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Peculiar Glass Transition Behavior and Miscibility in a Binary Mixture Comprising Amorphous Poly(ether imide) with Semicrystalline Poly(butylene terephthalate)

E. M. Woo* and S. N. Yau

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 701-01

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ABSTRACT: Miscibility and an asymmetric T_g−composition relationship have been demonstrated in the binary blends composed of amorphous poly(ether imide) (PEI) and semicrystalline poly(butylene terephthalate) (PBT). The peculiar T_g−composition behavior in the miscible PEI/PBT blends was analyzed using a free-volume approach, where uneven contributions to the mixtures free volumes were attributed to the vastly different crystallizing tendency of one constituent versus the other. A single T_g was observed in the PEI/PBT blends using differential scanning calorimetry (DSC) as well as dynamic mechanical analysis (DMA), which proved single relaxation and intimate mixing between these two components at the molecular scales. Additionally, homogeneous phase morphology in the blends was also substantiated using optical and scanning electron microscopy. Interactions between the polymers were investigated by analyzing the equilibrium melting point depression as well as the T_g dependence on composition.

Introduction

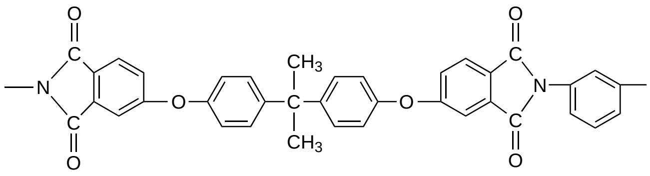
Thermoplastic polyesters are an interesting class of semicrystalline polymers. Of these, poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) are two of the most studied polyesters. Blend systems of these two thermoplastic polyesters with other amorphous or semicrystalline polymers have been widely studied. PBT has been known to form miscible blends with another polyester, PET, of similar chemical structure.[1] In addition, due to ester exchanges, PBT is also known to form immiscible but mechanically compatible blends with Bisphenol A polycarbonate (PC).[2]

In recent years, a significant amount of research has been directed at gaining better understanding of miscibility as well as compatibility of the blend systems comprising these polyesters and other polymers. Blending of polymers of different properties is usually an attractive route for development of new polymer materials that offer a special combination of performance characteristics. Especially, blends comprising an amorphous polymer and a semicrystalline one can lead to a unique combination of properties, particularly if the polymer pair is miscible. For example, poly(ether imide) (PEI) is an engineering thermoplastic polymer that is known for thermal stability, toughness, high T_g, and other excellent mechanical properties. It is, however, amorphous and susceptible to organic solvents. Structurally, PEI is quite different from poly(ether ketone) (PEEK), a semicrystalline polymer. However, miscibility issues of these two polymers have received extensive attention since first reporting.[3−7] It is expected that miscible blends of two polymers with proper compositions can offer properties suitable for specific applications. Although miscibility is not a prerequisite for applications of polymer blends, it is interesting since it allows easy design of new polymer materials. Special applications may also result. For example, miscibility in the PEEK/PEI blends has been exploited by proposals that PEI may be used as a potentially useful joining agent for PEEK composite parts.[8,9] Lately, in a rapid communication, we have demonstrated an interesting and rare case of ternary miscible blends comprising PEI, PET, and PBT.[10]

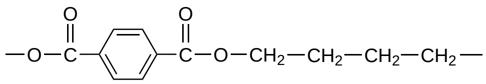
A detailed investigation on miscibility between imide-containing polymers with carbonyl-containing polyesters has been undertaken in our laboratory. A fundamental understanding of the miscibility thus will provide a guide for searching for potentially useful pairs of new miscible polymers. The objective of this study was to explore the phase behavior of blends comprised of amorphous PEI with semicrystalline PBT. Mechanisms and intermolecular interactions between the ester and imide functional groups were probed. Uneven contributions to the free volumes of blends from the amorphous vs semicrystalline polymer constituents as well as the effects on glass transition behavior were analyzed and reported in the present work.

Experimental Section

Materials. Poly(butylene terephthalate) (PBT) is a semicrystalline polyester polymer and was obtained as a research-grade resin with no additives from GE Laboratories (PBT-315). Poly(ether imide) (PEI) was a commercial-grade resin (GE Ultem-1010). Due to the asymmetry in the chemical structure, it is amorphous but has a high T_g of 215 °C because of the aromatic and imide rings in the backbone chains. The chemical structures of the repeating units of PEI and PBT are shown as follows:



PEI



Poly(butylene terephthalate), PBT

Other than a few high-boiling-point acids, no suitable organic solvents could be found to codissolve these two

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* To whom correspondence should be addressed. Fax: +886-6-234-4496. Phone: +886-6-275-7575 (x62670).

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polymers simultaneously. To avoid complicating effects from solvents on the true phase behavior of the blends, direct melt-mixing was used in sample preparation. Furthermore, to ensure that good mixing could be completed in the shortest time duration possible, the polymer components (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-g capacity) was used for the blending purposes. Heating was provided by mounting the mold on a hot stage, and mixing was accomplished by manual stirring. At the blending temperature of 280 °C, the viscous forces of the polymer melts of small quantities were rather low and blending 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. The temperature was controlled and monitored using a thermocouple inserted in the mold.

Apparatus. The glass transition (T_g), crystallization, and melting temperatures of the blend samples of various compositions were measured with a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with an intracooler. All T_g measurements were made at a scan rate of 20 °C min^{-1} in the range of 18−250 °C. The T_g values were taken as the onset of the transition (i.e., change in the specific heat) in the DSC thermograms. Since physical aging can affect T_g, one set of samples was prepared whose calorimetric measurements were performed immediately after the polymer samples were quenched from above their T_g's or melting points. This set of samples is designated "freshly quenched". Another set of samples was aged for 30 min at 10 deg below the T_g of the unaged samples. The T_g's of these aged blends were then determined using DSC. This set of samples is designated "aged".

A polarized-light optical microscope (Nikon 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 hand 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 examination.

Dynamic mechanical analysis (DMA) experiments were performed by using a Rheovibron DDV-II in a tensile deformation mode of film samples to examine the scales of phase homogeneity. Raw data were recorded manually, and tension adjustment was continually done by hand. Raw data were then entered into a computer and transformed to the storage and loss moduli for plotting. A heating rate of approximately 1−2 °C min^{-1} and a fixed frequency of 11 Hz were used. Film samples for DMA experiments were prepared by compression molding of the well-blended polymers of several compositions. The sample dimensions for DMA were about 5.0 cm × 0.3 × 0.015 cm, with the film thickness of all DMA samples being kept as uniformly as possible at about 0.01−0.02 cm.

Results and Discussion

Glass Transition Evidence. Figure 1 shows the DSC thermograms for the PEI/PBT blends with increasing PEI volume fraction (total 11 curves representing 11 different compositions investigated). There is clearly one single T_g in each of the blend compositions. The blend T_g's, as well as the peak location of the crystallization exotherm of the crystallizing PBT component in the blends, increase monotonously with an increase of PEI content. For the blends of low PEI contents, there exists an interesting trend that an increase in the PEI contents results in only a minimal increase in the blend T_g. For example, it appears that the T_g's of the 20/80 and 30/70 PEI/PBT blends closely resemble that of neat PBT (T_g = 34 °C). For high PEI contents, the trend is reversed. We will attempt to explain this peculiar T_g−composition behavior in later sections. Although there is only a slight increase of the blend T_g with the PEI content in this range, the peak location of the cold-crystallization exotherm rises considerably with increasing PEI content. This suggests that there are intimate molecular interactions between the PBT and PEI polymer chain segments, which cause chain stiffening of the PBT chain segments and result in elevation of cold-crystallization temperatures.

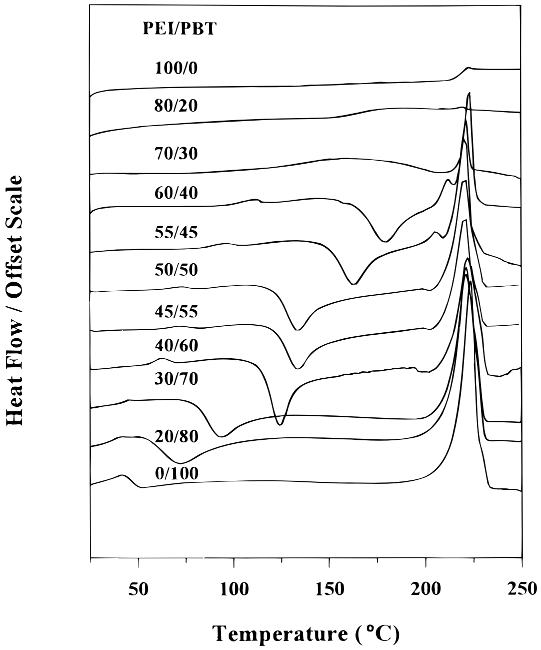

Figure 1. DSC thermograms for the PEI/PBT blends of 11 different compositions.

To more clearly reveal the T_g, physical aging was imposed on the blends at temperatures just 10 deg below the respective T_g. The T_g's of the aged blends were characterized again. The physical aging treatment resulted in a pronounced enthalpy relaxation peak appearing just above the T_g transition. Besides, the T_g's of the aged samples are more distinct and slightly higher than those of the quenched samples. On the other hand, the temperature location of the cold-crystallization peaks are not much affected by the physical aging treatment. The DSC thermograms of the aged blend samples further demonstrate that only a single T_g is discerned in the blend samples.

Figure 2 shows the glass transition breadth as a function of composition in the freshly quenched blend samples. For the blend compositions where PBT volume fractions are high (e.g., 20/80 and 30/70), the freshly quenched samples exhibited a relatively sharp T_g transition. The blends of these compositions showing a relatively sharp T_g transition were crystallizable, as evidenced by the cold crystallization of the PBT component upon thermal scanning. On the other hand, at high PEI compositions in the blends, the T_g transition is generally broader for the noncrystallizable blends whose compositions are such that cold crystallization is completely suppressed. This occurs at the blend compositions where the PEI contents are greater than 60 wt % (or PBT contents less than 40 wt %), and the maximum T_g transition breadth is found in the blend sample with 70 wt % of PEI.

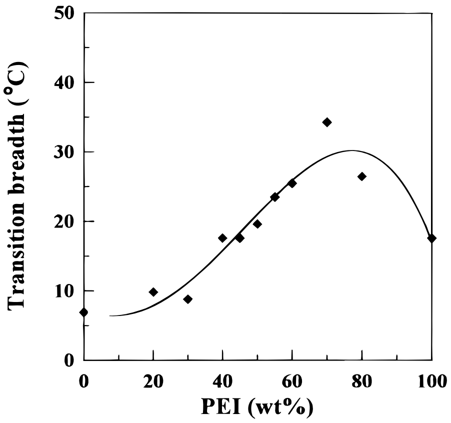

Figure 2. Glass transition breadth as a function of composition for the quenched (amorphous) PEI/PBT blend samples.

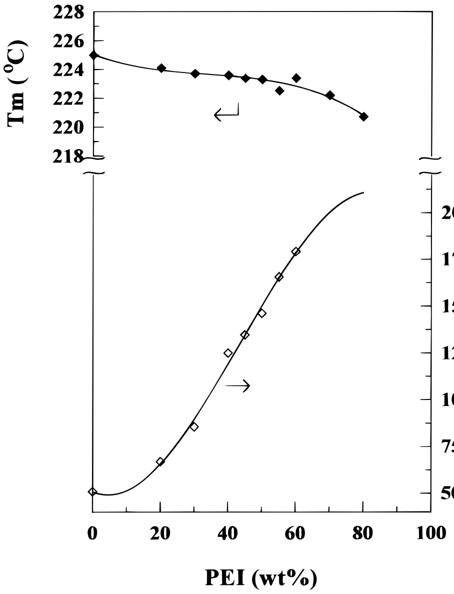

Figure 3. Apparent melting points and peak temperatures of the cold-crystallization exotherm of the PBT component in the blends.

Figure 3 shows the apparent melting points and peak temperatures of the cold-crystallization exotherm of the PBT component in the PEI/PBT blends plotted as functions of PEI content. Depression of the apparent melting point of PBT by the amorphous PEI constituent is obvious. Additionally, the temperature range of PBT cold crystallization is pushed to higher temperatures with increasing PEI content in the blends. For example, the neat PBT sample exhibits a T_g that is immediately followed by a crystallization exotherm located just above the T_g temperature. With increasing PEI content in the PEI/PBT blends, the cold-crystallization exotherm peak gradually moves from approximately 70 °C rapidly to higher temperatures of about 175 °C. The observation of the T_g behavior as well as the melting point depression and cold-crystallization temperature elevation suggests that intermolecular interactions between these two polymers may be present. To quantitatively determine the interactions, however, requires further analysis.

Intermolecular Interactions. The Flory–Huggins theory on melting point depression for polymer solutions can be written as[11,12]

$$1/T_m - 1/T_m{}^\circ = -(RV_1/\Delta H_{f1}V_2)[\ln(1-\phi_2)/n_1 + (1/n_2 - 1/n_1)\phi_2 + \chi_{12}\phi_2{}^2] \quad (1)$$

where T_m and $T_m{}^\circ$ are the equilibrium melting points of the polymer mixture and neat crystallizing polymer component, respectively. The subscript "1" indicates the crystallizing polymer (PBT), and "2" indicates the noncrystallizing polymer (PEI). V_1 and V_2 are the molar volumes of the repeat units of the crystallizing and amorphous (noncrystallizing) polymers, and n_1 and n_2 are the degrees of polymerization of these two polymer components, respectively. ΔH_{f1} is the heat of fusion of the fully crystalline polymer, and ϕ_2 is the volume fraction of the noncrystallizing polymer. In this equation χ_{12} is the Flory interaction parameter. It can be expected that the contributions from the first two terms are small due to relatively large n_1 and n_2. The melting point depression thus may be determined by the quantity of the interaction parameter. The above equation can be approximated by

$$\frac{1}{T_m} - \frac{1}{T_m{}^\circ} = -\frac{RV_1}{\Delta H_{f1}V_2}\chi_{12}\phi_2{}^2 \quad (2)$$

The interaction parameter may be expressed in terms of B, by

$$\chi_{12} = \frac{BV_2}{RT_m{}^\circ} \quad (3)$$

With the substitution of eq 3, eq 2 may be re-expressed as

$$\left(\frac{1}{T_m} - \frac{1}{T_m{}^\circ}\right)\Big/\phi_2 = -\frac{BV_1}{\Delta H_{f1}}\left(\frac{\phi_2}{T_m{}^\circ}\right) \quad (4)$$

Depression of the apparent melting points of the PBT in the blends was further analyzed. It was possible that the morphological factor might also vary in the blends. Thus, to determine the thermodynamic factor responsible for the observed melting point depression, the equilibrium melting point of PBT in the blends must be first estimated. By plotting the left-hand-side vs the right-hand-side terms of eq 4, the interaction energy density B was determined from the slope of the plot. In calculation, the physical constants used were $\rho_1 = 1.281$ g cm^{-3}, $\rho_2 = 1.70$ g cm^{-3}, $V_1 = 164.5$ cm^3 mol^{-1}, $V_2 = 399.5$ cm^3 mol^{-1}, and $\Delta H_{f1} = 29$ kJ mol^{-1}.[13,14]

Figure 4a shows a plot for the determination of the equilibrium melting points, and Figure 4b shows the plot for estimation of the B parameter. The slope in Figure 4b yielded $-BV_1/\Delta H_{f1}$. The interaction parameter was then determined to be $\chi_{12} = -0.62$ (at $T_m = 515$ K), which is a small negative value. The fact suggests that intermolecular specific interactions between dissimilar PEI–PBT are present but most likely quite weak and probably about the same as the average of the intermolecular interactions between the similar pairs (i.e., PEI–PEI or PBT–PBT pairs).

Phase Morphology. The PEI/PBT blends of all compositions appeared visually transparent and homogeneous. The blends of all compositions were examined using an optical microscope. The blends were first examined at ambient temperature; then the temperature was raised gradually to where degradation occurred in order to observe whether or not there was a cloud-point transition. Additionally, the optical micrographs showed that the blends of all compositions were transparent and that the phase morphology was homogeneous for all blends. Furthermore, no upper or lower critical solution point (UCST or LCST) phenomenon was observed while the blend samples were heated from

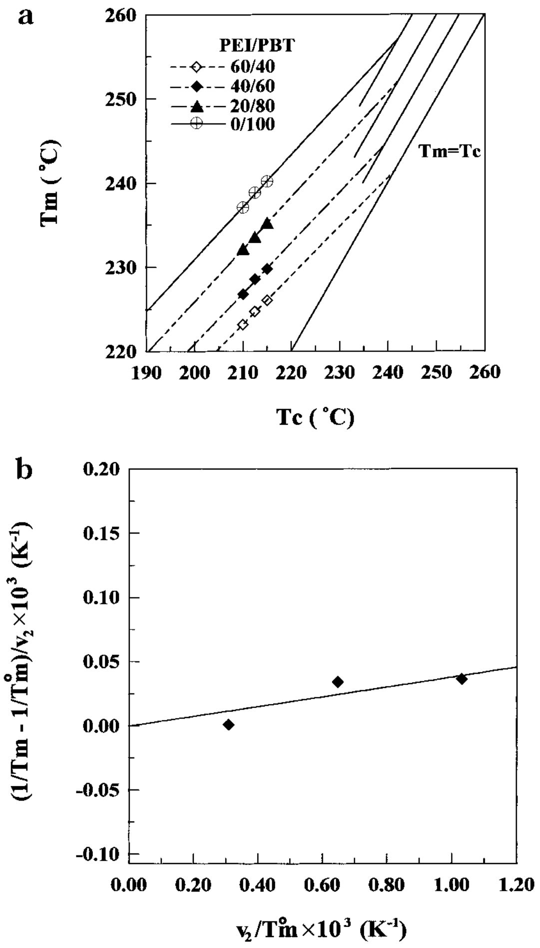

Figure 4. (a) T_m vs T_c plot for the determination of the equilibrium melting points. (b) Plot for estimation of *B*.

ambient temperature to above 300 °C where they started to thermally degrade.

In addition, the fractured surfaces of the PEI/PBT blends were examined using SEM to provide further evidence of phase homogeneity. Parts a−c of Figure 5 show the SEM micrographs of the fracture surface of three blend compositions: 80/20, 50/50, and 20/80, respectively, all at 5000× magnification (reduced to 75% for publication). The fracture surfaces of these three blend compositions demonstrate that the PEI/PBT blends within this wide composition range are homogeneous at least to the extent that no heterogeneous phase domains can be identified at 0.1−0.3 μm resolution or better.

Molecular Relaxation Behavior. There have been several cases reported for blend systems with detectable microheterogeneity showing one single T_g upon DSC scanning.[15] In those cases, SEM is performed to characterize the actual phase domains. Furthermore, DMA is usually capable of determining the molecular relaxation behavior of smaller chain segments and thus is able to detect phase heterogeneity on smaller scales, if present.

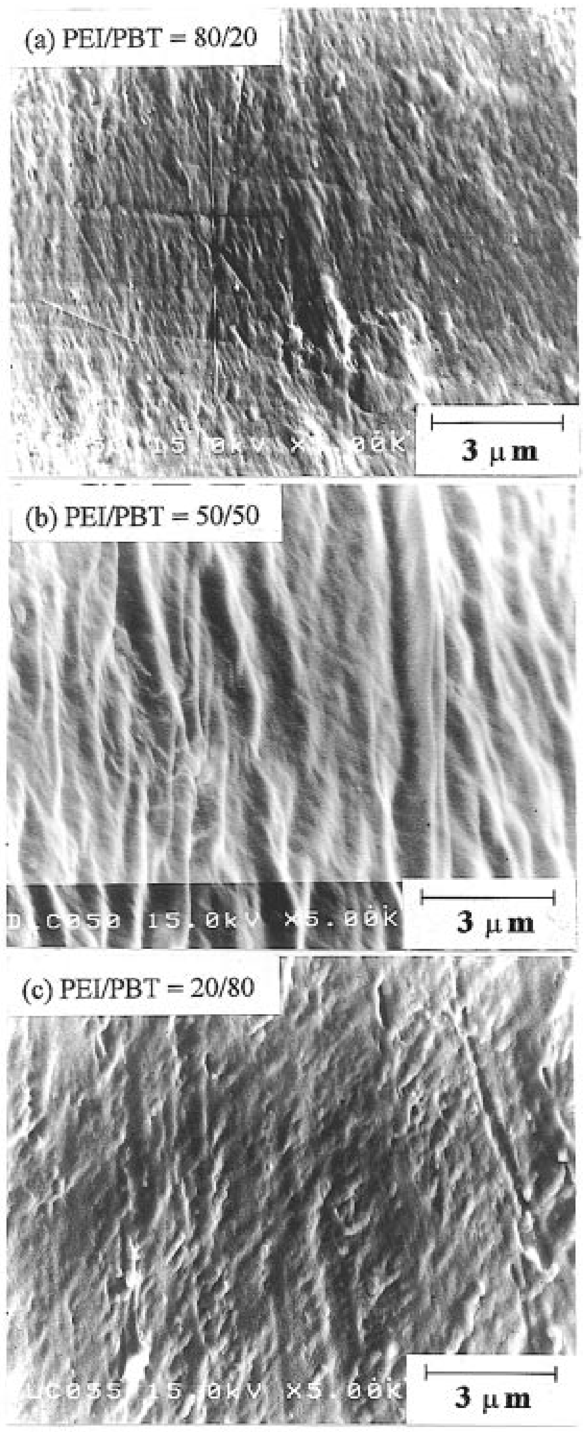

Figure 5. SEM micrographs of the fracture surface of three PEI/PBT blend compositions: (a) 80/20, (b) 50/50, and (c) 20/80 at 5000× (reduced to 75% for publication).

Parts a−c of Figure 6 show the storage and loss modulus curves for the PEI/PBT blends of a few representative compositions: 80/20, 70/30, and 60/40, respectively. Figure 6a shows that the loss modulus curve for the 80/20 PEI/PBT blend clearly shows a prominently single relaxation, with the peak temperature being about 175 °C. Between 25 and 175 °C, there is no other relaxation peak except that a small shoulder peak at 200−230 °C is identified, which is related to PBT cold crystallization occurring at temperatures above the T_g. Parts b and c of Figure 6 show that a similar behavior is observed for the 70/30 and 60/40 blends, except that the peak of the single relaxation is located at lower temperatures for the blends of lower PEI contents. The intensity of the crystallization-induced shoulder peak becomes greater for the samples with higher PBT contents, providing additional evidence that the shoulder peak is related to cold crystallization of PBT. Within the whole composition range, the peak temperatures of the loss modulus curves (T_α) increase with the PEI content in the blends.

DMA was also performed on the PEI/PBT blends of other miscellaneous compositions. Similar results were obtained, and they all clearly indicated a single relaxation peak, whose temperature location is dependent on

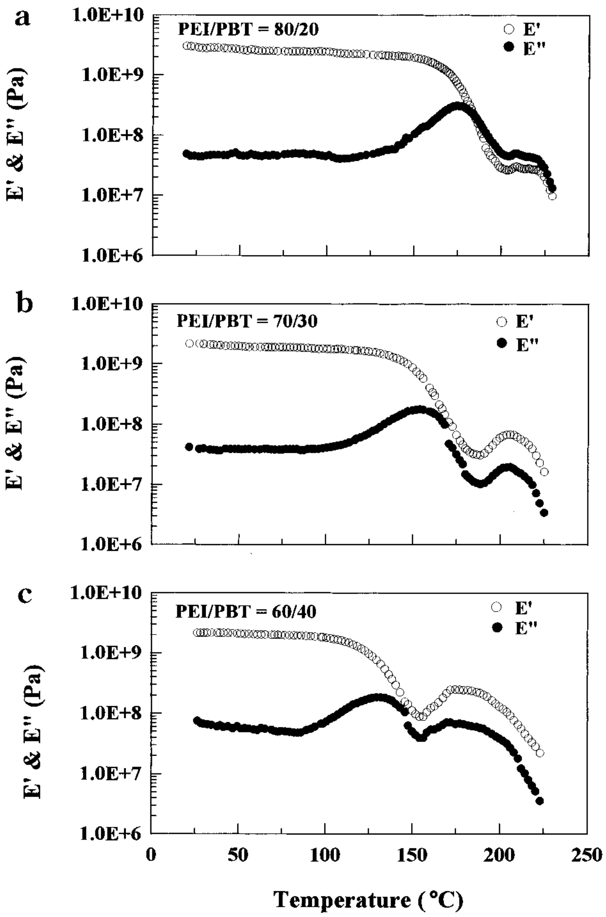

Figure 6. Storage and loss modulus curves for the PEI/PBT blends: (a) 80/20, (b) 70/30, and (c) 60/40.

Table 1. T_α of PEI/PBT Blends, Quenched and Annealed

composition (PEI/PBT)	T_α (°C) quenched	annealed
0/100 (neat PBT)	50	54
20/80	56	NA[a]
30/70	73	90
40/60	85	97
50/50	105	broad
60/40	130	180
70/30	155	195
80/20	175	NA
100/0 (neat PEI)	220	225

[a] NA: not available.

the composition. For the blends of intermediate compositions (60/40 and 50/50), the first relaxation peak related to T_g of the blend. The shoulder peak (at the higher-temperature side) is related to the crystallization/melting of PBT and is seen to become larger due to increasing contents of PBT. For the blends of high PBT compositions (30/70 and 20/80), the primary relaxation peak of the blend overlaps considerably with the chain-stiffening peak due to PBT crystallization. As a result, the overlapped relaxation peaks appear to be broadened. In all, if the chain stiffening due to crystallization is excluded, only a single T_g relaxation peak is observed. Other compositions were also investigated and similarly a single relaxation peak was observed in each of the PEI/PBT blends. Table 1 summarizes the T_α of the PEI/PBT blends (freshly quenched and annealed sample sets) of various compositions.

There are some interesting features in the DMA results that deserve special discussion. The DMA spectra of the blend samples of high PEI contents (80/20, 70/30, and 60/40) do not show this sub-T_g β-relaxation of the PEI component. The α-transition of the neat PEI polymer is located at 225 °C, and it is known that the neat PEI polymer also exhibits a pronounced sub-T_g β-relaxation peak between −25 and +175 °C.[16] It has also been suggested that intra- or interchain cooperative motions of one or several repeat units in PEI polymer chains are responsible for the observed β-relaxation peak.[17] This fact indicates that the interactions between PEI and PBT result in intimate mixing at the molecular scales of the polymer chains. Consequently, phase homogeneity at the scale of several repeat units is beyond the resolution of optical or electron microscopy.

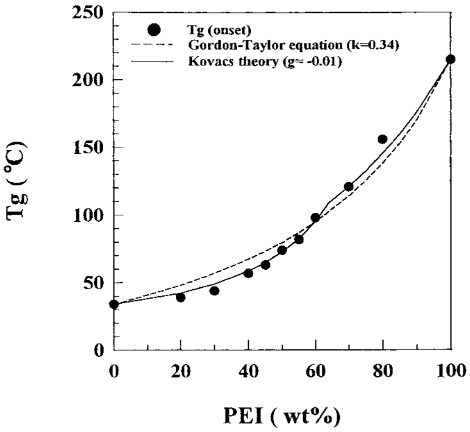

Figure 7. T_g of PEI/PBT blends as a function of composition. The solid and dashed curves represent fitting with eq 7 and the Gordon−Taylor equation, respectively.

Analysis of T_g Behavior. Having confirmed that the blends were thermodynamically miscible, the T_g−composition behavior of the blends was further analyzed. The T_g of PEI is 215 °C, and the T_g of PBT is 34 °C. Thus, an increase of the volume fraction of the high-T_g component (PEI) in the blends results in continuous elevation of the blend T_g. Interestingly, the T_g−composition of this blend system appears to be quite asymmetric. Qualitatively speaking, at small volume fractions of PEI in the blends, the contribution of PEI in raising the blend T_g is minimal. On the other hand, at small volume fractions of PBT (i.e., high volume fractions of PEI) in the blends, the contribution of the PEI component in raising the blend T_g is significant. A pronounced asymmetry clearly exists in the T_g−composition curve.

Figure 7 shows the T_g data of the blends plotted as a function of composition (weight fraction) of PEI. The asymmetry in the trend of variation of the data illustrates the dramatically uneven contributions of the polymer components to the blend T_g. Furthermore, there exists a discontinuity (cusp) in the otherwise continuous trend of variation. The cusp is located at the blend composition of ϕ_2 = 0.6−0.7, where the subscript "2" indicates the noncrystallizing (amorphous) component, PEI. A literature survey reveals that a few other miscible blend systems containing one crystalline polymer also exhibit such behavior.[18,19] Note that initial crystallinity is not a factor which influences the T_g in the blend samples. Experimental procedures of quenching were conducted carefully such that the amount of the initial (residual) crystalline portion was negligible in the blend samples for T_g measurements. Thus the cusp discontinuity in this figure is not due to a discrepancy in the experimental measurements.

Apparently, the widely-used Fox equation[20] does not fit the T_g data in this figure. The Gordon−Taylor equation[20] (dashed curve) overpredicts and underpredicts, respectively, the two portions of T_g data of the blends with low volume fractions ($\phi_2 < 0.60$) and high volume fractions ($\phi_2 > 0.60$) of PEI. We attempted to use Kovacs theory[21] 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 ($T_{g2} - T_{g1}$) 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) and volume fraction (ϕ_{2c}) at which this occurs are estimated as:

$$T_c = T_{g2} - (f_{g2}/\Delta\alpha_2) \tag{5}$$

$$\phi_{2c} = f_{g2}/[\Delta\alpha_1(T_{g2} - T_{g1}) + f_{g2}(1 - \Delta\alpha_1/\Delta\alpha_2)] \tag{6}$$

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 blend T_g is given by the following:

$$T_{g,\text{blend}} = T_{g,1} + (\phi_2 f_{g2} + g\phi_1\phi_2)/\phi_1\Delta\alpha_1 \tag{7}$$

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_e is the excess molar volume. The sign of the interaction parameter g depends on that of the excess volume (V_e). A negative value means that the interactions between the blend components (PEI−PBT pairs) are stronger than or at least equal to the average of those between the similar PEI or PBT molecules, and thus favorable for miscibility.

The solid curve in Figure 7 shows the best fit of eq 7 to the experimental T_g data. The best-fitted value of g was determined to be −0.01. The fact that the value of g is a small 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.

Conclusion

By using DSC, DMA, optical microscopy and SEM, this study has demonstrated that the polymer mixtures comprising an amorphous PEI and a semicrystalline PBT are thermodynamically miscible within the complete composition range. No LCST exists in the blends between the ambient and the degradation temperature. The interaction parameter obtained from the melting point depression indicates that intimate mixing does exist, although the intermolecular interactions may not be particularly strong. The interaction parameter obtained from the analysis on the T_g behavior also supported such a conclusion. It is expected that the capacity of mutual tailoring between semicrystalline PBT and amorphous PEI may offer a unique combination of properties. For example, PEI possesses toughness, high T_g, and thermal stability, while PBT offers crystallinity, excellent solvent resistance, and good flow property at processing temperatures.

The T_g−composition curve for the PEI/PBT blends is apparently asymmetric and exhibits a cusp at the PEI volume fraction of about $\phi_2 = 0.6$. With this cusp as a critical point, the T_g dependence on composition is dramatically different in these two composition ranges. Below this volume fraction, the blend T_g increases gently with an increase of the PEI component. On the other hand, above this critical volume fraction, the blend T_g increases sharply with an increase of the PEI component. Interestingly, this critical volume fraction of $\phi_2 = 0.6$, where the cusp is located seems to coincide with the composition beyond which the PBT crystallization tendency is now completely suppressed by the major component of amorphous PEI.

The peculiar T_g−composition curve with a discontinuous cusp is explained using an approach based on the free volumes. With one constituent being amorphous and the other being semicrystalline, uneven contributions from the two components to the free volume of the blends are responsible for the asymmetric T_g variation with composition. The phenomenon of uneven contributions is usually more obvious in blend systems in which one constituent is capable of crystallization while the other is not. Binary miscible blend systems comprising two amorphous polymers usually rarely exhibit such a peculiar T_g dependence on composition.

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References and Notes

(1) Avramova, N. *Polymer* **1995**, *36*, 801.
(2) Murff, S. R.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1984**, *29*, 3231.
(3) Hsiao, B. S.; Sauer, B. B. *J. Polym. Sci., Polym. Phys.* **1993**, *31*, 901.
(4) Crevecoeur, G.; Groeninckx, G. *Macromolecules* **1991**, *24*, 1190.
(5) Chen, H. L.; Porter, R. S. *Polym. Eng. Sci.* **1992**, *32*, 1870.
(6) Hudson, S. D.; Davies, D. D.; Lovinger, A. J. *Macromolecules* **1992**, *25*, 1759.
(7) Harris, J. E.; Robeson, L. M. *J. Appl. Polym. Sci.* **1988**, *35*, 1877.
(8) Silverman, J. E.; Griese, R. A. *SAMPE J.* **1989**, *25*, 34.
(9) Cogswell, F. N.; Meakin, P. J.; Smiley, A. J.; Harvey, M. T.; Booth, C. *Proc. Int. SAMPE Symp.*, 34th **1989**.
(10) Yau, S. N.; Woo, E. M. *Macromol. Rapid Commun.* **1996**, *17*, 615.
(11) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1978.
(12) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(13) Brandrup, J., Immergut, H., Eds. *Polymer Handbook*; Wiley: New York, 1989.
(14) van Krevelen, D. W. *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*; Elsevier Scientific Publishing Co.: Dordrecht, The Netherlands, **1976**.
(15) Woo, E. M.; Su, C. C. *Polymer* **1996**, *37*, 4111.
(16) Kuo, S. M. M.S. *thesis*, Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, 1996.
(17) Tamada, H.; Okita, S.; Kobayashi, K. *Polym. J.* **1993**, *25*, 339.
(18) Siciliano, A.; Seves, A.; De Marco, T.; Cimmino, S.; Martuscelli, E.; Silvestre, C. *Macromolecules* **1995**, *28*, 8065.
(19) Aubin, M.; Prud'homme, R. E. *Macromolecules* **1988**, *21*, 1945.
(20) Olabishi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979; Chapter 6, p 279.
(21) Kovacs, A. J. *Adv. Polym. Sci.* **1963**, *3*, 394.

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