

A calculator is permitted for the exam

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 could you use? What information must you know about the polymer in order to use this technique?

- d) i) You perform a DSC experiment on an amorphous polymer, but don't see a melting temperature curve. Why?

ii) What is the difference between heterogeneous and homogeneous nucleation?

- e) 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 whether a thermoplastic polymer

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contained any **aromatic (phenyl) rings in its structure**? 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 — *material properties*
- Why you chose the method — *data reference*

b) From the following thermal techniques (DSC and TGA), state which technique(s) you could use in the following scenarios to determine:

- The degradation temperature of a polymer
- Whether a thermoset polymer is completely cured (crosslinked)
- Whether a sample is a homopolymer or a blend of two polymers
- The crystallinity of a polymer

3. A Polypropylene (PP) rectangular rod attached to the ceiling (length 200 mm, width 25.0 mm, thickness 3.0 mm) is loaded with 30 kg's. How much will the polymer creep in two minutes when the creep compliance $J(t)$ follows the equation (t is time in minutes)?

$$J(t) = 1.5 - \exp(-t/6\text{min}) \text{ GPa}^{-1} \quad (1)$$

$$\epsilon(t) = J(t) \times \sigma \quad (2)$$

$$\sigma = \frac{F}{A} \quad (3)$$

4. Zero viscosity of a linear polyethylene (PE) was determined to be 676 000 Pa·s at 190°C. For polyethylene the constants for comparison of M_w and zero viscosity are $k = 3.4 \times 10^{-15}$ Pas and $\alpha = 3.5$. The temperature dependence of the viscosity of PE in melt can be estimated with an Arrhenius-type equation and the activation energy for HDPE is 27 kJ/mol.

- What is the molecular weight M_w of PE?
- How much should the temperature be altered in order to reduce the viscosity by half?

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EQUATIONS

$$n = \frac{m}{M} \quad c = \frac{n}{V} \quad \rho = \frac{m}{V}$$

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

$$\bar{M}_n = M_0 \bar{X}_n \quad p = 1 - \frac{[M]}{[M]_0}$$

$$\sigma = \frac{F}{A} \quad \varepsilon(t) = \frac{\Delta l}{l_0} = J(t) \times \sigma \quad Q = \frac{P \times A \times t \times \Delta p}{l}$$

Molecular weight:

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum n_i}$$

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

$$PD = \frac{\bar{M}_w}{\bar{M}_n}$$

Viscosity:

$$\eta_r = \frac{\eta}{\eta_0} \approx \frac{t}{t_0} \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \approx \frac{t - t_0}{t_0}$$

$$\eta_{red} = \frac{\eta_{sp}}{c} \quad \eta_{inh} = \frac{\ln \eta_r}{c} \quad [\eta] = \lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c} \right)$$

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

$$\eta = k \times \exp \left(\frac{E}{RT} \right) \text{ (Arrhenius)}$$

$$\eta_0 = k \times Z_w^{3.4}$$

$$T_{g,oligomer} = T_g^\infty - \frac{K}{M_n} \text{ (Fox-Flory)}$$

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \text{ (Fox)}$$

$$\log \frac{\eta}{\eta_{T_g}} = \frac{-C_1 \times (T - T_g)}{C_2 + (T - T_g)}$$

(Williams-Landell-Ferry / WLF)

$$\text{Reference temperature } T_s = T_g$$

$$C_1 = 17.44 \text{ and } C_2 = 51.6$$

$$\text{Reference temperature } T_s$$

$$C_1 = 8.86 \text{ and } C_2 = 101.6$$

Solubility:

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

$$\Delta G_M = kT \left(\frac{V}{V_r} v_1 v_2 \chi_1 \left(1 - \frac{2}{z} \right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) \right)$$

$$\chi_1 = \frac{V_{m,1}}{RT} (\delta_1 - \delta_2)^2$$

Constants:

$$R = 8.3145 \text{ J/(K mol)}$$

$$0^\circ \text{C} = 273.15 \text{ K}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$g = 9.80665 \text{ m/s}^2$$

Molar masses (g/mol):

$$\text{H } 1.008$$

$$\text{C } 12.011$$

$$\text{N } 14.007$$

$$\text{O } 15.999$$

$$\text{Al } 26.982$$

$$\text{Cl } 35.453$$

$$\text{Ti } 47.867$$

$$\text{Zr } 91.224$$