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Crystallisation in miscible blends of PEEK and PEI

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Abstract

The crystallisation of PEEK from miscible blends of PEEK and PEI has been measured and the results analysed in terms of the Avrami equation and the Hoffman and Lauritzen crystallisation theory. The melting of the crystals was analysed in terms of the Hoffman and Weeks theory and it was found that the β values were in excess of unity. The product of the surface free energies was found and discussed in terms of the variation in blend composition.

Keywords: PEEK/PEI blends; Crystallisation; DSC

1. Introduction

The aim in blending different homopolymers is to create new materials with controllable physical properties while attaining a significant reduction in cost. It also offers a systematic way of altering the mechanical and impact properties without chemical modification. In addition, the physical properties can also be altered by crystallisation of one or more of the blend components.

A blend system that has been frequently studied is that of the poly(ether ether ketone), PEEK and poly(ether imide), PEI blend [1,2]. Both are high temperature thermoplastic materials and are widely used as engineering plastics. PEEK is a costly material and consequently is only used in high technology applications such as aerospace materials. In the form of carbon fibre composites such as APC 2, the applications are much more varied, in particular the composites have been used in aircraft wing construction [3]. PEEK exhibits good thermal stability, in that it has a glass transition at 143°C and a crystalline melting point of 330°C. Poly(ether imide), PEI is less expensive but it has become more versatile and is widely used as an amorphous thermoplastic. PEI has a glass transition at 220°C [4].

The process of crystallisation in the blend system containing PEEK and PEI has been investigated previously and the kinetics were found to be strongly dependent on the blend composition. This was ascribed to the miscibility of the blend at all compositions [5]. The growth rate of crystals and the dependence on temperature was described by Turnbull and Fisher [6]

$$g = g_0 \exp\left(-\frac{\Delta E_{\mathrm{act}}}{\mathrm{R}T}\right)\exp\left(-\frac{\Delta fG^*}{\mathrm{R}T}\right) \tag{1}$$

where g_0 is constant, ΔE_{act} is the activation energy of viscous flow and ΔfG^* is the free energy of formation of the critical size nucleus. As the temperature approaches the glass transition, the first term in the above equation is dominant and the rate determining step is the diffusion of chains to the growth face. As the temperature approaches the melting point, the rate determining step is nucleation controlled and the second term becomes dominant. The opposing temperature dependencies of the two exponential terms result in a peak in the plot of growth rate against temperature.

This model was later refined by Hoffman and Lauritzen [7] to describe polymer crystallisation by the introduction of a modified nucleation term. In this modification, three regimes of nucleation are possible, each regime predominating at different temperatures. At temperatures approaching the melting point, each nucleation on the growing crystal surface leads to rapid completion of the growth strip by chain folding prior to the next nucleation event, this is referred to as regime I. At much lower temperatures there is prolific multiple nucleation on the growth surface and this is referred to as regime III. Between these two limits there is competition between chain folding and nucleation, growth in this region is termed regime II.

In this paper, crystallisation half life data previously reported has been analysed in terms of the Avrami and the Hoffman and Lauritzen crystallisation theories. Composite

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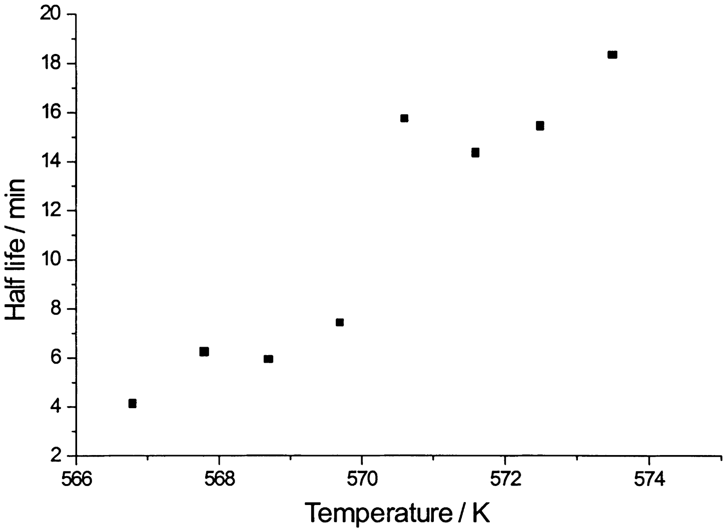

Fig. 1. Variation of half life with crystallisation temperature T_c for blends of PEEK and PEI in the composition range 10–80 wt% PEEK.

growth rates and the product of the surface free energies of the PEEK spherulitic crystals have been found and the effect of blend composition on the crystal free energy is discussed. The melting of the crystals was analysed in terms of the Hoffman and Weeks theory.

2. Experimental

2.1. Materials

A commercial grade of Poly(ether imide), ULTEM 1000, was used as supplied by General Electrics Ltd. The material had a weight average molecular weight of 20 kg/mol. Poly (ether ether ketone), PEEK, grade 450G was supplied by ICI Ltd, it had a weight average molecular weight of 99.2 kg/mol.

2.2. Instruments and apparatus

Blends of both materials were prepared using an APV model MP2000 twin screw extruder. Moulding pellets of PEEK and PEI were dried in a vacuum oven at 160°C for three hours prior to the production of a 50 wt% master batch. Blends containing 2, 5, 10 and 20 wt% PEEK were prepared by dilution of the dried master batch with PEI. The granules were premixed to ensure good dispersal of the components. The extruder was purged with 500 g of PEI and the first 200 g of each blend extruded from the die head were discarded. The barrel temperature was set to 380°C and the flow rate through the extruder was adjusted to maintain a high torque thereby ensuring thorough mixing. The moulding pellets produced from the extruder were subsequently dried prior to compression moulding at 380°C into sheets (150 × 150 × 2 mm). The sheets were quenched into ice/water to prevent crystallisation of the PEEK component.

The crystallisation and melting of the PEEK component from the blends was measured using a Perkin–Elmer differential scanning calorimeter, model DSC 2B which was interfaced to a personal microcomputer. The thermal response of the instrument was calibrated from the enthalpy of fusion of a known mass of indium (99.999% pure). The temperature scale of the calorimeter was calibrated using the melting points of indium, tin and lead. Plots of actual against experimental melting points were linear and used to calibrate the calorimeter temperature directly after correcting for thermal lag. Corrections were made for thermal lag by extrapolation to zero heating rate.

Samples in the form of discs (1 mm thick and 3 mm in diameter) were contained within aluminium pans, and an empty pan was used as a reference. The samples were first heated to 380°C and held at this temperature for 1 min and then quenched in icewater to ensure that the PEEK component was amorphous. Plots of heat capacity against temperature were obtained from the DSC at different heating rates. The glass transition temperatures were determined directly from a plot of heat capacity against temperature using the method outlined by Richardson and Savill [4].

The crystallisation and melting of the PEEK within the blends were also investigated using a Leitz polarised light microscope fitted with a Linkam TR600 hot stage. The hot stage consisted of a furnace which was flushed with nitrogen to create an inert atmosphere around the sample. The temperature was controlled to 0.1°C up to a maximum of 600°C using the Linkam LK600 controller. The temperature was calibrated using the melting point of sodium nitrate. A constant wavelength sodium light source was used to illuminate the sample and the transmitted light intensity was measured with a light dependent resistor. The resistance

Table 1
Variation of half life and mechanistic n value with crystallisation temperature for a 50 wt% blend

T_c/K	$t_{1/2}$/min	$n \pm 0.2$
566.8	4.1	2.31
566.8	4.1	2.31
567.8	6.2	2.00
568.7	5.9	2.23
569.7	7.4	2.14
570.6	15.7	1.97
571.6	14.3	1.87
572.5	15.4	1.79
573.5	18.3	1.92

was measured as a voltage in a bridge circuit and converted to a digital signal by a microcomputer based analogue to digital converter. The signal was displayed as a function of time.

The polarising filters in the microscope were crossed to exclude the light from the detector, so that the formation of birefringent regions in a crystallising polymer sample depolarised the light, thereby resulting in an increase in the transmitted light detected. The light intensity with time plots therefore reflect the development of crystallinity within the sample. This assumption has been shown to be correct by Pratt and Hobbs [8].

Sections, 30 μm thick, were cut from moulded plaques of the blends using a Leitz sledge microtome and placed between two glass coverslips. The sample was melted at 380°C for one minute and then cooled to the isothermal crystallisation temperature. The resulting light intensity with time plots were then used to measure the crystallisation kinetics. The melting points of the crystallised blends were also determined using Hot-Stage Microscopy. The decrease in light intensity was recorded as a function of time and temperature and the melting point was taken as the last trace of crystallinity.

3. Results and Discussion

3.1. Crystallisation of the blends

The technique of DSC was used to analyse the crystallisation kinetics of blend in the composition range 80–40 wt% PEEK. The variation of crystallisation half life with crystallisation temperature for a 50 wt% blend is shown in Fig. 1. The crystallisation isotherms were also analysed in terms of the Avrami equation [13,14,15] which relates the extent of crystallinity, X_t with time t,

$$1 - X_t = \exp(-Zt^n) \qquad (2)$$

where Z is a composite rate constant and n is an integer constant which is diagnostic of the crystallisation mechanism. The mechanistic n values determined for the 50 wt% blend are shown in Table 1. These were in the range 2–2.3 and very different from those observed for PEEK alone which were found to be in the range 3–4. These values of n are consistent with the growth either of homogeneously or heterogeneously nucleated spherulites, but reduced in the case of the blends by the rejection of uncrystallisable PEI. Composite rate constants were calculated from half life, $t_{0.5}$ and the n value data by applying the following relationship,

$$Z = \frac{\ln 2}{t_{0.5}^n} \qquad (3)$$

The variation of the composite rate constant with crystallisation temperature for blends in the composition range 80–40 wt% PEEK is shown in Fig. 2. The temperature dependence of the half lives shown in Fig. 1 and the composite rate constants in Fig. 2 can be explained by the existence of the two competing effects as described by Turnbull and Fisher. Nucleation control close to the melting point and diffusion control as the glass transition temperature is approached. Competition between the two resulting in a minimum in the half life and a maximum in the composite

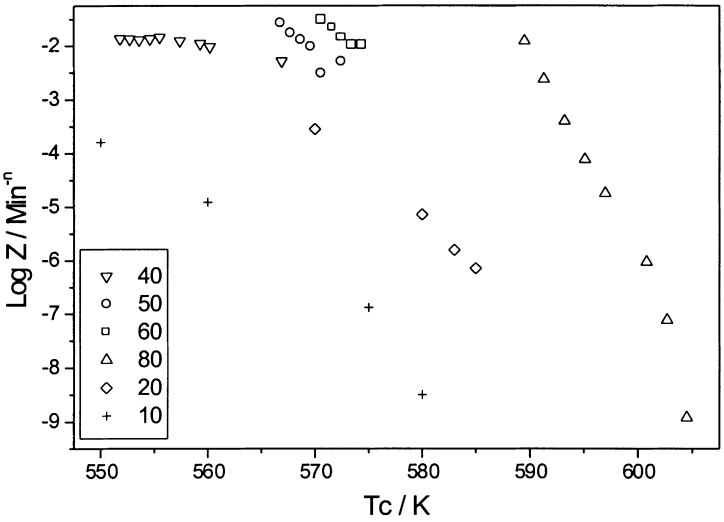

Fig. 2. Variation of composite rate constant with crystallisation temperature T_c for blends of PEEK and PEI in the composition range 10–80 wt% PEEK.

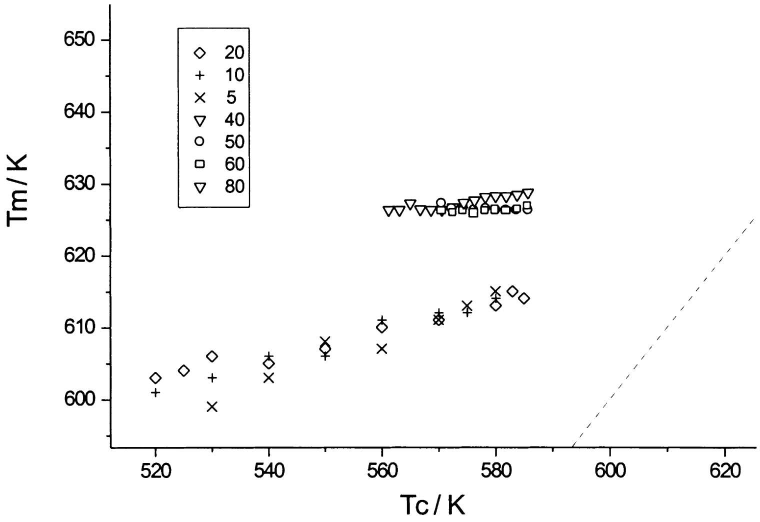

Fig. 3. Variation of melting point Tm with crystallisation temperature T_c for blends of PEEK and PEI in the composition range 5–80 wt% PEEK.

rate at a temperature midway between the glass transition and the melting point.

It can be seen that the rate of crystallisation at constant crystallisation temperature decreases with increasing PEI content, which is the result of the increased melt viscosity of the blends. The greater melt viscosity slows the diffusion of the PEI molecules away from the growth front giving rise to a slower crystallisation rate. Information on the phase morphology of the blends can also be inferred from this evidence. As the crystallisation rate of the blend is markedly slower than that of pure PEEK, it can be assumed that the components mix at the molecular level and large domains of pure PEEK do not exist in the blend.

The use of DSC for the measurement of crystallisation was found to be limited by the blend compositions to above 40 wt% PEEK, because of the reduced rate of heat evolution at longer half lives. For this reason, crystallisation in blends containing 20, 10 and 5 wt% PEEK was investigated using the technique of depolarised light microscopy. The light intensity at time t, was assumed to be a measure of the sample crystallinity. The relative degree of crystallinity, X_t, was then,

$$X_t = \frac{(I_t - I_0)}{(I_f - I_0)} \tag{4}$$

where I_0, I_f are the initial and final relative intensities and I_t is the relative intensity at time t. These crystallisation isotherms were also analysed in terms of the Avrami equation and composite rate constants were determined. The variation of the rate constants with crystallisation temperature is also shown in Fig. 2. As in the case of blends in the range 40–80 wt% PEEK, a maximum rate occurs which decreases with decreasing PEEK content. This is consistent with increasing melt viscosity as the level of PEEK decreases.

3.2. Determination of the equilibrium melting point

The equilibrium melting point of the PEEK component was investigated by applying the melting theory proposed by Hoffman and Weeks [9]. The melting points of the crystals formed by isothermal crystallisation were plotted against the crystallisation temperature, the resulting line was described by,

$$T_m = T_m^0\left(1 - \frac{1}{2\beta}\right) + \frac{T_c}{2\beta} \tag{5}$$

where $\beta = (\sigma_e l/\sigma l_e)$ and σ is the lateral surface free energy, l is the lamellae thickness and the subscript e refers to equilibrium conditions, i.e. no annealing. For crystallisation under equilibrium conditions β is equal to 1, which corresponds to a slope of 0.5 in the above equation. The equilibrium melting point was determined by the intersection of the above line with the $T_m = T_c$ line, when $\beta = 1$. The Hoffman and Weeks plots for the blend are shown in Fig. 3.

The β values calculated from the slopes of the Hoffman–Weeks plots for the blends were in excess of 1 indicating that melting of the thin crystals occurred during the warming process, this was then followed by recrystallisation on warming to the melting point. Only the homopolymer PEEK exhibited a β value that tended to 1 and the equilibrium melting point was found to be 663 K [10]. This value was used for all subsequent calculations involving the equilibrium melting point. It can also be seen from Fig. 3 that the melting temperature at a given crystallisation temperature decreases with increasing PEI content, this is consistent with PEI acting as a diluent which depresses the melting point.

3.3. Calculation of the crystal surface free energies

The relationship between the linear growth rate and the supercooling, ΔT, has been described by Hoffman and

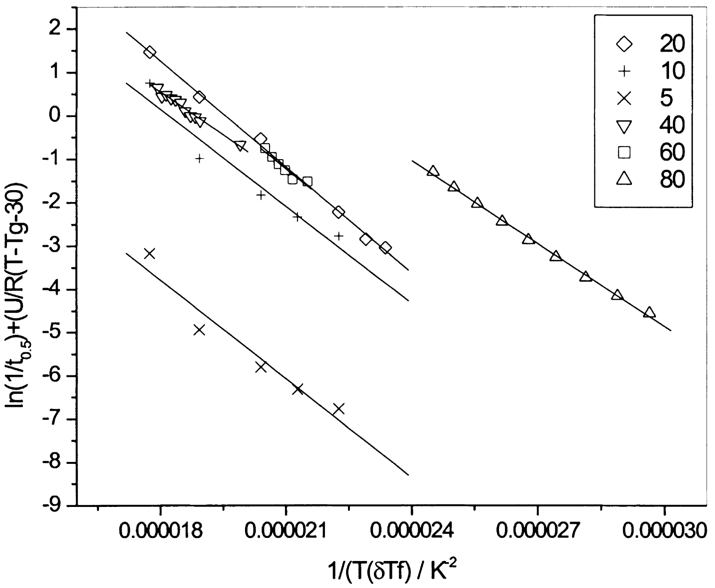

Fig. 4. A Hoffman–Lauritzen plot for blends of PEEK and PEI on the composition range 5–80 wt% PEEK.

Lauritzen as,

$$G_r = G_0 \exp\left(-\frac{U^*/\mathrm{R}}{T - T_\infty}\right)\exp\left(\frac{Kg}{T\Delta Tf}\right) \tag{6}$$

The first term describes the increased melt viscosity and reduced molecular mobility as the temperature approaches the equilibrium temperature T_∞ where molecular motion due to viscous flow ceases. This temperature is assumed to be 30 K below the glass transition temperature. U^* is the activation energy for segmental jumps that Hoffman has assigned a value of 6300 J/mol.

The second term accounts for the effect of primary nucleation on the crystallisation and is dominant at low degrees of supercooling, $\Delta T = T_m^0 - T$, where T_m^0 is the equilibrium melting point. The parameter $f = 2T/(T + T_m^0)$ is a correction factor which accounts for the change in the latent heat of fusion that occurs with reduced crystallisation temperatures.

The nucleation constant Kg is dependent on the surface free energy of the crystals and the heat of fusion and for regime III is defined by,

$$Kg = \frac{4b_0\sigma\sigma_e T_m^0}{\Delta H_f k} \tag{7}$$

where b_0 is the distance between two adjacent fold planes which in the case of PEEK is 0.592 nm [11], σ and σ_e are the surface free energies per unit area of the crystalline lamellae that run parallel and perpendicular to the chain direction, respectively. ΔH_f is the heat of fusion per unit volume and k is the Boltzman constant. The heat of fusion of PEEK was taken as 122.5 J/g [12].

The above equation has been modified such that the growth rate has been replaced by the reciprocal of the crystallisation half life. This enables the nucleation constant to be found from plots of ln $(1/t_{0.5}) + U^*/[\mathrm{R}(T - T_\infty)]$ against $1/(T/\Delta)$, the slope of the line being the nucleation constant Kg. Fig. 4 shows the Hoffman and Lauritzen plots for the blends studied.

It is clear that a transition from one regime to another did not occur in the temperature range studied. Since the grade of PEEK under investigation contains a high level of added nucleating agent and crystallisation occurred mainly at high supercoolings the mechanism is probably that of regime III, in which there is prolific multiple secondary nucleation. From the slopes of the above lines the product of the surface free energies was found. The variation of the product of the surface free energies with blend composition is shown in Table 2 and Fig. 5.

It can be seen that there is a trend apparent in the variation of the surface energy product with composition. There is an indication that increasing levels of PEI result in higher surface energies. The quantity σ_e is mainly determined by chainfolding, whereas the quantity σ varies with the nearest neighbours and will therefore depend on the composition of

Table 2
Variation of the nucleation constant and surface free energy product with blend composition

Weight % PEEK	$-Kg \times 10^5$ K^2	$\sigma\sigma_e$ ($\times 10^{-3}$ J^2 m^{-4}) ± 0.05
5	7.6 ± 0.1	1.24
10	7.4 ± 0.1	1.14
20	8.1 ± 0.2	1.16
40	6.6 ± 0.3	1.04
60	7.7 ± 1.1	1.19
80	6.4 ± 0.1	0.97

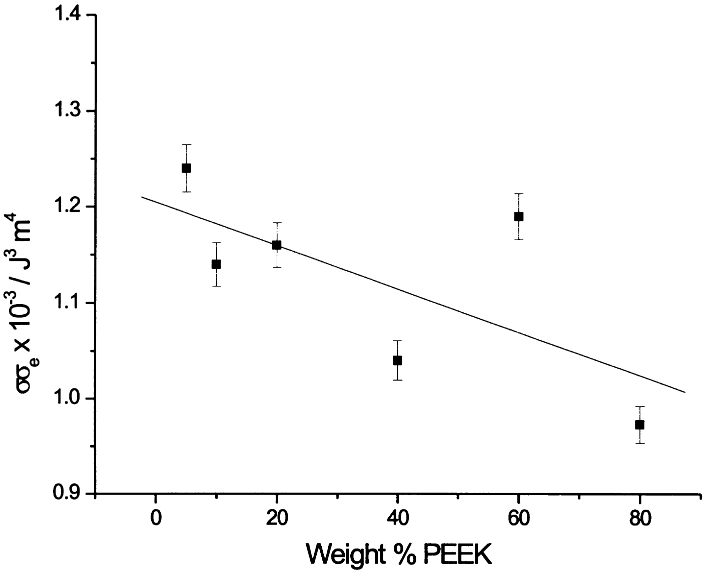

Fig. 5. Variation of surface energy product $\sigma\sigma_e$ with blend composition.

the melt which varies with the composition of the blend. This is consistent with the melting point depression observed in Fig. 3 and it also reflects the reduced tendency of PEEK to crystallise from the melt with increased levels of PEI. Hence the surface energy variation is another factor that determines the rate of crystallisation of PEEK.

4. Conclusions

The temperature dependence of the PEEK crystallisation rate can be described by the competing effects of nucleation and diffusion control. The maximum rate occurs at a similar temperature for all blend compositions studied, but the actual rate decreases with increasing PEI content. This can be explained by the shift in amorphous phase T_g and the corresponding increase in viscosity which reduces the chain mobility and the resulting growth rate.

While the technique of DSC is useful for determining the crystallisation kinetics of blends in the composition range of 40–80 wt% PEEK, the technique of hot stage microscopy was found to be more accurate in determining the crystallisation kinetics in blends in the composition range 20–5 wt% PEEK. This was attributed to the lack of sensitivity of DSC to very low heat flows, i.e. below 1 J/h.

Analysis of the melting behaviour of the blends showed that crystallisation did not occur under equilibrium conditions; the slopes of the T_m against T_c lines were not equal to 0.5. The only composition that did show a slope of 0.5 was that of pure PEEK, the intersection of this line with the $T_m = T_c$ line gave an equilibrium melting point of 663 K.

The surface free energies of the crystallites were found by analysing the crystallisation data in terms of the Hoffman and Lauritzen theory. It was found that there was an increase in surface free energy with increasing PEI content. This increase resulted from the increasing amounts of PEI within the amorphous matrix which also depressed the melting points and the reduced the rate of crystallisation.

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