Ternary blends of sulphonated PEEK and two aromatic polyimides

Robert J. Karcha and Roger S. Porter*
Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, USA
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Immiscibility has been confirmed by noting two glass temperatures for blends of two polyimides, a poly(ether imide) and a poly(amide imide). Phase diagrams provided here show how this pair can be compatibilized to show only a single glass transition by the addition of sulphonated PEEKs.

(Keywords: ternary blends; PEEK; aromatic polyimides)

Introduction

In earlier papers[1,2], it was reported that sulphonated poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) was miscible over the entire composition range with each of two aromatic polyimides: a poly(ether imide) (ULTEM 1000) and a poly(amide imide) (TORLON 4000T). Spectroscopic investigations of these blends suggested that formation of electron donor–acceptor complexes between the sulphonated phenylene rings of the PEEKs and the *N*-phenylene units of the polyimides are responsible for this miscibility. In this communication, the immiscibility of the binary blends of these two polyimides and the facility of sulphonated PEEK to compatibilize them in certain compositions are reported.

Experimental

Materials studied and the sulphonation procedures employed have been reported previously[1,2]. The degree of sulphonation (i.e. moles of sulphur per polymer repeat unit) was calculated from the elemental sulphur/carbon ratio. Sulphonated PEEKs (SPEEKs) with degrees of sulphonation (X_s) of 0.53 and 1.00 were used.

Binary blends of the two polyimides were prepared by mixing dimethyl acetamide (DMAc) solutions ($c = 10.0$ mg ml^{-1}) of each polymer in the desired proportions; the solutions were stirred until homogeneous. All of the blend solutions were observed to be clear and amber in colour. Films of these blends were obtained by solution casting; solvent was removed by drying for 36 h at 155°C *in vacuo*. Ternary blends of the two polyimides and a SPEEK were prepared in a similar fashion, mixing DMAc solutions ($c = 20.0$ mg ml^{-1}) of each of the three polymers in the desired proportion and stirring at room temperature until homogeneous. All ternary solutions were clear and amber in colour. Solvent was removed from cast films of the blends by drying for 24 h at 100°C *in vacuo*. The temperature of the oven was then gradually raised to 180°C, where the samples were held for an additional 24 h to remove any remaining solvent. All blend samples were stored in a vacuum desiccator over calcium sulphate until analysis.

The glass transition temperatures (T_gs) of the blends were determined by d.s.c. using a Perkin-Elmer DSC-4. Samples (5–12.5 mg) were scanned at 20°C min^{-1} under nitrogen to an upper temperature limit controlled by the thermal stability of the polymers [350°C for the poly(ether imide)/poly(amide imide) (PEI/PAI) binary blends, 325°C for all the SPEEK binary and ternary blends]. All samples were scanned twice to allow for the removal of absorbed water; results were determined from the second scan.

Results and discussion

Cast films of the binary PEI/PAI blends were visibly cloudy; d.s.c. analysis of the blends revealed two T_gs, approximately equal to those of the pure component polymers (*Table 1*). The immiscibility of binary polyimide blends seen here has also been reported for other polyimides[3,4].

The ternary phase diagrams for the $X_s = 0.53$ and 1.00 SPEEK polymers are shown in *Figures 1* and *2*, respectively. In both ternary systems, several compositions possess only one T_g, indicating the compatibilizing effect of the SPEEK. For the SPEEK ($X_s = 0.53$) system, samples which exhibited one T_g were composed of $\geqslant 60$ wt% SPEEK or $\geqslant 50$ wt% PEI; none had >15 wt% PAI. Compositions with >15 wt% PAI exhibited two separate and distinct T_gs. This behaviour is understood in light of the relative number of electron donor moieties in the polyimides[2]. For a given weight, PAI possesses 3.06 times as many *N*-phenylene rings as

Table 1 Glass transition temperatures of PEI/PAI blends

PAI weight fraction	T_g (°C)
0.00	218
0.25	217, 273
0.50	216, 274
0.75	214, 274
1.00	273

*To whom correspondence should be addressed

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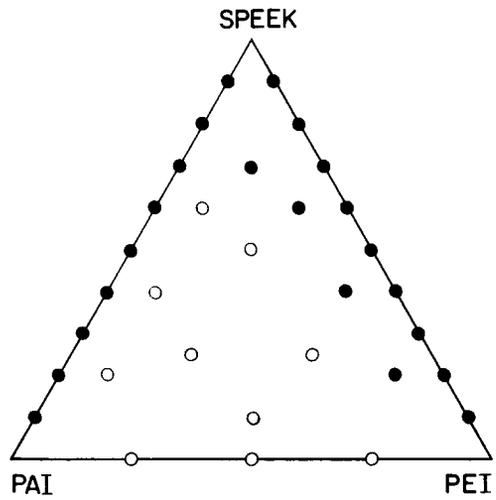

Figure 1 Phase diagram for the PAI/SPEEK/PEI ternary system ($X_s = 0.53$). Compositions showing (●) one and (○) two T_gs

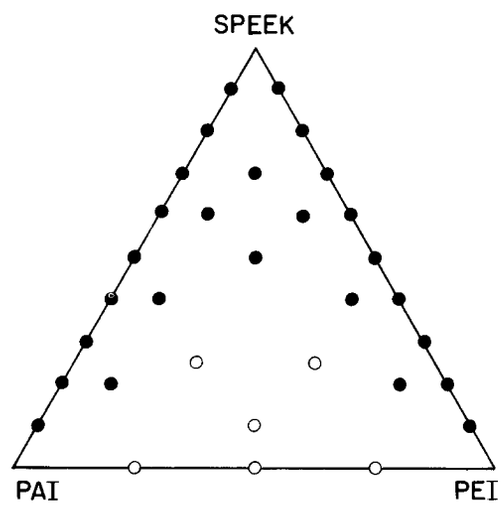

Figure 2 Phase diagram for the PAI/SPEEK/PEI ternary system ($X_s = 1.00$). Symbols as in *Figure 1*

does PEI, and is capable of forming a larger absolute number of electron donor–acceptor complexes, even at a PEI/PAI weight fraction as low as three. Thus, it was not unexpected that the PAI-rich compositions for which the SPEEK weight fraction was less than or equal to the weight fraction of both polyimides exhibited two glass transitions.

For the SPEEK ($X_s = 1.00$) ternary system, the region of compositions exhibiting a single T_g increased at the expense of the two-phase region, compared to the SPEEK (0.53) system. This indicates that the more highly sulphonated polymer is more effective as a compatibilizing agent, as expected, since the SPEEK (1.00) has a greater number of electron accepting moieties per unit weight (1.69 times as many) than the SPEEK (0.53). Four compositions exhibiting two T_gs in the SPEEK (0.53) system were found to have only one in the SPEEK (1.00) system. Only those compositions for which the SPEEK fraction was less than or equal to the weight fractions of both polyimides had two T_gs. For these compositions, SPEEK concentrations were insufficient to completely compatibilize the sample.

In both ternary systems, most of the blend samples were transparent; some of these compositions were found to have two separate T_gs. The condition of transparency cannot be assumed to be absolute proof of a single-phase system; in the two-phase, transparent samples, the indices of refraction of the two phases present must have been sufficiently close so that scattering was not observed by eye.

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