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Role of Entanglements on the Fracture Toughness of Incompatible Polymer Interfaces

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Introduction. In our previous publication[1] we have reported the effect of poly(styrene-*co*-acrylonitrile) (SAN) oligomers and acrylonitrile (AN) content on the interfacial fracture toughness of bilayers of polycarbonate (PC) and SAN. Commercial SAN copolymers can exhibit a distribution of both molecular weight and AN content, which can lead to the preferential segregation of oligomers and certain AN content species to the interfacial region.[2] We found oligomers to have a detrimental effect on interfacial toughness, reducing it by half with as little as 2% oligomer in SAN. We also found the interface toughness to vary markedly with AN content, reaching a maximum at 25% AN for the series of materials tested. The equilibrium interface width between PC and SAN at this optimum AN content has been measured experimentally using neutron reflectivity (NR) and is reported as 4.5 nm.[3] This is similar to the interface width measured for the well-studied polystyrene (PS)/poly(methyl methacrylate) (PMMA) system. Though both PC/SAN and PS/PMMA are both incompatible polymer pairs and exhibit similar interfacial penetration, their reported interfacial fracture toughness values differ by at least a factor of 2. In this paper, we report possible reasons for this difference based on the mechanistic origins of interfacial toughness. We also report on our own measurements of toughness for the PS/PMMA system and how crazing may be responsible for artificially high PS/PMMA toughness values reported by others.

Experimental Details. Polycarbonate was obtained from General Electric Co. having a weight-average molecular weight of 19 000. SAN with a 25% AN content and a weight-average molecular weight of 160 000 was supplied by Monsanto Co. PS and PMMA were purchased from Aldrich Chemical Co. and had molecular weights of 250 000 and 120 000, respectively. The SAN was dissolved and reprecipitated to remove oligomers. Prior to molding test specimens for fracture toughness measurements, the polymers were dried in vacuum for 2 days at 80 °C.

The polymers were compression molded in a vacuum press into rectangular plates of dimension 5.0 × 1.0 × 0.2 cm using a chrome-plated mold. The samples were joined together in their respective molds at 165 °C for 2 h under slight pressure. After 2 h, the samples were allowed to cool in the mold for 2–3 h until reaching room temperature, suppressing the formation of thermal stresses.

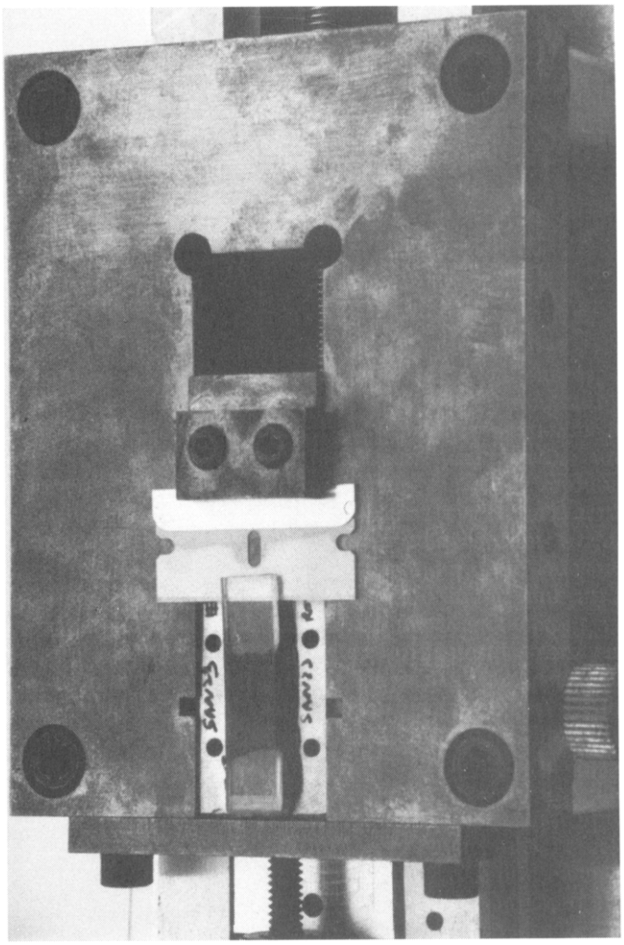

Figure 1. Experimental setup for the fracture toughness measurement.

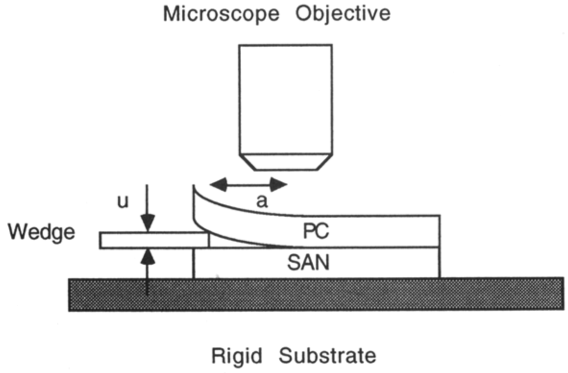

Figure 2. Geometry of the test method and parameters used in the calculation of fracture toughness.

The fracture toughness was measured using an asymmetric double-cantilever beam test geometry. The instrument setup and the schematic of the test method are shown in Figures 1 and 2, respectively. A wedge (a single-edged razor blade) was pushed with a constant velocity of 100 μm/s into the interface using a stepping motor controlled by a computer. The crack length ahead of the wedge was measured using an optical microscope to an accuracy of 0.1 mm. A minimum of 15 values of crack lengths were obtained, and the mean was used to calculate the fracture toughness. The validity of this type of test has been demonstrated by Brown[6] in measuring the interface strength between PS and PMMA. The choice of the asymmetric double-cantilever beam test geometry is necessitated by the difference in elastic moduli and crazing stresses between PC and SAN, as well as between PS and PMMA. A symmetric double-cantilever beam geometry creates a shear mode ($K_{\parallel}$) component in the stress intensity factor near the crack tip. This causes the crack to propagate toward the more compliant material, and, if the more compliant material has a lower crazing stress, small crazes will grow at an angle to the interface from the plane of the crack. Because of the energy dissipated upon craze formation, this will result in an apparent value for

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the bilayer fracture toughness much higher than the actual toughness of the interface.[7] To avoid this effect, the sample is made asymmetrical by varying the relative thickness of the layers.[8] In our case we have induced the asymmetry in the manner demonstrated by Brown through the attachment of one of the layers (SAN and PS) to a rigid substrate, a 3-mm-thick steel plate. A detailed discussion on the mixed mode effects on the fracture toughness of bilayer interfaces can be found elsewhere.[9,10]

Calculation of Fracture Toughness. Using the asymmetric double-cantilever geometry, the interfacial feature toughness (G_c) can be obtained with an assumption that upon fracture, all the elastic energy is dissipated in a very small region ahead of the crack tip. This model assumes that released elastic energy comes only from the bending of the two beams. Under this condition, G_c is given by[8]

$$G_c = \frac{3u^2E_1D_1^3E_2D_2^3}{8a^4[E_1D_1^3 + E_2D_2^3]}\ (\mathrm{J/m^2})$$

where u is the wedge thickness (Figure 2), E_1 and E_2 are Young's moduli of the materials, D_1 and D_2 are the thicknesses of the two layers, and a is the crack length. This approximation is valid only when the crack length is very large compared to the sample thickness, which is the case for a weak interface. When one layer is attached to a rigid substrate, Kanninen[11] has shown that the expression for G_c reduces to:

$$G_c = \frac{3u^2ED^3}{8a^4[1 + 0.64(D/a)]^4}\ (\mathrm{J/m^2})$$

where E and D are Young's modulus and the thickness of the top, unattached layer (PC and PMMA). This model was used by Brown[6] for the PS/PMMA system.

Results and Discussion. PS/PMMA Interfacial Fracture Toughness. Extensive studies have been reported on the adhesion between PS and PMMA.[6,7,12,13] Cho et al.[7] reported a very high value of 200 J/m^2. Brown[6] has demonstrated that this unusually high toughness for an incompatible pair is due to crazes developed in the PS side and attributed this to the effect of the loading mode on crack propagation. As explained above, the loading mode can be varied by changing the test geometry. When PS was attached to a rigid substrate, Brown found a G_c value of only 5–10 J/m^2. When the PMMA layer was attached, the value increased to 400 J/m^2. Brown also used a free-standing symmetric double-cantilever beam geometry, for which G_c was 60–90 J/m^2. In the two high-toughness cases, crazes were observed in the PS layer. No crazes were observed in either layer in the case where PS was attached to the rigid substrate. Thus, the value of 5–10 J/m^2 is representative of the true interface toughness. In our experiments, we have measured a G_c value of 4–10 J/m^2 for PS/PMMA with PS attached to a rigid substrate. Foster et al.[13] have recently reported G_c for PS/PMMA using the symmetric double-cantilever beam test geometry, obtaining a value of 40–60 J/m^2. This value, like Brown's for the same geometry, is probably misleadingly high due to crazes developed in the PS during crack propagation.

PC/SAN Interfacial Fracture Toughness. As reported in our previous paper, the interfacial fracture toughness between PC and SAN depends upon oligomer content and copolymer composition, and Figure 3 illustrates these effects. The maximum in adhesion at 25% AN is qualitatively similar to results reported by Keitz et al.,[14] using lap-shear adhesion methods. Callagham et al.[15] have calculated the interaction energy and interfacial width for the system and found a minimum and maximum, respectively, for these values at 25 wt % AN. Experimental measurements of the PC/SAN interfacial width by NR have been carried out by Mansfield[3] at the 25% AN composition and in the absence of oligomers. The value reported, 4.5 nm, is comparable to that reported for PS/PMMA using similar NR techniques, 5 nm.[4,5] Comparing the interfacial toughness of these two bilayer systems, the PC/SAN interface is significantly stronger, 17–20 J/m^2, than the PS/PMMA interface, 4–10 J/m^2.

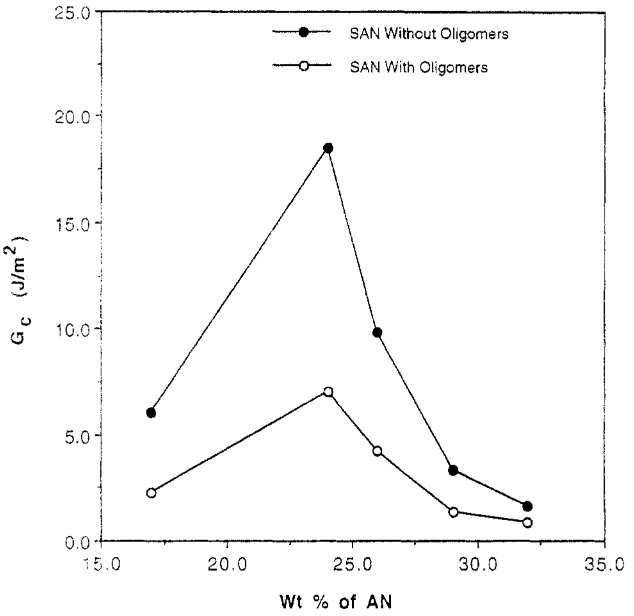

Figure 3. Fracture toughness, G_c, of the PC/SAN interface as a function of AN composition in SAN.

A possible explanation for this remarkable difference may be understood in terms of entanglement concepts. The adhesive failure may occur by two mechanisms: (1) pull out of chains from the bonded matrix or (2) breakage of chains. In either case, the failure energy will be proportional to the number of chains cross the interface. To develop appreciable interface strength, a chain from one of the polymer pairs must cross the interface and be entangled with chains of the second member, represented by probability P_I. Thus, the number of such chains will be proportional to the number of such entanglements. This depends upon the product of the entanglement density in the interfacial region with the volume of this region, proportional to its thickness. (We assume a layer of overlap of constant composition with a constant density of entanglements between the species. This is, of course, an oversimplification.) A chain emerging from such an entanglement may go back into its host polymer or else cross the interface and entangle with chains of the second polymer. For an isotropic polymer, the fraction of chains so entangling will be a constant. If the chain does entangle in this manner, separation of the two polymers may occur by its being pulled out of these entanglements or by breaking the chain (whichever requires lower energy) in the absence of crazes. In recent work,[8,16–18] a model was proposed and verified for blends reinforced with diblock copolymers predicting that the interface toughness varies with the square of the product of chain density of the copolymer and the force to break or pull out the chain. Molecular weight effects were also modeled, in that a chain length sufficient for entanglement to occur was required. In the case of PC/SAN and PS/PMMA interfaces, it is reasonable to assume that the force to break a chain is comparable in both systems, due to the similar polymer backbones. Pull-out forces for the two bilayers might differ, but our previous work[1] showed evidence for chain scission in PC/SAN, so that this process must be a contributor to the failure. The fraction of the chains that break (as opposed to pullout) depends upon temperature, rate of strain, and molecular weight.

It follows that

$$W_A = \rho_E \delta_I P_I (P_B W_B + P_P W_P)$$

where W_A is the adhesive failure energy and ρ_E is the density of entanglements between the two species, given by

$$\rho_E = \rho / M_E$$

where ρ is the (gravimetric) density of the polymer and M_E is the average molecular weight between entanglements of the two species. M_E is an "average" of the molecular weights between entanglements of the individual homopolymer species. δ_I is the thickness of the interfacial layer, P_B and P_P are the probabilities that a chain will break or pull out, respectively, and W_B and W_P are the energies for these processes.

For a given pair of polymers with specified molecular weights, temperatures, and rates of strain, the term $\delta_I P_I (P_B W_B + P_P W_P)$ will be constant, so W_A will depend on M_E. Thus, the difference in interface toughness can be explained by a difference in the entanglement density. Aharoni[19] has reported the spatial distance between entanglements of various polymers based on viscosity measurements above their entanglement molecular weights. For PC and PMMA, the distances given are 1.9 and 3.9 nm, respectively. This implies that PC can entangle effectively at shorter distances than PMMA. Within a 5-nm interface, then, the PC/SAN bilayer will likely form more entanglements than the PS/PMMA bilayer, resulting in higher interfacial toughness. Creton et al.,[20] in their study of adhesion between homopolymers reinforced with diblock copolymers, reported that in order to have good stress transfer at the interface there must be at least one average entanglement per chain between the copolymer and the respective homopolymer. Our results qualitatively agree with this, suggesting that interspecies penetration sufficient to allow effective entanglement is necessary to develop strength at the interface between incompatible polymers. Choosing species with smaller entanglement distances may thus be a route to optimizing adhesion and improving the mechanical properties of polymer blends.

The energy dissipation process at the interface depends upon the molecular weights of the materials, temperature, and strain rate in addition to the entanglement density at the interface since P_B and P_P depend upon these variables. In low molecular weight systems the energy is dissipated by the chain pull-out mechanism and P_P is high since the monomer friction coefficient depends upon the molecular weight of the material[21] and was demonstrated by Creton et al.[8] Also, with low molecular weights, the number of entanglements that a given chain will engage in following the first one will be low, so the net force required to pull the chain out will be low. Creton et al. also showed that, as the molecular weight of the blocks was increased above the entanglement molecular weight, an increase in adhesion was observed where the energy dissipation was from chain scission. This clearly indicates the effect of molecular weight on adhesion between immiscible blends reinforced with block copolymers. Similarly, the friction coefficient decreases with increasing temperature, resulting in a higher P_P. The force for pullout is proportional to the strain rate, so P_P decreases with increasing rate.

The effect of oligomers on interface toughness may also be considered in terms of the model described above. Oligomers are likely to segregate to the interface due to entropic effects. A high concentration of oligomers at the interface may dilute the polymer sufficiently to reduce the number of entanglements, thereby reducing the interface toughness. Certainly, the oligomers will plasticize the polymer, reducing the force required for chain pullout. If the pull-out force is reduced enough, interface fracture will occur by this mechanism rather than by chain scission and further reduce the interface toughness. In either case, there are advantages implied for polymer blend mechanical properties to the reduction of low molecular species content in the homopolymers.

In a typical weak interface (as in incompatible polymer bilayers) it is assumed that the elastic energy released upon fracture is dissipated in a region relatively small compared to the sample dimensions and that most of this energy is absorbed by the plastic deformation taking place ahead of the crack tip. For the test method used here, the only contribution for the released elastic energy comes from the bending of the two beams, and no energy is stored ahead of the crack tip. However, plastic energy dissipation can be estimated if microcrazes exist ahead of the crack tip, as demonstrated by Washiyama et al.[22] Although the difference in adhesion between PC/SAN and PS/PMMA may be due to differences in entanglement distances, there may also be very small contributions from microcrazes ahead of the crack tip in PC/SAN. Work is in progress to determine whether this is the case.

Summary. Brown's results showing that loading geometry can greatly affect the apparent interfacial fracture toughness of bilayers by inducing craze formation in the layer with lower crazing stress have been confirmed. The difference in interface toughness between PC/SAN and PS/PMMA bilayers having similar interfacial widths has been explained in terms of the distance required for effective interpolymer entanglement. The entanglement distance of PC (1.9 nm) is well within the interfacial thickness of 4.5 nm, whereas the entanglement distance of PMMA of 3.9 nm is not. The effect of oligomeric species on toughness has also been accounted for by entanglement concepts. The extension of this analysis to the development of incompatible blends with improved mechanical properties is an attractive area for future study, with implications for the use of commingled polymers obtained from waste streams.

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References and Notes

(1) Janarthanan, V.; Stein, R. S.; Garrett, P. D. *J. Polym. Sci., Polym. Phys. Ed.* **1993**, *31*, 1995.
(2) Mansfield, T.; Stein, R. S.; Composto, R. J.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A. *Physica B* **1991**, *173*, 207.
(3) Mansfield, T. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1993.
(4) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677.
(5) Russell, T. P.; Anastasiadis, S. H.; Menelle, A.; Felcher, G. P.; Satija, S. K. *Macromolecules* **1991**, *24*, 1575.
(6) Brown, H. R. *J. Mater. Sci.* **1990**, *25*, 2791.
(7) Cho, K.; Brown, H. R.; Miller, D. C. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, 28, 1699.
(8) Creton, C.; Kramer, E. J.; Hui, C.-Y.; Brown, H. R. *Macromolecules* **1992**, *25*, 3075.
(9) Charalambides, P. G.; Cao, H. C.; Lund, J.; Evans, A. G. *Mech. Mater.* **1990**, *8*, 269.
(10) Xu, D.-B.; Hui, C.-Y.; Kramer, E. J.; Creton, C. *Mech. Mater.* **1991**, *11*, 257.

(11) Kanninen, M. F. *Int. J. Fract.* **1973**, *9*, 83.

(12) Cho, K.; Gent, A. N. *J. Adhes.* **1988**, *25*, 109.

(13) Foster, K. L.; Wool, R. P. *Macromolecules* **1991**, *24*, 1397.

(14) Keitz, J. D.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1984**, *29*, 3131.

(15) Callagham, T. A.; Takakuwa, K.; Paul, D. R.; Padwa, A. R. *Polymer* **1993**, *34*, 3796.

(16) Brown, H. R. *Macromolecules* **1991**, *24*, 2752.

(17) Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* **1993**, *26*, 4155.

(18) Char, K.; Brown, H. R.; Deline, V. R. *Macromolecules* **1993**, *26*, 4164.

(19) Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722.

(20) Creton, C.; Kramer, E. J.; Hadziioannou, G. *Macromolecules* **1991**, *24*, 1846.

(21) Lee, L.-H. *Fundamentals of Adhesion*; Plenum Press: New York, 1991.

(22) Washiyama, J.; Creton, C.; Kramer, E. J. *Macromolecules* **1992**, *25*, 4751.