Completely Miscible Blend of Poly(trimethylene terephthalate) with Poly(ether imide)

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ABSTRACT: Miscibility in the amorphous region was discovered for the first time in a binary blend system composed of crystalline low- T_g poly(trimethylene terephthalate) (PTT) and amorphous high- T_g poly(ether imide) (PEI). The blends of all compositions exhibit a distinctly single T_g , whose temperature as well as broadening extent is dependent on the composition. Additionally, homogeneous phase morphology in the blends was also substantiated using optical and scanning electron microscopy results. Interestingly, discontinuity (a cusp near volume fraction of 0.5) and general asymmetry were noted in the T_g -composition relationship for this miscible blend system. This phenomenon is interesting but quite puzzling. The peculiar T_g -composition behavior in the miscible PTT/PEI blends was analyzed using a classical free-volume approach, where uneven contributions to the polymer mixtures' free volume were partially attributed to the vastly different T_g 's and free volumes of these two constituents. Furthermore, it was found that varying degrees of blend's T_g broadening with respect to the composition might have also contributed to the noted discontinuity. The asymmetry was partially attributed to the PTT crystalline domain-induced variation in the intermolecular interactions.

KEY WORDS Miscibility / Polymer Blends / Poly(trimethylene terephthalate) (PTT) / Poly(ether

imide) (PEI) / Asymmetry / Free Volume /

Thermoplastic polyesters are an interesting class of semicrystalline polymers that have attracted extensive studies. Of these, commercially important poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) are two of the most studied polyesters. On the other hand, poly(propylene terephthalate) (PPT), also called poly(trimethylene terephthalate) (PTT) and a semicrystalline polyester with emerging applications, is a relatively new comer as engineering plastics. Note that PTT possesses a structural repeat unit differing from either PET or PBT only by one methylene group.

Miscibility in blend systems comprising polyestesrs and polyimides (or polyetherimides) have in the past years attracted extensive interests. Especially, blends comprising a semicrystalline polymer and an amorphous polymer can offer potential synergistic balances in properties. For examples, poly(ether imide) (PEI) is an engineering thermoplastic polymer that is known for thermal stability, toughness, and high $T_{\rm g}$, and other excellent mechanical properties. PEI, however, is amorphous, and becomes susceptible to common organic solvents. It is expected that if PEI is blended with a semicrystalline polymer and forms a miscible blend, miscibility can offer greater chances of property balance for specific applications. In recent years, a significant amount of research has been directed at gaining better understanding of miscibility, compatibility, morphology, properties, and processing of the blend systems comprising of these polyesters and other polymers. $^{1-8}$

miscibility between imide-Investigation on containing polymers and carbonyl-containing polyesters has been undertaken by for a long time. PTT, as a relatively new engineering plastic, has not been a subject of miscibility studies, although studies related to its melting and crystalline morphology have appeared.^{9–18} The objective of this study was to explore the phase behavior of a new blend pair comprising amorphous PEI with semicrystalline PTT and factors that may influence phase behavior. Certain crystalline/amorphous blend systems have been shown to exhibit asymmetry in their $T_{\rm g}$ -composition relationships, which essentially suggests that $T_{\rm g}$ dependence on the blend composition is varying within the composition range. This behavior has been attributed to uneven contributions from the free volume differences between the amorphous vs. semicrystalline polymer constituents.^{1, 2, 19, 20} Other possible mechanisms and interpretations were examined and proposed in this study.

EXPERIMENTAL

Materials

Poly(trimethylene terephthalate) (PTT), also called

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poly(propylene terephthalate) (PPT), was synthesized and supplied as a research-grade resin with no additives by Industrial Technology Research Institute (ITRI, Taiwan). Poly(ether imide) (PEI) was a research-grade resin in pellet form (Polysciences, Inc., USA, with $M_{\rm w} = 30000 \,{\rm g}\,{\rm mol}^{-1}$). Due to the asymmetry in the chemical structure, PEI is amorphous, but has a high $T_{\rm g}$ of 215.6°C owing to the aromatic/imide rings in backbone chains. The chemical structures of the repeating units of PEI and PTT are shown as following:



To avoid complicating effects from solvents on true phase behavior of the blends, direct melt-blending (at ca. 280-290°C) was used in sample preparation. Care was exercised to control the temperature of blend to avoid heating-induced degradation. Furthermore, to ensure that good mixing could be completed in the shortest time duration possible, the neat polymers (originally in pellet forms) were pulverized into fine particles and dried prior to being blended. To ensure that good mixing was achieved, small sample sizes of about 1-2 g were used in each batch. A specially designed aluminum mold with a small mixing chamber (ca. 2-gram capacity) was used for the blending purposes. Controlled heating was provided by placing the mold on a hot stage, and blending/mixing was accomplished by careful manual stirring. For small quantities of mixtures at the blending temperature of 280°C, the viscosity could be comfortably maneuvered by hand-stirring. During the entire course of mixing, a continuous purge of dry nitrogen was maintained over the mixing chamber to minimize degradation/oxidation. Temperature was controlled and monitored using a thermocouple inserted in the mold.

Apparatus

The glass transition (T_g) temperatures, crystallization, and melting temperatures of the blend samples of various compositions were measured with a differential scanning calorimeter (Perkin–Elmer DSC-7) equipped with a coolant-circulated intracooler. All measurements of T_g , apparent cold-crystallization, and melting transitions were made at a scan rate of 20°C min⁻¹ in the range of $0-260^{\circ}$ C. The reported T_g values were taken as the onset of the glass transition (*i.e.*, change in the specific heat) in the DSC thermograms. Specific indications are noted if mid-point values of T_g (instead of the on-set) were used. The values of $T_{c,c}$ (cold-crystallization) and apparent melting point (T_m) were taken as the peak of the exotherms or endotherms.

polarized-light optical microscope (Nikon Α Optiphot-2 POL) with UFX-DX automatic exposure was used to examine and confirm the phase structure of the polymer mixtures. Samples for microscopy were placed between micro glass slides, then heated and gently pressed by hands to thin films on the microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer). To further confirm the phase homogeneity, the morphology of the fracture surfaces of the blends (compression-molded to films) was also examined using a scanning electron microscope (SEM) (JEOL, Model JXA-840). Thicker blend films (0.3 mm in thickness) for SEM were prepared by compression molding. They were then fractured across the thickness after dipping into liquid nitrogen; subsequently, the fractured surfaces were sputter-coated with gold for SEM characterization.

RESULTS AND DISCUSSION

Figure 1 shows the DSC thermograms for the PTT/PEI blends with increasing PEI fraction in compositions (traces representing 11 different compositions investigated). There is clearly only one single T_g (onset positions indicated with arrow marks) in each of the blend compositions. Table I also lists the onset T_{g} , midpoint values of $T_{\rm g}$, and extents of $T_{\rm g}$ broadening. The DSC traces show that both the blend T_g 's and the peak location $(T_{c,c})$ of cold crystallization exotherm (above respective T_{g}) of the crystallizing PTT component in the blends increase monotonously, though not fully proportionally, with increase of PEI content in blends. We will discuss the asymmetry of $T_{\rm g}$ variation with composition in later sections of this paper. Note that for the blends of low PEI contents (*i.e.*, PTT-rich), there exists a stagnant trend that an increase in the PEI contents results in only minimal increase in blend's $T_{\rm g}$. In other words, the T_g 's of two blend compositions, i.e., 90/10 and 80/20 (PTT/PEI) blends and all compositions in-between, closely resemble that of neat PTT $(T_g = 39.7^{\circ}C)$. In the same range of PTT-rich compositions, however, the $T_{c,c}$ of the PTT component in the blends is also slightly elevated with increasing PEI contents. But similarly, the extent of $T_{c,c}$ elevation is smaller in this PTT-rich range in comparison with the composition range in the middle (70/30, 60/40, and



Figure 1. DSC traces for quenched PTT/PEI blends of different compositions (wt. ratios), as indicated.

 Table I. Glass transition temperatures and breadth of transition for the PTT/PEI blend

PTT/PEI	$T_{g(onset)}$	$T_{g(mid-point)}$	Transition breadth
wt. ratios	°C	°C	°C
100/0	39.7	42.3	5.1
90/10	40.6	43.2	5.1
80/20	43.6	45.7	4.2
70/30	48.2	60.4	24.5
60/40	63.4	77.5	28.2
50/50	85.4	98.5	36.1
40/60	94.4	111.4	34.0
30/70	134.0	149.5	30.9
20/80	151.8	168.5	33.3
10/90	181.6	192.3	21.4
0/100	215.6	219.4	7.53

50/50, etc). Influence of the PEI component on the blend T_g and $T_{c,c}$ is seen to be qualitatively similar. For high PEI contents in blends, a drastically different trend is observed in that increase in PEI contents in the blends leads to T_g increase as well as variation of T_g broadening. In addition, $T_{c,c}$ is seen to be elevated more sensitively with respect to increasing PEI contents in the blends.

Figure 2 shows blends' apparent $T_{\rm m}$ and peaks of cold crystallization ($T_{\rm c,c}$) as a function of blend compositions. Slight but distinctly visible depression of the apparent melting point of the PTT component in the blends by the amorphous PEI constituent is obvious. In addition, it is of interest to note here that although there is only slight increase of blends' $T_{\rm g}$ with



Figure 2. Apparent melting points (T_m) and coldcrystallization peak temperatures $(T_{c,c})$ of the PTT component in the blends.

the PEI content in the range of PTT-rich compositions, the peak location of cold-crystallization exotherm rises considerably with increasing PEI content. The changes in $T_{c,c}$ is usually taken as an indication that there is intimate molecular interaction between the crystallizing PTT and stiffer but amorphous PEI polymer chain segments, which cause chain stiffening of PTT chain segments and result in elevation of cold-crystallization temperatures.

The PTT/PEI blends of all compositions, when quenched from above melt, appeared visually transparent and homogeneous; furthermore, the blends of all compositions were examined using an optical microscope. Figure 3 shows the optical microscopy result for as-quenched PTT/PEI blends: (A) 90/10, (b) 70/30, (C) 50/50, and (D) 10/90 (wt. ratios). The optical microscopy result revealed that the all blends (quenched to a fully amorphous state) contained a phase morphology that was homogeneous and free of any discernible domains (graphs not shown here for brevity). Furthermore, the blends were placed on a microscopy heating stage where the temperature was raised gradually in order to observe whether or not there existed a cloud-point transition. The result showed that no upper or lower critical solution point (UCST or LCST) phenomenon was observed up to above 350°C, beyond which the samples gradually started to chemically degrade and it was no longer possible for discerning any physical transitions.

In addition, SEM provides a greater magnification on revealing the phase morphology. Figure 4 shows complete homogeneity and lack of any discernible domains in the fractured surfaces of the quenched blends (show-

Miscible Blends of PTT with PEI



Figure 3. Optical microscopy result revealing morphology homogeneity in as-quenched PTT/PEI blends: (A) 90/10, (b) 70/30, (C) 50/50, (D) 30/70, and (E) 10/90 (wt. ratios).

ing four compositions, as indicated on the graphs) examined using SEM. The SEM result and related morphology evidence also confirmed the claimed miscibility in the amorphous region of the PTT/PEI blend system.

The evidence so far is quite clear to show that PTT/PEI is a miscible binary pair within the full composition range, although the peculiar asymmetry in molecular/chain interactions and apparent discontinuity (a jump-like cusp) in the T_g -composition relationship may require some further analysis. Having confirmed that the blends were indeed thermodynamically misci-



Figure 4. SEM graphs showing complete homogeneity and lack of any discernible domains in the fractured surfaces of the quenched PTT/PEI blends: (A) 90/10, (b) 70/30, (C) 50/50, (D) 10/90 (wt. ratios).

ble, the peculiar characteristics in the $T_{\rm g}$ -composition behavior of the blends were further analyzed. Figure 5 shows the $T_{\rm g}$ (onset) of the blends plotted as a function of composition (weight fraction) of PEI. A pronounced asymmetry clearly exists in the $T_{\rm g}$ -composition curve. Qualitatively speaking, at low volume fractions of PEI in the PEI/polyester blend, the contribution of PEI in raising the blend's T_{g} is minimal; on the other hand, at higher volume fractions of PEI in the blends, the contribution of the PEI component in raising the blend's $T_{\rm g}$ is more significant. The asymmetry in the trend of variation of the data illustrates the dramatically uneven contributions of the polymer components to blend's $T_{\rm g}$. Furthermore, there exists a discontinuity (cusp) in the otherwise continuous, though asymmetric, trend of variation. The cusp is located at the blend composition of $\phi_{2,c} = 0.619$ (or $\omega_{2,c} = 0.6$), where the subscript "2" indicates the non-crystallizing (i.e., amorphous) PEI.



Figure 5. T_g (onset values) *vs.* composition for the PTT/PEI blend. The data are compared with the Fox equation and the Kovac's equation, respectively.

Note the densities of PTT^{21} and PEI are: 1.377 g cm⁻³ and 1.27 g cm^{-3} , respectively. A literature survey reveals that a few other miscible blend systems containing one crystalline polymer and amorphous polymer can also exhibit such behavior.^{1,2} Experimental procedures of quenching were conducted in careful manners that the amount of initial (residual) crystalline portion was negligible in the blend samples for $T_{\rm g}$ measurements. As the initial crystallinity was totally suppressed in the quenched blend samples prior to the T_{g} measurements, it should not be a factor influencing the true $T_{\rm g}$ of the blend samples. Thus, the cusp discontinuity as well as the asymmetric $T_{\rm g}$ -composition relationship in this PTT/PEI system is not due to residual crystallinity in the samples. Blend samples were heated to 250° C (well above the $T_{\rm m}$) for extended time (4 h) before quenching to ensure complete erasure of any trace/residual crystallinity in the blend sample. DSC characterization performed on these samples revealed same values of $T_{\rm g}$ and $T_{\rm c.c.}$ The fact suggests that crystallinity was not a factor for the asymmetry or discontinuity in the $T_{\rm g}$ -composition relationship.

Apparently, the figure shows that the classic Fox equation:²² $1/T_g = (\omega_1/T_{g1} + k\omega_2/T_{g2})$ does not at all fit the T_g -composition relationship for the PTT/PEI blend system (in quenched amorphous state). An overprediction by the Fox model in the entire blend composition range is apparent, even not mentioning the specific cusp discontinuity or general asymmetry in the experimental T_g -composition relationship. The Kovacs model²³ was used again to explain the discontinuity in the T_g variation trend. According to the theory, if the difference of T_g between the two component polymers

Table II. Comparisons of critical volume fractions and fitted g-values for three polyester/PEI blend systems

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Blend systems	$T_{g,1}/^{\circ}C$	$\omega_{2,c}$	g
PTT/PEI	40	0.6	-0.025(this study)
PBT/PEI ^a	34	0.7	-0.01
PET/PEI ^b	75	0.6	-0.0025
^a ref.1. ^b ref.2.			

 $(T_{g2}-T_{g1})$ is larger than 50°C, there is a critical temperature (T_c) where the contribution of free volume of the polymer with the higher T_g is zero. The corresponding critical temperature $(T_c = 109.4^{\circ}C)$ and PEI volume fraction $(\phi_{2,c})$ at which this occurs were estimated as following:

$$T_{\rm c} = T_{\rm g2} - (f_{\rm g2}/\Delta\alpha_2) \tag{1}$$

$$\phi_{2c} = f_{g2} / [\Delta \alpha_1 (T_{g2} - T_{g1}) + f_{g2} (1 - \Delta \alpha_1 / \Delta \alpha_2)]$$
(2)

where f_g is the free volume fraction at the glassy state and $\Delta \alpha_i$ is the thermal expansion coefficient difference of the respective constituent polymer between the glassy and rubbery states. Below T_c , the blends' T_g is given by the

$$T_{\rm g,blend} = T_{\rm g,1} + (\phi_2 f_{\rm g2} + g\phi_1 \phi_2)/\phi_1 \Delta \alpha_1 \qquad (3)$$

In this equation, g is the parameter of interactions between the components and can be related to the excess volume. The relationship is defined as $g = V_e/(V\phi_1\phi_2)$, where V is the molar volume of the blend and $V_{\rm e}$ the excess molar volume. The sign of the interaction parameter g depends on that of the excess volume $(V_{\rm e})$. A negative value means that the interactions between the dissimilar components (i.e., PTT-PEI) are stronger than or at least equal the average of those between the same PEI or PTT molecules, and thus favorable for miscibility. The best-fitted value of g was determined to be -0.025. The calculated critical volume fraction (ϕ_1) was found at 0.495, which differed slightly with the experimental observation, suggesting reasonable agreement with some slight modeling deviation. The fact that the value of g is a negative suggests that the interactions between the blend components are about the same as the average molecular interactions within the polymer molecules of the respective neat components. This result is consistent with that obtained from the melting point depression discussed earlier. It would be interesting to compare the major characteristics among three know miscible pairs, PPT/PEI of this study, and PET/PEI, and PBT/PEI earlier documented in the literature. Table II shows the major comparisons. Similarity and consistence were found among these three miscible systems.

Figure 6 shows the glass transition breadth as a function of blend composition in the freshly quenched blend samples. The figure shows some interesting features of



Figure 6. Plot of broadening in glass transition breadth as a function of composition for the quenched (amorphous) PTT/PEI blend samples.

 $T_{\rm g}$ broadening variation with respect to compositions. For the blend compositions where PTT volume fractions are high (*e.g.*, $\omega_1 > 0.8$ or $\omega_2 < 0.2$), the freshly quenched PTT/PEI samples (*e.g.*, 90/10, 80/20) exhibited a relatively sharp $T_{\rm g}$ transition. On the other hand, as the PEI weight fraction in the blends increased beyond 0.2, the $T_{\rm g}$ transition breadth assumed a jumpincrease, reached a maximum, and then rapidly decreased again with further increase of PEI fraction in the blend. The maximum occurred at the blend composition near $\omega_{2,c} = 0.6$. The $T_{\rm g}$ breadth then rapidly decreases for the blend compositions where the PEI weight fractions are greater than 0.6.

The dramatic discontinuity in the $T_{\rm g}$ breadth with respect to compositions is apparent. Therefore, one may wonder how the transition broadening may influence the $T_{\rm g}$ -composition relationship if the mid-point values rather than the onset of T_g were used in analysis. Figure 7 shows T_g (mid-point of transition) of the blends plotted as a function of composition (weight fraction of PEI). The general asymmetry in the trend of $T_{\rm g}$ variation with respect to composition is still visible. However, the discontinuity cusp in Figure 3 (onset T_{g} vs. blend composition) no longer exists. Owing to the asymmetry, the figure shows that the Gordon-Taylor (G–T) equation:²² $T_{\rm g} = (\omega_1 T_{\rm g1} + k\omega_2 T_{\rm g2})/(\omega_1 + k\omega_2)$ either over-predicts (blend range of $\phi_2 < 0.5$) or underpredicts (blends with high PEI volume fractions, $\phi_2 >$ 0.5) the $T_{\rm g}$ -composition relationship. For the lower portion (PTT-rich blends) of the $T_{\rm g}$ -composition relationship, a G–T parameter of k = 0.30 was found to best fit the data, while for the upper portion (PEI-rich blends), a G–T parameter of k = 0.65 was obtained.



Figure 7. Mid-point values of $T_g vs$. composition for miscible PTT/PEI blend (The upper and lower portions of the T_g data are separately compared with the Gordon–Taylor equation).

Interestingly, similarly skewed $T_{\rm g}$ -composition relationship has also been reported for other crystalline/amorphous blend systems. For examples, blends of poly(ethylene oxide) (PEO, $T_g = -65^{\circ}C$) with poly(phenyl methacrylate) (PPhMA, $T_g = 115^{\circ}$ C) exhibit such an asymmetry in the $T_{\rm g}$ -composition curve.²⁴ Note that the T_g difference between these two constituents are 180°C, which is substantially greater than 50°C. That is, initially for the PEO/PPhMA blend at low PPhMA contents (i.e., PEO-rich, e.g., PEO wt% > 60), there exists a leveling trend in the T_{g} composition curve where an increase in PPhMA content does not seem to lead to substantial increase in the blend's $T_{\rm g}$. More steady increase of the blend $T_{\rm g}$ is observed only in the range of PPhMA-rich contents (PPhMA wt% > 50) in the blend. More thorough analysis for explaining the phase behavior in association with the $T_{\rm g}$ behavior has to be provided in more details. Note that not all miscible crystalline/amorphous blends exhibit an asymmetric $T_{\rm g}$ -composition dependence. For examples, miscible blends of crystalline polyarylates (e.g., poly(ether diphenyl ether ketone (PEDEK), $T_g = 156^{\circ}$ C) with amorphous PEI ($T_g =$ 215.6°C) are not known to show such asymmetry in their $T_{\rm g}$ -composition curves.²⁵ Note that in this case the $T_{\rm g}$ difference between PEDEK and PEI is much smaller (differing only by 60°C). Consequently, contribution of free-volume difference in the PEDEK/PEI blend system is probably smaller.

CONCLUSION

The polymer blend system comprising of crystalline

low- T_g PTT and amorphous but high- T_g PEI is for the first time shown to be thermodynamically miscible (in the amorphous region) within the complete composition range. Interestingly, the $T_{\rm g}$ -composition relationship for the PTT/PEI blends is apparently asymmetric and exhibits a cusp at the PEI volume fraction of about $\phi_{2,c} = 0.5-0.55$. With one constituent being amorphous and the other being semicrystalline and the constituents possessing drastically different T_{g} 's, uneven contributions from these two components to the free volumes of the blends are likely responsible for the peculiarly interesting characteristics in the $T_{\rm g}$ dependence on composition. With this cusp as a critical point, the $T_{\rm g}$ dependence on composition is dramatically different in these two composition ranges. Below this volume fraction, the blend's T_{g} increases only slightly or even stagnantly with an increase of the PEI component. On the other hand, above this critical volume fraction, the blend's $T_{\rm g}$ increases sharply with an increase of the PEI component. Interestingly, this critical volume fraction where the cusp is located seems to coincide with the composition beyond which the PTT crystallization tendency is completely suppressed by the amorphous PEI. The peculiar T_{g} -composition curve with a discontinuous cusp is explained using an approach based on the free volumes.

Owing to the asymmetry in the experimental T_{g} composition relationship, the Gordon-Taylor (G-T) equation either over-predicts (blend composition range of $\omega_2 < 0.6$) or under-predicts (blends with high PEI volume fractions, $\omega_2 > 0.6$) the T_g-composition relationship. For the lower portion (i.e., PTT-rich blends) of the T_g-composition relationship, a G-T parameter of k = 0.30 was found to best fit the data, while for the upper portion (*i.e.*, PEI-rich blends), a G–T parameter of k = 0.65 was obtained. If the values of G-T parameter are taken as a sign of molecular interactions between the constituents, the interactions leading to the PTT/PEI blend miscibility are apparently and systematically varying with the composition. The peculiar T_{g} -composition behavior in the miscible PTT/PEI blends was analyzed using a classical free-volume approach, where uneven contributions to the polymer mixtures' free volume were partially attributed to the vastly different T_{g} 's and free volumes of these two constituents. Furthermore, it was found that varying degrees of blend's T_{g} broadening with respect to the composition might also contribute to the noted discontinuity. The asymmetry was partially attributed to the PTT crystalline-domain-induced variation in the intermolecular interactions.

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