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Adhesion of Polymer Interfaces Reinforced with Random and Diblock Copolymers as a Function of Geometry

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ABSTRACT: The reinforcement effect of a thin layer of random copolymer at the interface between immiscible homopolymers was studied using an asymmetric double cantilever beam (ADCB) test. In this geometry, one can change the thickness of the homopolymer substrates and thus control the ratio of shear to tensile stress intensity (the mixity) at the crack tip. Polystyrene (PS) and polymethylmethacrylate (PMMA) were the constituent homopolymers and PS/PMMA random copolymers were used. The energy dissipated in propagating the crack, G_c, (the fracture energy of the interface), depends strongly on the degree of asymmetry in the ADCB sample, as well as the amount and type of copolymer present at the interface. A minimum in G_c occurred at a thickness ratio of the PS to PMMA beams of about 1.2. For both lower and higher thickness ratios, extra energy was dissipated in subsidiary crazes. The crack was found to propagate between the layer of random copolymer and the PS on a path that was quite independent of the sample geometry. Hence, the subsidiary crazes had no effect on the position of final failure. The effectiveness of the random copolymer as a toughening agent was found to increase as its molecular weight increased from 160 000 to 450 000.

Introduction

A thin layer of copolymer applied to the interface between two immiscible polymers can significantly affect the adhesion of the interface. When the copolymer acts as a compatibilizer between the different polymers, the strength and toughness of the interface is increased. Adhesion promotion through the use of diblock copolymers has been studied extensively.[1−6] The mechanism of reinforcement with diblocks can be considered as a form of stitching at the interface where each block of the copolymer chain mixes with the more miscible phase, and so, each copolymer molecule provides a single stitch. Random copolymers can also toughen the interface,[4,7,8] but the mechanism of reinforcement with random copolymers is not as clear. It has been suggested that each copolymer molecule can form loops that penetrate into the homopolymers on both sides[7,9] of the interface, and so, each copolymer molecule forms a number of stitches. There were suggestions that the loops may be longer than expected from the average Flory−Huggins parameter χ between the random copolymer and the homopolymer due to selection of particular random sequences, but it is now clear that such an effect is unlikely.[10] Hence, the mechanism of reinforcement is unclear in situations where χ is large and the interfaces between the copolymer and the homopolymers are expected to be narrow. However, in this paper, we present work using polystyrene (PS) and polymethyl methacrylate (PMMA) homopolymers and a copolymer where the χ is small and the interfaces are known to be broad.[8,11] Hence, the toughening can be understood qualitatively from the fact that the interfaces are expected to be wide with respect to the distance between entanglements.[3] The copolymer composition was chosen at 70% PS to give maximum interface strength and equal interface widths between the copolymer and both of the homopolymers. The fact that the optimum occurs at 70% PS rather than 50% PS is consistent with previous work on the copolymer miscibilities.[8,12−15]

Most recent work examining the mechanical effects of copolymer layers at homopolymer interfaces has employed the asymmetric double cantilever beam (ADCB) test specimen.[16] In this test geometry, a thin copolymer film is applied to a homopolymer sheet, and then, the latter is joined to a second homopolymer sheet. It has been shown that changes in the thickness ratio of the homopolymer sheets in the ADCB specimen strongly affect the measured fracture toughness of the interface.[17,18] Changing the thickness ratio of the two sheets changes the ratio of shear to opening stress intensity at the crack tip. The stress pattern at the crack tip is normally described by the mixity Ψ defined as $\tan^{-1}(K_{II}/K_I)$ where K_I and K_{II} are the opening and shear mode stress intensities at the crack tip, respectively. Previous observations[2,18] on PS and polyvinylpyridine (PVP) interfaces have revealed some important effects of altering the mixity in the ADCB test. A relatively flat-bottomed minimum in the variation of energy to propagate the crack, G_c, with Ψ was seen at a low but finite value of Ψ. For testing, one wishes to find the minimum value of G_c. Thus, the breadth of the minimum facilitates the selection of a good testing geometry. The dependence of G_c on Ψ has proved to be helpful in understanding how energy is dissipated in the system.

A crack that is propagated along the interface at $\Psi = 0°$ between two materials that differ in crazing stress can vacillate between the interface and the material that is less craze-resistant.[19] This effect can result in a combination of cohesive failure of the substrate material and adhesive failure of the reinforced interface, rather than pure adhesive failure. Even if the crack travels

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Table 1. Characteristics of the Random Copolymers[a]

designation	M_w	M_w/M_n
r160	160 000	1.51
r168-d[b]	168 000	1.36
r307	307 000	2.03
r450	450 000	1.38

[a] All of the copolymers contained about 70% styrene units. [b] The d indicates that the styrene component was perdeuterated.

along the interface, additional crazes may form in the less craze-resistant material. In both cases, measurements on the specimen fail to reveal the "correct", that is, minimum, fracture toughness of the interface. By alteration of the ratio of the beam heights in the sample, the propagation of the crack can be controlled to find the mixity that minimizes subsidiary craze formation and suppresses cohesive failure.

The purpose of the current work is to explore the effects of mixity on the failure process and resistance to crack propagation of a random copolymer toughened interface. In addition, the effects of changing the molecular weight of the random copolymer was examined. A comparison is also made to the case where a diblock copolymer is used as a toughening agent.

Experimental Section

Materials. This study was carried out using the immiscible pair of polymers, PS and PMMA. The PS (Styron 685) was obtained from Dow Chemical Company in pellet form; it has a molecular weight $M_w = 330\,000$. The PMMA (Elvacite 2021) was obtained from DuPont in granular form with $M_w = 127\,000$. Both materials deform at room temperature mainly by crazing, but the stress required to form crazes in PMMA is much higher than that in PS, making PMMA the more craze-resistant material.

The asymmetric random copolymer of PS and PMMA contained ~70% styrene segments. The molecular weights of the copolymers are given in Table 1. One copolymer, designated with a "d", contained perdeuterated styrene segments. All of the random copolymers were synthesized using a TEMPO free-radical polymerization techniques that yielded narrow molecular weight distribution copolymers.[20,21] The symmetric diblock copolymer of PS and PMMA had a weight-average molecular weight of 84 000.

Sample Preparation. Sheets of PS and PMMA (51 mm × 57.5 mm) were compression-molded in brass molds between two chrome steel ferrotype plates with mirror finishes at 165 °C, under a low pressure for 5−10 min and then under high pressure for 25−35 min. The samples were then rapidly cooled by being placed on a metal surface at room temperature. Mold thicknesses of 0.8, 1.6, 2.4, and 3.2 mm were used to vary the thickness of the sheets.

Thin copolymer films were spin-coated onto the PMMA sheets from toluene solutions. The nominal thickness was measured by ellipsometry on films spun from the same solution and spin-speed onto silicon wafers. Residual solvent was baked off in a vacuum oven for 1 h at 50−60 °C. The PMMA sheets with copolymer' films were then joined to the PS sheets by compression molding at low pressure. The resulting "polymer sandwiches" were cut with a diamond-tipped saw into strips 6−8 mm wide and 50 mm long. The specimens were tested a minimum of 6 h after being cut to ensure that small stresses incurred during the cutting process did not develop into cracks during testing.

Fracture Tests. A single-edge razor blade of thickness Δ was manually forced into the interface of the sandwich and pushed forward at a low speed until the crack was across the width of the specimen. One end of the sample was placed on a padded surface on top of a hard table, and the blade was pushed in from above. It is possible (but not experimentally verified) that this method gives rise to an additional compressional force along the direction of propagation. This force could help optimize the stress state near the crack tip for the crack to continue along the interface. Some specimens were tested after the PS side had been glued (with a cyanoacrylate adhesive) to a solid aluminum substrate for a comparison with previous results.[3] In either case, the crack was left to propagate for 24 h after insertion of the razor blade before measurement. The crack length, a (distance from the razor edge to the crack tip), was measured with optical microscopy. The critical energy release rate, G_c, or fracture toughness, of the interfacial crack, was obtained from the sample geometry and crack length using a model derived by Kanninen in which the beam is supported by an elastic foundation ahead of the crack tip:[2,22]

$$G_c = \frac{3\Delta^2 E_1 E_2 h_1^{\,3} h_2^{\,3}}{8a^4}\left(\frac{C_1^{\,2} E_2 h_2^{\,3} + C_2^{\,2} E_1 h_1^{\,3}}{(C_1^{\,3} E_2 h_2^{\,3} + C_2^{\,3} E_1 h_1^{\,3})^2}\right)$$

$$C_1 = 1 + 0.64\frac{h_1}{a}$$

$$C_2 = 1 + 0.64\frac{h_2}{a}$$

The subscripts 1 and 2 stand for PS and PMMA, respectively, the E represents Young's modulus, and h is the thickness of the beams. The error in G_c was taken as the standard deviation of the mean for each group of samples in the window mold.

Crazing near the fracture surfaces was examined using optical microscopy by splitting apart the beams at high speed. The high-speed cracking was an effective way of discriminating between features resulting from the original razor test and features resulting from the splitting. The fracture surfaces of the individual beams of either PS or PMMA could be viewed under transmission or reflection mode microscopy. Some beams were also cut in half along the long axis normal to the interface and viewed on their side after being polished with 1 micrometer grit sandpaper. With this method, crazes were seen to be oriented in two distinct directions with respect to the direction of crack propagation, about 45° and 135°.

Ion Scattering Techniques. Ion beam analysis was used with the deuterated copolymer to measure the amount of copolymer on each of the fracture surfaces. This method of analysis is expected to furnish information on how a crack propagates at a strengthened interface and thus how energy is dissipated in the system. For each experiment in which a layer of deuterated PS/PMMA random copolymer was added between PS and PMMA beams to improve adhesion, there were two "fracture surfaces": the PS side and the PMMA side. Each side was examined separately after fracture by splitting the beams completely apart. These samples were prepared for the experiment by being coated with a thin (~50 nm) layer of copper to avoid charging of the thick polymer substrate.

Forward-recoil spectrometry (FRES) and Rutherford backscattering (RBS) were measured simultaneously using a doubly ionized ^{4}He ion beam and a dual-detector apparatus to study the fracture surfaces. The forward scattering detector was responsible for counting ^{1}H and ^{2}H particles, and the backscattering detector was responsible for counting all heavier particles, for example, Cu, C, and O (in the case of PMMA). The copper coating was necessary for charge dissipation on the sample holder, but it was also useful as a standard among all of the probed samples because it exhibits a well-defined front energy edge. This front energy edge thus showed that each measurement was done under the same conditions (e.g., beam/sample geometry, beam energy, and layer thicknesses).

Scattering experiments were carried out for three copolymer layer thicknesses and three sample geometries or mixities. The copolymer layer thicknesses were chosen over a range from 15 to 40 nm because it is within this regime that the critical energy release rate, G_c, significantly increases for increasing ratios, h_{PS}/h_{PMMA}, above 1.2. It has already been shown that G_c increases as more copolymer is applied (for small amounts of copolymer) to the interface. This experiment was intended

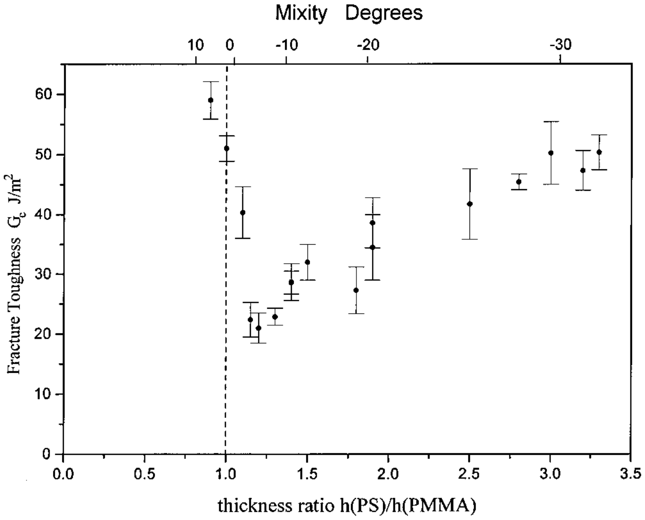

Figure 1. Fracture toughness vs h_{PS}/h_{PMMA} for 50 nm (nominal thickness) of the r160 random copolymer at the PS/PMMA interface. The mixity is shown on the upper x-axis.

to help find the location of final failure as a function of both copolymer layer thickness and crack tip stress pattern.

Results and Discussion

It is most convenient to consider the effects of sample geometry in terms of the effects of mixity at the crack tip. We used the analytical relations of Hutchinson and Suo[23] (their eqs 3.8−3.10) to estimate the mixity from the thickness ratios. The ratio of the plain strain moduli was assumed to be 1.1, and the crack was assumed to be long with respect to the sample thicknesses. The relationship can be seen by comparing the upper and lower abscissas axes in Figure 1. An alternative numerical technique to calculate mixity has been published by Xia et al.,[24] and so, mixities obtained using Suo and Hutchinson's relations were compared with some results obtained by Yun Sha (private communication) using an updated version of Xia's technique. The two techniques agreed to within about 1°.

A series of tests were performed on ADCB specimens with a 50 nm layer of random copolymer r-160 at the interface across a broad range of thickness ratios. From the plot of fracture toughness versus thickness ratio $h_{PS}/h_{PMMA} = h_r$ in Figure 1, it can be seen that a very sensitive relationship exists between the measured G_c and the thickness ratio. We shall assume that the "real" toughness of the interface is the mean value of the toughness obtained at the mixity that gives the minimum values of toughness. Clearly, the choice of sample geometry is critical in obtaining the "correct" toughness. In recent work, also on PS and PMMA, Sikka and coworkers have come to the same conclusion.[25]

Figure 1, owing to the dramatic dip in G_c around $h_r = 1.2$, demonstrates that this system is more sensitive to system geometry than those studied before,[18] though the patterns are qualitatively similar. These results can be understood with reference to Figure 2, which shows the principle stress directions in front of the crack for positive and negative mixities. Figure 1 can be considered to show two major sections. First, in the regime $h_r \leq 1.2$, where the mixity is either very small or positive, G_c increases steeply as the thickness of the PMMA beam approaches and then exceeds that of the PS beam. In this case, crazes formed in front of the crack tip extend out from the interface at an angle of about 45° with respect to the direction of crack propagation, as shown in the optical micrograph in Figure 3a. These crazes are 30−40 μm apart and several times this distance in length. The crack propagates partly along the interface and partly away from the interface into the PS along one of these subsidiary crazes. It is argued in the literature[16,18,19] that these crazes and the crack propagation mode are responsible for the large increase in G_c. Since much of the fracture energy is expended in forming these subsidiary crazes, the measured G_c can be much higher than the real toughness of the interface. In this region of mixity, crazes inclined at 45° form independently of whether or how much coupling agent is present at the interface. The fact that these crazes were observed in a system with no copolymer present emphasizes this fact.

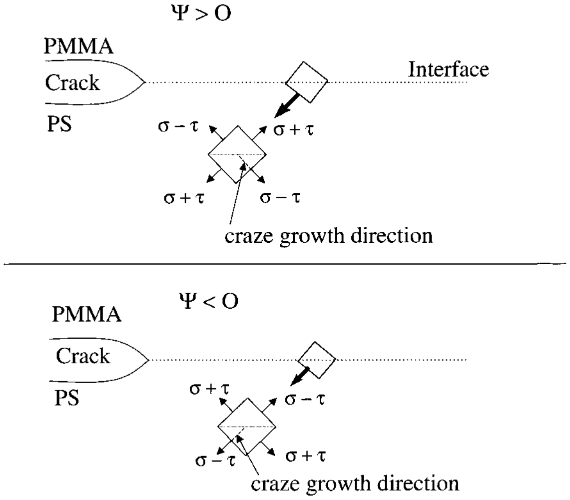

Figure 2. Illustration of the stress state in front of a crack showing the effects of negative and positive mixity and the direction of craze growth into PS.

Second, for $h_r > 1.4$, where the mixity is negative with an absolute value greater than 12°, G_c also increases. However, G_c is not such a strong function of h_r in this regime as when $h_r < 1.2$. The decreased sensitivity to mixity is because there is no tendency for crazes to grow in a forward direction into the easy crazing material, PS. This regime displayed the interesting (though previously observed[18]) phenomenon of crazes inclined at an angle of 135° with respect to crack propagation, as shown in Figure 3b. They appear to be more closely spaced and shorter than the forward crazes. It has been suggested that the growth of the "backward" crazes is responsible for considerable energy dissipation and, hence, the increase in G_c at high values of h_r.[18] Clearly, the backward crazes cause the increase in energy dissipation at high thickness ratios shown in Figure 1 for the case of a 50 nm layer of random copolymer. Backward crazes were not observed with smaller amounts of copolymer, consistent with the fact that G_c did not increase as much with h_r. It would seem likely that that these backward crazes initiate on the interface ahead of the crack tip and grow as the primary interface crack and craze approach. These secondary crazes tend to shield the crack tip zone from the applied stress intensity.

Forward crazes form for $h_r < 1$ independent of the presence of copolymer at the interface. However backward crazes form at $h_r > 1.4$ only when the interface is toughened with some copolymer. This difference can be understood from the different requirement for off-axis

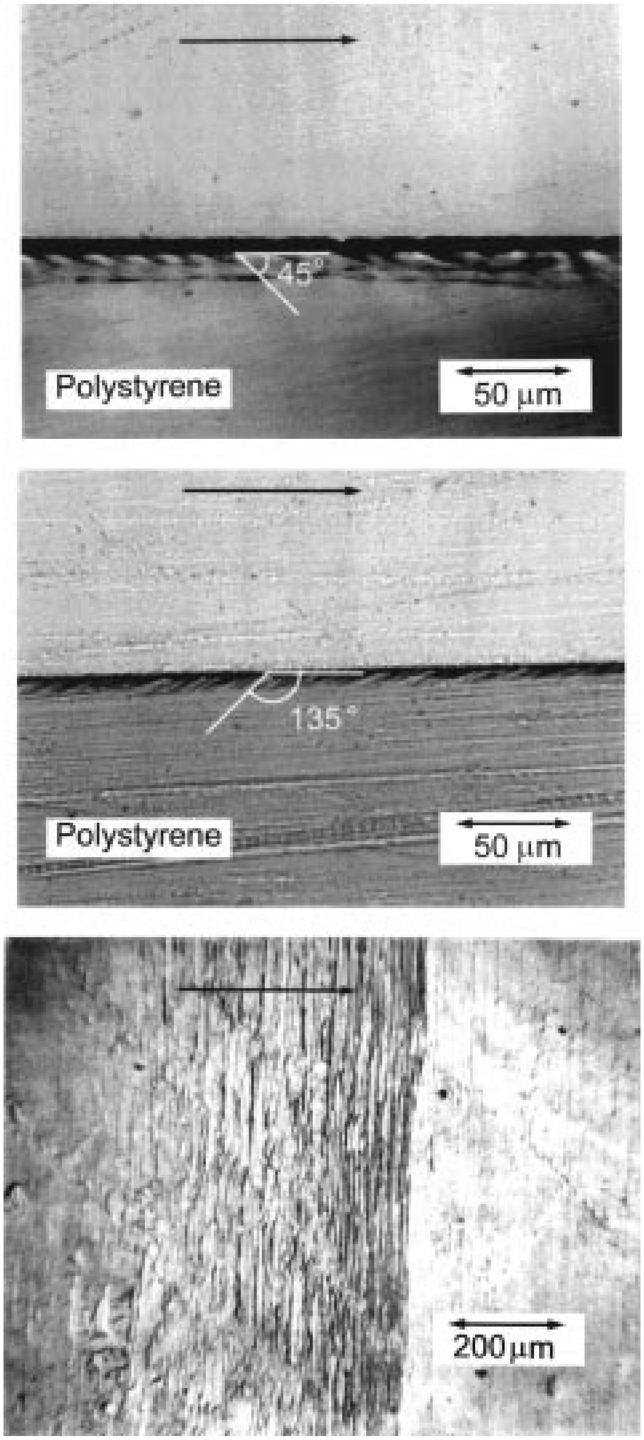

Figure 3. Optical micrographs of interfaces reinforced with 50 nm of random copolymer. The direction of crack propagation is shown by the arrows. (a) Side view of specimen with $h_r = 0.9$. PS side shows forward crazes inclined at angle of about 45° with respect to direction of propagation. (b) Side view of specimen with $h_r = 3.3$. PS side shows backward crazes inclined at an angle of 135° with respect to direction of propagation. Photos a and b were under the same magnification. Note the dimensions of the crazes in the two cases. (c) Top view of PS surface showing backward crazes ($h_r = 2$). There is an approximate correspondence with the crazes in b and the bands in c.

craze formation in the two different geometries. Kramer's[2,5] criterion for primary craze formation at an interface when there is a glassy diblock copolymer present is that there should be a high enough areal density of molecules crossing the interface to sustain the crazing stress, σ_c, without chain breakage or pullout. Hence, the criterion can be written as $\Sigma f_b \geq \sigma_c$ where Σ is the number of chains per unit interface area and f_b is the force to break or pull out a chain. This criterion is a necessary condition for stabilizing craze fibrils at the interface but does not consider if the initial meniscus instability process to form the fibrils can occur.[26] A primary stable interface craze will not form at zero mixity at a bare PS/PMMA interface because this criterion is not satisfied. However, a small crack tip yield zone probably exists within the mixed zone of the bare interface with some initial meniscus instability within this zone. When the crack tip stress pattern has a maximum principle stress that is not normal to the interface but is normal to a plane that goes into the PS in the forward direction, as will occur with a positive mixity ($h_r < 1.1$), then the crack tip yield zone and meniscus instability plane will grow into the PS where craze fibrils can stabilize, and so, a craze can form.

The situation for a negative mixity ($h_r > 1.2$) is different. The yield stress and craze stress for PMMA are larger than those for PS so, with a bare interface, a crack tip craze cannot form and easily grow into the PMMA. Of course, it cannot grow backwards into the PS. When the interface is toughened by the presence of sufficient copolymer that Kramer's criterion is satisfied, a primary crack tip craze can form on the interface plane but with fibrils growing into the PS. This primary craze will inevitably stay at the interface. Crazes can support no shear stress so, when the mixity is significant, the tensile stress across this primary craze can be less than the maximum principle stress (which is at 45° to the craze plane[18]) at a position in front of both the craze tip and its associated yield zone. Hence, if there are flaws or less-coupled areas on the interface, a craze can be initiated at the interface and grow normal to the maximum principle stress, i.e., in a backward direction into the PS. A minimum requirement for this latter process is that craze fibrils can stabilize at the interface so that Kramer's criterion for interface crazing is satisfied. Hence, in the PS/PMMA system, backward crazes can only occur in copolymer-toughened interfaces.

The striking new feature of the geometry dependence of G_c is the sharpness of the minimum seen near $h_r = 1.2$ in Figure 1. A consequence of such a feature is the difficulty it poses in measuring the fracture toughness of an interface. A curve with a broader minimum would imply that test samples need not be so meticulously designed. The nature of the sharp dip observed here, however, indicates that some previous testing[8] has not been done at an optimal geometry, i.e., one that drives the crack along the interface at minimum energy dissipation.

As discussed above, interfaces between immiscible homopolymers, in the absence of any modifying agent, are generally weak. Very little entanglement occurs at the pure interface between the two phases, so-backward crazes are less likely to initiate. This situation is the case for the results shown in Figure 4 for a bare interface where no significant minimum exists. The typical fracture toughness measured from a bare interface was $G_c \approx 3-4$ J/m^2. It would seem likely that G_c might increase slowly with the thickness ratio, as a shear yield zone could grow at high mixities. A test done at an asymmetry of $h_r = 8.5$ gave $G_c \approx 5$ J/m^2, suggestive of this trend but certainly not conclusive.

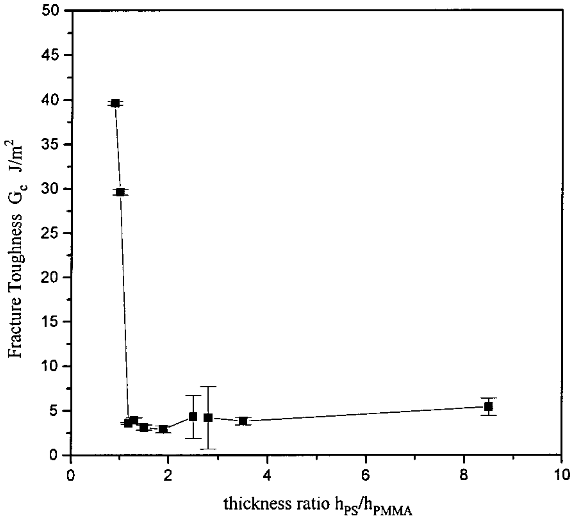

Figure 4. Fracture toughness vs h_{PS}/h_{PMMA} for a bare PS/PMMA interface.

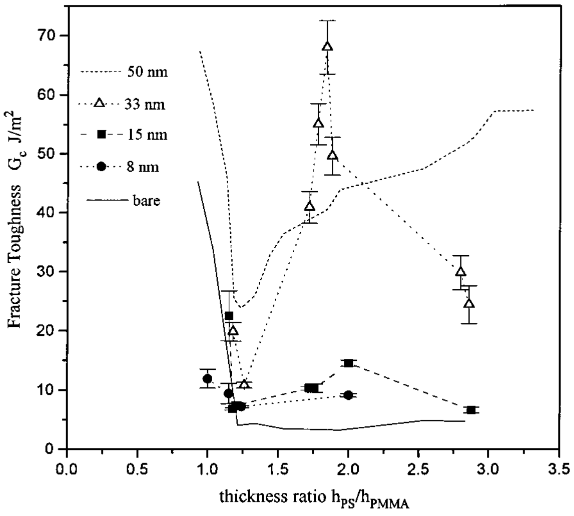

Figure 5. Fracture toughness vs h_{PS}/h_{PMMA} for random copolymer r160 toughened PS/PMMA interface for a range of layer thicknesses.

Figure 5 shows effects of varying the thickness of the random copolymer (r160) layer at the PS/PMMA interface, and Figure 6 gives equivalent results for the diblock copolymer at the same interface. For both systems, the fracture toughness increases with layer thickness (for a given h_r), but the effect is not strong, particularly at the toughness minimum. The random copolymer is only a little more effective than the diblock at equivalent layer thickness. For all the layer thicknesses for $h_r < 1$, crazes incline at an angle of about 45° in the forward direction, dissipating energy and causing a high measured toughness. These curves display a dip near $h_r = 1.2$, indicating a sensitive minimum, but none so clearly as the case in Figure 1. The increase in G_c persisted to high thickness ratios as at a ratio of $h_r = 8.5$ for 32.5 nm, G_c was about 25 J/m^2.

Something unusual is occurring at about $h_r = 1.8$ for 32.5 nm thickness random layers and 50 nm diblock layers (Figures 5 and 6). Both systems display a remarkable peak in toughness at this geometry. As this peak occurs with both diblock and random copolymers, it clearly is not related to any issue of copolymer organization at the interface or to the precise mode of interfacial coupling. At these negative mixities, we know that the fracture energy is dissipated in reverse crazes, and it is expected that such crazes initiate in front of the crack tip, probably at less coupled patches of the interface. It is plausible, if the coupling at the interface becomes "too good", that craze initiation on the interface will decrease. Hence, an optimum layer thickness would be expected. The optimum in mixity is probably related to the precise form of the stress pattern in front of the crack tip. As the mixity becomes more negative at constant applied G, the maximum principle stress on the interface in front of the crack tip increases, and so, crazes may initiate further from the crack tip. Initially, the crazes grow into regions of greater maximum principle stress, but the distance a craze can grow before it experiences a decreasing maximum principle stress and stops growing depends on the mixity. As the mixity increases, the expected craze length decreases; therefore, the toughness may decrease.

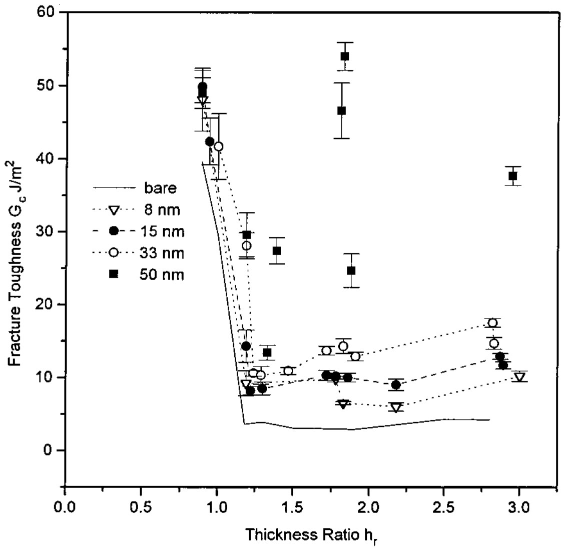

Figure 6. Fracture toughness vs h_{PS}/h_{PMMA} for the diblock copolymer-toughened PS/PMMA interface for a range of layer thicknesses.

In previous work, 11.5 nm of the diblock copolymer was found to give a $G_c \approx 116$ J/m^2 at the PS/PMMA interface,[3] much larger than values presented here. This value was obtained using a highly asymmetry sample where the PS sheet was glued to an aluminum block. Tests were done at high asymmetry in an attempt to reproduce this result, but when $h_r = 8-9$, values for G_c were only 20−40 J/m^2, depending on the quantity of copolymer used. However, when a symmetric sample was glued to an aluminum block, G_c was ~120−140 J/m^2, in agreement with the previous results. Clearly, the symmetric sample glued to the aluminum block is not equivalent to a highly asymmetric sample.

A series of experiments were carried out using the deuterated random copolymer rl68-d to find the locus of the final failure. Figure 7 shows the toughness obtained with this copolymer for three different layer thickness and three asymmetries. The results are fairly similar to those presented above. Figure 8 gives the amount of copolymer found on each of the fracture surfaces for the three total layer thicknesses and three asymmetries. The total amount of copolymer on the two fracture surfaces was significantly less than the amount placed at the interface. This difference did not originate in the process of spinning directly onto PMMA because FRES measurements of the amount of copolymer spin

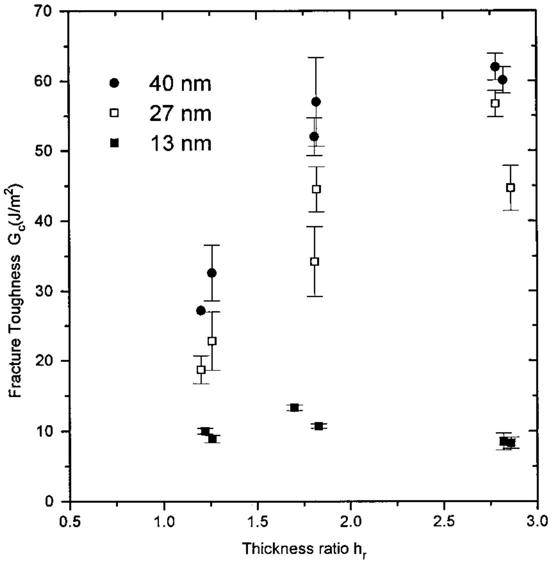

Figure 7. Fracture toughness results obtained using the deuterated copolymer r168-d at the PS/PMMA interface.

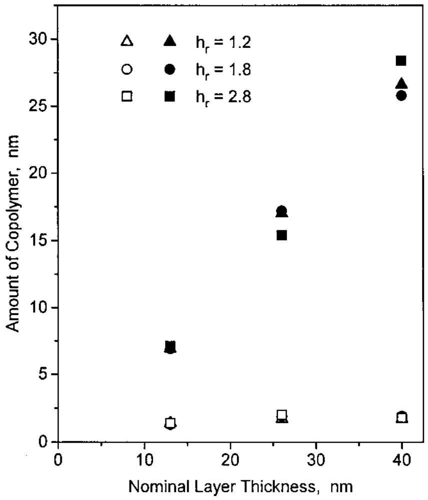

Figure 8. Results of FRES measurements of the amount of copolymer on each fracture surface for three specimen geometries. Data for the PMMA fracture surfaces is given by the filled symbols while that for the PS fractures by the open symbols.

coated onto PMMA were in good agreement with ellipsometric measurements of the amount spin-coated onto a silicon wafer. The difference must be caused by some copolymer dissolving in the homopolymers during the joining process. It is worth noting that good agreement was obtained between the amount of random copolymer placed at the interface and the amount present after welding when a higher molecular weight copolymer was used.[25]

It is immediately evident from Figure 8 that the sample geometry has absolutely no effect on the path of final failure. Failure occurs within one interface (the mixed region) between the copolymer layer and the PS homopolymer. We know that the interfacial thicknesses were about 11 nm[8] on each side and half the material within each of these interfaces would be copolymer so the total amount of copolymer required at the homopolymer interface to obtain two complete, independent interfaces with a separate copolymer phase would be at least 12 nm. When the nominal layer thickness was 13 nm, the measured amount of copolymer at the interface was just 8.4 nm, whereas the 26 and 40 nm nominal thickness layers actually had about 19 and 29 nm of copolymer. Hence, a separate copolymer phase would be expected for the two thicker layers but not for the thinner layer. Increasing the nominal layer thickness from 13 to 26 nm increased the amount of copolymer on the PS side from about 1.4 to about 1.8 nm, but a further increase of the nominal layer thickness to 40 nm had no effect on the amount of copolymer on the PS. These results show that the failure normally ran through the PS to copolymer interface perhaps about one-third of the interface depth in from the PS side.

It is clear from Figure 7 that increasing the nominal layer thickness from 26 to 40 nm increased the joint toughness, although the failure position was unchanged at the PS to copolymer interface. For both thicknesses, a discrete copolymer layer existed at the interface after annealing and so the increase of the copolymer layer thickness had little effect on the two copolymer to homopolymer interfaces. It is interesting to speculate on the mechanism of this toughness increase. It has been suggested that the remarkable effectiveness of the random copolymers in coupling the PS/PVP interface has its origin[27] in the concentration drift that occurs during free radical polymerization. This drift can cause the copolymer chains to have a considerable range of compositions, and so, a layer of random copolymer at an interface can segregate to cause a continuous composition'variation across the interface. Clearly, this effect can become more significant as the layer thickness increases. However, this effect could not be operative with the polymers considered here since with TEMPO-initiated polymerization most of the initiation occurs at the start of polymerization reaction, and so, composition drift could only occur within individual molecules. We have argued that the extra energy that is dissipated as the mixity becomes more negative goes into forming subsidiary crazes. It is possible that the initiation of these crazes occurs within the volume of the copolymer layer so an increase in copolymer layer thickness increases the initiation and, hence, the number of subsidiary crazes, thereby increasing energy dissipation. This argument cannot explain the increase in toughness with layer thickness at an h_r of 1.2 if, as we have assumed so far, the fracture energy is mainly dissipated in a primary craze at this geometry. However, we have no direct evidence for this assumption. It is possible that subsidiary crazes exist for all geometries.

In Figure 9 we show some toughness results obtained using the two higher molecular weight copolymers. It is evident from a comparison of these data with those of Figure 7 that the toughness continues to increase with the copolymer molecular weight even when the molecular weight is considerably higher than the entanglement molecular weight of either copolymer or the molecular weights of the homopolymers. This effect could be caused by the proposed increase of entanglement molecular weight at an interface.[28] Alternatively, it could have its origin in the tendency of the copolymer chain ends to concentrate within the interfaces.[29]

Conclusions

The effect of sample geometry on the fracture toughness of interfaces between PS and PMMA was studied for interfaces toughened by random and a diblock copolymer. The measured fracture toughness was found to depend strongly upon the geometry, showing a

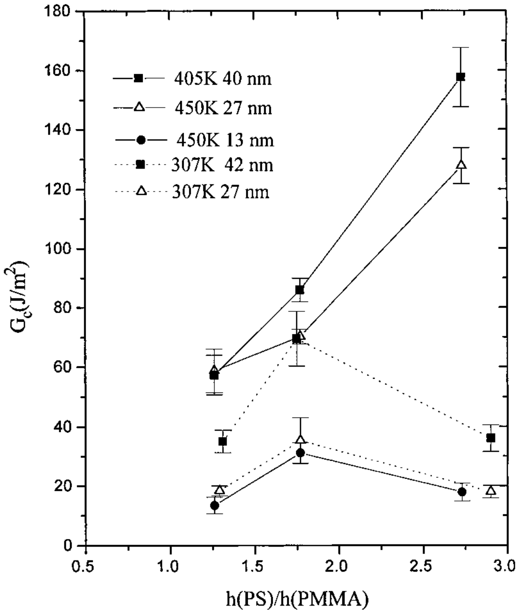

Figure 9. Fracture toughness vs h_{PS}/h_{PMMA} for the PS/PMMA interface toughened with the r307 and r450 random copolymers.

minimum at $h_r = 1.2$, particularly for the 50 nm layer of random copolymer. The extra fracture energy was dissipated in forward crazes when $h_r < 1.2$ and in backward crazes when $h_r > 1.2$. For negative mixities, where the PS layer was thicker than the PMMA layer, the crack was found to propagate between the layer of random copolymer and the PS on a path that was quite independent of the sample geometry. Hence, the subsidiary crazes had no effect on the position of final failure.

The effectiveness of the random copolymer as a toughening agent increased as its molecular weight increased from 160 000 to 450 000, consistent with the suggestion that entanglement molecular weight may increase at an interface.

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