

A Novel Quaternary Blend System of Poly(ethylene terephthalate), Poly(trimethylene terephthalate), Poly(butylene terephthalate), and Poly(ether imide)

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Summary

A quaternary blend system composed of three low- T_g semi-crystalline aryl-polyesters namely, [poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT)] and an amorphous high- T_g poly(ether imide) (PEI) was prepared and investigated using thermal and morphology characterization techniques. This study, for the first time, demonstrated miscibility and phase behavior of a quaternary blend comprising four different polymers. A single and composition-dependent T_g was found for each of all quaternary blend samples. In addition, various thermal transition characteristics, single and composition-dependent $T_{c,c}$, increasingly suppressed $\Delta H_{c,c}$ at higher PEI contents, are also indication of phase miscibility of the quaternary blend. SEM morphology characterization (3000X) revealed no discernible domains and homogeneous phase morphology in the quaternary blends was also substantiated using optical and scanning electron microscopy results.

Introduction

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. PTT has received much attention in various studies mainly related to its melting behavior and crystalline morphology. [1-6]

Binary blend systems [7-9] comprising any two of the PET, PTT, and PBT have been studied and proven to be miscible. Furthermore, it would be interesting to explore the phase behavior of a ternary blend system comprising all three aryl-polyesters, PET, PTT, and PBT [10]. Note that polymers with repeat units differing only by a methylene or methyl unit are not all miscible. For examples, polyethylene ($-\text{[CH}_2\text{-CH}_2\text{-]}$) and polypropylene ($-\text{[CH}_2\text{-CH(CH}_3\text{)]}$), which differ from each other only by a pendant methyl group in the repeat unit, are not miscible. Olefinic polymers are widely useful resins and the phase behavior in blends of different olefinic polymers has been studied by Graessley et. al. [11-13], who have reported interesting thermodynamic behavior of miscibility with LCST for some blends of polyolefins, while phase separation with a UCST behavior only at high temperatures for blends of other polyolefins.

Miscibility in blend systems comprising polyesters and polyimides (or polyetherimides) had in the past years attracted extensive interests. Especially, blends comprising a semicrystalline polymer and an amorphous one 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_g , and other excellent mechanical properties. PEI, however, is amorphous and becomes susceptible to common organic solvents. The weakness may be offset if PEI is

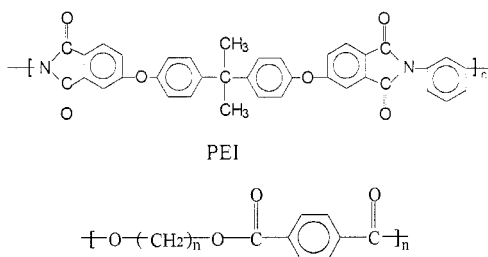
blended with other polymers that can offer what PEI does not possess. It is expected that if PEI is blended with a semicrystalline polymers and forms a miscible blend, then miscibility can offer advantages of delicate property balances for specific applications. In recent years, significant research effort has been directed at gaining better understanding of miscibility, compatibility, morphology, properties, and processing of the blend systems comprising these polyesters and PEI [14-20]. PEI is of interest for studies in blends owing to the fact that it shows tendency of being miscible with some polyesters as well as polyarylates. For examples, miscible blends of crystalline polyarylates, e.g., poly(ether diphenyl ether ketone) (PEDEK) or poly(ether ether ketone) (PEEK) have been proven to be miscible with PEI ($T_g = 215.6^\circ\text{C}$). [21]

Although there have been ample examples of demonstrated binary miscible polymer pairs in the literature, it is known to most polymer scientists that the number of ternary miscible systems is relatively limited. It is expected that quaternary polymer blends would be least likely to become miscible. To our knowledge, there have been no studies directed at examining the phase behavior, morphology, properties, and miscibility of quaternary blend systems. Although realistically it is rarely encountered that four polymers are incorporated to form a quaternary blend system, it would be intellectually interesting and critical to examine the phase behavior and prospect of miscibility of a blend comprising four different polymers. The objective of this study was to demonstrate the first case of a miscible quaternary blend, by using an amorphous PEI and three semicrystalline aryl polyesters as models. Possible mechanisms leading to quaternary miscibility were examined and causes were proposed for interpreting the changes in heterogeneity in the multi-polymer blend systems.

Experimental

Materials

Three aryl polyesters, poly(ethylene terephthalate), PET (from Shin-Kwang Co. Taiwan), poly(trimethylene terephthalate), PTT, poly(butylene terephthalate), PBT (GE Corp. USA) were used in this study. PET and PBT were obtained from commercial sources in pure-grade state. Poly(trimethylene terephthalate) (PTT), also called 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 (purchased from Polysciences, Inc., USA, with $M_w = 30,000$ g/mol). PET, PTT, and PBT are all semicrystalline and have apparent T_g 's = 76.7°C , 42.8°C , 33.4°C , and T_m 's = 255.6°C , 228.5°C , 221.9°C , respectively. PEI is amorphous, but has a high T_g of 215.6°C owing to the aromatic and imide rings in the backbone chains. The chemical structures of the repeating units of PEI and aryl-polyesters are shown as following:



Where $n = 2, 3, 4$ for PET, PTT, PBT, respectively

Hot melt-blending (at ca. $280\text{--}290^\circ\text{C}$) was first attempted for preparation of quaternary blends, but turned out to be not successful. The viscosity of the mixtures prohibited easy maneuvering of melt-blending of all four constituents simultaneously at high temperatures. Thus, insteads, three aryl-polyesters (PET/PTT/PBT of weight ratio 1/1/1) were first co-dissolved in dichloroacetic acid (4wt%) at 60°C by continuous stirring, then precipitated in large quantity of distilled water. The precipitated pre-blend of three polymers was left to dry by keeping at room temperature for several days. The residual solvent was then removed in vacuum oven at higher temperatures. The pre-blend of co-precipitated aryl-polyesters (PET/PTT/PBT=1/1/1) was then treated as a single

component, and then was further blended with various quantities of PEI by using the same procedures as stated above. The final quaternary blend material was then compression-molded into thin-film samples for various thermal and microscopy characterization, to be described as following.

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. Measurements of T_g , cold-crystallization, and melting transitions were made at a scan rate of 20°C/min in the range of 0-260°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 will be noted if the mid-point values of T_g (instead of the on-set values) are used in plots. The values of $T_{c,c}$ (cold-crystallization) and apparent melting point (T_m) were taken as the peak of the exotherms or endotherms.

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 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

Thermal characterization

For convenience and balance of covering as much range of compositions, the quaternary blend samples were prepared in such way that the relative ratios of arly polyesters (PET/PTT/PBT) were kept at fixed (1/1/1). The three aryl polyesters in the well-mixed form were treated as a pseudo-single component for further blending with various fractions of PEI in the quaternary blend. Realistically, it would be difficult to exhaust all possible quaternary blend compositions; but representative compositions for the quaternary blend system had been characterized in this study. Figure 1 shows the DSC thermograms for the quaternary PET/PTT/PBT/PEI blends with increasing PEI fractions in the quaternary compositions. The figure shows that there is clearly only one single T_g (onset positions indicated with arrow marks) for each of the quaternary blend compositions examined in this study. All these representative quaternary compositions exhibited a characteristic behavior of miscibility by the conventional criterion. Other characteristics of the thermal transitions also yielded evidence leading to a conclusion of state of miscibility in this quaternary blend system. For examples, the DSC traces in Figure 1 show that not only the blend T_g 's but also the peak location of cold crystallization exotherm ($T_{c,c}$ located at above the respective T_g) of the crystallizing components (PET, PTT, PBT) in the blends increase monotonously with increasing PEI contents. This will be discussed in more details in the following paragraphs.

Qualitative treatments on the T_g 's of the quaternary blend system were attempted. As the initial crystallinity was totally suppressed in the quenched blend samples prior to the T_g measurements, the measured T_g reflected the state of the blend samples in totally amorphous chains. Figure 2 shows the T_g -vs.-composition plot for the quaternary blends plotted as a function of increasing weight fractions of PEI but with the relative wt. ratio of PET/PTT/PBT fixed at 1/1/1 in the quaternary blend. The T_g data are further compared to two quantitative models (Fox or Gordon-Taylor equations). Apparently, the figure shows that the classic Fox equation for the quaternary blend systems: $[22] 1/T_g = (\omega_1/T_{g1} + \omega_2/T_{g2} + \omega_3/T_{g3} + \omega_4/T_{g4})$ might deviate from the prediction of the T_g-composition relationship. In this expression the Components-1, -2, -3 are PET, PTT, and PBT, respectively, and Component-4 is PEI. The figure shows that there is slight over-prediction by the Fox model in the entire quaternary blend composition range. As the Fox model

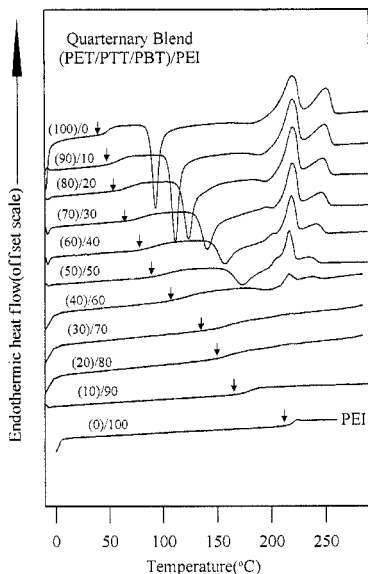


Figure 1. DSC thermograms for the quaternary PET/PTT/PBT/PEI blends with increasing PEI fractions.

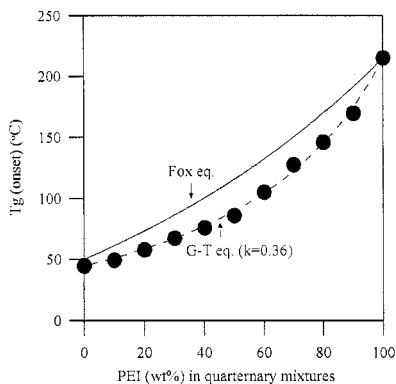


Figure 2. T_g (onset values) vs. composition for the quaternary PET/PTT/PBT/PEI blend. The plot also shows comparison with the Fox equation (solid curve) and Gordon-Taylor model (dashed curve), respectively.

showed some deviation from experimental data, alternative models may be more desirable. The quaternary is treated as a pseudo-binary blend system, where the three aryl-polyesters (PET, PTT, PBT) were treated as a well-mixed ternary polymer constituent (Component-A), and PEI is Component-B. The experimental T_g of Component-A (PET/PTT/PBT = 1/1/1) was measured and it exhibited a $T_{g,A} = 44.5^\circ\text{C}$. Then, the Gordon-Taylor (G-T) equation for this quaternary blend, by using a pseudo-binary expression, is: [23] $T_g = (\omega_A T_{g,A} + k_{A-B} \omega_B T_{g,B}) / (\omega_A + k_{A-B} \omega_B)$, where A and B are the lower- T_g Component (ternary blend of aryl-polyesters) and higher- T_g component (PEI), respectively, i.e., $T_{g,A} < T_{g,B}$, and k is a fitting parameter for this pseudo-binary blend system (actually a quaternary blend). Figure 2 shows that the fitted curve of the G-T model agrees well with the experimental T_g 's of the quaternary blend of all compositions. The fitting result showed a parameter of $k_{A-B} = 0.36$, where the three semicrystalline polyesters were collectively treated as A and the amorphous PEI as B. This parameter represents an average state of miscibility in the quaternary blend system that comprises at least three set of interactions between the three polyesters and PEI, i.e., an average of interactions among those of PET-PEI, PTT-PEI, and PBT-PEI.

Influence of the PEI component on the blend T_g and $T_{c,c}$ appears to be qualitatively similar. For examples, as the quenched quaternary blend samples were scanned in DSC, a cold-crystallization exotherm was observed in most blend compositions of high-polyester contents. $T_{c,c}$ is seen to increase sensitively with respect to increasing PEI contents in the blends but $\Delta H_{c,c}$ is significantly suppressed. Figure 3 shows blends' peak temperatures ($T_{c,c}$) of cold-crystallization exotherms and the integrated peak area ($\Delta H_{c,c}$) of cold crystallization as a function of blend compositions (PEI contents in the quaternary blend). Distinct elevation of $T_{c,c}$ of the aryl-polyesters component in the blends by the amorphous but high- T_g PEI constituent is obvious. The changes in $T_{c,c}$ is usually taken as an indication that there is intimate molecular interaction between the crystallizing components (PET, PTT, PBT) and stiffer PEI polymer chain segments, which cause chain stiffening of chain segments of the aryl-polyesters, which result in significant elevation of the cold-crystallization peak temperatures. Furthermore, the quaternary blends contain three crystallizable constituents (PET, PTT, PBT) as well as PEI, but the blend exhibited only a single and composition-dependent $T_{c,c}$ peak, indicating that the polymer chains are mixed in such fine molecular/segmental scales that the thermal responses of the crystallizing chain segments act

collectively as a single chain, whose behavior is the averages of these three aryl-polyester polymers. Thus, upon scanning, the chains in the miscible polymer mixtures responded collectively to the temperature in crystallization from an amorphous/rubbery state to crystalline state. In addition, the suppressed $\Delta H_{c,c}$ with increasing PEI is also related to the intimate mixing among the four polymers in the quaternary blend. Note that the reported values $\Delta H_{c,c}$ have been adjusted (normalized) to per gram of the aryl-polyesters in the quaternary blend; therefore, the decrease of $\Delta H_{c,c}$ cannot be attributed to the proportional decrease of the crystallizing components in the quaternary blend. The stiffened chains of the aryl-polyesters in the quaternary blend reflected a state of increasing difficulty in crystallization when subjected to heat scanning. This led to an increasingly suppressed $\Delta H_{c,c}$ of the blends with increasing PEI contents. All these thermal evidences indicate a state of intimately mixed chains of quaternary blend system.

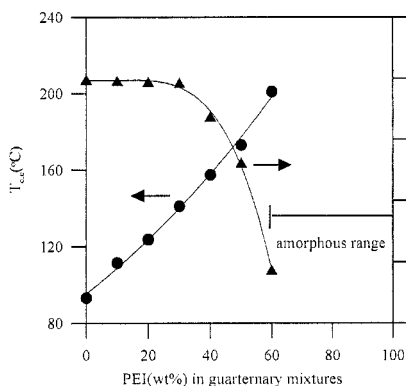


Figure 3. Peak temperature ($T_{c,c}$, filled circles) of cold-crystallization exotherms and their integrated enthalpy ($\Delta H_{c,c}$ adjusted to per g of aryl-polyesters, filled triangles) of the crystallizing aryl-polyesters (PET, PTT, PBT) in the quaternary blends.

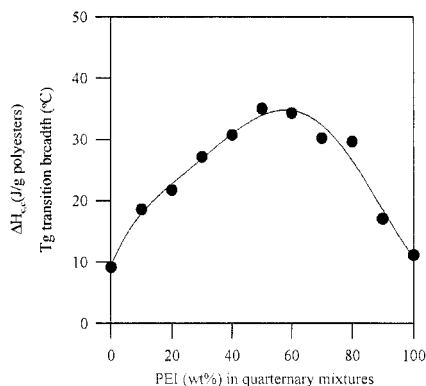


Figure 4. Glass transition breadth as a function of quaternary blend compositions (increasing PEI contents).

The broadening of the glass transition of the blends usually can be taken as an indication of variation of micro-heterogeneity of the mixture state with respect to compositions. Figure 4 shows the glass transition breadth as a function of quaternary blend compositions (increasing PEI contents). The figure shows some interesting features of T_g broadening variation with respect to compositions. For the blend compositions where the weight fractions of the crystallizing aryl-polyesters are high, the samples exhibited a relatively sharp T_g transition. As the PEI weight fraction in the blends increased, the T_g transition breadth reached a maximum, and then decreased again with further increase of PEI fraction in the blend. The maximum of T_g breadth occurred at the blend composition near $\omega_{PEI}=0.6$, and the T_g breadth then rapidly decreases for the blend compositions where the PEI weight fractions are greater than 0.6.

Morphology characterization

For morphology characterization, the PET/PTT/PBT/PEI blends of all compositions were subjected to rapid quenching (dipping into liquid nitrogen) from above the melt state. The OM characterization (for brevity, graphs not shown) revealed that the quenched samples (with the crystallinity being suppressed) appeared optically transparent and homogeneous (at 800X). 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 cloud-point or lower-critical-solution-temperature (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, the SEM result

(for brevity, graphs not shown here) showed homogeneity (at 3,000X) and lack of any discernible domains in the fractured surfaces of the quenched blend samples.

Conclusion

This study, for the first time, demonstrated miscibility and phase behavior of a quaternary blend comprising four different polymers of PET, PTT, PBT, and PEI. A quaternary polymer blend system comprising three semi-crystalline aryl-polyesters, PET, PTT and PBT) and a high- T_g amorphous PEI was for the first time shown to be thermodynamically miscible (in the amorphous region) within the representative composition range studied. A single and composition-dependent T_g was found for each of all quaternary blend samples. The experimental T_g data of the quaternary blend system were further analyzed and compared with some quantitative models. All thermal evidences indicate a state of intimately mixed chains in the quaternary blend system. Furthermore, the quaternary blend contain three crystallizable constituents (PET, PTT, and PBT) and an amorphous PEI, but the quarterly blend exhibited only a single and composition-dependent $T_{c,c}$ peak. This indicates that the polymer chains are mixed in such fine molecular/segmental scales that the thermal responses of the three crystallizing chain segments in the blend act collectively as a single chain, whose behavior is the averages of these three aryl-polyester polymers. In addition, the increasingly suppressed $\Delta H_{c,c}$ at higher PEI contents is also an indication of miscibility and chain intermixing of the quaternary blend. SEM morphology characterization (at 3000 X) revealed no discernible domains.

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