POLYMERS

Examples Sheet 5

Crystallisation

1 . In an isothermal spherulitic crystallization process the rates of nucleation and radial growth are first order. Prove that, in the early stages, the ratio of the mass of crystallized material, m_c, to the mass of initially molten material, m_o, is given by

$$\frac{\mathbf{m_c}}{\mathbf{m_o}} = \mathbf{z\,t^{4}},$$

where t is the time since crystallization began and z is a composite constant.

Show that this equation applies to the following data for the isothermal crystallization of a certain molten polymer.

t(s) ...	30	60	75	90	105
weight fraction of molten polymer	0.9984	0.9756	0.9405	0.8766	0.7725

Determine the value of the nucleation constant, given that the radial rate of growth of the spherulites has been observed to be 150 /min by optical microscopy. The densities of molten and crystalline polymer are 872 kg/m^3.

Indicate how the theoretical treatment might be modified to allow for the impingement of spherulites at higher degrees of crystallization.

2 . Derive an expression for . The weight fraction of polymer crystallized as a function of time t. Assume spherulite crystallization with no impingement, a constant nucleation rate and a linear growth of the spherulite radius with time.

Show how this expression can be modified by including spherulite impingement to yield an expression of the form:

$$\theta = 1 - \exp(-zt^{p})$$

where z and p are constants.

The following data for θ as a function of time have been obtained for samples of polyethylene terephthalate, crystallized isothermally at three different temperatures. For each temperature, determine the time at which the rate of crystallization was a maximum and also determine the magnitudes of the maximum rates of crystallization. Comment on your results.

Data:

Values of θ as a function of time t and temperature T

T (°C)				Time (s)				

100					0.009	0.042	0.500	0.995
210	0.002	0.041	0.489	0.966				
240				0.005	0.451	0.952		

3. And finally, do **98.3.4 and 99.3.2**