

Chapter 14 and 15 Polymer viscoelasticity

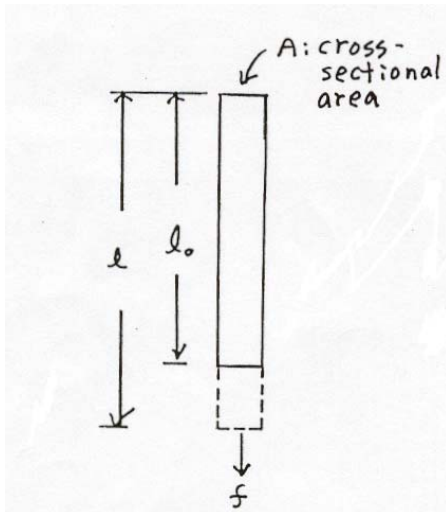
(Ref. John.D.Ferry, Viscoelastic Properties of polymers, John Wiley(1980))

- Hooke's Law :

$$\sigma = Y \epsilon$$

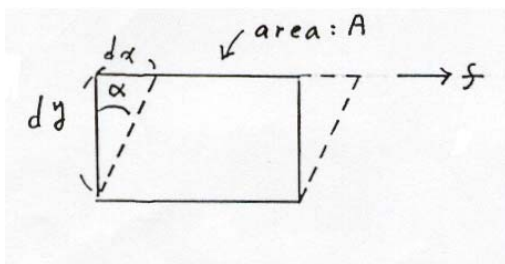
the strain ϵ is proportional to the stress σ , Y is Young's modulus(tensile strength)

(a) tensile deformation

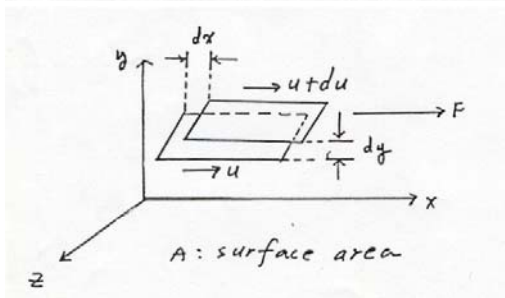


- tensile strain $\epsilon = \frac{l - l_0}{l_0}$
- tensile stress $\sigma = \frac{f}{A}$
- tensile modulus $Y = \frac{\sigma}{\epsilon}$
- tensile compliance $D = \frac{\epsilon}{\sigma}$

(b)



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



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

- shear strain : $\gamma = \frac{dx}{dy}$ (dimensionless)

- shear rate : $\dot{\gamma} = \frac{d}{dt}(\gamma) = \frac{d}{dt}\left(\frac{dx}{dy}\right) = \frac{d}{dy}\left(\frac{dx}{dt}\right) = \frac{du}{dy}$ (time⁻¹)

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

- shear stress : $= \frac{F(\text{in } x \text{ direction})}{A(\text{in } y \text{ direction})} \left(\frac{\text{force}}{\text{length}^2} \right)$

- viscosity : $\eta \equiv \frac{\tau}{\dot{\gamma}}$

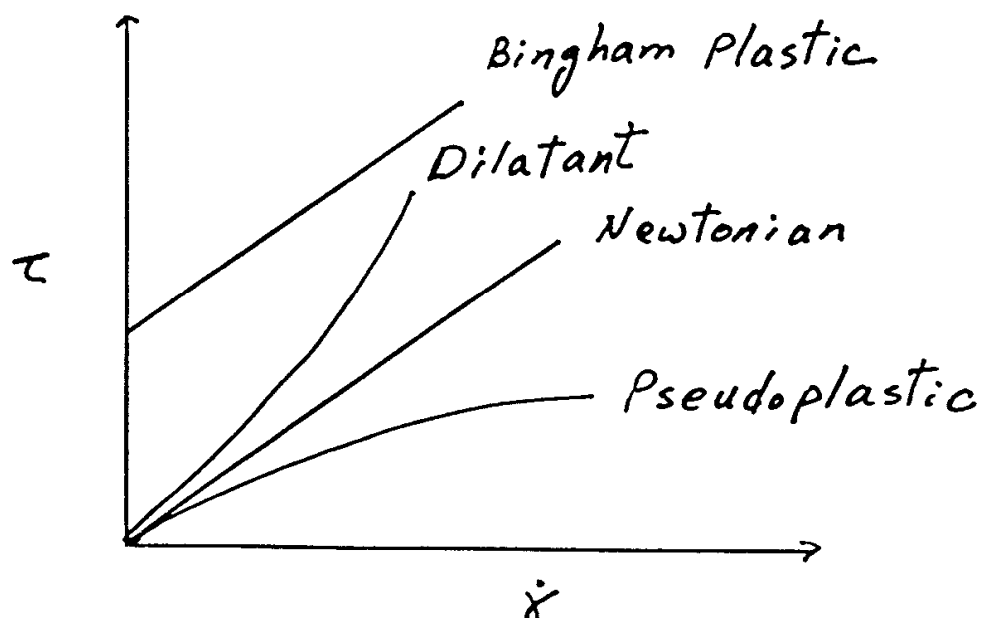
- Relations between τ and $\dot{\gamma}$ - Flow curves.

- Newton's law : shear stress is linearly proportional to the shear rate, the proportionality constant being the viscosity η .

$$\tau = \eta \dot{\gamma} \quad (\eta = \text{dyne sec/cm}^2)$$

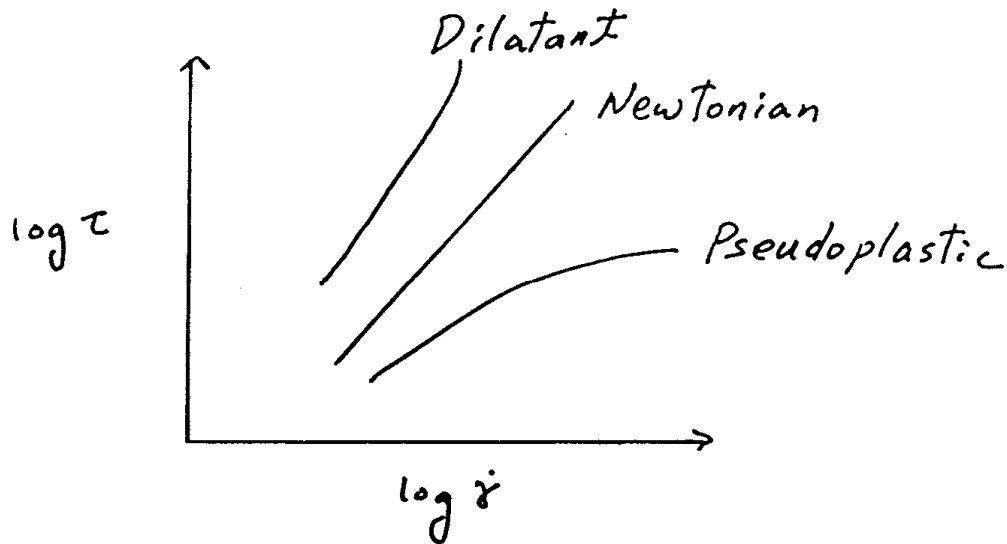
Taking logarithm :

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



• $\tau = \dot{\gamma}^n$

taking logarithm : $\log \tau = \log \tau_0 + n \log \dot{\gamma}$



(a) $n = 1$ () : Newtonian flow
(= constant)

- for small molecules (ex : silicone polymer)
- the structure, the resistance to flow does not change with the intensity of shearing

(b) $n < 1$: pseudoplastic flow (shear - thinning)

decreases with increase of $\dot{\gamma}$: $\tau = f(\dot{\gamma})$

(e.g.) polymer melts and solutions

- resistance to flow decreases with the intensity of shearing.

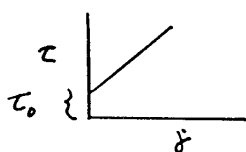
(c) $n > 1$: dilatant flow (shear - thickening)

increases with the increase of $\dot{\gamma}$

(e.g.) slurries, suspension()

- resistance to flow increases with the intensity of shearing

• Bingham plastic



(ex) emulsion ()

- three types of fluid

(a) Newtonian fluid

(b) Non-newtonian fluid $\left(\begin{array}{l} \text{pseudoplastic flow} \\ \text{dilatant flow} \end{array} \right)$

-these two fluids, though shear dependent, are time independent ;
(constant) shear rate stress가 maintain , the
same viscosity will be observed at equilibrium.

- Time dependent behavior :

(a) Rheopetic

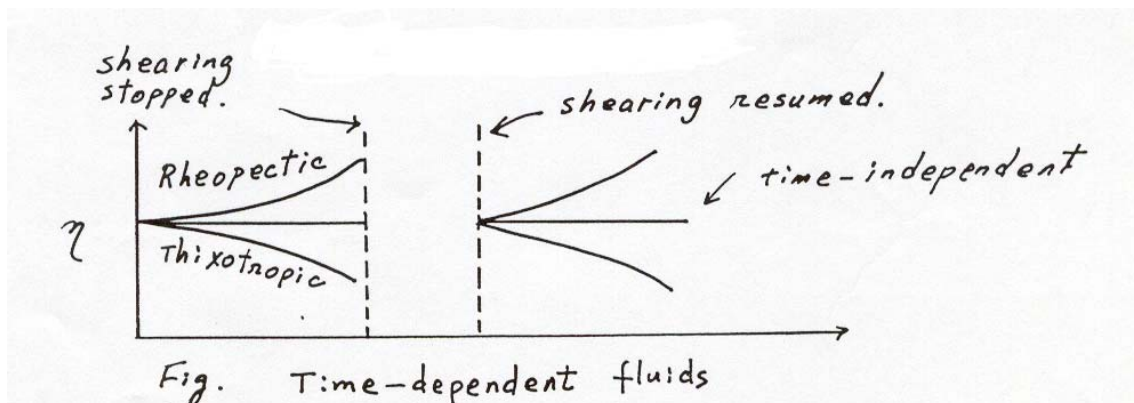
(b) Thixotropic

(a) Rheopetic fluid – when sheared at a constant rate or stress, the
viscosity will increase over a period of time.

(e.g.) muds

(b) Thixotropic fluid – when sheared at a constant rate or stress, the
viscosity will decrease over a period of time.

(e.g.) ketchup, paint



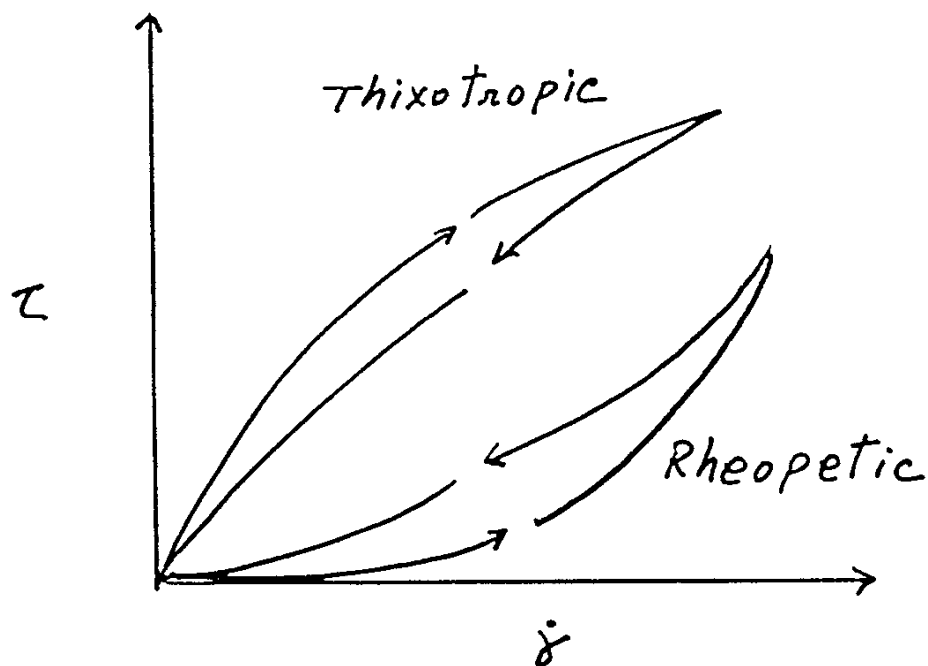


Fig. Flow curves for time-dependent fluids under continuously increasing and then decreasing shear.

- the system is not reversible and that is due to degradation or crosslinking of the polymer when in the viscometer for long periods of time, particularly at elevated temperatures.
- but for chemically stable polymer melts or solutions, the equilibrium viscous properties are time independent.

◦ Polymer Melts and Solutions

(a) at low shear rates, a "lower Newtonian "

region is reached with a so – called zero – shear viscosity (η_0).

(b) In intermediate range of shear rates, the material is pseudoplastic.

(c) at very high shear rates, "upper Newtonian " region with viscosity η_∞ is attained.

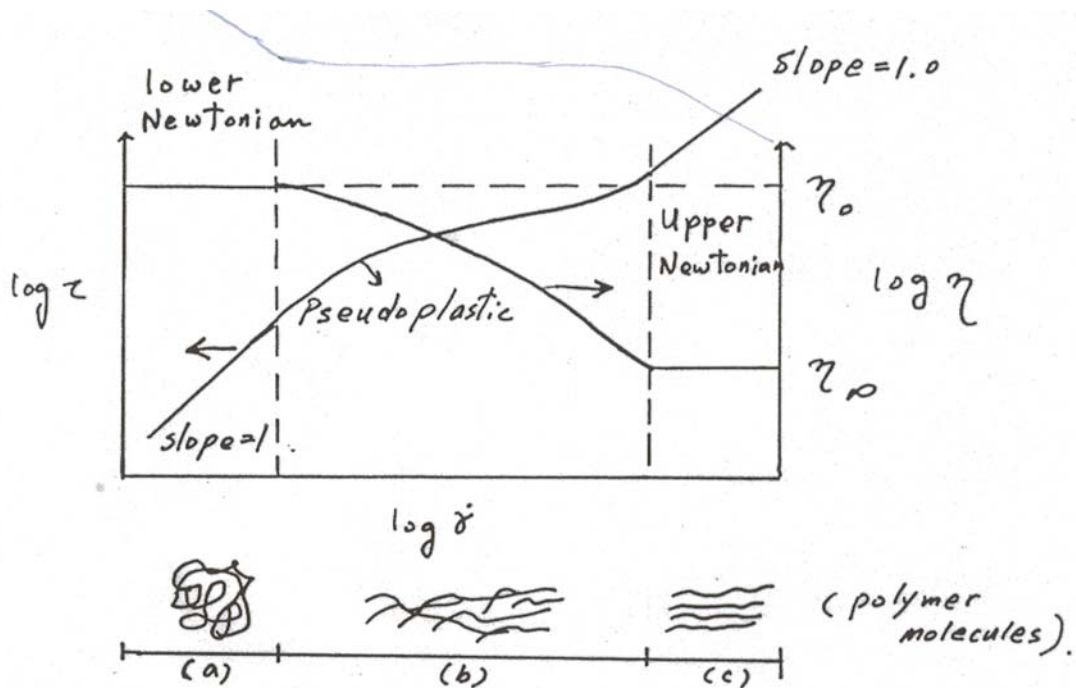


Fig. Generalized flow properties for polymer melts and solutions

- (a) The molecules are in their most random and highly entangled state, and have their greatest resistance to slippage(flow).
- (b) The molecules begin to unentangle and align in the shear field, reducing their resistance to flow.
- (c) Pretty much completely untangled and aligned, and reach a state of minimum resistance to flow. Sometimes mechanical degradation.

Quantitative representation of flow behavior

- for purely viscos non -Newtonian flow

$$\tau = K(\dot{\gamma})^n \quad (\text{power law})$$

where K =consistency (depend on n)
 n =flow index

$$\tau = K(\dot{\gamma})^n \quad (\dot{\gamma})^n \quad \text{dimension} \quad :$$

$$\tau = K \left| \dot{\gamma} \right|^{n-1} \dot{\gamma}$$

(K has the usual viscosity units)

when $n=1$: Newton's law

$n < 1$: Pseudoplastic fluid

$n > 1$: Dilatant fluid

- Melt flow in screw extruder channel

$$10 < \dot{\gamma} < 10^2$$

- Melt flow in injection molding

$$10^2 < \dot{\gamma} < 10^3$$

- n : PE 0.3~0.6
 PP 0.3~0.4
 PVC 0.2~0.5
 Nylon 0.6~0.9

(ex) Determine the equation relating viscosity to shear rate for a power-law fluid.

$$\text{(sol)} \quad \eta \equiv \frac{\tau}{\dot{\gamma}} = \frac{K (\dot{\gamma})^n}{\dot{\gamma}} = K (\dot{\gamma})^{n-1}$$

Temperature dependence of flow properties

$$\eta = f(\tau, T) \quad \text{or} \quad \eta = f'(\dot{\gamma}, T)$$

- zero-shear viscosity, $\eta_0 = Ae^{E/RT}$

E=flow activation energy

- $\eta_0 = Be^{E/RT}$ (τ : constant)
- $\eta_0 = Be^{E/RT}$ ($(\dot{\gamma})$: constant)

A more general expression for the variation of η_0 with temperature:

$$\log \frac{\eta_0(T)}{\eta_0(T_g)} = -\frac{17.44(T - T_g)}{51.6 + (T - T_g)}$$

William-Landell-Ferry (WLF) equation

-good for a wide variety of polymers in the temperature range of T_g to $T_g + 100^\circ\text{C}$

Influence of molecular weight on Flow Properties.

- by empirical equation

$$\eta_0 \propto (\bar{M}_w)^1 \quad \text{for } \bar{M}_w < \bar{M}_{wc}$$

$$\eta_0 \propto (\bar{M}_w)^{3.4} \quad \text{for } \bar{M}_w > \bar{M}_{wc}$$

where \bar{M}_{wc} is a critical molecular weight.

\bar{M}_{wc} depends on the temp and polymer type, but most commercial polymers are well above \bar{M}_{wc} .

$$\bar{M}_{wc} \approx 4000 \sim 50000 (\text{g/mole})$$

-entanglement가 M.W.(500~600 carbon atom)

$$\text{p.s} = \bar{M}_{wc} (40000)$$

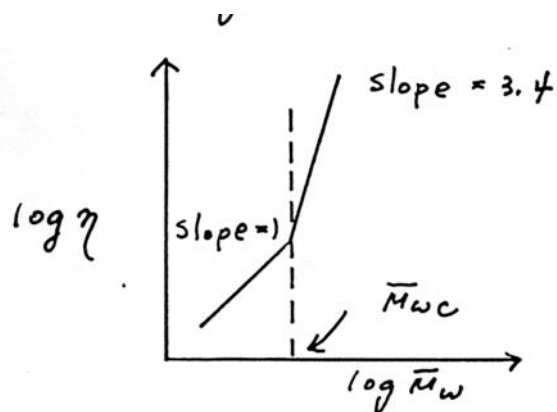
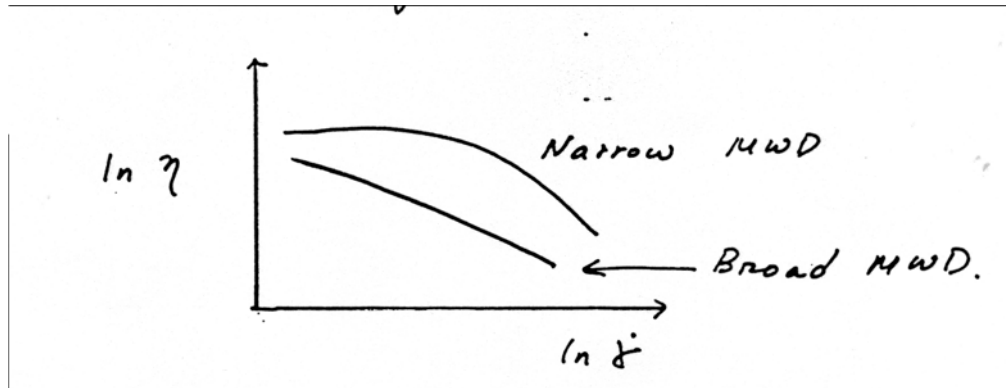


Fig. The effect of molecular weight on viscosity.

MWD(Molecular weight distribution)effects on η



Broad MWD →

chain braching effects on η .

Short branch - η . decrease

Longbranch - η . Increase(entanglement가)