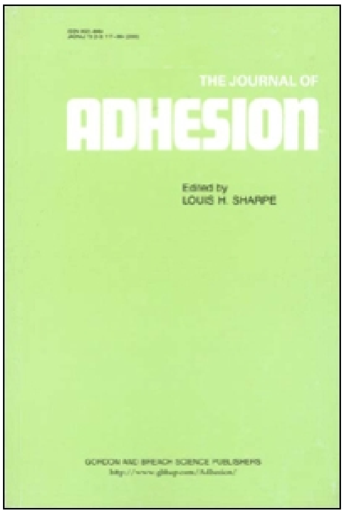

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

On The Strength of Adhesive Bonds Between Rigid, Non-Crystalline Polymers

Richard E. Robertson[a]
[a] Scientific Research Staff, Ford Motor Company, Dearborn, Michigan, U.S.A.

To cite this Article Robertson, Richard E.(1972) 'On The Strength of Adhesive Bonds Between Rigid, Non-Crystalline Polymers', The Journal of Adhesion, 4: 1, 1 — 13

To link to this Article: DOI: 10.1080/00218467208072206

URL: http://dx.doi.org/10.1080/00218467208072206

J. Adhesion, 1972, Vol. 4, pp. 1–13

Printed in Northern Ireland

On The Strength of Adhesive Bonds Between Rigid, Non-Crystalline Polymers

RICHARD E. ROBERTSON

Scientific Research Staff, Ford Motor Company
Dearborn, Michigan 48121, U.S.A.

(*Received September* 27, 1971)

The relatively high strengths exhibited by well-prepared, rigid adhesive bonds partly reflect the crack-growth inhibiting properties of the surrounding bulk. Dispersion forces alone are unable to inhibit crack growth significantly, as is indicated, for example, by the low strengths of low molecular weight glassy polymers. The source of crack-growth inhibition of adhesive bonds was revealed by examining crack fronts with a microscope. Examined were crack fronts along the self-bond between pieces of poly(methyl methacrylate) and along the adhesive bond between pieces of poly(methyl methacrylate) and polystyrene. Associated with each crack front were two sets of interference fringes, indicating the presence of a craze preceding the crack. Crazes form in high molecular weight brittle polymers, and their presence along the adhesive bond ahead of the crack indicates the involvement of the high molecular weight bulk polymer adjacent to the bonding plane. Crazes ahead of cracks are known to inhibit fracture by distributing the load surrounding the cracks and causing any growth to consume large amounts of energy.

INTRODUCTION

The high strengths exhibited by well-prepared adhesive joints must depend on something more than the intrinsic strength of the dispersion forces across the bonding plane, because relying on the same forces for cohesion, low molecular weight polymers do not exhibit strengths nearly as high. For example, Merz, Nielsen, and Buchdahl[1] reported being unable to cast from solution a crackfree film of polystyrene because of low strength when the weight-average molecular weight was below 130,000. Also, Vincent[2] has reported that below a viscosity-measured molecular weight around 30,000 the strength of poly(methyl methacrylate) was so low that he was unable to prepare a crackfree film either by compression molding or solution casting with very slow drying.

These low strengths exhibited by low molecular weight polymers are not due to a lack of intrinsic strength, but rather the inability of the molecular contact forces to provide an adequate mechanism for inhibiting the growth of inherent flaws or cracks. Huntsberger[3] has pointed out that the dispersion forces can provide intrinsic strengths of the order of 10^9 to 10^{10} dyn/cm^2 for atomic separations of 4 to 5 Å. This may represent a lower limit to the intrinsic strength of polymers with even a low molecular weight because some of the atoms are connected by covalent bonds. But the macroscopic strengths will not necessarily be as large as the intrinsic strength. Fracture generally occurs by the nucleation and growth of a crack, and the crack can greatly magnify the applied stress, allowing the intrinsic strength to be exceeded at the crack tip by application of a relatively small stress. Though the stress required to nucleate a crack can approach a value equal to the intrinsic strength, this stress level is rarely realized because plastics always have an abundance of flaws that can develop into cracks. In addition, crazing often produces a weakness that is equivalent to a crack. For example, Berry found that the crazes that form in polystyrene were equivalent to cracks of length 0.04 in. and in poly(methyl methacrylate) of length 0.002 in.[4] Thus, failure usually requires only the growth of "inherent" cracks, and it is the resistance of the polymer to crack-growth that is reflected in the exhibited strength.

Several mechanism can operate to inhibit crack growth in high molecular weight polymers. For ductile polymers inherent cracks tend to be blunted through yielding. For brittle polymers like polystyrene (PS) and poly(methyl methacrylate) (PMMA), the stress concentration at the crack tip tends to be reduced by the formation of a craze ahead of the crack.[5] Crazing is usually associated with a weakening of the plastic, as in producing the crack-equivalents; but in forming ahead of the crack, the craze tends to strengthen the plastic. By allowing the bulk to rarefy and yet retain the ability to bear a load,[5,6] the craze tends to distribute the high stress concentration that would otherwise exist at the crack tip. The inhibitory effect of crazes on crack growth can also be viewed as requiring the expenditure of large amounts of energy.[7] Rather than allowing the crack to run through the polymer expending energy only in the severing of bonds across a single plane, crazing causes a thick region of the polymer to be involved in the fracture process. In high molecular weight PMMA, a layer thicker than 0.5 μm and in PS a layer perhaps as thick as 3μm is involved, dissipating plastic energy and absorbing unrecoverable elastic strain energy.[8] As a result, fracture energies, i.e., the energies required for the crack to grow, are found to be some 1000 times higher than would be expected for the severing of a closely packed collection of covalent bonds across a single plane.[4]

But this tendency to craze ahead of the crack decreases as the degree of molecular entanglement diminishes at lower molecular weights. Kambour[7] found for PMMA, for example, that the thicknes of the craze layers left on the fracture surfaces decreases by perhaps one-half as the viscosity-measured molecular weight of the bulk is reduced from 6×10^6 to 90,000. (The craze thickness is indicated by the color of the reflected light resulting from the interference between the light reflected from the upper and lower surfaces). Kambour further points out that enhancing the fracture energy of the 6×10^6 molecular weight polymer were numerous crazes that formed on planes roughly parallel but slightly displaced from the plane of primary crack growth. At 90,000 molecular weight most of this secondary crazing was absent. For polystyrene the secondary crazing was present when the viscosity-measured molecular weight was 350,000 but was mostly absent when the molecular weight was 130,000. The reduction of crazing with decreasing molecular weight is reflected in the fracture energy: for example, from cleavage tests at room temperature Berry[9] found that the fracture energy of PMMA decreased with decreasing molecular weight and extrapolated to zero at the viscosity-measured value of 25,000; the fracture energy for polystyrene found by Benbow[10] for slow crack propagation also decreased with decreasing molecular weight and seemed to extrapolate to zero near 50,000.

Because in adhesive joints at least the adhesive, if not the adherend, is usually composed of a high molecular weight polymer, it seems possible that the high strength of adhesive joints is due to the participation in the fracture process of the adjacent bulk polymer. That is, the lack of crack-growth inhibition from the molecular contact forces could be compensated by that of the highly entangled adjacent bulk. To test this possibility we have compared light microscope observations of the fracturing process at the adhesive interface with those found by Kambour for bulk fracture.[8] We have examined fracture at the self-adhesive joint between pieces of PMMA in which the mixing of polymer chains across the interface was incomplete and at the adhesive joint between PS and PMMA where only the forces of molecular contact operate.

EXPERIMENTAL

The poly(methyl methacrylate) (PMMA) used had the viscosity-measured molecular weight of 3.1×10^6 and was a commercial material in the form of a cast sheet 4.5 mm thick. The polystyrene (PS) used had a broad molecular weight with the weight average of 453,000 and had been cast as a film 0.20 mm thick. Both polymers were cut into strips 55 mm long and 18 mm wide and then washed with methanol, water and a mild nonionic detergent, and finally rinsed with distilled water and with methanol, and air-dried. To guard against dust, the samples were stored in covered dishes and were exposed to a stream of Freon gas just prior to bonding.

Specimens of PMMA were solvent-bonded to each other with methylene chloride by first applying a thick layer of the solvent onto one of the pieces to be joined. On this was placed the mating strip, squeezing out air and excess solvent. To further decrease the thickness of the solvent layer, the pieces were squeezed together under a pressure of 2.5 kg/cm^2. The PMMA-PS-PMMA specimens were prepared in the same manner with the PS film placed between the two PMMA pieces. The bonds set after about one hour, and the pressure was then removed. Further diffusion of the solvent out of the specimens was allowed for an additional two weeks at room temperature with all specimen surfaces exposed. Though some traces of methylene chloride may have remained after this drying, the polymer at the interface behaved as a typical glassy plastic in subsequent experiments.

The adhesive bonds were fractured by cleavage. A 7 mm-deep saw cut was made in one end of each specimen, removing regions on both sides of the bonding interface. Into this was forced a wedge, which initiated a crack along the adhesive plane with a width equal to the width of the specimen. Saw cuts 2 mm deep were also made along the side edges to constrain the path of the crack, though this precaution proved unnecessary as there was no tendency for the crack to leave the vicinity of the bond. This was true also of the PMMA-PS-PMMA sandwich specimens, where the crack might have jumped back and forth across the PS layer from one interface with the PMMA to the other as it moved through the specimen. After having started near a particular interface, though, the crack always travelled in the vicinity of that interface.

The observations were made with a light microscope using incident illumination with a green filter (5400 Å). The crack front and the craze ahead of it were viewed through the top piece of PMMA.

RESULTS

The PMMA Self-Bond

Figure 1 shows the region of a crack front that had moved along the bonding plane between two pieces of PMMA. The crack is here stationary but had been moving rapidly, so that the fracture surface behind the crack front is relatively smooth. In this photograph the crack is moving toward the left and has not yet penetrated the black area. The main features of the photograph are the two sets of fringes labelled *A* and *B*.

Figure 1 is similar to a photograph obtained by Kambour[8] of the region of

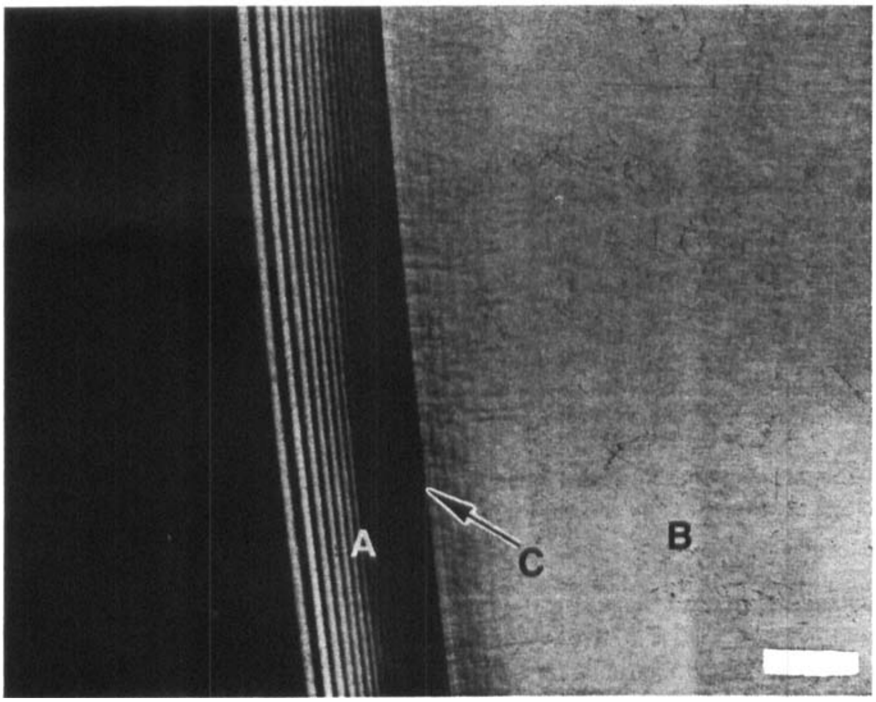

FIGURE 1 The region of the crack front along the bond between two pieces of poly(methyl methacrylate). The region of the craze is denoted by (*A*), the crack by (*B*) and the crack front by (*C*). The marker represents 50 μm.

the crack front in bulk PMMA. According to Kambour the two sets of interference fringes are indicative of a craze preceding the crack front, which would be the dark line separating the two sets labelled *C*. Behind the crack front, in the lighter region of the photograph labelled *B*, the fringes are almost uniformly spaced, with the fringe spacing decreasing only slightly in the direction of crack-growth, which suggests almost a simple V-shaped opening for the crack. (See Fig. 2.) Ahead of the crack front the spacing between fringes increases in the direction of crack motion, suggesting a "hollow-ground" razor shape (Fig. 2). Though the specimen shown in Fig. 1 is PMMA that had been bonded to itself, only a limited amount of polymer mixing can be expected to have occurred during bonding. At a molecular weight of 3.1×10^6 PMMA swells and dissolves relatively slowly even in methylene chloride, a good solvent. For the crack in the bulk, Kambour found the craze width, i.e. the distance from the crack front to the most forward fringe, to be always 25 μm. Also, he found approximately 6 fringes when the stress applied to the crack had been removed. The craze shown here is about 90 μm

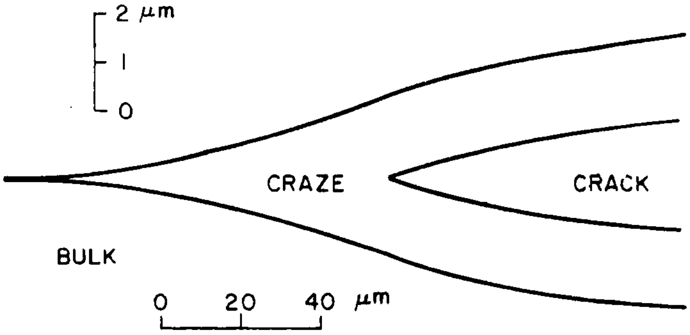

FIGURE 2 The shape of the craze and crack at the crack front as plotted from the fringes in Fig. 1 for the PMMA self-bond. The vertical scale is expanded about 12 times from that of the horizontal scale.

wide and contains 17 fringes. The number of fringes (m) can be converted to craze thickness (d) by the equation

$$d = \lambda(m + \tfrac{1}{2})/2n$$

where λ is the wavelength of the light (5400 Å) and n is the refractive index of the craze material. Being a mixture of polymer and voids the craze is expected to have a variable refractive index, but it must remain between 1.49, the refractive index of PMMA, and 1.00, that for air. The value 1.32 that Kambour[5] measured for a particular unstressed craze is a reasonable value to use, since the calculated thickness can never be in error by more than one-quarter. For Fig. 2 the craze thickness was calculated assuming this value of n; the crack thickness was calculated taking $n = 1.00$ for air and a constant craze thickness. The maximum craze thickness for the PMMA self-bond and Kambour's result for the bulk are given in Table I. We find that the ratio of width to maximum thickness, which is a measure of the sharpness of the craze, is nearly the same for crazes in bulk PMMA and along the self-bond, even though the craze widths and maximum thicknesses differ. The dimensions

TABLE I

Dimensions of craze preceding fracture crack

	PMMA Self-Adhesive Joint	PMMA-PS Adhesive Joint	PMMA Bulk[a]	PS Bulk[a]
Craze width (μm)	90	65 to 165	25	550
Maximum craze thickness (μm)	3.5	0.9 to 1.9	1.3	≤6.0
Width/max thickness	25	~80	20	100

[a] From Kambour.[8]

of the craze in the self-bonded specimen may be larger than those in the bulk because of remaining traces of bonding solvent.

The PMMA-PS Adhesive Bond

Figure 3 shows the region of the crack front of a rapidly moving crack after it had stopped in a PMMA-PS-PMMA sandwich specimen. By measuring the thicknesses of the two pieces after the specimen had been completely cleaved, we found that the crack had run exclusively along the upper interface between the PS and the PMMA. The crack had been moving toward the left in Fig. 3 but had not yet penetrated the black region. Again there are two sets of fringes—the crack front is the "furrow" that runs through what seems to be a speck of dirt. The speck may have influenced the path taken by the crack, but it has not influenced the qualitative features of the crack, the crack front, or the craze. By serving as an identification mark, though, the speck did make it easier for us to return to the same region of the specimen for subsequent examination.

We again take the two sets of fringes as evidence that the crack is preceded by a craze. In the crack region the fringes, which unfortunately are not easily visible here, were about evenly spaced, indicating an almost V-shaped crack opening. In the craze, the fringes increased in spacing in the direction of crack motion; the number of fringes from the craze region varies from 5 to about 9. A further indication that the band of intense fringes is a craze rather than a crack came shortly after this photograph was taken. Starting from beyond the top of the photograph, the region began to rupture and the rupture travelled into the field of the photograph. Figure 4 shows the result several minutes after the photograph in Fig. 3 was taken. The rupture is seen to have even moved ahead of the most forward craze fringe to give what was better seen with transmitted light, a rippled crack that we find associated with slow crack growth and is perhaps due to a stop-start crack-growth pattern.

The craze widths and maximum thicknesses measured for the crack front in Fig. 3 as well as for three other examples in other specimens are given in Table I. For the craze thickness we again used the craze refractive index 1.32. Craze widths and thicknesses may also be compared with Kambour's results for polystyrene. The ratio of width to maximum thickness is similar to that for PS bulk; but evidence is mentioned below suggesting that the craze near the PMMA-PS interface remained in the PMMA.

Figure 5 and 6, taken with incident illumination, show the surfaces of the two pieces after they had been cleaved apart. The surface of the bottom piece (Fig. 5) has the same orientation as that in Figs. 3 and 4; this piece consists of the PS film bonded to the bottom PMMA strip. The upper piece (Fig. 6) has the orientation of the mirror image of that in Figs. 3 to 5, as

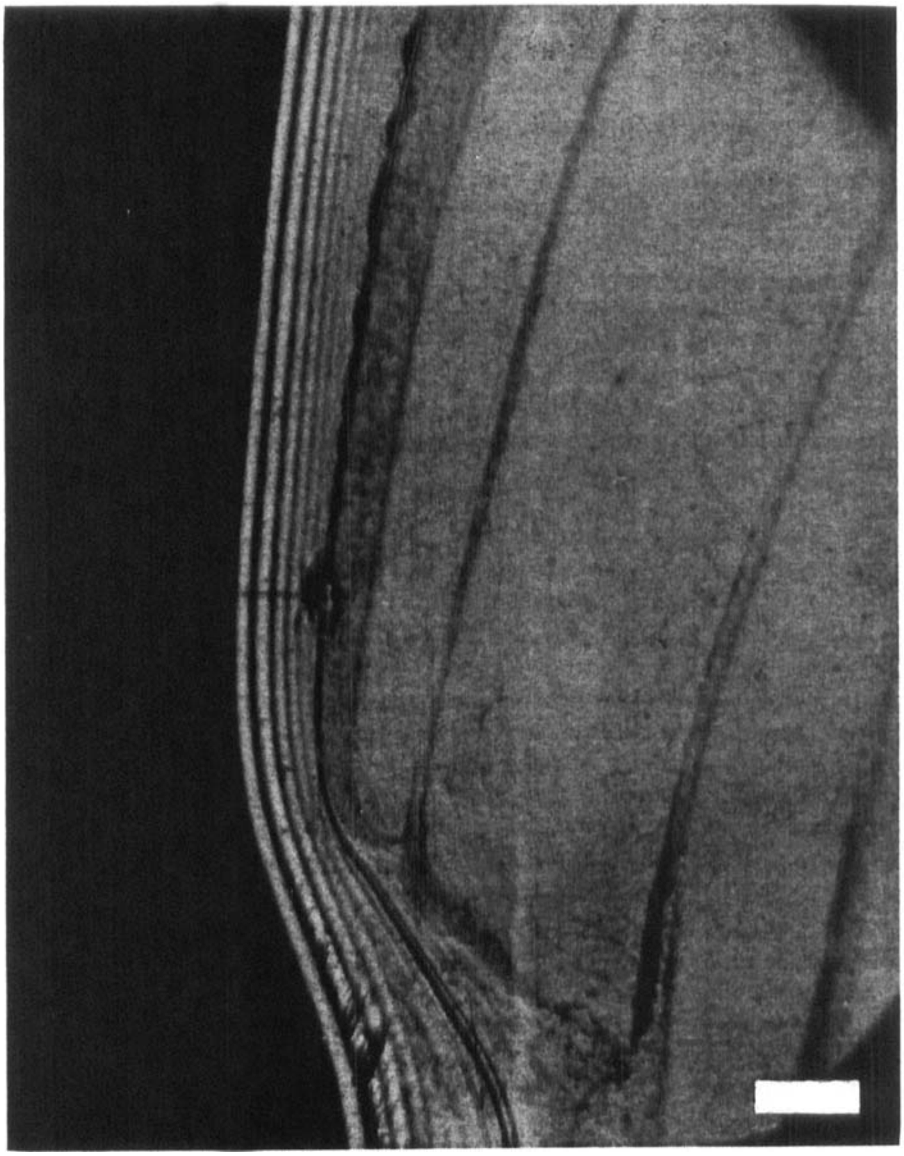

FIGURE 3 Crack front along the bond between polystyrene and poly(methyl methacrylate). (Marker = 100 μm).

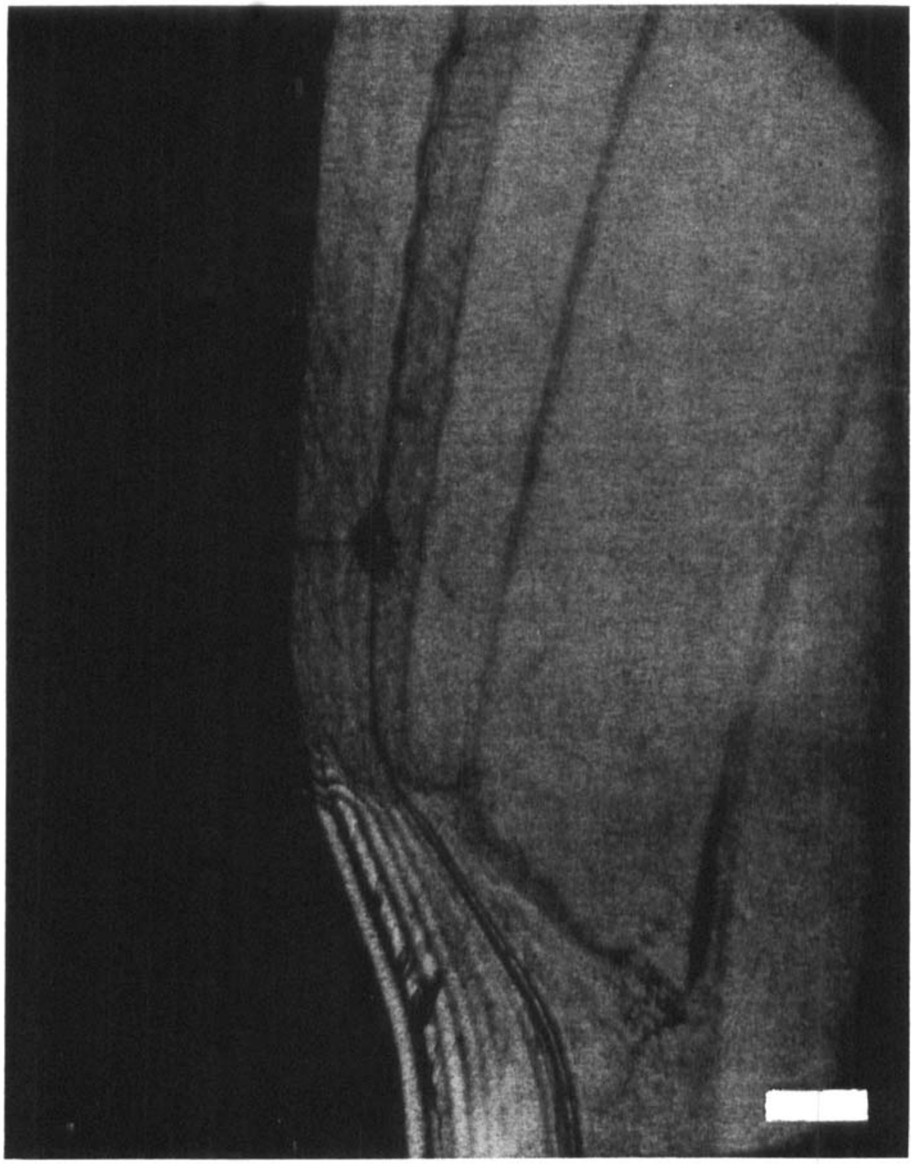

FIGURE 4 The same crack front as in Fig. 2 photographed several minutes later, after part of the craze ruptured.

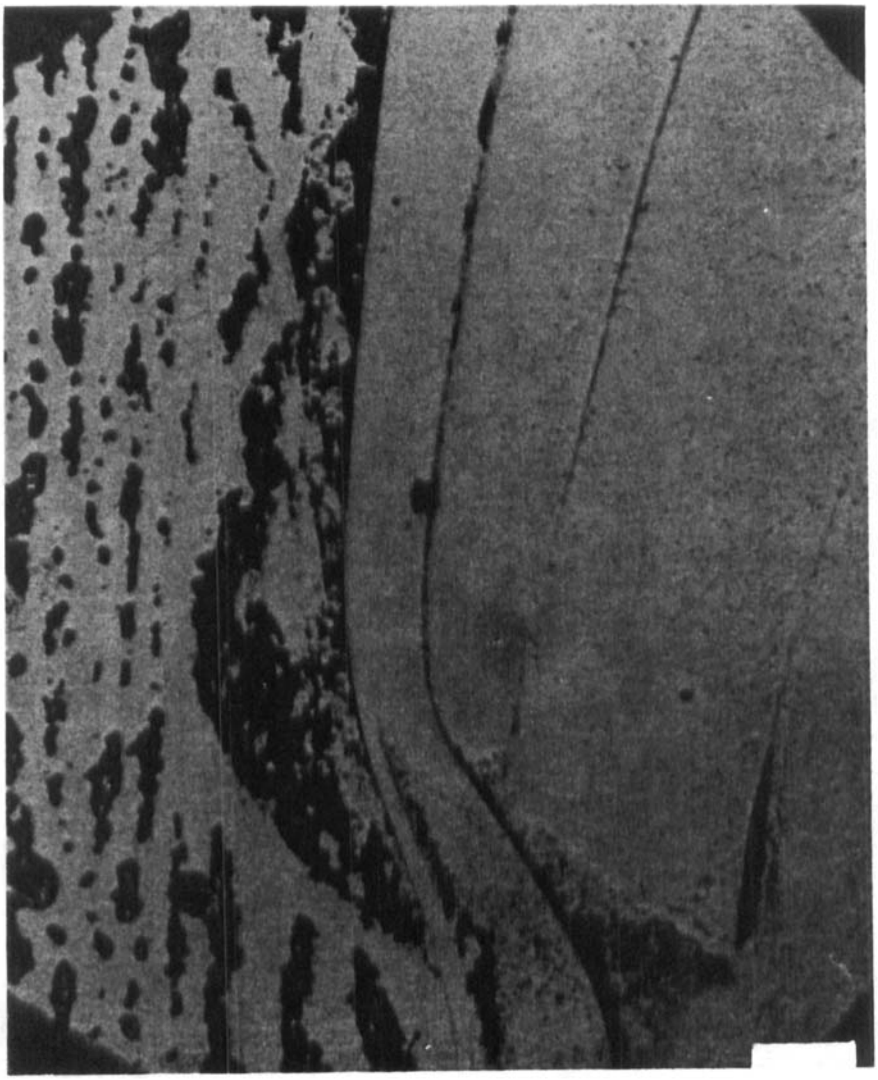

FIGURE 5 The bottom part of the specimen shown in Figs. 2 and 3, consisting of the polystyrene side of the joint. (Marker = 100 μm).

reflected in a horizontal plane; this piece consists of the top PMMA strip only. For both, the crack had moved toward the left, and the regions to the left, which had not yet been severed in Figs. 3 and 4, have the slow-growth, rippled texture.

The reflection of light from the surface of the cleaved pieces shown in Fig. 6 is yet another indication that the crack is accompanied by crazing. Because

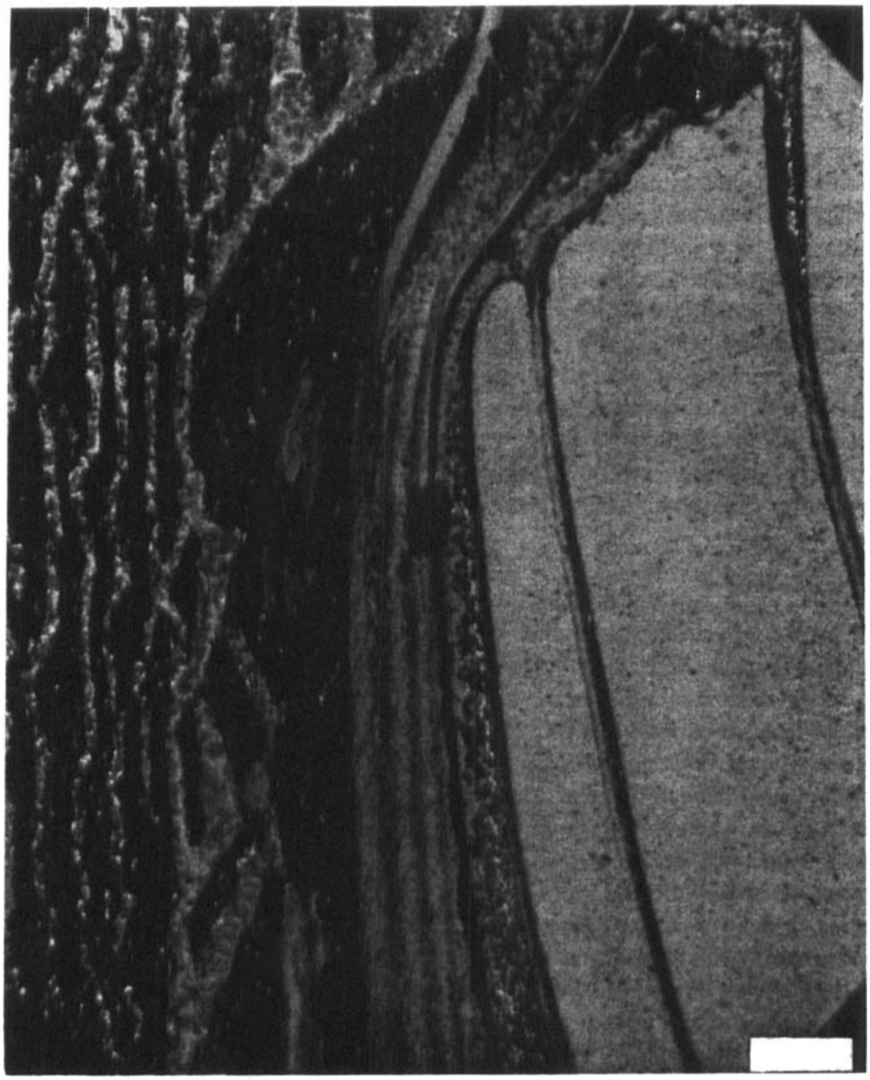

FIGURE 6 The upper part of the specimen shown in Figs. 2 and 3, consisting of the poly(methyl methacrylate) side of the joint. (Marker = 100 μm).

Fig. 6 was photographed with green light while much of the reflected light had a reddish cast, the colored regions appear dark. In the region corresponding to that of the craze in Fig. 3, though, green and reddish light alternated to yield fringes. The interference colors are often seen in fracture and are believed caused by a craze moving with the crack, which can produce a layer of material with a refractive index different from that of the bulk.[5]

The surface of the cleaved piece shown in Fig. 5 has many fewer dark regions associated with craze matter, which indicates that rupture occurred along the boundary of the craze with the bulk, a not uncommon observation.[11] An examination of the surfaces of both pieces revealed that when the crack followed the craze boundary, it always followed the lower craze boundary, suggesting something unique about this boundary. The only unique plane along which the crack might tend to follow more than any other is the PS-PMMA interface. If indeed the crack followed along the PS-PMMA interface, the piece on which the craze layer is usually found is then the PMMA side of the boundary, which suggests that the craze was principally or even wholly within the PMMA. We have not been able to test this suggestion experimentally, though in view of Berry's findings[4] that the energy to move a crack is less in PMMA than in PS, the suggestion seems plausible. Nonetheless, this suggestion is in conflict with that from the ratio of craze width to maximum craze thickness given in Table I, and it is not presently clear which suggestion is correct.

DISCUSSION

The crack always seemed to follow a path in the vicinity of the adhesive bond, though not necessarily along the interface. Two possible reasons for this are, first, whenever the volume of the region surrounding the bond tends to decrease as the bond is being formed, stresses develop. This would be true of our "glueing" of the pieces together with methylene chloride. The resulting stress superimposes on the applied cleavege stress and causes the crack to remain near the bond. Second, it is unlikely that our specimens had uniformly good molecular contact over the whole area of the bond. With a fairly small amount of solvent and pressure and a short contact time in the softened state to smooth natural irregularities and chance asperities, perfect mating over the whole interface is not easily accomplished. The lighter regions in Fig. 3 on the right half of the photograph are probably examples of regions that did not make contact; Figs. 5 and 6 show that on neither side of the cleavage plane did any crazing occur in these regions.

Where molecular contact was established, though, our results indicate that fracture was accompanied by crazing in the bulk adjoining the interface. This is expected for adhesive joints generally whenever the adhesive is a rigid, high molecular weight, non-crystalline polymer. Considering that the craze may have remained in the PMMA during the fracture of the PMMA-PS joint, crazing would not seem to require that both adhesive and adherend be polymers. Since crazing significantly enhances the strength of bulk polymers by inhibiting the growth of cracks, it is expected to do the same for the strength of adhesive joints.

Thus, as has been emphasized by Bikerman[12] for perhaps different reasons, the observed adhesive performance may depend more on the properties of the bulk adjoining the bond than on the strength of the forces of molecular contact holding the bond together. For good adhesive strength, the bulk adjoining the interface must have good mechanical strength. And a region of low molecular weight polymer, for example, surrounding the bond will clearly act as a "weak boundary layer." Yet it is evident: for crazing to occur in the bulk the resistance of the adhesive bond to separation must be at least comparable with the bulk's resistance to the plastic deformation and void formation chracteristic of crazing. Because the forces in the bulk inhibiting crazing are again the forces of molecular contact, the resistance of the adhesive bond to separation should be comparable if good molecular contact has been established. Where intimate molecular contact has been established, then, the strength of the adhesive joint depends on the strength of the bulk materials surrounding the joint.

Acknowledgement

I want to thank my colleagues of the Ford Scientific Research Staff, especially Drs. D. R. Fitchmun, S. Newman and S. Rabinowitz, for their helpful comments.

References

1. E. H. Merz, L. E. Nielsen, and R. Buchdahl, *Ind. Eng. Chem.* **43**, 1396 (1951).
2. P. I. Vincent, "Fracture: Short-term Phenomenon," in *Encyclopedia of Polymer Science and Engineering*, (Interscience Publ., New York, 1967).
3. J. R. Huntsberger, "The Mechanism of Adhesion," Chap. 4, in *Treatise on Adhesion and Adhesives*, R. L. Patrick, ed. (Marcel Dekker, Inc., New York, 1967), Vol. 1.
4. J. P. Berry, *J. Polym. Sci.* **50**, 107, 313 (1961).
5. R. P. Kambour, *Appl. Polym. Symp.* **7**, 215 (1968).
6. R. P. Kambour and A. S. Holik, *J. Polym. Sci., Part A-2*, **7**, 1393 (1969).
7. R. P. Kambour, *Polym. Eng. Sci.* **8**, 281 (1968).
8. R. P. Kambour, *J. Polym. Sci., Part A-2*, **4**, 349 (1966).
9. J. P. Berry, *J. Polym. Sci.* **A2**, 4069 (1964).
10. J. J. Benbow, *Proc. Phys. Soc.* (*London*) **78**, 970 (1961).
11. J. Murray and D. Hull, *J. Polym. Sci., Part A-2*, **8**, 583 (1970).
12. J. J. Bikerman, *The Science of Adhesive Joints* (Academic Press Inc., New York, 1968).