Interfacial adhesion and toughening mechanisms in an alloy of polycarbonate/polyethylene

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Interfacial adhesion and toughening mechanisms in an alloy of polycarbonate/polyethylene (PC/PE) are investigated using transmission electron microscopy. In contrast to the general speculation, it is found that the PE particles strongly adhere to the PC matrix. The toughening mechanisms in the PC/PE blend are found to be debonding of the PC/PE interface, which relieves the triaxial tension in front of the crack tip, followed by shear banding of the PC matrix. Possible causes for such an unexpected strong interfacial adhesion between PC and PE are discussed. Also, the importance of the cavitational strength of the toughener phase in toughness optimization is addressed.

(Keywords: PC/PE blend; interfacial adhesion; toughening mechanism; cavitational strength; thermal stress)

Introduction

Toughening of polycarbonate (PC) via polyethylene (PE) particles has been previously studied by Yee *et al.*[1–5] and the toughening effect found to be quite remarkable[4,5]. However, the operative toughening mechanism(s) in the PC/PE† blend is still unclear owing in part to the lack of appropriate tools and/or techniques for probing the properties of the interface between PC and PE. This results in considerable speculation and debate as to how the PC is toughened. Although there exists no experimental evidence, the thermal expansion coefficient mismatch between PC and PE as well as observations of the fracture surface[1–3,6] lead one to believe that the PE particles only serve to create randomly dispersed holes in the PC matrix. In other words, the PE particles are hosted by bigger holes in the PC matrix due to the larger thermal contraction of the PE particles when the temperature drops from the processing temperature (~230°C) to room temperature (~25°C). Consequently, holes are thought to be suitable for toughening PC. Notwithstanding these deductions, the possibility that some bonding exists between the two phases still remains. The present study focuses on clarifying whether or not PC and PE are interfacially bonded. The resulting operative toughening mechanisms in PC/PE are also discussed.

Experimental

PC (Lexan® 141, $M_w \sim 26\,000$), obtained from the General Electric Company, was blended in a Brabender mixer with 3.3 wt% low density PE for 20 min. The PC/PE blend was then compression moulded into a 6.35 mm thick plaque at 230°C. The plaque was slowly cooled to room temperature and cut into rectangular bars (76.2 × 12.7 × 6.35 mm). These bars, which were pre-notched using a jeweller's saw and pre-cracked using a liquid nitrogen chilled razor blade, were used for fracture toughness evaluation using single-edge-notch three-point-bend specimens and for the double-notch four-point-bend (DN-4PB) experiment[6–8] (*Figure 1*). A screw-driven Instron testing machine (model 1137) was used to conduct the DN-4PB test with a crosshead speed of 0.847 cm s^{-1}.

The sub-fracture surface zone (SFSZ) (*Figure 1*) was probed using two microscopic techniques. The first technique involved petrographic polishing to the mid-plane of the specimen[6–9] and subsequent examination using an optical microscope in transmitted light (TOM). The second technique involved microtomy: sections were removed until the mid-plane was reached, then the surface was sectioned cryogenically at −160°C to obtain ultra-thin sections with a thickness of ~80 nm. These thin sections were then examined using a JEOL 2000FX ATEM transmission electron microscope (TEM) operated at an accelerating voltage of 100 kV. The fracture surface of the DN-4PB specimen was coated with 20 nm of Au–Pd and investigated using a Hitachi S-520 scanning electron microscope (SEM).

Results

Blending of the incompatible PC and PE using the Brabender mixer produces a good dispersion of PE with an average particle size of 0.3 μm in the PC matrix (see below). The high toughness of the blend made it necessary to evaluate the fracture toughness using the J-integral techniques. Details of this technique have been given previously[10]. The J_{IC} of the blend was found to be 5.67 kJ m^{-2}, which is considerably higher than that of PC without PE (2.5 kJ m^{-2})[5,10]. These results are consistent with the much higher notched Izod toughness previously found for a similar system[1–3].

The fracture surface of the stress-whitened zone (slow crack growth region) of the PC/PE blend is shown in *Figure 2*. Plastic flow of the matrix is evident. The interfacial adhesion between PE and PC appears to be

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†The first listed polymer, i.e. PC in this case, indicates the matrix phase; the second listed polymer, i.e. PE, indicates the inclusion phase

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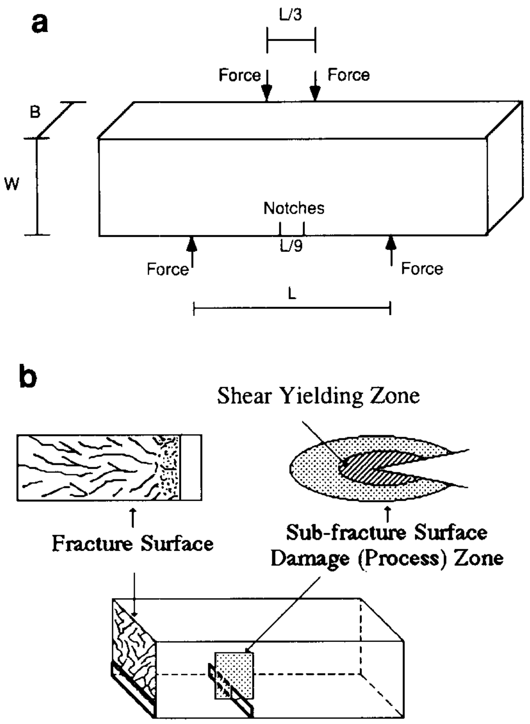

Figure 1 Schematic diagrams of (a) the DN-4PB geometry and (b) the region studied by microscopy

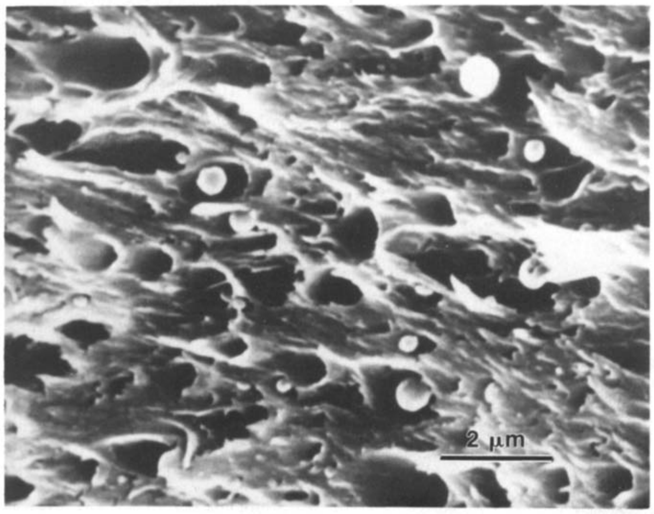

Figure 2 SEM micrograph of the plane strain stress-whitened region of PC/PE. The PE particles appear to be hosted by bigger holes. The crack propagates from right to left

poor. The seemingly detached PE particles are distinctly smaller than the holes that host the PE particles. However, the SEM micrograph shown in *Figure 2* does not necessarily indicate that the PE particles were detached from the PC matrix before deformation. The holes may have been induced by the debonding of the PE particles in the PC matrix during slow crack growth and had subsequently grown in size around the crack tip before unstable fracture proceeds.

In order to find out whether or not the PE particles are interfacially bonded to the PC matrix, cryogenic (−160°C) thin sectioning of an undamaged PC/PE specimen was carried out. As shown in *Figure 3*, it is clear that the PE particles are still bonded to the PC matrix even after experiencing a dramatic temperature drop from room temperature (25°C) down to −160°C, and back to room temperature. The thermal stress at the interface corresponding to the maximum temperature excursion can reach as high as ~30 MPa if the equation derived by Boyce *et al.*[11] for calculating the interfacial thermal stress between the isotropic spherical inclusion and the matrix is utilized*. This implies that the interfacial strength between PC and PE must be 30 MPa or higher. This finding prompted an investigation of the toughening mechanisms using the DN-4PB technique[6–8].

As shown in *Figure 4*, the TOM micrographs taken both in bright field and with crossed polars indicate the existence of a dark cavitational zone (*Figure 4a*) and a birefringent shear yielded region (*Figure 4b*) in the SFSZ. The size of the shear yielded zone appears to be comparable to the size of the cavitational zone. This type of damage feature is significantly different from that of the MBS (KM 653, Rohm & Haas) rubber-modified PC system[6,10], where the size of the cavitational zone is considerably bigger than the size of the shear yielded zone.

The origin of the cavitational zone in the PC/PE system could be internal cavitation of the PE particles, detachment of the PE particles from the PC matrix, or just a simple plastic dilatation of the pre-existing holes. In order to acquire a definitive picture of the toughening mechanisms in the PC/PE blend, a more detailed study at the SFSZ was conducted using TEM.

When preparing the TEM thin sections, care was taken to make sure that the observed damage features were not

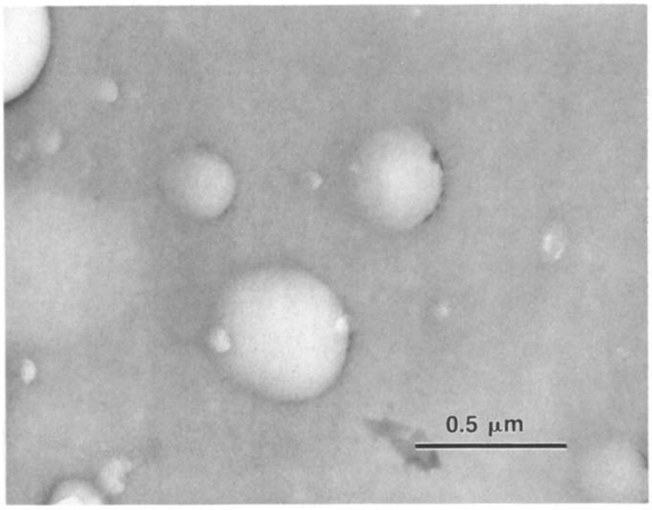

Figure 3 TEM micrograph of an undamaged PC/PE sample. PC and PE appear to be well-bonded to each other

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*The equation derived by Boyce *et al.* is given below[11]:

$$\sigma = \frac{K_p(\gamma_m - \gamma_p)\Delta T}{1 + \frac{K_p}{K_m}\frac{(1+\nu_m)}{2(1-2\nu_m)}}$$

where σ is the thermal stress, K is the bulk modulus, γ is the volumetric thermal expansion coefficient, ΔT is the temperature difference, ν is the Poisson's ratio, and the subscripts p and m denote particle and matrix, respectively. In this study, $K_m = 5$ GPa, $K_p = 3$ GPa, $\gamma_m = 2 \times 10^{-4}$ K^{-1}, $\gamma_p = 4 \times 10^{-4}$ K^{-1}, $\nu_m = 0.42$ and $\Delta T = [(-160°C) - 25°C] = -185°C$ are used. As a result, $\sigma \sim 30$ MPa. Note that the thermal stress due to the previous sample preparation procedures is neglected. Furthermore, the molecular relaxation at the PC/PE interface is not considered

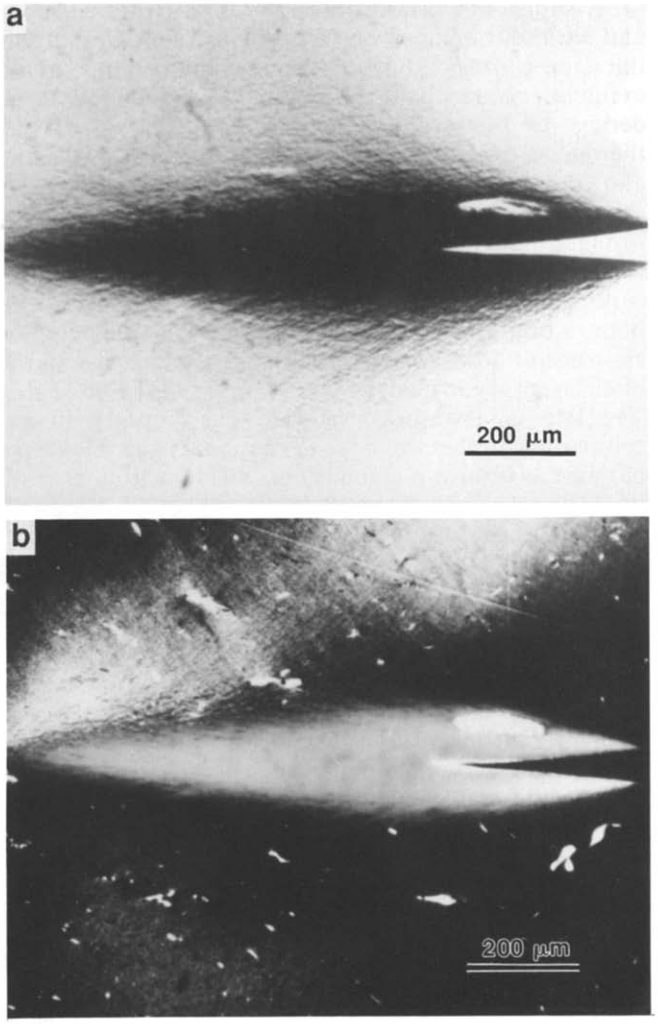

Figure 4 TOM micrographs taken of the DN-4PB damage zone of PC/PE under (a) bright field and (b) crossed polars. The crack propagated from right to left

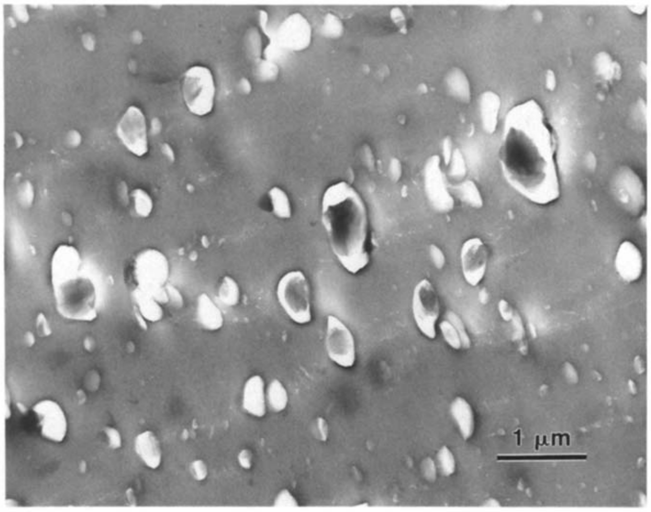

Figure 5 TEM micrograph taken at the crack tip of the DN-4PB damage zone. It is clear that debonding occurs in this region. The holes have grown not only in size but also in shape. This indicates that large deformation of the PC matrix has taken place. The crack propagated from right to left

due to the ultra-thin sectioning process. In the crack tip region, the originally spherical PE inclusions appear to have become elongated, indicating the occurrence of some shear plasticity (*Figure 5*). Detachment of the PE particles from the PC matrix is readily observed. The holes that hosted the PE particles have grown to a size larger than the particles and changed substantially in shape. This observation implies that the PC matrix has undergone both dilatational plasticity and shear plasticity around the crack tip. The significant shape change of the holes indicates a rather large shear deformation of the matrix around the crack tip region (~150%). In regions farther away from the crack tip region, a less pronounced but still measurable degree of debonding at the PC/PE interface and deformation of holes is found (*Figure 6*). In regions outside the SFSZ (*Figure 7*), the PE particles are undeformed and appear to be fully attached to the PC matrix. *Figures 3–7* demonstrate that an interpretation based on fracture surface (*Figure 2*) observation alone can be misleading. Furthermore, the assumption that thermodynamic incompatibility would necessarily lead to no adhesion between the two phases appears to be groundless. The above study clearly suggests that a rather strong interfacial adhesion between the PE particles and the PC matrix is present.

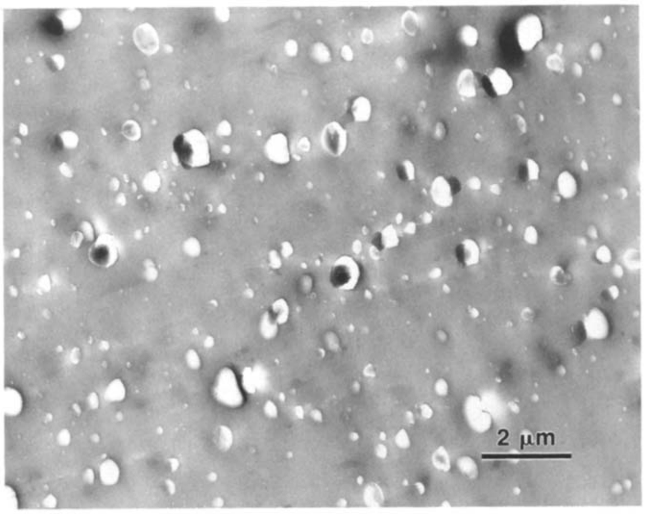

Figure 6 TEM micrograph taken farther away from the crack tip than in *Figure 5* of the DN-4PB damage zone. The size of the hole and the degree of matrix deformation (change in shape of the hole) are smaller. The crack propagated from right to left

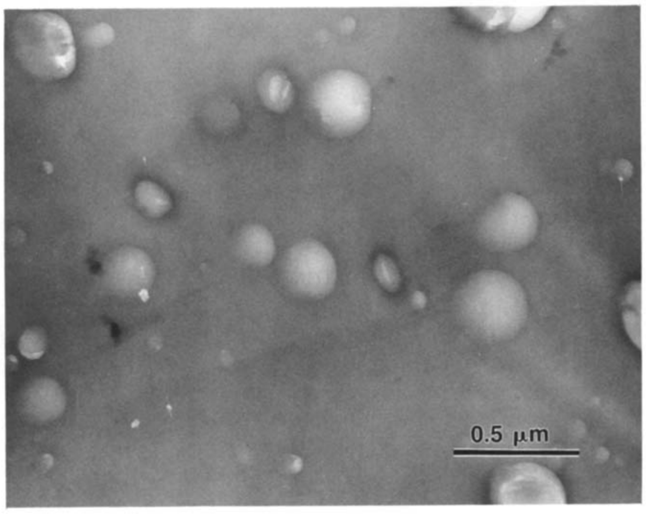

Figure 7 TEM micrograph taken outside the DN-4PB damage zone. No observable debonding or deformation is found. The crack propagated from right to left

Discussion

Our previous work on toughened plastics involving ductile matrices indicated that internal cavitation of the toughening particles served as the key role in relieving plane strain, thus allowing extensive shear plasticity to occur. The present study suggests that the toughening process in the PC/PE blend begins with debonding of the PE particles from the PC matrix, instead of internal cavitation of the toughener phase as in the case of the MBS rubber-modified PC system[5,6,10]. This cavitational process relieves the triaxial tension in front of the crack tip, and is immediately followed by massive matrix shear banding. While the extents of the birefringent shear yielded zones are comparable between the two types of toughened systems, the size of the cavitational zone in PC/PE is far smaller than that of the MBS rubber-modified PC system. This implies that the cavitational strength of the MBS rubber is probably weaker than the interfacial adhesion between PC and PE. Since the fracture toughness of PC/PE is higher than that of PC/MBS (5.67 *versus* 4.58 $\mathrm{kJ\,m^{-2}}$) at a comparable level of toughener[5,10], we surmise that in the PC matrix, this particular MBS rubber cavitates too early. In other words, the stress state for the cavitational process to occur may be critical for toughness optimization[12–14]. It seems reasonable that the optimal cavitation resistance depends on the polymer.

At this stage, it is not known what mechanism(s) cause the strong interfacial adhesion between the PE particles and the PC matrix. For an interface to be able to withstand the rather high thermal stress ($\sim$30 MPa) without failure, there must exist a mechanism or mechanisms that allow the PE to interact with the PC matrix either physically or chemically, or both. PE lacks functionalities along its backbone and at its chain ends that could react with PC. A possibility exists that the vigorous mixing in the Brabender mixer, which produces the fine dispersion of PE particles, has oxidized the PE chain, thus creating reactive sites. This possibility will be the subject of a future investigation.

Conclusion

The interfacial bonding between the PE and PC is found to be surprisingly strong (as high as 30 MPa). The toughening mechanism(s) in PC/PE is found to be due to a late cavitational process (i.e. debonding at the interface between PC and PE) which relieves the plane strain constraint, followed by extensive shear yielding of the matrix. This study suggests that debonding at the interface between the toughener phase and the matrix is as effective as the internal cavitation of the inclusion phase. The present work also implies that the stress state at which the cavitational process takes place is important for effective toughening of polymers. At this point, however, it is still uncertain whether or not holes can be as effective as PE and rubber particles in toughening PC. Further experimental studies have to be conducted to reveal these differences, if any.

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