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Miscibility

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

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Summary

The miscibility of blends of poly(butylene terephthalate) and poly(bisphenol A-carbonate) was investigated using differential scanning calorimetry. Contrary to previously reported data, PBT and PC were found to be almost completely immiscible over the entire compostion range studied. The minor change in T_g's observed for samples quenched form the melt can be attributed to transesterification at elevated temperatures. The melting behavior and normalized enthalpy of fusion are somewhat dependent on composition but the behavior is erratic.

Introduction

There has been considerable interest in creating new useful materials through the formation of polymer blends. A number of such mixtures have been commercialized recently including those based on poly(butylene terephthalate) (PBT) and poly(bisphenol A-carbonate)(PC). However, despite their commercial importance, very little has been published regarding the phase behavior of PBT/PC blends (1,2). The results of previous research indicate that the polymers are partially miscible with two or three glass transitions usually shifted from the temperatures observed for the pure components.

A complication in determining the inherent miscibility of polyester-polycarbonate mixtures is the potential for transesterification when blending or processing the polymers. A small amount of transesterification would lead to formation of copolymers which could complicate the phase behavior. Several recent papers (3-7) have shown that transesterification can take place between PBT and PC within the temperature range often used to melt blend these materials, even for relatively short residence times. Since the previous investigations of the miscibility of PBT/PC mixtures have focused on melt processed materials (1,2), we decided to examine the phase behavior of blends in which the possibility of transesterification had been minimized. In the course of our studies we also examined the melting behavior and degree of crystallinity of these blends.

Experimental

The poly(butylene terephthalate) (Celanex 2001) and poly(bisphenol A-carbonate) (Lexan 131) used in this study were provided by the Celanese and General Electric Corporations, respectively. Blends were prepared from two different solvents: 1,1,1,3,3,3, hexaflouro-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 in the appropriate solvent at room temperature. The solutions were mixed in volume ratios to form a range of compositions. Films of the pure polymers and all blends were initially dried in air then dried above the highest possible glass transiton temperature (i.e. that for PC, 150 °C) in a vacuum oven for 5 hours.

The glass transition temperature (T_g), melting point (T_m), and heat of fusion (ΔH_f) of each blend were measured with either a Perkin-Elmer DSC-2 or DSC-4 differential scanning calorimeter. All DSC curves were recorded and analyzed using a Perkin-Elmer Thermal Analysis Data Station. A heating rate of 20 °C/min was used for all measurements except where noted. Large sample sizes (14 to 22 mg) were used to determine T_g and ΔH_f. To minimize complications due to low polymer thermal conductivity (8), the melting behavior was determined using small samples (0.3 to 2 mg). All values reported are the average of at least two measurements. The endothermal areas and transition temperatures were corrected using an indium standard.

A complication inherent in dealing with solution-cast blends is that the presence of solvent may induce phase separation in a normally miscible system due to the greater affinity of one of the polymers for the solvent ('$\Delta\chi$ effect') (9). This could lead to phase separation in the final dry film if the polymer chains do not have the time or mobility to intermix as the solvent evaporates. We used two approaches to avoid the possibility of reaching erroneous conclusions due to solvent effects. First, in order to mimic the thermodynamics appropriate for melt processing at elevated temperatures, while avoiding long residence times in the melt, the thermal properties were determined for both as-cast blends and for as-cast materials that were heated to temperatures in excess T_m and quenched to room temperature. The quenched samples, which should not be influenced by solvent, were prepared by heating the as-cast films to 257 °C at 20 °C/min and then quenching at the highest possible rate in the DSC. In addition, as described previously, the blends were cast from two different solvents: any differences in behavior would indicate a $\Delta\chi$ effect.

Results and Discussion

A. Amorphous Phase Miscibility

DSC thermograms for selected compositions are shown in Figure 1 for samples cast from HFIP and T_g's for all compositions are summarized in Figure 2. The behavior of blends prepared from TCE/Ph is similar to those cast from HFIP. Two T_g's are observed over the entire composition range for both the as-cast and quenched blends. In addition, the T_g's are mostly independent of composition. For the case of the as-cast materials, the high temperature transition is approximately constant near 150 °C (i.e. the T_g of pure PC). Similarly, the high temperature glass transition for the quenched blends is invariant with composition. No transition was detected for the 90% PBT sample, but this is thought to be more of a problem with instrument sensitivity than any indication of miscibility.

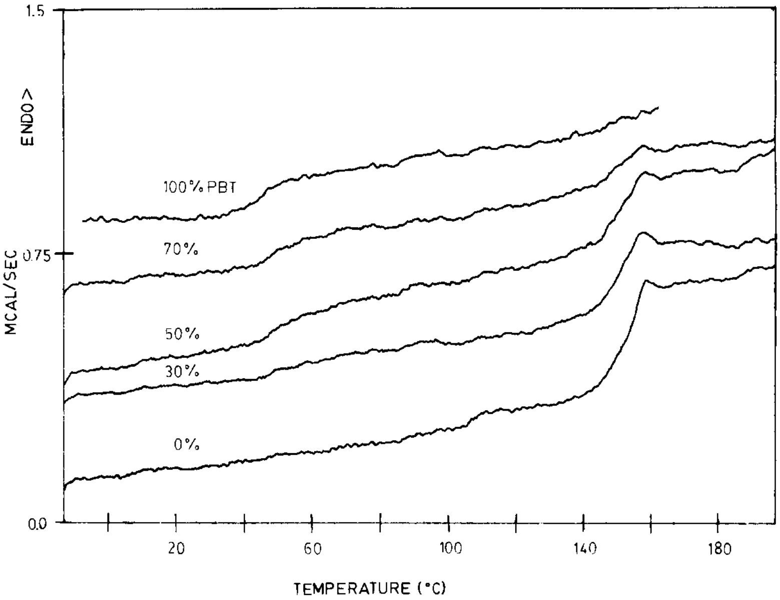

Figure 1. DSC thermograms for PBT/PC blends cast from HFIP

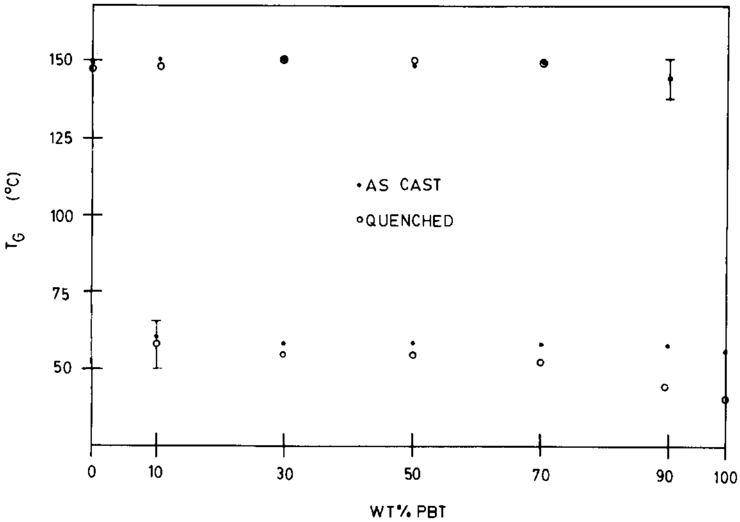

Figure 2. T_g versus weight percent PBT for as-cast (HFIP) and quenched blends. Unless otherwise noted, the estimated error in T_g is ± 3^o

The lower temperature transition of the as-cast films also remains approximately constant with composition, near the value for pure PBT. In contrast, the lower T_g for the quenched blends shifts from 42 °C for pure PBT to 54 °C for samples with lower PBT contents. The transition is essentially independent of composition for blends with less than about 70% PBT. Several possible explanations exist for this variation in T_g. There may be some level of partial miscibility as suggested previously (1). However,one would expect the as-cast blends to behave in a similar manner in the absence of any solvent effects. We believe that movement in the lower T_g is associated with a small amount of transesterification. All quenched samples were subjected to temperatures up to 257 °C before any measurements were obtained and, while the residence times at the elevated temperatures are relatively short, even a small amount of ester interchange may be sufficient to cause a change in the observed T_g's.

To determine if the use of elevated temperatures for short times could lead to a significant change in phase behavior, samples of a 70 PBT/30 PC blend were subjected to several thermal treatments. One sample was heated to 245 °C at 180 °C/min., held at 245 °C for 10 minutes and then quenched at the highest possible rate in the DSC before determining its thermal properties. The same procedure was followed for another 70/30 blend, except that it was held at 255 °C for 10 minutes. In Figure 3 the results are compared for the two heat treated samples described above as well as for a sample quenched in the normal manner. The position of the low temperature transition increases with more severe treatment while the melting point (not shown) decreases. However, for the conditions used, the high temperature transition appears to be independent of treatment, presumably indicating that any copolymers formed at the higher temperatures mix with the amorphous PBT phase.

B. Melting Behavior

No evidence was observed for the crystallization of the PC portion of the blends when cast from HFIP and endothermal areas observed in DSC curves were therefore attributed to the PBT portion of the blend. The normalized heat of fusion (i.e. ΔH_f per unit weight of PBT) for pure PBT and the 90% PBT blend is $\sim$16 cal/gram as opposed to $\sim$13 cal/gram for samples with less than 70% PBT. Taking the perfect crystal heat of fusion to be 34 cal/gram (10), these values correspond to a degree of crystallinity based on the weight of PBT in the blend of between 38 and 47%. In contrast, the adjusted heat of fusion is independent of composition for the quenched blends ($\Delta H_f \simeq 9$ cal/gm).

The polycarbonate portion of the blends crystallized when cast from TCE/Ph, complicating interpretation of the melting behavior for these films. Therefore, the discussion of the influence of blending on ΔH_f and T_m is ignored for this solvent.

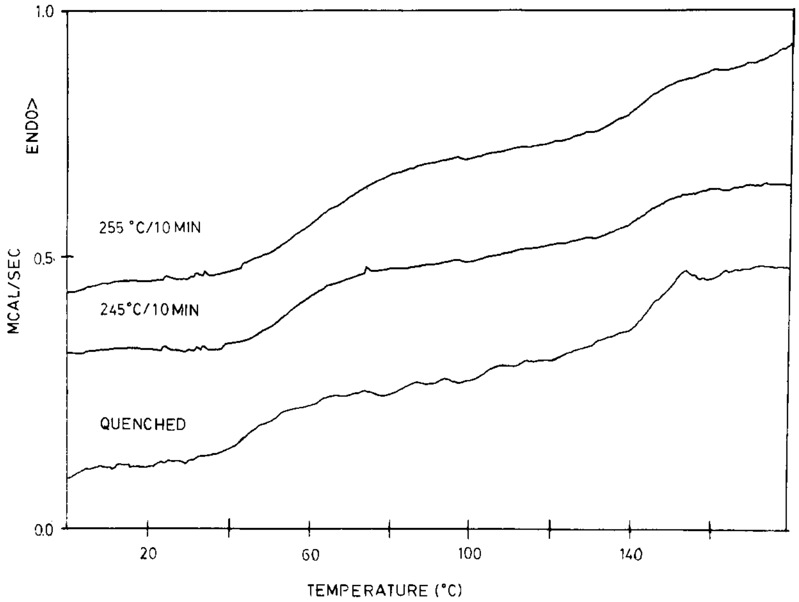

Figure 3. DSC thermograms for heat treated and quenched 70 PBT/30 PC blends

DSC thermograms of the PBT melting region for each composition are illustrated in Figures 4 and 5 for the as cast and quenched samples, respectively. A summary of the T_m data is presented in Figure 6. The thermograms of the as-cast samples display two melting endotherms. As can be seen in Figure 4 the lower peak temperature is erratic while the higher T_m remains constant at a temperature of approximately 219 °C. Multiple melting has been reported previously for pure PBT (11,12). To further understand this phenomenon in our blends and the possible influence of PC on the melting of PBT, the melting behavior of a 50 PBT/50 PC blend was determined using a range of heating rates (Figure 7). These results are generally in agreement with the concept of lamellar reorganization to a more stable form during heating in the DSC, which has been reported to be the cause of multiple melting in pure PBT (11). However, the rationale for the movement of the low temperature peak to lower temperatures with increasing heating rate is not clear at this time.

In contrast to the as-cast blends, quenched specimens display a single melting peak, presumably also complicated by reorganization during heating. The melting point of the quenched samples decreases by about 4 ° with decreasing PBT content. This depression is consistent with the possibility of a small amount of ester interchange during specimen preparation and with the decrease in T_m observed in our heat treatment experiments.

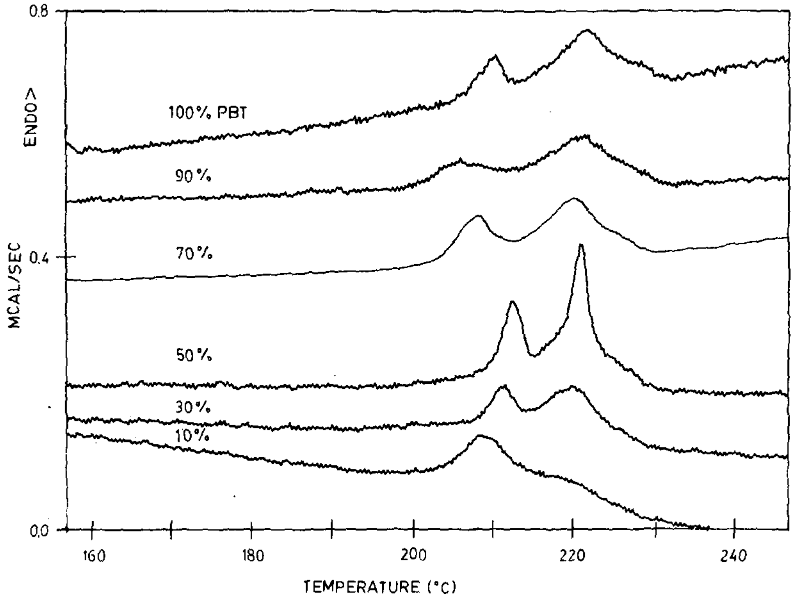

Figure 4. Melting behavior of as-cast (HFIP) PBT/PC blends

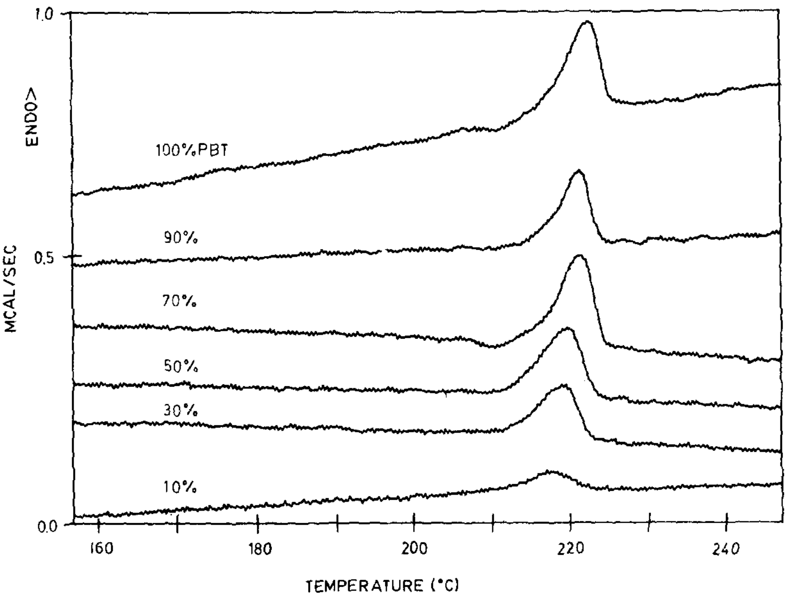

Figure 5. Melting behavior for quenched PBT/PC blends

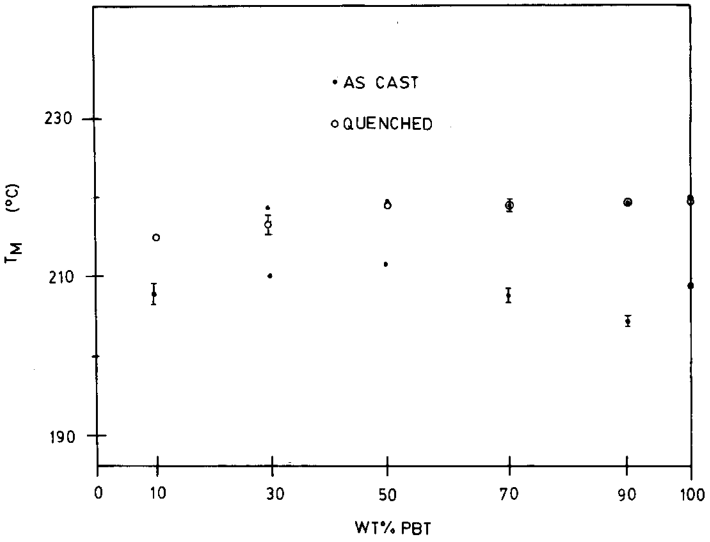

Figure 6. Summary of T_m's for as-cast (HFIP) and quenched blends. The error in T_m is approximately the size of the open circles unless otherwise noted. A T_m could not be confidently assigned to the high temperature melting endotherm of the as-cast 10% PBT blend due to poor peak resolution

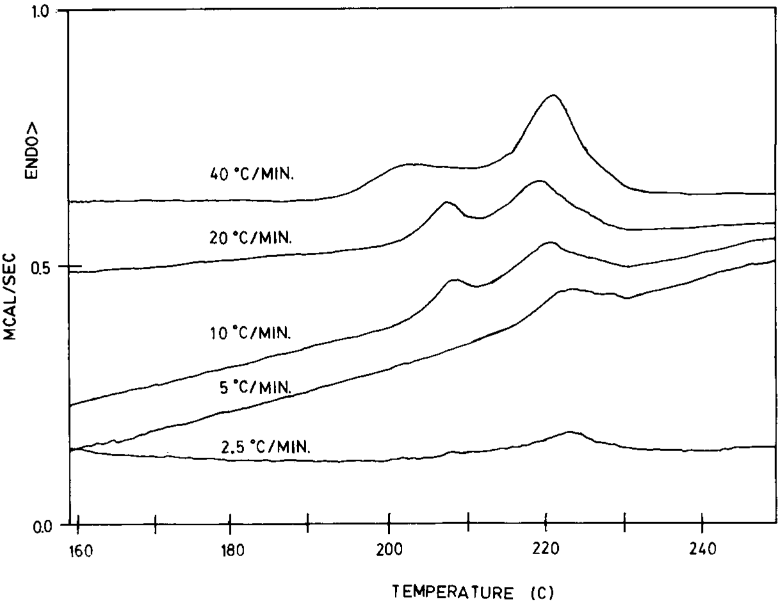

Figure 7. Heating rate dependence of the melting behavior of an as-cast 50 PBT/50 PC blend

Acknowledgments

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