# Thermal Properties of a Thermoplastic Polyimide Blend

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ABSTRACT: Differential scanning calorimetry and dynamic mechanical analysis of blends of a new thermoplastic polyimide (TPI) and poly(ether imide) (PEI) have confirmed the full miscibility of the system over the whole composition range. Annealing of the blends above the glass transition temperature of TPI, but below its crystallization temperature, did not produce a shift in the glass transition, while physical ageing of the annealed blends also failed to reveal any indication of phase separation. The rate of crystallization of TPI was slowed by the addition of PEI, and the temperature of the blends followed a linear trend between the response of the component polymers, while the low-temperature  $\gamma$ -relaxation was unchanged by blending. The time scale of physical ageing of the blends did not behave in a linear fashion, and the enthalpy loss on ageing also deviated from the average. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 543–552, 1999

**Key words:** thermoplastic polyimide; poly(ether imide); thermal properties; physical ageing

## INTRODUCTION

High-performance polyimides are used across a broad range of engineering applications. The presence of aromatic and imide groups in the monomer unit impart rigidity and strong interchain interactions to the polymer and, thus, result in high thermal stability and good mechanical properties. Polyimides can also be designed with a low dielectric constant, which makes them suitable for use as insulation in electrical and electronic applications. The development of a new thermoplastic polyimide (TPI) based on the monomers pyromellitic dianhydride and 3,3'-bis (4aminophenoxy) biphenyl diamine has been the subject of a number of research groups,<sup>1–3</sup> and the crystal structure, morphology, crystallization behavior and relaxation behavior have been reported. This polymer, the structure of which is shown below,



contains flexible ether and meta-phenyl linkages which allow the polymer to be processed by conventional thermoplastic melt-processing techniques. The amorphous material has a  $T_g$  around 250°C and, when crystallized, has an experimental melting temperature of about 385°C.

Blends of TPI with other high-performance polymers have been reported. Sauer and Hsiao et al. investigated blends of TPI with various poly-(aryl ether ketones)<sup>4,5</sup> and reported that a higher percentage of ketone linkages in the poly(aryl ether ketones) correlated with a higher degree of miscibility. TPI blends with polymer liquid crys-

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tals (PLC) have been studied,<sup>6,7</sup> and it was found that the presence of a PLC-enhanced orientation in the system lowered the crystallization temperature and modified the melt viscosity. Zone drawing of TPI-PLC blends resulted in highly oriented materials with increased dynamic moduli in the drawing direction, compared with the transverse direction.8 TPI has been blended with PEEK, PTFE, and other chemical and fiber additives to determine the wear resistance.<sup>9</sup> It was observed that, at elevated temperatures, the mechanism of wear changed from adhesive wear to fatigue fracture of the composite as the modulus decreased. Ma and Takahashi investigated the miscibility and phase behavior of TPI-PEI blends by annealing different compositions above the TPI  $T_g$  to induce phase separation, which was detected using differential scanning calorimetry (DSC).<sup>10</sup> They also used small-angle X-ray scattering (SAXS) to study the semicrystalline morphology of the blends and found that four states developed, depending on the temperature of heat treatment and blend composition. The amorphous PEI segments were incorporated between the stacked TPI crystals.

In this work, we report on the dynamic mechanical behavior of amorphous and semicrystalline TPI-PEI blends and also the use of DSC to investigate the physical ageing of the blends as well as their crystallization kinetics.

# **EXPERIMENTAL**

#### **Materials**

Poly(ether imide) is an amorphous thermoplastic with a  $T_g$  of 215°C. It was supplied by GE Plastics as Ultem 1000 with  $M_w$  equal to 30000 g mol and  $M_n$  equal to 12000 g mol. The structure is shown below.



TPI was supplied by Mitsui Toatsu Chemical Co as Aurum 450 with  $M_w$  equal to 27000 g mol. The polymers were blended at 400°C using a CSI Mini-Max blender. The blender output was compression-molded and then quenched into iced water to form amorphous sheets.

### **Dynamic Mechanical Analysis**

Dynamic mechanical analysis (DMA) was performed using a Rheometric Scientific MK II DMTA in the bending mode with dual cantilever geometry and a Perkin-Elmer DMA 7 in the probe penetration mode. With the dynamic mechanical thermal analysis (DMTA), rectangular samples measuring 25 imes 10 imes 1 mm were scanned at various frequencies in the temperature scanning mode over the frequency range of 0.1-30 Hz. The main parameters determined were tan  $\delta$  and loss modulus E''. The glass transition temperature was defined as the temperature corresponding to the peak maximum,  $f_{\text{max}}$ . For the Perkin–Elmer DMA 7, small sample discs were temperature-scanned at 1 Hz and 1°C min in a probe penetration mode. The main parameter of interest was loss modulus, E''.

## **Differential Scanning Calorimetry**

The glass transition temperature of each blend was determined by a computer-controlled Perkin-Elmer DSC 7. Samples were either heated directly from ambient to determine the transition or were heated to 400°C and then rapidly cooled to room temperature before scanning to determine the  $T_{g}$ , which was taken as the midpoint of the heat capacity change. For the physical ageing studies, a consistent thermal history was applied to each sample prior to ageing as follows: the sample was heated to 400°C, held for 5 min, and then rapidly cooled to 100°C. The sample was then rapidly heated to the required ageing temperature and held for an appropriate length of time. After ageing, the sample was once again rapidly cooled to 100°C, followed by a scan through the  $T_g$  at a heating rate of 10°C min to reveal the endothermic overshoot caused by the enthalpy relaxation. At a set temperature beyond the  $T_g$ , the deaged sample was then rapidly cooled to 100°C and scanned through the  $T_{\sigma}$  to the same set temperature. This was done to establish a baseline for the physical ageing process. The calorimeter was calibrated for temperature and heat flow using high purity indium, tin, and zinc standards. Crystallization kinetics of TPI and blends were determined by rapid cooling from 400°C to the desired isothermal crystallization temperature, and the evolution of heat was monitored as a function of time. An indication of the crystallization kinetics was achieved by recording the time taken to reach the peak of the exotherm.



**Figure 1** Composition dependence of  $T_g$  for amorphous TPI–PEI blends: ( $\bullet$ ) DSC; ( $\bigcirc$ ) DMA.

#### Density

Density measurements were carried out at room temperature on a Micromeritics AccuPyc 1330 pycnometer using samples that had been dried overnight at 150°C.

## **RESULTS AND DISCUSSION**

### Glass Transition of Amorphous and Crystallized Blends

All of the amorphous blends exhibited a single glass transition temperature over the whole composition range, as shown in the Figure 1 plot of the composition dependence of the DSC and DMA  $T_{\sigma}$  for TPI and blends. The slight negative deviation from linear additive behavior is typical of miscible binary blends where the specific interactions between the two polymers are weak and indicates the full miscibility of this system in the amorphous state. This is consistent with that reported by Ma and Takahishi<sup>10</sup> for amorphous TPI-PEI blends, although their investigation used only DSC to detect the glass transition. PEI is known to form miscible systems with other polyimides<sup>11</sup> and with poly(aryl ether ketones).<sup>12</sup> Ma and Takahishi successfully induced phase separation of the amorphous blends by annealing at 260°C, which is above the calorimetric  $T_{\sigma}$  of TPI and below the temperature at which crystal-

lization occurs. Their annealed blends showed two  $T_g$ s, which were only slightly shifted from the pure polymer  $T_g$ s, indicating almost complete separation of the phases. Due to the problems associated with the interpretation of DSC scans of immiscible or phase-separated binary blends where the component polymer  $T_{\rm g}{\bf s}$  are similar, we repeated and expanded the work described above, and the results are presented in Figures 2 and 3. Figure 2 shows DSC scans of an amorphous 50/50 TPI-PEI blend that has been subjected to various thermal treatments. Curve 1 shows a broad glass transition region typical of miscible blends, while curve 3 shows little change in the DSC response, except for the absence of the slight overshoot in 1, which is due to residual stresses. Physical ageing has previously been used to reveal the individual  $T_{\sigma}$ s of phase-separated blends with similar  $T_{\sigma}$ s as the development of an endothermic overshoot on scanning across the glass transition of aged materials is generally quite visible; so for single phase blends, a single endothermic peak is observed, while in two phase blends, the endothermic overshoot appears as a double peak. Bosma et al.<sup>13</sup> used this method to investigate the miscibility of PVC blends, while Konda et al. also proved



**Figure 2** DSC heatings scans of amorphous TPI–PEI 50/50 blend after different thermal treatments: (1) sample cut from a compression-molded sheet; (2) quenched amorphous sample aged at 200°C for 1 week; (3) quenched amorphous sample annealed at 260°C for 2 h; (4) quenched amorphous sample annealed at 260°C for 2 h and then aged at 200°C for 1 week.



**Figure 3** (a) Temperature dependence of the storage modulus for amorphous TPI and PEI and a 50/50 blend: (—) pure TPI and PEI; (----) amorphous 50/50 blend; (— —) amorphous 50/50 blend annealed at 260°C for 2 h. (b) Temperature dependence of tan  $\delta$  for amorphous TPI and PEI and a 50/50 blend [symbols are as (a)].

the utility of enthalpy recovery in investigating the phase structure of polymer liquid crystal blends with TPI and PEI.<sup>14</sup> To establish if phase separation had occurred in the annealed blends, we physically aged the quenched and annealed blends at 200°C for 1 week before rescanning in the DSC for enthalpy recovery. The ageing temperature was chosen as it is below the  $T_g$  of PEI and would therefore allow ageing of both components. Curve 2 displays an endothermic overshoot typical of ageing with an area of 4.2 J g, the peak of which is located a few degrees above the unaged  $T_g$ , at about 241°C. This is very similar to the behavior shown by a quenched and aged sample (curve 4), where the endotherm area is 4.5 J g and the peak location is the same. To further investigate the phase separation process, we also used the more sensitive technique of dynamic mechanical analysis on quenched and annealed blends. Figure 3 shows the temperature dependence of tan  $\delta$  and storage modulus for the 50/50 blend and the component polymers. The similar response of both parameters in the blend confirms that annealing at 260°C does not induce any significant change in the phase structure, as observed by DMA. The data shown in Figures 2 and 3 are also typical of the DSC and DMA response of the other TPI–PEI blend compositions, and this is summarized by Figure 4, which plots the composition dependence of the DSC and DMA  $T_g$  for annealed samples. The data in this figure are virtually identical to those shown in Figure 1, and we conclude that phase separation did not occur in our blend samples upon annealing at 260°C.

It is well known that phase separation does occur when one component of a miscible binary blend crystallizes, and in doing so, the noncrystallizing polymer is excluded from the growing crystals. This has been observed in detail in PEEK-PEI blends by DSC, DMTA, dielectric relaxation spectroscopy, electron microscopy, and X-ray scattering.<sup>15</sup> The semicrystalline morphology of these blends can be controlled by careful choice of the isothermal crystallization temperature, which is consistent with kinetic control of the evolving morphology; lower crystallization temperatures, for example, lead to trapping of the amorphous PEI between the PEEK crystal lamellae as a result of the low mobility of PEI. A mixed amorphous interlamellar phase coexisting with



**Figure 4** Composition dependence of  $T_g$  for amorphous TPI-PEI blends annealed at 260°C for 2 h: ( $\bullet$ ) DSC; ( $\bigcirc$ ) DMA.



**Figure 5** Temperature dependence of the loss modulus for semicrystalline TPI–PEI 50/50 blend: annealed at ( $\Box$ ) 300°C and ( $\triangle$ ) 360°C for 2 h.

pure PEI residing in interfibrillar or interspherulitic regions are responsible for the two glass transition processes in PEEK-PEI blends. The DSC scans of TPI-PEI blends crystallized at different temperatures, presented by Ma and Takahashi,<sup>10</sup> are also suggestive of differences in morphology. For melt-quenched blends annealed at 290 to 340°C, a single  $T_g$  corresponding closely with that of pure PEI is found, while for blends annealed at 360°C, the  $T_g$  tends to change with composition according to the Gordon-Taylor relation, and this suggests that mixed amorphous regions of TPI and PEI are dominant. SAXS studies indicated that PEI chains are incorporated in the amorphous layer between the TPI crystals, regardless of phase separation. We employed DMA and repeated some of the annealing studies described above to establish if the effects seen by DSC were real or simply artifacts due to baseline changes in the DSC. Figure 5 shows the temperature dependence of tan  $\delta$  for a crystallized 50/50 TPI-PEI blend. Certainly, with an annealing temperature of 300°C, the resulting  $T_g$  (at 222°C) is very close to that of pure PEI, and the high temperature skew of the plot may be due to the TPI phase, so this finding is qualitatively similar to the DSC findings of Ma and Takahashi. However, when the blend is annealed at 360°C and then subsequently scanned by DMA, the  $T_g$  is observed at 253°C, which is close to that of pure TPI (257°C), and there is no obvious sign of a glass transition due to either a pure PEI phase or a mixed TPI– PEI phase. Clearly, further DMA studies across the whole composition range and with different annealing temperatures are required to shed more light on these observations.

# Sub-T<sub>g</sub> Behavior of Amorphous Blends

Polyimides are well known for exhibiting sub- $T_{\sigma}$  $\beta$ -relaxations at temperatures above ambient. In polyimides synthesized from diamines and dianhydrides, this relaxation usually occurs between 50 and 250°C and is influenced by small-scale motions originating in both chemical units.<sup>16,17</sup> Fluorination of the polyimide structure shifts the temperature location of the  $\beta$ -process to higher temperatures with an increasing weight percent of fluorine in the diamine unit.<sup>18</sup> The origin of subambient processes in rigid aromatic polymers has been shown to comprise a range of mechanisms, including methyl group rotations, phenyl flips, main chain wiggling, defect migration, and disentanglement of chain ends.<sup>19</sup> This process is also considered to be a superposition of lower temperature intrachain motions and high-temperature cooperative motions that are influenced by moisture, thermal history, and morphology.<sup>20</sup> A dielectric, dynamic mechanical, and nuclear magnetic resonance (NMR) study on a semicrystalline thermoplastic polyimide assigned a  $\gamma$  tran-



Figure 6 Temperature dependence of tan  $\delta$  for amorphous TPI–PEI 50/50 blend.



**Figure 7** Composition dependence of the peak temperature location for the  $\beta$ -process in TPI–PEI blends.

sition at -100°C and 0.1 Hz to motions of phenoxy rings and a  $\beta$ -transition at 100°C and 0.1 Hz to motions of aromatic imide groups.<sup>21</sup> Figure 6 shows the dynamic mechanical response of an amorphous 50/50 TPI blend scanned across a wide temperature range. The blend exhibits the typical sub- $T_g$  transitions described above, and the composition dependence of the  $\beta$  process is shown in Figure 7. The temperature location of the  $\beta$ -process follows a weighted average between the TPI and PEI locations, and as the TPI process occurs at a lower temperature, this indicates that it is relaxing at a faster rate compared with PEI. It is interesting to note that this process in TPI is very weak, and our findings in this regard were very similar to previous DMA studies on amorphous TPI.<sup>22</sup> Thus, much of the  $\beta$ -peak intensity apparent in Figure 6 is due to PEI. The shifts in peak position in the blends suggest that the processes responsible for the  $\beta$ -process in TPI and PEI are unaltered by blending and obey simple dilution effects and approximate estimates of the change in peak height, as an indicator of the relaxation strength of the process, confirmed this view. The apparent activation energy for the process in both TPI and PEI was equal to  $200 \pm 20$  kJ mol and was unchanged by blending.

Subambient secondary relaxations in miscible blends have been reported to follow a range of behavior including no effect, suppression, and enhancement.<sup>23</sup> For blends of PC and PMMA, for example, the local backbone motions of PC are inhibited by the presence of PMMA; such phenomena can have important implications for the mechanical behavior of polymer blends, particularly with regard to loss of toughness.<sup>24</sup> The  $\gamma$ process in both TPI and PEI were very similar in terms of temperature location, peak height, and broadness and very little change was found in the blends. This is not surprising given the structural similarity of the two polymers and the likelihood that the localized motions responsible for the  $\gamma$ process arise from the same subunits. The apparent activation energy for this process was equal to  $62 \pm 10$  kJ mol.

#### **Crystallization Kinetics**

The relatively slow rate of crystallization of TPI, under both melt and cold-crystallization conditions, due to its rigid aromatic structure, makes it an ideal polymer for investigation using isothermal DSC and related techniques. The kinetics of crystallization, thermodynamics of crystallization, and crystalline morphology of pure TPI have been studied in some detail.<sup>25,26</sup> To examine the effect of blending with TPI on the rate of crystallization, we carried out some simple scanning and isothermal DSC studies on the TPI-rich blends. As the scans in Figure 8 show, only the 90% TPI and 75% TPI-containing blends were able to crys-



Figure 8 DSC heating scans of amorphous TPI-PEI blends. Heating rate was 10°C min.



**Figure 9** Temperature dependence of the crystallization rate for TPI–PEI blends: ( $\bullet$ ) TPI; ( $\blacktriangle$ ) 90/10 TPI–PEI blend; ( $\bigcirc$ ) 75/25 blend; ( $\bigtriangledown$ ) 50/50 blend.

tallize on heating from the quenched glass with sufficient rate and energy output to be detected by the DSC. The 50/50 blend was also heated at rates as low as 1°C min, but a crystallization exotherm was not observed. The heat of crystallization reduced from 26.1 to 14.2 J g for TPI and the 75% TPI blend, respectively, while the peak temperature of the exotherm increased from 322 to 329°C. The melting endotherm decreased in area from 30 J g for TPI to 22 J g for 75% TPI, while the temperature location of the melting peak was unchanged at  $379 \pm 2^{\circ}$ C. The fact that these changes are not in proportion to the mass fraction of TPI present is probably due to the different rates of dynamic crystallization occurring during heating. It is also apparent that the crystallization of the TPI occurs over a broader temperature range as the proportion of TPI decreases. An inspection of the amorphous heating thermograms reported previously<sup>10</sup> showed detectable exotherms in blends containing as little as 20% TPI, erratic changes in the peak location of the crystallization exotherm with composition changes, and a decrease in the peak temperature of the melting endotherm with increasing TPI concentration. In order to confirm the PEI-induced changes in crystallization behavior indicated by our heating data, we carried out isothermal DSC studies of crystallization in TPI, 90% TPI, 75% TPI, and 50% TPI. From a plot of rate versus

time, the crystallization peak time was obtained at various temperatures, and the data are plotted in Figure 9. Since the crystallization peak time is inversely proportional to the crystallization rate, we can see that the maximum rate of crystallization for TPI occurs at 320°C, and this is in excellent agreement with previous studies on TPI.<sup>25,26</sup> Blending of TPI with PEI decreases the rate of crystallization, significantly so for the 50/50 blend, and also shifts the maximum rate to slightly higher temperatures. These are also features of the crystallization of miscible blends, such as PEEK–PEI,<sup>27</sup> although the TPI–PEI system is guite different from PEEK-PEI in that the crystallizing component (that is, TPI) has the higher  $T_g$ . Therefore, it would be expected that addition of PEI to TPI would shift the maximum to lower temperatures due to the slight lowering of  $T_{g}$ . However, the fact that the noncrystallizing PEI has to be excluded from the growing TPI crystals is probably more influential in retarding crystallization than any possible plasticization effects. It would be desirable to investigate this further by conducting spherulite growth rate and nucleation density studies using optical microscopy; unfortunately, the high melt temperature of TPI and the small size of TPI spherulites (1–15 nm depending on crystallization temperature<sup>27</sup>) prevented us from carrying out such studies. Similar work carried out on blends of PEI with PEEK and PEKK<sup>27</sup> have indicated that PEI can have a significant effect on the rate and density of nuclei formation, and that for slow crystallizing polymers, the nucleation density can be significantly reduced. These factors are probably also important in the crystallization of TPI-PEI blends.

#### **Physical Ageing**

Physical ageing is a reversible phenomenon that results in changes in polymer properties as a function of annealing time at a temperature below the glass transition temperature. It occurs as a result of the nonequilibrium state of the glass and because of the time scale of molecular mobility, its effects are usually most important in a narrow temperature range below the  $T_g$ . Physical ageing has engineering significance since it can produce quite profound changes in mechanical behavior as well as other bulk properties, such as enthalpy, specific volume, refractive index, and dielectric response. Thus, it is a subject that has received wide attention.<sup>28</sup>

The physical ageing of miscible polymer blends is more complex since changes in relaxation behavior and the presence of concentration fluctuations can affect the process. For a 50/50 blend of polystyrene (PS) and poly(phenylene ether) (PPE), Oudhuis and ten Brinke<sup>29</sup> noted that the lost enthalpy was significantly lower that of either homopolymer. However, since other compositions did not show this effect, they attributed it to concentration fluctuations in the blend resulting in a range of  $T_{\rm g}$  values and, therefore, a range of molecular environments ageing to different extents at different rates. Cowie and Ferguson also noted a similar finding for a 50/50 blend of polystyrene and poly(vinyl methyl ether) (PVME); in addition, they reported that the characteristic relaxation time for physical ageing in the 50/50 blend behaved in a nonaverage manner compared with the pure polymers.<sup>30</sup> They attributed these observations to changes in relaxation behavior and retardation of physical ageing in PVME by PS. In a stress relaxation study on ageing of miscible blends, Chang et al.<sup>31</sup> examined the relaxation behavior and free volume properties of PS-PPE, PS-PVME, and poly(methyl methacrylate) (PMMA)-poly(ethylene oxide) (PEO) blends. In the first two cases, the rate of stress relaxation was faster in the blend compared with the pure PS, while in the latter system, stress relaxation in the blend occurred at a slower rate than either homopolymer. Positron annihilation lifetime measurements of fractional free volume showed that the free volume increased in PS-PPE and PS-PVME and decreased in PMMA-PEO blends, compared with the pure polymers. The differences in ageing behavior were therefore attributed to changes in packing density of the blends.

The typical time dependence of enthalpy relaxation through physical ageing is shown in Figure 10 for a 50/50 blend. Each value of  $\Delta H_t$  was determined by scanning the aged polymer through the glass transition region and measuring the area under the ageing endotherm, with a scan of the unaged glass taken as the baseline. From such curves, as shown in Figure 10, the time to reach equilibrium  $t_e$  and the enthalpy lost at equilibrium  $\Delta H_{\rm max}$  were determined, and it was found that both parameters varied in a linear fashion with temperature, which is typical behavior over the narrow temperature range often employed in physical ageing studies. The composition dependence of these parameters is shown in Figure 11. with each value corresponding to a constant degree of undercooling below the  $T_g$ . The positive



**Figure 10** Time dependence of physical ageing for TPI-PEI 50/50 blend at various temperatures: ( $\bullet$ ) 222°C; ( $\Box$ ) 215°C; ( $\blacktriangle$ ) 200°C.

deviation from linear additive behavior shown in Figure 11(a) indicates that the rate of physical ageing is slower in the blends, compared with the component polymers. This nonaverage behavior is consistent with other studies discussed above and also with the ageing study of Morales and Acosta<sup>32</sup> in which blends of PPO and PEO were found to age at a faster rate compared with the pure polymers. The values of maximum enthalpy in Figure 11(b) also showed a positive deviation from the average, and, similarly, this type of behavior has also been observed in the ageing studies described above. An insight into the possible cause of the slowing of physical ageing may be gained by examining the composition dependence of the density, measured at room temperature and plotted in Figure 12. The slight increase in density of the blends, compared with the pure polymers, is an indicator of increased chain packing, and this, as previously suggested,<sup>31</sup> is likely to result in a decrease in mobility of the relaxing segments. Similar trends in relaxation behavior can also be seen in miscible blends above the calorimetric glass transition.<sup>33</sup> These studies have also shown that changes in relaxation rate above the  $T_g$  occur for miscible blends with relative changes in density,<sup>34</sup> and it is therefore reasonable to assume that the rate of molecular motion above and below  ${\cal T}_g$  is influenced by similar factors, of which the amount of unoccupied volume available for mobile segments to move in is of primary importance. Deviations of the maximum relaxed enthalpy away from linear behavior are usually attributed to concentration fluctuations in the blend, and their presence in TPI-PEI blends was checked by measuring the width of the glass transition region by DSC, which is related to larger-scale fluctuations. Even through the  $T_{\sigma}$  of TPI and PEI differ by less than 30 K, we still observed an increase in  $T_g$  width of between 20 and 75% for the blends, compared with the pure polymers, and this is less than the DSC broadening found in a previously studied miscible PEI blend system with very different  $T_g {\rm s.}^{11}$  Generally, the range of relaxing environments caused by fluctuations produces a relative decrease in maximum enthalpy of miscible blends, particularly when the  $T_g$  of each polymer is far apart; whereas the TPI-PEI blends studied here show a positive deviation in ageing enthalpy. We cannot establish from our studies alone if this is connected with the close proximity of the  $T_g$  of TPI



**Figure 11** (a) Composition dependence of the time to reach equilibrium during physical ageing with  $\Delta T = 10$  K. (b) Composition dependence of the enthalpy loss at equilibrium during physical ageing with  $\Delta T = 10$  K.



**Figure 12** Composition dependence of the room temperature density of amorphous TPI–PEI blends.

and PEI affecting concentration fluctuations or with a fundamental change in the mechanism of physical ageing in the blends.

# **CONCLUSIONS**

The melt mixing and quenching of TPI and PEI was found to produce single-phase blends according to the variation in amorphous  $T_g$ , as monitored by DSC and DMA. Annealing of the blends above the  $T_g$  did not induce shifts in the  $T_g$  of any composition, nor did it produce any changes in the magnitude and location of the endothermic overshoot arising from physical ageing. Thus, we concluded that the blends did not phase separate. The intensity and location of the sub- $T_{\sigma}$   $\beta$ -relaxation behavior varied in a linear manner with blend composition while the low-temperature  $\gamma$ -process was virtually unchanged by blending. From DSC heating experiments of amorphous samples, the PEI was clearly seen to influence the crystallization and melting behavior of TPI, and isothermal DSC studies revealed that the rate of TPI crystallization decreased as the PEI content increased, and the temperature of maximum crystallization rate shifted upwards width increasing PEI. DMA scans on a 50/50 blend crystallized at different temperatures indicated that the rate and extent of demixing of PEI and TPI, as TPI crystallizes, is temperature-dependent. Physical

ageing studies revealed that the enthalpy relaxation behavior of the pure polymers is affected in a nonaverage manner upon blending, and that the accompanying changes in density and the presence of concentration fluctuations in the blends exert an influence on physical ageing.

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