Aalto University
School of Chemical
Technology

CHEM-E2130 Polymer Properties

Exam 13.12.2016

1. a) Die swell and melt fracture (spiraling or 'sharkskin' effect) are two phenomena which can occur during polymer processing. For each of these phenomena, explain:
   i) What causes this behaviour
   ii) How you can prevent/reduce the likelihood of their occurrence

   b) You have a single-layer polymer film which is being used as a gas-barrier. If you wish to **reduce/slow down** permeation, what are **three** things you could do to the polymer structure and/or morphology? You are not allowed to add additional polymer layers.

   c) i) List **three** property changes that can be utilised to determine the number average molecular weight

   ii) If you wish to determine the number average molecular weight of a polymer which is insoluble in most solvents, what technique(s) could you use? What information must you know about the polymer in order to use this technique?

   d) Polymers generally have three geometric isomers (tacticities)
   i) Name these three tacticities
   ii) List which ones are usually semi-crystalline and which are usually amorphous
   iii) Blends of two and sometime three different tacticities are common; what benefit does this have on polymer properties?

2. a) If you had access to the following characterization methods but were only allowed to use **two** of the methods, which would you use when asked to determine the **chemical structure** of a thermoplastic polymer? You can choose from FTIR, UV, GPC, DSC, TGA, NMR and SEM. In your reasoning, explain briefly;
   - The operating principle of the methods
   - What data you can obtain from it
   - Why you chose the method

b) From the following thermomechanical/rheological techniques (stress-strain, creep-recovery, DMA, rheometry) state which technique(s) you could use in the following scenarios to determine:

i) The glass transition of a polymer DMA, rheometry

ii) Whether a thermoset polymer is completely cured (crosslinked) DMA

iii) How stiff a polymer is Stress strain / creep recovery

iv) The temperature at which a polymer can be processed

3. What is optimal **operating temperature range** (that is, the temperature at which you would use the polymer) for;

- a semi-crystalline polymer
- amorphous thermoplastic polymer
- elastomer (rubber)
- thermoset

4. Polymers A and B are monodisperse polystyrenes. The molecular weight of Polymer A is three times the molecular weight of polymer B. Polymer C is polydisperse PS with M_w=2.0×10^5 g/mol. A mixture containing 25g of polymer A, 50g of polymer B and 25g of polymer C was measured with light scattering (↳ Mw), and molecular weight obtained was 112500 g/mol. With osmotic pressure (↳ Mn), the molecular weight was determined to be 60000 g/mol. Estimate the number average molecular weight M_n of the polymer C.

5. There is a novel polymer available for the production line with the following properties: melt viscosity at 140 °C is 1×10^5 Pa×s, glass transition temperature 110 °C but some decomposition starts at 160 °C. The production line is tailored for polymer viscosity 2×10^2 Pa×s running at 160 °C.

a) What would the processing temperature have to be for the novel polymer grade in order to have viscosity in the range appropriate for the production line?

b) What could be done to increase the decomposition temperature of the polymer? Don't worry about any effects on processing or material properties.

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EQUATIONS

$n = \frac{m}{M}$ $c = \frac{n}{V}$ $\rho = \frac{m}{V}$ $V_m = \frac{V}{n} = \frac{M}{\rho}$ $pV = nRT$ $k = Ae^{-\frac{E}{RT}}$

$\bar{M}_n = M_0 \bar{X}_n$ $p = 1 - \frac{[M]}{[M]_0}$ $\sigma = \frac{F}{A}$ $\varepsilon(t) = \frac{\Delta l}{l_0} = J(t) \times \sigma$ $Q = \frac{P \times A \times t \times \Delta p}{l}$

Molecular weight:

number of molecules ↓ ↙ molecular weight

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum n_i} \qquad \bar{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \qquad PD = \frac{\bar{M}_w}{\bar{M}_n}$$

$\bar{M}_n = M_0 \times \bar{X}_n$

Viscosity:

$$\eta_r = \frac{\eta}{\eta_0} \approx \frac{t}{t_0} \qquad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \approx \frac{t - t_0}{t_0} \qquad \eta_{red} = \frac{\eta_{sp}}{c} \qquad \eta_{inh} = \frac{\ln \eta_r}{c} \qquad [\eta] = \lim_{c \to 0}\left(\frac{\eta_{sp}}{c}\right)$$

$[\eta] = k \times M_v^{\alpha}$ (Mark-Houwink)

$\eta = k \times \exp\left(\frac{E}{RT}\right)$ (Arrhenius) $T_{g,oligomer} = T_g^{\infty} - \frac{K}{\bar{M}_n}$ (Fox-Flory)

$\eta_0 = k \times Z_w^{3.4}$ $\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$ (Fox)

$\log \frac{\eta}{\eta_{T_g}} = \frac{-C_1 \times (T - T_g)}{C_2 + (T - T_g)}$ (Williams-Landell-Ferry / WLF)

Reference temperature $T_s = T_g$	Reference temperature T_s
$C_1 = 17.44$ and $C_2 = 51.6$	$C_1 = 8.86$ and $C_2 = 101.6$

Solubility:

$$\Delta G_M = \Delta H_M - T\Delta S_M = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2)$$

$$\Delta G_M = kT\left(\frac{V}{V_r} v_1 v_2 \chi_1 \left(1 - \frac{2}{z}\right) + N_c \left(v_1 \ln v_1 + v_2 \ln v_2\right)\right) \qquad \chi_1 = \frac{V_{m,1}}{RT}(\delta_1 - \delta_2)^2$$

Constants:

$R = 8.3145$ J/(K mol) $N_A = 6.022 \times 10^{23}$ mol^{-1} $g = 9.80665$ m/s^2

0 °C = 273.15 K 1 bar = 10^5 Pa

Molar masses (g/mol):

H 1.008	C 12.011	N 14.007	O 15.999
Al 26.982	Cl 35.453	Ti 47.867	Zr 91.224