Toughening of poly(butylene terephthalate) with core–shell impact modifiers dispersed with the aid of polycarbonate

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Commercial emulsion-made impact modifiers with a shell of poly(methyl methacrylate) (PMMA) chains grafted onto a rubber core, either acrylate or butadiene based, cannot be adequately dispersed in a matrix of poly(butylene terephthalate) (PBT) to achieve useful toughening. However, it is known that tough materials can be achieved when these blends also contain polycarbonate (PC). It is demonstrated here that 10 wt% or less of PC greatly facilitates the dispersal of such core–shell impact modifiers in a PBT matrix and leads to tough blends even at low temperatures. It is known that PC wets PBT and PMMA better than PBT and PMMA wet each other, which allows the PC to act as a dispersing agent for these impact modifier particles in the PBT matrix. The morphology and mechanical properties of ternary blends where PC is a major matrix component rather than simply a dispersing agent are also examined.

(Keywords: core–shell impact modifiers; poly(butylene terephthalate); polycarbonate)

INTRODUCTION

Many engineering thermoplastics lack adequate mechanical toughness, particularly at low temperatures, which has led to an interest in rubber toughening of these materials. A number of approaches have been used to achieve an appropriate blend morphology and coupling between phases[1–12]. Rubber particle size or interparticle distance appears to be a key factor in obtaining 'supertough' engineering materials[6–12]. One particularly attractive method is the use of emulsion-made core–shell impact modifiers (IMs) since they offer particles of a predetermined size, in contrast to rubber in other forms where the size of the particles formed may depend on the details of the mixing process. Of course, the problems for fixed particles are to ensure their uniform dispersion in the matrix material and, presumably, to create an adequate interfacial coupling of the particles to the matrix.

These core–shell materials typically have a core of crosslinked butadiene or acrylic rubber and a shell of grafted chains that may physically interact with the matrix in ways that ensure dispersion and coupling[13–17]. The optimum case may be when there is a favourable enough thermodynamic interaction between the shell chains and the matrix polymer to cause their miscibility. Indeed, a practical example approaching this is the toughening of poly(vinyl chloride) (PVC) by IM particles having grafted shells composed of poly(methyl methacrylate) (PMMA) or styrene/acrylonitrile (SAN) copolymer chains that are miscible with PVC at least under some circumstances[13,18,19]. However, it appears that even less favourable interactions that lead only to a physical wetting may provide a useful strategy for creating tough blends. It has been observed that polycarbonate (PC) tends to wet or encapsulate small particles of PMMA simply through surface interactions at the interface[20]. This mechanism has been used to disperse IM particles with PMMA shells to produce toughened PC blends with far better sharp notch impact properties than pure PC[21]. Finally, for polymer pairs which demonstrate no miscibility or wetting, a more aggressive chemical approach may be considered. This involves the production of grafted shell chains containing active sites, chemically incorporated during the final stage of emulsion polymerization, that are capable of reacting with the matrix polymer. Such materials are now commercially available. Solubilization of reactive polymers in the shell has also been shown to be a useful strategy[3]. For example, certain styrene/maleic anhydride (SMA) copolymers are miscible with PMMA[22], and relatively small amounts of SMA lead to drastically improved dispersion of impact modifier particles with a PMMA shell in a matrix of nylon 6[23].

This paper demonstrates that additive polymers which function in a purely physical way can also be used to disperse core–shell impact modifiers in matrices where there is no effective interaction between the shell of the particles and the matrix. What is sought is a third polymer that has greater affinity for both the shell and the matrix than these have for each other. A practical example of this suggested in the patent literature[24–26] uses polycarbonate (PC) to disperse impact modifiers with a PMMA shell in poly(butylene terephthalate) (PBT). For some time it has been known that there is a certain amount of partial miscibility and good adhesion between PC and PBT[27–30]. Recent work[31,32] has shown that the interaction between PC and PMMA is very near the critical limit for miscibility. The fact that PMMA-based impact modifiers cannot be readily dispersed in PBT is

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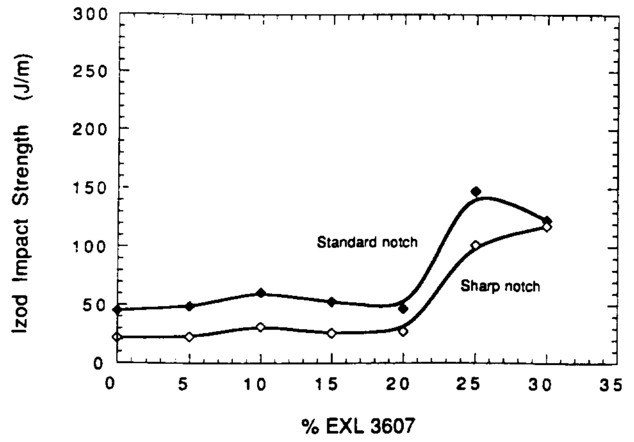

Figure 1 Room temperature notched Izod impact strengths of PBT/EXL 3607 binary blends

evidence of the less favourable PMMA–PBT interaction; recall that such impact modifiers can be dispersed in PC. These interactions, which can be formally expressed in terms of interfacial tensions, and classical analyses of wetting are useful[20,33]. Indeed, Hobbs *et al.*[20] have demonstrated that in ternary blends PC tends to encapsulate PMMA domains (not core–shell particles) dispersed in a PBT matrix. Thus, it seems reasonable to propose that PC should be an effective additive for dispersing PMMA-grafted rubber particles in a PBT matrix for toughening purposes.

The purpose of this paper is to demonstrate the usefulness of this technique for toughening PBT. The effects of mixing order and composition on blend morphology and mechanical properties, including especially the ductile–brittle transition temperature, are explored.

EXPERIMENTAL

The PBT used in this work was Valox 310 from General Electric, while the PC was Calibre 300-4 from Dow. To avoid hydrolysis of these polymers, all materials were dried at 80°C for at least 12 h in a vacuum oven to remove absorbed water before all melt-processing steps.

Two types of core–shell impact modifier from Rohm and Haas were employed. Paraloid EXL 3607 contains a butadiene rubber core with a T_g of -60°C, measured by dynamic mechanical analysis[23], and has a particle diameter of 0.18 μm[16,17]. Paraloid EXL 3300 has a core based on n-butyl acrylate rubber with a T_g of -30°C and a particle diameter of 0.30 μm[16,17]. Both types of modifier particle have a grafted poly(methyl methacrylate) shell. Additional details about these particular materials can be found elsewhere[13–17].

All blends were prepared in a Killion single-screw extruder ($L/D=30$, $D=2.54$ cm) at a melt temperature of 265°C and a screw speed of 30 rev min^{-1}. Various mixing protocols for producing the ternary blends were examined. A procedure involving two separate extrusions was finally adopted since it resulted in blends with the best mechanical properties. The first pass was used to disperse the impact modifier particles in the polycarbonate. This concentrate, after drying again, was blended with the PBT matrix in the second pass. The pelletized extrudates were dried again prior to forming test bars in an Arburg Allrounder screw injection moulding machine. All moulded test specimens were then sealed in plastic bags and stored under vacuum in a desiccator prior to testing. Tensile testing was performed in accordance with ASTM D638 on an Instron at a crosshead speed of 5.08 cm min^{-1}. An extensometer strain gauge with a 5.08 cm gap was used in the determination of elastic modulus. Notched Izod impact tests were conducted in compliance with ASTM D256 using both standard and sharp notch specimens. Sharp notch test bars were produced by pressing a fresh razor blade firmly into the bottom of a standard notch. All test specimens were 0.318 cm thick.

Blend morphology was determined by transmission electron microscopy (TEM) using a JEOL 200CRX operating at an accelerating voltage of 120 kV. Ultrathin samples were obtained from Izod bars by microtoming perpendicular to the flow direction using a Reichert–Jung ultramicrotome at -40°C. Proper staining technique is essential to attain sufficient contrast. Typically, the rubber cores of the impact modifier particles were stained using an aqueous solution of OsO_4 (2%) over a period of at least 9 h. Polycarbonate was stained with an aqueous solution of RuO_4 (5%) for about 20 min.

BINARY BLENDS

The properties of binary blends of the polyester with the core–shell modifier without polycarbonate present are useful for comparison with subsequent data for the ternary blends. Izod impact results at room temperature for PBT/EXL 3607 blend specimens with both standard and sharp notches are shown in *Figure 1*. Up to 20 wt% impact modifier, there is no improvement in toughness. Blends with higher concentrations of rubber particles showed some increase in Izod values; however, even these blends failed in a brittle manner. The tensile properties shown in *Table 1* reveal that expected losses in both yield strength and elastic modulus resulting from the presence of the rubbery component. The elongation at break for these blends is also lower than that for pure PBT, which is a further indication of the failure to produce improved materials by this simple binary blend. The TEM photomicrograph shown in *Figure 2* offers a revealing insight into the cause for the poor mechanical properties of these blends. This 80/20 blend of PBT/EXL 3607 was stained with OsO_4 solution, which makes the unsaturated butadiene-based rubber cores of the impact modifier particles appear black against the lighter PBT matrix phase. The modifier particles form large agglomerations and are poorly dispersed in the polyester matrix. This extremely poor dispersion and the weak bonding to the matrix are responsible for the very poor properties observed. As will be discussed later, addition of polycarbonate to these blends greatly improves the dispersion of the IM particles throughout the matrix phase and the toughness.

Table 1 Tensile properties of PBT/EXL 3607 blends

PBT/EXL 3607 blend	Yield stress (MPa)	Elastic modulus (GPa)	Elongation at break (%)
100/0	46.6	2.24	186
90/10	43.0	1.16	10
80/20	37.0	1.54	11
70/30	30.9	1.74	14

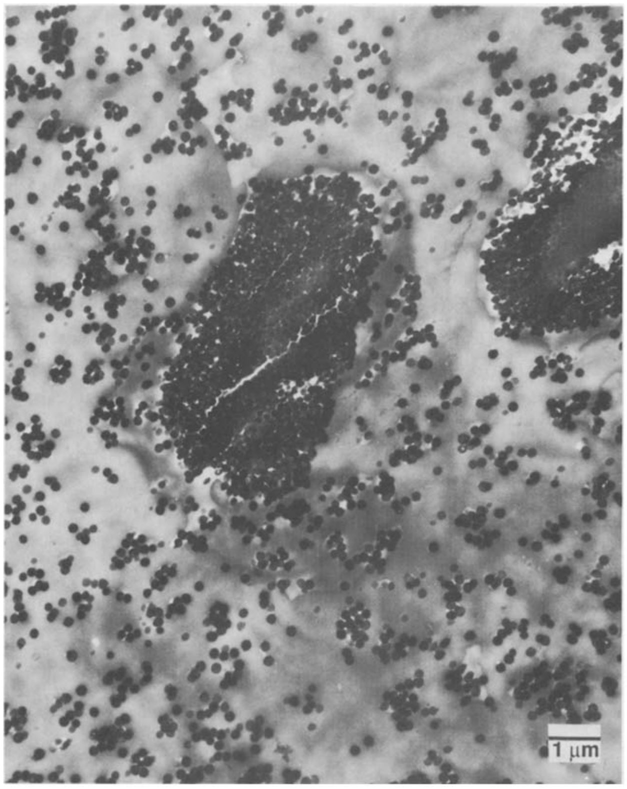

Figure 2 TEM photomicrograph of an 80/20 PBT/EXL 3607 blend stained with OsO$_4$

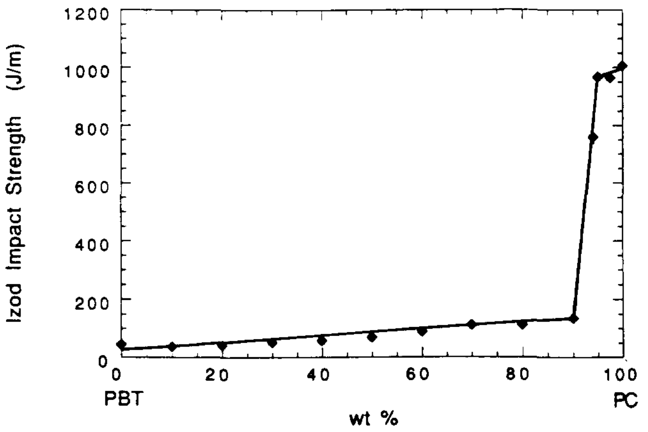

Figure 3 Izod impact strengths (standard notch) of PBT/PC binary blends

Binary blends of the polyester with polycarbonate were also examined for comparison with the subsequent ternary blends. These data are needed to show that the toughening observed for the ternary blends is not simply a result of incorporating sufficient amounts of polycarbonate into the brittle matrix phase to induce ductility even without the use of impact modifiers. *Figure 3* shows the Izod impact values at room temperature for binary blends of PBT and PC with a standard notch. There is no significant change in toughness or ductility until the blend contains about 90 wt% PC. The ternary blends discussed later show significant toughening at far lower concentrations of polycarbonate in the blend. Tensile properties for selected blends are shown in *Table 2*. It is useful to examine the trend in the elongation at break in more detail (see *Figure 4*). Addition of small amounts of PC to PBT causes a dramatic reduction in the elongation at break. At about 40 wt% or more of PC there is a large increase in ductility that corresponds to the formation of a continuous PC phase. Evidently, PC particles in the PBT matrix give rise to the significant loss in ductility below the additive relation suggested by the dashed line, whereas PBT particles dispersed in the PC matrix do not result in such a loss. It seems that PC is more tolerant of such hard particle inclusions than is PBT. On the other hand, PBT-rich materials containing impact modifier particles are very tough and ductile.

Ester interchange reactions in PBT/PC blends have been discussed extensively in the recent literature$^{34-37}$. These reactions can influence blend performance. While such reactions may be useful in very limited amounts, they are not easily controlled and excessive reaction can result in a loss in mechanical properties. Accordingly, commercial materials contain small amounts of additives, such as organophosphites, that inhibit interchange reactions. For this study, blends were prepared with and without 1 wt% Ultranox 626 organophosphite (General Electric). The blends prepared under these controlled laboratory conditions with or without this stabilizer showed no measurable difference in mechanical properties. Of course, under more abusive melt-processing conditions significant differences can be expected. Interchange reactions will reduce the ability of the blend to form PBT crystallinity owing to copolymer formation. Thus, examination of the heat of fusion for the PBT component via differential scanning calorimetry (d.s.c.) would be a useful indicator of any reaction. *Figure 5* shows the heats

Table 2 Tensile properties of PBT/PC blends

PBT/PC blend	Yield stress (MPa)	Elastic modulus (GPa)	Elongation at break (%)
100/0	46.6	2.24	186
80/20	51.2	2.28	37
60/40	54.3	2.28	107
50/50	55.7	2.26	173
40/60	58.8	2.21	134
20/80	62.5	2.30	122
0/100	61.1	2.29	111

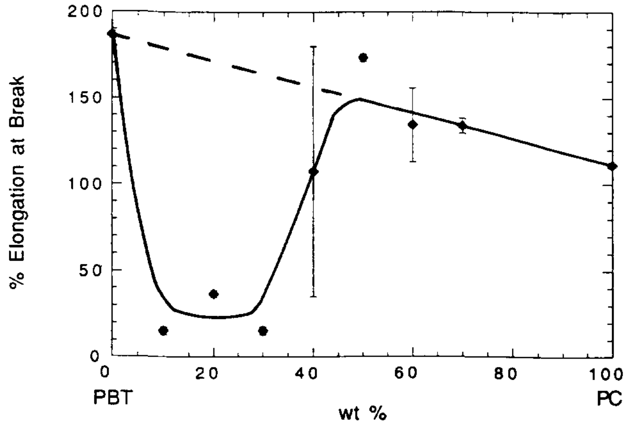

Figure 4 Elongation at break of PBT/PC blends as a function of composition. The vertical bars indicate average deviations from the mean. In most cases the deviation is about the same size as the point itself

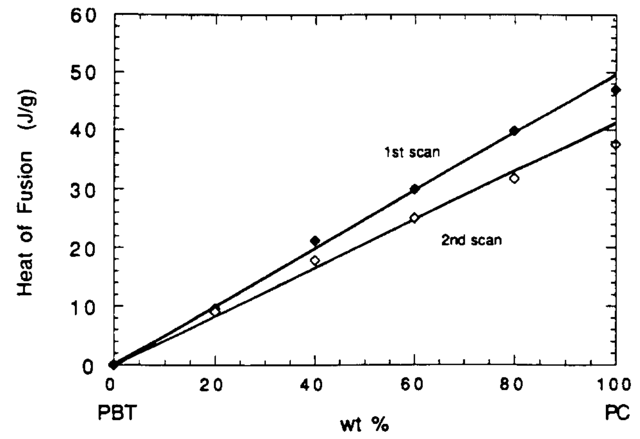

Figure 5 Heats of fusion of the PBT/PC blends. The first d.s.c. scan represents the crystallinity of the injection-moulded specimen

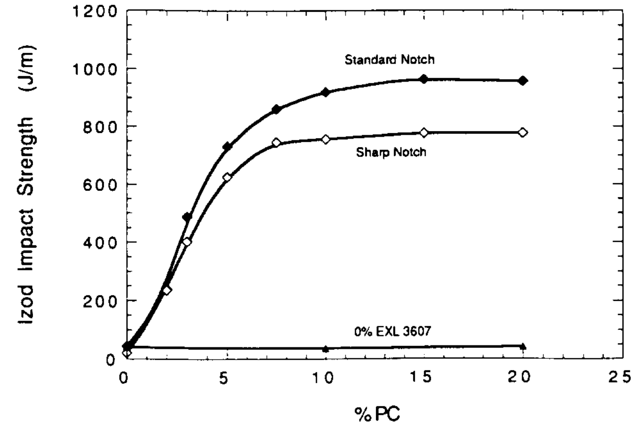

Figure 6 Effect of PC (x wt%) content on the notched Izod impact strength of PBT ($80-x$ wt%)/EXL 3607 blends. All blends contain 20 wt% EXL 3607 except for the indicated control

of fusion, estimated from the area of the PBT melting endotherm, of blends taken from moulded bars without any stabilizer. There is a higher heat of fusion after the first scan than after the second scan because of differences in crystallization conditions between moulding and cooling in the d.s.c. For both scans, the heat of fusion is directly proportional to the PBT content of the blend. Samples that contained 1 wt% of the above-mentioned stabilizer showed identical results to those shown in *Figure 5*. This suggests that there were no effects of interchange reactions within the sensitivity of this method of observation.

TERNARY BLENDS

Several different mixing protocols for formulating ternary PBT/PC/IM blends were examined. These procedures included adding all three component polymers to a single-screw extruder at the same time; combining PBT with PC first and then adding the IM particles in a second extrusion; combining PBT with IM particles first and then adding PC; and combining PC with IM particles first and then adding PBT. The last of these options seemed to provide blends with the best mechanical properties. This mixing protocol is a logical choice since the impact modifier is easily dispersed in PC, as noted earlier, and because the envisioned final goal is one where impact modifier particles are individually dispersed in the PBT matrix via a thin coating of PC around them. In a more intensive mixing device, such as a corotating twin-screw extruder, the order of mixing may possibly be less important. For a variety of practical reasons, a single extrusion step would be preferred. A compounding extruder with multiple feed ports might also be useful for achieving this objective.

Polycarbonate as a dispersing agent

The mechanical properties of a series of PBT blends containing 20 wt% EXL 3607 with small amounts of polycarbonate were determined. *Figure 6* shows the variation in Izod impact strength for specimens with both standard and sharp notches as the PC content is increased; data for the binary blend of PBT and PC without impact modifier (*Figure 3*) are shown for reference. Even relatively small amounts of PC, less than 5 wt%, lead to significant toughening, and as the PC content approaches 10 wt% the blends become 'supertough'. The specimens showed increasingly ductile fracture behaviour (i.e. lateral contraction and whitening in the deformation zone) as the PC content was increased. Tensile properties for these blends are shown in *Table 3*. The addition of polycarbonate does not significantly alter the modulus or yield stress until its content exceeds 10 wt%. The elongation at break data for these blends are shown in *Figure 7*. There is a rapid rise in this indicator of ductility as PC is added. At 10 wt% PC, the elongation at break is about 100%, while at 20 wt% PC, the elongation at break is nearly 300%. These results

Table 3 Effect of PC content on the tensile properties of PBT/PC/EXL 3607 (20 wt%) blends

PC content (wt%)	Yield stress (MPa)	Elastic modulus (GPa)	Ultimate stress (MPa)
0.0	37.0	1.54	35.3
2.0	36.5	1.53	30.1
3.0	37.4	1.51	27.1
4.0	37.1	1.50	28.2
5.0	37.7	1.57	28.4
7.5	38.0	1.55	28.5
10.0	39.8	1.60	30.7
20.0	43.2	1.66	33.3

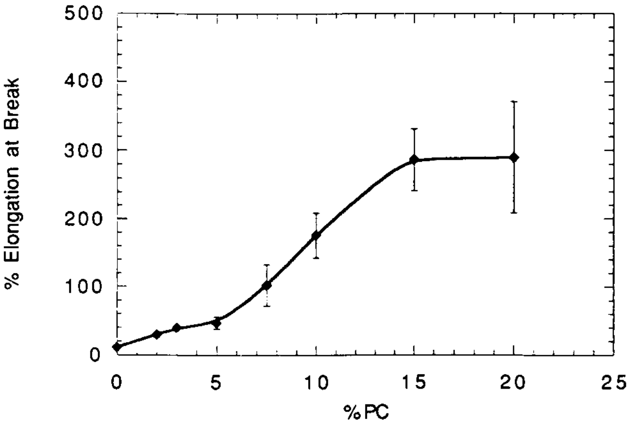

Figure 7 Effect of PC (x wt%) content on the elongation at break of PBT ($80-x$ wt%)/EXL 3607 (20 wt%) blends

plus the ultimate strengths shown in *Table 3* indicate that small amounts of PC greatly influence the stress–strain behaviour after yield and the failure mode.

Impact properties at reduced temperatures are of great practical concern since many applications of toughened thermoplastics involve outdoor usage. *Figure 8* shows the impact strengths of ternary blends with a standard notch at 25°C, 0°C and −20°C. Even at the lower temperatures, ternary blends with as little as 10 wt% PC remain 'supertough'. However, as the temperature is reduced, more PC is required to achieve equivalent toughening. For example, an impact strength of 250 J m^{-1} can be achieved with 2 wt% PC at 25°C, while about 6 wt% PC is needed to attain 250 J m^{-1} at −20°C. At relatively low concentrations of PC, the toughness of these blends is very sensitive to the amount of PC present. This is consistent with the concept that polycarbonate acts as an interfacial wetting agent between the matrix and the dispersed phase.

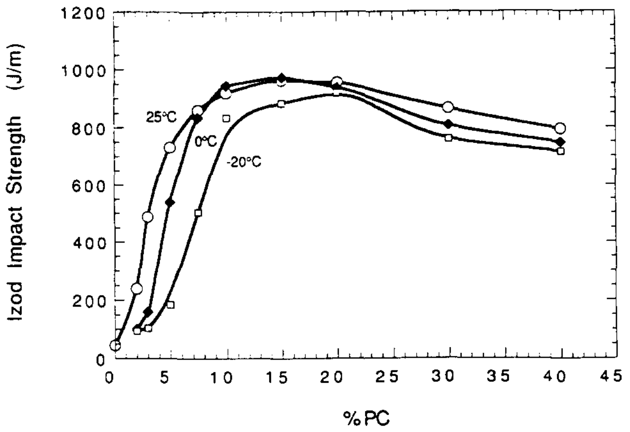

Figure 8 Izod impact strength (standard notch) of PBT/EXL 3607 (20 wt%) blends at 25°C, 0°C and −20°C as a function of PC content

Transmission electron microscopy provides direct evidence for the proposed effect of PC on the blend morphology, as shown by the photomicrographs in *Figure 9*. Osmium tetroxide stains the butadiene-based rubber core of EXL 3607 and makes the impact modifier particles appear black on the lighter PBT background. The blends containing no polycarbonate show very large agglomerations of IM particles, as seen in *Figure 2*. Addition of PC results in the break-up of these clusters, and the IM particles become increasingly better dispersed in the PBT matrix. Osmium tetroxide staining does not provide discrimination between the PC and PBT phases.

Polycarbonate as a matrix component

As larger amounts of PC are incorporated into the ternary blend, the PC ceases to act only as a wetting agent; eventually it must be thought of as a discrete matrix component. Indeed, such blends are commercially useful and have been extensively studied[38,39]. *Figure 10* shows a series of TEM photomicrographs for ternary blends containing 0 wt%, 20 wt%, 40 wt% and 60 wt% PC which have been stained with ruthenium tetroxide to make the PC appear dark against a lighter PBT background. The butadiene core material of the IM

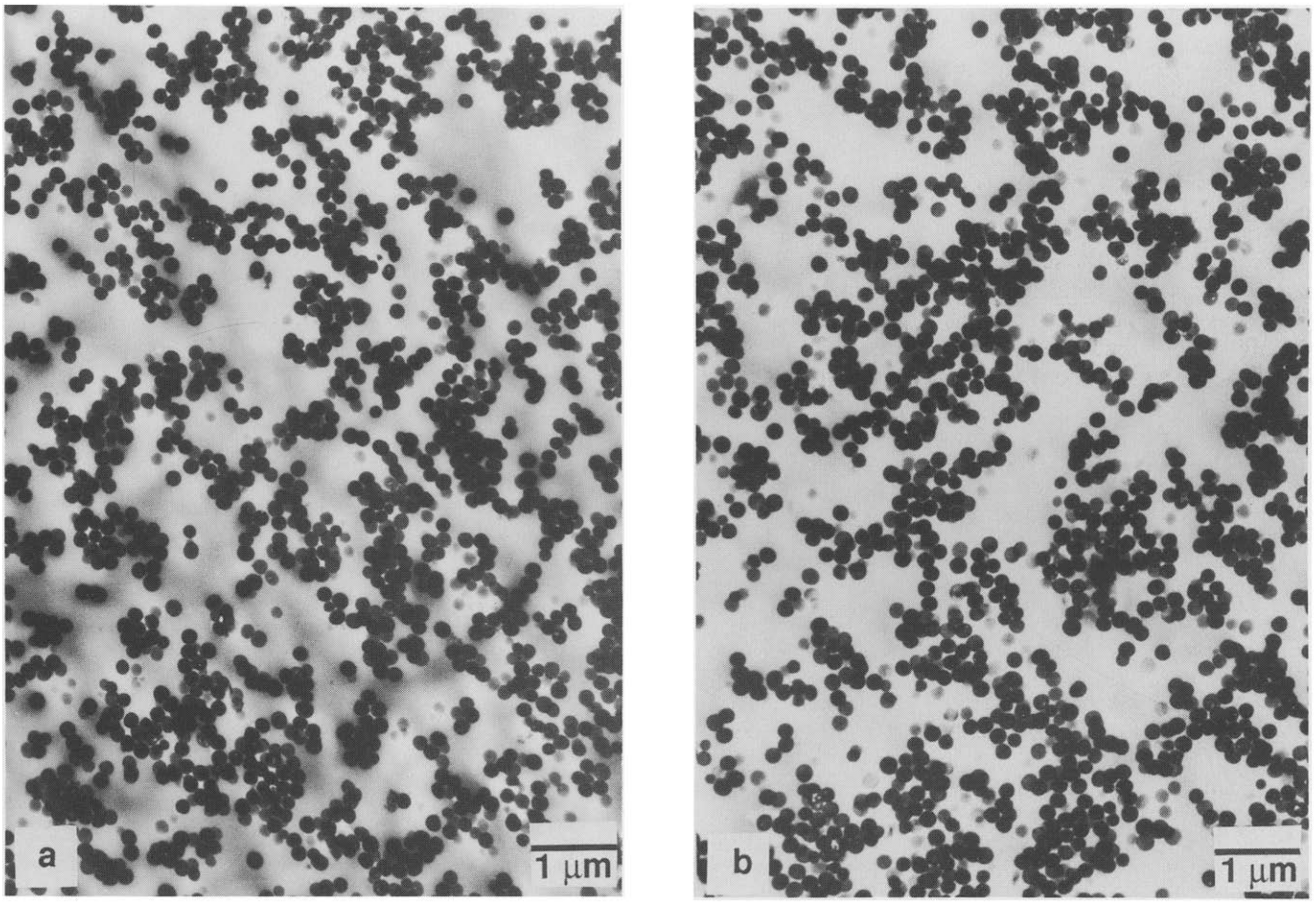

Figure 9 TEM photomicrographs of OsO_4-stained PBT/PC/EXL 3607 blends: (a) 77/3/20; (b) 70/10/20

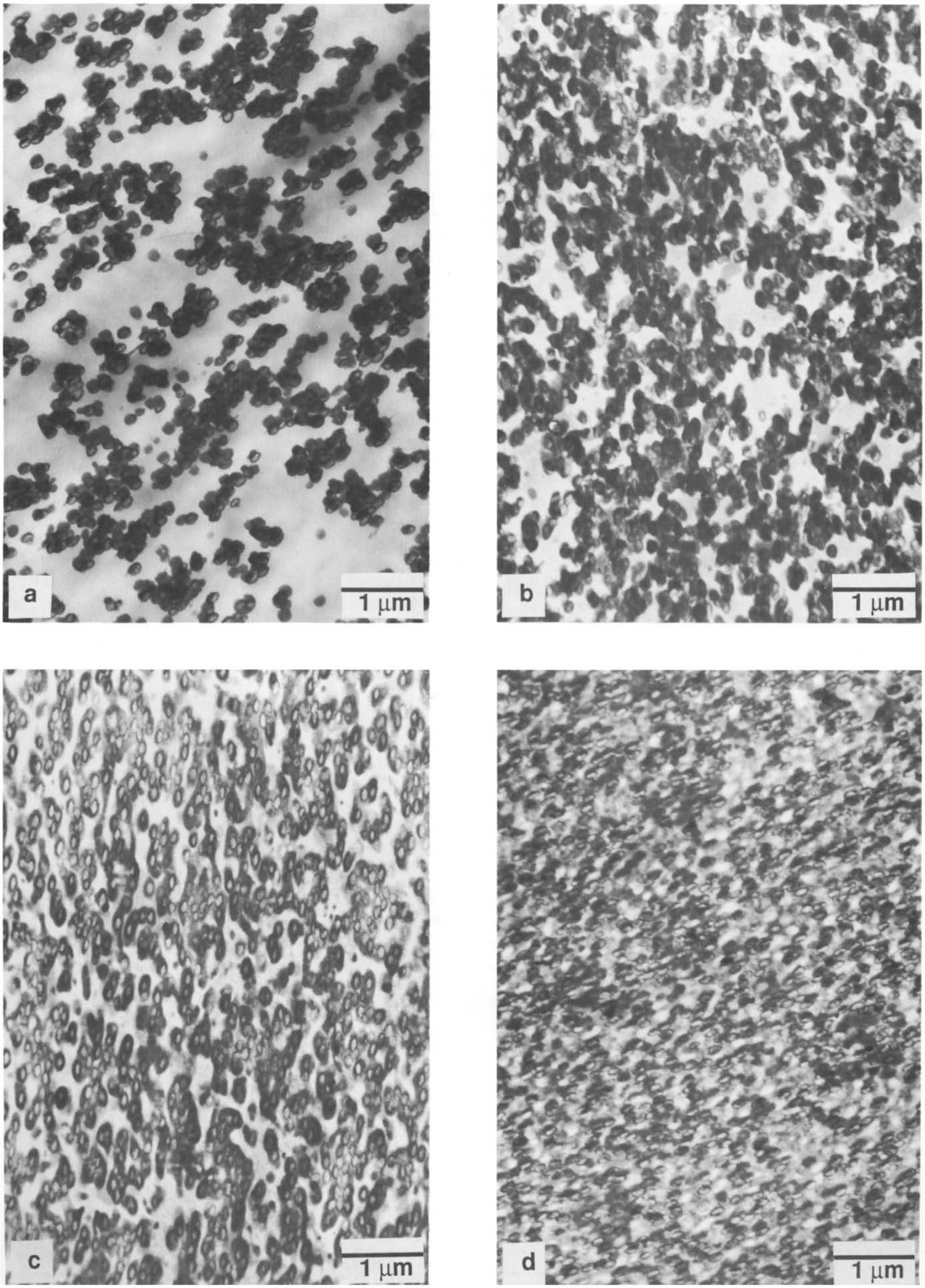

Figure 10 TEM photomicrographs of PBT/PC/EXL 3607 blends (RuO_4 staining causes darkening of the PC phase): (a) 80/0/20; (b) 60/20/20; (c) 40/40/20; (d) 20/60/20

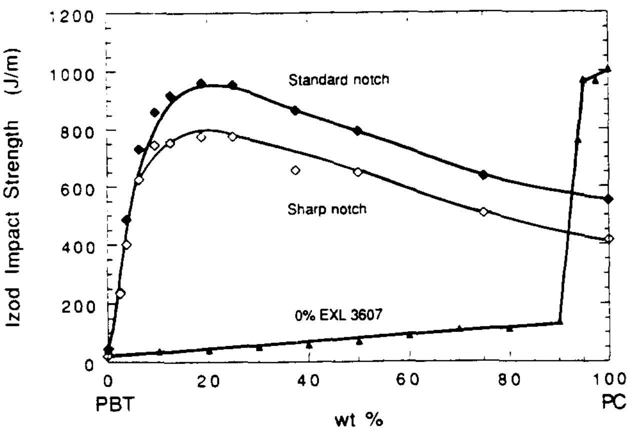

Figure 11 Izod impact strength of ternary PBT/PC/EXL 3607 (20 wt%) blends *versus* PBT/PC ratio. Data from *Figure 3* for a binary control with no EXL 3607 are also shown

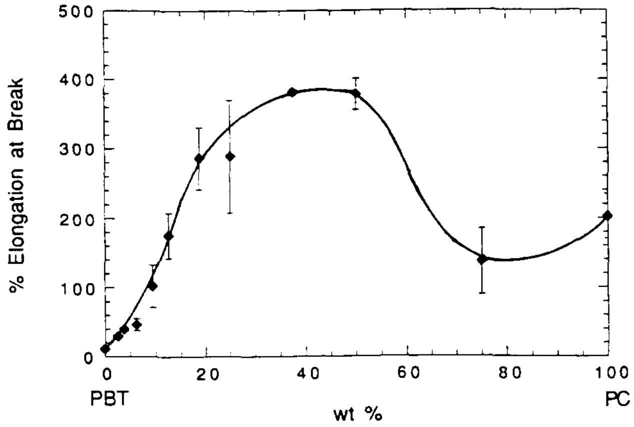

Figure 12 Elongation at break for PBT/PC/EXL 3607 (20 wt%) blends *versus* PBT/PC ratio

particles is not readily stained by RuO_4; thus, these particles appear as light circles with dark shells, indicating the grafted PMMA material coating the surface. At very low PC concentrations, the only darkened regions in the stained samples are the spherical surfaces of the EXL 3607 particles. At 20 wt%, a shadowy polycarbonate phase becomes visible in and around the IM particles. By 40 wt%, this PC phase has formed a co-continuous network throughout the PBT matrix. It must be noted that all of the IM particles reside in the PC phase domains, as predicted earlier on the basis of the surface interactions of these three polymers. At 60 wt%, a matrix phase inversion occurs with PC assuming the role of the major constituent component. This is shown by the blackening of the entire matrix material. *Figure 11* shows that as the polycarbonate content increases above 20 wt%, there is a small, steady decline in the Izod impact strength of the ternary blend. As *Figure 12* shows, the elongation at break of the ternary blend decreases after the PC content exceeds about 50 wt%.

The ductile–brittle transition temperatures shown in *Figure 13* provide additional insight into the toughness of these blends. The temperatures shown are the median values within the range between the lowest temperature at which all specimens failed in a ductile manner and the highest temperature at which all specimens failed in a brittle manner. The ductile–brittle transition temperature shows steady improvement as the polycarbonate content increases from 0 wt% to about 10 wt%. By about 30 wt% PC, it reaches a plateau at about −35°C. This plateau temperature is considerably above the glass transition temperature of the butadiene core of the EXL 3607 particles. The use of the poly(n-butyl acrylate)-based impact modifier (EXL 3300) in these blends gives a ductile–brittle transition temperature of about −27°C. This value is very similar to the glass transition temperature of the rubber core. As pointed out in another recent study of core–shell modifiers in nylon 6[23], the degree of dispersion and interfacial behaviour in addition to the T_g of the rubber are apparently critical in determining blend toughness at low temperatures.

CONCLUSIONS

Poly(butylene terephthalate) cannot be effectively toughened by the introduction of typical core–shell impact modifier particles since they fail to achieve the degree of dispersion required when blended in a single-screw extruder. This is a direct result of insufficient physical interaction between the polyester and the grafted PMMA shell of the modifier particles employed here. It is also possible that this same characteristic would lead to inadequate interfacial adhesion between the matrix and the modifier even if well-dispersed blends could be achieved. It was proposed that the addition of some type of dispersant or 'wetting agent' might provide a solution to these two problems and yield tough polyester blends. Polycarbonate was selected for its tendency to wet both PBT and PMMA better than these two wet each other, which should therefore lead to dispersion of the core–shell modifier particles throughout the polyester matrix. It has been shown that the PC phase material does indeed locate preferentially between the PBT matrix and the PMMA shell of commercial emulsion-made core–shell impact modifiers. Additionally, the evidence is clear that small amounts of polycarbonate (less than 10 wt%) greatly improve both the dispersion of modifier particles and the mechanical properties of the ternary blends. The improved impact properties of these blends, particularly at low temperatures, seem to arise more from better dispersion and adhesion of the IM particles than simply from the presence of the more ductile polycarbonate material in the blend.

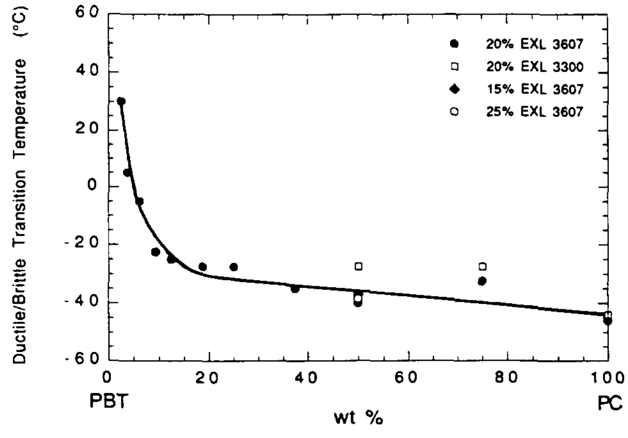

Figure 13 Ductile–brittle transition temperature for PBT/PC/IM blends *versus* PBT/PC ratio. The line is shown for the general trend and as a reference for the multiple compositions at high PC content

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