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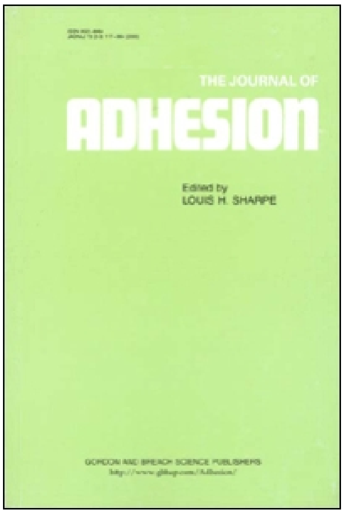

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The Strength of an Adhesive Weak Boundary Layer

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The strength of model adhesive joints composed of different thicknesses of low (10,300 narrow distribution) molecular weight polystyrene sandwiched between high molecular weight poly(methyl methacrylate) has been studied. The joints model a polymer-to-polymer adhesive bond across a low-strength boundary layer. As an appraisal of strength, the fracture toughness was measured by driving a cleavage wedge into the specimens along the polystyrene layer and analyzing the results with Kanninen's equation. The fracture toughness for both crack growth initiation K_{Ic} and arrest K_{Ia} was essentially that for bulk poly(methyl methacrylate) until the polystyrene layer exceeded 1 μm, at which K_{Ic} and K_{Ia} fell by approximately 85%. Examination of the fracture surfaces of specimens with polystyrene layers less than 1 μm thick revealed that the fracture path was predominantly in the poly(methyl methacrylate). Possible reasons for this are discussed.

INTRODUCTION

Weak boundary layers have been a convenient concept for explaining adhesive failure. The concept has arisen from the assumption that two solids in contact, such as adhesive and adherend, cannot fail exactly at the interface between them.[1] Hence, if failure occurs at or near the interface and at relatively small applied stresses, a weak boundary layer is assumed to have been present. In many cases, a weak boundary layer is probably an accurate description of the cause of adhesive failure. Bikerman, in his book, *The Science of Adhesive Joints*,[1] has listed numerous examples of low adhesive strength and has suggested for each how weak boundary layers might have been interposed between adhesive and adherend.

The question is whether any boundary layer is a weak boundary layer. That is, under what circumstances does a layer at the interface between adhesive and adherend, such as a layer of oxide or contamination on the substrate, cause bond strengths to fall and the rupture to follow the interface? Or does a layer of any thickness of a material having less cohesive strength than either the adhesive or adherend constitute a weak boundary layer? The investigation described here was an attempt to give a partial answer to these questions.

The investigation employed boundary layers of low molecular weight (10,000) polystyrene (PS) interposed between plates of poly(methyl methacrylate) (PMMA). Though the boundary layers were actually an adhesive between two adherends of the same material, it may also be viewed as a layer between an adhesive and a polymeric adherend. The boundary layer employed, being a glass at room temperature, has roughly the same modulus as that of PMMA, but has a much lower fracture toughness. This model system might correspond to boundary layers that arise from (a) weathered and depolymerized paint or plastic surfaces on which an adhesive is applied, (b) a surface contamination that inhibits the cross-linking reaction of a structural adhesive, or (c) a surface contamination that is absorbed into the adhesive.

The features of the PMMA-low mol. wt. PS-PMMA system that make it attractive as a model are (a) the incompatibility between the polystyrene and poly(methyl methacrylate) so they remain as separate phases, (b) the ready availability of PMMA as a cast sheet with surface roughness amplitude of 3000 Å or less, (c) similar glass transition temperatures for both polymers so that shrinkage and thermal stresses can be virtually eliminated by annealing, and (d) specimen transparency so that optical means can be used for determining the PS layer thickness.

EXPERIMENTAL

Specimen preparation

The materials employed were ¼-inch thick cast poly(methyl methacrylate) with a molecular weight around 3 million (American Cyanamid Co.'s Acrylite) and polystyrene with a narrow molecular weight distribution around 10,300 (ArRo Laboratories, Inc.). The faces of the PMMA sheets appeared smooth within at least one-half fringe of green light, indicating a roughness amplitude of 3000 Å or less.

Before assembling the specimens, the PMMA was cut into 2¼ inch square plates. To obtain a close fit between pairs of PMMA plates, the cut surfaces were mill-finished and the edges slightly beveled to remove burrs. After removing the protective paper covering, the plates were washed for 2 minutes with ultrasonic agitation in reagent-grade methanol, which was repeated with fresh methanol. The plates were then rinsed with another change of methanol and then with water. The water was removed by draining, with the few remaining drops blown off by a stream of freon gas. The plates were stored in covered dishes; but before use, the surfaces were again blown free of any dust with a stream of freon gas.

To obtain thin layers, a dilute solution of PS in methylene chloride was spread across the surface of one of the pair of PMMA plates to be joined and the second plate immediately brought down on top of it. The plates were pressed together with a weight of 5 lb to squeeze out the excess solution. This typically resulted in a solution layer approximately 0.1 mm thick being retained between the two pieces.

To determine the thickness of the PS layer, a dye of very high extinction, rhodamine B, was also added to the solution. Like the methylene chloride the rhodamine B diffuses into the PMMA (leaving only the PS at the interface); but most of it was found to remain within 0.1 mm of the interface. By measuring the light absorption of the PMMA–PS–PMMA composite at the absorption maximum of the dye (around 560 nm), the amount of dye and thence the PS in the joint could be obtained. The ratio of rhodamine B to polystyrene was adjusted for each solution to yield approximately the same amount of dye per unit area of bonded surface. This amount averaged 2 μg/cm^2, which gave an absorbance of nearly 0.4.

Two weeks were allowed after bonding for the solvent to diffuse away from the boundary layer. Then, the composites were cut into test specimens $\frac{1}{2}$ inch wide. A groove $\frac{1}{16}$ inch wide and $\frac{1}{4}$ inch deep was machined into the top of each for insertion of the cleavage wedge. Because of shrinkage stresses, a crack was very easily initiated along the bond. After initiating the crack, but before testing, the specimens were annealed 1 hour at 140°C to remove the shrinkage stresses.

Mechanical tests

As a measure of strength for the PMMA–PS–PMMA sandwich, the fracture toughness was chosen rather than the tensile strength. The fracture toughness describes the growth of flaws or cracks in a body subjected to mechanical stresses.[2] The tensile strength also depends on the growth of flaws or cracks, but, in addition, is a function of the size of the largest flaw or crack existing in the body,[3] which to a certain extent is a result of the quality of specimen manufacture. Hence, to avoid the emphasis contained in the tensile strength on the skill of specimen assembly, the fracture toughness was measured instead.

The fracture toughness was measured in the cleavage experiment shown in Figure 1, in which the wedge was driven downward into the specimen along the polystyrene layer. This procedure superimposes a small compressive stress

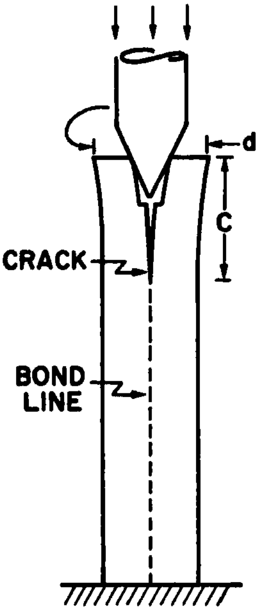

FIGURE 1 The cleavage experiment in which the wedge is driven downward into the specimen. The crack is initiated before the experiment begins. The parameters needed to compute the fracture toughness are *c*, the length of the crack below the application of the stress at the top, and *d*, the distance between the outside edges of the specimen at the top, as the crack begins to grow and then at its arrest.

parallel with the layer that helps to guide crack growth. In a more commonly employed cleavage test, rather than driving a wedge into the specimen, the ends are simply pulled apart. To guide crack growth in this test, it is then generally necessary to machine grooves along the sides of the specimen, particularly in the absence of a layer of a much weaker material. Since it was desired to include in the series of tests, specimens with layers of polystyrene so thin that they would not appear weak to the growing crack, it was felt necessary to guide the crack along the layer. Since any groove machined into the sides of the specimen would still have a root that would be quite gross compared to the thickness of the PS layer, the cleavage method in Figure 1 was used. Once the crack is initiated along the layer, as is done before the specimens are annealed, the superimposed compressive stress can help keep the crack in or near the layer.[4, 5]

Crack growth in the double-cantilever beam specimen shown in Figure 1 is controlled by the length of the crack *c*, from where the stress is applied at the top of the specimen, and the separation between the ends. For a given crack length, the crack remains stationary as the ends are separated until a critical separation is reached. On reaching this separation, the crack will begin growing. But if the separation is held fixed, crack growth will cease, or is arrested, at a new crack length c'. The critical separation of the ends and the original crack length describe crack growth initiation, while this separation and the final crack length describe crack growth arrest. Both can be measured in the same experiment; indeed, each can be measured a number of times with a single specimen because the position of crack arrest for one measurement serves as the position of crack growth initiation for the next.

The fracture toughness for crack growth initiation K_{Ic} and arrest K_{Ia} in the cleavage method employed, in which a wedge is forced into the specimen, is given approximately by the following equation based on the work of Kanninen[5, 6]

$$K_I = (\sqrt{3}/2)Eh^{3/2}\delta c^{-2}[1+0.64(h/c)]^{-2} \tag{1}$$

where E is the elastic modulus (450,000 psi), h is the width or height of the beams, depending on how these words are used (see Figure 2), and 2δ and c are the separation of the ends and crack length at crack growth initiation or arrest. This equation is for the specimen without the machined slot of depth l present in our specimens, which reduces the width of each beam at the top from h to h' (see Figure 2). Because of the slot, the specimen legs will be more highly flexed with a larger separation of the ends for the same applied force. The greater flexure due to the slot can be corrected easily to an adequate approximation by considering the cantilever beam problem, which leads to the following equation for fracture toughness

FIGURE 2 The right half of the specimen.

$$K_I \approx \frac{0.433E(d-2h)h^{3/2}}{c^2[1+0.64(h/c)]^2}\left\{1+\left[\left(\frac{h}{h'}\right)^3-1\right]\left(\frac{l}{c}\right)^3\right\}^{-1} \tag{2}$$

The separation of the ends of the specimen is obtained by measuring the full width of the specimen at the upper end, *d*, which includes the width of the two beams, $2h$.

RESULTS

The fracture toughness for crack growth initiation K_{Ic} and the toughness for crack arrest K_{Ia} obtained from Eq. (2) are shown as a function of the polystyrene layer thickness in Figures 3 and 4, respectively. The fracture toughness for both growth initiation and arrest are seen to remain relatively constant at values corresponding to bulk PMMA for PS thicknesses up to about 1 μm. The mean fracture toughness seems even to increase slightly with thickness in this region, though the variance also increases. This retention of a high fracture toughness up to thicknesses as large as 1 μm is surprising. Above 1 μm, the fracture toughness plummets to values that are only about 15% of those for bulk PMMA.

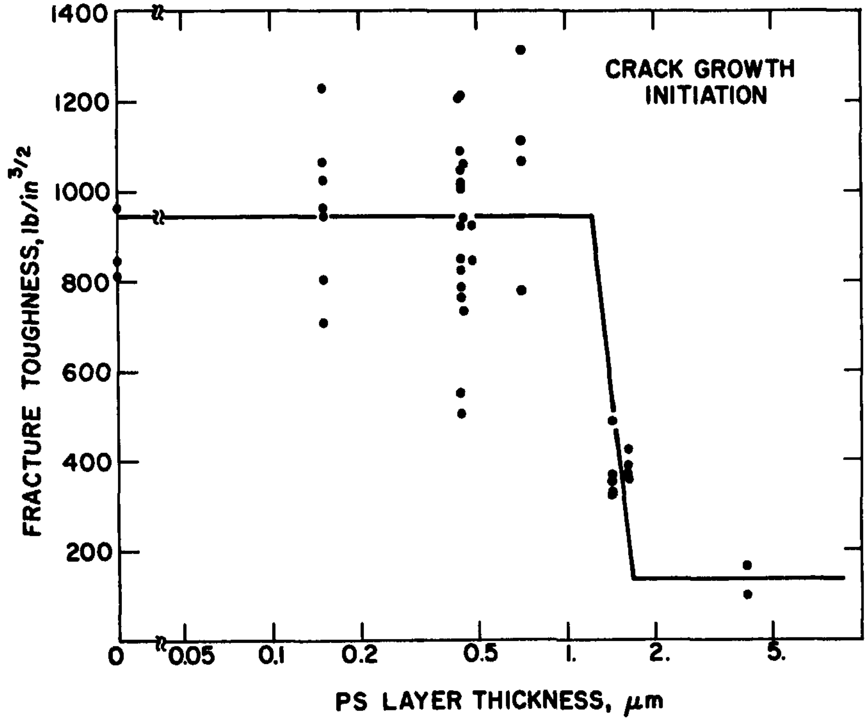

FIGURE 3 Fracture toughness for crack growth initiation (K_{Ic}) versus thickness of the 10,300-molecular-weight polystyrene layer.

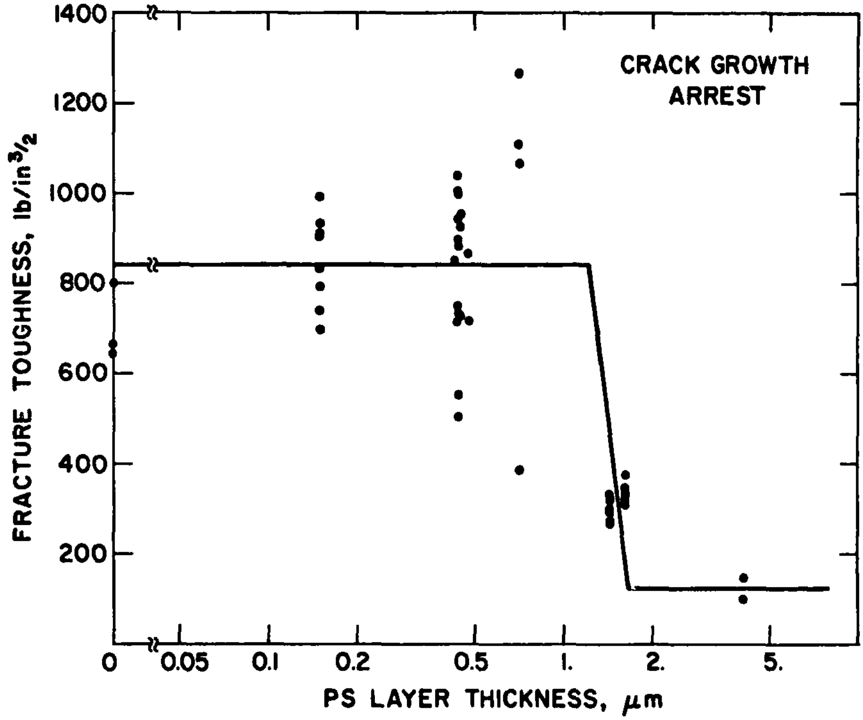

FIGURE 4 Fracture toughness for crack growth arrest (K_{Ia}) versus the polystyrene layer thickness.

DISCUSSION

The unusual aspect of this investigation has been the finding that a boundary layer of low-molecular-weight polystyrene does not manifest its weakness until its thickness exceeds 1 μm. Though macroscopically small, this is still many molecules thick.

To try to learn why joints with PS boundary layers thinner than 1 μm have a fracture toughness close to that of bulk PMMA, the fracture surfaces of these specimens were examined with a light microscope. Though the fracture surfaces were generally disordered, which discourages complete decipherment, Figure 5 shows an example in a smooth area with two characteristics that could be found at higher magnification in the disordered areas. The first characteristic is the field of what look like small circular pits or pocks, extending from near the top in the left half of the photograph down and over toward the right at the bottom. The second is the smooth striated field to the right of the first. The fracture path ran from the smooth, striated region at the top left into the pocked region, and then back into the smooth region in the center and right of the figure.

FIGURE 5 Fracture surface micrograph obtained with reflected green light. The low-molecular-weight polystyrene layer between the poly(methyl methacrylate) plates had a thickness of approximately 0.1 μm. The white bar represents 20 μm.

The pocks are typical of the fracture surfaces of lower molecular weight glassy polymers. They are found in increasingly greater profusion as the molecular weight decreases [7] and seem to arise from ruptures in the craze ahead of the main crack front.[8] The craze that precedes the crack in glassy polymers, or is the vanguard of the crack, is a sponge-like network of the polymer spanning the opening. It can be seen easily with a microscope through the PMMA in the fracturing specimen by illuminating the plane of the craze perpendicularly with reflected light.[8, 9] The ruptures in the craze probably initiate just as the craze begins to thicken and then spread outward through increasingly thicker layers of craze that have been forming while the ruptures were growing. It is the increasing thickness of the craze outward from the center of the pocks that gives rise to the rings in Figure 5, which are really sequences of interference colors. For each pock on the fracture surface shown here, there is opposite, on the other fracture surface, a corresponding pock. The sequence of interference colors outward from the center is the same for all pocks on both surfaces, implying that the craze thickness increases away from the center for all. The increasing profusion of pocks with decreasing molecular weight indicates either an increase in inherent flaws or an increase in the propensity for ruptures to initiate, perhaps from small crazes, as a result of the decreasing chain entanglement.

The smooth, striated area, on the other hand, has the characteristics of a fracture through high-molecular-weight PMMA. Most characteristic are the very strong interference colors that alternate over the surface, with the complementary color appearing opposite on the surface of the companion fracture piece.[10]

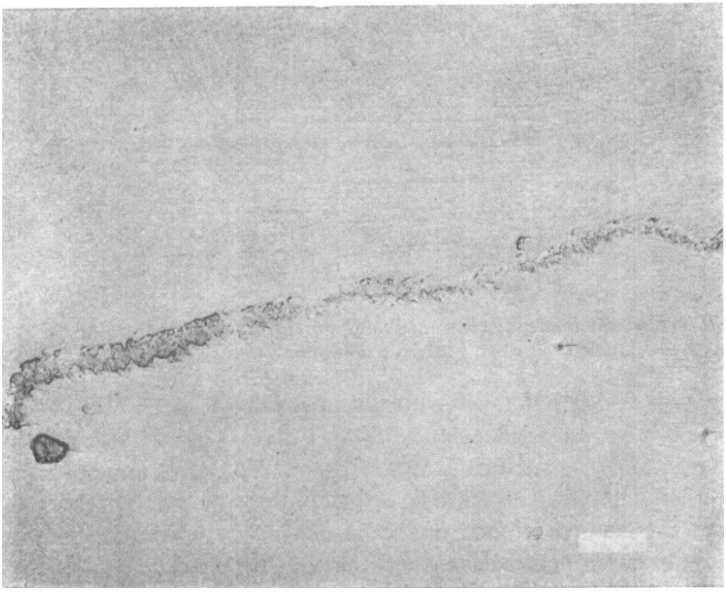

FIGURE 6a Fracture surface micrograph obtained with green reflected light for a specimen having a polystyrene layer approximately 0.1 μm thick. The white bar represents 100 μm.

The fracture path was found to meander between the PS layer and the PMMA bulk over the entire surface including the disordered regions. This probably explains why the fracture toughness remained near that for bulk PMMA when the PS layers were thin: at any point, the crack path was more likely to be in the PMMA than in the PS layer. The scatter of the data in Figures 3 and 4 may be due in part to the crack path meandering in and out of the PS layer. It may also be due to the uncertainty in the measurement of *d*, the separation of the ends at the top of the specimen. Note that the mean of the data remains near that of the fracture toughness of PMMA.

Though the polystyrene layer should represent an easy path for crack growth, and the crack often passed through the layer, there was little tendency for it to channel the crack. Examples of this are given in Figures 6 and 7, showing the fracture path intersecting the PS layer from different directions. (Because Figure 6a is at relatively low magnification to indicate the extensiveness of these fractures, the band running from left to right may not appear as a row of pocks, but higher magnification reveals that it is.) In Figure 6 the path runs roughly parallel with the intersection line, while in Figure 7, the path is shown intersecting the PS layer at two points along its path at roughly right angles to the direction of travel. Note that in neither example is there a tendency for the PS layer to "capture" the crack path. The intersection in Figure 6 continued in the specimen for a distance considerably beyond that shown here before the fracture became very irregular. Though pock bands meandered across the path more elsewhere than shown here, it never widened, as would happen if the crack were to be captured by the layer. The path in Figure 7 never did intersect the PS layer again after it ran out of the photograph to the right, but eventually ran off through the PMMA to the side of the specimen.

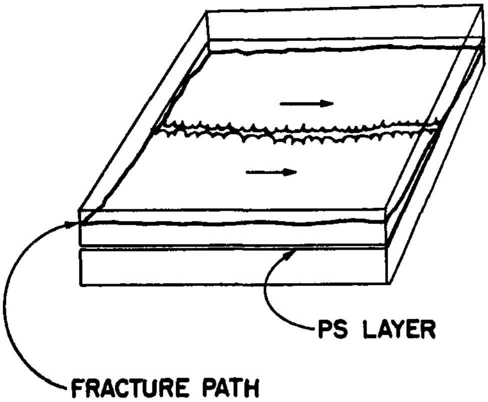

FIGURE 6b A schematic diagram showing the position and direction of the crack relative to the PS layer and the two PMMA plates adjoining.

To map the fracture path for Figures 6b and 7b, use was made of the rhodamine B dye that had diffused equally into the two PMMA pieces. Most of the dye remained within a distance of 100 μm on either side of the polystyrene. Within this distance, then, the position of the fracture path could be obtained simply by assessing the amounts of dye in the two fracture pieces. This assessment was aided by the orange fluorescence of rhodamine B produced by green light, to which the eye seems to be more sensitive than to differences in the green absorption. It was from this type of examination that we first found the pocked regions on the surface to be associated with the PS layer.

To supplement the light micrographs, the specimen shown in Figure 6 was examined with a scanning electron microscope after being given a light gold deposition. From the region shown in Figure 6 was obtained the scanning micrograph in Figure 8. (Unlike that in Figure 6, the crack here had traveled from right to left.) We see that the band is wider than simply the width of the intersection with the PS layer. The fracture path away from the intersection occasionally jumped over to the PS layer. This has caused small pieces, presumably PMMA, to have been plucked out of the specimen above the intersection region and for other pieces, plucked from the opposite fracture member, to be deposited below the intersection. These pieces are more or less round in shape and not greatly elongated in the direction of crack propagation, which reinforces the conclusion that there was no tendency for the PS layer to channel the crack path.

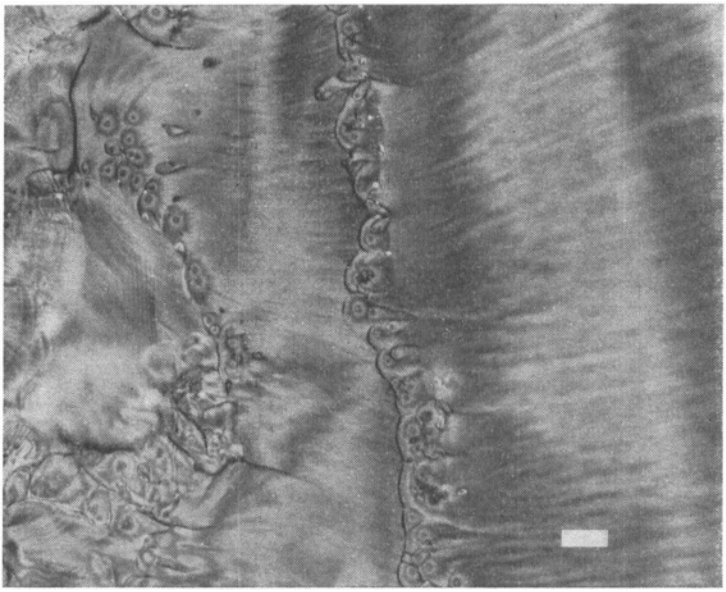

FIGURE 7a Fracture surface micrograph obtained with green reflected light for a specimen having a polystyrene layer approximately 0.1 μm thick. The white bar represents 10 μm.

The region of the intersection is seen at higher magnification in Figure 9. Numerous intersecting steps or ridges are seen, which suggest that many secondary cracks had initiated on a number of different levels ahead of the

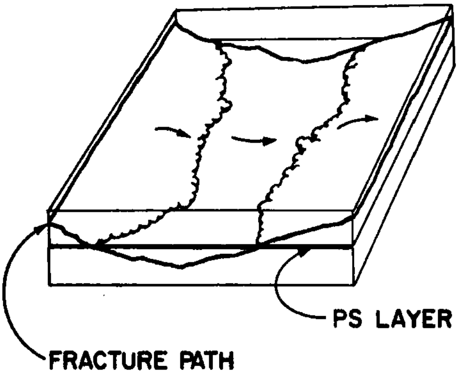

FIGURE 7b A schematic diagram showing the position and direction of the crack relative to the PS layer and the two PMMA plates adjoining.

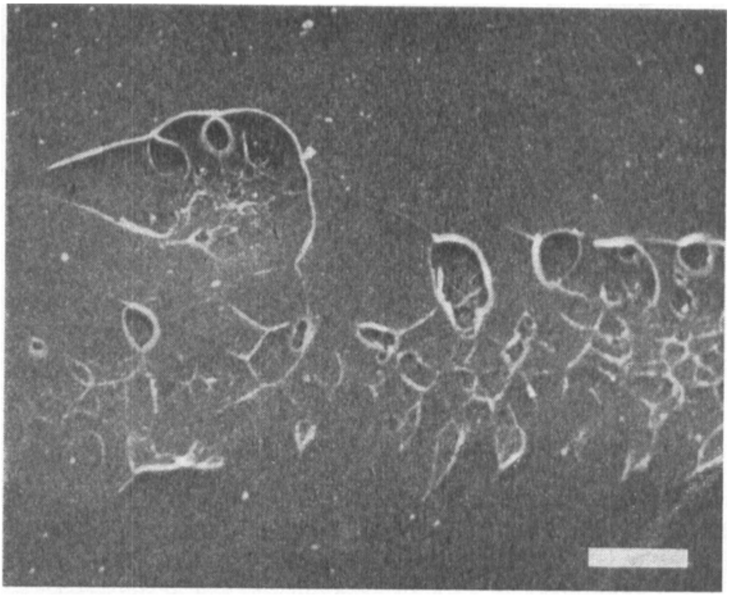

FIGURE 8 The fracture surface in Figure 6 as seen by a scanning electron microscope. Crack growth was from right to left. The white bar represents 10 μm.

main crack front, and the steps are a result of these cracks joining together to become the extension of the main crack. But from a part of the intersection band different from that shown in Figure 6 is observed the morphology shown in Figure 10. Here is seen a strip with almost no surface detail. The strip width, which is surprisingly uniform, may represent the extent to which

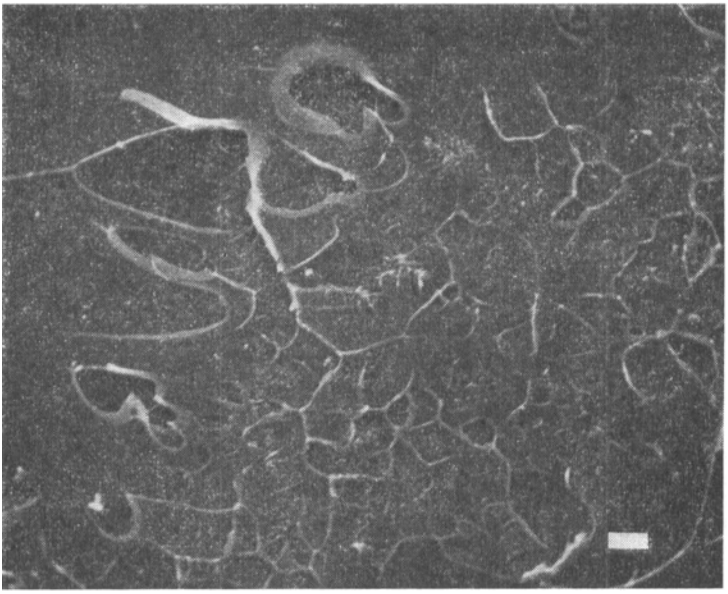

FIGURE 9 The region of the intersection by the crack of the polystyrene layer in the same specimen. The bar represents 2 μm.

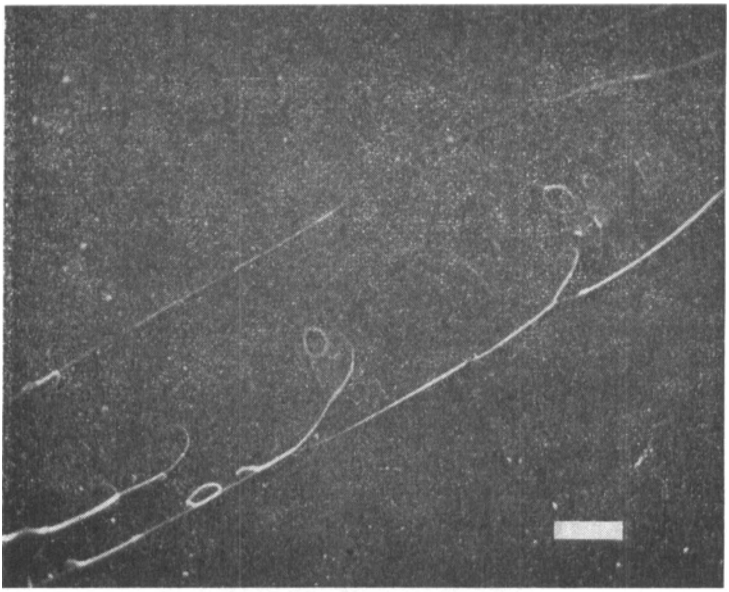

FIGURE 10 Another region of the same specimen showing the intersection of the crack with the polystyrene layer. The bar represents 10 μm.

the crack deviated from the generally inclined plane of the crack to follow the PS layer. Clearly, there is no tendency for the crack to be further channeled by the PS layer.

The apparent lack of effect by the PS layer on the propagating crack might suggest that the layer is as strong as the bulk. Because the polystyrene, being a glass, has approximately the same modulus as the poly(methyl methacrylate), the layer has roughly the same intrinsic strength. But the reduced load-bearing ability of the polymer when crazed, as indicated by the pocks, does represent a true weakness for crack growth and accounts for the low fracture toughness of the joint for thicknesses above 1 μm.

One possible explanation for the high fracture toughness of the joint when the layer is thinner than 1 μm is suggested by the crack's generally wavy path. A craze in the low-molecular-weight polystyrene is expected to have less load-bearing capacity than one in the PMMA, which will affect the stress intensity ahead of the craze where the path direction is being determined. But if the crack is passing in and out of the PS layer, as in Figure 7, by the time the weakness of the PS is manifested, the tip of the craze may have already entered the PMMA again. Thus, a crack following a wavy path would simply not "see" the layer.

Because this explanation depends on the presence of a craze, we would expect that the critical thickness for a weak boundary layer would depend on the molecular weight, falling to perhaps less than 100 Å for a non-polymeric layer.

Another possible explanation for the high toughness with thin polystyrene layers depends on the polystyrene being discontinuous and dispersed as droplets in the PMMA. Though the morphology of the PS layer is unknown, it may in places exist as such. The droplets could arise from the PMMA plates having been bonded with approximately 100 μm thick layers of dilute solutions of polystyrene in methylene chloride. Thin ternary solution layers containing a large amount of PMMA relative to PS might have arisen, then, which would have phase separated into globules of PS solution surrounded by PMMA solution as the solvent diffused away. Since the PS is unable to diffuse through the PMMA, the globules would be confined to a relatively narrow band. Whether a polystyrene dispersion occurs is uncertain, however, because the PMMA of this molecular weight is very slow to dissolve after swelling.

If the PS were dispersed, it would probably enhance the initiation of secondary fractures ahead of the main crack. The secondary fracturing would probably tend to blunt the crack and require that more energy be expended propagating it. Also, it might tend to slow crack propagation. If this were to allow the crack to propagate faster in the PMMA than in the region of the polystyrene, it could explain why there was no tendency for the polystyrene layer to channel the crack when the crack propagated roughly parallel with the intersection of the PS layer, as in Figure 6. The propagation of the crack in the PMMA near the intersection would be retarded by the slower moving segment in the PS. This would cause the crack in the PMMA to move at an angle into the intersection, which would continually narrow the spreading crack front in the PS. This effect is consistent with the markings along the edges of the bands in Figures 9 and 10. If the crack propagation rates were the same in the PS and the PMMA, the markings would extend outward as undistorted parabolas. Instead, the outer edges are reoriented parallel with the general direction of propagation. This is best seen in Figure 10.

Of these two possible mechanisms for explaining the high fracture toughness for polystyrene layers thinner than 1 μm, the first is directed more toward explaining the fracture morphology in Figure 7, and the second toward the fracture morphology in Figure 6. Each also depends on the nature of the layer, the first assumes a continuous layer and second, a discontinuous layer. Hence, both mechanisms may operate to give the high fracture toughness observed, the operation of each depending on the nature of the layer at each location.

CONCLUSION

The problem of when does a boundary layer constitute a *weak* boundary layer has been examined for a layer of polystyrene having a narrow distribution molecular weight of 10,300 sandwiched between high molecular weight poly(methyl methacrylate). The boundary layer was found not to constitute a weakness until its thickness exceeds 1 μm. Why such a large thickness is needed before the layer exhibits a weakness is not known. It may be related, though, to the general waviness of the fracture path and the ability of a craze, even in 10,300 molecular weight PS, to bear enough load to disguise the position of the weakness from the stress field ahead of the craze front. In addition, if and when the polystyrene layer is dispersed as globules in the PMMA, the polystyrene may act to frustrate easy movement of a crack.

Acknowledgement

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