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Miscibility and Melting in Poly(Ethylene Terephthalate)/ Poly(Bisphenol-A-Carbonate) Blends

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Summary

In the absence of significant tranesterification, blends of poly(ethylene terephthalate) and poly(bisphenol-A carbonate) were found to be almost completely immiscible over the range of compositions studied. Although the observed behavior was sometimes erratic, poly(bisphenol-A carbonate) appears to exert a significant influence on PET melting behavior and normalized heat of fusion.

Introduction

In a recent paper (1) we investigated the amorphous phase miscibility of blends of poly(butylene terephthalate) (PBT) with poly (bisphenol-A carbonate) (PC). The motivation for this work stemmed from several reports which indicated that a significant concentration of PBT-PC copolymers could be formed through a transesterification reaction at the temperatures and times used in melt processing (2,3). Copolymer formation could alter the observed transition temperatures and perhaps mask the "inherent" phase behavior of mixtures of pure PBT and PC. In order to avoid exposure to elevated temperatures for prolonged time periods, we prepared our blends by solution casting. In addition, in order to mimic the thermodynamics appropriate to melt processing, all blends were also heated above the melting point of the polyester for a relatively short period of time, cooled to ambient temperature and the phase behavior determined. Contrary to previous reports (4,5), PBT/PC blends were found to be almost completely immiscible over the composition range studied.

It has been suggested that melt processed mixtures of poly(ethylene terephthalate) (PET) and PC also exhibit significant intermolecular mixing (6-8). Blends containing greater than about 70% PET have been reported to show complete miscibility while those with lower polyester content are considered to be partially miscible. Again, however, there are indications that substantial transesterification can occur during melt processing (9). In the current paper we have conducted a set of experiments similar to those we performed on PBT/PC blends in an attempt to more clearly understand the inherent phase behavior of mixtures of

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the pure homopolymers. In the course of our studies we also performed a preliminary evaluation of the melting behavior of these blends.

Experimental

The poly(bisphenol-A carbonate) used in this study (Lexan 131) was obtained from the General Electric Corporation. The PET was obtained from Scientific Polymer Products, Inc. and was designated as having an inherent viscosity of 0.7. Blends were prepared from two different solvents: 1,1,1,3,3,3, hexafluoro-2-propanol (HFIP), and a mixed solvent of tetrachloroethane and phenol (TCE/Ph) in a 40/60 ratio by weight.

Two percent by weight of each polymer was dissolved into the appropriate solvent at room temperature. The solutions were mixed in volume ratios to form a range of compositions. Cast films were initially dried in air then dried under vacuum above the highest possible T_g (i.e., 150°C) for five hours.

Glass transition temperatures (T_g) and melting behavior were determined by differential scanning calorimetry (DSC). All measurements were conducted with either a Perkin-Elmer DSC-2 or DSC-4. Thermograms were recorded and analyzed using a Perkin-Elmer Thermal Analysis Data Station. A heating rate of 20°/min was used for all measurements except where noted. All samples were weighed on either a Perkin-Elmer Autobalance AD-2 or AD-2B. Large samples sizes (14-22 mg) were used to determine T_gs and heats of fusion (ΔH_f). To minimize any complications due to low polymer thermal conductivity, T_ms were obtained using relatively small sample sizes (0.3 to 2 mg) (10). All values reported are the average of at least two measurements. Baselines used to determine the endothermal areas were constructed from approximately 160°C to a temperature above which no more melting was observed. The endothermal areas and transition temperatures were calibrated using an Indium standard.

The problem of reaching an erroneous conclusion due to the so-called $\Delta\chi$ effect was approached in two ways. As mentioned previously, films were cast from two different solvents and differences in the behavior of the blends would indicate solvent effects. Experimentally, we found that the phase behavior of films cast from HFIP and TCE/Ph to be very similar and consequently, only the results for films cast from HFIP will be discussed. In addition, samples with two different thermal histories were characterized for each blend. First, the phase behavior of the blends was determined for samples which had been removed from the vacuum oven and stored at room temperature. Samples with this thermal history will be designated as 'as-cast'. In order to mimic melt processing conditions while avoiding long residence times in the melt, the as-cast blends were heated above the PET melting point (to 277°C) then cooled at 10°/min. ('slow cooled'). This cooling rate was chosen to provide the PET with sufficient time to crystallize. Otherwise, during the second DSC heating run, the PET crystallization exotherm made it impossible to determine the position of the higher T_g.

Dielectric loss spectra were obtained only for as-cast samples from HFIP. Films with an average thickness of approximately 100 μ were metallized with evaporated aluminum over an area of approximately 0.5 cm^2.

The sample geometry used was that of a parallel plate capacitor. Measurements of dielectric constant and loss were made using a Hewlett-Packard Model 4274A LCR meter. Measurements were obtained at 11 discrete frequencies ranging from 0.1 to 100 kHz. A heating rate of 4^{o}/min was used for all samples. For the blends and pure polymers we will designate the relaxation associated with T_g-like motion as the β transition.

Results and Discussion

A. Amorphous Phase Miscibility

Typical DSC thermograms for several slow cooled blends are shown in Figure 1. A summary of glass transition temperatures (defined as the midpoint of the heat capacity change) versus weight percent PET are presented for both as-cast and slow cooled blends in Figure 2. In contrast with previous reports (6-8), two T_gs are observed over the entire composition range studied. For the as-cast materials the lower T_g increases from 82 to 90^{o}C as PET content decreases. The experimental error in measuring the lower temperature T_g is at least 4^{o}C, therefore, the observed variation (although progressively lower with PET content) is within experimental error. A more accurate determination of the lower T_g is difficult due to its small magnitude and what would appear to be a crystallization exotherm just above T_g. The position of the higher temperature transition was found to be independent of composition and is close to the value observed for pure PC.

Dielectric loss spectra at 4 kHz for selected blends as-cast from HFIP, are illustrated in Figure 3. In agreement with the results from DSC, two β transitions are observed over the entire composition range. There is a minor, erratic variation in transition temperature with composition but most were within experimental error of those of the pure components.

For slow-cooled blends (Figure 2), the lower T_g increased progressively by about 5^{o}C with decreasing PET concentration, but this variation is again within the estimated experimental error. However, the higher temperature transition is approximately 8^{o}C below that observed for pure PC and outside the range of experimental error. This depression could indicate a limited degree of mixing masked in the as-cast blends by a $\Delta\chi$ effect. However, recall that these samples were subjected to elevated temperatures for a short, although significant time period on heating and cooling in the DSC and it is possible then that the small change in the higher T_g may be the result of transesterification/copolymer formation.

To determine if the use of elevated temperatures for short times would alter the phase behavior of our blends, films of 70 PET/30 PC mixtures were heated in a press to 280^{o} and 300^{o}C for 10 min using minimal pressure. All films had been placed under vacuum prior to heating to remove moisture. After heating, the blends were quenched into room temperature water. The samples were then loaded into the DSC and heated to 277^{o}C at 180^{o}/min then cooled at 10^{o}/min to below the T_g of PET, in order to mimic the thermal history of the slow cooled blends. DSC thermograms for samples which were subjected to these thermal histories along with a regular slow cooled 70 PET/30 PC blend are illustrated in

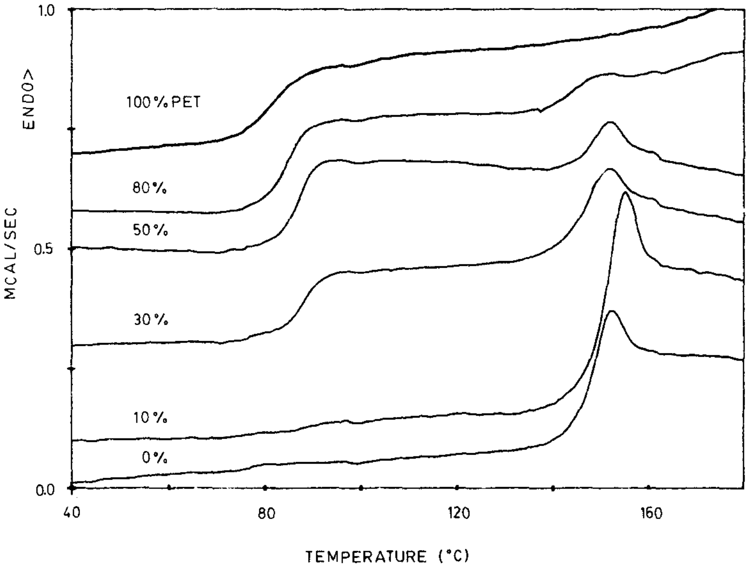

Figure 1. DSC thermograms for slow cooled PET/PC blends.

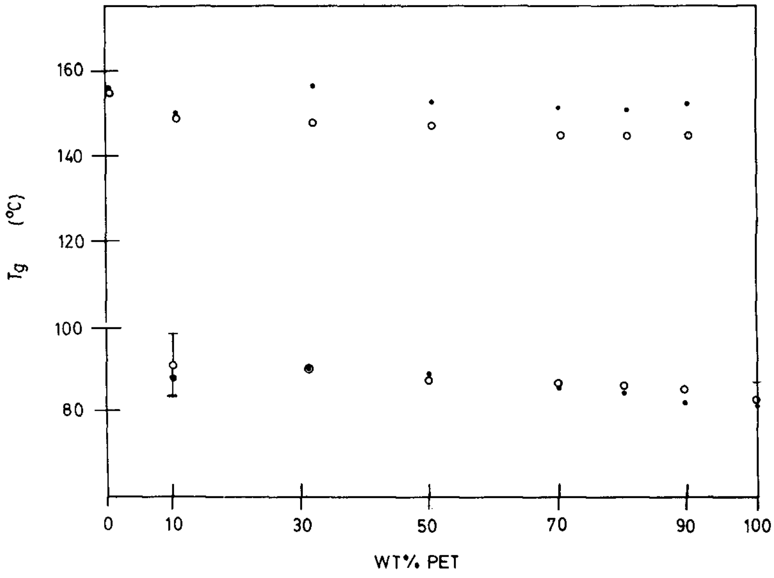

Figure 2. T_g versus weight percent PET (• as-cast, 0 slow cooled). Estimated error is ±4° for the lower T_g and ±2° for the higher T_g unless noted otherwise.

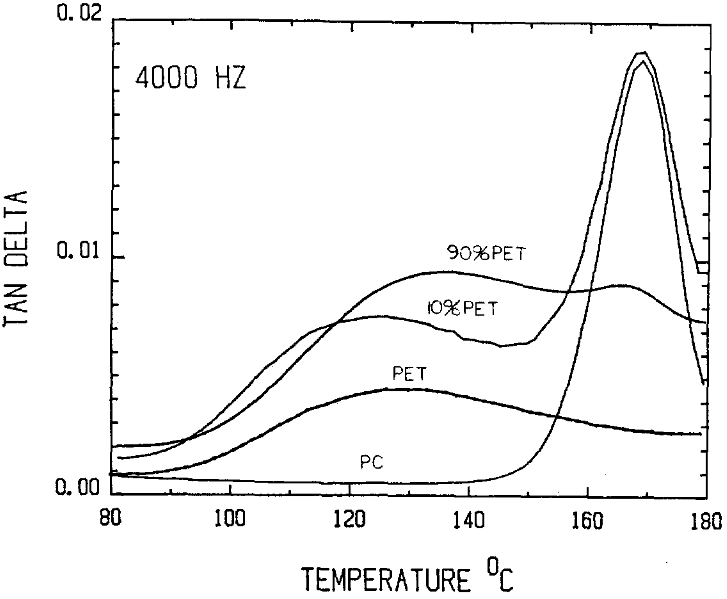

Figure 3. Dielectric loss spectra of as-cast (HFIP) blends obtained at 4 kHz.

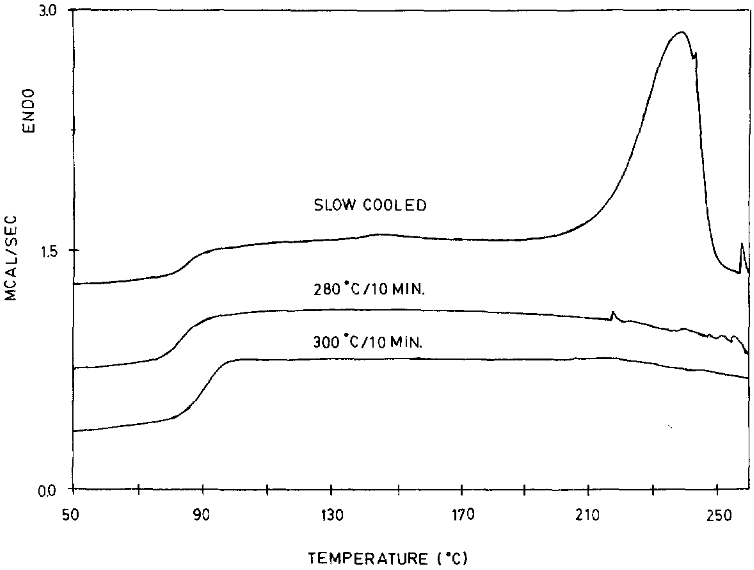

Figure 4. DSC thermograms for 70 PET/30PC blends provided with different thermal histories prior to cooling in the DSC.

Figure 4. The thermal treatments have clearly altered the phase behavior. The position (and intensity) of the lower T_g increases as the treatment becomes more severe, but this change is within the estimated experimental error. Interestingly, the higher T_g is not observed for either of the heat treated blends. In addition, despite the fact that the blends were cooled at 10°C/min from the melt, no melting or crystallization on heating is observed for either of the heat treated samples.

B. Degree of Crystallinity and Melting Behavior

The ΔH_f (adjusted for the weight of PET in the blend) for the as-cast blends are all approximately 13 cal/gram. Taking the perfect crystal heat of fusion to be 33 cal/gram (11), these values correspond to a degree of crystallinity of about 40 percent. In contrast, the adjusted ΔH_f for slow cooled blends decreases from approximately 10 to 4 cal/gram with decreasing PET concentration. This decrease is broadly similar to the behavior observed by Murff, et al. (8). For PET/PC blends heated to 290°C for various time periods then crystallized at 167°C, Murff, et al. found that the heat of fusion was reduced as the residence time at 290°C increased. In addition, the relative amount of the decrease was greatest for blends with less PET. As these and other authors point out, the degree of transesterification obtained for any given melt processing conditions depends strongly on the type and amount of residual polymerization catalyst. This could explain the relatively greater decrease in ΔH_f in our studies as compared to the work of Murff, et al.

DSC thermograms of PET melting behavior for selected compositions are illustrated in Figures 5 and 6 for as-cast and slow cooled samples, respectively. The thermograms of the as-cast blends display multiple melting endotherms, whose shape and position vary somewhat erratically with composition. Pure PET displays a low temperature peak at 197°C while the 90% PET blend contains a collection of small endotherms located between 210 and 230°C. Samples containing 80 to 10% PET exhibit a lower temperature melting endotherm which alternates between approximately 225 and 228°C. The high temperature transition moves in a more regular way, progressively decreasing from 248 to 239°C as PET content decreases. For at least some compositions, the higher melting endotherm appears to be composed of more than one peak. Despite the lack of amorphous phase miscibility, the melting behavior of the PET is clearly influenced by the presence of PC. A number of papers have appeared recently in which immiscible second components have been reported to affect the melting behavior of a crystallizable polymer through their effect on nucleation or spherulitic growth rate (eg. 12-14).

Multiple melting has been reported previously for pure PET and has been attributed to reogranization of the lamellar structure to a more stable form during heating in the DSC (15). To further understand this phenomenon in our blends, the melting behavior of a 50 PET/50 PC blend was determined using a range of heating rates (Figure 7). In general agreement with the concept of lamellar thickening in the DSC, the relative intensity of the highest temperature melting peak becomes larger as heating rate decreases. However, further work is necessary to fully understand the origin of the individual melting endotherms.

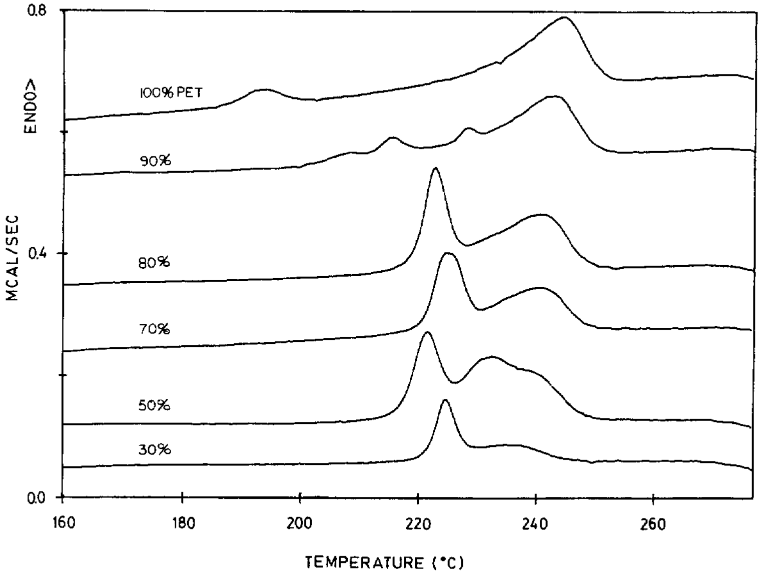

Figure 5. Melting behavior of as-cast (HFIP) blends

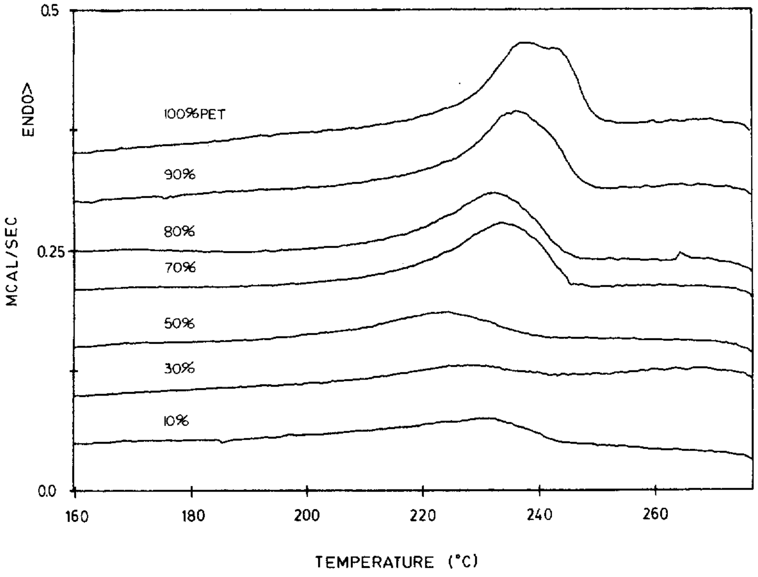

Figure 6. Melting behavior of slow cooled blends.

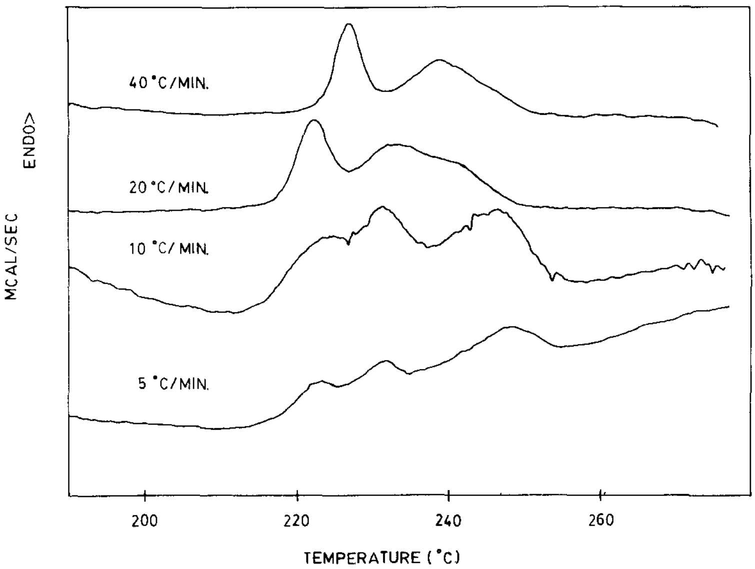

Figure 7. Heating rate dependence of the melting behavior of an as-cast (HFIP) 50 PET/50 PC blend. 40° and 20°/min runs plotted on a range of 0.8 mcal/sec. 10° and 5°/min runs plotted on a range of 0.25 and 0.3 mcal/sec., respectively.

Slow-cooled blends (Figure 6) display a broad melting endotherm which in some cases appear to consist of multiple peaks. In general, T_m decreases as PET content decreases, but the T_m of the 10% PET sample is out of line with the trend.

Acknowledgments

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