

# Thermal Behavior of Poly(ether ketone ketone)/Thermoplastic Polyimide Blends

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Received 12 January 2004; accepted 4 May 2004

DOI 10.1002/app.21032

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The phase behavior and crystallization of poly(ether ketone ketone)/polyimide blends was investigated by differential scanning calorimetry and dynamic mechanical analysis, and chemical interactions in the blends were probed by Fourier-transform infrared spectroscopy. Amorphous blends were miscible over the entire range of composition, although mixing was most favorable at higher thermoplastic polyimide concentrations. Blending suppressed crystallization, especially of the minor component, but crystallization of both components, however, did occur in most of the blends. While blends quenched from the melt

exhibited only a single amorphous phase, melt crystallized blends appeared to possess two amorphous phases with different compositions. Shifts in the vibration frequencies of the carbonyl and imide bonds were inconsistent with the development of strong, specific intermolecular interactions, but may be explained by a disruption of the packing of the two homopolymers by nature of the mixing. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1227–1235, 2004

**Key words:** blends; thermal properties; poly(ether ketone ketone); polyimides

## INTRODUCTION

Poly(aryletherketones), PAEK, are a family of semicrystalline, engineering thermoplastics with high-temperature stability, excellent chemical and solvent resistance, and high modulus, strength, and toughness. PAEKs differ by the ratio of ether to ketone linkages; the most common commercial PAEKs are shown in Table I. The glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) increase with increasing ketone/ether (K/E) ratio. Polyimides are also high-temperature, engineering resins, and the wholly aromatic thermoplastic polyimide (TPI) formed from 4,4'-bis(3-aminophenoxy)-biphenyl and pyromellitic dianhydride possesses excellent solvent resistance and thermal and oxidative stability.<sup>1</sup>

PEKK is actually a family of polymers with different ratios of terephthaloyl (T) and isophthaloyl (I) moieties; see Scheme 1. The T/I ration can be varied to control the crystallization rate and crystallinity of poly(ether ketone ketone) PEKK without substantially changing the end-use temperature.<sup>2,3</sup> As the T/I ratio decreases, the chain becomes more disordered and the crystallinity decreases. Sauer et al.<sup>4,5</sup> reported that PEKK(T/I = 6/4) and TPI are miscible in the amorphous state for all blend compositions. They also reported that PEK is only miscible with TPI at high and low PEK concentrations and PEEK and TPI are immis-

cible for all compositions. The origin of the miscibility or partial miscibility of the PAEKs with TPI and the differences in miscibility due to the K/E ratio of the PAEK was not determined. Sauer et al.<sup>5</sup> suggested that there may be a specific intermolecular interaction, such as has been observed in other blends involving polyimides,<sup>6–9</sup> but they were not able to detect either charge transfer or hydrogen bonding interactions in the PAEK/TPI blends. The T/I isomer ratio of the PEKK also affected the phase behavior with TPI. PEKK(T/I = 8/2) was less miscible with TPI than was PEKK(T/I = 6/4),<sup>5</sup> and Sauer et al. suggested that that might be a consequence of the more disordered chain conformation for the polymer with the lower T/I ratio.

PEKK and TPI are crystallizable polymers, which complicates characterization of the phase behavior of their blends. Crystallization of either or both components in a blend depends on the miscibility of the two polymers in the melt, as well as the temperature history when cooling the blend from the melt. In this paper, we report on studies of the specific interactions between PEKK and TPI using Fourier transform infrared (FTIR) spectroscopy and the effect of thermal history of the blend on crystallization and miscibility using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and wide-angle X-ray diffraction (WAXD).

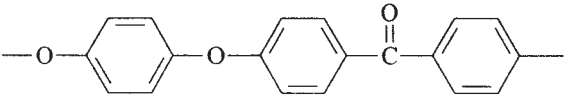
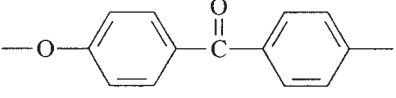
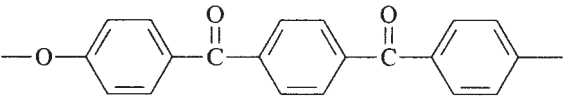
## EXPERIMENTAL

### Materials

The polymers used in this study were obtained from commercial sources. The PEKK, OXPEKK-C from Ox-

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TABLE I  
Common Poly(aryl ether ketone)s

Polymer	Repeat Unit	K/E <sup>a</sup>	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
poly(ether ether ketone)		0.5	142 <sup>b</sup>	340 <sup>b</sup>
poly(ether ketone)		1.0	156 <sup>b</sup>	370 <sup>b</sup>
poly(ether ketone ketone)		2.0	155	358

<sup>a</sup> Ketone/ether ratio.

<sup>b</sup> Ref. 4.

ford Performance Materials (Enfield, CT), had a T/I ratio of 8:2 and glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ), measured by differential scanning calorimetry, of 155 and 360°C, respectively. The TPI, Aurum PD450C, was obtained by Mitsui Chemical Co. (Purchase, NY) and had a  $T_g$  and  $T_m$  of 250 and 385°C, respectively.

PEKK/TPI blends were prepared in a Plasti-Corder intensive batch mixer (C. W. Brabender, South Hackensack, NJ) using a 50-cm<sup>3</sup> mixing head and mixing for 7 min at 405°C. Compression molded films were prepared using a 2-platen Wabash hydraulic press (Wabash, IN) with a set temperature of 410°C. Amorphous PEKK/TPI blends were achieved by first melting the sample in the press for 5 min without pressure, applying pressure and holding it for another 5 min, and then quenching the sample directly into ice water. Melt crystallized PEKK/TPI blends were obtained by slow cooling from 410°C to ambient temperature at a rate of ~2°C/min in the press. Samples were also crystallized isothermally by heating the quenched blends, i.e., the amorphous specimens, in the heat press at constant temperature for 1 h and then quenching the film to room temperature. The resulting film thickness was about 0.6 mm.

#### Blend characterization

Thermal transitions between 50 and 420°C were measured with a TA Instruments (New Castle, DE) DSC,

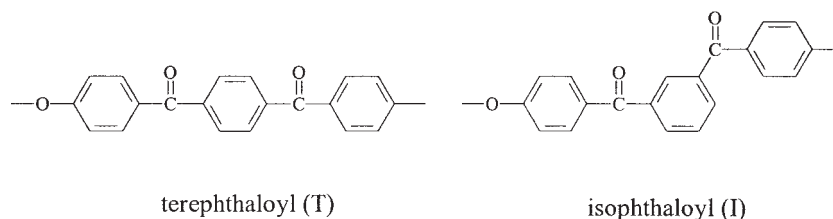
Model DSC2920. The temperature and enthalpy were calibrated using indium. A nitrogen atmosphere was used and unless indicated otherwise the heating rate was 20°C/min. DMA was carried out on molded films using a TA Instruments Model 2980 DMA, using a tensile fixture, a fixed frequency of 1 Hz, and a heating rate of 2°C/min. The specimens had a gauge length of ~15 mm and a cross section of ~3.5 mm<sup>2</sup>.

FTIR spectroscopy measurements were carried out with a Spectra Tech IR-Plan Microscope accessory interfaced with a Nicolet 560 FTIR (Thermo Nicolet, Madison, WI) using 32 scans with a resolution of 2 cm<sup>-1</sup>. WAXD data were obtained with a Bruker AXS, Inc. (Madison, WI) D5005 X-ray diffractometer equipped with a scintillation counter detector and using CuK $\alpha$  radiation. The scattering angle,  $2\theta$ , was scanned from 5 to 40° at 0.5°/min.

## RESULTS AND DISCUSSION

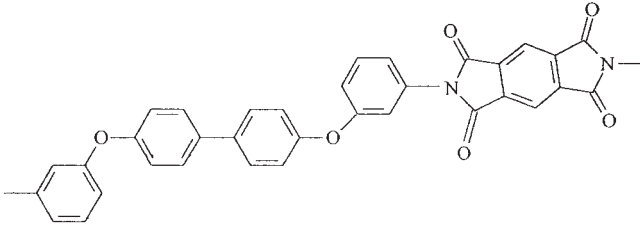
### Glass transition temperature and interaction parameter of PEKK/PI blends

DSC heating thermograms for the amorphous blends of varying composition from pure PEKK to pure TPI are shown in Figure 1. Only a single  $T_g$  was observed in each thermogram, which indicates that the two polymers were miscible in the amorphous phase at all compositions. The values of  $T_g$  are plotted against composition in Figure 2; the solid line is the Fox equa-



Scheme 1

TABLE II  
Thermoplastic Polyimide

Polymer	Repeat Unit	$T_g$ (°C)	$T_m$ (°C)
Thermoplastic polyimide (TPI)		249	385

tion prediction of  $T_g$  for miscible blends, which agrees reasonably well with the experimental values. The miscibility of PEKK and TPI shown here is consistent with the previous observation by Sauer et al.<sup>4,5</sup> Because the amorphous samples were prepared by quenching the blend from the melt at  $\sim 410^\circ\text{C}$ , the miscibility indicated by Figure 1 actually represents the phase behavior of the blend at that elevated temperature prior to the rapid cooling. The assumption here is that the sample temperature was quenched rapidly enough to below  $T_g$  so that the state of the sample at  $410^\circ\text{C}$  was preserved. In addition, since most partially miscible, high molecular polymer blends exhibit lower critical solution temperature phase behavior, the data in Figure 1 suggest that PEKK and TPI are miscible in the amorphous state at all temperatures below  $410^\circ\text{C}$ .

Dynamic moduli,  $E'$ , and  $\tan \delta$  data for the glass transition region for the amorphous PEKK/PI blends are shown in Figure 3. Both homopolymers exhibited a relatively narrow peak in  $\tan \delta$  at the glass transition;

see Figure 3b. The blends showed a single peak associated with  $T_g$ , plus a shoulder immediately after the glass transition. The single  $\tan \delta$  peak is consistent with the DSC data that indicated miscibility over the entire range of composition, although the  $\tan \delta$  peak for the blends was broader and lower in intensity than that for the homopolymers. The  $T_g$ 's of the blends as defined as the temperature of the  $\tan \delta$  peak in Figure 3b are also plotted in Figure 2 and the Fox equation fit is also shown by the dotted curve. The differences in the  $T_g$ 's measured by DSC and DMA reflect the frequency of the experiment; the higher frequency measurement, i.e., DMA, measures a higher  $T_g$ . The broadening of the glass transition in miscible blends is common, due to the distinct segmental mobility of each component.<sup>11-17</sup> The high-temperature shoulder in the  $\tan \delta$  data is probably a result of cold crystallization, although the temperature at which the shoulder appeared was much lower than the crystallization exotherm seen in the DSC thermograms in Figure 1. That

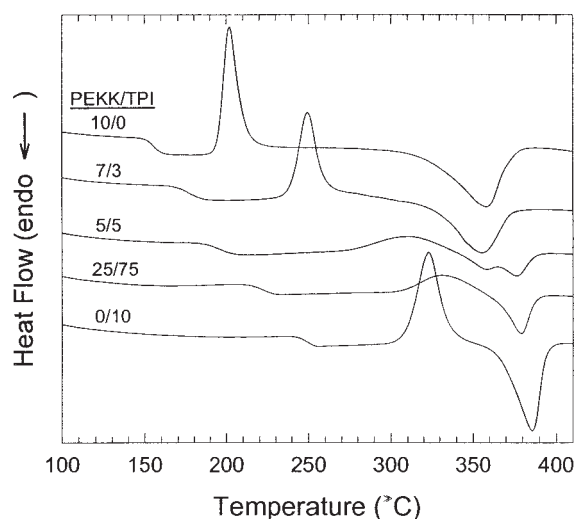


Figure 1 DSC heating thermograms (heating rate =  $20^\circ\text{C}/\text{min}$ ) of amorphous PEKK/PI blends prepared by rapidly quenching sample from the melt at  $410^\circ\text{C}$ .

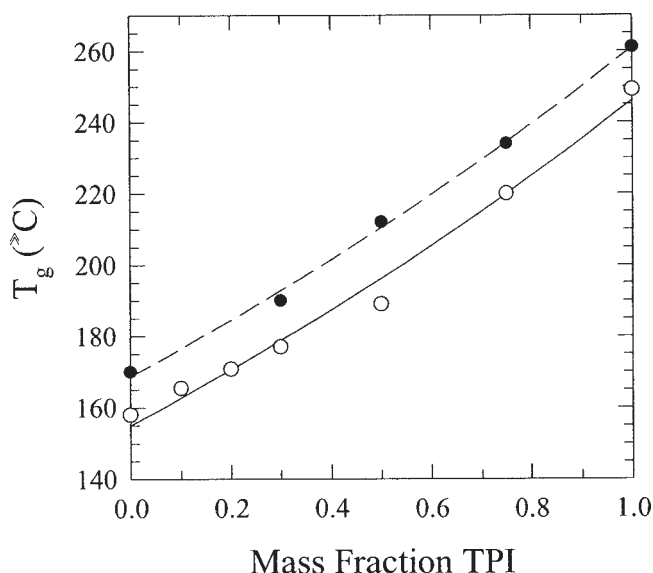
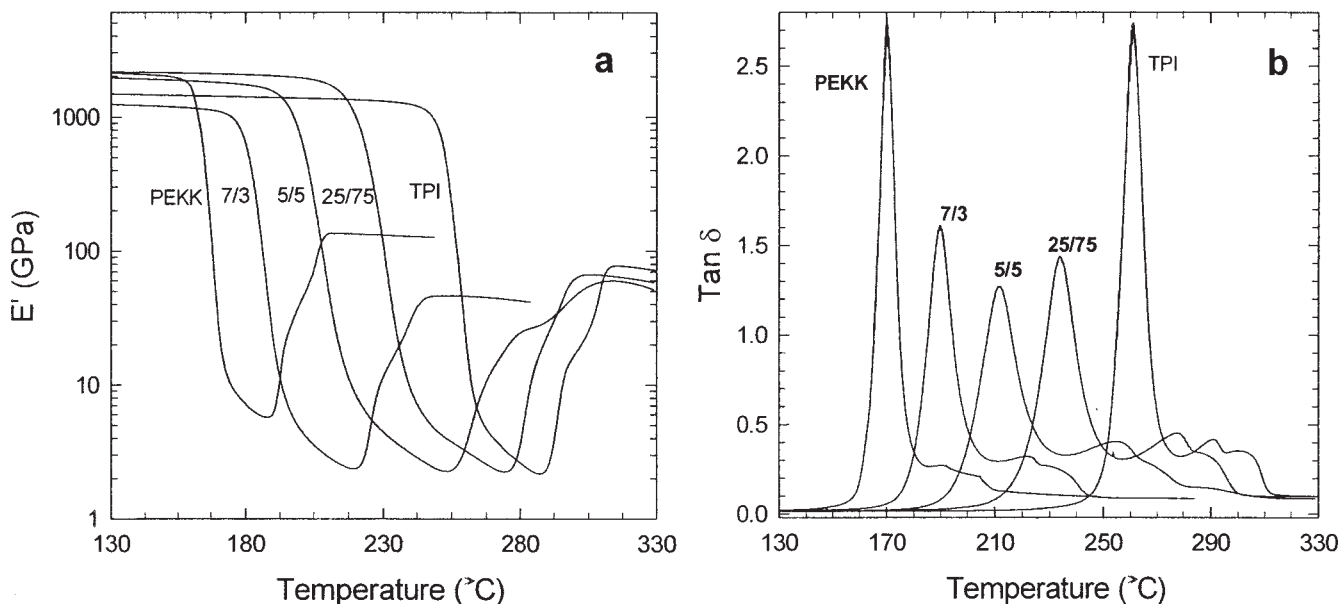


Figure 2 Effect of blend composition on the  $T_g$  of PEKK/PI blends: (○) DSC, (●) DMTA.



**Figure 3** Effect of blend composition on the dynamic mechanical properties of amorphous PEKK/PI blends: (a)  $E'$ ; (b)  $\tan \delta$

may be due to the slower heating rate used for the DMA experiment and/or to more sensitivity of the mechanical response to the initial stages of the crystallization. The shoulder in  $\tan \delta$  was also accompanied by a corresponding increase in the storage modulus, see Figure 3a, which is consistent with an increase in stiffness due to crystallization. A similar observation was reported for blends of poly(ether ether ketone) and poly(ether imide) by Goodwin and Simon.<sup>18</sup>

Miscibility of high-molecular-weight polymers requires a small or negative binary interaction energy density, which is usually characterized by an interaction parameter,  $\chi$ .<sup>19,20</sup> The commonly used experiments for measuring  $\chi$  for binary polymer blends, e.g., melting point depression and neutron scattering, are not particularly practical for the PEKK/TPI system. Instead, we chose to estimate  $\chi$  and its dependence on composition using an equation based on glass transition and change in heat capacity measurements:<sup>20</sup>

$$T_{gm} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_2)(w_1 + c w_2)^2} \quad (1)$$

$$A = \frac{-\chi^{R(T_{g1}-T_{g2})c}}{M_1 \Delta C_{p1}} \quad (2)$$

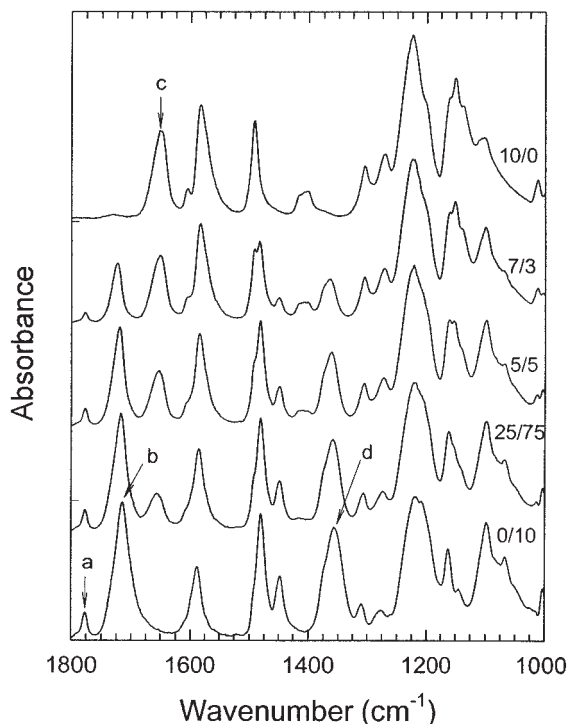
$$k = \frac{\Delta C_{p2} - w_1 \delta C_p^1}{\Delta C_{p1} - w_2 \delta C_p^{g'}} \quad (3)$$

where  $T_{gm}$  is the measured  $T_g$  of the blend,  $w_i$  and  $T_{gi}$  are the mass fraction and glass transition temperature of polymer  $i$ ,  $b = M_2/M_1$ , where  $M_i$  is the molecular weight of the repeat unit for polymers  $i$ ,  $c = \rho_1/\rho_2$ , where  $\rho_i$  is the density of polymer  $i$ , and  $\chi$  is the polymer-polymer interaction parameter.  $\Delta C_p = C_p^l(T_g) - C_p^g(T_g)$  is the specific heat change at  $T_g$  and  $\delta C_p$  is the specific heat change due to mixing. The  $T_g$ 's and  $\Delta C_p$ 's for PEKK and TPI were measured by DSC using quenched (i.e., amorphous) samples. Densities at 405°C were estimated using a group contribution method described by Van Krevelen.<sup>21</sup> It was assumed that  $\delta C_p$  was negligible, so that Eq. (3) was simplified to  $k = \Delta C_{p2}/\Delta C_{p1}$ .

The values of  $\chi$  calculated from Eqs. (1–3) for the 7/3, 5/5, and 25/75 PEKK/PI blends were -0.1, -1.0, and -2.4, respectively. The negative  $\chi$  indicates an attractive interaction between PEKK and TPI, and the decreasing trend of  $\chi$  (i.e., more negative value) with increasing TPI concentration indicates that miscibility improves with increasing TPI composition.

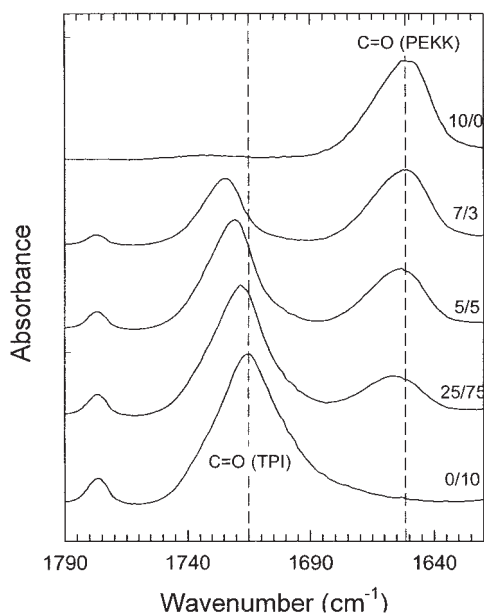
#### Infrared spectra of amorphous PEKK/TPI blends

FTIR spectroscopy was used to assess specific interactions between PEKK and TPI. Figure 4 shows the FTIR spectra (1800–1000  $\text{cm}^{-1}$ ) of the amorphous PEKK/TPI blends. Since both polymers have similar chemical units, the C–C bands in the phenyl ring and the diphenyl-ether overlap. However, the C = O stretching vibrations for the two polymers occurred at slightly different frequencies. For the TPI, the C = O stretch was composed of a doublet peak at 1776  $\text{cm}^{-1}$  (sym-

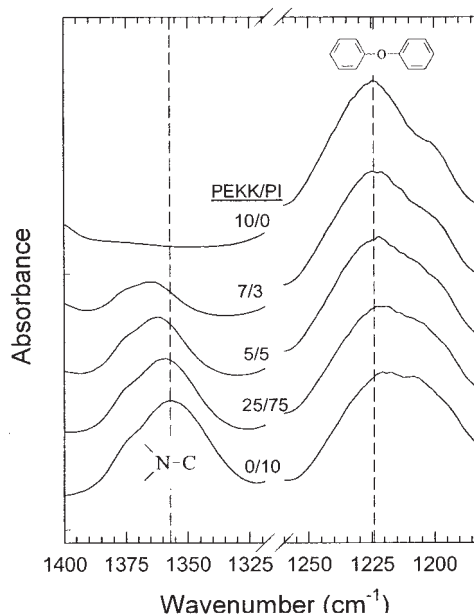


**Figure 4** FTIR spectra (1800–1000  $\text{cm}^{-1}$ ) of amorphous PEKK/TPI blends. (a,b) ( $\text{C}=\text{O}$ )<sub>TPI</sub>; (c) ( $\text{C}=\text{O}$ )<sub>PEKK</sub>; (d) ( $\text{CNC}$ )<sub>TPI</sub>

metric stretching)<sup>22</sup> and 1715  $\text{cm}^{-1}$  (antisymmetric stretching),<sup>22</sup> while a single  $\text{C}=\text{O}$  stretching vibration was observed for PEKK at 1651  $\text{cm}^{-1}$ . A vibration for the CNC axial stretching<sup>22</sup> in the imide ring of TPI occurred at 1357  $\text{cm}^{-1}$ . A reasonable assumption is



**Figure 5** FTIR spectra of carbonyl region for PEKK/PI blends.



**Figure 6** FTIR spectra of imide and ether region for PEKK/PI blends.

that any favorable intermolecular interaction between PEKK and TPI should involve the carbonyl, ether, or imide groups and, therefore, should be evident by changes in the IR vibrations due to those chemical groups.

Figure 5 shows the  $\text{C}=\text{O}$  absorbance region of the IR spectra of the PEKK/TPI blends. The frequency of the  $\text{C}=\text{O}$  stretching band for TPI at 1715  $\text{cm}^{-1}$  increased with PEKK concentration; e.g., the band moved to 1725  $\text{cm}^{-1}$  for the blend with 70% PEKK. The  $\text{C}=\text{O}$  band of the PEKK at 1651  $\text{cm}^{-1}$  also shifted slightly to higher frequency as the TPI concentration increased. Figure 6 shows the IR absorbance bands of the imide ring and the diphenyl-ether group of TPI. As the PEKK concentration increased, the imide ring absorption increased from 1357 to 1365  $\text{cm}^{-1}$ . The ether band also shifted to an intermediate position between the frequency for the two polymers (1221  $\text{cm}^{-1}$  for the TPI and 1224  $\text{cm}^{-1}$  for PEKK) as the blend composition changed, but changes in the ether absorptions were much less noticeable than the changes in the carbonyl and imide absorptions.

The shifts of the IR absorbance bands for the two polymers indicate that the local chemical environment near the carbonyl and imide groups changed upon mixing the two polymers. However, the formation of specific interactions between the  $\text{C}=\text{O}$  of the PEKK and the  $>\text{N}-\text{C}$  groups of the TPI would be expected to increase those absorptions, unless specific intramolecular interactions involving those groups that were present in the homopolymers were weakened or disappeared in the blend. For PEKK, dipole-dipole interactions between the carbonyl groups and the ether

groups are possible, and for TPI, the carbonyl group may interact with the ether via dipolar interactions or with the imide group by an electron donor-acceptor interaction.<sup>22</sup> Dissociation of the electron donor-acceptor complex should produce an increase in the vibration frequencies of the C = O and >N-C bonds. It does not appear, however, that the IR spectrum can be explained by a simple substitution of intra- by intermolecular associations involving the C = O groups. That would produce a decrease in the C = O bond vibration of one polymer, a corresponding increase in the C = O vibration for the other polymer, and little or no change in the imide absorption. The observed results may be accounted for by a disruption of the packing of the two homopolymers by nature of the mixing. That could weaken the intramolecular donor-acceptor complexes and/or substitute strong intramolecular electron donor-acceptor complexes due to close packing of chain segments with weaker intermolecular dipolar interactions due to poorer packing, which could increase the frequencies of both C = O vibrations and the >N-C vibration. Competition between the C = O groups on the two polymers for interaction with the imide appears to still be an important factor in the mixing as judged by the differences in the miscibility of PEEK, PEK, and PEKK with TPI.<sup>4,5</sup> That is, increasing the percentage of carbonyl groups in the PAEK increases its miscibility with TPI.

#### Cold crystallization and melting of PEKK/TPI blends

Both components of the blends were crystallizable polymers. The exotherm and subsequent endotherm above  $T_g$  in the thermograms in Figure 1 are due to cold-crystallization and melting transitions. For each

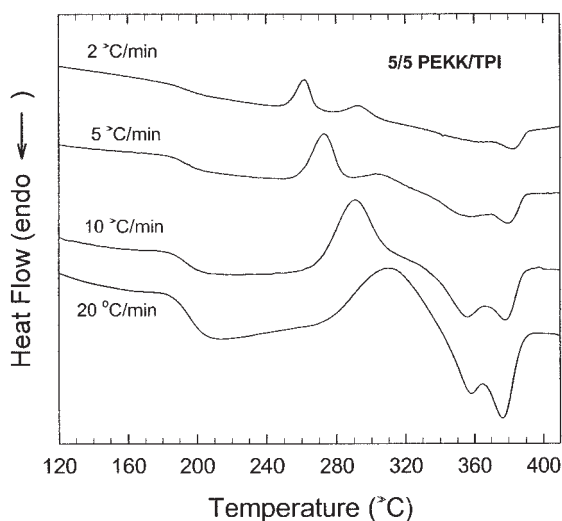


Figure 7 Effect of DSC heating rate on the thermal behavior of amorphous 5/5 PEKK/PI blend.

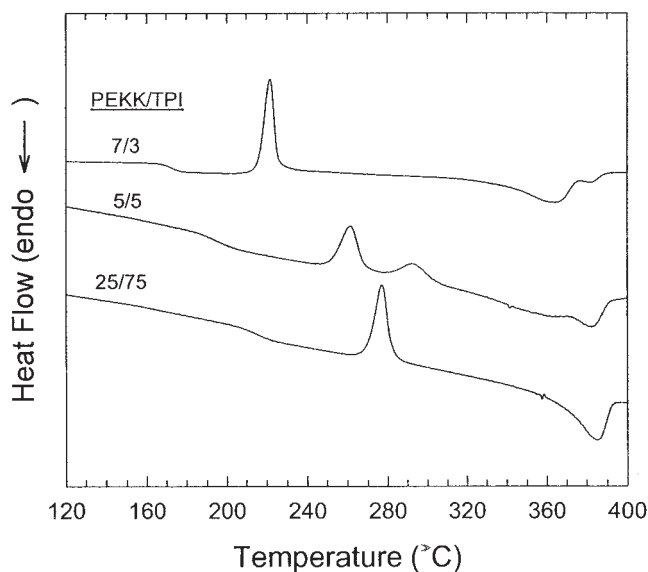
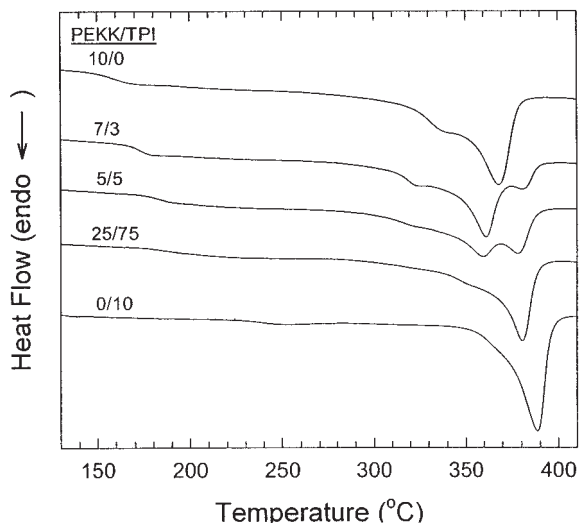


Figure 8 DSC thermograms of amorphous PEKK/PI blends using a heating rate of 2°C/min.

blend, only a single cold-crystallization peak is apparent in Figure 1, although for the 5/5 and 25/75 PEKK/TPI compositions, the peak was rather broad. The peak maximum,  $T_{cc}$ , increased as the amount of TPI in the blend increased. For PEKK-rich compositions (e.g., 7/3 PEKK/TPI),  $T_{cc}$  was about 50°C higher than for the pure PEKK, but the  $T_m$  was close to that of PEKK. Similarly, for the TPI-rich compositions (e.g., 25/75 PEKK/TPI),  $T_{cc}$  was greater than that for the neat TPI and  $T_m$  was close to that of TPI. Those results indicate that crystallization of the minor component in the blends was suppressed, probably due to the dilution of the polymer by the other miscible component, and only the major component of the blend crystallized.

The thermal behavior for the 5/5 PEKK/TPI blend shown in Figure 1 is distinctly different from that of the other blends; in this case, two melting endotherms are apparent. The effect of heating rate on the heating thermogram of the amorphous 5/5 PEKK/TPI blends is shown in Figure 7. The data for the lower heating rates show that the broad cold-crystallization exotherm seen in Figure 1 was actually composed of two crystallization processes, which is consistent with the observation of two melting peaks. For the 5/5 composition, both the PEKK and the TPI crystallized, although the  $T_m$ 's were each lower than that of the pure components due to a melting point depression as a result of the single amorphous phase in the blend.

DSC heating thermograms for the 7/3, 5/5, and 25/75 PEKK/PI blends using a heating rate of 2°C/min are shown in Figure 8. Although only a single, relatively narrow  $T_{cc}$  was observed for the 7/3 PEKK/TPI blend, a small high-temperature peak occurred above the main melting peak, which suggests that in addition to the PEKK crystallization, some TPI crys-



**Figure 9** DSC heating thermograms (heating rate = 20°C/min) of melt crystallized PEKK/PI blends

tallization also occurred in that sample. No evidence for PEKK crystallization or melting, however, was observed in the 2°C/min heating thermogram for the 25/75 PEKK/TPI blend; only a peak corresponding to melting of TPI was resolved. These results suggest that the TPI is more effective at suppressing crystallization of the PEKK than *vice versa*, which is consistent with the higher  $\chi$ -values for the TPI-rich blends.

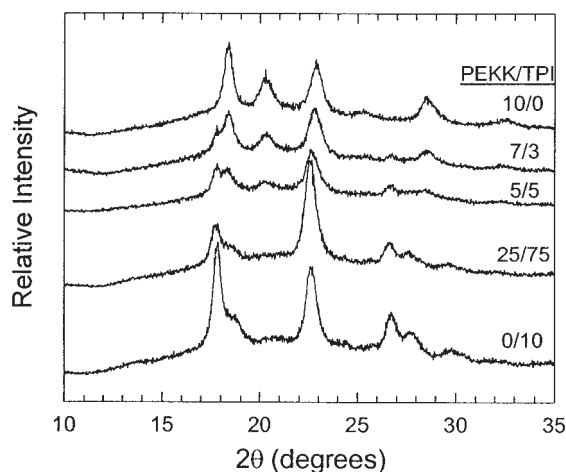
#### Melt crystallization and phase separation of PEKK/PI blends

DSC heating thermograms for the homopolymers and blends, melt crystallized by cooling relatively slowly, 2°C/min, from the melt, are shown in Figure 9. Because of the relatively high degree of crystallinity of the blends, the glass transition was relatively weak and broad. The thermograms for the 7/3 and 5/5 PEKK/TPI blends showed distinct melting endotherms for both PEKK and TPI. The melting transitions for the neat PEKK and for PEKK in the 7/3 PEKK/TPI blend exhibited a second endotherm prior to the main endothermic peak, probably due to melting of small, imperfect crystallites. A less distinct shoulder can also be seen on the lower temperature side of the main PEKK endotherm for the 5/5 blend. A weak shoulder is visible on the low-temperature side of the TPI melting endotherm in the 25/75 PEKK/TPI thermogram. That may be due to small TPI crystallites or, perhaps some PEKK crystallinity, which contrasts with the cold-crystallization result for that blend, in which only TPI melting was observed. However, as is shown below, no evidence of PEKK crystals was found in the WAXD of that sample.

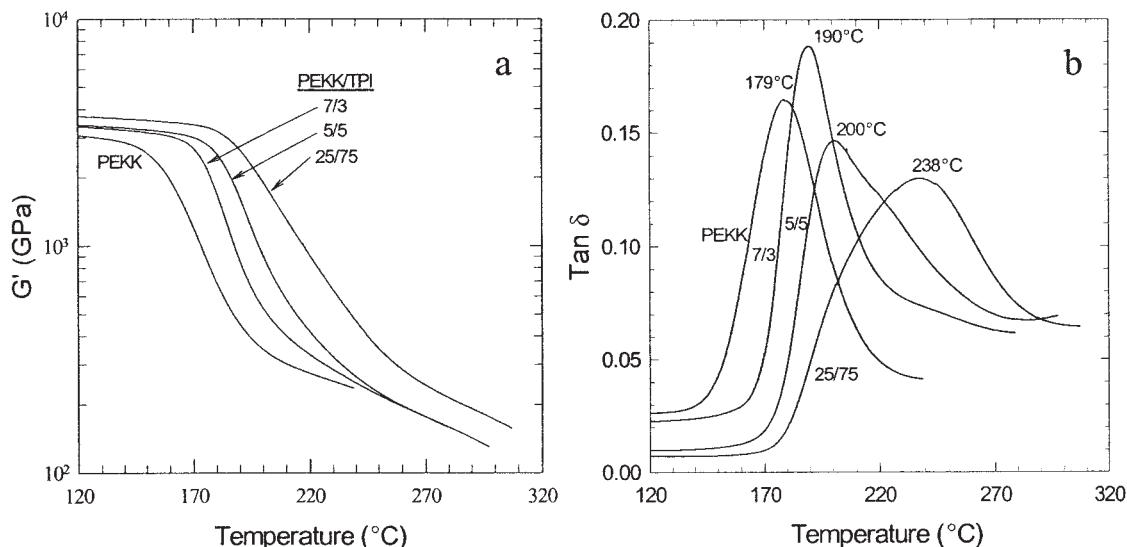
WAXD patterns for the melt crystallized PEKK/TPI blends are shown in Figure 10. For the pure PEKK,

four dominant reflections were observed: at  $2\theta = 18.5^\circ$  (110),  $20.6^\circ$  (111),  $23.0^\circ$  (200), and  $28.7^\circ$  (211) (The numbers in parentheses correspond to the Miller indices of the crystal planes<sup>2</sup>). To the best of our knowledge, the crystal diffraction assignments for the WAXD of TPI has not been reported in the literature. The 7/3 and 5/5 PEKK/PI blends showed X-ray peaks characteristic of both PEKK and TPI, which supports the conclusion from the DSC study that both polymers may crystallize in these blends. The WAXD pattern of the 25/75 PEKK/TPI blend is similar to that of the pure TPI, which supports the earlier conclusion that PEKK crystallization was completely suppressed in that blend.

The dynamic mechanical behavior of the melt crystallized PEKK/TPI blends in the glass transition region is shown in Figure 11. The  $G'$  data show only a single glass transition process for each of the blends, although the transition became broader as the TPI concentration increased. A single  $\tan \delta$  peak associated with  $T_g$  was also observed for each blend, though the  $\tan \delta$  peak was broader for these blends than for the amorphous blends shown in Figure 3. The  $\tan \delta$  peak for the 5/5 had a shoulder on the high-temperature side and that for the 25/75 PEKK/TPI blends was exceptionally broad, which suggests that those peaks may actually involve two overlapping processes. Crystallinity in the two TPI-rich blends was largely from the TPI, so that the amorphous phase should be richer in PEKK than the overall blend composition. Two distinct amorphous phases have been previously reported for miscible crystalline/amorphous blends of PEEK/PEI,<sup>23,24</sup> which was attributed to a pure PEI amorphous phase and a mixed interlamellar amorphous phase. The similarity of that blend with the PEKK/TPI blends suggests that something similar may have occurred in the TPI rich blends. Only a single amorphous phase containing both polymers



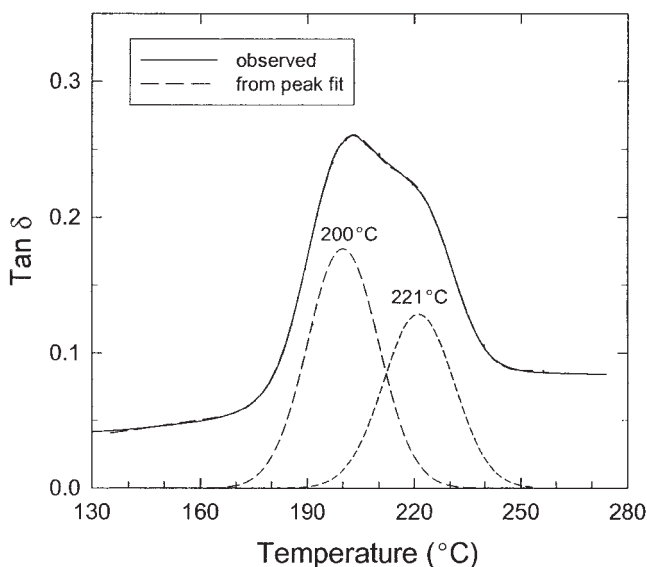
**Figure 10** WAXD patterns of melt crystallized PEKK/PI blends.



**Figure 11** Effect of blend composition on the dynamic mechanical properties of melt crystallized PEKK/PI blends: (a)  $G'$ , (b)  $\tan \delta$ .

was observed in the quenched, amorphous blends, see Figure 1, which further suggests that phase separation of a second amorphous phase may have occurred during melt crystallization of 5/5 and 25/75 blends.

Figure 12 shows  $\tan \delta$  data for the 7/3 PEKK/TPI blend crystallized isothermally at 250  $^{\circ}\text{C}$ ; it exhibited a peak at 202  $^{\circ}\text{C}$  and a shoulder at  $\sim 220^{\circ}\text{C}$ . These were deconvoluted into two Gaussian peaks (using PeakFit software, SPSS, Inc.) centered at 200 and 220  $^{\circ}\text{C}$ , as shown by the two dotted curves in Figure 12. Neither peak corresponds to the  $T_g$  of a pure PEKK or TPI phase. Based on the Fox equation fit of the DMA data



**Figure 12**  $\tan \delta$  of cold crystallized 7/3 PEKK/PI blends and peak fit result. The sample was crystallized isothermally at 250  $^{\circ}\text{C}$  for 1 h.

in Figure 2, the  $T_g$ 's represented by the deconvoluted  $\tan \delta$  peaks correspond to two amorphous phases with TPI mass fractions of 0.38 and 0.62. The data for the melt crystallized blends shown in Figures 11 and 12 indicate that during crystallization of the miscible blend, a second amorphous phase, rich in TPI forms, possibly in the crystalline interlamellar regions, similar to what was described for PEEK/PEI blends by Hsiao et al.<sup>24</sup>

## CONCLUSION

Blends of PEKK and TPI are miscible in the amorphous phase. If it is assumed that the blends exhibit lower critical solution temperature behavior, the miscibility extends to  $>400^{\circ}\text{C}$ .  $\chi$ -interaction parameters estimated from  $T_g$  data indicate that mixing becomes more favorable as the TPI concentration increases. This origin of the miscibility has not been determined, but shifts of the infrared vibrations of carbonyl and imide bonds indicate that there are no strong, specific intermolecular interactions responsible. Rather, it appears that mixing may be entropic in origin, in that a disruption of intramolecular interactions and packing of the two homopolymers increases the chain flexibility.

Mixing suppresses crystallization of both polymers, although crystallization of both can occur in the blends. The dominant crystal form was the major component, and the melting point of each was suppressed due to mixing of the amorphous phase. Melt crystallized blends also appeared to possess two different amorphous phases, one rich in PEKK and one rich in TPI. These may arise from different amorphous



phases within the interlamellar regions of the TPI and PEKK crystallites.

This work was supported by a Yankee Ingenuity grant from Connecticut Innovations, Inc (99CT007). We are also grateful to Oxford Performance Materials for supplying the polymers used in this research.

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