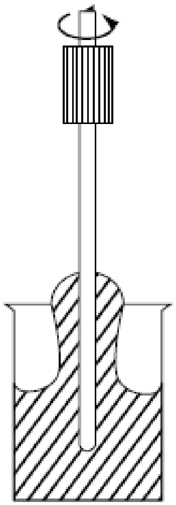
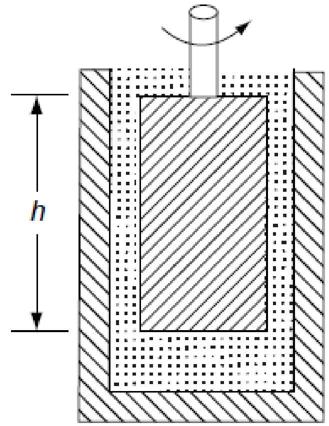


Fig 3.28

Rheometry or viscometry

- rotational viscometers
  - cylinder [cup & bob]
    - Brookfield [bob only]
  - parallel plate
  - cone-and-plate
- capillary viscometers
  - melt indexer
    - melt (flow) index [M(F)I] = g of resin/10 min
      - at specified T and P

➢ MI and MW? GPC, IV



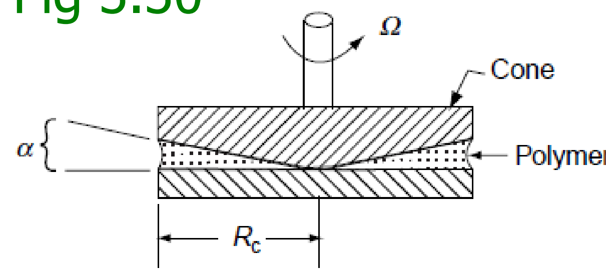


Fig 3.30

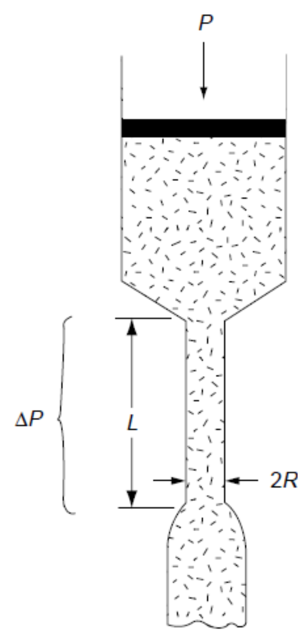


Fig 3.32