National Examinations December 2010

98-Met-B9: Polymers and Fibre-Reinforced Polymers

3 hours duration

Notes:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.

2. Candidates may use one of two calculators, the Casio or Sharp approved models. This is a closed book examination.

3. Any five (5) questions constitute a complete paper (100 marks total). Only the first five questions as they appear in your answer book will be marked.

4. Each question is of equal value.

5. All lettered parts **(a), (b)**... and numbered sub-parts [i], [ii]... of the five selected questions must be answered. Do use all the available time to answer particularly the descriptive questions as fully as possible, to show what you know.

Question 1 (20 marks)

(a) An ideal rubber, made from isoprene (C_5H_8), has shear modulus $G = 200$ kPa at 25°C. [i] With $k = 1.38 \times 10^{-23}$ J/K, theory gives $G = NkT$. Briefly state the meaning of N and find the density of the rubber, if the average number of isoprene units between cross-linking points is 170. (Atomic weights in g/mol: H 1.0, C 12.0; $N_0 = 6.02 \times 10^{23}$ mol^{-1}.) [ii] For a sample of constant volume V deformed by extension ratios λ_x, λ_y, λ_z in three perpendicular directions, $W = \frac{1}{2}VG(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$. Briefly state the meaning of W and comment on the assumptions made in deriving this equation for W. [iii] A cylindrical disk (similar to a puck used in ice hockey) is made from this rubber. The disk is compressed by forces f_x on its circular faces so as to decrease its thickness L by an elongation ratio λ, and to increase its diameter, with V remaining constant. How does W depend on the one variable λ? [iv] A disk of this rubber has initial diameter 100 mm and initial thickness 25.0 mm. The disk is compressed so as to reduce its thickness by 5.00 mm. What force f_x is needed? Here $f_x = (dW/d\lambda)(d\lambda/dL)$. **(12 marks)**

(b) [i] What is the most widely used reinforcement for rubber, and why is it effective? What processes occur in real rubber, ignored in the ideal theory of part **(a)**, that influence stress-strain curves for loading and unloading? [ii] How can rubber and other polymers be protected against thermal and oxidative degradation? **(8 marks)**

Question 2 (20 marks)

(a) At 25°C, amorphous isotactic polypropylene (PP) has a density of 854 kg/m^3. [i] Using diagrams where appropriate, briefly define or explain the meaning of: "amorphous", "isotactic", and "polypropylene". [ii] Isotactic PP can also form crystals, which have a density of 946 kg/m^3 at 25°C. In a molding of PP, the fraction by mass that is crystalline is $x = 0.60$. What is its density? [iii] A thin section of PP with $x = 0.60$ is observed with the optical (light) microscope, between crossed polarizers. What is seen, and what structural features account for the observations? **(6 marks)**

(b) Reaction of ethylene glycol HO–C_2H_4–OH (molar mass 62 g/mol) with terephthalic acid HOOC–C_6H_4–COOH (molar mass 166 g/mol) yields poly(ethylene terephthalate) (PET). [i] What is the repeating unit in PET? What is the by-product of the reaction? [ii] A reaction mixture initially contains 1001 mol of ethylene glycol and 1000 mol of terephthalic acid. Reaction continues until all of the limiting reacting group is completely used up, with every polymer molecule terminated by the excess reacting group. What are the amounts in moles, and masses, of polymer and of by-product present? [iii] Find a molecular weight for this polymer, and state what kind of molecular weight it is, giving a reason. [iv] Name another kind of molecular weight, and find it for this polymer or tell why it cannot be found. **(8 marks)**

(c) [i] There are two categories of polymers, PP being in one and PET in the other. What are these categories? Name one other polymer from each of these categories, that is used in engineering applications, having a higher price than commodity plastics, and show its chemical structure. [ii] For the four polymers, PP, PET, and the two of part [i], name a product or article that would be appropriately made from that polymer, and state what processing or forming operation would be used to make that product or article. **(6 marks)**

Question 3 (20 marks)

(a) Think of an engineering design familiar to you from your reading or from your engineering work or from an undergraduate design project, that involves a polymer or fibre-reinforced polymer. [i] What were its purpose, its requirements and constraints? Mention numerical values if possible. [ii] What polymer or fibre-reinforced polymer was selected for this design, and why? Give details of important property requirements. [iii] What method of processing was chosen, and what advantage did it have over alternatives? [iv] What was necessary to prevent premature failure in use? [v] What plans for disposal at the end of the useful lifetime were made? **(10 marks)**

(b) A thermosetting polymer resin is reinforced with 55% by volume of continuous stiff fibres, all aligned in one direction. Mechanical testing of the composite shows that its tensile strength parallel to the fibres $\sigma_1^* = 950$ MPa, its tensile strength transverse to the fibres $\sigma_2^* = 30.0$ MPa, and its shear strength parallel to the fibres $\tau_{12}^* = 60.0$ MPa. Here the 1 direction is parallel to the fibres and the 2 direction is perpendicular to them. [i] Choose <u>one</u> of these strengths, and briefly explain how it can be calculated from properties of the polymer resin and of the fibres. [ii] A tensile force is applied to the composite in a direction at an angle θ to the fibres (to the 1 direction). Three expressions can be written for the failure strength σ_θ^* in this θ direction: $\sigma_1^*/\cos^2\theta$, or $\tau_{12}^*/\sin\theta\cos\theta$, or $\sigma_2^*/\sin^2\theta$. To which mode of failure does each of these expressions apply? [iii] A rectangular plate, 450 mm × 600 mm × 4.00 mm, is cut from this composite with the fibres aligned along the diagonal of the plate. A tensile force is applied to the plate parallel to 600 mm side. At what force will the plate fail, <u>and</u> what is the mode of failure? **(10 marks)**

Question 4 (20 marks)

(a) If a torque Γ is applied to a thin-walled tube which is clamped at one end, the tube twists with the other end rotating through an angle θ given by $\theta = (l/2\pi r^3 s)\Gamma J$, where l, r, and s are respectively the length, outer radius, and wall thickness of the tube. For polymers J depends on the time t elapsed after the torque is first applied. J can be modeled as a function of t by $J(t) = J_R - (J_R - J_U)\exp(-t/\tau_\sigma)$. [i] What is this behavior of a polymer called, and what are the names given to $J(t)$, J_R, and J_U? [ii] A polyvinyl chloride pipe (or tube) has outer diameter 80.0 mm and inner diameter 76.0 mm. A torque Γ = 15.0 N m is applied to a section of this pipe 1.20 m in length. Immediately after application of the torque, the angle θ of twist is 1.5°. Later, at t = 30 minutes, θ = 5.0°; at t = 12 hours, θ =12.0°; and at t = 1 week, θ =12.0°. What was the twist at t = 10 minutes? **(10 marks)**

(b) The relationships of part **(a)** only apply to small deformations. [i] Sketch a tensile stress-strain curve continuing to large deformations for a ductile polymer such as polyethylene (PE). What happens in the tensile specimen as it is stretched, visibly, and at the microscopic level? Identify the yield stress σ_y on the stress-strain curve. [ii] For a brittle polymer, crazes or cracks influence failure. Under what conditions will a craze or crack grow? What environments make crazing worse? What can be added to a brittle polymer to toughen it, and why is this addition effective? [iii] If a polymer is reinforced with short (discontinuous) fibres, in what ways can it fail? Discuss how the strength of such a reinforced polymer can be increased. **(10 marks)**

Question 5 (20 marks)

(a) Values of the specific volume v and enthalpy H of amorphous polystyrene (PS) are tabulated for eight temperatures in °C.

Temp. °C	0	20	40	60	80	100	120	140
v cm^3/kg	945.7	951.0	956.4	961.7	967.1	972.4	983.4	994.4
H kJ/kg	157	180	205	231	260	291	328	367

[i] How do the volume coefficient of expansion and specific heat capacity c_p depend on temperature? [ii] What can be learned about the behavior and properties of PS from the temperature dependence of volume coefficient of expansion and c_p? Comment on molecular motions, mechanical properties, and any other aspects of interest. [iii] A cylindrical rod of PS has length 280 mm and diameter 18.0 mm at 15°C. It gains 6.00 kJ of heat. By how much does its length extend? [iv] How can the thermal conductivity of PS be decreased? **(10 marks)**

(b) At temperatures high enough to melt them, or in solution, polymers flow under an applied stress. [i] Define shear flow. How do the flow properties of Newtonian and non-Newtonian fluids differ? Suggest an equation to characterize non-Newtonian flow, and comment on its limitations. What experiment could be used to find the parameters in this equation, and how are the results of the experiment analyzed? [ii] How does elongational flow differ from shear flow? In what processes does elongational flow occur? What quantities are important in calculations for elongational flow, and how are they related? **(10 marks)**

Question 6 (20 marks)

(a) A fluid flows with volumetric flow rate Q through a cylindrical tube of radius R and length ΔL under a pressure drop ΔP. [i] Equations for shear rate and stress are $\dot{\gamma} = 4Q/\pi R^3$ and $\tau = \frac{1}{2} R\Delta P/\Delta L$. For <u>both</u> these equations, state what kinds of fluid they are valid for, <u>and</u> where in the tube they are valid. [ii] In the melt flow index test (ASTM D1238), molten polymer is forced out of a barrel of diameter 9.550 mm, by gravity acting on a piston of mass 2.16 kg that fits closely in the barrel. The polymer flows out of the barrel through a die (tube) of diameter 2.095 mm and length 8.000 mm. In a test of polyethylene (PE) at 190°C, 7.40 g of PE flows out of the die in 10.0 minutes. At 190°C the density of PE is 761 kg/m^3. Find the melt flow index (MFI) of this PE, <u>and</u> estimate the viscosity of this PE at 190°C.
[iii] Explain why this viscosity value is unlikely to be accurate, and discuss ways to obtain better viscosity values, using equations where appropriate.
[iv] If the viscosity value is inaccurate, why is the melt flow index test used?
(10 marks)

(b) When a polymer is cooled from the melt down to a lower temperature, it becomes viscoelastic. [i] What viscoelastic behaviors are observed when strain is constant, and when stress is constant? When are these behaviors desirable and undesirable in applications? Describe a model to represent viscoelastic behavior, and show how it responds to applied strain or stress. [ii] How do strain and stress depend on time in a determination of dynamic viscoelastic properties, characterized by the complex modulus and the damping? State the equations relating these quantities. Discuss how the dynamic properties typically depend on temperature. **(10 marks)**

Question 7 (20 marks)

(a) [i], [ii], [iii]: For <u>three</u> different processing methods used for forming polymers or fibre-reinforced polymers, answer the following questions: Name the processing method, and sketch a diagram of the equipment used. State what form and qualities the input or feed to the method must have, and what kind of product is best made using the method. Describe how the method operates, and comment on anything else important about it.
(12 marks)

(b) To check the quality of a polycarbonate, a specimen having compact tension (CT) geometry is tested; the specimen has thickness 5.40 mm and an effective width 30.0 mm, with a crack of effective length 7.0 mm. [i] On a sketch of the specimen geometry, indicate where the fracturing force is applied. [ii] In the equation $K_{IC} = Y\bar{\sigma}_F(\pi a)^{1/2}$, what are the meanings of K_{IC}, $\bar{\sigma}_F$, and a? [iii] Here $Y = 6.2$; in general, why does Y appear in the equation, and what is Y a function of? [iv] What force will fracture this CT specimen of polycarbonate, for which $K_{IC} = 2.78$ MPa $m^{1/2}$? **(8 marks)**

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Formula sheet

Characterization of polymers: $\bar{M}_n = W/\Sigma n_i$, $\bar{M}_w = \Sigma w_i M_i / W$.

Crystallization: $x = (v_a - v)/(v_a - v_c)$.

Specific heat capacity: $c_p = dH/dT$.

Thermal conductivity: $dH/dt = -kA\, dT/dL$.

Thermal expansion: $\alpha = (1/L)dL/dT$.

Properties of polymers

rubber: $G = NkT$. $f_x = (dW/d\lambda)(d\lambda/dL)$. $W = \frac{1}{2}VG(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$.

small deformations: $\sigma = \Gamma/2\pi r^2 s$; $l\gamma = r\theta$. $G = E/2(1+\nu)$.

viscoelasticity:

$G(t) = G_R + (G_U - G_R)\exp(-t/\tau_\gamma)$. $J(t) = J_R - (J_R - J_U)\exp(-t/\tau_\sigma)$.

$\gamma^* = \gamma_0 e^{i\omega t}$; $\sigma^* = \sigma_0 e^{i(\omega t + \delta)}$;

$G^* = G' + iG'' = \sigma^*/\gamma^* = 1/(J' - iJ'')$; $\tan\delta = G''/G' = J''/J'$.

Failure mechanisms: $\bar{\sigma} = F/BW$. $K_{IC} = Y\bar{\sigma}_F(\pi a)^{1/2}$.

Polymer processing: $\dot{\gamma} = 4Q/\pi R^3$; $\tau = \frac{1}{2}R\Delta P/\Delta L$.

$\dot{\gamma} = (Q/\pi R^3)(3 + d\log Q/d\log \Delta P)$. $\tau = K\dot{\gamma}^n$.

Fibre-polymer composites

Rule of mixtures e.g. $\rho = \varphi_f \rho_f + (1 - \varphi_f)\rho_m$:

holds for ρ, E_1, $1/E_2$, ν_{12}, $1/G_{12}$, $\alpha_1 E_1$, $\alpha_2 + \alpha_1\nu_{12}$. $\nu_{12}E_2 = \nu_{21}E_1$.

failure: $\sigma_\theta^* = \sigma_1^*/\cos^2\theta$ or $\tau_{12}^*/\sin\theta\cos\theta$ or $\sigma_2^*/\sin^2\theta$.