

Toughened blends of poly(butylene terephthalate) and BPA polycarbonate

Part 1 *Morphology*

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The morphologies of melt blends of poly(butylene terephthalate) (PBT) and bisphenol A polycarbonate (PC) toughened with a core/shell impact modifier have been characterized by transmission and scanning electron microscopy. Selective staining with ruthenium and osmium tetroxide and etching with diethylene triamine have been used to assess the distribution of the various blend components and investigate the effects of thermal history on morphology. Strong evidence for partial melt miscibility of PC and PBT and rate-dependent segregation during cooling is presented.

1. Introduction

Impact-modified blends of poly(butylene terephthalate) (PBT) and polycarbonate (PC) are being used to an increasing extent in engineering applications requiring superior low-temperature toughness. In order to optimize the performance of these materials in such demanding situations, it is essential to develop a thorough understanding of the factors affecting their microstructure and deformation behaviour. To date, however, these issues have received relatively little attention in the published literature [1-4] with most of the reported work on PBT/PC blends dealing primarily with the limited issue of miscibility between the two polymers [5-7]. As a consequence, major questions involving phase segregation, distribution of blend components and morphological changes which occur during deformation, remain.

In response to this deficiency, a more complete investigation of the microstructure and deformation characteristics of several PBT blends containing various combinations of PC and an unsaturated core/shell impact modifier (IM) was recently carried out in our laboratory. All of the studies were performed on melt blends of the various components. While transesterification was minimized by the addition of appropriate stabilizing agents, the primary purpose of the work was to assess the behaviour of blends prepared under realistic processing conditions rather than to address more fundamental miscibility issues. Comments on phase separation which appear in the following text should be considered in this context. The success of the work rests heavily on the complementary use of scanning (SEM) and transmission (TEM) electron microscopy, optical microscopy (OM), differential scanning calorimetry (DSC), tensile dilatometry and impact testing which were employed to advantage in earlier studies of nylon/polyphenylene oxide blends [8]. The morphological studies are reviewed in this

paper and the mechanical deformation results are discussed in Part 2 [9].

The key to the successful analysis of polymer blends by electron microscopy is the development of sufficient contrast between the various components. In transmission electron microscopy (TEM), contrast arises from variations in electron density and can be most conveniently enhanced by incorporation of a heavy metal in one of the components. In the current system, various combinations of osmium and ruthenium tetroxide were employed to selectively stain the different phases. The IM could be differentiated from PBT and PC by reaction with OsO_4 which is known to form well-defined chemical complexes with double bonds. In a similar fashion, PC could be distinguished from the other components as a result of its greater ability to absorb RuO_4 . While differences in the capacities of different polymers to pick up RuO_4 have been reported in the literature [10], we believe this to be the first reported instance in which this characteristic has been used to differentiate PBT and PC.

TEM observations were complimented by SEM studies of specimens which were etched with diethylene triamine (DETA). The amine aggressively degrades PC while having little effect on either the amorphous or crystalline components of PBT. This etching procedure was found to be preferable to solvent or plasma etches which attack both components to various degrees and obscure finer structural features. Comparison of SEM and TEM results provided a convenient internal check for artefacts associated with a particular sample preparation technique.

2. Experimental techniques

2.1. Sample preparation

The blends used in this study were prepared from commercial grades of PBT and PC obtained from the

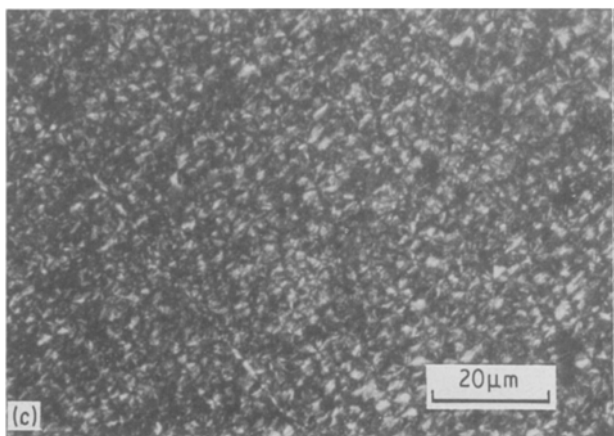
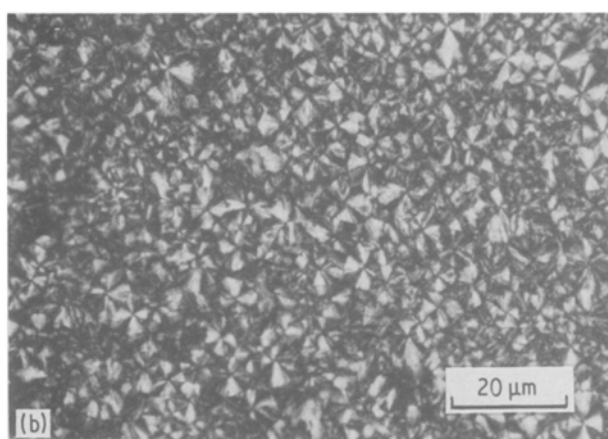
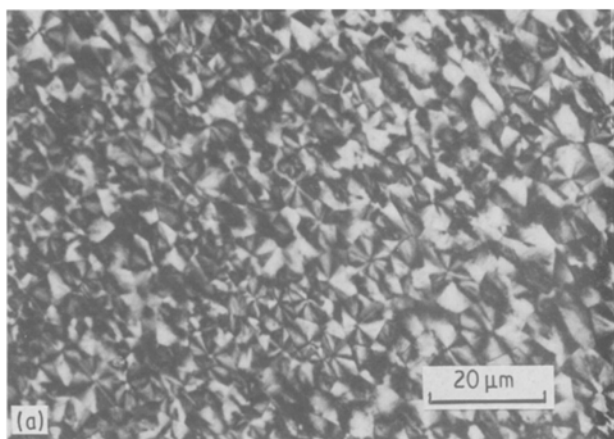


Figure 1 Optical micrographs, polarized light, showing spherulitic structure in injection-moulded samples of (a) pure PBT, (b) Blend 2, and (c) Blend 3.

General Electric Plastics Division. These resins were compounded in various compositions with a core/shell IM on a single screw extruder. Low levels of organic phosphites and thermal stabilizers were added to prevent transesterification and molecular weight degradation [6]. The extrudates were pelletized and injection moulded into ASTM Type D 638 tensile dogbones and Type D 256 Izod bars for mechanical testing. The blend compositions are summarized in Table I.

2.2. Microscopy

Samples for TEM, SEM and OM analyses were cut directly from the moulded test specimens. In some cases specimens with more carefully controlled thermal histories were prepared by remelting pieces of the moulded bars in a Mettler FP-2 hot stage blanketed with nitrogen. Well-crystallized samples were prepared by melting for 3 min at 270°C, cooling rapidly to 200°C and holding for 5 min, and then cooling at 10°C min⁻¹ to room temperature. Other samples were rapidly quenched after melting in an attempt to preserve the structure of the melt.

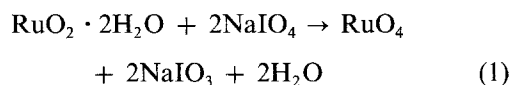
Microtomy was carried out at room temperature using a Reichart Ultracut E ultramicrotome. Samples to be stained with osmium tetroxide were first faced

TABLE I Blend compositions (wt %)

Blend no.	PBT	PC	IM
1	90	10	
2	85		15
3	70	15	15
4	40	45	15

and then immersed in a 1% solution of OsO₄ in hexane for 30 min. Thin sections were subsequently sectioned from the stained block and mounted on copper grids for examination.

Both osmium-stained and unstained thin sections were stained with ruthenium tetroxide using the procedure outlined by Trent *et al.* [10]. The staining solution is prepared by adding 0.3 g NaIO₄ and 0.15 g RuO₂ to 25 ml H₂O. As the solution is mixed, RuO₄ is generated *in situ* turning the solution yellow while the unreacted dioxide settles to the bottom of the vessel.



To stain the specimens, the copper grids containing the thin sections were glued to a glass slide and suspended above the RuO₄ solution in a stoppered bottle. Satisfactory results were obtained after exposure times of approximately 30 min. TEM observations were made on a Hitachi H 600 transmission electron microscope.

SEM studies were carried out on both the free surfaces of specimens crystallized in the hot stage and on cross-sections faced with the ultramicrotome. The samples were etched by immersing them in diethylene triamine for 1 min at room temperature. The specimens were subsequently rinsed in distilled water and sputtered with a thin coating of Au/Pd. SEM observations were made on a Jeol 840 scanning electron microscope.

2.3. DSC measurements

DSC measurements were carried out on a Perkin Elmer DSC 2. Scans were typically made from room temperature to 270°C at a rate of 10°C min⁻¹.

3. Results and discussion

A preliminary examination of the blends was carried out by optical microscopy and DSC in order to determine if additions of IM and PC produced significant changes in the gross morphology or crystallinity of the PBT phase. Optical micrographs of thin sections cut from the core areas of moulded bars of pure PBT and Blends 2 and 3 are presented in Fig. 1. A small

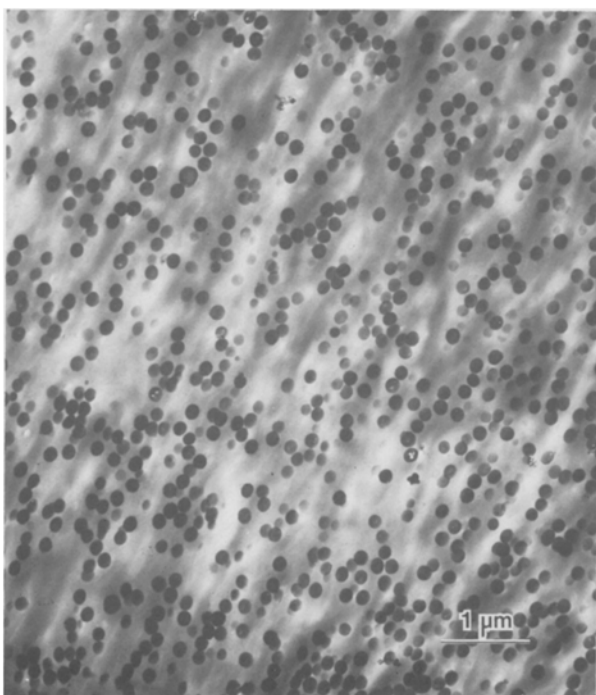


Figure 2 Transmission electron micrograph of OsO_4 -stained section of injection-moulded sample of Blend 3 showing dispersion and uniform size of IM particles. There is little, if any, differentiation of the PBT and PC phases.

decrease in spherulite size is evident, especially in Blend 3 and the spherulites become less well defined as the PBT concentration drops. The coarsening in the spherulite structure is discussed more fully below. DSC studies showed that the PBT crystallinity remained essentially constant at 33% over the entire range of compositions.

As noted above, the IM was readily visible in all of the blends after treating with OsO_4 . The TEM photograph of Blend 3 in Fig. 2, in which the IM particles

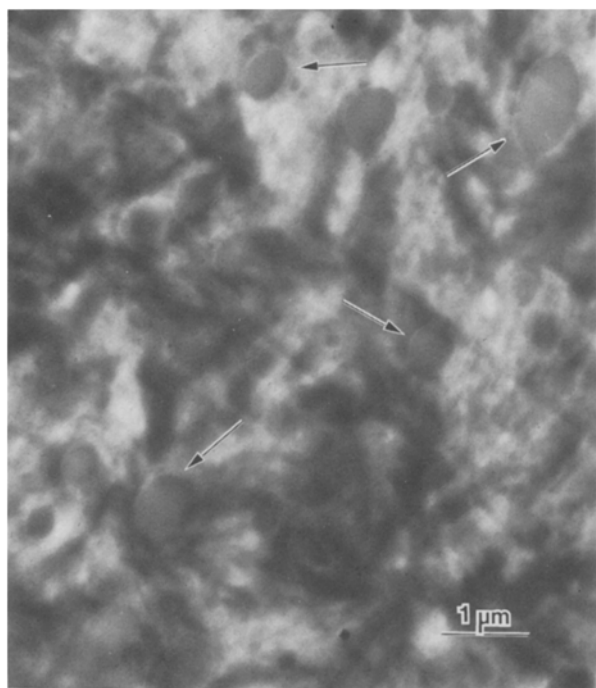


Figure 3 Transmission electron micrograph of injection-moulded sample of Blend 1 showing low inherent contrast between PBT and PC phases. Arrows indicate the dispersed PC domains.

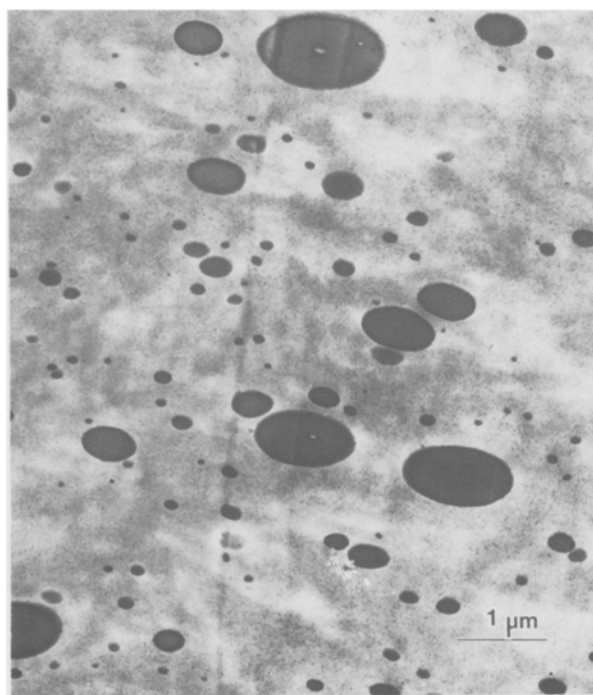


Figure 4 Transmission electron micrograph of injection-moulded sample of Blend 1 showing contrast improvement after staining with RuO_4 . Note the faint feathery quality of the PBT/PC interface.

appear as uniform, darkened spheres of $0.2\ \mu\text{m}$ diameter, is typical. It was not possible to differentiate the PBT and PC phases in any of the specimens. Uniform dispersions of the impact modifier were observed in the absence of PC. In the three-component blends having low PC concentrations there appeared to be some agglomeration of the rubber particles although this effect was less obvious at higher PC levels. The reason for the increase in rubber particle association at low PC levels became obvious in the RuO_4 -stained samples described below.

The ability of ruthenium tetroxide to selectively stain PC was first evaluated on a 90/10 PBT/PC blend where the ratio of the two components was sufficiently high to permit unambiguous assignment of the major and minor phases. An unstained and a RuO_4 -stained specimen cut from a moulded bar of this blend are shown in Figs 3 and 4. The polycarbonate domains are visible in the unstained section, probably as the result of slight differences in thickness (see arrows), but contrast is poor. By comparison, the PC phase in Fig. 4 is markedly darkened with respect to the PBT as a result of greater uptake of the RuO_4 . The interface between the two components is more sharply defined and the overall contrast in the specimen is significantly improved. The irregularities at the PBT/PC interface and the fine structure in the major phase, which are not visible in the unstained sections, are true features of the blend rather than artefacts of the staining process and are discussed more fully below.

The advantage of using RuO_4 in characterizing toughened PBT/PC blends is evident in comparing Figs 2 and 5. In Fig. 2 only the IM is stained and no contrast develops between the PBT and PC phases. When ruthenium tetroxide is used, preferential staining

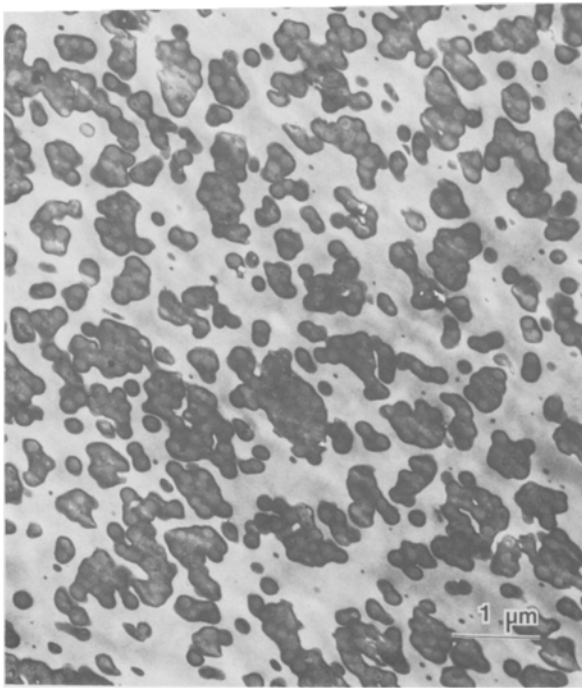


Figure 5 Transmission electron micrograph of RuO_4 -stained section from injection-moulded sample of Blend 3 showing excellent contrast between the three phases. All of the IM particles are isolated in the PC phase.

of the PC occurs and it is easily distinguishable from the surrounding PBT as shown in Fig. 5. Although the IM particles do not react with RuO_4 they are readily visible as subinclusions which are totally isolated within the PC phase. In contrast to the OsO_4 -stained specimen, some compression of the impact modifier particles occurs during room temperature cutting because the rubber is not hardened by reaction with OsO_4 . This problem does not occur in samples cut

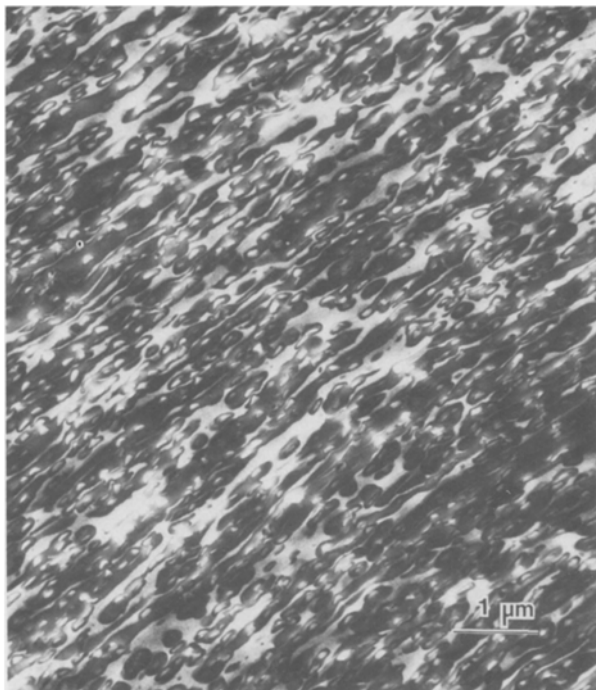


Figure 6 Transmission electron micrograph of RuO_4 -stained section from injection-moulded sample of Blend 4 showing interpenetrating network formed at high PC concentrations.

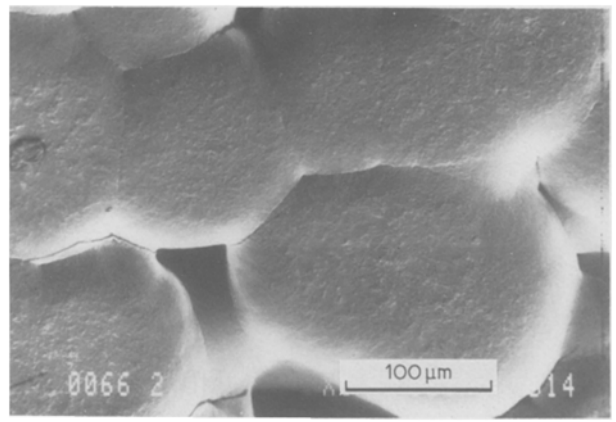


Figure 7 Scanning electron micrograph of DETA-etched free surface of recrystallized PBT showing spherulites.

at low temperatures or those sequentially treated with OsO_4 and RuO_4 . As the PC concentration is raised, the dispersed domains become more highly interconnected until at around 40% PC by weight an interpenetrating network of the two polymers is formed. Isolation of the impact modifier in the PC phase continues to be observed. These changes are shown in Fig. 6.

It is worthwhile to emphasize the importance of developing an unambiguous staining procedure for the analysis of complex blends such as those considered in this paper. In early experiments in which toughened PC/PBT blends containing high levels of PC were exhaustively extracted with chloroform, it was possible to remove quantitatively the PC. Infrared analyses of the dissolved and undissolved components showed that the IM was retained in the PBT phase. From these results it was concluded, in contrast to the microscopic evidence, that the impact modifier was dispersed within the PBT phase. The explanation for the discrepancy appears to lie in the fact that the rubber particles, which are undoubtedly swollen by the chloroform, are not able to pass through the narrow passages which link many of the PC regions. As a result, they are retained in the matrix after extraction.

Additional insight into the microstructure of melt-compounded PBT/PC blends was provided by analysis of samples which were slowly cooled from the melt. Scanning electron micrographs of the melt-crystallized free surfaces of PBT and Blend 2 are shown in Figs 7 to 9. All the samples were etched with diethylene triamine. In both cases individual spherulites can be seen in the lower magnification micrographs and the radiating lamellar sub-structure can be seen at higher magnifications. In contrast to pure PBT, which was unaffected by the DETA, a large amount of interlamellar etching is visible in the PBT/PC blend. The extremely small scale on which this segregation occurs is even more evident in Fig. 9 and strongly suggests that in the melt phase PC is partially miscible with PBT and phase separates during crystallization.

Even more striking evidence for this process is supplied by transmission electron micrographs of ruthenium-stained thin sections such as that shown in

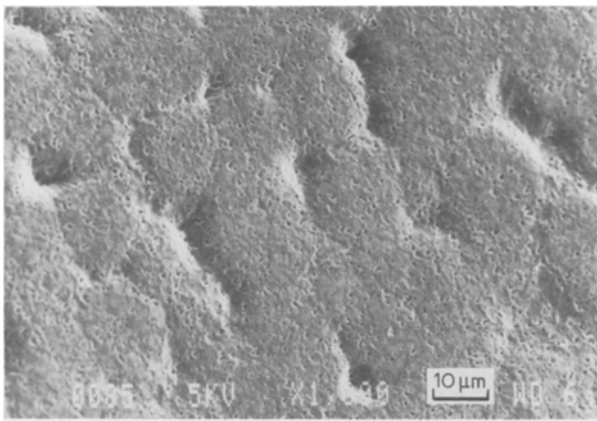


Figure 8 Scanning electron micrograph of DETA-etched free surface of recrystallized Blend 3 showing surface spherulites and etched regions high in PC.

Fig. 10. In this slowly crystallized sample containing 15% PC and 15% impact modifier, the growth of the PBT lamellae into the PC envelope containing the impact modifier and the extremely fine segregation of PC between the PBT lamellae in the bulk of the sample are visible in high detail. As the cooling rate is increased the structure in the matrix becomes less distinct and the PBT/PC interface becomes more even as seen in Fig. 4. Significantly, the PC envelope is still observed in quenched specimens indicating that a large fraction of the PC remains phase separated in the melt. As expected, injection-moulded specimens display a range of morphologies between these extremes depending on sample location, moulding conditions, etc.

The foregoing morphological observations are not definitive with respect to the role copolymer formation may play in the PBT/PC mixing/demixing process. In an extensive DSC study of melt-processed and solution-mixed PBT/PC blends, however, we have been able to demonstrate that a significant amount of melt mixing of the two resins occurs in the absence of copolymer formation. This conclusion is based on the observation that melt blends in which the PC T_g is depressed show a normal PC T_g after dissolving and evaporating the solvent. This behaviour is strong evidence that the partially mixed components simply phase separate during dissolution because, if copoly-

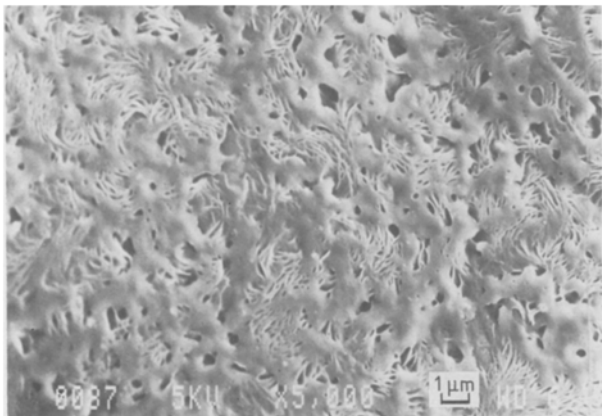


Figure 9 Higher magnification photograph of Fig. 8 showing lamellar bundles of PBT remaining after etching of PC areas.



Figure 10 Transmission electron micrograph of thin section of recrystallized Blend 3 showing detailed morphology of PBT and PC phases separated during slow cooling.

mer were present, the depression should be retained. A paper describing these experiments in detail is in preparation [11].

4. Conclusions

1. Various combinations of OsO_4 and RuO_4 staining have proved to be remarkably effective in elucidating the morphology of toughened PBT/PC blends by transmission electron microscopy.

2. In all of the melt-compounded blends examined PBT forms the continuous phase. In three component systems, the core/shell impact modifier remains isolated in islands of polycarbonate. As the PC concentration is increased, the dispersed phase becomes more highly interconnected. Photomicrographs suggest that above approximately 40% PC an interpenetrating network is formed. This conclusion is supported by exhaustive extraction studies with chloroform which are effective in removing essentially 100% of the PC from the blends.

3. Both SEM studies of specimens etched with diethylene triamine and TEM studies of specimens stained with RuO_4 provide convincing evidence of melt miscibility and phase separation of the two resins during crystallization of the PBT. It seems likely that the incorporation of PC in the interlamellar regions of the PBT spherulites may have a significant effect on their deformation behaviour. Perhaps more importantly, the complicated interpenetration of the two polymers which develops during phase separation ensures that the interfacial region is extremely strong. The integrity of the PBT/PC interface is further substantiated by the tensile dilatometry experiments discussed in Part 2 of this study [9].

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