5.4 Theories for the glass transition

: free volume theory, kinetic theory, thermodynamic theory

* **Free volume theory**

Polymers have a certain universal free volume at T_g .

← (Doolittle equation & WLF equation)

• *WLF (Williams-Landel-Ferry) equation*

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

Shift factor $a_T = \eta_T / \eta_{T_r} = \tau_T / \tau_{T_r}$

η_T : temperature T에서의 점도

η_{T_r} : reference T에서의 점도

τ_{T_r} : reference T에서의 완화시간

When T_r is set equal to T_g ,

$$\log a_T = \frac{-17.44(T - T_r)}{51.6 + T - T_r} \quad \Leftarrow \quad C_1 = -17.44, \quad C_2 = 51.6K$$

이것을 Doolittle viscosity equation

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

과 비교해 보면,

$\Rightarrow$ $f_g = 0.025$ 를 얻을 수 있다.

5.5 Mechanical behavior

* Phenomenological model

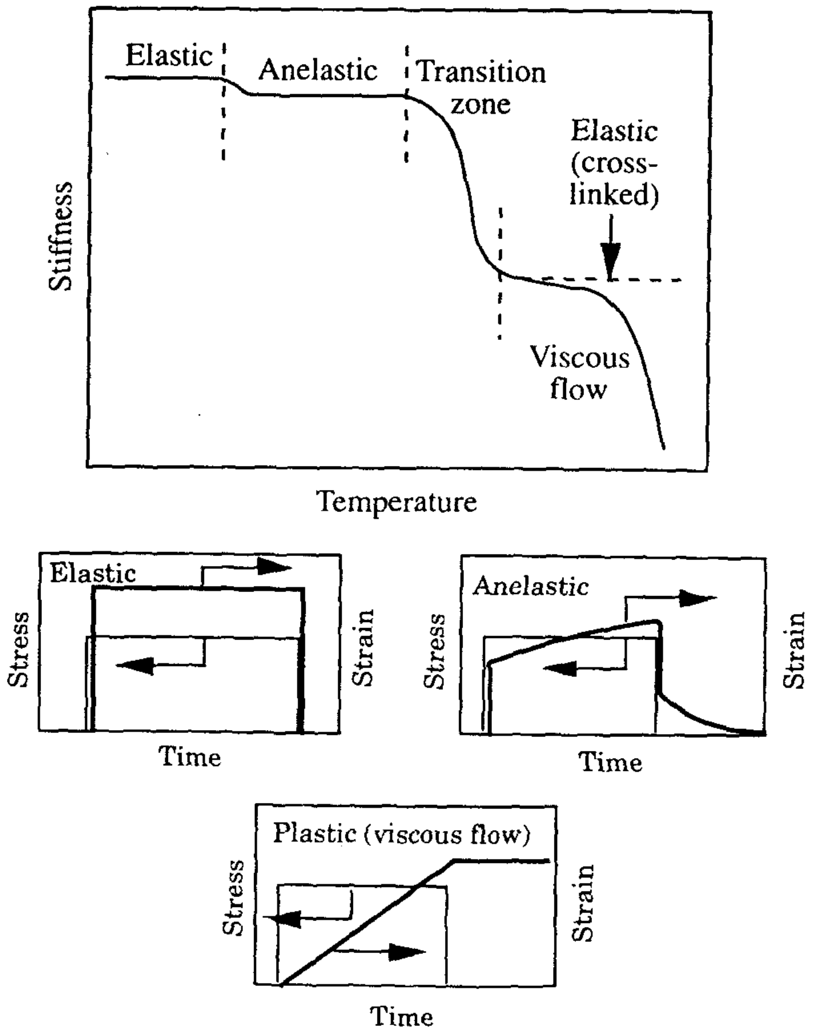
- Creep test

Measuring $\varepsilon(t)$ under the constant stress σ_0

↘ time-dependent strain $= \dfrac{\Delta L}{L_0}$

$$\varepsilon(t) = J(t)\sigma_0$$

↘ compliance



Behavior of amorphous polymers

. Elastic

. Anelastic (= viscoelastic)

. Viscous

- Stress relaxation test

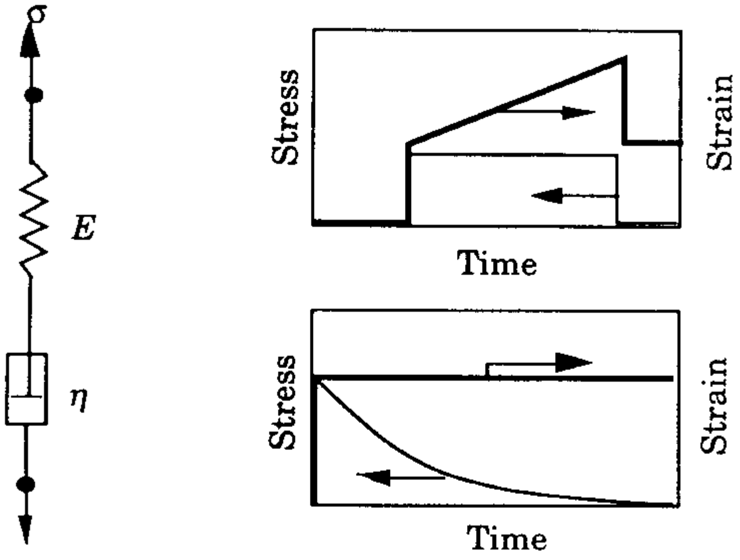
Measuring $\sigma(t)$ under the constant strain ε_0

$$\sigma(t) = G(t)\varepsilon_0$$

↘ modulus

• Maxwell model

: an elastic spring & a viscous element (dashpot) coupled in series



$$\sigma + \tau\dot{\sigma} = \eta\dot{\varepsilon} \quad \leftarrow \quad \varepsilon = \varepsilon_e + \varepsilon_v$$

- Creep test (constant stress σ_0)

$$\varepsilon = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta}t = \frac{\sigma_0}{\eta}(\tau + t)$$

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

- Relaxation test (constant strain ε_0)

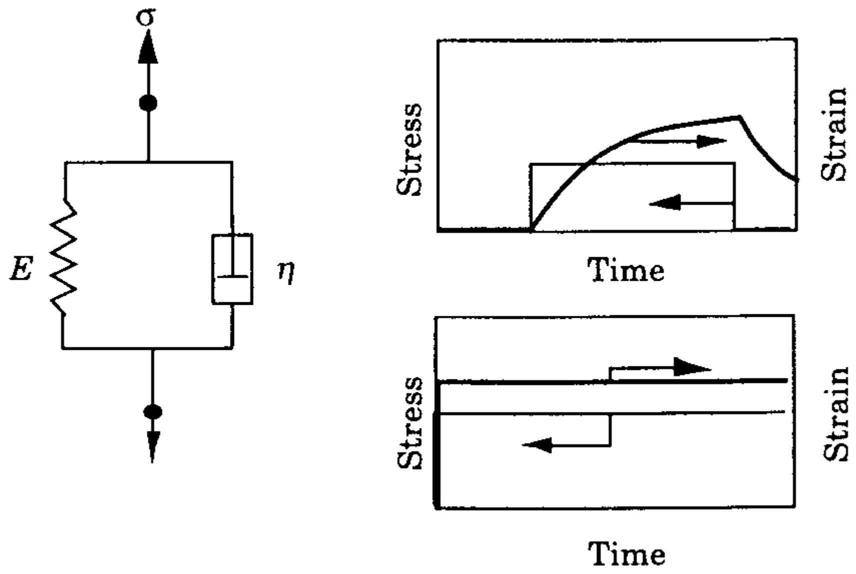
$$\sigma = E\varepsilon_0 e^{-t/\tau}$$
$$= \sigma_0 e^{-t/\tau}$$

τ 는 time constant라 불리기도 함.

(σ_0 로부터 σ_0 / e 로 될 때까지 걸리는 시간)

• Voigt-Kelvin model

: an elastic element & a viscous element coupled in parallel



$$\frac{\sigma}{E} = \tau \dot{\varepsilon} + \varepsilon \quad \leftarrow \quad \sigma = \sigma_e + \sigma_v$$

$$\tau = \frac{\eta}{E} \text{ (retardation time)}$$

- Creep test (constant stress σ_0)

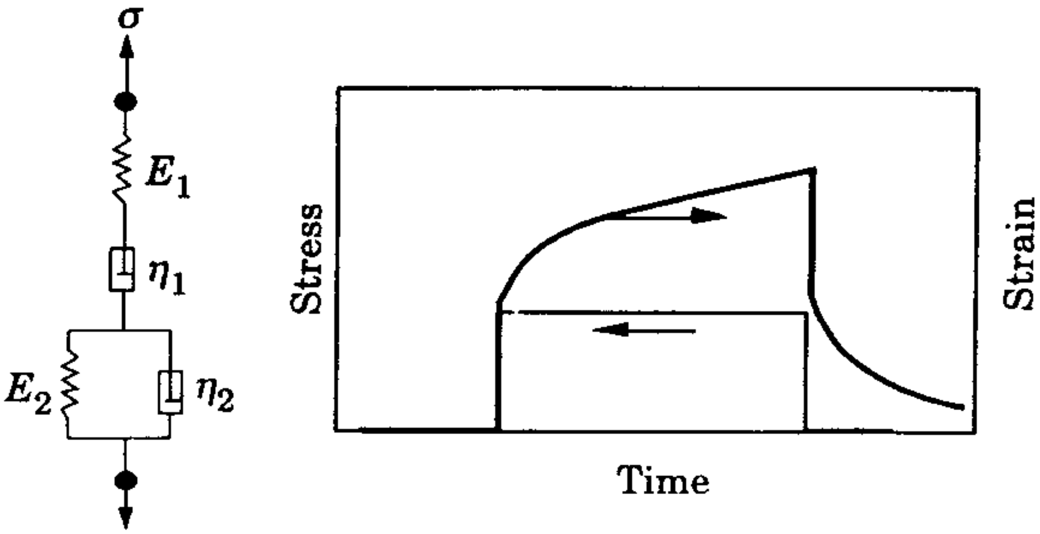
$$\varepsilon = \frac{\sigma_0}{E}\left(1 - \exp\left(-\frac{t}{\tau}\right)\right)$$

- Relaxation test (constant strain ε_0)

$$\sigma = \varepsilon_0 E$$

- Burger's model

: the Maxwell and Voigt-Kelvin elements in series



* Dynamic mechanical behavior

Under a sinusoidal strain $\left(\varepsilon^* = \varepsilon_0 \exp(i\omega t)\right)$ in the Maxwell element

$\leftarrow \omega$: angular velocity

$$E^* = E' + iE''$$

$$E' = E\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) : \text{storage modulus}$$

$$E'' = E\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) : \text{loss modulus}$$

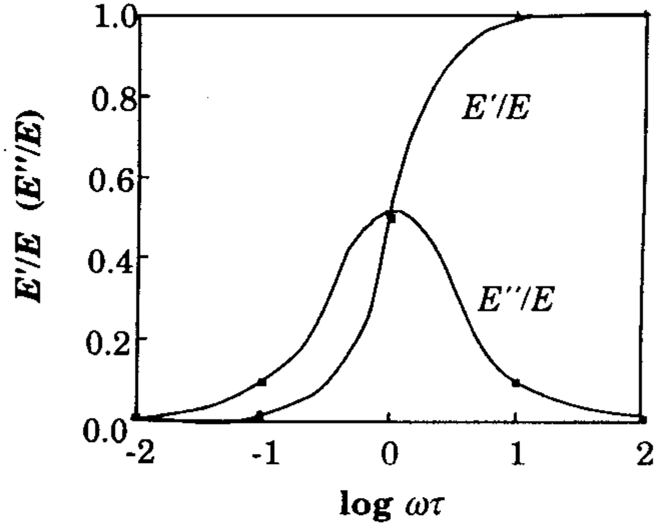


Figure 5.25 Storage and loss modulus as a function of frequency (angular velocity ω) for a single Maxwell element.

Polymers need a number of Maxwell elements coupled in parallel.

$$E(t) = \sum_{i=1} E_i \exp\left(-\frac{t}{\tau_i}\right)$$

$$= \underline{E_{eq}} + \int_{-\infty}^{\infty} \underline{H(\tau)} \exp\left(-\frac{t}{\tau}\right) \overline{d \ln \tau}$$

$\frac{1}{\tau} d\tau$

$\tau E(\tau)$: relaxation time spectrum

modulus at time $\rightarrow \infty$

* ***Molecular interpretation***

Experimental data show a series of relaxation processes.

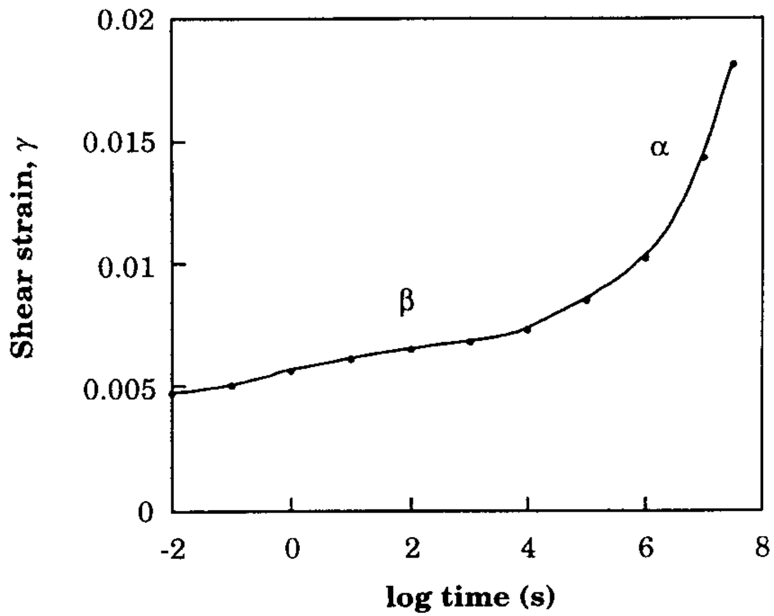


Figure 5.27 Shear strain as a function of time (log scale) for polymethyl methacrylate (PMMA) at a constant shear stress of 7.3 MPa at 30°C. Drawn after data from Lethersich (1950).

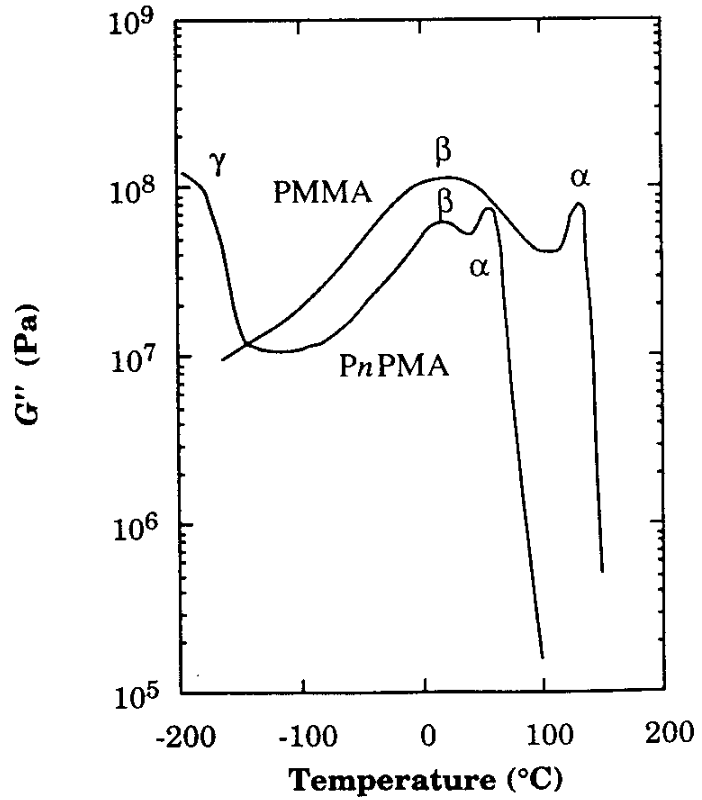


Figure 5.28 Temperature dependence of loss modulus (G'') as a function of temperature at 1 Hz for polymethyl methacrylate (PMMA) and poly(*n*-propyl methacrylate) (P*n*PMA). Drawn after data from Heijboer (1965).

PnPMA

$T_g(\alpha)$: free volume

subglass processes

T_β : physical ageing

T_γ : motions in the flexible methylene sequence

PS

$T_g(\alpha)$: 100 ~ 105 ℃

β process ($T_g - 100$ ~ T_g)

: due to a rotation of the phenyl group with a main-chain cooperation

γ process (180K)

: due to oscillatory motions of the phenyl group

δ process (55K)

: due to oscillatory motions of the phenyl group or from defects associated with configuration

5.6 Structure

Typical glassy amorphous polymers -- transparent

-- very low light scattering

-- no Bragg reflections (in XRD)

- DSC -- amorphous (T_g)

  -- crystalline (T_m)

- WAXS -- amorphous (diffuse)

  -- crystalline (sharp Bragg reflections)