

P287

Chap. 10 Optical properties

P296 (EX 10.1) Estimate the refractive index of PF

P303 (Ex10.2) Estimate the optical stress coeff. For polycarbonate with $V_w=144$ cm^3/mol

P311 (Ex 10.3) Estimate the specific refractive index increment (dn/dc) of polystyrene in 1,4-dioxane ($n_d=1.422$)

Chap. 11 Electrical properties

P324 (Ex11.1) Estimate the dielectric constant and the average dipole moment of polycarbonate

P325 correlation between dielectric constant and solubility parameter (see Table 11.4)

$$\delta = 7.0 \text{ \AA} \quad (11.5)$$

p330 conductivity (see Fig 11.5)- p.332

p343

Chap. 12 Magnetic properties.

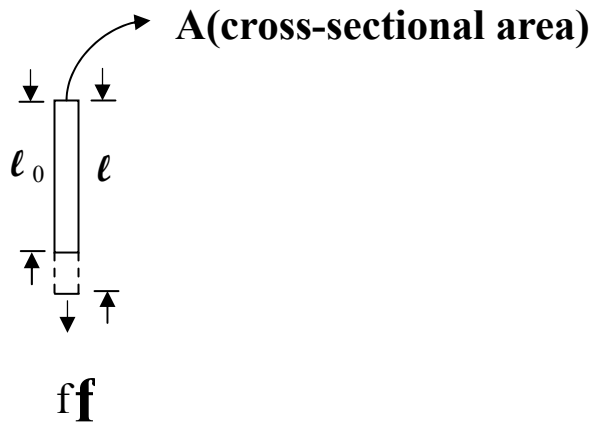
Chap. 13 Mechanical Properties of Solid Polymer

p.367 • Hook's Law

$\tau = Y\epsilon$, stress is proportional to the strain

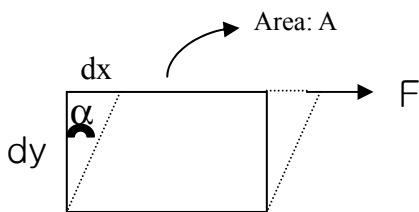
$$\left\{ \begin{array}{l} \tau : \text{stress} \\ \epsilon : \text{strain} \\ Y : \text{young's modulus} \end{array} \right.$$

(a) Tensile deformation



- tensile strain : $\epsilon = \frac{\lambda - \lambda_0}{\lambda_0}$
- tensile stress : $\sigma = f/A$
- tensile modulus : $Y = \tau / \epsilon$
- tensile compliance : $D = \epsilon / \tau$

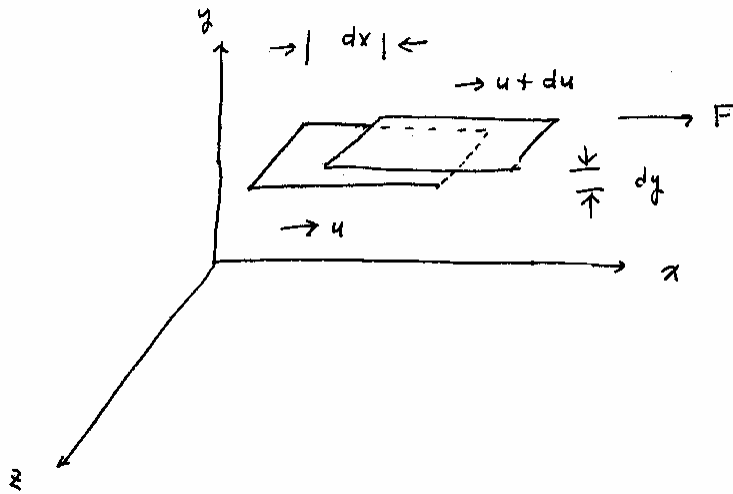
(b) shear deformation



- shear strain: $\gamma = \tan \alpha = \frac{dy}{dx}$
- shear stress: $\sigma = f/A$
- shear modulus : $G = \sigma / \gamma$
- shear compliance : $J = \gamma / \sigma$

(see Table 13.1)

- A modulus is the ratio between the applied stress and the corresponding deformation.



- a fluid surface at y :
velocity : $y = \frac{dX}{dt}$
- a fluid surface at $y+dy$:
velocity : $y+dy$:

- shear strain : $\gamma = \frac{dX}{dy}$
- shear rate : $\dot{\gamma} = \frac{d}{dt}(\gamma) = \frac{d}{dt}\left(\frac{dx}{dy}\right) = \frac{d}{dy}\left(\frac{dx}{dt}\right) = \frac{dx}{dt}$

an alternate definition of the shear rate is the velocity gradient du/dy

- shear stress : $\tau = \frac{F(\text{in } x \text{ direction})}{A(\text{in } y \text{ direction})} = \frac{(\text{force})}{(\text{length}^2)}$
- viscosity : $\eta \equiv \tau / \dot{\gamma}$

p369• Poisson Ratio : $\nu \equiv \frac{\text{change in width per unit width}}{\text{change in length per unit length}}$

$$= \frac{\text{lateral contraction}}{\text{axial strain}}$$

- poisson ratio 비교,
Table 13.4 (p.374)로부터

{	PMMA,	$\nu = 0.40$
	PS	0.38
	Copper	0.34
	Glass	0.23

p. 377

(Ex.13.1) Estimate the bulk modulus of a medium density polyethylene,
density of 0.95 (degree of crystallinity = 70%)

(sol.)

(a) Estimation by Rao function:

식 (13.22)로부터 (p. 375)

$$K/\rho = \left(U_R/V \right)^6$$

$$\text{molar volume, } V = \frac{M}{\rho} = \frac{28}{0.95} = 29.5 \text{ (cm}^3/\text{mol)}$$

여기서 U (Molar elastic Wave Function)를 구하기 위하여 Table 14.2 참조 (p.447)

$$U_R = 2 \times 880 \text{ (cm}^3/\text{mol) (cm/sec)}^{1/3}$$

$$= 1760$$

$$\text{그러므로 } \left(U_R/V \right)^6 = \left(\frac{1760}{29.5} \right)^6$$

$$= 4.5 \times 10^{10} \text{ (cm}^2/\text{sec}^2)$$

$$\therefore K = 4.5 \times 10^{10} \times 0.95 \text{ g/cm} \cdot \text{sec}^2$$

$$= \underline{4.3 \times 10^9 \text{ (N/m}^2)}$$

p378 (Ex 13.2) Estimate the moduli and Poisson ratio of polycarbonate,

(sol.) Poisson ratio ;

식 (13.10) (p. 370)으로부터

$$\nu = \frac{1 - \frac{2G}{3K}}{2(1 + \frac{G}{3K})} = \frac{1 - 0.15}{2(1 + 0.075)} = 0.39$$

$$\nu \text{ (exp)} = \underline{0.39}$$

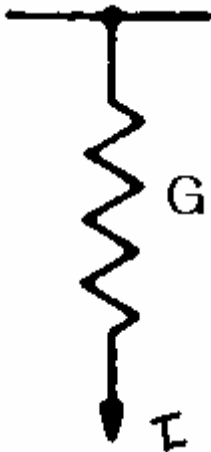
p388. • Linear Viscosity.

-Two linear model
 $\left\{ \begin{array}{l} \text{linear elastic} \\ \text{linear viscous} \end{array} \right.$

i) Linear elastic model : OR Hookean Solid.

$$\tau = G \gamma$$

G= shear modulus



Linear elastic model
Or Hookean solid

$$\tau : G \gamma$$

G: shear modulus

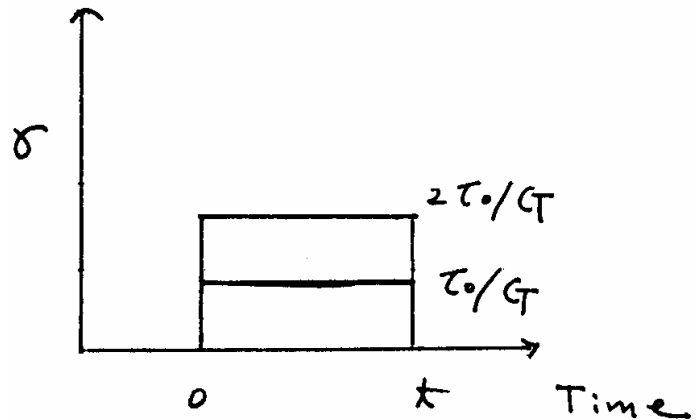


Fig. Response of spring

• The overall modulus is a function of time only, no the magnitude of Stress or strain.

$$G \equiv \frac{\tau}{\gamma} = G$$

(t only for linear response)

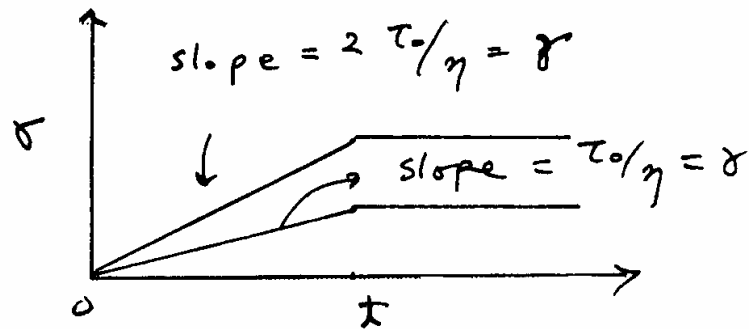
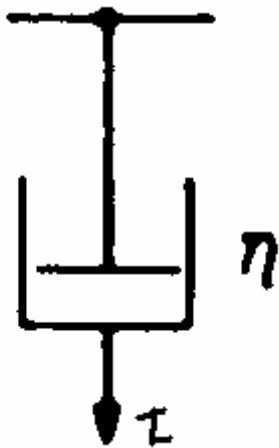


Fig. Response of dashpot

Linear viscous model

Or Newtonian fluid

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

η : viscosity

• **Mechanical Models for linear viscoelastic response**

(1) **The Maxwell Element.**

- a simple series combination of a linear viscous element (dashpot) and a linear elastic element (spring)

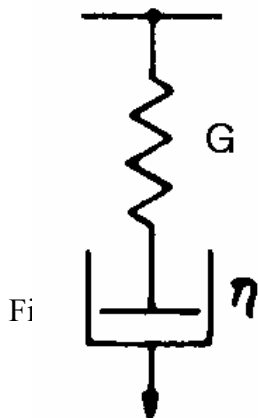


Fig. Maxwell element

-the spring and dashpot support the same stress:

$$\tau = \tau_{\text{spring}} = \tau_{\text{dashpot}}$$

-the overall strain of the element :

$$\gamma = \gamma_{\text{spring}} + \gamma_{\text{dashpot}}$$

differentiation with time, t

$$\dot{\gamma} = \dot{\gamma}_{\text{spring}} + \dot{\gamma}_{\text{dashpot}}$$

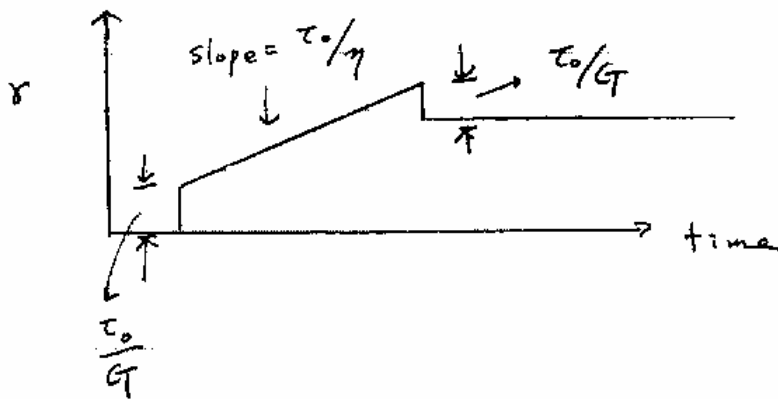
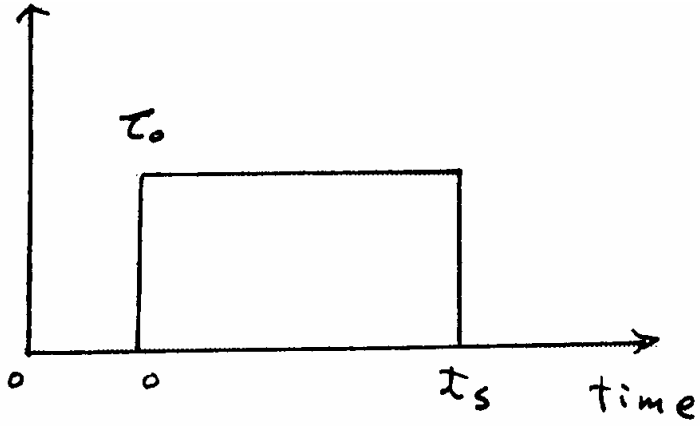
$$\dot{\gamma} = \dot{\gamma}/G + \tau/\eta$$

$$\tau = \eta \dot{\gamma} - (\eta/G) \dot{\tau}$$

$$= \eta \dot{\gamma} - \lambda \dot{\tau}$$

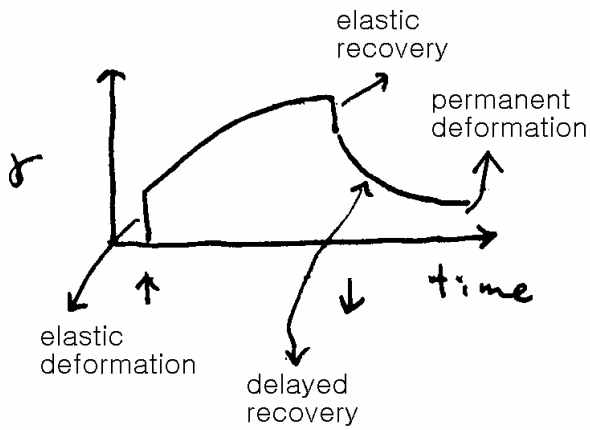
where ($\lambda = \eta/G$: relaxation time)

- creep test – a constant stress is instantaneously applied to the material, and the resulting strain is followed as a function of time

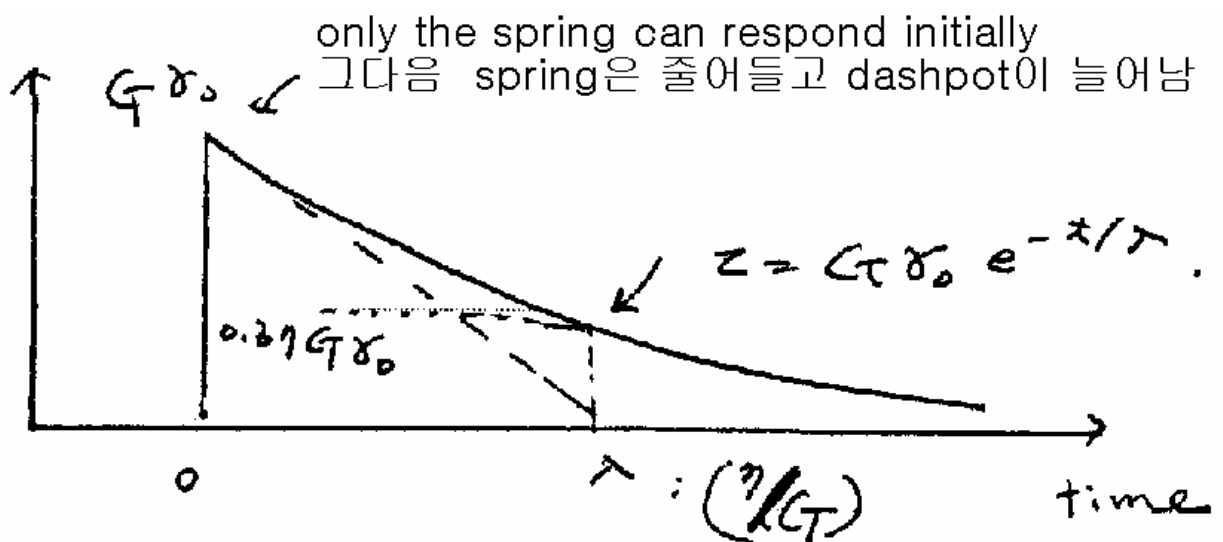
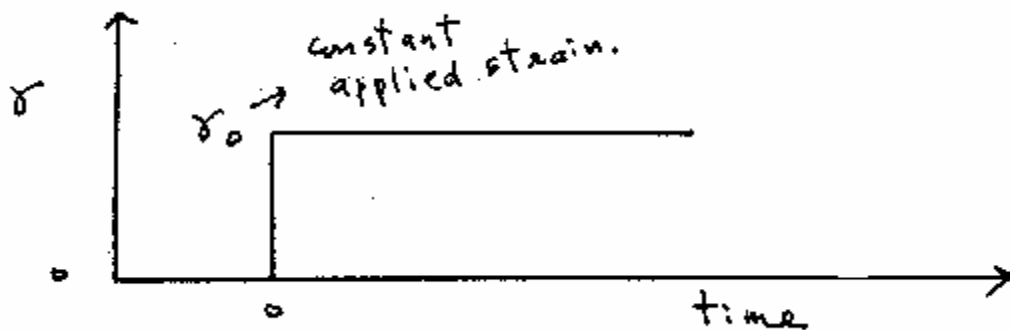


ex)

Fiber:



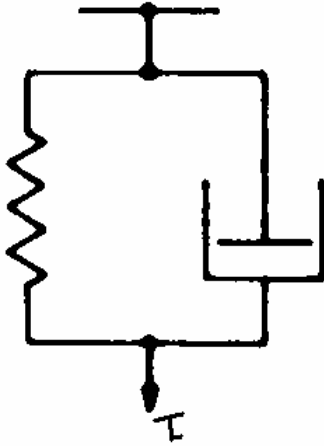
- creep recovery : deformation after removal of the stress.
- τ_0/G : instantaneous stretching of the spring to an equilibrium value with the sudden application of stress (τ_0)
- Elastic Recovery : when the stress is release the spring immediately contracts by an amount equal to its original extension
- **Stress relaxation test** : Suddenly applying a strain to the sample and following the stress as a function of time as the strain is held constant.



λ : (relaxation time)- time required for the stress to decay to a factor of $1/e$ or 37% of its initial value.

- 실제 linear polymer 의 stress-relaxation curve 와 비슷함

(ii) The Voigt-kelvin Element : for crosslinked polymer



- strain in each element is same

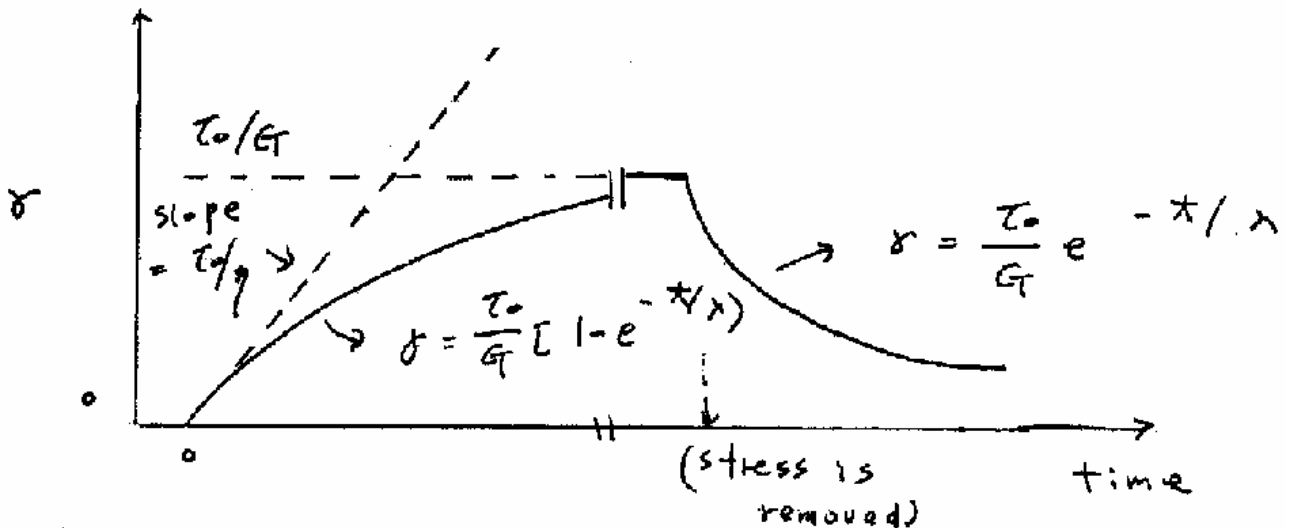
$$\gamma = \gamma_{\text{spring}} = \gamma_{\text{dashpot}}$$

- The stress is the sum of the stresses:

$$\tau = \tau_{\text{spring}} + \tau_{\text{dashpot}}$$

$$\tau = G\gamma + \eta\dot{\gamma}$$

- Creep response of a Voigt-kelvin Element : stress is constant



-initial slope of the strain vs time curve is

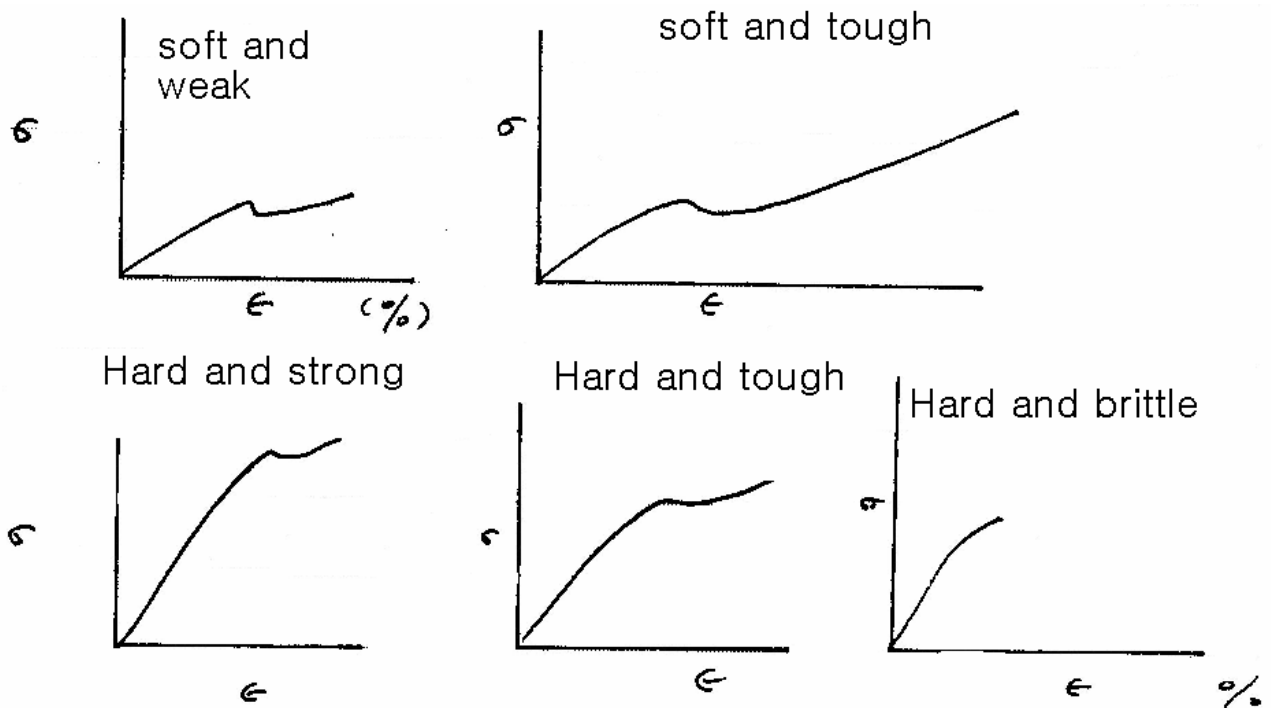
- as the element is extend, the spring provides an increasingly greater resistance

to further extension, and so the rate of creep decreases.

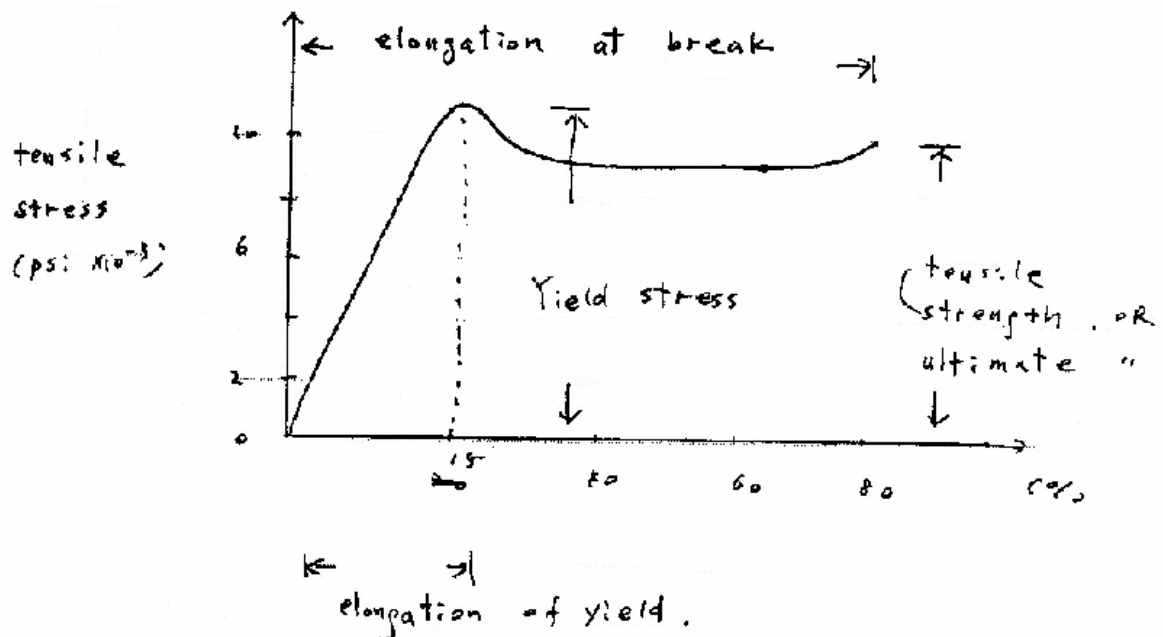
- Eventually, the system curves to equilibrium with the spring alone supporting the stress. (rate of strain = 0 , resistance of the dashpot=0)
- The equilibrium strain = τ_0/G
- Voigt-kelvin model : a fair qualitative picture of the creep response of some crosslinked polymers.

- characteristics of tensile stress-strain curves of polymer samples.

See page 413 in V. K.



- polymer 사이에 dipole-dipole interaction 이 없기 때문에 soft 하다.
- strongly polar polymer: Nylon, PC, acetal (Engineering plastics) see P.426



- yield stress : 11000psi
- strain at yield : 15%
- ultimate elongation : 80%
- Filled thermosetting polymers:
일반 engineering 고분자와 비교했을 때 stiffness 가 4-5 배

• high modulus, high strength polymer – Aramid Fiber (Kevlar) – aromatic polyamid.
Thermosetting resin, carbon Fiber 등의 액정고분자

p402 C5. The time-temperature superposition principle (TTSP)

- Above T_g , the stress relaxation and the creep behavior of amorphous polymers obey the “time-temperature superposition principle”
- In viscoelastic maters, time and temperature are equivalent to the extent that data at one temp. can be superimposed upon data taken at a different temperature
- The amount each reduced modulus has to be shifted along the logarithmic time axis in making the master curve, the so-called shift factor, is a function of temp.

$$\left[\begin{aligned} \log a_r = \log \frac{t}{t(T_g)} &= \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \\ &\text{W.L. Ferry Eq.} \end{aligned} \right.$$

P. 405 Ex 13.3

25°C, measuring time 1h 에서 polyisobutylene 의 stress relaxation modulus 는 $3 \times 10^5 \text{ N/m}^2$ 이다.

(a) time 1h, 80°C 에서 modulus 는?

(b) 식(13.70)에서 그리고 PIB 의 $T_g = 197\text{k}$

$$\begin{aligned} \log a(273+25) &= \frac{-17.44(298-197)}{51.6+101} \\ &= \frac{-1760}{152.6} = -11.5 \end{aligned}$$

$$\log a \frac{273-80}{193} = \frac{17.44 \times 4}{51.6-4} = \frac{70}{47.6} = 1.5$$

$$\log \frac{a(193)}{a(298)} = 1.5 + 11.5 = 13.0 \quad \left(\log \frac{a(298)}{a(193)} = -13 \right)$$

the master curve at $t \approx 10^{-13}$ 에서의 modulus 는 약 $2 \times 10^9 \text{ N/m}^2$