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Adhesion enhancement in immiscible polymer bilayer using oriented macroscopic roughness

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The use of oriented macroscopic roughness to enhance the effective adhesion between two immiscible polymers was demonstrated. Bilayer specimens of polycarbonate and poly(styrene-*co*-acrylonitrile) (SAN) were produced with rough interfaces by scribing grooves of varying depths and spacings into the polycarbonate (PC) before joining the layers. The SAN, having a significantly lower glass transition temperature than polycarbonate, flows into the grooves during annealing at temperatures just over the PC glass transition, creating a mechanically interlocking interface. Subsequent measurements of bilayer interfacial fracture toughness showed up to a twenty-fold increase from that of a smooth interface when grooves were oriented perpendicular to the direction of interfacial crack propagation. The increase in toughness was shown to be greater as grooves were spaced closer together, and as groove depths were increased. Propagation of interface cracks followed a stick–slip mechanism, slowing considerably at each groove. Analysis of fracture surfaces indicates the increase in toughness to be mainly due to cohesive failure and deformation of the polymers at the grooves. Interface toughness was also enhanced with grooves scribed parallel to the propagation direction, but to a lesser degree than with perpendicular orientation.

(Keywords: adhesion; blends; surface enrichment)

INTRODUCTION

Adhesion in a bilayer comprised of immiscible polymers is generally weak due to limited interdiffusion, which results in a sharp interface. Many commercially available polymer blends are immiscible systems, and it is therefore important to devise methods to enhance the adhesion, or compatibility, between the phases present to improve the blend's mechanical properties. It has been shown previously[1–4] that adhesion between immiscible polymers can be enhanced by placing a di-block copolymer at their interface. The di-block acts as a physical bridge between the two immiscible polymers and enhances the interfacial bonding between the homopolymers. In this case, the adhesive strength depends upon the areal density of the di-block copolymers at the interface. Practical application of this method is limited, due to the expensive nature of the di-block polymer. It has also been shown that adhesion may be enhanced through the addition of a third molecule into the system which reacts chemically with both species[5]. This reactive compatibilization has been utilized commercially, and can be significantly less expensive than using di-block compatibilizers. However, not all immiscible polymers pairs will be easily amenable to interface strengthening by this method. In our previous publications[6,7] we have demonstrated how adhesion between two immiscible polymers, polycarbonate (PC) and poly(styrene-*co*-acrylonitrile) (SAN), can be enhanced by manipulating molecular parameters such as copolymer content and entanglement density, the latter through control of oligomer concentrations.

In this paper we demonstrate a new method of enhancing adhesion in a bilayer of two immiscible polymers through the introduction of *oriented* macroscopic roughness in one of the polymer layers prior to formation of the interface. This roughness is introduced by the creation of patterned grooves in the polymer

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surface. This method does not address blend compatibility, but rather adhesion in macroscopic constructs or laminates of immiscible polymer layers. Although the use of macroscopic roughness for adhesion enhancement between metals and polymers is not new, the use of oriented roughness is novel. In previous studies on the use of roughness for adhesion enhancement, Malpass *et al.*[8] showed that the adhesion mechanism between polyethylene and porous alumina is due to mechanical interlocking of polyethylene in the pores, and that adhesion is controlled by pore size. Similar enhancement of adhesion between a Kevlar fibre and a polymer matrix was reported by Breznick *et al.*[9]. They induced a roughness on fibre surfaces using chemical etching, and found that the increased contact area between the fibres and matrix resulted in a stronger interface. Other studies have also emphasized the importance of surface roughness in adhesion between metals and polymers[10–13]. In this study, we illustrate with a specific example how adhesion between two immiscible, glassy polymers can be enhanced significantly using oriented macroscopic roughness, and explain in detail the mechanism of this enhancement.

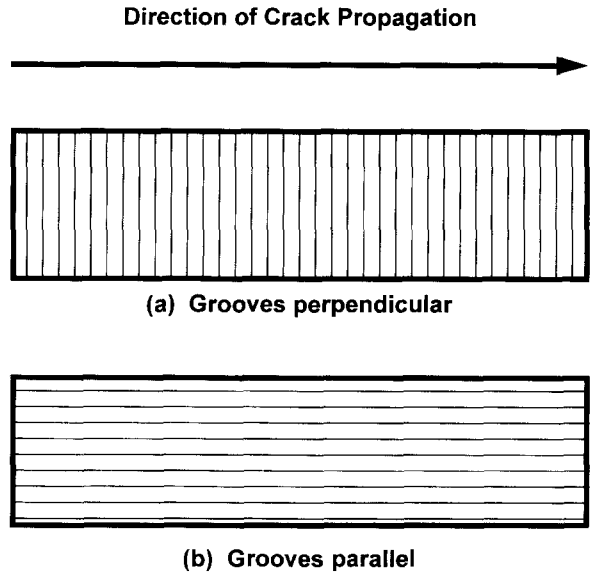


Figure 1 Schematic diagram illustrating orientation of macroscopic grooves relative to crack propagation direction. (a) Grooves perpendicular to propagation direction. (b) Grooves parallel to propagation direction

EXPERIMENTAL

Materials

The materials used to form the bilayer described in this study were polycarbonate (PC) and poly(styrene-*co*-acrylonitrile) (SAN). The PC was obtained from General Electric Co., and had a weight average molecular weight of 19 000. The SAN was supplied by Monsanto Company, and had a weight average molecular weight of 160 000. The copolymer composition of the SAN was 24% acrylonitrile by weight. The glass transition temperatures of (T_gs) of the two polymers as measured by differential scanning calorimetry (d.s.c.) at a heating rate of 20°C min^{-1} were 150 and 105°C, respectively. Both materials were studied as-received, and so contained some small percentage of additives and oligomeric species.

Formation of bilayer

The individual polymers, supplied in pellet form, were dried and then compression moulded in a vacuum press into separate rectangular plates of dimension 4.0 × 1.0 × 2.0 cm using a chrome-plated mould. After cooling to room temperature, but while still in the mould, roughness was created on the PC plate by scribing grooves of specific dimensions and orientation with a diamond-edged knife. The grooves were created either parallel or perpendicular to the direction of subsequent crack propagation measurements (see *Figure 1*). The width, depth and spacing of the roughness was characterized using an optical microscope in reflection mode. The initial cross section of the grooves was 'V' shaped. Groove depths were varied from 4 to 35 μm, and the spacing between the grooves was either 1 mm or 0.5 mm. Control samples were also produced with no grooves in the PC surface. After the roughness was created and characterized on the PC, the polymers were joined together in their respective moulds at 165°C for 2 h under slight pressure. The bilayer formed was then allowed to cool for 2–3 h in the mould prior to removal, suppressing the formation of thermal stresses. To gain information about the shape of the grooves and mechanism of adhesion, a thin section of the bilayer perpendicular to the direction of the grooves was microtomed before fracture and analysed using a phase contrast microscope in transmission mode.

Interfacial fracture characterization

The fracture energy of the bilayer was measured using an asymmetric double-cantilever beam test geometry. The instrument setup and the schematic of the test method are reported in our previous publication[6]. In this method, a wedge (single edged razor blade) is pushed with a constant velocity of 100 μm s^{-1} into the bilayer interface using a stepping motor. The crack length ahead of the wedge is measured using an optical microscope to an accuracy of 0.1 mm. A minimum of 15 values of crack length are obtained at various stages of propagation, and

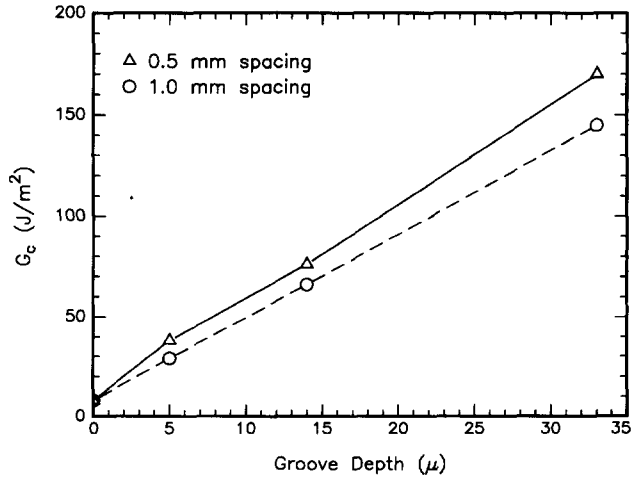


Figure 2 Fracture toughness, G_c of the PC/SAN interface as a function of groove depth for 0.5 and 1.0 mm groove spacings with grooves perpendicular to the crack propagation direction. SAN acrylonitrile level is 24 wt%

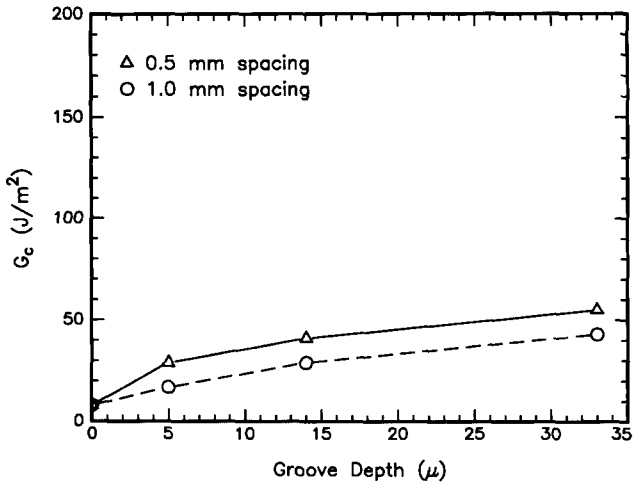


Figure 3 Fracture toughness, G_c of the PC/SAN interface as a function of groove depth for 0.5 and 1.0 mm groove spacings with grooves parallel to the crack propagation direction. SAN acrylonitrile level is 24 wt%

the mean is used to calculate the fracture toughness. The validity of this type of test has been demonstrated by Brown[14] in measuring the interface strength between polystyrene and poly(methyl methacrylate).

After fracture, the separated surfaces were analysed using an optical microscope in reflection mode to obtain information about the mode of failure at the grooves.

RESULTS AND DISCUSSION

Effect of groove orientation, depth, and spacing on interfacial fracture toughness

Figures 2 and *3* show the interfacial fracture toughness as a function of groove depth for the PC/SAN bilayer with grooves oriented perpendicular and parallel to the direction of crack propagation, respectively. Also shown is the effect of groove spacing for each orientation. An interfacial fracture toughness of $8\,J\,m^{-2}$ for the PC/SAN control without any grooves was reported in our previous publication, and is represented in the figures by the zero depth data point. As can be seen in the figures, the oriented macroscopic roughness created on the PC prior to bonding enhances the interfacial fracture toughness of the bilayer considerably, in both orientations. In the case of grooves oriented perpendicular to the crack propagation direction (*Figure 2*), the interfacial toughness increases from $8\,J\,m^{-2}$ (no grooves) to $145\,J\,m^{-2}$ (groove depth 35 μm) for groove spacings of 1.0 mm. A further increase to $170\,J\,m^{-2}$ is seen when the groove spacing is reduced to 0.5 mm. This increase is especially dramatic when considering that, as shown previously[7], optimization of acrylonitrile content and removal of oligomers for this system resulted in a maximum interface toughness of only $19\,J\,m^{-2}$. Samples with grooves created parallel to the direction of crack propagation also showed an increase in interfacial fracture toughness (*Figure 3*), but to a lesser degree

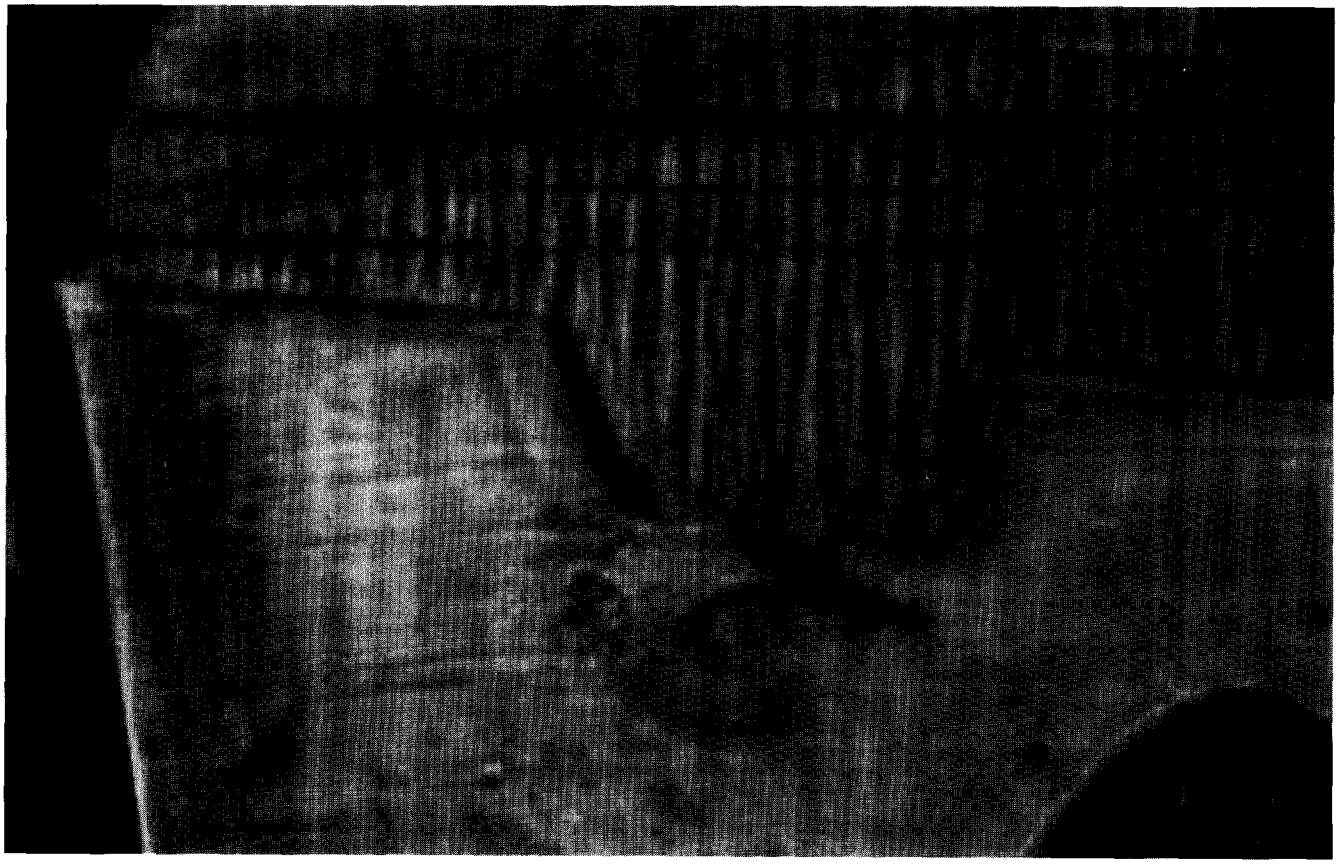
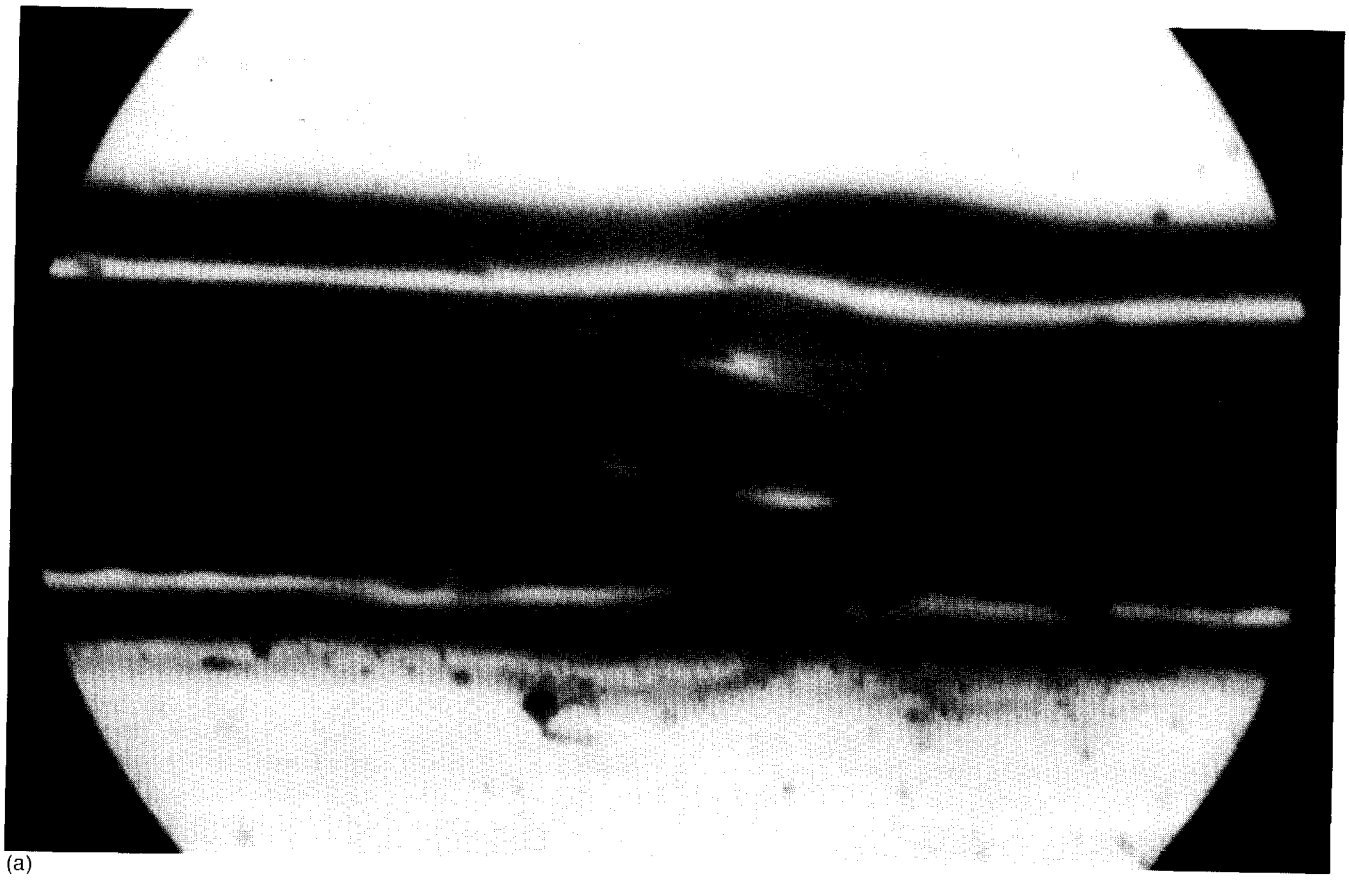
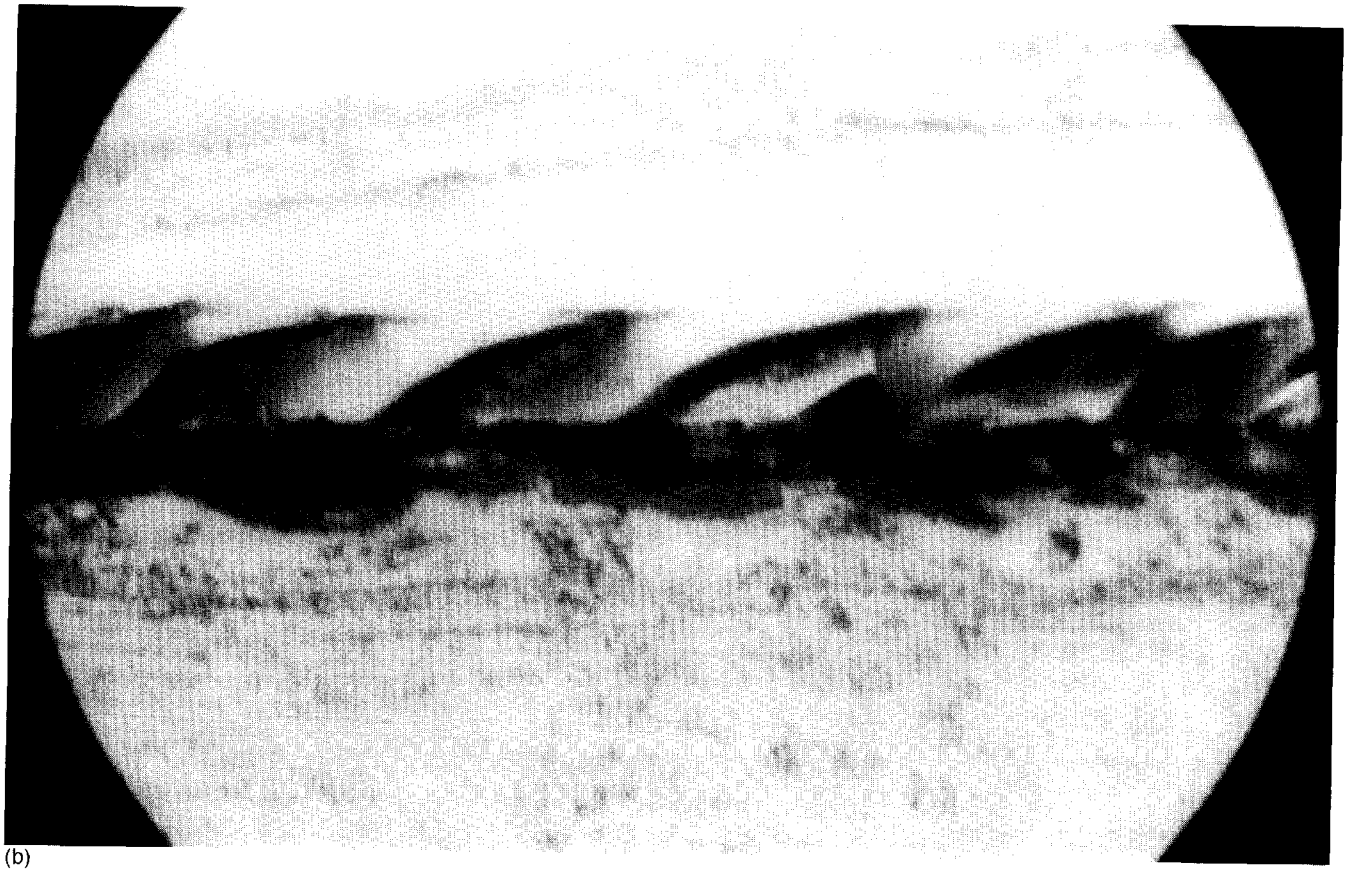


Figure 4 Optical micrograph (16 × magnification) of groove cross section after annealing showing mechanical interlocking morphology. Polycarbonate layer is below the interface, SAN layer above

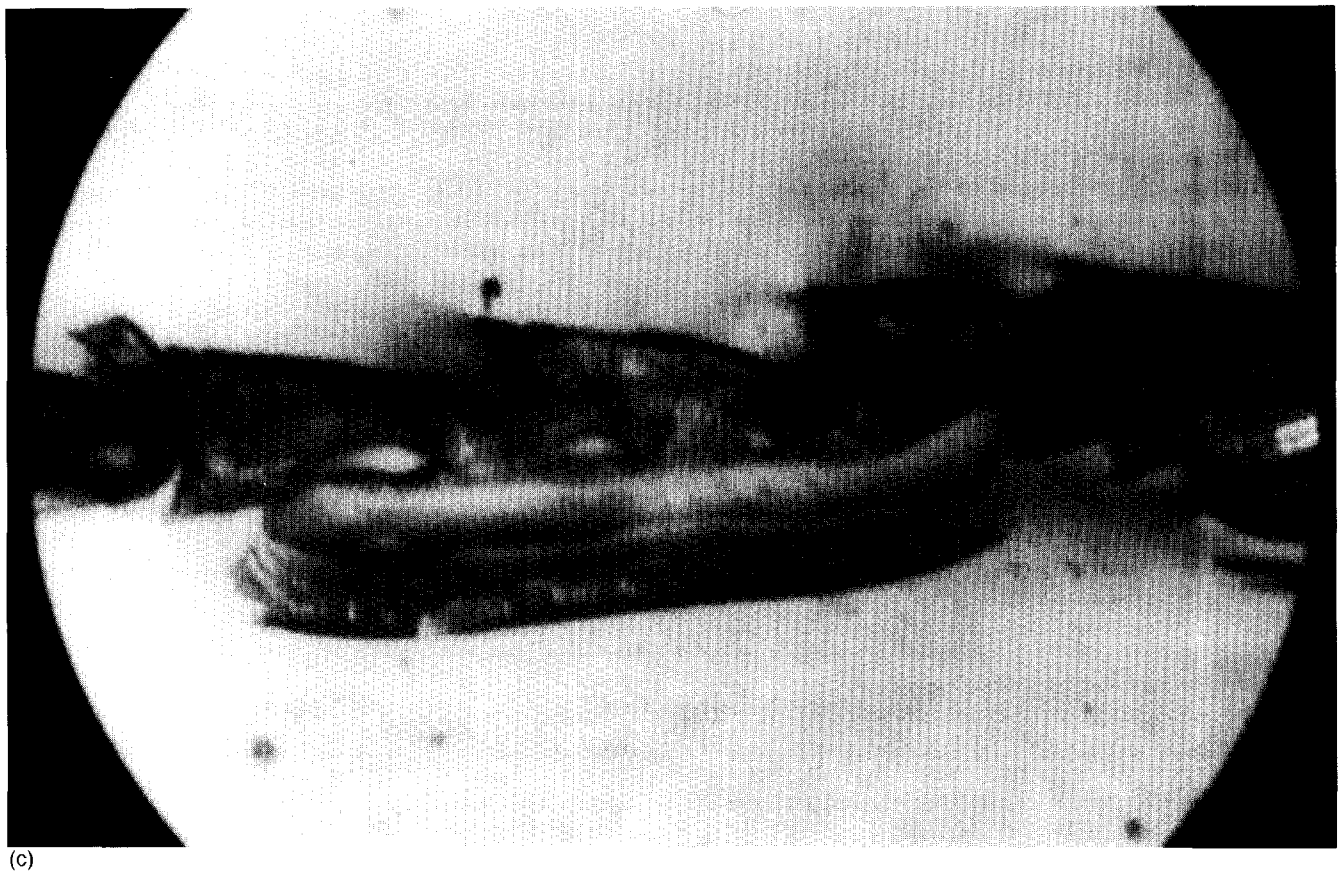


(a)



(b)

Figure 5 (a) Optical micrograph (16 × magnification) looking down on a groove in the polycarbonate surface before joining the two polymers. (b) Post-fracture optical micrograph (16 × magnification) of SAN surface at a groove. (c) Post-fracture optical micrograph (16 × magnification) of PC surface at a groove after fracture of the interface. Original groove depth in the PC was 35 μm



(c)

Figure 5 (*Continued*)

than the perpendicular grooves, up to $55\,J\,m^{-2}$. This directional dependence is analogous to a wall slip mechanism during the flow of polymeric melts described by Chen *et al.*[10]. They reported that wall slip velocities for linear low density polyethlene on metal capillaries were decreased with increasing wall roughness. More resistance was seen by the polymer when the roughness was perpendicular, rather than parallel, to the direction of slip. In the bilayer system considered here, the orientation dependence suggests that mechanical interlocking occurs at the interface, producing a stick–slip mechanism during crack propagation. The stick–slip effect would be expected to be strongest when the growing crack encounters grooves spanning the entire crack front, as in the perpendicular case. During crack propagation, the stick–slip mechanism was observed directly by optical microscopy, with growth of the interfacial crack being noticeably slowed at the grooves when the grooves had depths over $5\,\mu m$. This mechanism is also consistent with the change in toughness with smaller groove spacing, since the crack will encounter a higher density of barriers as it propagates. The strong effect of groove depth suggests that it is a determining factor in the crack-arresting effectiveness of the grooves.

Formation and morphology of the rough interface

Figure 4 shows a micrograph of the interface cross section for a $35\,\mu m$ deep groove taken with phase contrast microscopy prior to crack propagation. From the figure it is clear that the initial 'V' shape of the groove has become hemispherical, and that the SAN has flowed into the groove, creating an interlocking morphology. That the SAN should flow into the grooves is not unexpected since the annealing temperature used in forming the bilayer was 65°C above the SAN T_g but only 15°C above the PC T_g. At this temperature, the SAN will flow much more readily than the PC, which will tend to hold its shape. The sample is under slight pressure during annealing, which also contributes to flow. With additional time subsequent to flow, however, the driving force to decrease surface area will lead to the surfaces getting smoother, which is likely to be the reason for the rounding of the PC groove. The rounded shape of the groove will be beneficial to the interface strength, as it surrounds some amount of SAN, creating a mechanically stronger joint. Thus, the interface toughness may first increase as the interlocked morphology forms, but then with enough time the toughness may decrease as the PC pinches off more of the SAN beneath the original surface. It is therefore important that the sample be cooled below the T_g of both components at some optimum annealing time which will give the most effective interlocking morphology. Other factors could also be manipulated so as to maximize effective interfacial strength, such as the annealing temperature, pressure and molecular weight and surface tension of the components. All of these will affect the rheology of the two materials, and thus their ability to form a mechanically strong interface.

Deformation mechanisms during interface fracture

After completing the fracture toughness measurements, the fracture surfaces were examined using optical

microscopy in reflection mode to determine the mode(s) of failure. *Figure 5a* shows a micrograph looking down on a groove in the polycarbonate before joining the two polymers. The initial groove depth was approximately 35 μm. The edges of the groove are smooth and uniform. The roughness visible in the micrograph is at the bottom of the groove, and was created by the diamond-edged knife in the scribing process. *Figures 5b* and *5c* show grooves after fracture of the interface, looking at the SAN side and the PC side, respectively (but for different grooves). The patterns observed on both sides suggest that fracture was cohesive at the groove site. Adhesive failure at the interface would result in the observation of SAN mounds on the SAN side, and depressions on the PC side corresponding to the original groove pattern. Instead, extensive deformation appears to have occurred in both materials in the vicinity of the grooves, with smooth, apparently adhesive, failure away from the grooves. On the SAN side (*Figure 5b*) a one-sided brush-like pattern is visible just ahead of the groove, suggesting that the SAN crazes before undergoing cohesive failure. This is an indication of higher stress near the grooves than away from them, where the debonded interface is smooth. On the PC side (*Figure 5c*), the brush pattern also appears, and on both sides of the groove. Note that the groove runs through the centre of the micrograph, above a long, straight feature that is material from the SAN layer which remained on the PC side after separation. This pattern is evidence that a significant amount of deformed SAN remains in the groove on the PC side. Similar results were observed for the grooves created parallel to the direction of crack.

For a sample with shallow grooves (4–5 μm), a post-fracture micrograph is shown in *Figure 6*. Here, none of the features seen in the *Figure 5* micrographs are visible. Instead, a smooth surface was observed, similar to that reported in our previous publications[6,7]. This suggests that at this groove depth, the failure mechanism at the grooves is adhesive, with the SAN pulling completely from the grooves. The resolution of the optical microscope was not sufficient to observe whether SAN mounds existed on the surface.

CONCLUSION

Enhancing the adhesion between immiscible polymers has been traditionally approached from the standpoint of changing molecular interactions through monomer or co-monomer structural changes, or through the addition of compatibilizer molecules that create chemical or physical crosslinks at the interface. The results of this study demonstrate that enhanced adhesion in a bilayer construct can be achieved through the introduction of macroscopic roughness, and controlled through the orientation and morphological features of the roughness. Specifically, the effective interfacial fracture toughness is increased by creating grooved depressions in the polymer with the higher T_g prior to interface formation. The lower T_g material then flows into the grooves to create a mechanically interlocking interface. It is expected that a

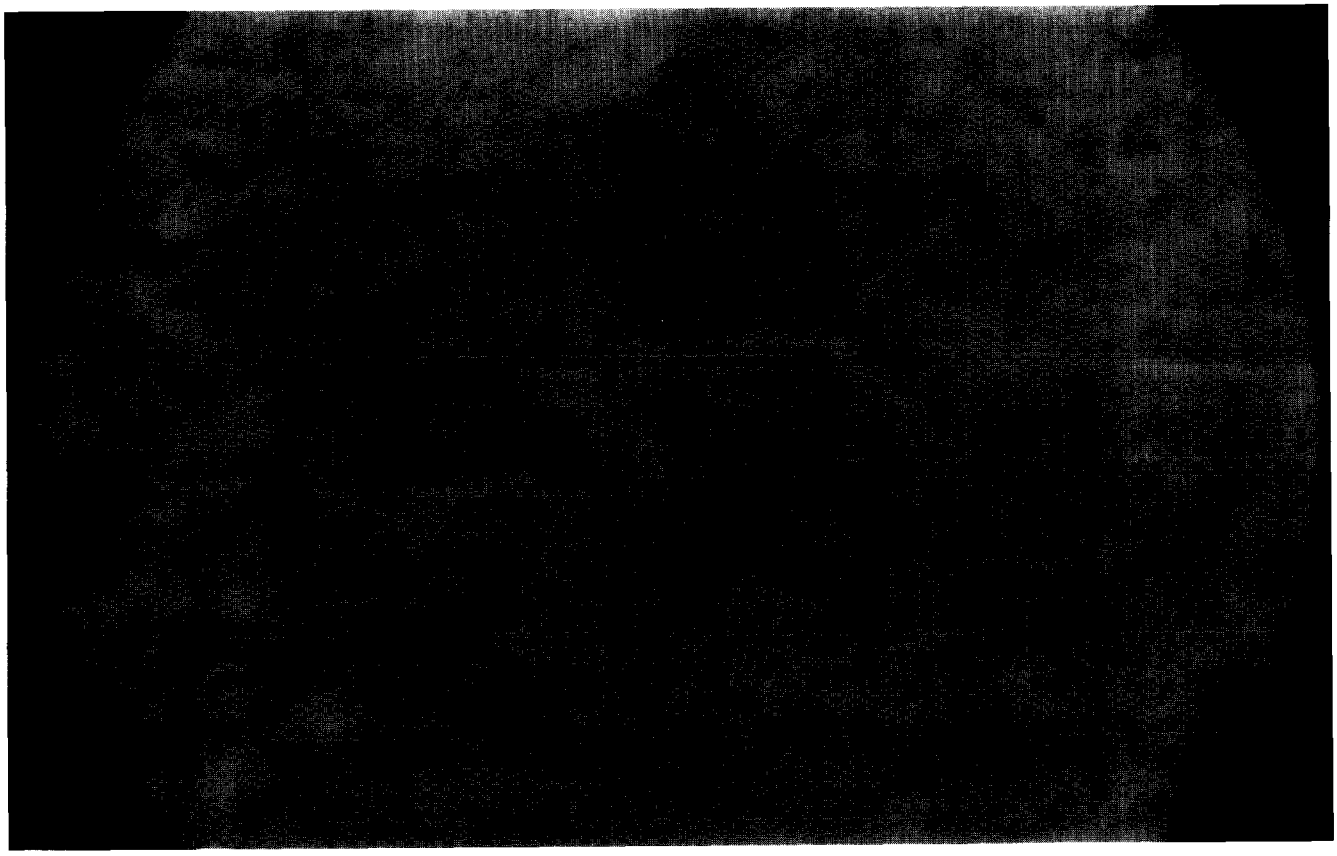


Figure 6 Post-fracture optical micrograph (16 × magnification) of PC surface with original groove depth of 4–5 μm

sufficient difference between the T_gs is required for an effective interface to be formed, but other parameters affecting melt flow behaviour could be manipulated to achieve the same result in cases were the difference in T_g is small. The morphology of the grooves determines the efficiency of the adhesion enhancement, with toughness increasing as groove spacing was decreased and groove depth was increased. The groove orientation with respect to the crack propagation direction also strongly affected interface toughness, with perpendicular being more effective than parallel. This indicates that adhesion could be optimized by imparting a mixture of groove orientations, or perhaps even a curved pattern of grooves depending on the application in question.

Although this method has been shown to work well in a bilayer system, it cannot be applied to improve the properties of a polymer blend or alloy, since the interfaces in such a system are on a microscopic level. Instead, this approach is useful in applications such a coextrustion, or lamination of bi- or multi-layer polymer constructs, where increased adhesion is desired.

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