Chapter 20

Viscoelasticity

Mechanical models

Superposition

Transitions

Entanglement

3 types of response (to small ε)

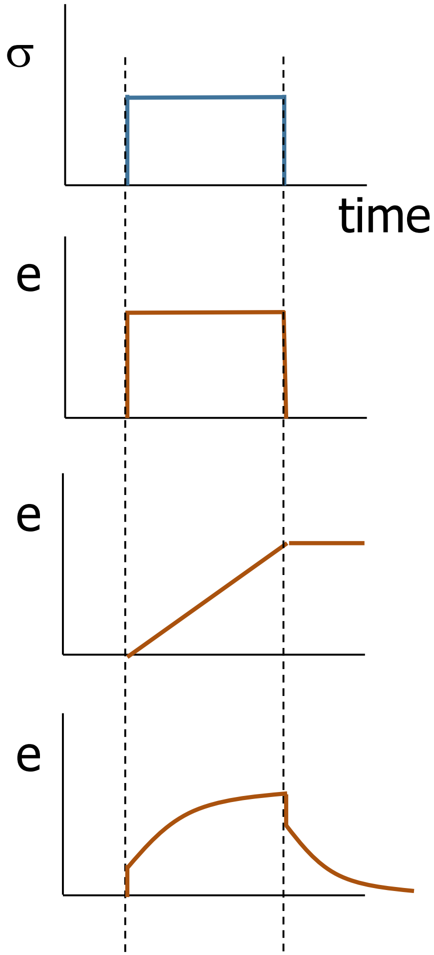
- elastic [彈性]
  - instantaneous; $\sigma = E\, e$ ~ Hooke's law
  - solid-like; $De = \tau/t > 1$
- viscous [粘性]
  - rate-dependent; $\sigma = \eta\, (de/dt)$ ~ Newton's law
  - liquid-like; $De < 1$
- viscoelastic [粘彈性]
  - betw elastic and viscous
    - elastic at short time [high rate] and low Temp
  - time-dependent; $\sigma(t) = E(t)\, e$
  - polymer-like; $De \approx 1$

anelastic = VE that recovers

plastic = deformation at $\sigma > \sigma_y$

- Every material is viscoelastic.
  - $De = \tau/t \rightarrow$ elastic/VE/viscous depending on t

- strain response to stress

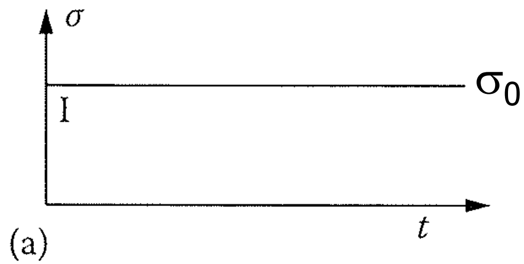


	tensile	*shear*
	$e = \sigma/E = D\sigma$ $1/E = D$	$\gamma = \tau/G = J\tau$
	$de/dt = \sigma/\eta_E$	$d\gamma/dt = \tau/\eta_{(s)}$
	$e(t) = \sigma/E(t) = D(t)\sigma$ $1/E(t) = D(t)?$	$\gamma(t) = \tau/G(t) = J(t)\tau$

Two transient tests for VE

- creep

apply



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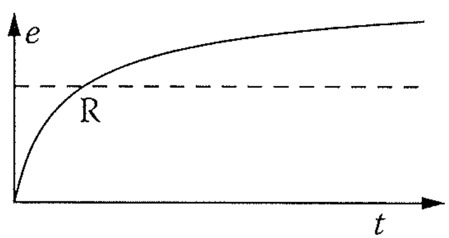
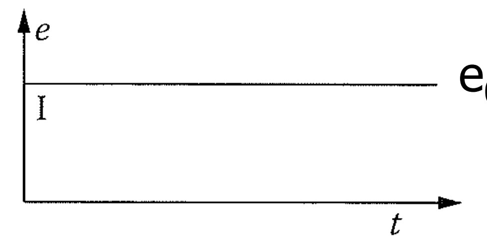


- stress relaxation

apply



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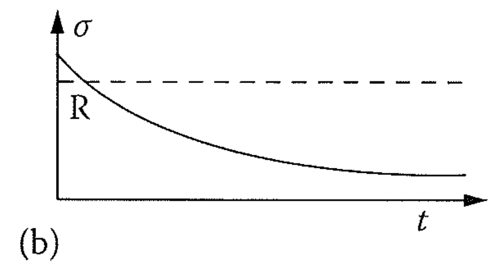


Fig 20.1 p488

- $D(t) = e(t)/\sigma_0$
  - D(t) = creep compliance
  - $\sigma_0 \sim \sigma$ at t=0 and constant
- $E(t) = \sigma(t)/e_0$
  - E(t) = SR modulus
  - $e_0 \sim e$ at t=0 and constant

1/E(t) = D(t)? No, if from different experiment

Mechanical models

- elements
  - spring ~ elastic, $\sigma = E\,e$
  - dashpot ~ viscous, $\sigma = \eta\,(de/dt)$

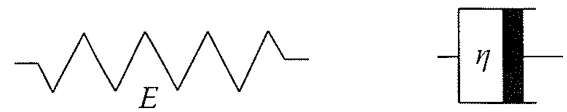


Fig 20.2

- Maxwell model ~ serial
  - stress the same and strain additive

$$\sigma_1 = \sigma_2 = \sigma \qquad e = e_1 + e_2$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = E\frac{\mathrm{d}e_1}{\mathrm{d}t} \quad \text{and} \quad \sigma = \eta\frac{\mathrm{d}e_2}{\mathrm{d}t} \qquad \frac{\mathrm{d}e}{\mathrm{d}t} = \frac{\mathrm{d}e_1}{\mathrm{d}t} + \frac{\mathrm{d}e_2}{\mathrm{d}t} = \frac{1}{E}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{\sigma}{\eta}$$

  - creep

$$\mathrm{d}\sigma/\mathrm{d}t = 0 \longrightarrow \frac{\mathrm{d}e}{\mathrm{d}t} = \frac{\sigma_0}{\eta}$$ ~ viscous only

from spring

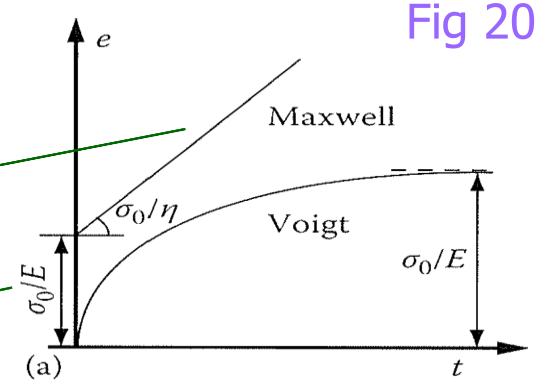


Fig 20.3

- stress relaxation

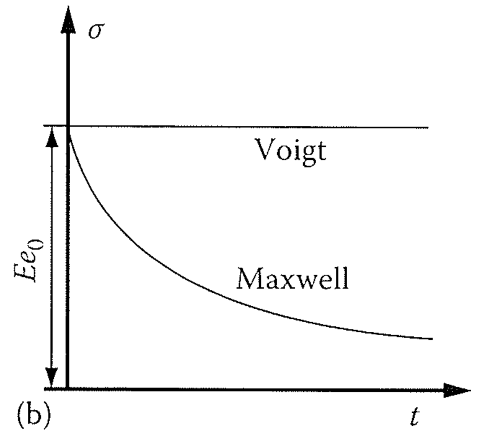
$$\mathrm{d}e/\mathrm{d}t = 0 = \frac{1}{E}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{\sigma}{\eta} \longrightarrow \frac{\mathrm{d}\sigma}{\sigma} = -\frac{E}{\eta}\mathrm{d}t$$

$$\sigma = \sigma_0 \exp\left(-\frac{Et}{\eta}\right) = \sigma_0 \exp\left(\frac{-t}{\tau_0}\right)$$

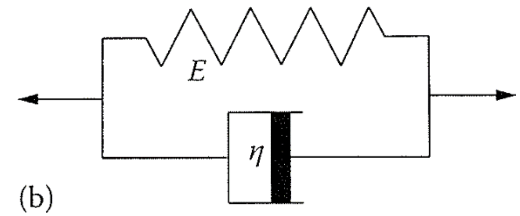
at $t = 0,\ \sigma = \sigma_0$

$\tau = \eta/E$ ~ relaxation time

$De = \tau/t$



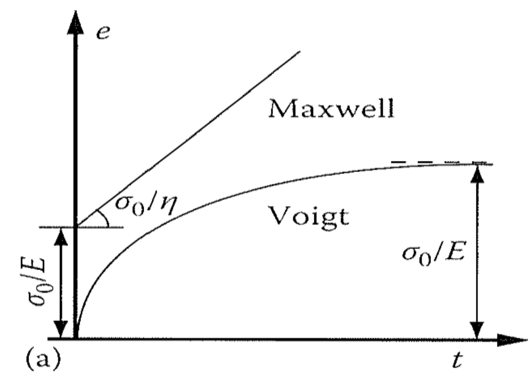
- Voigt [Kelvin] model ~ parallel
  - strain the same and stress additive



$$e = e_1 = e_2 \quad \text{and} \quad \sigma = \sigma_1 + \sigma_2$$

$$\sigma_1 = Ee \quad \text{and} \quad \sigma_2 = \eta \frac{de}{dt} \longrightarrow \frac{de}{dt} = \frac{\sigma}{\eta} - \frac{Ee}{\eta}$$

  - creep



$$\frac{de}{dt} = \frac{\sigma}{\eta} - \frac{Ee}{\eta} \xrightarrow{\sigma=\sigma_0} e = \frac{\sigma_0}{E}\left[1 - \exp\left(-\frac{Et}{\eta}\right)\right]$$

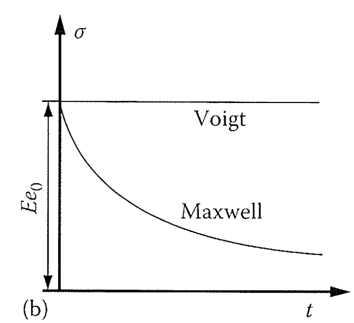
$$= \frac{\sigma_0}{E}\left[1 - \exp\left(\frac{-t}{\tau_0}\right)\right]$$

$\tau = \eta/E$ ~ retardation time

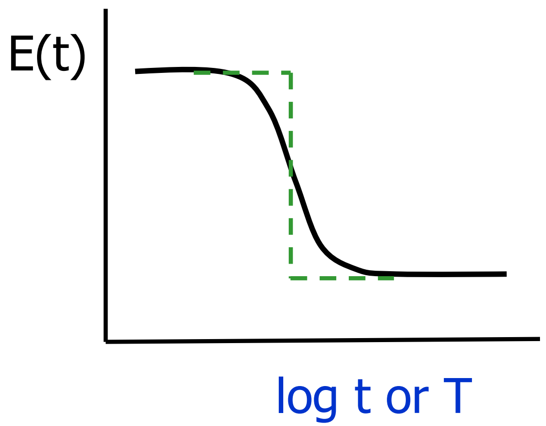
one relaxation time?

  - SR

$$\frac{de}{dt} = \frac{\sigma}{\eta} - \frac{Ee}{\eta} \xrightarrow{de/dt=0} \sigma = Ee_0$$ ~ elastic only

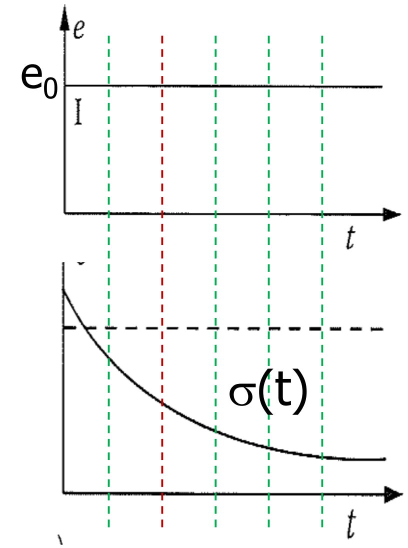


- relaxation time



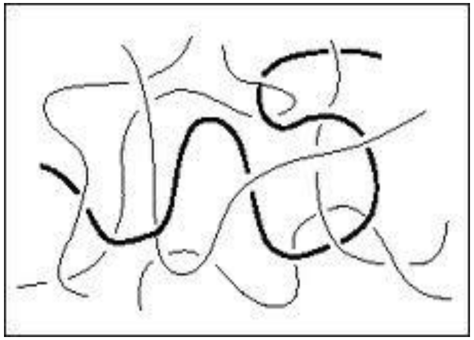
SR modulus
$E(t) = \sigma(t)/e_0$

at different time, one Temp
or
at different Temp, one time

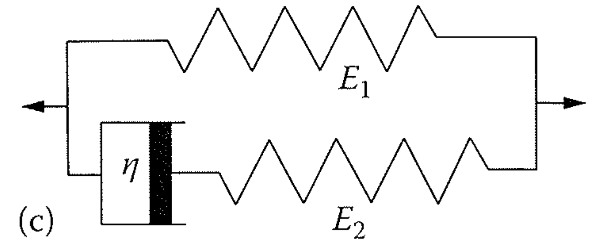


✓ time-temp superposition

- one relaxation time?
- many relaxation times

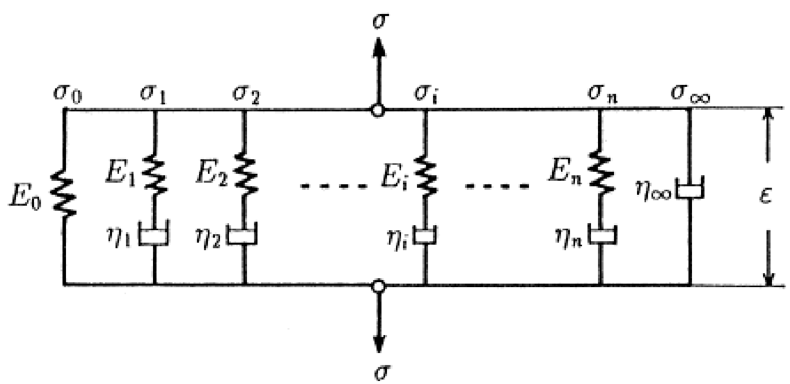


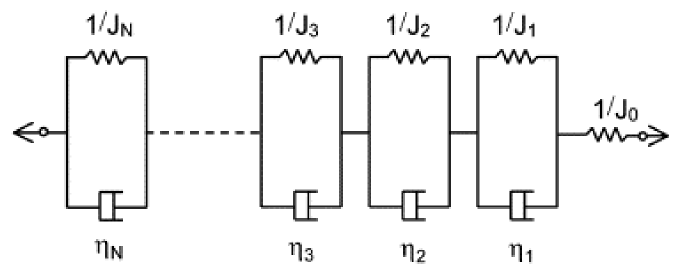
- composite models
  - 3-, 4, --- element models
  - standard linear solid [SLS] model
  - math improved, not physics



SLS model (2 τ's)

- generalized Maxwell (or Voigt) model





  - spectrum [distribution] of relaxation times
  - physics improved, but not real

Boltzmann superposition principle

- In linear deformation [small strain] range,
  strains (and stresses also) at different times are additive.

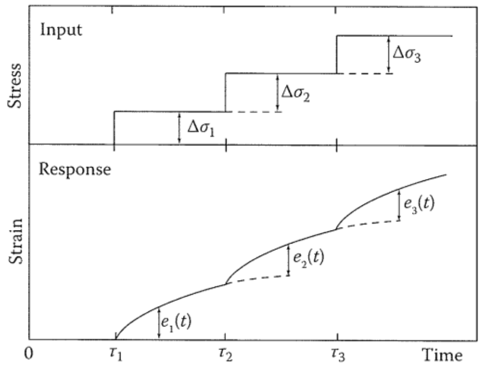


Fig 20.4

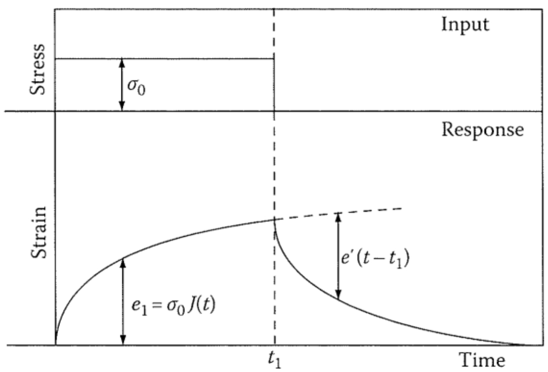
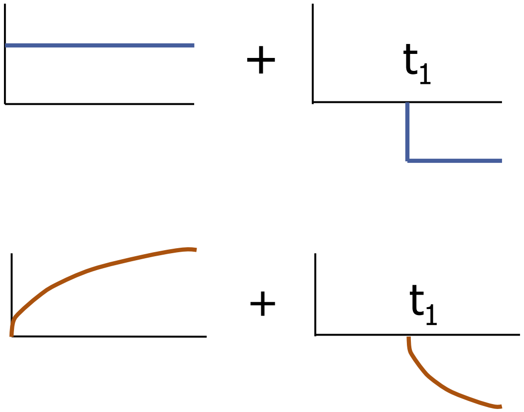


Fig 20.5



$$e(t) = e_1(t) + e_2(t) + \ldots$$

$$= \Delta\sigma_1 J(t-\tau_1) + \Delta\sigma_2 J(t-\tau_2) + \ldots$$

$$= \sum_{n=0}^{n} J(t-\tau_n)\Delta\sigma_n$$

$$e(t) = \int_{-\infty}^{t} J(t-\tau)\mathrm{d}\sigma(t)$$

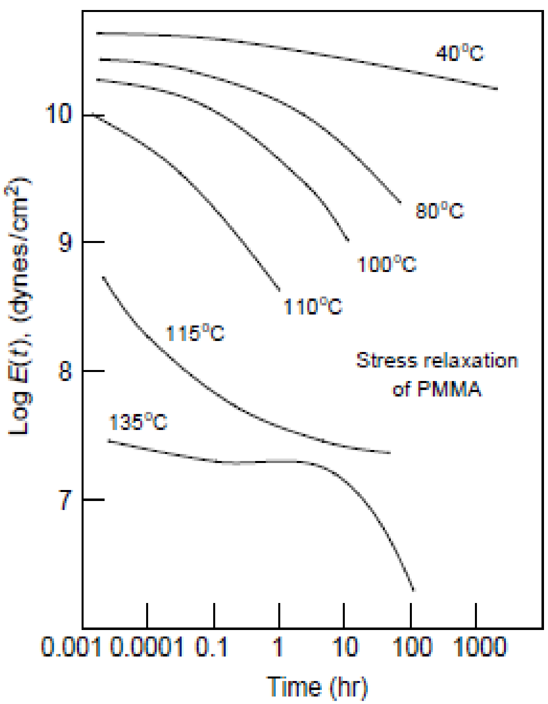
$$e(t) = \int_{-\infty}^{t} J(t-\tau)\frac{\mathrm{d}\sigma(\tau)}{\mathrm{d}\tau}\mathrm{d}\tau$$

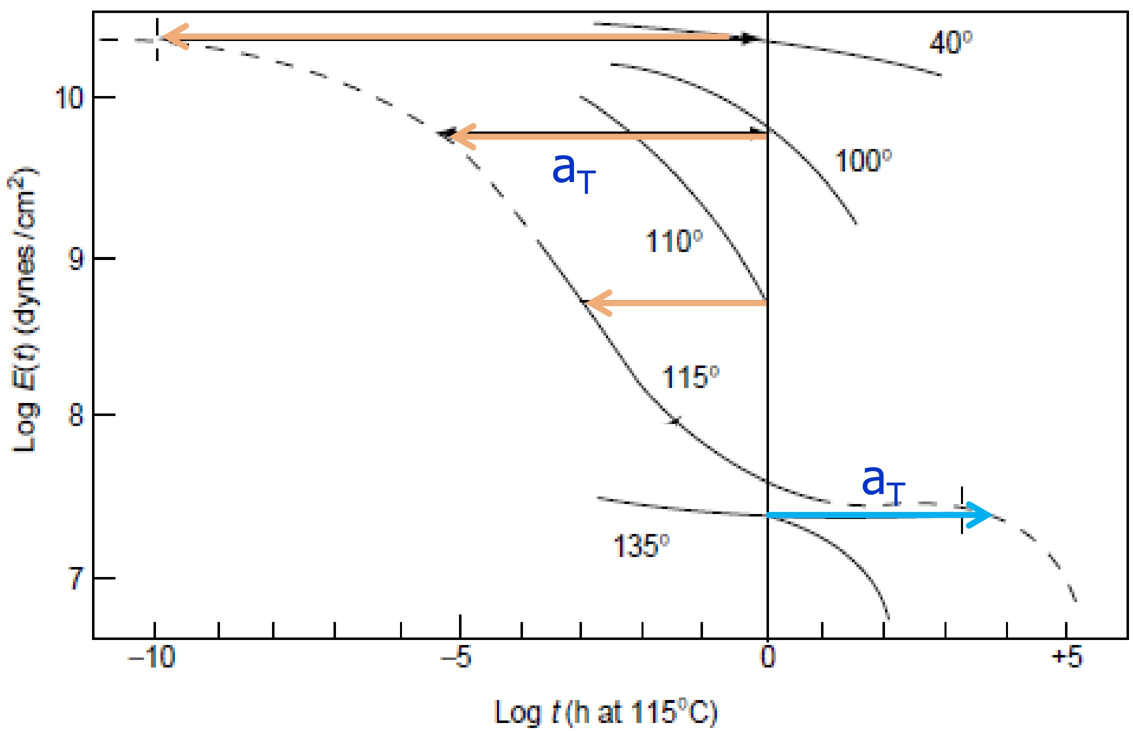
Time-temperature superposition

§20.7 pp503-505

- time-Temp equivalence
  - Long time and high temperature is equivalent.
    - for chain motion and viscoelasticity
  - Data can be superposed (log t and T) → 'master curve'

SR tests at different T's, shifted to fit on curve at reference Temp T_s





- shifting

$$\frac{E(T_1, t)}{\rho(T_1)\, T_1} = \frac{E(T_S, t/a_T)}{\rho(T_S)\, T_S}$$

~ horizontal shift

~ vertical shift ~ negligible

← $E = \rho RT/M$

Chapt 21

$$\log a_T = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)}$$

a_T = shift factor

- when T_S [$T_{reference}$] is T_g → WLF equation

$$\log a_T = \frac{-C_1^g(T - T_g)}{C_2^g + (T - T_g)}$$

  - C_1 = 17.44 and C_2 = 51.6 K ~ 'universal constants'
  - holds very well for most polymers

- WLF equation
  - by Williams, Landel, and Ferry

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

why η not E?
E indep of T? p504
Glass is frozen liquid.

  - Doolittle eqn $\eta = A \exp\left(\frac{B}{f}\right)$

$$\ln \eta = \ln A + \frac{B(V - V_f)}{V_f}$$ p505

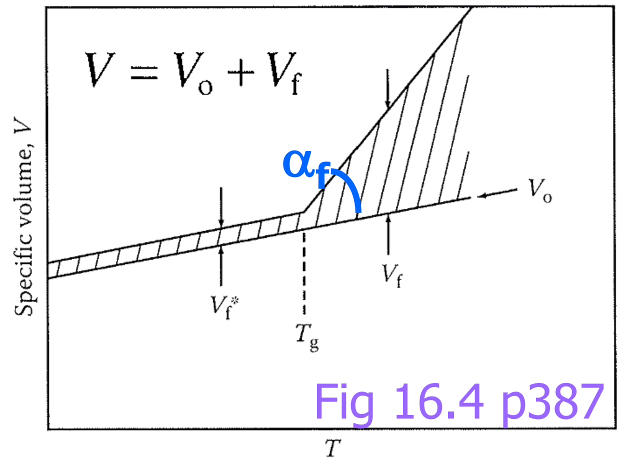


Fig 16.4 p387

  - fractional free vol $f_V = f_g + (T - T_g)\alpha_f$
  - shift factor a_T

$$\ln \frac{\eta(T)}{\eta(T_g)} = B\left(\frac{1}{f_g + \alpha_f(T - T_g)} - \frac{1}{f_g}\right)$$

$$\log \frac{\eta(T)}{\eta(T_g)} = \log a_T = \frac{-(B/2.303 f_g)(T - T_g)}{f_g/\alpha_f + (T - T_g)}$$

putting B=1 (arbitrary)
→ f_g = 0.025 (← C_1=17.44)
→ $\alpha_f = 4.8 \times 10^{-4}\ K^{-1}$ (← C_2=51.6)
"T_g is an iso-free-volume state."

Dynamic mechanical test

- oscillating stress and strain

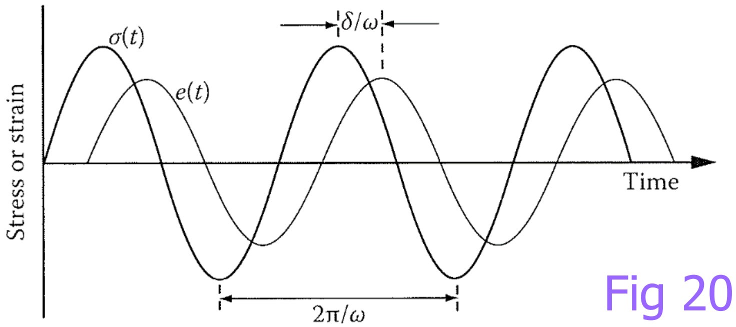


Fig 20.6

$$\sigma = \sigma_0 \sin \omega t$$

$$e = e_0 \sin(\omega t - \delta)$$

δ = phase lag, phase angle
loss angle, 'damping'

$$e = e_0 \sin \omega t$$

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$
$$= \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta$$
$$= e_0 E_1 \sin \omega t + e_0 E_2 \cos \omega t$$

in-phase with e
elastic
energy stored

$\pi/2$ out-of-phase with e
viscous
energy dissipated

$E_1 = (\sigma_0/e_0)\cos\delta$ storage modulus

$E_2 = (\sigma_0/e_0)\sin\delta$ loss modulus

$\tan\delta = \dfrac{E_2}{E_1}$ loss tangent

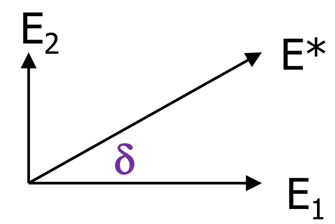
more generally, E′ and E″
instead of E_1 and E_2

- in complex expression

$$e = e_0 \exp i\omega t$$

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

overall complex modulus $E^* = \sigma/e$



$$E^* = \frac{\sigma_0}{e_0}\exp i\delta = \frac{\sigma_0}{e_0}(\cos\delta + i\sin\delta) = E_1 + iE_2$$

$$\tan\delta = \frac{E_2}{E_1}$$

- instruments
  - torsion pendulum
    torsional braid analyzer
    - log decrement Λ

$$\Lambda = \ln\left(\frac{\Theta_n}{\Theta_{n+1}}\right) \qquad \tan\delta \simeq \frac{\Lambda}{\pi}$$

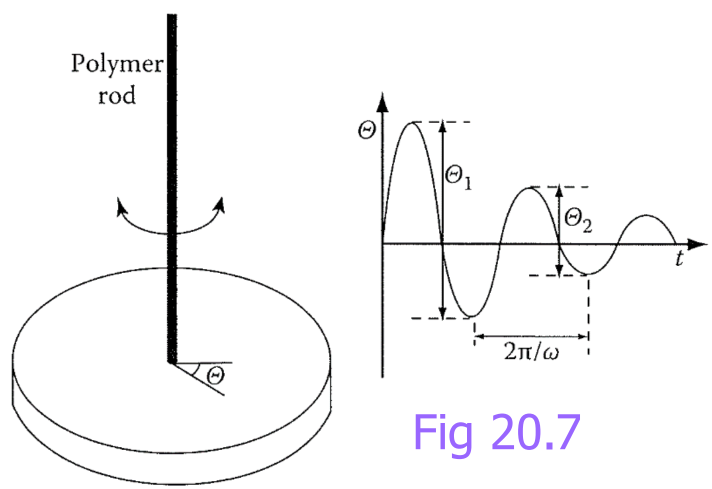
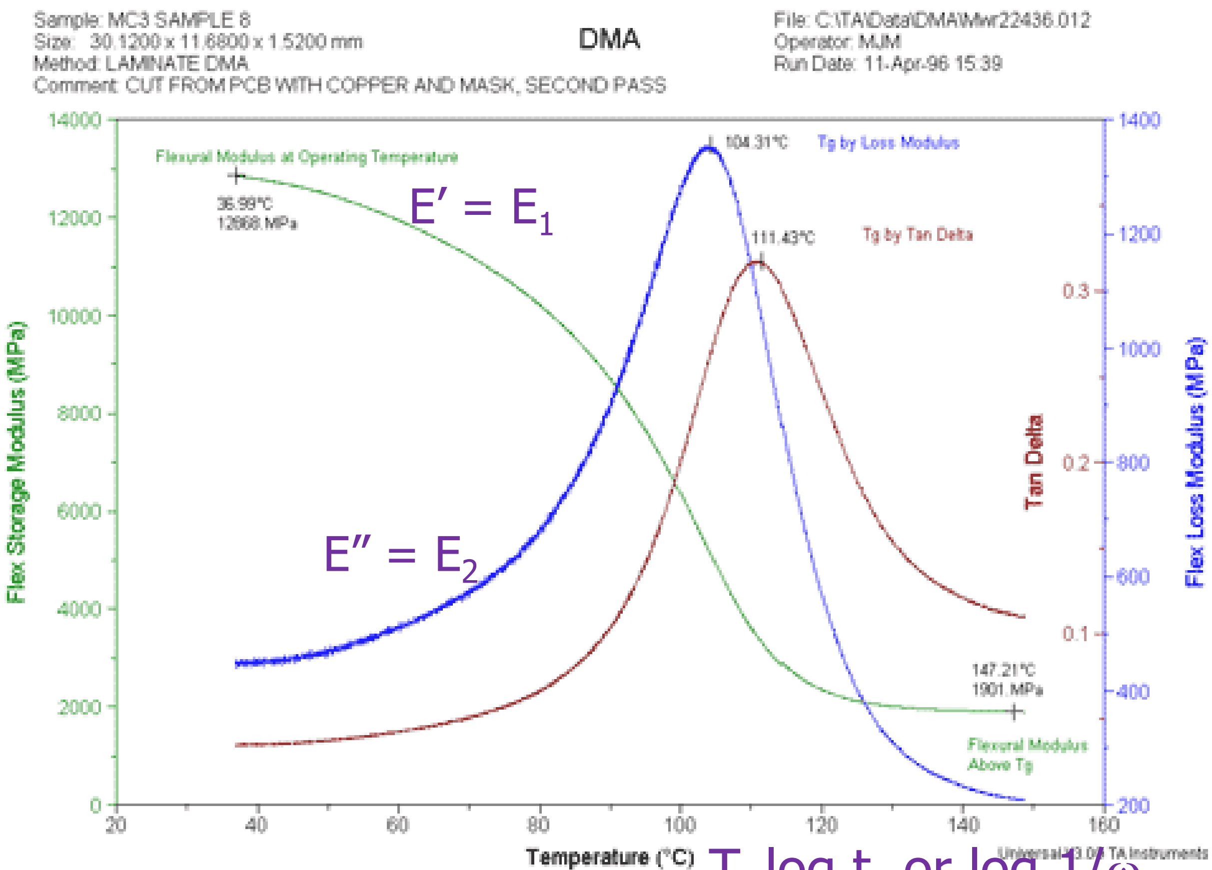
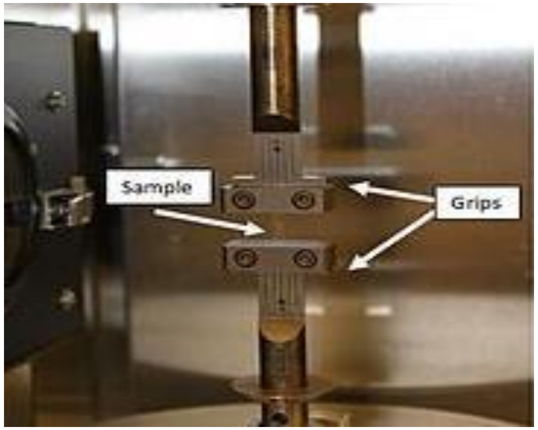


Fig 20.7

- dynamic mechanical (thermal) analysis [DM(T)A]
  - tensile or bending strain
  - temperature or frequency scan

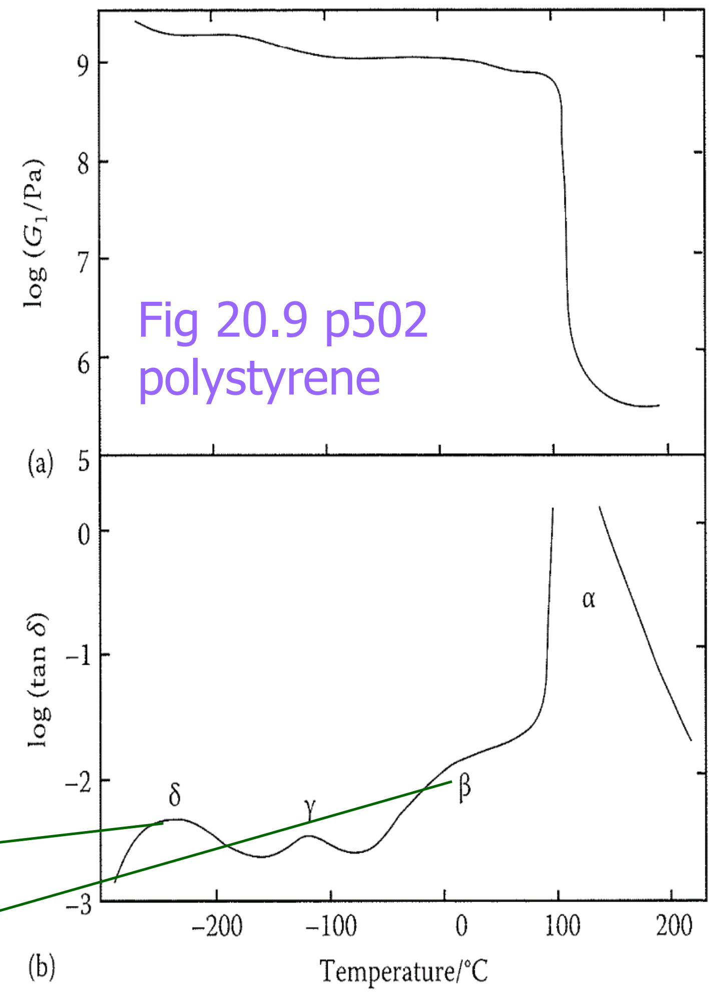




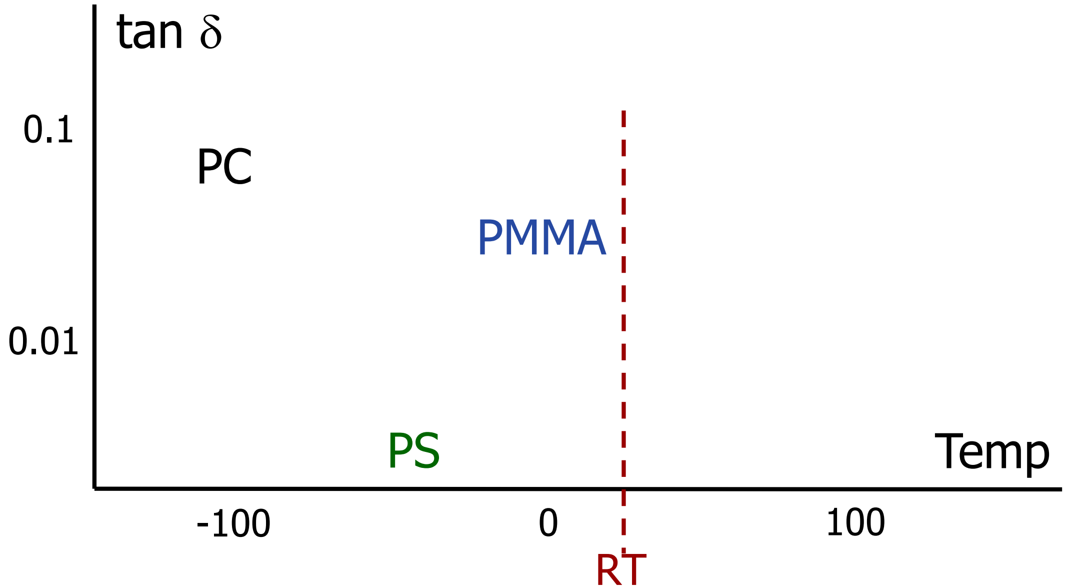
tan δ = E″/E′ is small →
E ≈ E* ≈ E′ (in magnitude)

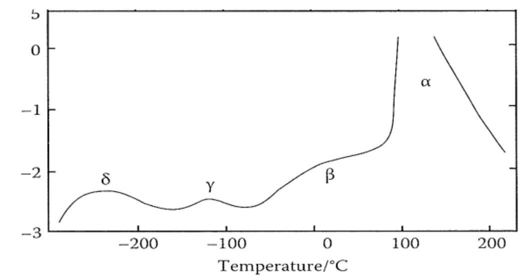
Transitions and relaxations in polymers

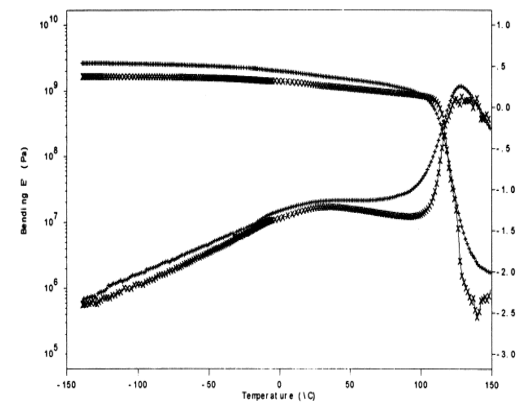
- transition [轉移]
  - change in property
- relaxation [緩和]
  - response by molecular motion
- glass transition
  - primary [α] relaxation
  - segmental motion
- secondary relaxation
  - β-, γ-, δ- -- (in the order of T↓)
  - motion smaller than that for T_g
    - local main chain
    - side-chain, part of side-chain
    - cooperative main and side-chain
    - plasticizer

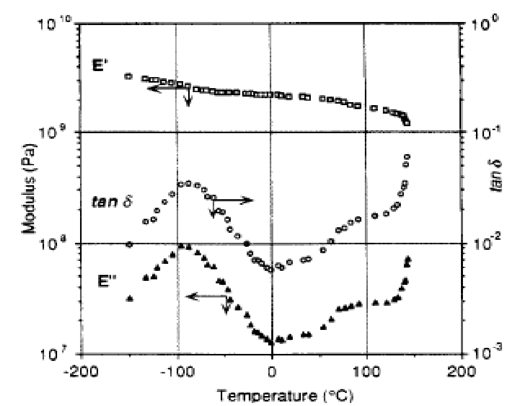


- 2ndary relaxation affects property at room temp.





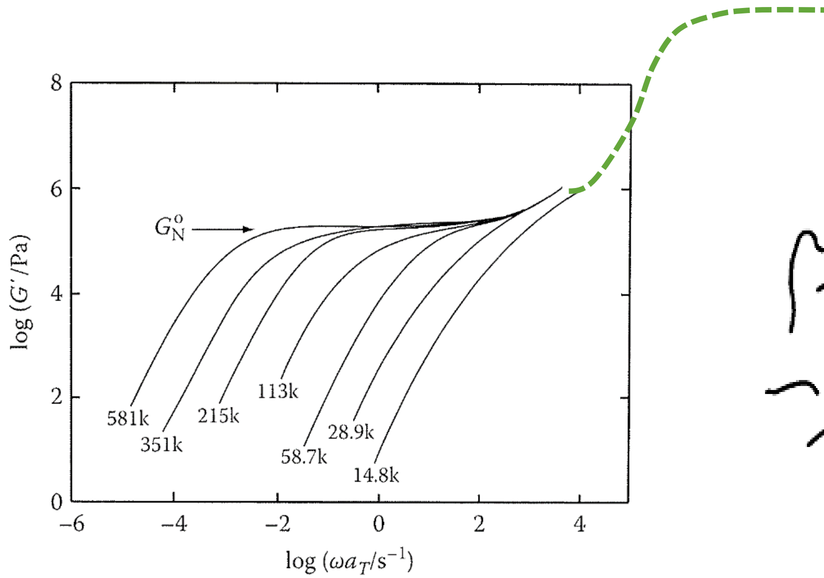


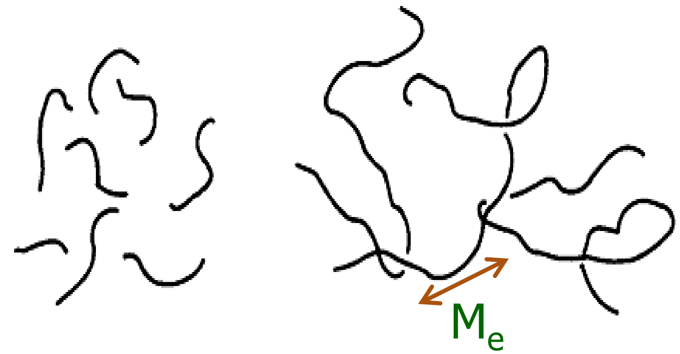


- property like toughness
- especially with larger-scale motion
- T_g? heat resistance, use temperature

Entanglement

- rubbery plateau region





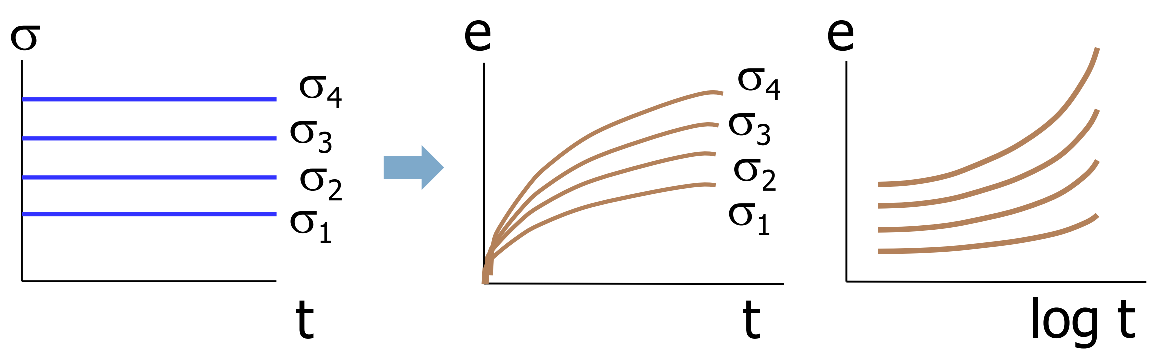
- width of plateau ∝ molar mass
  - motion of chains between [inside] entanglements
- level [plateau modulus $G_N{}^0$] depends on M_e, <u>not</u> on MM of chain

$$M_e = \frac{\rho \mathbf{R} T}{G_N^o} \qquad\qquad G_N^o \propto M^0$$

Chapt 21 reptation

Applying VE data to product design

- Correspondence principle
  - viscoelastic equation → elastic equation
  - $\sigma(t) = E(t)\, e \;\rightarrow\; \sigma = E\, e$
- Pseudoelasticity
  - From creep, SR, or isochrone s-s curve,
  - estimate long-term stress-strain relation,
  - and design the product.



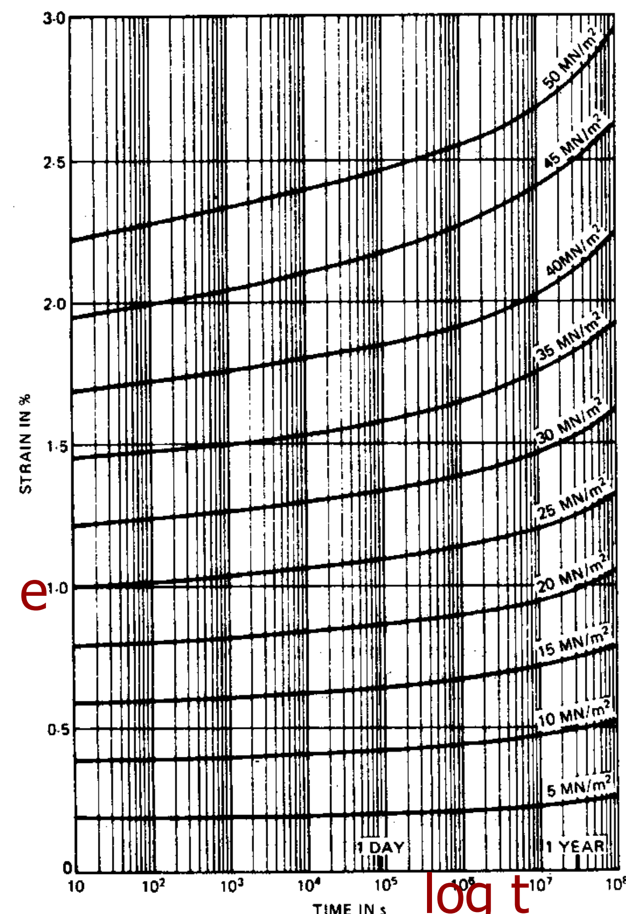
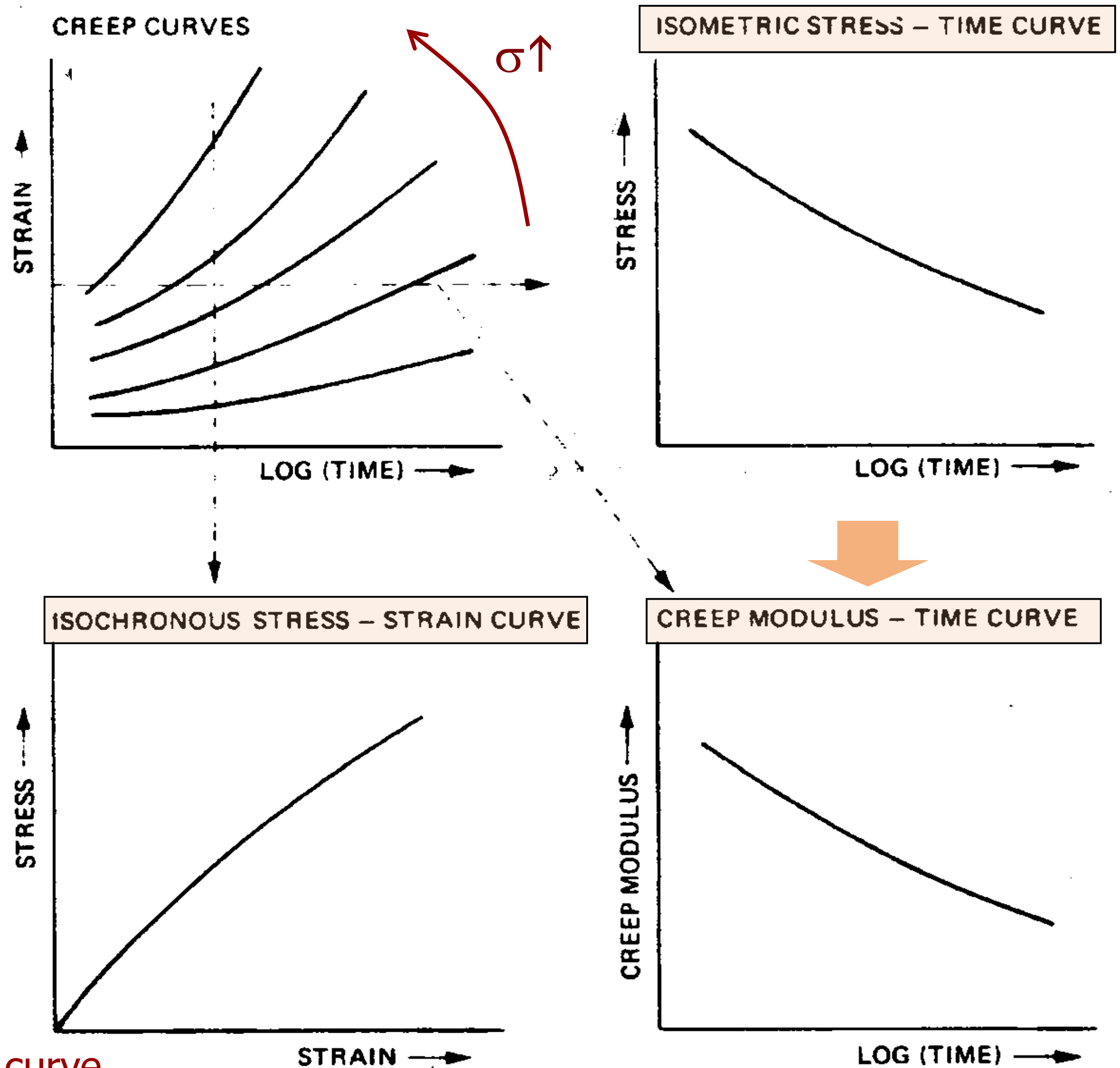
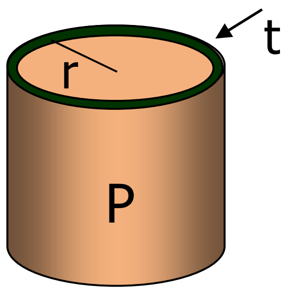


Figure 9.9. Curves for creep in tension of a commercial polysulphone (Polyethersulphone 300P–ICI) at 20°C. (From ICI Technical Service Note PES 101, reproduced by permission of ICI Plastics Division)



different from transient σ–ε curve

- An example
  - To design a pressure vessel that is required to be used for 1 year without yielding or fracture (say 5% maximum allowable strain),



largest stress $\sigma = P\,r\,/\,t$