Miscibility of three different poly(aryl ether ketones) with a high melting thermoplastic polyimide

Bryan B. Sauer* and Benjamin S. Hsiao†
E. I. du Pont de Nemours and Company, Inc., Central Research and Development, and † Fibers Experimental Station, Wilmington, DE 19880, USA

Three poly(aryl ether ketone)s (PAEKs) were melt blended at 415°C with a new thermoplastic polyimide (N-TPI) composed of (4,4′bis(3-aminophenoxy) biphenyl) and pyromellitic dianhydride. The PAEKs studied were poly(aryl ether ether ketone) (PEEK), poly(aryl ether ketone ketone) (PEKK) and poly(aryl ether ketone) (PEK). Although chemically similar, these three show distinctly different behaviour when blended. We have concentrated on amorphous blends in this work so the difference in the crystallization rates of the PAEKs is not a factor in our determination of miscibility. It was found that PEEK was immiscible with N-TPI at all proportions. PEKK is the slowest crystallizing polymer and is miscible at most proportions, as evidenced by single glass transitions. PEK is miscible at N-TPI contents of less than ~50% and partially phase separated in the N-TPI rich blends. It is apparent that the higher percentage of ketone linkages in the PAEKs correlates with the higher degree of miscibility. Charge transfer complexation could also be a factor but this has yet to be explored.

(Keywords: thermoplastic polyimide; melt blending; miscibility)

Introduction

Semicrystalline, melt processable polyimides with high glass transition temperature, T_g (>220°C) have only become available recently, and studies of the phase morphology in melt-mixed blends of these are apparently non-existent. Many studies of solution blending of polyimide precursors (polyamic acids)[1-3] or solution blending of polyimides[2,4-10] have reported unique material properties in the cast films. Interesting examples include 'molecular composites' consisting of mixtures of rod-like and flexible polyimides[1].

Work on polyimide blends has been reviewed[11,12], including several examples where chemical interactions occur[11]. For many of the solvent-cast polyimide blends, apparent miscibility was due only to kinetic constraints which evolved due to the solvent-casting process[9,10,12]. For instance, for originally homogeneous solvent-cast blends of Ultem 1000 with polybenzimidazole[4,9], or Matrimid 5218 (Matrimid is another amorphous polyimide) with polyethersulphone[10], it was shown that heating at temperatures above the blend T_g leads to irreversible phase separation. Other examples of this type of metastable state below T_g have been reviewed[12]. Ultem 1000 ($T_g = 216$°C) is an amorphous polyimide that has been used in a variety of blending studies[4,5,7,12,13]. Ultem is only miscible with other polymers in rare instances. A well studied example is the miscible blend with poly(aryl ether ether ketone)[13] ($T_g \approx 150$°C).

The wholly aromatic new thermoplastic polyimide (N-TPI) studied here is different from the amorphous polyimides mentioned above. Ultem 1000 and Matrimid 5218 contain methyl groups which are known to lower thermal and oxidative stability. They are not
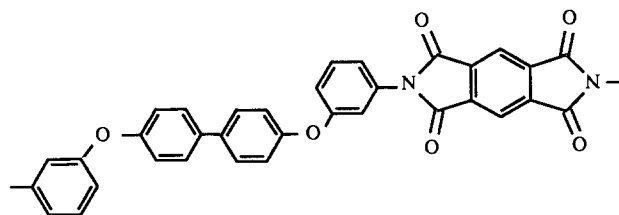
N-TPI

semicrystalline and therefore thermal and solvent resistance properties are diminished. N-TPI is composed of (4,4′ bis(3-aminophenoxy) biphenyl) and pyromellitic dianhydride (PMDA), has a T_g of ~250°C, a melting point of ~380°C and a moderate degree of crystallinity of ~20%. The N-TPI diamine unit, (4,4′ bis(3-aminophenoxy) biphenyl), imparts some flexibility to the polymer chain because of the ether linkages. Many similar all-aromatic polyimides are intractable. The melting point of N-TPI is lowered beneath the degradation temperature partly because of the meta linkages in the diamine, which presumably give rise to symmetry defects in the crystallites.

Thermal analysis studies of neat N-TPI has been reported recently[14]. Properties of poly(aryl ether ketone) (PEK)/N-TPI blends[15] and liquid crystalline polymer blends with N-TPI have been reported[15,16]. Presumably the N-TPI processability can be modified by addition of PEK, although not much information is given on the miscibility[15]. A related study[17] has shown that the processability of a poly(imide sulfone) was improved by the addition of another thermoplastic polyimide with a similar T_g.

We have melt blended three poly(aryl ether ketone)s (PAEKs) with N-TPI. The PAEKs studied were poly(aryl ether ether ketone) (PEEK), poly(aryl ether ketone

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* To whom correspondence should be addressed

ketone) (PEKK) and poly(aryl ether ketone) (PEK). Although chemically similar, the three PAEKs have distinctly different properties in the blends. We have concentrated on amorphous blend properties so the differences in crystallization rates between the PAEKs do not influence our conclusions on miscibility. The crystallization rates are in the order PEK $\approx$ PEEK $\gg$ PEKK. The fact that we do see significant differences in the blend miscibility, given the structural similarity of the three PAEKs, indicates the degree of complexity of the system. Besides the technological interest of developing these very high temperature melt-processable blends, there is a fundamental interest in understanding the driving forces for miscibility in high-temperature, semicrystalline polyimides.

Experimental

N-TPI with a weight average molecular weight, $M_w \approx 20\,000\ g\,mol^{-1}$ was supplied by Mitsui Toatsu and had the chemical structure given above. The PEEK (150G) and PEK (Victrex 220P) were supplied by ICI. Both PEEK and PEK contained wholly 1,4 linked aromatic moieties. The PEKK sample was an experimental polymer from DuPont and was effectively a copolymer with a mixture of 1,3 and 1,4 ketone linkages[18] in the ratio 0.4/0.6, respectively. The M_ws are believed to be around $30\,000\ g\,mol^{-1}$ for the PAEKs.

The blending temperatures were $415\pm5°C$ for the N-TPI/PAEK blends. All polymers were dried at $\sim T_g$ under vacuum for 24 h before melt blending. We have developed procedures for blending very small amounts of materials because of their limited availability. The blending method used consisted of pressing and shearing molten polymer films (0.1–0.5 g total) on a hot plate between sheets of Kapton® (release film), and then quenching. The sample was then folded and the process repeated 5–10 times. The blend was only exposed to $415°C$ for less than 1 min for the entire procedure in order to minimize decomposition. Owing to the small film areas ($A \approx 200\ mm^2$), relatively high shear forces can be applied. Very fast quenches ($\approx 300°C\,s^{-1}$) were applied by quenching between blocks of cold brass, so the first d.s.c. run always corresponded to a mostly amorphous film. At least 10 mg of material was used for d.s.c. to improve sensitivity. Two thermal analysis stations were used: a DuPont 9900 and a DuPont 2100. The d.s.c. heating rate was $20°C\,min^{-1}$ unless indicated otherwise.

Results and discussion

The T_gs for all three blend systems are given in *Figure 1*. T_g is defined as the centre point of the d.s.c. transition. *Figures 1A* and *2* indicate that the PEKK/N-TPI blends have single T_gs which roughly follow the Gordon–Taylor equation[19]:

$$T_g = (T_{g,1} + rT_{g,2}W_2/W_1)/(1 + rW_2/W_1) \tag{1}$$

where T_g is in kelvin, $r = \rho_1\Delta\alpha_2/\rho_2\Delta\alpha_1$ with ρ the density and $\Delta\alpha$ the change in thermal expansion coefficient from the solid to liquid state, and W is the weight fraction. It is generally necessary to use r as an adjustable parameter[20]. We have used $r = 0.65$ for all Gordon–Taylor curves in *Figure 1*.

There is a slight deviation from the solid curve in *Figure 1A* at weight fractions (W) of PEKK $\leqslant 0.3$. For $W > 0.5$ the T_gs of the amorphous blends are sharp and are comparable with those seen previously for amorphous

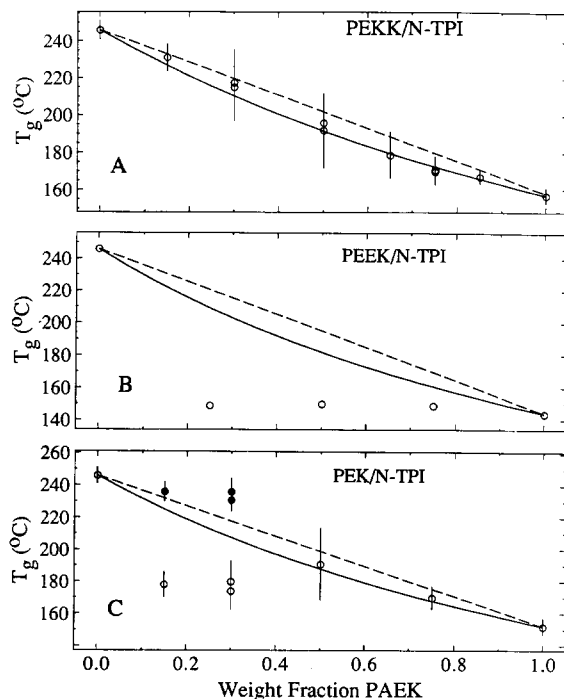**Figure 1** Glass transitions from d.s.c. results at $20°C\,min^{-1}$ vs. weight fraction of the different PAEKs indicated. The vertical bars represent the breadth of the glass transition as determined from the departure points from the d.s.c. baseline. The solid symbols in *Figure 1C* are for the higher temperature glass transition of the N-TPI rich phase (see text). The solid curves were calculated using the Gordon–Taylor equation and the dashed lines (linear average) are shown for comparison
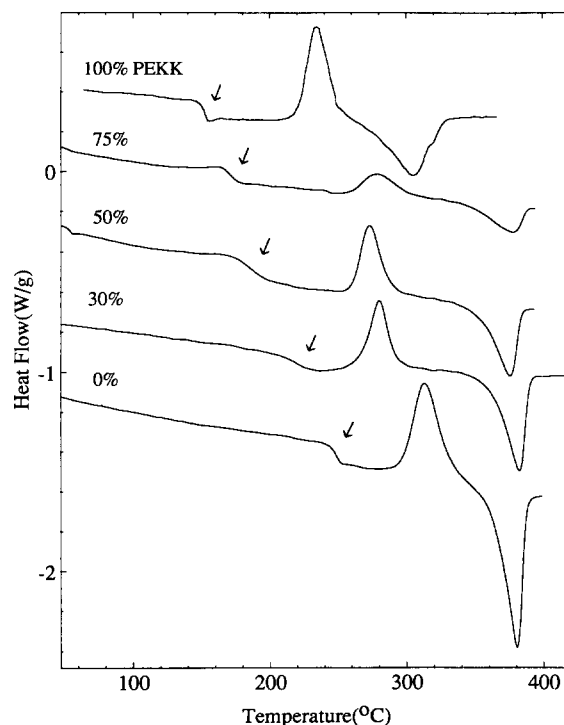

Figure 2 D.s.c. data taken at $20°C\,min^{-1}$ are shown for the different PEKK/N-TPI blend compositions. All samples were originally amorphous

PEEK/Ultem[13,21] and PEKK/Ultem[21] blends at all compositions. For $W = 0.3$ and 0.5, the T_gs become quite broad, as indicated in *Figure 1* by the vertical bars. This is likely due to a small amount of phase separation at these two concentrations.

The raw d.s.c. traces in *Figure 2* illustrate crystallization and melting behaviour of the originally amorphous blends. The PEKK crystallization rate is reduced significantly by addition of N-TPI due to a reduction in mobility (increase in T_g) and also the dilution effect. In fact, a clear PEKK exotherm is not observable even at 75% PEKK. The converse is true for N-TPI where crystallization is accelerated because of increased mobility due to lowering of the T_g by PEKK. The melting points for N-TPI in the blends are essentially the same as for neat N-TPI (380°C).

PEEK was found to be immiscible with N-TPI at all concentrations studied. Two T_gs were seen in each case, and were almost identical to those for the pure components (*Figure 1B*). D.s.c. data for a representative amorphous blend (*Figure 3*, 1st run) show that cold crystallization of the PEEK phase occurs at 190°C, which is below the T_g of the N-TPI phase ($T_{g,2}$). After $T_{g,2}$ the crystallization exotherm of the N-TPI phase is seen at 307°C and then separate melting endotherms of both phases are seen. For the second run in *Figure 3* the T_gs are broadened and weakened due to crystallinity of both PEEK and N-TPI in their respective phases.

For the N-TPI/PEK blends rather interesting behaviour is seen. A sharp T_g is seen for PEK weight fractions $(W) = 0.75$ (*Figures 1C* and *4*), while the T_gs are quite broad for $W = 0.5$. At $W = 0.3$ they separate into two individual sharp T_gs although the higher temperature T_g at 235°C is partially obscured by the crystallization peak at $\sim 210°C$ in *Figure 4*. The T_g at 235°C for the crystallized sample is shown more clearly in *Figure 5* for $W = 0.3$. Samples that were melt blended at different times give reproducible results for this composition. It should also be noted that neither of the T_gs at $W = 0.3$ are the same as those for the pure components (*Figure 1*), indicating some partial phase mixing.

The raw d.s.c. data for the PEK blends (*Figure 4*) indicate that the crystallization of PEK is hindered as is expected due to both the dilution effect and the increase in T_g (for the case where the blends are miscible). Crystallization temperature, T_c for pure PEK is 175°C, while for $W = 0.75$ and 0.5 it increases to 210 and 225°C, respectively. For the $W = 0.3$ blend, which is partially phase separated, T_c for the PEK phase decreases compared to the miscible $W = 0.5$ blend. This is because of the high mobility in the almost pure PEK phases in the $W = 0.3$ blend. For the $W = 0.75$ blend, the N-TPI
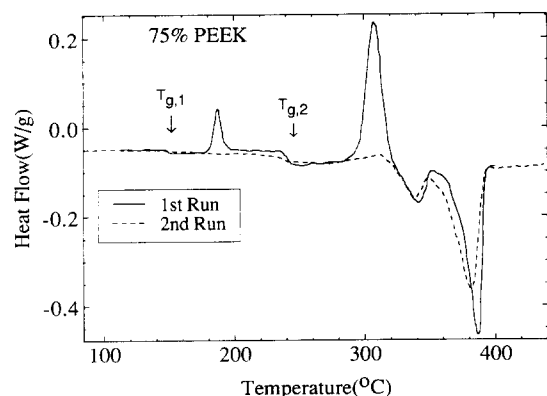

Figure 4 D.s.c. data for originally amorphous blends taken at 20°C min⁻¹ are shown for the different PEK/N-TPI blend compositions. No data are shown for pure amorphous PEK because of difficulties in quenching fast enough to prevent crystallization. For reference, T_g is estimated to be 156°C and T_c is 175°C for amorphous PEK
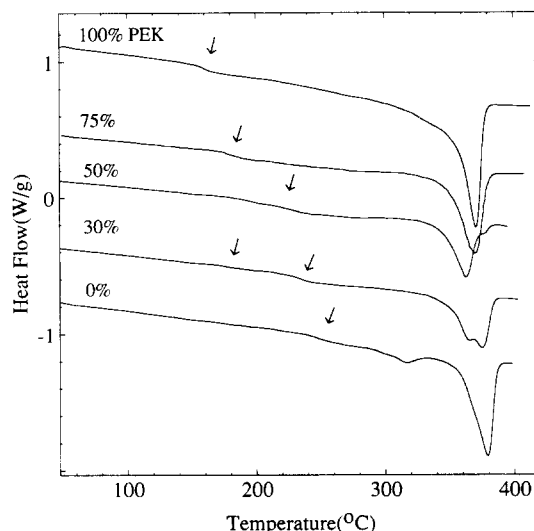
Figure 5 D.s.c. data for PEK/N-TPI blends taken at 20°C min⁻¹. The blends were crystallized by cooling from 410°C at 5°C min⁻¹

crystallization is reduced significantly, as indicated by the lack of a clear crystallization exotherm. For $W = 0.5$ and 0.3, the higher temperature T_c for the N-TPI phase stays constant at $\sim 307°C$, comparable to that for pure N-TPI. Individual melting endotherms for both PEK (370°C) and N-TPI (380°C) can be distinguished (*Figure 4*) for some of the blends.

The data for the semicrystalline blends are shown in *Figure 5*. Pure N-TPI was crystallized by annealing at 300°C for 10 min and the rest of the blends and neat PEK were crystallized in the d.s.c. pans by cooling from 410°C at $\sim 3°C min⁻¹$. The T_gs for the blends (and the pure semicrystalline materials) are broader and weaker

Figure 3 D.s.c. data taken at 10°C min⁻¹ are shown for an N-TPI blend with 75% PEEK. The first run is for an amorphous fast quenched sample and the second run is for a sample crystallized after cooling at 3°C min⁻¹ from 400°C
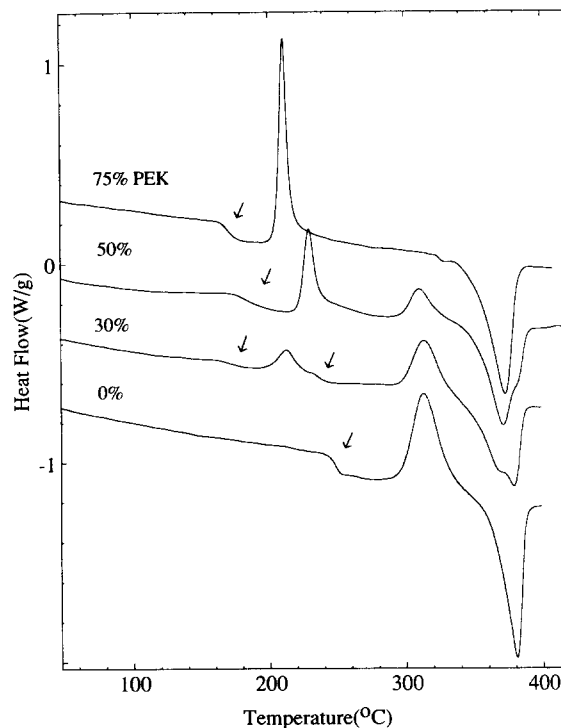
due to the constraining effect of crystallites on the amorphous regions. The data are consistent with the amorphous blend data considering the rather complicated effect of crystallinity in modifying the morphology in terms of both constraining effects and also depletion of the amorphous phase of the crystallized species.

It was found that PEEK was immiscible with N-TPI at all proportions. PEKK is the slowest crystallizing polymer and is miscible at most compositions, as evidenced by single T_gs. At some intermediate concentrations a broadened T_g indicates the presence of two phases with varying compositions. PEK is miscible at N-TPI contents of less than $\sim 50\%$. Significant phase separation is observed at the other compositions. The results indicate that increased miscibility of PAEKs with N-TPI correlates with the higher percentage of ketone linkages in the PAEKs. Polyimides are well known to form charge transfer complexes[22,23], which are known to be the driving forces for miscibility[24]. U.v.–vis. spectra of the PAEK/N-TPI blends could shed some light on the nature of these interactions. Although the processing window is rather narrow, it may be possible to construct a phase diagram for these materials in the future.

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