Aalto University
School of Chemical
Technology

CHEM-E2130 Polymer Properties

Exam 15.12.2016

1. a) Describe two types of degradation which polymers can experience, and what can be done to prevent or reduce the effects of degradation.

   b) The viscosity of the polymer you are processing is too low, but you cannot increase the processing temperature since it would start to degrade the polymer. What are three things you can do to increase the polymer's viscosity? (Don't worry about the influence on material properties, just mention how the viscosity could be increased).

   c) 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?

   d) What action could you take in order to:

   i) Increase the thermal stability of a polymer (prevent thermal degradation)

   ii) Increase the ductility/elongation of a brittle polymer

   iii) Increase the strength of a weak polymer

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 contained any **ceramic filler**? 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

3. Define the following terms:
   - Glass transition temperature
   - Melting temperature
   - Homogenous nucleation
   - Heterogeneous nucleation

4. A sample of polystyrene is composed of a series of fractions of different sized molecules
   a) Calculate the number average and weight average molecular weights of this sample as well as the PDI.
   b) How would adding styrene oligomer change the average molecular weights? The added amount is 5 %wt of polymer mass and M=1000g/mol.

Table 1. PS fractions.

Fraction	weight fraction	Molecular weight [g/mol]
A	0.130	11000
B	0.300	14000
C	0.400	17000
D	0.170	21000

5. Poly(vinyl alcohol) film (thickness 0.20 mm) is laminated in between two LDPE films (thickness of each film 0.2 mm). The oxygen transfer coefficient for LDPE is 2.2×10^{-13} (cm^3(STP)×cm)/(cm^2×s×Pa) and for PVOH 6.65×10^{-16} cm^3(STP)×cm)/(cm^2×s×Pa). Atmospheric pressure is 101 kPa.
   a) What is the oxygen transfer coefficient for the laminate at 25 °C?
   b) A product is packed in this laminate material. The gas volume of the package is 20 cm^3 and surface area is 250 cm^2. How long is shelf life of the product when the oxygen concentration in the packet must not exceed 1.0 mol%? Oxygen concentration is 0.0 mol% just after packaging.
   c) What would be the shelf life of a product packed in similar LDPE packaging at room temperature?

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EQUATIONS

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

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

Molecular weight:

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

Viscosity:

$$\eta_r=\frac{\eta}{\eta_0}\approx\frac{t}{t_0} \qquad \eta_{sp}=\frac{\eta-\eta_0}{\eta_0}\approx\frac{t-t_0}{t_0} \qquad \eta_{red}=\frac{\eta_{sp}}{c} \qquad \eta_{inh}=\frac{\ln\eta_r}{c} \qquad [\eta]=\lim_{c\to0}\left(\frac{\eta_{sp}}{c}\right)$$

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

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

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

$$\Delta G_M=\Delta H_M-T\Delta S_M=kT(N_1\ln v_1+N_2\ln v_2+\chi_1N_1v_2)$$

$$\Delta G_M=kT\left(\frac{V}{V_r}v_1v_2\chi_1\left(1-\frac{2}{z}\right)+N_c\left(v_1\ln v_1+v_2\ln v_2\right)\right) \qquad \chi_1=\frac{V_{m,1}}{RT}(\delta_1-\delta_2)^2$$

Constants:

$R = 8.3145$ J/(K mol) $\qquad N_A = 6.022\times10^{23}$ mol^{-1} $\qquad g = 9.80665$ m/s^2
0 °C = 273.15 K $\qquad$ 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