Review

Structure —— Molecular Chain Motion / Polymer Processing ——→ **Properties**

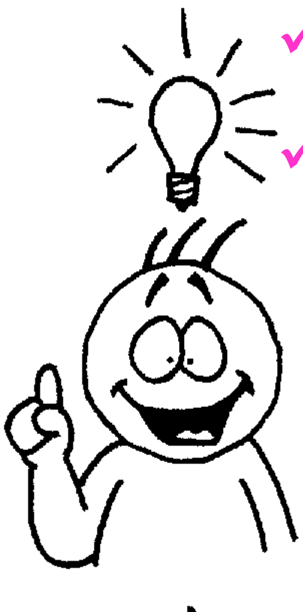
Basic concept

- Segment
- Relaxation and relaxation time
- the free energy of activation
- Free volume
- T_g /T_f/T_d/T_m/T_b/T_s
- Cross-link density
- Simple Shear Deformation
- Simple Extensional Deformation
- Viscous deformation
- Elastic deformation
- Segments motion and polymer flow

- **Non-Newtonian fluid**
- **pseudoplastic fluid**
- ***Viscosity***
- **non- Newtonian index**
- **Shear thinning**
- **Shear viscosity**
- **Elongation viscosity**
- **apparent viscosity η_a**
- **zero-shear-rate viscosity η_0**
- **Melt Index**
- **Weissenberg effect**
- **Unsteady flow**
- **Melt fracture**
- **Die swell**

Relationship

- ✓ Characteristics of molecular chain motion
- ✓ T－ε curves （thermo-mechanical curve）
- ✓ Dependences of T_g on various parameters
- ✓ Effect factors on flow temperatures of polymers
- ✓ Effect factors on shear viscosities of polymer melts



Equations

Temperature Dependence

$$\tau = \tau_0 e^{\Delta E / RT}$$

The specific free volume

$$v_f = K + (\alpha_R + \alpha_G)T$$

$$f_r = f_g + \alpha_f \left(T - T_g \right)$$

0.025

WLF equation

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

if we set $T_r = T_g$, commonly $C_1 = -17.44$ and $C_2 = 51.6K$, then

$$T_g^{'} = T_g + \frac{51.6 \log \alpha_t}{17.44 - \log \alpha_t}$$

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

T_g~T_g+100℃

Gordon —Taylor equation

$$T_g = \frac{W_1 \Delta\alpha_1 T_{g1} + W_2 \Delta\alpha_2 T_{g2}}{W_1 \Delta\alpha_1 + W_2 \Delta\alpha_2}$$

Fox equation:

$$\frac{1}{\mathrm{T}_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}}$$

$$T_g = \chi_A T_{gA} + \chi_B T_{gB}$$

Fox-Flory equation

$$T_g = T_g(\infty) - \frac{K}{\overline{M}_n}$$

$$T_g = T_{g,\infty} - \frac{y\rho N_{Av}\theta}{\alpha_f \overline{Mn}}$$

Time Dependent Effect of Tg

$$\log\nu = a - b/T_g$$

Arrhenius equation

$$\eta = Ae^{\Delta E_\eta / RT}$$

Power Law

$$\sigma_s = k\dot{\gamma}^{n}$$

$$\eta_a = \frac{\sigma(\dot{\gamma}_s)}{\dot{\gamma}} = K\dot{\gamma}^{n-1}$$

Fox-Flory

$$\overline{M_w} > M_c \qquad \eta_0 = k_1 \overline{M_w}^{3.4}$$

$$\overline{M_w} < M_c \qquad \eta_0 = k_2 \overline{M_w}^{1.0-1.5}$$

$$\log(MI) = A - B \log \overline{M}$$

Lee, White

$$\ln \eta = \varphi_1 \ln \eta_1 + \varphi_2 \ln \eta_2$$

Alle

$$1/\eta = \varphi_1 / \eta_1 + \varphi_2 / \eta_2$$

First normal-stress difference

$$N_1 = \sigma_{11} - \sigma_{22} = \psi_1(\dot{\gamma})\dot{\gamma}^2$$

Die swell ratio

B＝D/ D$_0$

Measurements

- T_g
- T_m
- T_f
- Shear viscosity

Questions?

1 A polymer sample with the viscosity of 1.0×10^4 poises at 0 ℃ is considered the temperature-viscosity relation is according with WLF equitation, what is the viscosity of the polymer at 25 ℃ if the viscosity at T_g is about 1.0×10^{13} poises.

A new linear amorphous polymer has a T_g of 10 ℃, at 27 ℃it has a melt viscosity of 4×10^8 poises. Estimate its viscosity at 50 ℃.

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

2 A new polymer is reported to soften at 60℃. Describe a very simple experiment to determine whether this softening is a glass transition or a melting point.

Show schematically the results that would be expected from the following experiments with the new polymer of above mentioned if the reported softening temperature is indeed a T_g/T_m.

1) Specific volume as a function of temperature

2) Differential scanning calorimeter

3) Young's modulus as a function of temperature

3 Account for the differences in glass transition temperatures for the following pairs of isometric polymers:

(a) Poly(but-1-ene) and poly(but-2-ene)

(b) Poly(ethylene oxide) and poly(vinyl alcohol)

(c) Poly(methyl acrylate) and poly(vinyl acetate)

(d) poly(ethyl acrylate) and poly(methyl methacrylate)

4 The T_g of a linear polymer with M_n=2500 is 120℃, while for a sample of the same linear polymer with M_n=10,000, T_g is 150℃. On the other hand, a branched product of the same polymer with M_n=6000 has a T_g of 114℃. Determine the average number of branches per chain of the branched polymer.

5 Please give the repeat units of the following materials and arrange them in the probable order of their increasing crystalline melting points or glass transition temperature and justify your answer.

T_g

- **Polypropylene**
- **Poly(vinyl chloride)**
- **Poly(vinylidene chloride)**
- **Polyisobutylene**

T_g

- **Polycarbonate**
- **Polyethylene**
- **Poly(2,6-dimethyl -1,4-phenylene oxide)**
- **Polydimethylsiloxane**

T_g

- **Polyethylene**
- **Polystyrene**
- **Polypropylene**
- **Poly(α-methylstyrene)**
- **Poly(m-methylstyrene)**
- **Poly(o-methylstyrene)**
- **Poly(α-vinyl naphthalene)**

T_m

polycaprolactone

Nylon 6

Nylon 66

Nylon 12

6 What is the T_g of butadiene-styrene copolymer containing 10 vol % styrene?

(T_g Polybutadiene=-80℃, T_g Polystyrene=100℃)

7 Toluene behaves as a plasticizer for polystyrene. Estimate T_g of a polystyrene ample containing 20 vol% toluene.

(T_g Polystyrene=100℃, melting point of toluene=-50℃)

8 What is the T_g of polystyrene of M_n=3000?
（K=2×105 T_g Polystyrene=100℃

9 **Monomers A and B are copolymerized with the following results:**

Wt. Fraction A in polymer	T_g/ ℃
1.000	108.0
0.850	75.0
0.260	28.0

If B forms a copolymer with equal weights of B and C, and the same K applied, that T_g can be expected? (The T_g of C is -37.0 ℃)

10 Please draw out the T –Deformation curves of PS with different molecular weights.

1 M_n=360 g/mol
2 M_n=400 g/mol
3 M_n= 500 g/mol
4 M_n= 1140 g/mol
5 M_n= 3000 g/mol
6 M_n= 1.2×10^4 g/mol
7 M_n= 5.5×10^4 g/mol
8 M_n= 6.3×10^5 g/mol

11 As we all known, the activation energy for viscous flow of PE and PIB is 23.3kJ/mol and 36.9 kJ/mol respectively, then at which temperature their viscosities will be the half of their values at 166.7 ℃.

12 What is the melting point of a copolymer of ethylene and propylene with 90 mol% ethylene?

$\triangle H_m$ (PE)=7.8×10^{3}J/mol

$$\frac{1}{T_m} = \frac{1}{T_m^o} - \frac{R}{\Delta H_m} \ln x$$

13 The polyester, polycaprolatone and poly(ethylene terephthalate), have T_g value of -60℃ and +60℃ and T_m value of 60℃ and 250 ℃, respectively. Which of the two polymers would be more suitable for a study of the effect of the degree crystallinity on biodegradability at 30 ℃ ?

14 A new atactic polymer of the type ($CH_2CH_X)_n$ has a T_m of 80℃, what is its T_g likely to be?

Di-n-ethylhexyl phthalate(DEHP) and related compounds are commonly used to plasticize poly(viyl chloride)(PVC) to produce the pliable material genercally referred to as "vinyl." a good plasticizer is miscible with the polymer in question, does not crystallize itself, ad has a very low vapor pressure. What fraction of DEHP should be added to PVC to bring T_g down below room temperature(300K), given that Tg for DEHP is about -86℃.

(Tg PVC: 360K)

(0. 22)