

## **Partial miscibility of poly(butylene terephthalate)/BPA polycarbonate melt blends**

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### **SUMMARY**

Differential scanning calorimetry (DSC) measurements have been carried out on a number of poly(butylene terephthalate) (PBT)/BPA polycarbonate (PC) blends prepared by melt compounding and solution casting from hexafluoroisopropanol (HFIP). The results clearly indicate that appreciable mixing of the two polymers takes place in the melt phase whereas complete separation is observed in cast films. The failure of the casting procedure to mimic the melt blending results is related in part to liquid-liquid phase separation and to crystallization of both polymers from the casting solvent.

### **INTRODUCTION**

The issue of miscibility between PBT and PC has been addressed by several researchers in recent years with conflicting results. In early experiments, Paul and his coworkers concluded from measurements of glass transition temperature shifts that partial mixing of the two polymers occurred during melt compounding (1). Following these studies, however, Mercier et al., pointed out that transesterification can take place in the temperature range used for melt blending and that the observed  $T_g$  drops could be accounted for by copolymer formation rather than miscibility (2,3). Most recently, Hanrahan et al., attempted to avoid the ambiguities associated with melt reactivity by analyzing solution-cast blends of the two polymers (4). Noting the absence of  $T_g$  shifts in these samples the authors concluded that the two polymers were immiscible. This conclusion is at odds with morphological studies carried out in our laboratory on well-stabilized, melt-mixed PBT/PC blends (5-7). We believe the calorimetric investigations in this communication clarify this discrepancy and provide convincing evidence for true melt-miscibility between PBT and PC in the absence of copolymer formation.

The experiments described herein are unique in that the blends were carefully stabilized to inhibit transesterification and both melt-mixed samples and solution-cast films prepared from the melt-mixed samples were examined. This procedure provided a measure of the extent of demixing which occurred during solvent evaporation and an assessment of the relative importance of copolymer formation and miscibility in depressing the PC  $T_g$ . The analysis is based on the following argument: If copolymer were generated in the melt, the PC  $T_g$  in both the extrudate and the cast film should be depressed since the copolymer is necessarily carried along during the casting process. If, on the other hand, the two resins form a mixed phase in the melt which segregates during solvent casting (4), the PC  $T_g$  in

the extrudate should again be depressed but that of the cast film should be close to that of the homopolymer. Additional insights into the extent of copolymer formation and the degree to which the stabilizer plasticized the resin were provided by  $^{13}\text{C}$  NMR studies of extracted samples and DSC analyses of stabilized PC homopolymers.

#### EXPERIMENTAL

The melt blends used in this study were prepared from commercial PBT (Valox 315\*) and PC (Lexan 141\*) resins obtained from the General Electric Plastics Business Group. Compounding was carried out on a single screw extruder and a proprietary chemical stabilizer was added to inhibit transesterification. After extrusion the pelletized resins and melt blends were cryogenically ground to improve their homogeneity and handling characteristics. Dry blends of the homopolymer were prepared by tumbling the powdered resins on a roll mill.

Cast films were prepared by dissolving the individual resins and blends in HFIP at a concentration of 2% by weight and allowing the solvent to evaporate in air overnight. Final drying was carried out by placing the films in a vacuum oven at  $150^\circ\text{C}$  for five hours. Films prepared in this way showed weight losses of less than 0.3% during subsequent melting and recrystallization experiments.

Melting points,  $T_g$ 's, and heats of fusion ( $\Delta H_f$ ) were determined on a Perkin Elmer DSC-2. All runs were carried out at  $20^\circ\text{C}/\text{minute}$  over a temperature range of  $270^\circ\text{K}$  to  $540^\circ\text{K}$  using samples of 15-25mg. After the first heat, the specimens were cooled to room temperature at  $320^\circ\text{K}/\text{min}$ . and rerun in order to eliminate any  $T_g$  elevation associated with crystallization of the PC.

#### RESULTS AND DISCUSSION

The measured  $T_g$ 's for the various 50:50 blends used in this study are shown in Figure 1. Rather than reproducing the DSC scans, the data are presented as a bar plot to provide a more convenient visual means of comparing the results and estimating the uncertainty in the data. Before continuing the discussion, it seems worthwhile to comment on the film casting process since several observations made in our studies differ from those reported elsewhere (4).

First, both the melt-processed and dry-mixed blends gave cloudy solutions in HFIP. For example, 0.25 gm PC + 0.25 gm PBT + 10 ml HFIP was mixed by shaking at  $50^\circ\text{C}$  in a cylindrical vial and then allowed to stand at room temperature for one week. The initially turbid solution separated into two clear layers. 24% of the mixture volume was in the upper (PC-rich) layer and 76% of the mixture volume was in the lower (PBT-rich) layer. Second heat DSC measurements on the film (0.258 gm) cast from the upper layer gave a  $T_g$  for PC identical to that of pure PC and a PBT fusion heat of  $3.6 \text{ J/gm}$ . Second heat DSC measurements on the film (0.232 gm) cast from the lower layer gave a PBT of  $35.1 \text{ J/gm}$  and a PC  $T_g$  that was

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\* Valox and Lexan are registered trademarks of the General Electric Company

too small to detect. These data indicate a very appreciable separation of the polymers by partitioning between the liquid phases.

Secondly, PC crystallization was observed in all of the cast films during first heat DSC measurements. This was evidenced by both a 2-3°C elevation in the PC  $T_g$  (Figure 1, Bars B,D) and the appearance of a melt endotherm (29.4 J/gm) centered at 232°C for pure PC cast from HFIP. (In the blends the PBT and PC melt endotherms were unresolved.) The extent of PC crystallization from solution-cast films varied considerably for different castings. Figure 2 presents the first and second melting heats for PC, PBT and PC/PBT (dry blend) films cast from HFIP. Due most likely to some variation in the extent of PC crystallization, a linear increase (broken line) in the heat is not observed on moving from the PC melting heat of 29.4 J/gm to the PBT melting heat of 52.9 J/gm in the first heat. Only the PBT crystallizes from the melt during cooling between the DSC runs and the heat of melting for the film is linear in PBT weight fraction from 0 to 39.5 J/gm in the second heat. The second heat  $T_g$  values for the PC in the PC/PBT blend lay within 2°C of that of the pure PC film and did not vary with blend composition. These data indicate that the combined effect of liquid-liquid phase separation and crystallization of both polymers produces complete separation of the polymers in the cast films within the DSC detection limits.

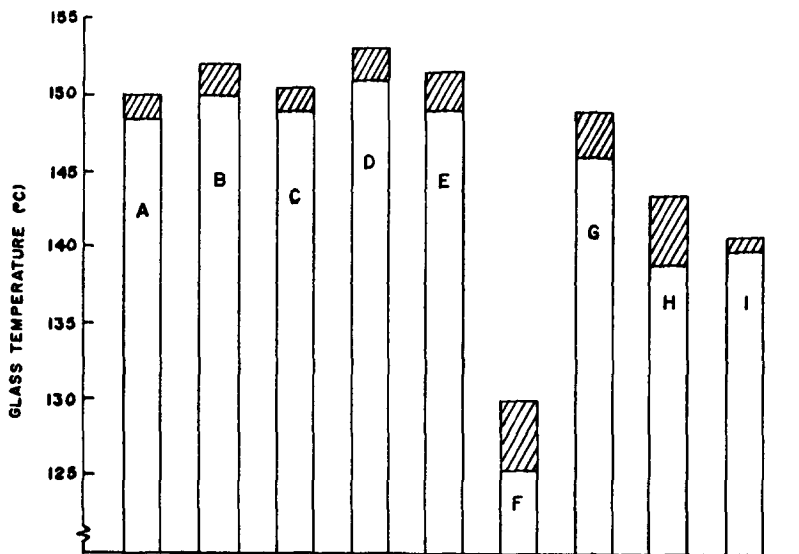


FIGURE 1: PC Glass transition temperatures for PC and PC/PBT 50:50 blends. Shaded areas indicate range of measured  $T_g$  values. A) as-received PC pellets; B) PC pellets cast from HFIP (1st heat); C) PC pellets cast from HFIP (2nd heat); D) PC/PBT dry blend cast from HFIP (1st heat); E) PC/PBT dry blend cast from HFIP (2nd heat); F) PC/PBT melt blend; G) PC/PBT melt blend cast from HFIP (2nd heat); I) PC + stabilizers cast from HFIP (2nd heat).

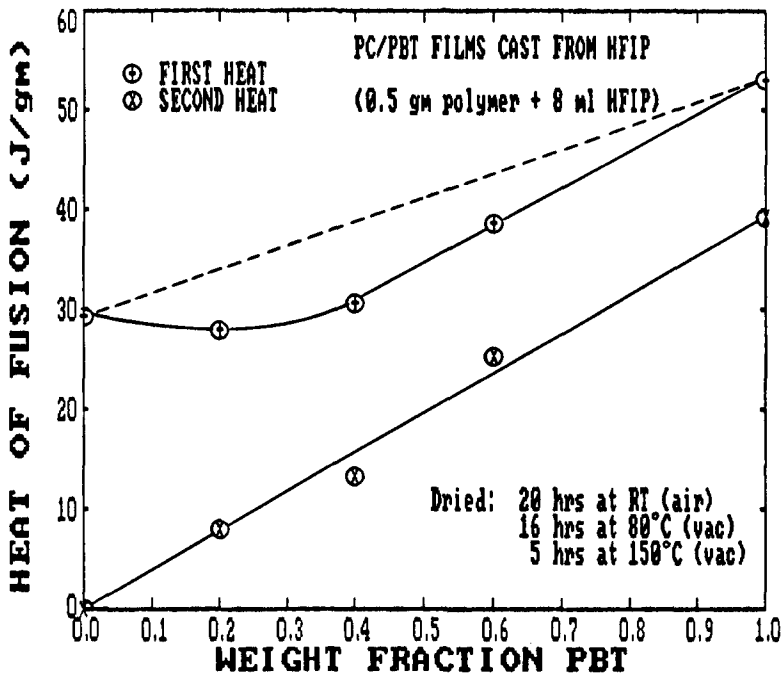


FIGURE 2: Heats of fusion vs. weight % PBT in PBT/PC cast films.

Comparison of bars A, C and E in Figure 1 reveals that the second run  $T_g$ 's of PC cast from HFIP solutions of the homopolymer and a PBT/PC dry blend are identical to that determined for the starting material. These results agree with Hanrahan's observation that no mixing of the two polymers occurs when they are codissolved and cast from solution or briefly melted in the calorimeter. It also confirms that solvent removal is complete and that the relatively mild DSC heating history does not depress the  $T_g$  as the result of degradation, etc.

In contrast to these samples, the stabilized, melt-blend of PBT and PC showed a sharp drop in  $T_g$  to 126 - 130°C. When this sample was dissolved and cast into a film, however, the  $T_g$  rose to a value only slightly below that of the homopolymer (Figure 1, Bar H). This reversible  $T_g$  shift provides convincing evidence that PBT and PC show an appreciable degree of thermodynamic miscibility in the melt phase when sufficient contact time and agitation are provided. It is also consistent with recently reported morphological observations which show phase-separated PC in the interlamellar regions of PBT spherulites (5-7). Finally, these observations point out the danger of using solution-cast films or short-term exposure to elevated temperatures to assess miscibility.

It was noted that the  $T_g$  of the solution-cast melt blend of PBT and PC remained slightly below that of the homopolymer. This effect could be accounted for either by the presence of a small amount of copolymer or

by the stabilizer added to the mixed melt. To check on the former, the melt-compounded blend was ground to a fine powder and exhaustively extracted with chloroform. The soluble (PC) and insoluble (PBT) phases were examined by  $^{13}\text{C}$  NMR and the spectra compared with those of the original components and that of the stabilizer package. A 1:1 match of all of the peaks in the melt blend with those in the spectra of the individual components was obtained. The minimum detectable impurity level was estimated to be less than 0.5%.

The second effect was evaluated by solution casting a film of PC and stabilizer from HFIP maintaining the same composition ratio as that in the melt blend. This film was dried in the same fashion as the previous samples and examined by DSC. The  $T_g$  is shown by Bar I in Figure 1 and is seen to be identical to that of the  $T_g$  of the solution-cast melt blends of PBT and PC. The amount of PBT dissolved in the PC phase after the depression due to the stabilizer is eliminated can be estimated from the additivity of reciprocal  $T_g$ 's to be approximately 12%.

#### CONCLUSIONS

1. The PC  $T_g$  in well-stabilized melt blends of PBT and PC is significantly depressed compared to that of the homopolymer.
2. The largest part of the depression is due to partial miscibility between the PBT and PC phases and is not due to copolymer formation.
3. When plasticization due to transesterification stabilizers is properly accounted for, the amount of PBT dissolved in PC is calculated to be about 12% for high molecular weight commercial resins used in this study.
4. Solution blending is an inappropriate method for assessing miscibility because of spontaneous phase separation driven by liquid-liquid phase separation and crystallization of both components during evaporation of the solvent. Short exposure of the segregated samples to elevated temperatures in the quiescent state is insufficient to allow the components to remix.

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