Spherulitic Growth Kinetics in Miscible Blends of Poly(ether ether ketone) and Poly(ether imide)

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Abstract: Growths of poly(ether ether ketone) (PEEK) spherulites from both pure melt and its miscible blends with poly(ether imide) (PEI) have been studied by polarized optical microscopy. The nucleation density of PEEK spherulites was depressed upon blending with PEI, which can be attributed to the reduction in degree of supercooling arising from equilibrium melting point depression. A modified Lauritzen-Hoffman (L-H) theory was adopted to analyze the growth kinetics. Regime III-II transition was observed with the transition temperature decreasing with increasing PEI composition. Assuming free rotations of the virtual bonds in PEEK molecule, the side surface free energy of 12.0 erg/cm² was calculated from the characteristic ratio. The fold surface free energy of 188 erg/cm² and work of chain folding of 12.3 kcal/mol were then obtained from the modified L-H analysis.

Keywords: Poly(ether ether ketone), Poly(ether imide), Blend, Spherulite growth rate, Surface free energy.

Introduction

Poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) are both high performance polymers. PEEK is semicrystalline with a $T_g$ of 145 °C and an equilibrium melting point (M.P.) of 384 °C [1-3]. PEI is an amorphous material with a $T_g$ of 215 °C.

PEEK and PEI formed miscible blends in the melt but liquid-solid phase separation took place below M.P. due to the crystallization of PEEK [3-8]. Blending with PEI served as a method to systematically control the crystallization kinetics of PEEK, as the crystallization rate of PEEK was depressed by blending [4,5]. In this paper, we report a detailed investigation on the spherulite growth kinetics of PEEK in its blends with PEI. The spherulite growth rates of PEEK/PEI are analyzed using a modified Lauritzen-Hoffman (LH) theory. Crystallization regime behavior and molecular parameters such as the fold surface free energy and the work of chain folding deduced from the modified L-H analysis will be critically discussed.

Experimental

PEEK powder was acquired from Imperial Chemical Industries (ICI), Wilton, U.K. The molecular weights are $M_n$=16,800, $M_w$=39,800. Poly (ether imide), PEI, was obtained from General Electric (GE, Ultem 1000). The molecular weights are $M_n$=12,000, $M_w$=30,000.

PEEK/PEI blends were prepared by solution-precipitation from dichloroacetic acid. The concentration of the polymers in the solvent was 4% (w/v). The mixtures were heated with stirring to 150 °C and were held at this temperature until homogeneous solutions were observed. After cooling to room temperature, the solutions were poured into a tenfold excess volume of methanol and water mixture (50/50 (v/v)). The precipitates were filtered, washed with a large amount of water, and then dried in vacuo at 95 °C to constant weight.

Spherulite growth was monitored with a Carl

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Zeiss cross-polarized optical microscopy. The sample under study was first melted on a Thomas Model 40 Micro hot stage at 400 °C for 1 min followed by quickly moving to a Mettler FP2 hot stage equilibrated at the desired crystallization temperature (T_c). Micrographs were taken at intervals for measuring the spherulite radii (R) at various time periods. The growth rate was calculated from the change of spherulite radius with time, dR/dt.

Results and discussion

1. Nucleation density

Figure 1 displays the optical micrographs of PEEK spherulites grown from the pure melt and 75/25 blend. The nucleation density of neat PEEK is high as manifested by the small spherulites. Blending with PEI increases the average spherulite size, suggesting depression of nucleation density upon blending. The average size of spherulites or nucleation density is determined by the competition between the rates of nucleation and subsequent growth of spherulites. Fast nucleation and slow growth rate induce the formation of small spherulites after impingement and thus yields high nucleation density. Reduction in nucleation density suggests that the nucleation rate of PEEK was depressed by a greater extent upon blending than the growth rate.

The difference between the rates of nucleation and growth may be revealed by comparing their respective thermodynamic driving force. For the sake of simplicity, the nucleation is approximated as a homogeneous primary nucleation, the rate of nucleation can then be written as [9]:

$$i = \exp \left( -\frac{-32\sigma^2 \sigma e}{k_BT_c \Delta h_0^0 (T_m^0 - T)^{\alpha}} \right)$$  \hspace{1cm} (1)

where $\sigma$ and $\sigma_e$ are the side and fold surface free energy, respectively, $\Delta h_0^0$ is the bulk enthalpy of melting, $T_m^0$ is the equilibrium M.P., and $(T_m^0 - T)$ = $\Delta T$, i.e., the degree of supercooling. The growth rate in regime III can be written as [10]:

$$G \propto \exp \left( -\frac{-4\sigma^2 \sigma e}{k_BT_c \Delta h_0^0 (T_m^0 - T_c)} \right)$$  \hspace{1cm} (2)

Comparing Eqs.(1) and (2), it can be seen that the primary nucleation rate varies with $\exp[-1/\Delta T^2]$ while the growth rate varies with $\exp[-1/\Delta T]$. This means that the primary nucleation rate is more susceptible to change in degree of supercooling than the growth rate. In other words, a perturbation in degree of supercooling would bring about a greater change in nucleation rate.

At a given T_c, blending may actually lower the degree of supercooling via depression of $T_m^0$. A slight depression in $T_m^0$ is expected to induce a strong depression in nucleation rate due to the amplification by the exponential factor. A simple calculation is performed here to demonstrate the effect of PEI on the rates of nucleation and growth of PEEK. Considering $T_c=250$ °C, the ratios of $i/i_0$ and $G/G_0$ of PEEK/PEI are calculated from Eqs.(1) and (2), where the subscripts 0 and b denote the rates of pure PEEK and PEEK/PEI, respectively. The values of the parameters used in this calculation will be indicated in the later discussion of the growth kinetics. The result indicates that as the equilibrium M.P. of PEEK is depressed by 1 °C due to blending with PEI, $i/i_0 = 0.36$ and $G/G_0 = 0.87$. This means that depression of M.P. by 1 °C would reduce the nucleation rate by 64%, while this M.P. depression reduces the growth rate by only 13%. Depression of equilibrium M.P. by 2 °C decreases the nucleation rate by 87%, whereas the crystal growth rate is only decreased by 25%. This simple calculation demonstrates that dilution by PEI exerted a more pronounced effect in decreasing the nucleation rate of PEEK and hence explains the depression of nucleation density upon blending.

2. Growth regimes

The crystal growth kinetics of homopolymers have been widely analyzed by the Lauritzen-Hoffman (L-H) theory [10]. The crystal growth theory for crystalline/amorphous blends has been formulated with minor modification by taking account of the equilibrium M.P. depression and change of T_c upon blending [11,12]. More rigorous treatments considering the diffusion mechanism associated with crystallization have also been proposed [13,14]. The modification adopted in the present study was proposed by Boon and Azcue [15]. This modification considered the effect of the probability of selecting a crystallizable sequence from the mixture on the free energy of formation of a two-dimensional nucleus. The crystal growth rate is given by [15]:

$$G = G_0 \exp \left( -\frac{U^*}{RT_c} \right) \exp \left[ -\frac{K_e}{T_c(T_m^0 - T_c)} \right] \exp \left\{ -\frac{\lambda \sigma h_0^0}{b_0 \Delta h_0^{0'} (T_m^0 - T_c)} \right\}$$  \hspace{1cm} (3)

where $U^*$ is the activation energy required to transport the chain segments across the solid-liquid