

# Phase behaviour of amorphous and semicrystalline blends of poly(butylene terephthalate) and poly(ether imide)

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The phase behaviour of amorphous and semicrystalline poly(butylene terephthalate) (PBT)/poly(ether imide) (PEI) blends has been investigated. PBT and PEI were miscible in the melt over the entire composition range. Upon the crystallization of PBT at temperatures lower than 210°C, a strong segregation of PEI was observed. The morphological observation by optical microscopy indicated that PBT crystallization was coupled with a liquid–liquid phase separation, and the modulated morphology created in the early stage of spinodal decomposition was preserved due to the rapid crystallization of PBT. The phase diagram for PBT/PEI blends was also determined. This binary pair exhibited a UCST phase diagram with the binodal line located below the equilibrium melting point. Investigation on the multiple melting behaviour showed that recrystallization of PBT after the initial melting was hindered by the presence of PEI. The results presented here have indicated that PBT/PEI exhibited quite similar phase behaviour to poly(ethylene terephthalate) (PET)/PEI blends. © 1997 Elsevier Science Ltd

(Keywords: poly(butylene terephthalate); poly(ether imide); phase behaviour)

## INTRODUCTION

Blends of high performance polymers have attracted attention recently because of the technological importance of these materials. 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<sup>1,2</sup>. PET/PEI blends exhibited several interesting features when PET was allowed to crystallize from the blends. For example, PET crystallization was found to proceed simultaneously with a liquid–liquid phase separation, and such competitive processes led to a modulated morphology identical to the structure created in the early stage of spinodal decomposition<sup>2</sup>.

Poly(butylene terephthalate) (PBT) is also an engineering polymer whose chemical structure differs from PET by two methylene moieties per repeating unit. PBT is semicrystalline with  $T_g$  and melting point located around 35 and 220°C, respectively. Because of the similarity between the chemical structures of PBT and PET, it is of interest to blend PBT with PEI and see if the phase behaviour of this system would differ from that of

PET/PEI. In this paper, the phase behaviour of PBT/PEI blends is studied. The miscibility of this binary pair in both the melt and the semicrystalline state will be characterized and compared with that of PET/PEI. In addition, the effect of blending with PEI on the crystallizability and melting behaviour of PBT will be described.

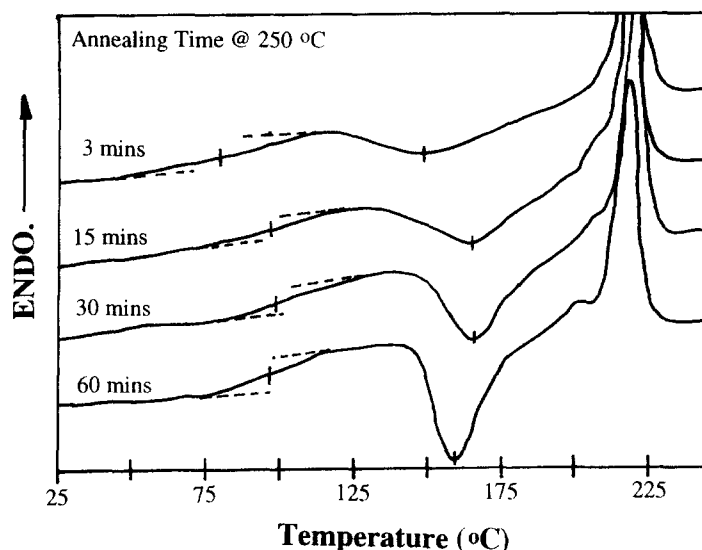
## EXPERIMENTAL

PBT used in this study was supplied by the Far Eastern Textiles Co. Ltd., Taiwan. Its molecular weight was about 20 000. PEI was obtained from General Electric (GE, Ultem 1000), and its molecular weights were  $M_n = 12 000$  and  $M_w = 30 000$ .

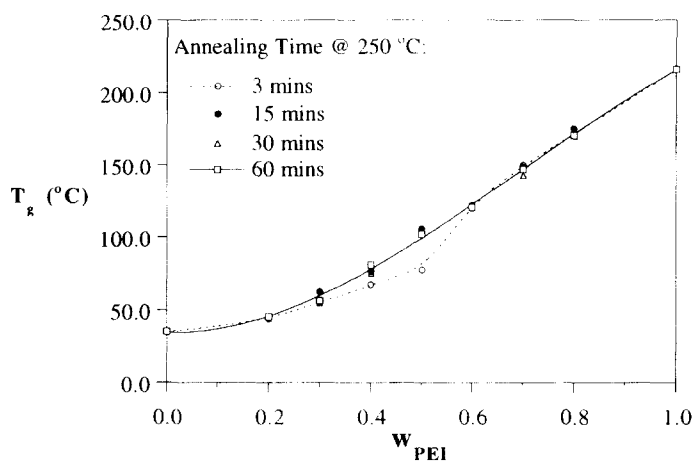
Blending of PBT and PEI was carried out by solution precipitation. PBT and PEI were dissolved in dichloroacetic acid at room temperature, yielding a 4 wt% solution. The blends were subsequently recovered by precipitating them in twenty-fold excess volume of water. The blends were washed with a large amount of water and then dried *in vacuo* at 90°C for seven days.

Thermal transitions of the blends were measured with a Perkin–Elmer DSC-7 differential scanning calorimeter (d.s.c.). Samples of the weight of *ca.* 5 mg were used for

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**Figure 1** D.s.c. thermograms of melt quenched PBT/PEI 50/50 blend. The scans were recorded after annealing the as-prepared blend at 250 °C for the time periods indicated in the figure. The glass transition regions are shown by the dash lines



**Figure 2** Composition variation of  $T_g$  for melt quenched PBT/PEI subject to different annealing periods at 250 °C

the d.s.c. measurement except for those used for the melting behaviour study, where samples of *ca.* 0.5 mg were used in order to reduce superheating effect. Unless otherwise indicated, the d.s.c. scanning rate was 20 °C min<sup>-1</sup>. The morphologies of PBT/PEI blends were observed by a Nikon FX-A cross-polarized optical microscopy. The sample was first melted on a Linkam TP92 hot stage at 250 °C for 3 min. The sample was then quickly transferred to another hot stage equilibrated at the desired crystallization temperature ( $T_c$ ), where the resultant morphology was observed.

## RESULTS AND DISCUSSION

### Miscibility in the melt

In the present study, PBT/PEI blends were prepared via precipitation from their solutions with dichloroacetic acid. It was found previously for PET/PEI that the as-precipitated blends did not exhibit full compatibility, but the compatibility could be enhanced upon melt annealing<sup>2</sup>. Similar phenomenon was also observed here for PBT/PEI. *Figure 1* displays the d.s.c. thermograms of the melt quenched PBT/PEI 50/50 blend. The d.s.c. scans were recorded after annealing the as-prepared blend at

250 °C for various time periods. A broad glass transition with  $T_g \approx 85$  °C is observed for the annealing time of 3 min. The glass transition becomes narrower and  $T_g$  shifts to higher temperature as the annealing time was increased to 15 min, indicating that the compatibility between PBT and PEI was enhanced. The cold crystallization temperature ( $T_{cc}$ ) also moves to higher value as the annealing time was increased to 15 min because the difficulty of PBT crystallization during heating was augmented owing to the improvement in compatibility. No noticeable change in  $T_g$  width and  $T_{cc}$  is observed for further increasing the annealing time from 15 min, showing that 15 min was sufficient to homogenize the blends.

The effect of melt annealing on the compatibility of PBT/PEI can also be manifested in *Figure 2*. *Figure 2* displays the composition variation of  $T_g$  for melt quenched PBT/PEI subject to different annealing periods at 250 °C. For the annealing time of 3 min, the composition variation of  $T_g$  exhibits an abrupt jump at  $w_{PEI} = 0.5$ . The  $T_g$ -composition relationship becomes a typical monotonic curve after annealing for more than 15 min. The  $T_g$  values coincide on the same curve for the annealing time longer than 15 min, supporting that the as-prepared blends could be homogenized by annealing at 250 °C for more than 15 min. Therefore, in the following

reported studies, all PBT/PEI blends have been homogenized by annealing at 250°C under N<sub>2</sub> atmosphere for 20 min before further investigations were conducted. The possibility of thermal degradation at 250°C was precluded by thermogravimetric analysis (t.g.a.), which did not indicate any noticeable weight loss for 1 h annealing under N<sub>2</sub> atmosphere. PBT and PET are also known to undergo transesterification with other polyesters such as polyarylate and polycarbonates at high temperature<sup>3-5</sup>; however, such a reaction between PBT and PEI is also precluded because of the great difference between the chemical structures of PEI and polyesters, and also the high thermal and chemical stabilities of PEI.

Figure 3 plots  $T_g$ ,  $T_{cc}$ , and the observed melting point ( $T_m$ ) of the homogenized blends against the weight fraction of PEI.  $T_{cc}$  increases with increasing PEI concentration, indicating that the crystallization rate of PBT decreased with increasing PEI content. If the observed  $T_g$  (35°C) of pure PBT is disregarded in the figure, the  $T_g$ -composition dependence in the region of  $w_{PEI} \geq 0.20$  can be described by the linear additivity rule. The failure of the observed  $T_g$  of pure PBT to fall on the linearity may be due to the high crystallinity (17%) associated with the quenched PBT sample. Cheng *et al.* have found that quenched PBT with very low crystallinity has the  $T_g$  of -25°C while normal semicrystalline PBT has a  $T_g$  between 37 and 59°C<sup>6</sup>. If -25°C was substituted as the  $T_g$  for PBT, a good linearity is observed over the entire composition range, as also displayed in Figure 3. The linearity for  $T_g$ -composition dependence would suggest a fairly weak intermolecular interaction between PBT and PEI, which is similar to the case of PET/PEI blends<sup>2</sup>.

#### Phase behaviour in the semicrystalline state

The phase behaviour of semicrystalline PBT/PEI is also investigated. Figure 4 displays the d.s.c. thermograms of PBT/PEI scanned after crystallization at 200°C for 5.5 h. A glass transition located at *ca.* 175°C is observed for the blends whereas this  $T_g$  does not appear for pure PBT. It is noted that the observed  $T_g$  is independent of initial blend composition. A  $T_g$  of 175°C would correspond to the glass transition occurred in the amorphous regions containing *ca.* 80 wt% PEI. This means that a strong segregation of PEI must have occurred upon the crystallization of PBT. Of course, in order to accommodate the crystallization of PBT, PEI must be segregated away from the crystal growth front. However, it seems quite unlikely that the observed segregation was solely induced by crystallization considering the very high observed PEI concentration. Suppose the segregation of PEI was induced solely by crystallization such that during PBT crystallization PEI was continuously segregated to the remaining miscible melt, then the composition of the miscible amorphous phase may be calculated from the simple mass balance relationship

$$w_{PEI} = \frac{w_{PEI}^0}{w_{PEI}^0 + (w_{PBT}^0 - \Delta h_f / \Delta h_f^0)} \quad (1)$$

where  $w_{PEI}^0$  and  $w_{PBT}^0$  are the initial weight fraction of PEI and PBT, respectively,  $\Delta h_f$  is the measured enthalpy of melting, and  $\Delta h_f^0 = 145.5 \text{ J g}^{-1}$ <sup>6</sup>, the bulk enthalpy of melting.  $\Delta h_f / \Delta h_f^0$  gives the weight fraction of PBT crystal, i.e. the degree of crystallinity, in the blend. The amorphous composition calculated from equation (1) can then be compared with that evaluated from the observed  $T_g$ . Figure 5 shows such a comparison for 50/50

blend crystallized at various temperatures for 11 h. It can be seen that for  $T_c$  higher than 215°C, the calculated compositions are in accord with the observed composition. On the other hand, the observed PEI composition is always about 20% higher than the calculated value for  $T_c \leq 215^\circ\text{C}$ . This disagreement would suggest that the

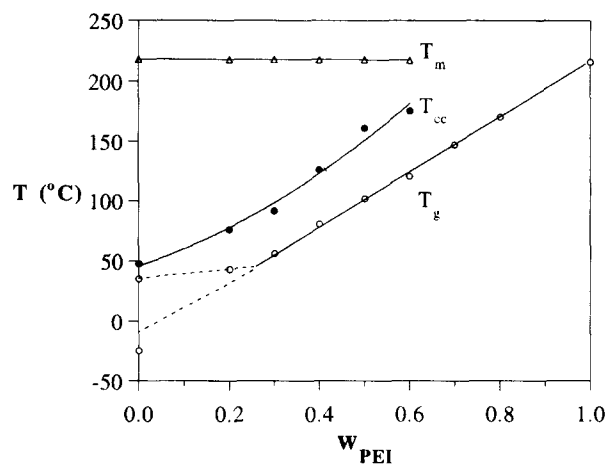


Figure 3  $T_g$ , cold crystallization temperature ( $T_{cc}$ ), and melting point ( $T_m$ ) of PBT/PEI. The observed  $T_g$  of pure PBT is 35°C. When the reported value of -25°C is substituted as the  $T_g$  of PBT, a linear composition dependence of  $T_g$  is observed over the entire composition range

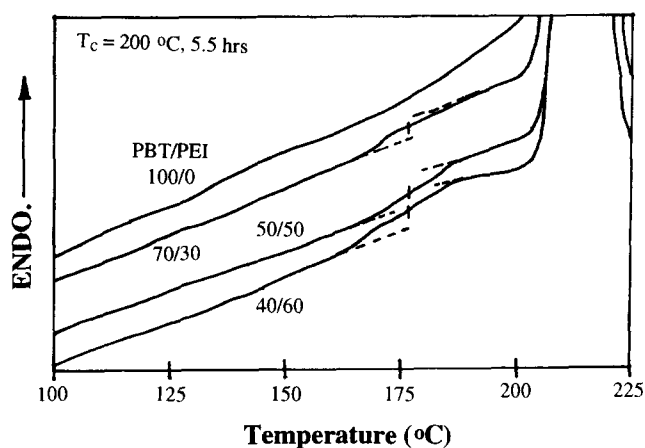


Figure 4 D.s.c. thermograms of PBT/PEI after crystallization at 200°C for 5.5 h. A  $T_g$  located at *ca.* 175°C is observed for the blends whereas this  $T_g$  does not appear for pure PBT

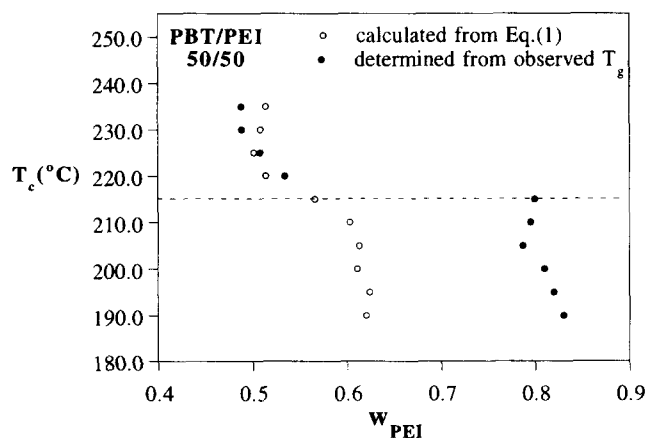
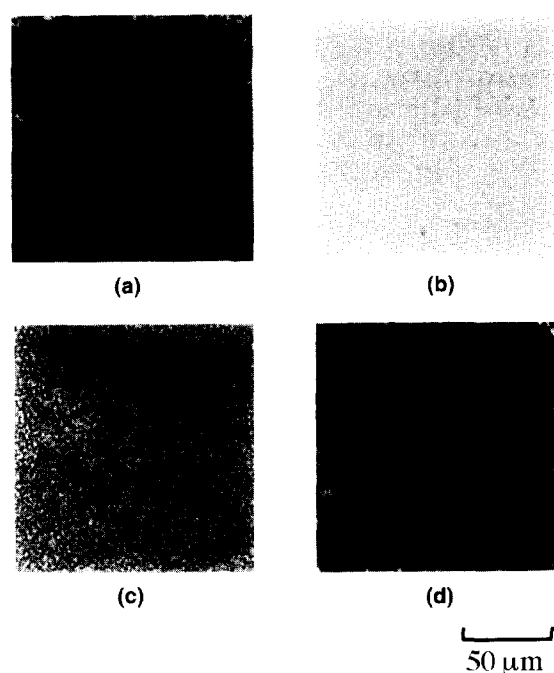
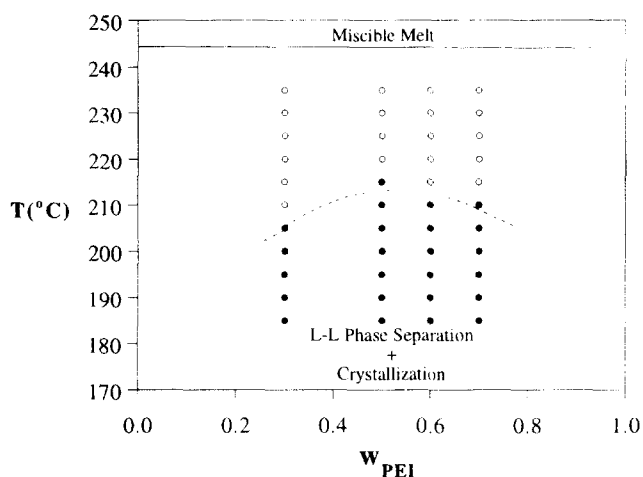


Figure 5 Comparison between the amorphous composition calculated by equation (1) and that evaluated from the observed  $T_g$  for PBT/PEI 50/50 after crystallization at various temperatures for 11 h



**Figure 6** Optical micrographs showing the morphologies of (a) pure PBT at 200°C (spherulitic morphology), (b) 50/50 blend at 250°C (homogeneous melt), (c) 50/50 blend at 200°C (modulated structure), and (d) 50/50 blend at 200°C. Micrographs (a) and (d) were viewed under cross polarization



**Figure 7** Phase diagram of PBT/PEI blends

observed PEI segregation at  $T_c \leq 215^\circ\text{C}$  may not simply be induced by crystallization.

In order to gain further insight into the nature of the PEI segregation, the semicrystalline morphology of PBT/PEI was monitored by optical microscopy. Figure 6 shows the morphology of pure PBT and 50/50 blend observed at 200°C. Pure PBT displays typical spherulitic morphology, while on the other hand, a coarsening structure deviating from the spherulitic morphology was developed from the homogeneous melt for the 50/50 blend. The coarsening structure appears like the modulated structure developed in the early stage of spinodal decomposition<sup>7</sup>, and is similar to the morphological pattern previously observed in PET/PEI<sup>2</sup>. Thus, it is concluded that PBT/PEI exhibited a similar phase behaviour to PET/PEI in that a liquid-liquid phase

separation took place simultaneously with the crystallization of PBT. The coupling between crystallization and liquid-liquid phase separation occurs when the binodal curves intersect the melting point depression curves<sup>8-14</sup>. Thermodynamically, the binodal curve has no equilibrium significance below the melting point, because crystallization is the favourable phase transformation<sup>12</sup>. Nevertheless, because of the high nucleation barrier in polymer crystallization, formation of a stable nucleus may be preceded by liquid-liquid phase separation<sup>12</sup>.

Since both processes occur simultaneously, liquid-liquid phase separation can compete with crystallization in producing its own morphology, and the final blend morphology is strongly dependent on the outcome of such a competition<sup>9-14</sup>. Inaba *et al.* have shown that the modulated structure resulting from spinodal decomposition in isotactic-polypropylene (i-PP)/ethylene-propylene random copolymer (EPR) blends could be locked in as the crystallization rate of i-PP was sufficiently fast<sup>9,10</sup>. The morphology shown in Figure 6 is indeed such a case where the spinodal modulated structure was conserved throughout the crystallization process. The crystallization of PBT from the blends appeared to be sufficiently rapid to compete with the spinodal decomposition to lock in the modulated structure.

The temperature and composition range within which liquid-liquid phase separation was coupled with crystallization can be evaluated by observing the resultant morphology for various blend compositions crystallized at different temperatures, as well as comparing the calculated amorphous composition by equation (1) with the observed composition evaluated from  $T_g$ . The determined phase diagram is shown in Figure 7. It is seen that PBT/PEI exhibits a UCST phase diagram with the binodal curve located below the equilibrium melting point. The equilibrium melting point of PBT was 245.5°C<sup>6</sup>; therefore, assuming melting point depression is negligible, all PBT/PEI blends were in the form of miscible melt above this temperature. Within the temperature and composition range bounded by the dashed line, crystallization was found to proceed simultaneously with liquid-liquid phase separation. The critical temperature was found to locate at *ca.* 215°C.

#### Crystallizability and melting behaviour

The effect of blending with PEI on the crystallizability of PBT is displayed in Figure 8. The degree of crystallinity was determined from the enthalpy of melting and was normalized by the weight fraction of PBT in the blends. Figure 8 shows that the crystallinity stays approximately at 40% when the blends contained less than 50 wt% of PEI. The crystallinity decreases with increasing PEI content as  $w_{\text{PEI}}$  exceeds 0.5, which shows that blending reduced the crystallizability of PBT at moderate to high PEI concentration.

The effect of blending on the melting behaviour of PBT was also evaluated. PBT exhibited multiple melting endotherms, and such a behaviour has been attributed to the occurrences of melting, recrystallization, and remelting in the melting region<sup>15</sup>. Figures 9a and b display, respectively, the melting endotherms of PBT and 40/60 blend crystallized at 190°C for 30 min followed by scanning at different rates. For PBT, the higher melting endotherm located at *ca.* 220°C was presumably associated with the melting of the crystals formed

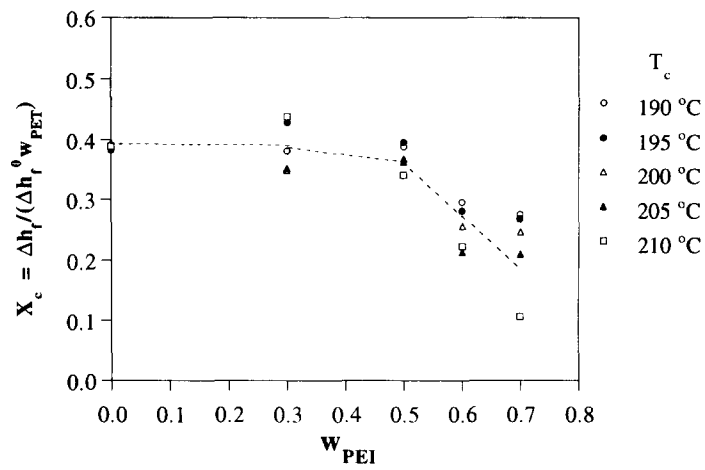


Figure 8 Effect of blending on the degree of crystallinity of PBT

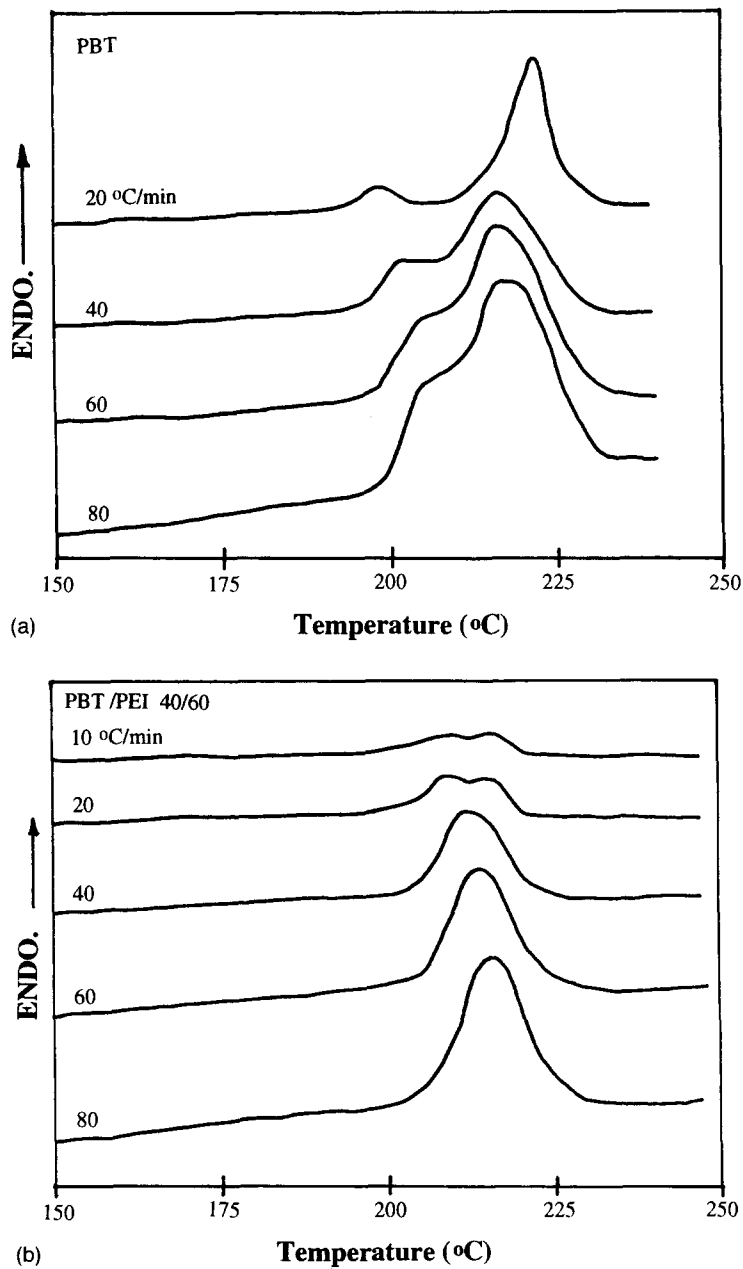
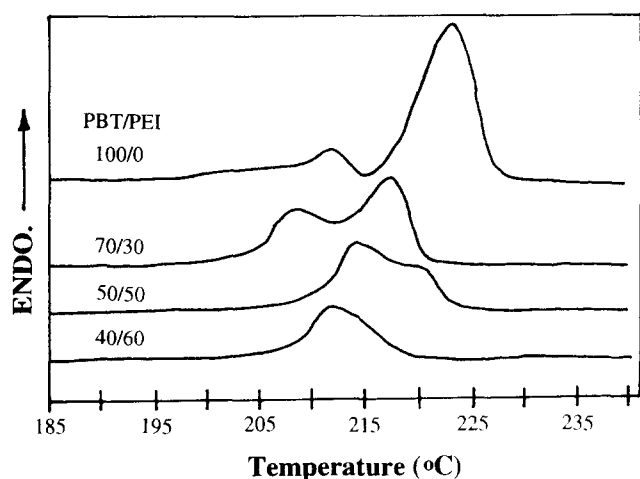


Figure 9 D.s.c. thermograms of (a) PBT and (b) PBT/PEI 40/60 blend scanned at different heating rates. All samples have been crystallized at 190°C for 30 min prior to scanning



**Figure 10** Effect of blend composition on the melting curves of PBT/PEI blends. All samples have been crystallized at 190°C for 11 h prior to scanning

from the recrystallization process during d.s.c. heating. This higher melting endotherm shifts to lower temperature as the heating rate was increased from 20 to 40°C min<sup>-1</sup>, which may indicate that recrystallization was hindered by raising the heating rate. The effect of heating rate on the melting behaviour was even more drastic for 40/60 blend, as shown in *Figure 9b*. For the lower heating rates of 10 and 20°C min<sup>-1</sup>, two melting endotherms are observed. As the heating rate was raised to 40°C min<sup>-1</sup>, the two endotherms merged into one, showing clearly that the higher melting endotherm was associated with the melting of the crystals formed through recrystallization.

The effect of blend composition on the melting behaviour of PBT is shown in *Figure 10*. It is evident that the height of the higher melting endotherm relative to that of the lower melting endotherm becomes smaller with increasing PEI content. The higher melting endotherm even becomes a shoulder of the lower melting endotherm for the 50/50 blend and it disappears as PEI content exceeds 60 wt%. Combining the observations in *Figures 9* and *10*, it can be concluded that increasing PEI concentration in the blends for a given heating rate had a similar effect to increasing the heating rate for a given blend composition. This suggests that pure PBT can undergo recrystallization more easily than its blends with PEI in the melting region. In other words, the presence of PEI in the blends hindered the recrystallization of PBT. The recrystallization of PET was also found to be hindered in PET/PEI blends<sup>16</sup>. The hindrance of recrystallization may be ascribed to the remixing between PBT and PEI after initial melting<sup>2,16</sup>. Since a large part of the melting range is located in the one-phase region in the phase diagram of *Figure 7*, as PBT crystals were melted, the melted PBT would remix with the

remaining miscible melt. Since the subsequent recrystallization required the diffusion of PBT chain segments out of the melt, such a diffusion was impeded by PEI and hence the recrystallization was hindered.

## CONCLUSIONS

The phase behaviour of PBT/PEI blends has been discussed in this paper. This binary pair was found to exhibit quite similar phase behaviour to the PET/PEI system. PBT/PEI was found to be miscible in the melt over the entire composition range. However, PBT/PEI as precipitated from its solution with dichloroacetic acid into water was not fully compatible. The compatibility could be enhanced by melt annealing. As PBT was allowed to crystallize from the blends at temperatures lower than 210°C, the crystallization was found to take place simultaneously with a liquid-liquid phase separation. The reason for this behaviour is that PBT/PEI displayed the UCST phase diagram and the binodal line was located below the equilibrium melting point. The melting behaviour study has indicated that the recrystallization of PBT in the melting region was hindered by the presence of PEI.

## ACKNOWLEDGEMENT

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