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Toughened blends of poly(butylene terephthalate) and BPA polycarbonate

Part 2 *Toughening mechanisms*

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The toughening mechanisms of blends of poly(butylene terephthalate) (PBT) and bisphenol-A polycarbonate (PC) toughened with core/shell impact modifier have been studied by transmission electron microscopy, notched impact testing and uniaxial tensile dilatometry. It was found that in both toughened PBT and toughened PBT/PC blends, shear deformation is the major toughening mechanism. Brittleness at low temperatures is caused by a reduction in the ability of the matrix to undergo shear deformation. In tensile dilatometry this effect is indicated by an increase in the extent of internal cavitation of the impact modifier particles. The low-temperature impact toughness of toughened PBT/PC blends is significantly greater than that of toughened PBT. Modification of PBT with partially miscible PC appears to have a beneficial effect on the ability of PBT to undergo shear deformation. This effect has been attributed to the PC residing in the amorphous interlamellar regions of the PBT spherulites, thus facilitating interlamellar slip.

1. Introduction

Blends of poly(butylene terephthalate) (PBT) and bisphenol-A polycarbonate (PC) can be made extremely tough by the addition of core/shell impact modifier. The morphology of these blends was studied in Part 1 of this series [1]. The present paper deals with the toughening mechanisms.

The mechanical tests performed in this study are notched impact tests and uniaxial tensile dilatometry. Tensile dilatometry is a unique test to gain information about the deformation mechanisms in multiphase resins [2–4]. The volume strain of a sample placed in uniaxial tension is measured by simultaneously measuring the axial and transverse strains. The volume strain behaviour provides an insight into the extent to which shear deformation and cavitation occur because shear deformation takes place without a significant volume change whereas cavitation gives rise to a volume increase. Unfortunately, from tensile dilatometry it is not possible to discriminate between the various cavitation processes that may occur. Therefore, transmission electron microscopy (TEM) was used to study deformed tensile specimens in order to identify the cavitation processes. The deformation mechanisms as revealed by tensile dilatometry and TEM will be correlated to the failure mode observed in notched impact testing.

2. Experimental details

2.1. Materials

The blends used in this study were prepared from commercial grades of PBT and PC obtained from the General Electric Plastics Division. The impact modifier (IM) consists of a rubbery core and a glassy shell. The average particle diameter is about 0.2 μm. The blends under investigation are listed in the first column of Table I. In the impact-modified blends the level of impact modifier was held constant at 15wt %. Details on blend preparation and stabilization can be found elsewhere [1].

2.2. Notched impact tests

The notched impact tests were performed in a three-point bend geometry. Injection-moulded samples were used having the dimensions of 62 mm × 12.5 mm × 3 mm. Notches with a depth of 2.5 mm and a notch tip radius of 0.25 mm were prepared using a multitooth fly cutter. This notch tip radius of 0.25 mm is recommended by ASTM D256 for standard notched Izod and Charpy impact tests. The single-edge notched specimens were tested on a thermostatted Instron 1350 servo-hydraulic testing machine using a span of 50 mm. All tests were done at the maximum attainable piston speed of 2 m sec^{-1}, at temperatures ranging from −30 to +25° C.

2.3. Uniaxial tensile dilatometry

Tensile dilatometry experiments were carried out on the same Instron 1350 testing machine at temperatures ranging from −30 to +25° C. Standard ASTM D638 injection-moulded tensile specimens were used (gauge section 25 mm × 12.5 mm × 3 mm). Volume changes were measured by simultaneously measuring the axial strain, ε_A, and the transverse strain, ε_T, with two extensometers. The volume strain, $\Delta V/V_0$, was calculated using the formula:

$$\frac{\Delta V}{V_0} = (1 + \varepsilon_A)(1 + \varepsilon_T)^2 - 1 \qquad (1)$$

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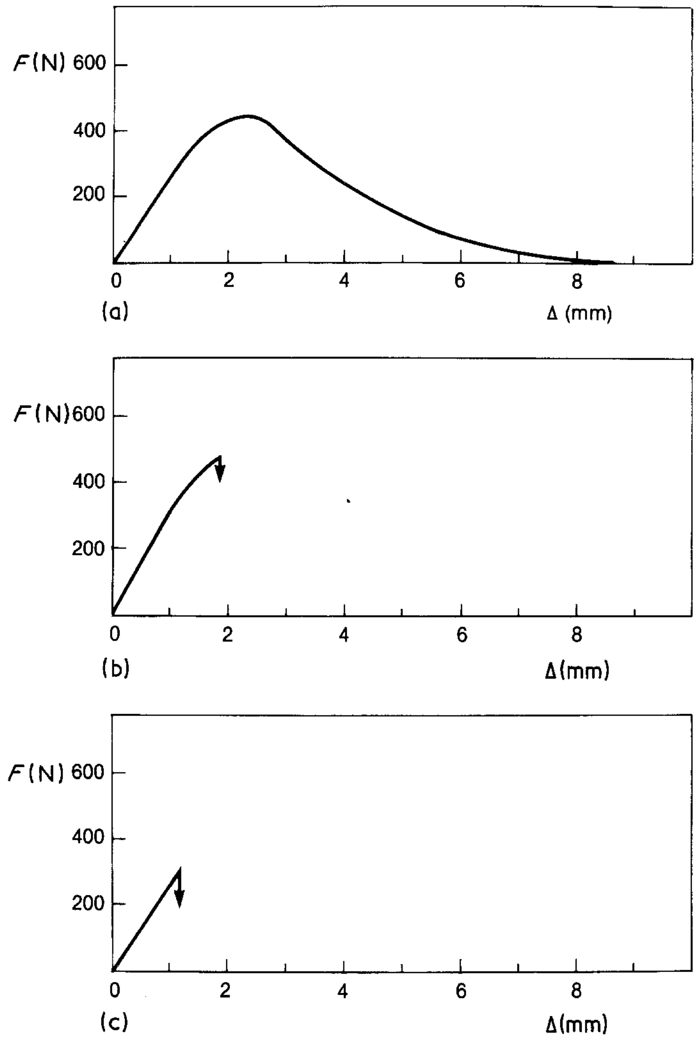


Figure 1 Load–piston displacement curves for PBT/IM 85/15 tested in three-point bending at a piston speed of $2\,m\,sec^{-1}$. Test temperature: (a) 25° C; (b) 0° C; (c) −30° C.

All tensile tests were performed at a constant axial strain rate of $0.1\,sec^{-1}$. This is the highest strain rate at which acceptable accuracy could be achieved. The axial strain was carried to a maximum of 14%. In those cases where the sample formed a neck, $\Delta V/V_0$ is reported only up to the point where necking begins, which is shortly after yielding.

3. Results

3.1. Notched impact tests

Three different failure modes were observed in the notched impact tests: ductile failure, semi-brittle failure and brittle failure. Table I lists the failure modes for the materials under investigation. The three failure modes will be discussed on the basis of the PBT/IM 85/15 blend which exhibits all three modes in the temperature range from −30 to +25° C.

Fig. 1 shows the load–piston displacement (F–Δ) curves for the PBT/IM 85/15 blend at +25, 0 and −30° C. A light micrograph of the three corresponding fracture surfaces is shown in Fig. 2. At 25° C the blend exhibits the type of failure that will be referred to as ductile. The F–Δ curve shows a gradual fall from the peak load which indicates stable, ductile crack propagation throughout the whole width of the specimen [5]. The corresponding fracture surface shows evidence of extensive plastic deformation with shear lips and lateral contraction along the whole width of the specimen.

At 0° C the PBT/IM 85/15 blend exhibits the type of

TABLE I

Materials	Temperature range (° C)	Failure mode in notched impact	Deformation mechanisms in tensile dilatometry
PBT	−30–+25	Brittle	Shearing
PBT/PC 45/55 wt %	−30–+25	Brittle	Shearing
PBT/IM 85/15 wt %	−30–−10	Brittle	Shearing and cavitation
	−10–+10	Semi-brittle	Shearing and cavitation
	+10–+25	Ductile	Shearing
PBT/PC/IM 70/15/15 wt %	−30–−20	Semi-brittle	Shearing and cavitation
	−20–+25	Ductile	Shearing
PBT/PC/IM 40/45/15 wt %	−30–+25	Ductile	Shearing

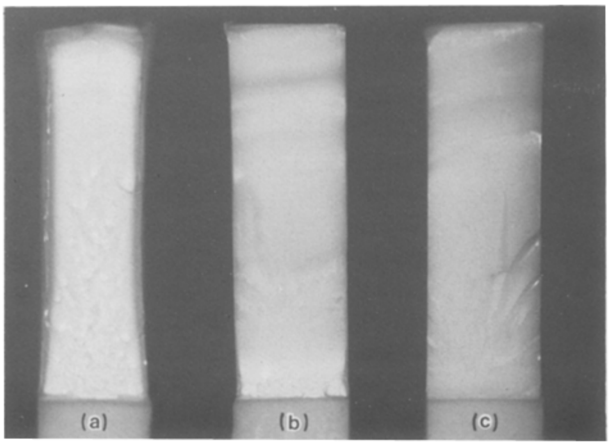


Figure 2 Fracture surfaces of PBT/IM 85/15 tested in three-point bending at a piston speed of $2\,\mathrm{m\,sec^{-1}}$. Test temperature: (a) 25° C; (b) 0° C; (c) −30° C. The notches are visible at the bottom of the photograph.

failure that will be referred to as semi-brittle. After significant deviation from linear elastic behaviour, the F–Δ curve shows a steep fall from the peak load (indicated by the arrow in Fig. 1b). The fracture surface shows signs of plastic deformation only in the immediate vicinity of the notch tip. These features indicate that crack initiation is preceded by plastic deformation at the base of the notch, but that almost immediately after initiation the crack becomes unstable and propagates rapidly through the rest of the sample with little additional energy absorption.

At −30° C the F–Δ curve shows no deviation from linear elastic behaviour. The curve is linear up to the point of failure and is fully determined by the elastic response of the specimen. The fracture surface shows no signs of plastic deformation. These features indicate that at this low temperature the initiation of the rapidly propagating crack is no longer delayed by plastic deformation at the base of the notch. This type of failure will be referred to as brittle.

3.2. Uniaxial tensile dilatometry

The volume strain curves measured in tensile dilatometry provide information about the deformation mechanisms that cannot be gained from the stress–axial strain curves alone. In the present study two different types of volume strain behaviour were observed. One type indicates that no significant cavitation takes place and that shear deformation is the only non-Hookean deformation mechanism. The other type indicates a mixed mode of deformation, with shear deformation and cavitation occurring at the same time.

Figs 3 to 5 show engineering stress–axial strain–volume strain (σ–ε_A–$\Delta V/V_0$) curves of selected blends at some selected temperatures. The two curves for the PBT/PC 45/55 blend shown in Fig. 3 are typical examples of volume strain behaviour observed when no significant cavitation takes place. After the initial volume increase due to elastic deformation (Poisson effect), the $\Delta V/V_0$–ε_A curve levels off and becomes flat (or nearly flat) at the axial strain at which the yield point in the σ–ε_A curve is reached

$$\frac{\mathrm{d}\,(\Delta V/V_0)}{\mathrm{d}\varepsilon_A} \sim 0 \quad \text{when} \quad \frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_A} = 0 \qquad (2)$$

This behaviour indicates that shear deformation is the only non-Hookean deformation mechanism. The volume increase of the sample is entirely due to elastic deformation [4]. The same type of behaviour can be seen in Figs 4a, 5a, and 5b. All the samples that exhibit this type of volume strain behaviour show distinct neck formation shortly after yielding.

Figs 4b, 4c and 5c are typical examples of volume strain behaviour indicative of a mixed mode of shear deformation and cavitation. After the initial volume increase, the volume strain does not level off but keeps increasing, indicating that besides shear deformation considerable cavitation takes place. The samples that exhibit this type of behaviour do not form a neck at axial strains up to 14%. Therefore, volume strain measurements are still valid after yielding.

Table I lists the deformation mechanisms as revealed by tensile dilatometry for the materials under investigation. It is interesting to note that none of the samples broke at an axial strain lower than 14%.

4. Discussion

4.1. Toughened PBT

From Table I it appears that the notched impact toughness of PBT can be greatly improved by the addition of 15% impact modifier. As illustrated by

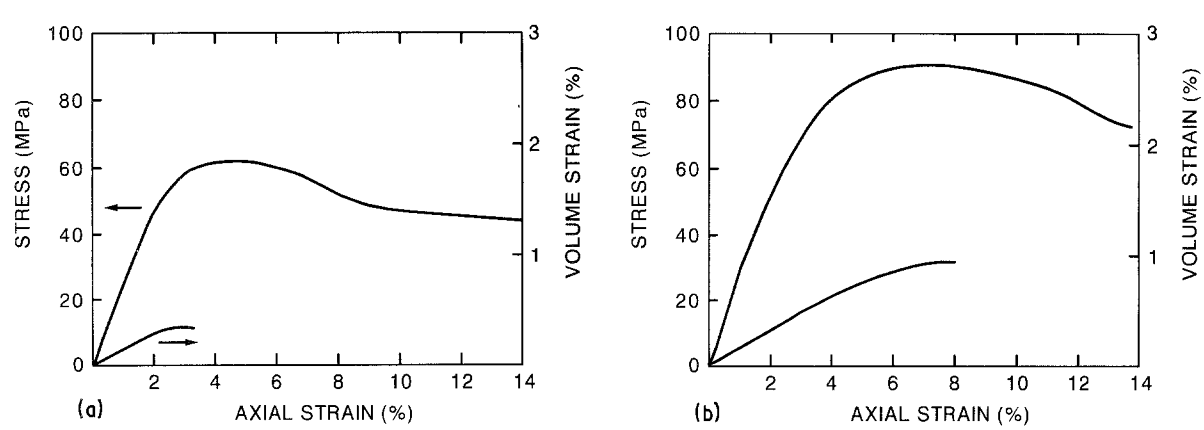
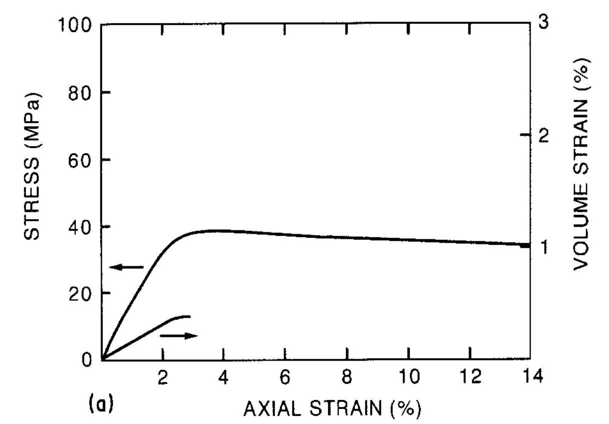
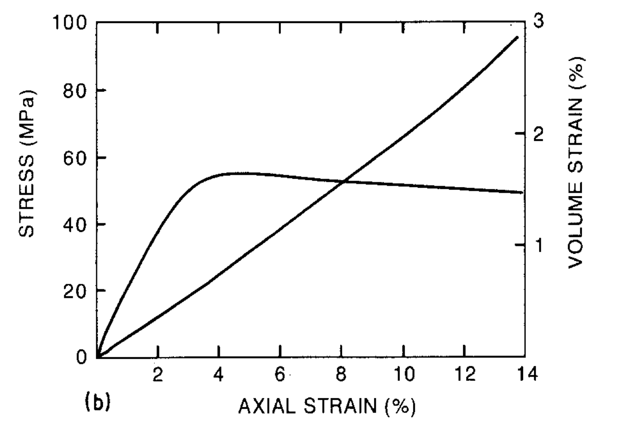


Figure 3 Stress–axial strain–volume strain curves for PBT/PC 45/55 tested at an axial strain rate of $0.1\,\mathrm{sec^{-1}}$. Test temperature: (a) 25° C; (b) −30° C.





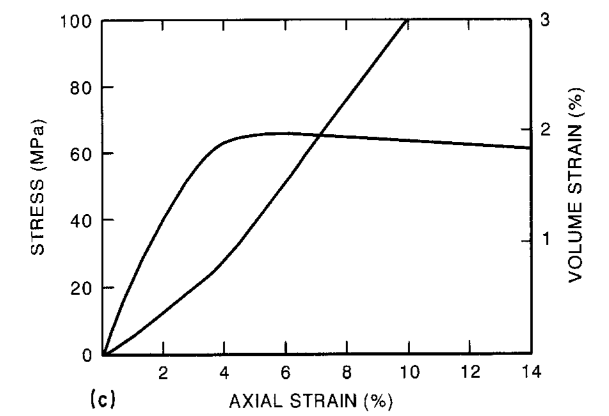
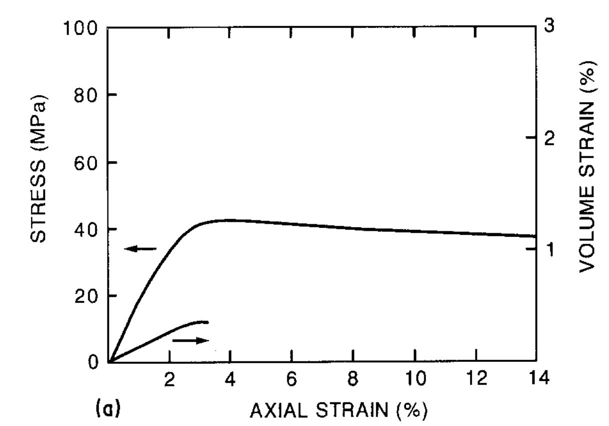
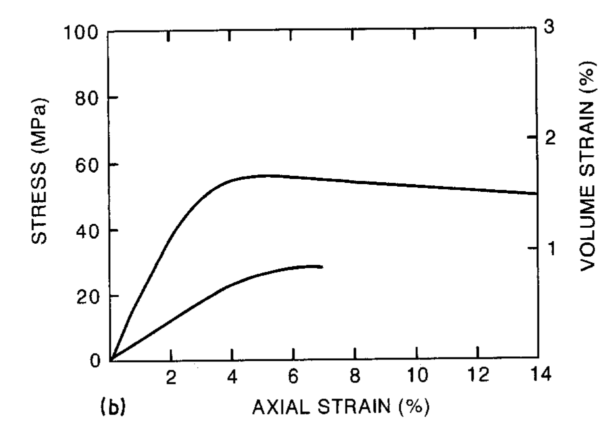


Figure 4 Stress–axial strain–volume strain curves for PBT/IM 85/15 tested at an axial strain rate of $0.1\,\mathrm{sec}^{-1}$. Test temperature: (a) 25° C; (b) 0° C; (c) −30° C.

Fig. 1, the degree of toughening depends strongly on temperature. It must be realized that the notched impact test and the uniaxial tensile test are different in test speed as well as stress configuration. At the base of the notch of a 3 mm thick specimen the stress field is essentially biaxial, whereas in the tensile test the stress field is predominantly uniaxial. In spite of the differences, for PBT/IM 85/15 there appears to exist a distinct relation between the failure mode in the notched impact test and the deformation mechanisms in tensile dilatometry (Table I and Figs 1 and 4). In the temperature region of ductile failure, shear deformation is the only deformation mechanism. In the regions of semi-brittle and brittle failure, a mixed mode of shear deformation and cavitation occurs, with less cavitation in the semi-brittle region than in the brittle region (Fig. 4). In unmodified PBT no cavitation occurs over the entire temperature range. This result directly indicates that the cavitation in PBT/IM 85/15 must be the result of the presence of the impact modifier.

Fig. 6 shows a transmission electron micrograph of a thin section of a PBT/IM 85/15 specimen that was highly deformed in tension at −30° C. The impact modifier particles have been stained with OsO_4 and appear dark in the micrograph [1]. An appreciable fraction of the particles has cavitated internally. This cavitation is not observed in undeformed specimens. No crazes and no signs of debonding at the particle–matrix interface are discernible. The latter observation indicates that there is good adhesion between the PBT matrix and the shell of the impact modifier particles. This adhesion enables stress transfer from the matrix to the particles and, thus, enables the hydrostatic





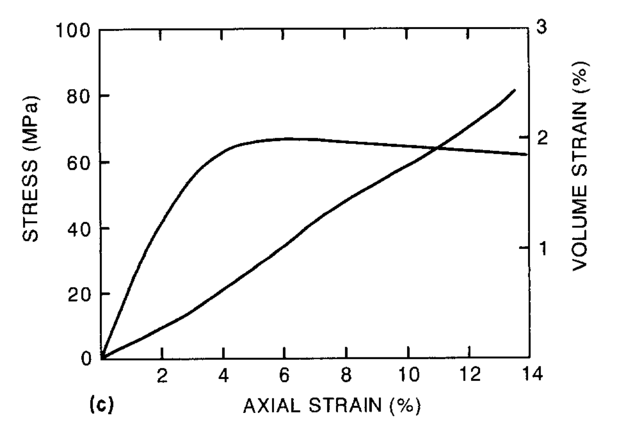


Figure 5 Stress–axial strain–volume strain curves for PBT/PC/IM 70/15/15 tested at an axial strain rate of $0.1\,\mathrm{sec}^{-1}$. Test temperature: (a) 25° C; (b) 0° C; (c) −30° C.

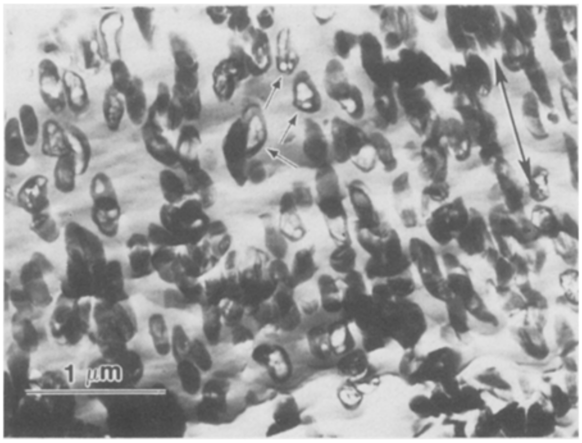


Figure 6 Transmission electron micrograph of PBT/IM 85/15 highly deformed at $-30°$ C. The small arrows indicate cavitated impact modifier particles. The large arrow indicates the tension direction.

tensile stresses in the particles to become large enough for internal cavitation. The fact that no crazes are observed in specimens deformed in tension does not mean that crazing never occurs in toughened PBT. Similar to toughened nylon [6], in specimens that fail in a brittle or semi-brittle manner in the impact test, some crazes are observed above and below the plane of the rapidly propagating crack.

From the relation between the failure mode in notched impact and the deformation mechanisms in tensile dilatometry, it is clear that in toughened PBT shear deformation of the PBT matrix is the major toughening mechanism. This shear deformation is initiated by the stress concentrations associated with the impact modifier particles. Because of overlapping stress fields between neighbouring particles, a very high volume of matrix material is involved in shear deformation, resulting in high energy dissipation. This mechanism of toughening is similar to that reported for toughened nylon [6–8] and toughened epoxies [3, 9]. Reduction of the test temperature leads to brittleness because of a decrease in the extent of shear deformation. This decrease may be partly caused by a lower effectiveness of the impact modifier particles in producing stress concentrations. However, the glass transition temperature of the rubbery core is sufficiently low ($-80°$ C) that at temperatures above $-30°$ C the impact modifier is not believed to have lost its rubbery character. The main reason for the decrease in shear deformation with lower temperatures is the reduced inherent ductility of the matrix or, in other words, the reduced ability of the matrix to respond to the presence of impact modifier particles by undergoing shear deformation. In tensile dilatometry this reduced inherent ductility is indicated by an increase in the extent of internal cavitation of the particles. This cavitation is caused by the fact that the hydrostatic tensile stresses in the particles can build up higher as a result of the reduced shear deformation. The extent of internal cavitation can thus be considered to be a measure of the inherent ductility of the matrix. For optimum toughening, internal cavitation is an undesirable deformation mechanism because the energy dissipation involved in this cavitation process is clearly lower than that involved in extensive shear deformation of the matrix.

4.2. Toughened PBT/PC blends

4.2.1. Interfacial adhesion

Before discussing the toughening mechanisms of toughened PBT/PC blends, it is important to deal with the adhesion at the interface between PBT and PC. In an earlier paper [4], tensile dilatometry studies on PC resins filled with 10 vol % of small glass beads were reported. It was found that the degree of adhesion at the PC–glass interface has a distinct effect on the extent of cavitation as measured by tensile dilatometry. Resins with good interfacial adhesion show no cavitation whereas resins with poor interfacial adhesion show substantial cavitation as a result of debonding at the PC–glass interface. As shown in Fig. 3 and Table I, tensile dilatometry on the PBT/PC 45/55 blend reveals no significant cavitation over the entire temperature range from -30 to $+25°$ C. This result indicates good interfacial adhesion between PBT and PC. This adhesion can be understood from the partial miscibility of PBT and PC which leads to complicated interpenetration of the two polymers at the interface [1].

4.2.2. Toughening mechanisms

Table I shows that the low-temperature impact toughness of PBT/IM 85/15 can be greatly improved by replacing 15% of the PBT with PC. The transition temperature from ductile failure to semi-brittle failure is shifted from 10° C for PBT/IM 85/15 to $-20°$ C for PBT/PC/IM 70/15. At first sight this beneficial effect of such a relatively small amount of PC is surprising. In the impact-modified blends containing PC, the impact modifier is exclusively contained in the PC [1]. Therefore, as can be seen in Fig. 5 of Part 1 [1], addition of only 15% PC leads to severe agglomeration of the impact modifier particles. This effect alone would be expected to be detrimental for toughness. Nevertheless, the low-temperature toughness is greatly improved, and from Table I and Figs 4 and 5 it appears that the relation between the failure mode in notched impact and the deformation mechanisms in tensile dilatometry is the same for PBT/PC/IM 70/15/15 as for PBT/IM 85/15; brittleness in impact is coupled to cavitation in tensile dilatometry. Fig. 7 shows a transmission electron micrograph of a thin section of a PBT/PC/IM 70/15/15 specimen that was highly deformed in tension at $-30°$ C. Similar to PBT/IM 85/15, the source of the cavitation is internal cavitation of the impact modifier particles. This internal cavitation indicates that there is good interfacial adhesion between PBT and PC as well as between PC and the shell of the impact modifier.

From these results it is clear that the improvement in low-temperature toughness obtained through replacing 15% of the PBT with PC is caused by an increase in the extent of shear deformation. As discussed previously [1], addition of PC changes a few important features of the microstructure of the blend. Therefore, it is difficult to determine unambiguously the reason (or reasons) for the increased extent of shear deformation.

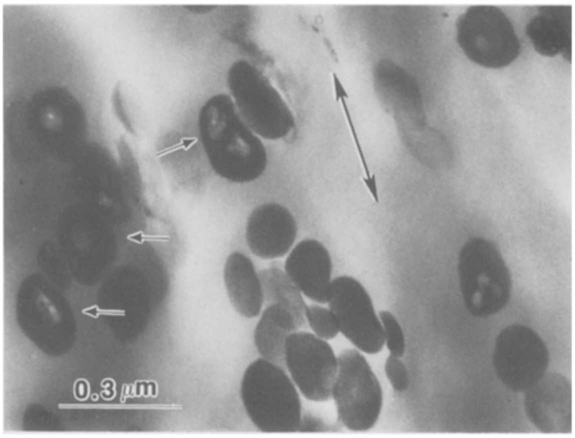


Figure 7 Transmission electron micrograph of PBT/PC/IM 70/15/15 highly deformed at $-30°$ C. The small arrows indicate cavitated impact modifier particles. The large arrow indicates the tension direction.

One reason may be that the impact modifier particles are embedded in a thin envelope of PC. PC is a polymer of high inherent ductility. It will, therefore, be relatively easy to deform the PC envelope by shearing. This may hamper the building-up of hydrostatic tensile stresses in the particles which would suppress internal cavitation in favour of shear deformation. The PC envelope, however, is so thin that it seems unlikely that this effect fully accounts for the large increase in shear deformation. Another, and probably more plausible reason for the increase in shear deformation is an increased inherent ductility of the matrix induced by modification of the PBT with partially miscible PC. Although the degree of crystallinity of PBT remains fairly constant upon PC addition, the microstructure of the PBT spherulites changes significantly. The spherulites become smaller, more diffuse and, perhaps most importantly, PC is found to reside in the amorphous regions between the PBT lamellae as a result of phase separation during crystallization of the PBT. It seems very likely that this modification of the amorphous interlamellar regions by PC increases the inherent ductility of the matrix by increasing the ability of the PBT spherulites to undergo interlamellar slip.

Raising the concentration of PC to 45% leads to an interpenetrating network of PC and PBT [1]. Because more PC is present, the impact modifier particles are well dispersed in the PC phase and no longer agglomerated as in the blend containing 15% PC. The high level of highly ductile PC leads to further improvement of the low-temperature impact toughness. For PBT/PC/IM 40/45/15 the transition from ductile to semi-brittle failure occurs below $-30°$ C (Table I). Tensile dilatometry reveals no cavitation in the temperature range of ductile failure, indicating that also in this blend shear deformation is the major toughening mechanism.

5. Conclusions

1. The combination of notched impact testing and uniaxial tensile dilatometry is very useful in elucidating toughening mechanisms. For the impact modified blends a distinct relation was found between the failure mode in notched impact and the deformation mechanisms in tensile dilatometry. Ductile failure in impact is coupled to shear deformation in dilatometry; brittle failure is coupled to a mixed mode of shear deformation and internal cavitation of the impact modifier particles.

2. In toughened PBT shear deformation of the PBT matrix is the major toughening mechanism. The brittleness at low temperatures is caused by a reduction in the ability of the PBT to undergo shear deformation. In tensile dilatometry this reduced inherent ductility of the PBT is indicated by an increase in the extent of internal cavitation of the impact modifier particles.

3. Addition of PC to toughened PBT significantly improves the low-temperature impact toughness. This improvement is the result of an increase in the extent of shear deformation. At first sight the significant improvement obtained with a PC level as low as 15% is surprising. A likely explanation is a higher inherent ductility of the matrix induced by modification of the PBT with partially miscible PC. It is conceivable that the PC residing in the amorphous interlamellar regions of the PBT spherulites promotes the ability of the spherulites to undergo interlamellar slip.

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