04-CHEM-B8, POLYMER ENGINEERING

May 2016

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. Property data required to solve a given problem are provided in the problem statement or are available in the recommended texts. If you are unable to locate the required data, do not let this prevent you from solving the rest of the problem. Even in the absence of property data, you still have the opportunity to provide a solution methodology.
3. The examination is an **open book exam.**
4. Candidates may use any **non-communicating** scientific calculator.
5. Regular graph papers will be provided.
6. Each problem is worth **20 points**. **Five problems** constitute a complete paper.
7. **Only the first five** questions as they appear in the answer book will be marked.
8. State all assumptions clearly.

1. A seeded emulsion polymerization of methyl methacrylate (MMA) is carried out in a batch process using sodium persulfate ($Na_2S_2O_8$) at 60 ^oC. Assuming an initiator efficiency of 50%, estimate the number average molecular weight of the polymer formed when the monomer concentration in the particles is 4 kmol/m^3.

<u>DATA</u>:

Propagation rate coefficient of MMA (k_p) = 830 m^3/kmol.s
Volume fraction of particles in the reaction mixture = 0.4
Particle diameter = 80 nm
Density of particles = 1000 kg/m^3
Initiator concentration = 10^{-3} kmol/m^3
Thermal dissociation rate coefficient of initiator (k_d) = 4 x 10^{-3} s^{-1}
Average number of radicals per particle = 0.5
Molecular weight of methyl methacrylate = 100.121 kg/kmol
Avagadro's number = 6.023 x 10^{26} particles/kmol

2. Two polymer fluids are flowing within a tube of inside radius 5 mm. In the central region of the tube (r = 0 to 4 mm), a Newtonian polymer fluid **A** is flowing as a core of fluid. Within the annular region (r = 4 mm to 5 mm), a Power law polymer fluid **B** is flowing in the same direction as polymer fluid A. Assume there is no slip boundary conditions at the tube walls, and stress and velocity continuity across interface of polymer fluids A and B. Given a pressure gradient of 5 x 10^4 Pa per meter along the tube, determine

(a) The maximum velocity within the tube.
(b) The velocity at the interface of polymer fluids A and B.
(c) The volumetric flow rate of the two fluids.

<u>DATA</u>:

Viscosity of fluid A = 10 Pa.s
Zero-shear viscosity of fluid B = 10 Pa.s
Power law index of fluid B = 0.5

3. The osmotic pressure of a polymer solution at 23 °C was measured at several concentrations and following data obtained:

Concentration (g/cm^3)	**Osmotic Pressure** ($dynes/cm^2$)
2×10^{-3}	508
4×10^{-3}	1040
6×10^{-3}	1580
8×10^{-3}	2150
1×10^{-2}	2740

Determine the number-average molecular weight of the polymer and the second virial coefficient of the solution.

4. Polyethylene is most commonly sold as one of three grades; high density (HDPE), low density (LDPE) and linear low density (LLDPE).

(a) [4 points] Briefly explain the main differences in material morphology and their molecular origin.

(b) [4 points] Briefly describe the polymerization mechanisms by which these three grades are commonly produced.

(c) [4 points] HDPE can be produced using heterogeneous or homogeneous catalysts. Briefly explain the main differences in final product.

(d) [4 points] When studying the kinetics of ethylene polymerization using heterogeneous Ziegler-Nata catalysts in a gas-phase reactor, one often observes an increasing rate of polymerization in the initial stages of the process. Briefly explain this rate increase.

(e) [4 points] LDPE is produced industrially in either autoclave or tubular reactors. In both processes, the ethylene conversion is rather limited (~ 20% per pass in autoclave and ~ 40% in tubular reactor). Briefly explain these rather low conversions.

5. Nylon 6,6 is extruded at 285 °C under isothermal conditions in a temperature-controlled chamber, and it is fiber-spun in such a way that length is 400 cm and the draw ratio is 100. The take-up speed is 1000 meters/minute, the polymeric volumetric flow rate is 0.1 cm^3/s, and the die swell diameter is three times the die diameter. Assume that Nylon 6,6 is a Newtonian at the spinning temperature of 285 °C with a viscosity of 250 Pa.s.

(a) [6 points] Calculate the maximum stretching rate of the melt.

(b) [3 points] Compare this stretching rate with shear rate inside the die, if the die diameter is 0.16 cm.

(c) [5 points] Assess the validity of the approximation that V_r is nearly zero.

(d) [6 points] Determine the maximum tensile stress in the melt and the force required to draw melt.

6. Determine the viscosity (η), the steady-state compliance (J_{eq}) and the longest relaxation time (τ) from the following data for a monodisperse polystyrene with M = 60,600 g/mol at 180 °C

Angular Frequency (ω), in rad/s	**Storage or Elastic Modulus (G')**, in Pa	**Viscous or Loss Modulus (G")**, in Pa
57.54	17400	49000
36.31	7590	33100
22.91	3090	21900
14.45	1260	14100
9.12	525	9120
5.75	200	5750
3.63	83.2	3720
2.91	33.1	2900