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Multiple melting and crystal annealing of poly(ethylene terephthalate) in its blends with poly(ether imide)

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The melting behaviour and crystal annealing of poly(ethylene terephthalate) (PET) in its blends with poly(ether imide) (PEI) have been investigated by differential scanning calorimetry (d.s.c.). The multiple melting endotherms of PET were considered to arise from the occurrences of initial melting, recrystallization, and remelting processes in the melting region. The effects of blend composition, heating rate and crystallization duration on the multiple melting behaviour of PET/PEI blends were examined. It was found that the extent of recrystallization during d.s.c. heating decreased with increasing PEI composition and crystallization duration. The extent of recrystallization was suggested to be controlled by the degree of undercooling, $T_m^\circ - T_m$, and the remixing after initial melting. The reduction in extent of recrystallization of PET upon blending with PEI was attributed to the remixing between PEI and PET after the initial melting. The effect of blend composition on the annealing rate of PET crystals was also evaluated from the change of the onset of melting with annealing time. The results showed that the PET crystals exhibited a slower annealing in the blends than in the pure state. This observation was correlated with the molecular morphology in the crystalline/amorphous blends. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); poly(ether imide); multiple melting)

INTRODUCTION

Since blending is an effective method to tailor the properties of polymers, it is expected that this method may lower the cost of using high-performance polymers as well as extend their application windows. Poly(ether imide) (PEI) is an amorphous high-performance polymer with a glass transition temperature (T_g) of 215°C. PEI has been found to form a miscible blend with poly(ethylene terephthalate) (PET) in the melt[1,2]. Because of the crystallizable nature of PET, PET/PEI blends are basically crystallizable in the temperature range between the melting point and T_g. The crystallization behaviour and semicrystalline state of PET/PEI blends have been characterized in a previous study[2]. It was found that both the degree of crystallinity and the bulk crystallization rate decreased with increasing PEI composition[2]. A coupling between liquid–liquid demixing and crystallization was observed in PET/PEI blends. Such competitive processes led to an interconnected morphology identical to the structure created in the early stage of spinodal decomposition[2].

The multiple melting behaviour of PET in PET/PEI blends was briefly discussed in the previous study[2]. The presence of multiple melting peaks in the differential scanning calorimetry (d.s.c.) scan is not an unusual phenomenon for semicrystalline polymers. Nevertheless, the origin of such a phenomenon varies from polymer to polymer. Different crystal structures have been found to cause the multiple melting endotherms for *trans*-1,4-polyisoprene[3], isotactic polypropylene[4] and poly(vinylidene fluoride)[5]. Different lamellar thickness has been suggested for *cis*-1,4-polyisoprene[6] and poly(ether ether ketone) (PEEK)[7]. Simultaneous melting, recrystallization and remelting have been proposed for PET[8–10] and isotactic polystyrene[11,12]. Sometimes more than one reason has been suggested as being responsible for the multiple melting peaks[13,14].

Although there are many studies in the literature on the melting behaviour of homopolymers, similar investigations on polymer blends are relatively rare. Besides, most melting studies for polymer blends have mainly concerned the equilibrium melting point depression, the effect of blending on the melting of the metastable equilibrium crystals being subject to much less attention. In this paper, a study on the melting behaviour of PET in its blends with PEI is reported. The effects of blend composition, heating rate and crystallization duration on the multiple melting of PET will be discussed. In addition, the annealing of PET crystals in PET/PEI

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blends will also be reported. The effect of blend composition on the annealing rate of PET crystals will be discussed, and the results will be correlated with the molecular morphology in crystalline/amorphous blends.

EXPERIMENTAL

The PET sample used in this study was obtained from Goodyear Tire and Rubber Co., carrying the identification of Vituf. PEI was obtained from General Electric (GE, Ultem 1000), and its molecular weights were $M_n = 12\,000$ and $M_w = 30\,000$.

Blending of PET and PEI was carried out by solution precipitation. PET and PEI were dissolved in dichloroacetic acid at room temperature, yielding a 4 wt% solution. The blends were subsequently recovered by precipitating them into an excess (10×) of water. The blends were washed with a large amount of water and then dried *in vacuo* at 100°C for 5 days. It has been reported previously that PET/PEI blends as precipitated from dichloroacetic acid are not fully compatible and about 15 min of annealing at 280°C is required to homogenize the blends[2]. Therefore, all the samples used in this study were homogenized by melt-annealing in a differential scanning calorimeter at 280°C for 60 min under nitrogen atmosphere.

Crystallization, annealing and thermal analysis of PET/PEI were performed with a TA Instrument 2000 differential scanning calorimeter. To reduce the superheating effect, samples weighing approximately 0.5 mg were used for the d.s.c. measurements. For the crystallization experiment, the sample was annealed at 280°C for 3 min to erase previous thermal history, followed by quenching into liquid nitrogen to obtain a fully amorphous sample. The sample was then moved into the calorimeter pre-equilibrated at 200°C, where crystallization was carried out for the desired duration. Unless otherwise indicated, the d.s.c. scanning rate was $20°\mathrm{C\,min^{-1}}$.

RESULTS AND DISCUSSION

Multiple melting of PET in PET/PEI blends

The multiple melting behaviour of PET has been studied extensively[8-10]. The majority of evidence has demonstrated that multiple melting endotherms of PET are due to the occurrences of initial melting, recrystallization and remelting processes in the melting region[8-10]. Rim and Runt proposed that, as three processes are operative, the melting curve observed by d.s.c. is the superposition of three contributions, i.e. an endotherm associated with the melting of crystals formed prior to the d.s.c. scan, an exotherm corresponding to recrystallization following the initial melting and an endotherm associated with the melting of crystals formed from recrystallization[15]. This melting model, which should be applicable to PET, is displayed in *Figure 1*.

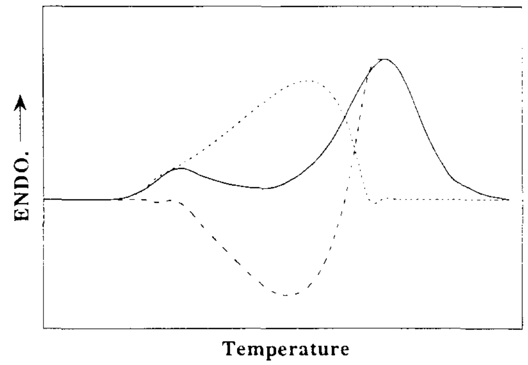

Figure 1 Schematic representation of the double melting endotherms arising from the superposition of an initial melting endotherm, a recrystallization exotherm and a remelting endotherm

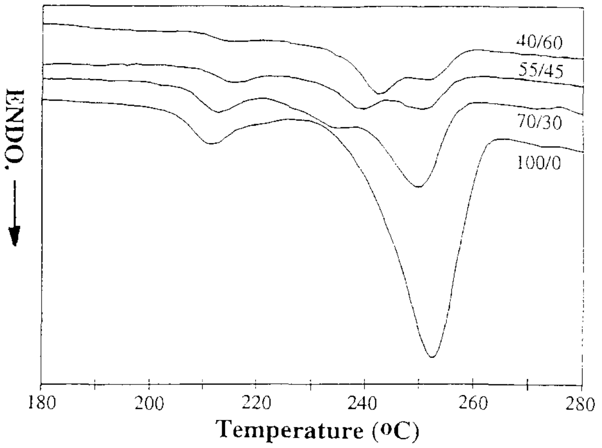

Figure 2 D.s.c. melting curves of PET/PEI blends after crystallizing at 200°C for 30 min. The scanning rate was $20°\mathrm{C\,min^{-1}}$

Figure 2 shows the melting endotherms of PET/PEI blends crystallized at 200°C for 30 min. It can be seen that the appearance of the melting endotherms varies with blend composition. As is usually observed, PET exhibits two melting endotherms with the lower endotherm (denoted by 'L-endotherm') located at 213°C and the higher endotherm (denoted by 'H-endotherm') located at 254°C. In contrast to PET, PET/PEI blends display three melting endotherms; an additional mid-endotherm (denoted by 'M-endotherm') is observed for the blends. It is noted that the peak temperature of the L-endotherm shifts to higher temperature with increasing PEI composition. The model in *Figure 1* suggests that recrystallization starts after a certain amount of PET crystals has melted and the peak temperature of the L-endotherm approximately represents this point. Therefore, the shift of the L-endotherm peak temperature to higher value implies that recrystallization started later in the blends than in pure PET. The variation of the H-endotherm with blend composition also deserves attention. The height of this endotherm relative to that of the M-endotherm decreases with increasing PEI composition. For the 70/30 blend, the M-endotherm appears as the shoulder of the H-endotherm, whereas the opposite is observed for the 40/60 blend.

To gain further insight into the above observation, the effect of heating rate on the melting behaviour of PET/PEI blends was evaluated. *Figures 3a* and *b* show, respectively, the d.s.c. thermograms of PET and the 40/60 blend crystallized at 200°C for 30 min followed by scanning at different rates. The variation of heating rate did not appear to influence the appearance of the pure PET melting endotherms significantly. The peak of the H-endotherm shifts slightly to lower temperature as the heating rate was increased from 10 to $40°\mathrm{C\,min^{-1}}$, indicating that recrystallization was slightly hindered by

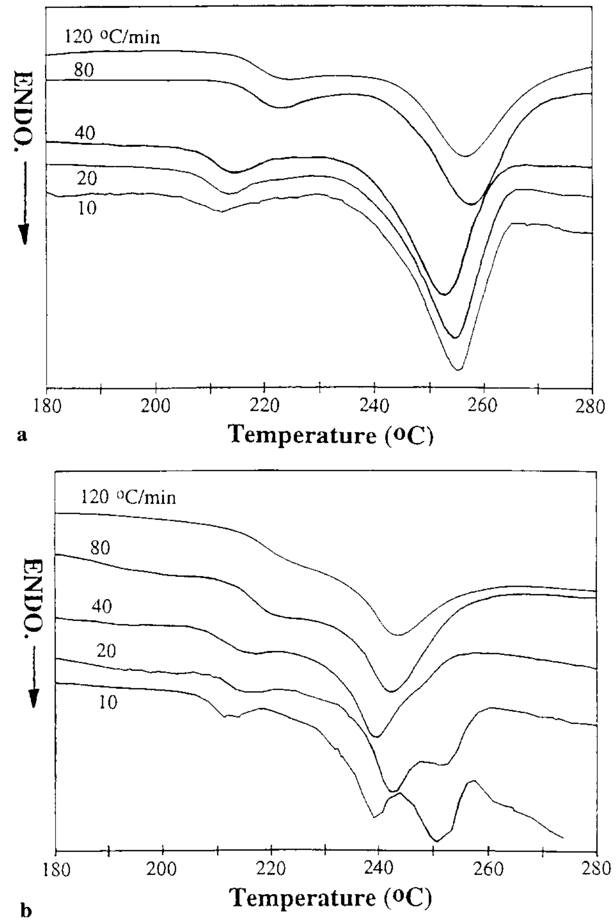

Figure 3 D.s.c. melting curves of (a) PET and (b) PET/PEI 40/60 blend scanned at different heating rates. The samples were scanned after crystallizing at 200°C for 30 min

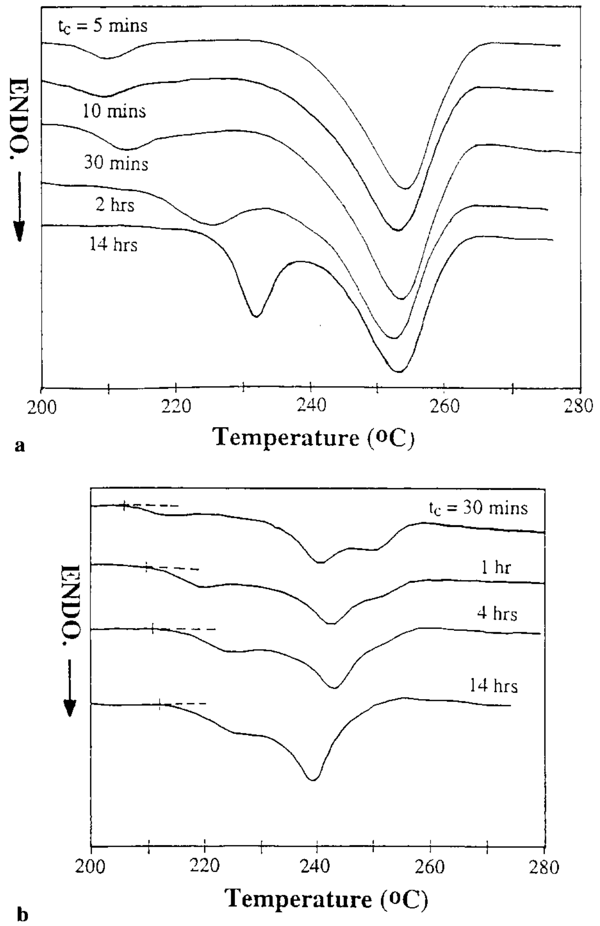

Figure 4 D.s.c. melting curves of (a) PET and (b) PET/PEI 40/60 blend scanned after crystallizing at 200°C for different time periods. The scanning rate was 20°C min^{-1}

raising the heating rate. On the other hand, the peak of the H-endotherm moves to higher temperature with increasing heating rate for heating rates >40°C min^{-1}, showing that superheating has played a role in the melting process. In contrast to PET, the variation of heating rate significantly affected the appearance of the melting endotherms of the 40/60 blend, as shown in *Figure 3b*. For the lowest heating rate of 10°C min^{-1}, three melting endotherms are observed. With increasing heating rate, the H-endotherm gradually diminishes, and the melting curve appears as two endotherms for heating rates >40°C min^{-1}. This evidently indicates that the H-endotherm observed in PET/PEI blends is due to melting of the PET crystals formed from recrystallization during the d.s.c. heating. Combining the observations in *Figures 2* and *3*, it can be concluded that increasing PEI concentration in the blends for a given heating rate has a similar effect to increasing the heating rate for a given blend composition. This suggests that pure PET can undergo recrystallization more easily than its blends with PEI in the melting region.

The effect of crystallization duration at 200°C on PET/PEI melting behaviour was also evaluated. *Figures 4a* and *b* display, respectively, the melting endotherms of PET and the 40/60 blend crystallized at 200°C for different time periods. It can be observed for pure PET that the L-endotherm moves to higher temperature with increasing crystallization duration as a result of crystal thickening. On the other hand, the H-endotherm peak temperature decreases slightly with increasing crystallization time, which may suggest that prolonged annealing tended to suppress the recrystallization in the melting region. This effect is more evident in the 40/60 blend. It can be seen in *Figure 4b* that the size of the H-endotherm relative to that of the M-endotherm decreases with increasing crystallization time, showing that recrystallization did become more difficult with prolonged annealing prior to the d.s.c. scan. Lemstra *et al.* have proposed that the rate of recrystallization should decrease as the melting point of the crystals formed prior to the d.s.c. scan increases, since the degree of undercooling decreases[11]. Certainly an increase in crystallization duration allows the already-formed crystals to undergo more thickening and, as a result, the melting point was increased and the driving force for subsequent recrystallization was reduced.

The above results have demonstrated the effects of blend composition, heating rate and crystallization duration on the melting behaviour of PET/PEI blends. The extent of PET recrystallization in the melting region was reduced by increasing PEI composition, heating rate and crystallization time. To provide a more quantitative measure for the extent of recrystallization, the melting endotherm of the crystals formed prior to the d.s.c. scan was obtained by a mathematical distribution. Once the shape of the initial melting endotherm had been determined, the recrystallization exotherm and remelting endotherm could be obtained easily by subtracting the initial melting endotherm from the observed melting curve, and the extent of recrystallization could subsequently be determined from the area of the recrystallization exotherm. According to Nichols and Robertson, the shape of the melting endotherm of a polymer can be described by the following distribution[16]:

$$C_{\mathrm{m}}(T) = N(T_{\mathrm{m}}^* - T)(1-p)^2 p^{(T_{\mathrm{m}}^* - T)} - K \qquad (1)$$

where T_{m}^* is the maximum melting of the crystals formed initially, p is a shape factor ($p < 1$), N is a normalization constant which is proportional to the height of the melting endotherm, and K is a constant required to force $C_{\mathrm{m}}(T)$ to zero at the onset of melting. At the onset of melting T_{ob}, $C_{\mathrm{m}}(T_{\mathrm{ob}}) = 0$, thus

$$K = N(T_{\mathrm{m}}^* - T_{\mathrm{ob}})(1-p)^2 p^{(T_{\mathrm{m}}^* - T_{\mathrm{ob}})} \qquad (2)$$

T_{m}^* in equation (1) can be related to the peak temperature (T_{p}) of the melting endotherm by recognizing that $\mathrm{d}C_{\mathrm{m}}(T)/\mathrm{d}T = 0$ at T_{p}, thus

$$T_{\mathrm{m}}^* = T_{\mathrm{p}} - \frac{1}{\ln p} \qquad (3)$$

Substituting equations (2) and (3) into equation (1) gives

$$C_{\mathrm{m}}(T) = N(1-p)^2 \left[\left(T_{\mathrm{p}} - \frac{1}{\ln p} - T \right) p^{(T_{\mathrm{p}} - 1/(\ln p) - T)} - \left(T_{\mathrm{p}} - \frac{1}{\ln p} - T_{\mathrm{ob}} \right) p^{(T_{\mathrm{p}} - 1/(\ln p) - T_{\mathrm{ob}})} \right] \qquad (4)$$

The initial melting endotherm can be obtained from equation (4) if N, p, T_{p} and T_{ob} are known. The value of the onset of melting, T_{ob}, can be determined directly from the observed melting curve. The proper values of the remaining parameters can be chosen by considering two conditions. First, it has been noted that the recrystallization of PET was likely to start at the peak temperature of the L-endotherm, and hence the endothermic portion below this peak temperature should represent the unperturbed part of the initial melting endotherm. Thus, in the temperature range between T_{ob} and the peak temperature of the L-endotherm, the melting curve calculated by a proper set of T_{p}, N, p and T_{ob} should fit that of the observed endotherm. The second condition to be considered is the area of the calculated melting endotherm. The area (or the enthalpy of melting) of the experimentally observed melting curve is given by:

$$A_{\mathrm{obs}} = A_{\mathrm{im}} - A_{\mathrm{rx}} + A_{\mathrm{rm}}$$

where A_{im}, A_{rx} and A_{rm} are the areas of the initial melting endotherm, the recrystallization exotherm and the remelting endotherm, respectively. Because the remelting endotherm is associated with the melting of crystals formed in the recrystallization process, its area should be identical to the area of the recrystallization exotherm, i.e. $A_{\mathrm{rx}} = A_{\mathrm{rm}}$. Thus,

$$A_{\mathrm{obs}} = A_{\mathrm{im}}$$

The area of the calculated initial melting endotherm is equal to that of the experimentally observed endotherm.

Equation (4) was used to fit the endothermic portion below the peak temperature of the L-endotherm. Once a set of N, p, T_{p} and T_{ob} provided a good fit to this endothermic portion, then the area of the endotherm determined by this set of parameters was calculated. The set of parameters was discarded if the calculated area did not agree with the area of the observed melting curve. Since T_{ob} can be determined experimentally, the curve fitting by equation (4) was basically a three-parameter fit. However, the curve fitting may be simplified by recognizing that the value of T_{p} of PET/PEI blends after crystallizing at 200°C may be extrapolated from the T_{p} *versus* crystallization temperature (T_{c}) plot. It was found that more than two melting endotherms were always observed for $T_{\mathrm{c}} \leq 200$°C, while only one endotherm was present after 14 h of crystallization at $T_{\mathrm{c}} \geq 200$°C. This indicates that recrystallization during d.s.c. heating was inhibited by the high melting point of the PET crystals formed at $T_{\mathrm{c}} \geq 200$°C. Therefore, the observed T_{p} corresponding to $T_{\mathrm{c}} \geq 200$°C can be regarded as the true melting point of the PET crystals formed prior to the d.s.c. scans. Because the T_{p} *versus* T_{c} plot is normally linear for polymers, the T_{p} of the initial melting endotherm corresponding to $T_{\mathrm{c}} = 200$°C can then be extrapolated linearly on the T_{p} *versus* T_{c} plot. Such a plot for PET/PEI blends is shown in *Figure 5*. The blend composition did not seem to affect T_{p} noticeably. The linear extrapolation to $T_{\mathrm{c}} = 200$°C yielded a T_{p} of $\sim$237.5°C for PET/PEI blends. This value was used as the initial guess for T_{p} in the curve fit for the samples crystallized for 14 h. For the samples crystallized for 30 min at 200°C, the annealing study (which will be reported in the following section) showed that the onset of melting was about 7 to 10°C lower than that for the sample crystallized for 14 h; thus the value of 230°C was used as the initial guess for T_{p}.

Table 1 lists the values of N, p and T_{p} for the

Table 1 Values of N, p and T_{p} used to calculate the initial melting endotherm of PET/PEI blends crystallized at 200°C for 14 h

PET/PEI	N	p	T_{p} (°C)
100/0	208	0.776	237.65
70/30	106	0.904	241.27
55/45	89	0.881	236.89
40/60	81	0.866	239.88

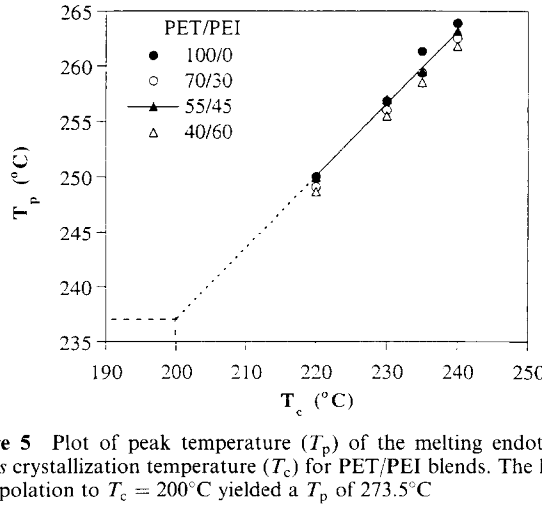

Figure 5 Plot of peak temperature (T_{p}) of the melting endotherm *versus* crystallization temperature (T_{c}) for PET/PEI blends. The linear extrapolation to $T_{\mathrm{c}} = 200$°C yielded a T_{p} of 273.5°C

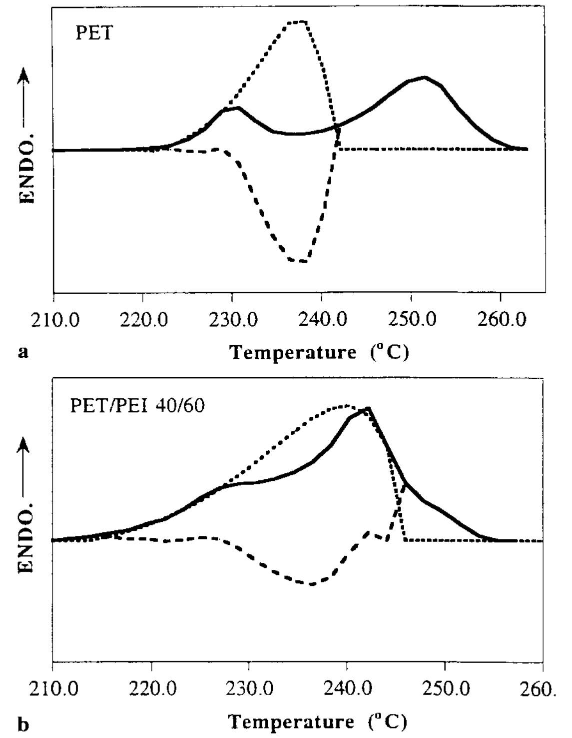

Figure 6 Calculated initial melting endotherm, recrystallization exotherm and the remelting endotherm, along with the observed melting endotherms, of (a) PET and (b) PET/PEI 40/60 blend. Both samples were crystallized at 200°C for 14 h

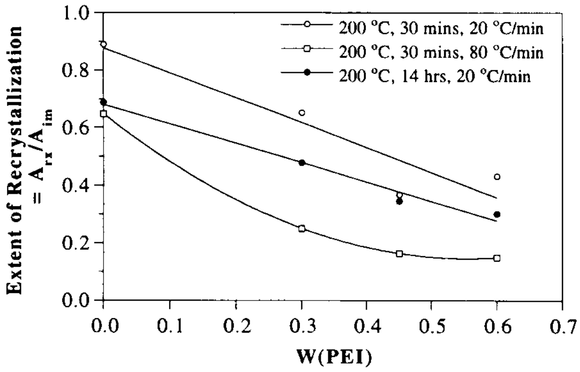

Figure 7 Composition variation of the extent of recrystallization of PET/PEI blends. The extent of recrystallization was calculated by the ratio of the area of the recrystallization exotherm (A_{rx}) to that of the initial melting endotherm (A_{im})

calculated initial melting endotherms of PET/PEI blends crystallized at 200°C for 14 h. The calculated initial melting endotherm, recrystallization exotherm and remelting endotherm of PET and the 40/60 blend are displayed in *Figure 6* along with the experimentally observed melting curves. The extent of recrystallization can be expressed by the ratio of the area of the recrystallization exotherm (A_{rx}) to that of the initial melting endotherm (A_{im}). This ratio signifies the weight fraction of the melted PET that was able to undergo subsequent recrystallization. The variation of this ratio with composition is shown in *Figure 7*. The extent of recrystallization decreases monotonically with increasing PEI composition. For pure PET crystallized at 200°C for 14 h, as much as 65% of the crystals could undergo recrystallization after their initial melting but, on the other hand, the extent of recrystallization dropped to 15% when there was 60 wt% of PEI contained in the blend. As expected, the samples exhibited less recrystallization at 80°C min^{-1} than at 20°C min^{-1}, and the samples undergoing shorter crystallization prior to the d.s.c. scan displayed higher extent of recrystallization.

The results presented thus far have demonstrated that a melting/recrystallization/remelting process was operative in both PET and PET/PEI blends during d.s.c. heating. The recrystallization of PET was hindered upon blending with PEI. A similar phenomenon has also been observed in poly(styrene-*co*-acrylonitrile) (SAN)/poly(ϵ-caprolactone) (PCL) blends. It is noted that the increased hindrance to recrystallization upon blending is not a universal phenomenon. A melting study on blends of isotactic and atactic poly(β-hydroxybutyrate) (PHB) indicated that the blends were actually more prone to recrystallize than pure i-PHB[17]. Such an observation was attributed to the lower melting point of the i-PHB crystals formed from the blends, and hence a larger undercooling towards recrystallization. The degree of undercooling towards recrystallization may be expressed by ($T_m^\circ - T_m$), with T_m° being the equilibrium melting point and T_m the observed melting point. In an ideal mixture like i-PHB/a-PHB, T_m° is essentially unaffected by blending; consequently the degree of undercooling is determined by T_m. Since the i-PHB crystals formed from the blends have a lower T_m than those formed from its pure melt, they exhibited a stronger tendency towards recrystallization.

In the present study, both PET and PET/PEI blends were found to start to melt at about the same temperature, thus the reduction of extent of recrystallization might be due to the depression in T_m° upon blending. The equilibrium melting point depression should be very small for PET/PEI blends, because the Hoffman–Weeks extrapolation in *Figure 5* would lead to a very minor difference in the equilibrium melting point between PET and PET/PEI blends. In addition, a glass transition (T_g) study of this binary pair has also suggested a fairly weak interaction between PET and PEI; thus a significant depression in T_m° is not expected.

The strong reduction in the extent of recrystallization in PET/PEI blends may alternatively be ascribed to the remixing between PET and PEI after initial melting. As the PET crystals were melted, the melted PET entered into the mixed melt. Since the subsequent recrystallization of PET required the diffusion of PET chain segments out of the melt, such a diffusion of PET was impeded by PEI and hence the recrystallization was hindered. As a consequence, the recrystallization rate was reduced due to remixing, leading to a decrease in the extent of recrystallization. Based on this discussion, it can be concluded that the extent of recrystallization during d.s.c. heating in a crystalline/amorphous blend is determined by two factors: (1) the degree of undercooling, $T_m^\circ - T_m$, which is determined by the crystal perfection (such as the crystal thickness) and the equilibrium melting point depression; and (2) the remixing after initial melting. In the blends of i-PHB and a-PHB the first factor dominated, since the melting point of the i-PHB crystals formed from the blends was considerably lower than that of crystals formed from pure i-PHB; as a result, the blends showed a stronger tendency towards recrystallization. On the other hand, in PET/PEI blends, the remixing effect is more dominant, and hence the blends exhibited a lower extent of recrystallization.

Isothermal annealing of PET crystals in PET/PEI blends

It is known that chain-folded polymer crystals may undergo thickening during crystallization. Such an annealing process is presumably different from crystallization, where the latter involves nucleation and growth from the melt while the former proceeds primarily in the solid state[18]. The crystal annealing of homopolymers has been the subject of extensive investigation[9,19,20], however, such a study for polymer blends is rare. The presence of the amorphous component in crystalline/amorphous blends may affect the crystal annealing significantly. It has been observed in PEEK/PEI blends that the thickening of PEEK crystals during d.s.c. heating was hindered by PEI[14]. A similar phenomenon has also been observed for i-PHB/a-PHB blends, where the annealing of i-PHB crystals during d.s.c. heating was impeded by a-PHB[17].

Previous studies on the crystal annealing in polymer blends have primarily concerned the crystal thickening in a dynamic d.s.c. heating process[14,17]. In the present study, the effect of blending with PEI on the isothermal annealing of PET crystals at 200°C was evaluated. Because the melting point of a chain-folded crystal is related to the crystal thickness, the variation of crystal thickness upon annealing may, in principle, be followed by observing the change of melting point during annealing. It has been shown that a significant portion of the initial melting endotherm overlapped with the recrystallization exotherm for PET/PEI blends, therefore the variation of the onset instead of the peak temperature of the initial melting endotherm was monitored during isothermal annealing. The onset of melting is the melting point of the thinnest crystals present in the sample and, according to the crystal annealing theory of Sanchez and co-workers[19,20], these crystals exhibit the largest tendency towards thickening. Although these crystals accounted for only a very small fraction of the total crystal population, investigating the annealing of these crystals should also reveal the general effect of PEI on the thickening of PET crystals.

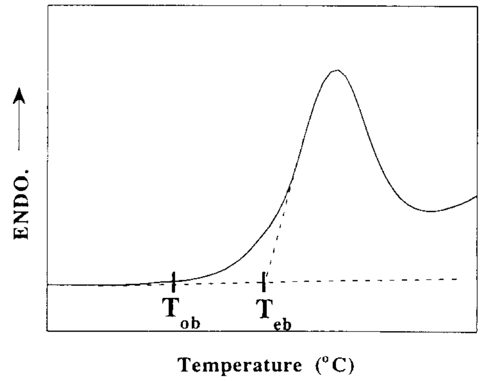

Figure 8 Schematic representation of the two onsets of melting, T_{ob} and T_{eb}, used to monitor the annealing of PET crystals in PET/PEI blends. T_{ob} is the onset of melting observed directly on the melting curve. T_{eb} is the onset of melting extrapolated from the tangent of the melting curve

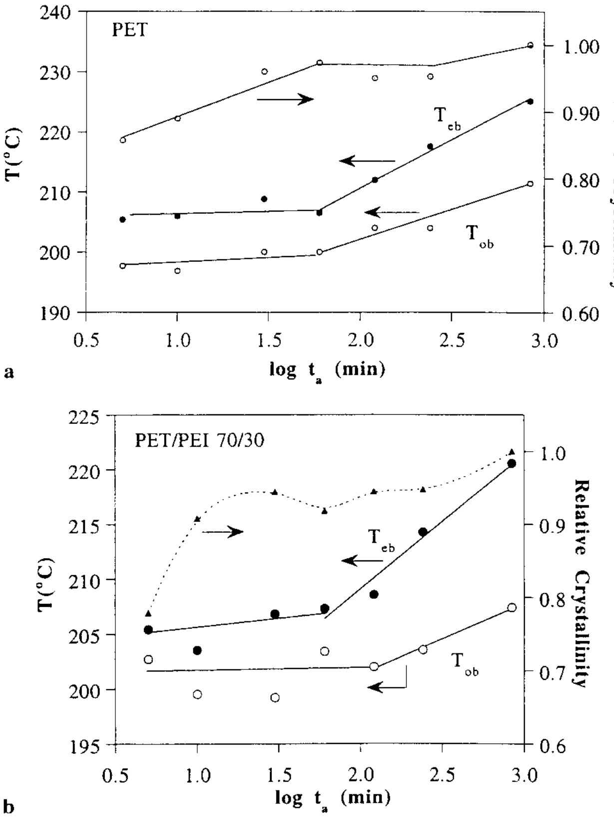

Figure 9 Variations of the onset of melting and the relative crystallinity of (a) PET and (b) PET/PEI 70/30 blend during isothermal annealing at 200°C. The relative crystallinity was obtained by $\Delta h_f(t_a)/\Delta h_f(14\,h)$

There are two onsets of melting considered here: the first is the observed onset T_{ob} and the other is the extrapolated onset T_{eb}, which was obtained by the manner shown in *Figure 8*. *Figures 9a* and *b* display the variations of T_{ob}, T_{eb} and relative crystallinity with logarithmic annealing time (t_a) at 200°C for pure PET and the 70/30 blend, respectively. The relative crystallinity was calculated by $\Delta h_f(t_a)/\Delta h_f(14\,h)$, with $\Delta h_f(t_a)$ and $\Delta h_f(14\,h)$ being the enthalpy of melting of the sample crystallized for t_a and 14 h, respectively. It is interesting that two regimes of the annealing time dependence of T_{ob} and T_{eb} can be identified for both PET and the 70/30 blend. Both T_{ob} and T_{eb} remain approximately constant for $t_a < 60$ min, while they increase linearly with $\log t_a$ thereafter. This observation can be readily understood if the variation of the relative crystallinity with t_a is considered. *Figure 9* shows that, in the region where the onsets of melting are approximately invariant, the relative crystallinity indeed increases with t_a. This indicates that crystallization was still taking place during this time period. T_{ob} is the melting point of the thinnest crystals present in the sample. As long as crystallization was still occurring, the thinnest unannealed PET crystals should always be produced. Because these crystals were always present in the sample during this time period, T_{ob} should correspond to the melting point of these crystals, and it should remain constant during this time period. On the other hand, after crystallization has ceased, T_{ob} should then correspond to the melting point of the thinnest crystals developed latest that have already undergone annealing. Since crystal thickness increases with annealing time, the observed onsets of melting should also

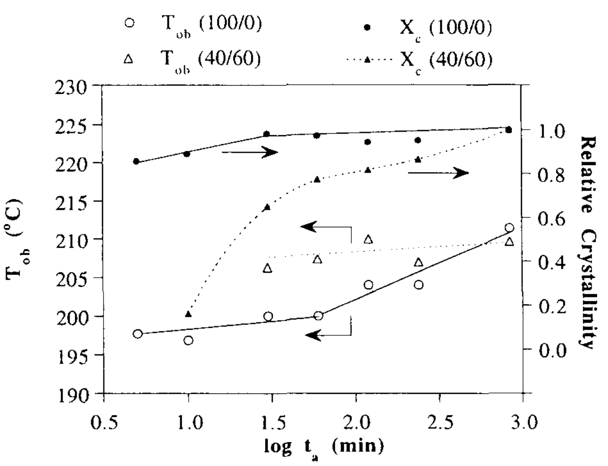

Figure 10 Variations of T_{ob} and relative crystallinity of PET and PET/PEI 40/60 blend during isothermal annealing at 200°C. T_{ob} of the 40/60 blend stays approximately constant throughout the crystallization period, while the relative crystallinity increases monotonically with annealing time

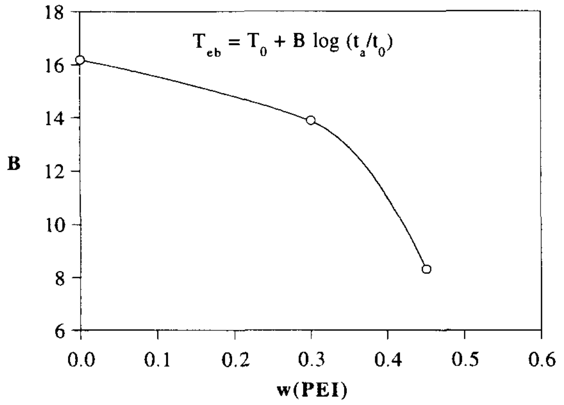

Figure 11 Variation of parameter B with PET/PEI blend composition

increase with annealing time. The above conclusion is further supported in *Figure 10*, which compares T_{ob} and relative crystallinity of PET and the 40/60 blend. Apparently, while the relative crystallinity of the 40/60 blend increases monotonically with $\log t_a$ throughout the annealing period, T_{ob} stays approximately constant.

As for many polymers[9], the linear portion in the melting point *versus* $\log t_a$ plot in *Figure 9* can be described by the following equation:

$$T_m(t_a) = T_0 + B \log(t_a/t_0) \qquad (5)$$

B is a parameter expressing the rate at which T_m increases with $\log t_a$, and hence it can be used as an index to reflect the rate of crystal annealing: a higher value of B should correspond to faster crystal annealing. The values of B obtained from the variation of T_{eb} with $\log t_a$ are plotted against PEI composition in *Figure 11*. A monotonic decrease of B with increasing PEI composition is observed, indicating that crystal thickening was more difficult in the blends than in pure PET.

The hindrance of crystal annealing in PET/PEI blends may be understood by considering the resultant molecular morphology after crystallization. If PEI was trapped in the crystalline interlamellar regions after crystallization, the crystal–amorphous interphase should contain chain segments of PEI as a requirement for the concentration transition from a pure PET crystalline phase to a mixed amorphous phase[21,22]. The presence of PEI chain segments in the interphase would restrict the cooperative motion of the crystalline chain segments in the crystal thickening process[14]. Consequently, a greater hindrance to crystal thickening is expected in the blends. In addition, because PEI has a higher T_g than PET, after crystallization from the blends the PET crystals were embedded in a stiffer amorphous matrix than they were before blending. Such an effect would also impede the crystal thickening of PET.

CONCLUSIONS

The results presented in this paper show that blending with PEI has a strong effect on the melting behaviour and crystal annealing of PET. Both recrystallization during heating and crystal annealing were hindered by the presence of PEI. The hindrance of recrystallization by blending may be rationalized by proposing that remixing between PET and PEI takes place after initial melting of the PET crystals, and such a remixing renders more difficult the diffusion of PET out of the melt in the subsequent recrystallization. It is suggested that the extent of recrystallization in a crystalline/amorphous blend is controlled by the degree of undercooling, $T_m^\circ - T_m$, and the remixing effect. They tendency towards recrystallization may either be increased or decreased by blending, depending on which factor dominates. The hindrance of PET crystal annealing by PEI may be attributed to the presence of PEI segments in the crystal–amorphous interphase, and also to the increase in viscosity of the amorphous matrix in which the PET crystals were embedded after crystallization from the blends.

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