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The morphology and deformation behavior of poly(butylene terephthalate)/BPA polycarbonate blends

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SUMMARY

In this communication the results of a series of recent studies of the morphology and deformation behavior of toughened poly(butylene terephthalate) (PBT)/BPA polycarbonate (PC) blends are briefly summarized. Several papers containing a more detailed account are currently in press (1-3). Among the unique morphological features of these blends are the consistent isolation of the core/shell impact modifier (IM) in the PC phase and the crystallization and phase separation of the PBT from the partially miscible PBT/PC melt on slow cooling. DSC studies provide corroborating evidence for melt miscibility of the two resins. The blends deform through a combination of cavitation and shear processes. In all cases cavitation occurs exclusively within the IM particles and is suppressed at higher PC concentrations and elevated temperatures.

INTRODUCTION

Impact modified blends of BPA polycarbonate (PC) and poly (butylene terephthalate) (PBT) are being used to an increasing extent in engineering applications requiring superior low temperature toughness (e.g., automotive bumpers). In order to optimize performance of these materials in such demanding situations, it is essential to develop a thorough understanding of the factors affecting their microstructure and deformation behavior. To be successful in this endeavor, an interdisciplinary effort involving detailed microscopic characterization, sophisticated mechanical testing, and careful analytical studies is required. Although some work of this type has appeared in the literature (4,5) together with more fundamental research on PBT/PC miscibility (6-9), major questions with respect to phase segregation, distribution of blend components, and morphological changes which occur during deformation remain.

In response to these issues, a more complete investigation of the microstructure and deformation characteristics of several PBT blends containing various combinations of PC and IM was recently carried out in our laboratory. Scanning (SEM) and Transmission (TEM) electron microscopy, tensile dilatometry, and differential scanning calorimetry (DSC) were used in a complimentary fashion in this effort. Staining with RuO_4 and etching with diethylene triamine (DETA) were found to provide excellent contrast between the blend components in the samples analyzed by electron microscopy. The structural details visualized by these methods provided a unique perspective for interpreting DSC and tensile dilatometry data.

EXPERIMENTAL

Blend Preparation

The blends used in this study were prepared from commercial grades of PC (Lexan 141) and PBT (Valox 315) obtained from the General Electric Plastics Group. These resins were compounded in various compositions with a core/shell impact modifier on a single screw extruder and injection molded into suitable test specimens. A proprietary stabilizer was added to each of the blends to inhibit transesterification. All subsequent melting and recrystallization experiments were carried out in a Mettler FP-2 hot stage.

Microscopy

Transmission electron microscopy was carried out on a Hitachi H-600 TEM. Thin sections were stained by immersion in a hexane solution of OsO_4 or by suspension in RuO_4 vapor following the method described by Trent (10). Scanning electron microscopy was carried out on a Jeol 840 SEM. The samples were typically etched by immersion in DETA for 1 minute at room temperature and sputter-coated with an Au/Pd alloy.

Mechanical Testing

Notched impact tests and tensile dilatometry were carried out on a thermostatted Instron 1350 servohydraulic testing machine. The impact tests were performed in three-point bending at a piston speed of 2 m/s. Volume changes were measured on ASTM tensile specimens using nested axial and transverse strain gauges.

RESULTS AND DISCUSSION

The efficacy of RuO_4 staining was first evaluated on a 90/10 PBT/PC blend to permit unambiguous assignment of the major and minor phases. In comparison to unstained samples, contrast and interface definition in the stained specimens was excellent and the dispersed PC particles ranging from 2 to 5 μm in diameter were readily visible. This improvement was even more apparent in the toughened specimens where the IM was found to be uniformly encapsulated by PC (Figure 1). It is noteworthy that although the IM is unsaturated and reacts readily to OsO_4, it is not effectively stained by RuO_4. This result suggests that, in contrast to OsO_4, the uptake of RuO_4 is controlled by differential absorption and does not involve a discrete chemical reaction. At higher PC concentrations the impact modifier remains encapsulated in PC although the dispersed PC/IM phase becomes increasingly interconnected and eventually forms an interpenetrating network.

The extent of intermixing between the PBT and PC phases in the melt blend was highlighted in samples which were melted and slowly recrystallized. The SEM photograph in Figure 2 shows the free surface of a recrystallized 70/15/15 PBT/PC/IM blend after etching with DETA. In this specimen the PC has been selectively removed from between the PBT lamellae. The extremely small scale of this segregation suggests that there is some melt miscibility of the components and the phase separation occurs during cooling and recrystallization of the PBT. This process is more strikingly

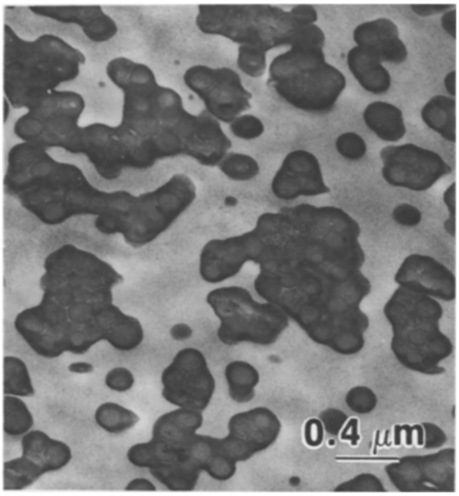

FIGURE 1: (TEM) PBT/PC/IM (70/15/15) stained with RuO_4. IM particles are visible as sub-inclusions in stained PC.

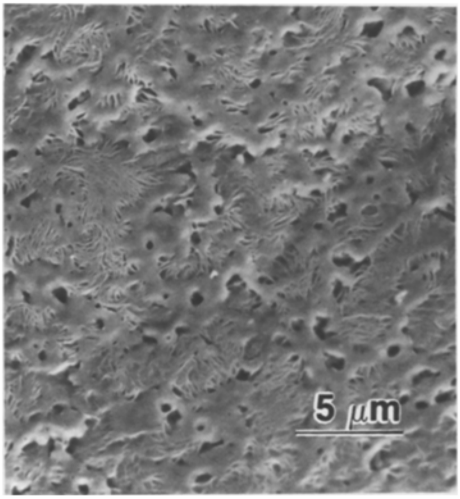

FIGURE 2: (SEM) Free surface of slowly crystallized PBT/PC/IM (70/15/15) etched with DETA.

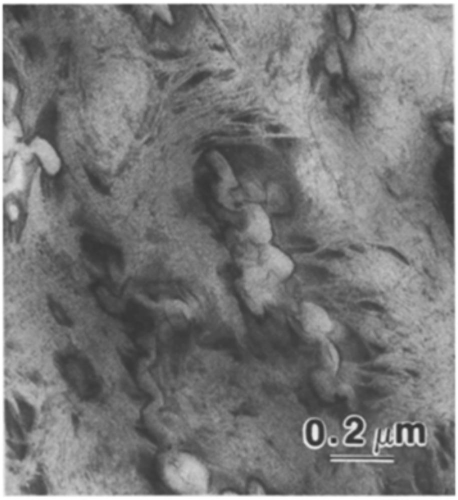

FIGURE 3: (TEM) Slowly crystallized PBT/PC/IM stained with RuO_4.

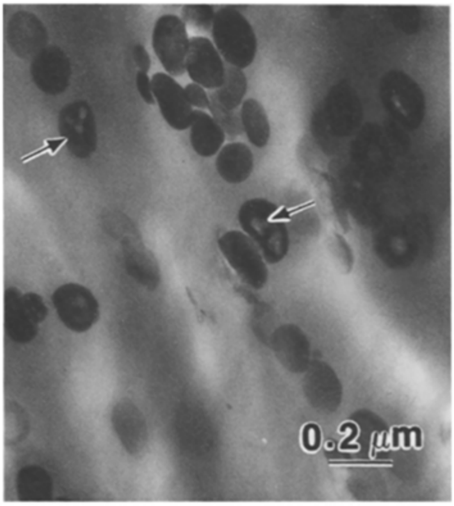

FIGURE 4: (TEM) Cavitated rubber particles in PBT/PC/IM (40/45/15) stained with OsO_4.

illustrated in Figure 3 showing a RuO_4-stained cross section of the same sample viewed by TEM.

The apparent melt miscibility of PBT and PC was confirmed by DSC analyses of the extruded blends. In these samples, the PC T_g's were depressed by approximately 20°C compared with that of the pure resin. In order to insure that the depression was due to melt-mixing and not copolymer formation, the blends were dissolved in hexafluoroisopropanol and cast into thin films. T_g depressions resulting from copolymer formation should be preserved after such treatment, experimentally, however, the PC glass temperatures were observed to rise sharply in the cast films indicating that the melt-mixed resins simply phase-separated during evaporation of the solvent. The details of these experiments are described more fully elsewhere (3).

Additions of IM and PC were found to have a synergistic effect on the low temperature toughness of PBT. In three-point bend tests pure PBT was observed to be brittle over the entire range of test temperatures (-30°C to 25°C) while the 40/45/15 PBT/PC/IM blend was ductile at all temperatures. Intermediate compositions exhibited ductile/brittle transitions at various temperatures between the two extremes. Tensile dilatometry revealed that the extent of shear deformation vs. cavitation was independent of the fracture mode but related to the presence or absence of IM. Only those blends containing IM showed appreciable cavitation. TEM photographs taken beneath the fracture surfaces of specimens containing impact modifier showed that cavitation was localized within the cores of IM particles (Figure 4). At higher PC levels, where shear deformation appeared to be facilitated by the presence of PC in the interlamellar region of the PBT spherulites, the level of cavitation decreased.

CONCLUSIONS

1. Selective staining with OsO_4 and RuO_4 and etching with DETA have been shown to be extremely effective in elucidating the morphology of toughened PBT/PC blends.
2. In all of the blends the impact modifier is isolated within the PC phase. The PC/IM domains become increasingly interconnected as the PC level is raised until an interpenetrating network is formed.
3. There appears to be appreciable melt solubility between PBT and PC although the major fraction of PC forms a separate melt phase. Phase separation of the soluable PC fraction appears to take place on cooling and the PC becomes segregated between the PBT lamellae. DSC results are consistent with this observation.
4. During high speed deformation, toughened PBT/PC blends exhibit both dilation and shear deformation. Dilation occurs only in those blends containing IM and appears to be localized within the core of the IM particles. Addition of PC drops the initiation stress for shear deformation allowing triaxial stresses to be relieved by plastic flow rather than cavitation. Dilation gives way to shear at higher temperatures and lower rates and toughness is enhanced.

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