

# Partially Miscible Blends Based on a Polyarylate and Poly(trimethylene terephthalate)

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Received 22 April 2003; accepted 7 November 2003

**ABSTRACT:** The miscibility of blends of a polyarylate (PAr) with poly(trimethylene terephthalate) (PTT) was investigated in the whole composition range by DSC measurements. With the exception of the 90/10 composition, which was fully miscible, the blends showed partial miscibility,

and contained a nearly pure PTT phase and a PAr-rich phase with 18% PTT. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1559–1561, 2004

**Key words:** blends; miscibility; thermoplastics

## INTRODUCTION

It is known that immiscibility of the components is the norm in polymer blends, and that it usually leads to poor mechanical properties. Partial miscibility, however, through the presence of at least one component in each of the two phases of the blend, often leads to mechanical compatibility. In the case of miscible polymers, compatibility is obvious. Therefore, the production of new miscible or partially miscible polymer blends is an interesting research objective.

Poly(trimethylene terephthalate) (PTT) is a thermoplastic polyester that has been recently commercialized. As a consequence, few PTT blends have been studied to date. Thus, to our knowledge, only blends with second components such as poly(etherimide),<sup>1,2</sup> polycarbonate,<sup>3,4</sup> poly(ethylene terephthalate) (PET),<sup>5–8</sup> poly(butylene terephthalate) (PBT),<sup>6,8,9</sup> poly(ethylene naphthalate),<sup>10,11</sup> poly(trimethylene naphthalate),<sup>12</sup> and a linear aliphatic polyketone<sup>13</sup> have been studied.

PTT has a chemical structure intermediate between that of PBT and that of PET. Therefore, considering miscible or partially miscible PTT blends, those based on both PBT and PET should be taken into account. Several blends based on both PBT and PET have been found to be either miscible<sup>14–20</sup> or partially miscible,<sup>21–26</sup> and some of them have been commercialized. For instance, blends of PBT with a copolyester of bisphenol A and 50/50 isophthalic/terephthalic acids (PAr) are miscible,<sup>14</sup> and PET/PAr blends are partially miscible.<sup>21</sup> Therefore, the existence of some miscibility

in PAr/PTT blends is probable but, to our knowledge, these blends have not been studied.

In this work, the miscibility of PAr/PTT blends was studied across the entire composition range. The blends were prepared by melt mixing, and the miscibility was analyzed by means of the thermal transitions determined by differential scanning calorimetry (DSC).

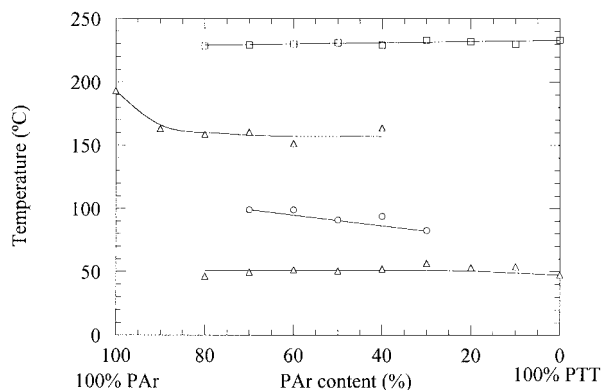
## EXPERIMENTAL

The polymers used in this work were PTT (Corterra CP509200), kindly supplied by Shell Chemical (Houston, TX), and PAr (U-Polymer, Unitika Ltd., Tokyo, Japan). PTT has an viscosity-average molecular weight  $M_{\eta} = 69,000$ , determined by viscosimetry in a phenol/tetrachloroethane mixture (50% by weight) at 20°C. PAr had number- and weight-average molecular weights of  $M_n = 21,500$  and  $M_w = 51,500$ , respectively, determined by GPC in tetrahydrofuran at 30°C.

Before blending, PTT was dried for 4 h at 150°C in a circulating-air oven, and PAr for 24 h at 80°C in vacuum. The blends were obtained by melt mixing in a Collin ZK25 corotating twin-screw extruder-kneader (Ebersberg, Germany) at 30 rpm. The barrel temperature varied from 260 to 315°C as the PAr content in the blends increased because of its high viscosity. The rod extrudates obtained were cooled through a water bath and pelletized.

To analyze the phase structure and the crystallization-melting behavior of the blends, a Perkin-Elmer DSC-7 calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) was used at a heating rate of 20°C/min in a nitrogen atmosphere. Two heating scans were carried out from 15 to 280°C. In the first scan, the thermal history was deleted, and in the second scan the thermal transitions were determined. Cooling be-

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**Figure 1** Melting ( $\square$ ) and crystallization ( $\circ$ ) temperatures of PTT, and  $T_g$  values ( $\triangle$ ) of the PTT- and PAr-rich phases of PAr/PTT blends versus PAr content.

tween both heating scans was carried out at the maximum speed provided by the calorimeter. The glass-transition temperatures ( $T_g$ ) were determined at the midpoint of the transitions, and the crystallization and melting temperatures ( $T_c$  and  $T_m$ , respectively) at the maxima of the corresponding peaks. The melting enthalpies ( $\Delta H_m$ ) were determined from the area of the peaks.

## RESULTS AND DISCUSSION

All the blends were practically transparent in the melt state. In the solid state, the PAr/PTT (90/10) blend was also transparent, but the 80/20 composition was translucent, and the remaining compositions opaque. The different transparency levels of the blends in the solid state are probably attributable to change of the crystallinity of PTT. The transparency of the 90/10 blend is not fully indicative of miscibility because biphasic blends appear transparent if the refractive indices of both components are very similar,<sup>27</sup> and the refractive index of PTT in the literature<sup>28</sup> (between 1.59 and 1.61) and that calculated<sup>29</sup> by group contribution (1.58) are similar to that calculated for PAr (1.62). The transparency of the blends in the melt state also indicates miscibility. However, given that the refractive indices of melt PTT and PAr are unknown, the miscibility in the melt state cannot be inferred.

The miscibility level of the blends in the solid state was studied by DSC. Figure 1 shows the  $T_g$  values (triangles),  $T_c$  values (circles), and  $T_m$  values (squares) of the blends as a function of composition. As can be seen, a single  $T_g$  was observed in the 90/10 blend. This indicates miscibility, or at least that the size of a hypothetical dispersed phase is smaller than the wavelength of the visible light.<sup>27</sup> Reasons for the miscibility of this blend composition are stated later. As can also be observed, in the rest of the blends, two  $T_g$  values located between those of the neat components ap-

peared, which indicated the presence of two amorphous phases in the blends. The low-temperature  $T_g$  was similar to that of PTT, indicating the presence of a practically pure PTT phase. The high-temperature  $T_g$  was at 163°C in the 90/10 blend and, when observed, it appeared at almost the same temperature (157°C) in the rest of the blends. It could barely be observed in the 50/50 and 40/60 compositions at the same temperature, and could not be observed in the other blends because of the small intensity of the PAr  $T_g$ . This high-temperature  $T_g$  was clearly below that of pure PAr (192°C), indicating the presence of some PTT in the PAr-rich phase and partial miscibility. This must also occur in PAr-poor blends because, at these compositions, the large PTT presence ensures the partial presence of PTT in the PAr-rich phase.

The constancy of the  $T_g$  of the PAr-rich phase of the blends indicates that its composition was almost constant and that there was a maximum amount of PTT miscible in PAr. This maximum amount can be estimated by means of the Fox equation<sup>30</sup>

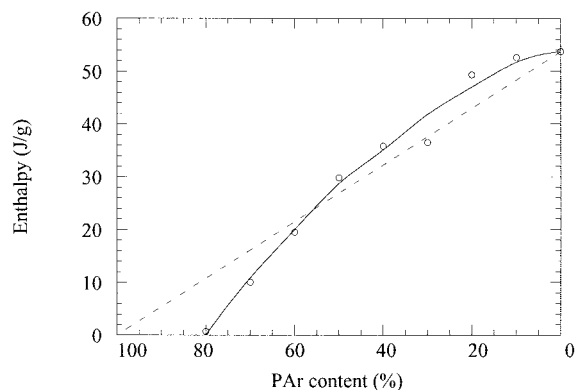
$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

where  $T_g$  is the glass-transition temperature of the PAr-rich phase;  $T_{g,1}$  and  $T_{g,2}$  are those of PTT and PAr, respectively; and  $w_1$  and  $w_2$  are the respective weight fractions in the PAr-rich phase. When the experimental  $T_g$  value of 157°C was used in eq. (1), the calculated PTT presence in the PAr-rich phase was 18%.

In the 90/10 blend, a single  $T_g$  was seen. The lack of low-temperature  $T_g$  could be attributed to the low PTT level. However, besides the single  $T_g$ , there is another reason that supports the miscibility of this composition; taking into account that 18% PTT was mixed in the PAr-rich phase of the rest of the blends, 10% PTT has to be fully miscibilized in a blend with 90% PAr. Thus, it is concluded that the 90/10 blend has a single amorphous phase.

The phase behavior of these PAr/PTT blends is qualitatively comparable to that found in PAr/PET blends.<sup>21</sup> This is because, as in this study, the PAr-rich blends (80/20 and 90/10 compositions) were miscible, and in the rest of the blends, a pure PET phase and a partially miscibilized PAr phase were observed. Both PAr/PET and PAr/PTT blends differ from the fully miscible PAr/PBT blends.<sup>14</sup>

As can also be seen in Figure 1, cold crystallization occurred in the blends with PTT contents between 70 and 30%. This indicated that these blends crystallized only partially during cooling in the calorimeter, and that the blends very rich in PTT crystallized fully. As can also be seen, the crystallization temperature ( $T_c$ ) increased slightly with the PAr content, indicating that PAr made the cold crystallization of PTT slower. As



**Figure 2** Melting heats of PAr/PTT blends versus PAr content.

can also be seen, the melting temperature of PTT was almost constant with composition, indicating the absence of reactions between the blend components.

Figure 2 shows the melting enthalpy of the blends as a function of composition. As can be seen, in PTT-rich blends, slight positive deviations with respect to linearity were seen. This indicated that, at these compositions in the presence of PAr, PTT crystallized slightly more than in the neat state. This is not an unexpected result, given that the incorporation of PAr also led to greater crystallinity in blends with both PBT<sup>14</sup> and PET,<sup>31</sup> despite the miscible and partially miscible nature, respectively, of the blends. The decrease in the melting enthalpy below linearity in PAr-rich blends is attributed to the small amount of unmiscibilized, and thus crystallizable, PTT at these PAr contents.

## CONCLUSIONS

The 90/10 PAr/PTT blend appears as completely miscible, as inferred from its transparency, single  $T_g$ , and ability of PTT to be miscible in PAr up to 18%. The rest of the PAr/PTT blends constitute, besides a crystalline PTT phase, an almost pure PTT amorphous phase and a PAr-rich phase containing 18% PTT. The presence of

PAr makes the crystallization of PTT slower, but allows PTT to crystallize to a slightly greater extent.

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