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Mixed-mode effects on the toughness of polymer interfaces

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Normal, symmetric fracture toughness tests can give high values for the toughness of the joint between the immiscible polymers polystyrene and polymethylmethacrylate. These high values, which are caused by crazes growing away from the interface into the polymer with lower craze resistance, are not a fair characterization of the toughness of the joint. Much lower, and more realistic, toughness values are obtained by the use of an asymmetric test that tends to drive the crack and crazes more along the interface.

1. Introduction

Crack propagation on the interface between different materials is normally examined using fracture mechanics. Thus, it is assumed that the criterion for crack propagation can be expressed in terms of a critical value for the strain energy release rate G or the stress intensity factor K. An important distinction between an interface crack and a crack in a bulk material is that in the former, if the interface is weak, the direction of crack propagation is defined so that changing the loading geometry can change the mode of crack-tip loading (e.g. the ratio of K_I to K_{II}) that occurs at the crack tip during crack propagation. This is in distinction from a crack in bulk material which normally grows in such a direction that it experiences a pure opening mode, which means that K_{II} equals zero. Hence, in general, only with interfacial failure is it necessary (or possible) to consider the effects of varying the ratio of mode I to mode II loading on crack propagation.

Interfacial failure is complicated in another way. It has been known for some years [1] that the elastic stress situation very close to a crack tip at an interface between materials of different moduli cannot be described by a simple stress intensity factor. The stresses show an oscillating singularity that is not physical, as the oscillations correspond to interpenetration of the crack faces. This problem can normally be ignored in practice as the region of oscillation is small and where, in real materials, non-elastic deformation is to be expected. A second problem is that K on a material interface cannot, in principle, be separated into the opening and shear modes K_I and K_{II}. However, Rice [2] has shown, for only moderate differences in moduli between the materials, that this effect is small and also can be ignored because combined changes in the specimen geometry and loading that are not huge, and do not change the classical K_I and K_{II}, will give about the same interface crack stress field.

A little experimental information is available on the effect of loading mode on crack propagation. Anderson *et al.* [3] examined the cracking of a urethane adhesive bonded to polymethylmethacrylate and found that the fracture energy was lowest for mode I and increased by factors of 2 and 3 for modes II and III. Much larger effects were observed by Bascom *et al.* [4] when testing rubber-toughened epoxies. They found that the rubber toughening only occurs for mode I loading, so the toughness could be a factor of 30 lower for mixed modes I and II than for pure mode I. This observation is consistent with the belief that voiding is an integral part of the toughening mechanism in these systems. More recently Cao and Evans [5] have examined the effect of K_I/K_{II} ratio (phase angle of a complex K) on crack propagation at interfaces. It is worth noting that, in all these cases, although a significant effect of loading mode could be observed, there was no evidence that small changes in K_{II} might have a very large effect.

The impetus for the work described here comes from a study of the toughness of the interface between two incompatible polymers, polystyrene (PS) and polymethylmethacrylate (PMMA), and in particular the effect of placing a thin layer of a PS–PMMA diblock copolymer on the interface [6]. Using both compact tension and double torsion samples, it was found that the PS–PMMA interface (without block copolymer) was surprisingly tough with a G_c of about $200\,J\,m^{-2}$ which is equal to about half that of the individual polymers. This result is in agreement with Cho and Gent's [7] previous work but very different from that obtained by Wool *et al.* [8] ($50\,J\,m^{-2}$) using wedge-opened double cantilever beam samples. The fracture surfaces of the PS–PMMA samples were examined using a number of techniques including reflection optical microscopy. A typical micrograph of the PS side of the fracture is shown in Fig. 1. Such images have been interpreted as showing that crazes grew down into the polystyrene from the interface and the crack tended to follow one such craze and then jump back to the interface. This interpretation is shown in Fig. 2. Observation of a moving crack showed that propagation occurred in discrete increments, each one corresponding to a single

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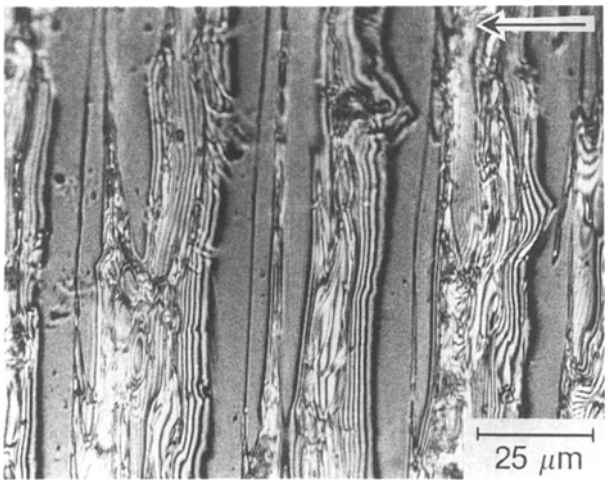

Figure 1 A reflection optical micrograph of the PS side of the fracture surface of a PS–PMMA joint. A symmetric test was used to break the joint. The interference fringes were emphasized by observation with monochromatic light.

cycle of the craze moving into the polystyrene and then jumping back to the interface. Also each increment of growth initiated at the side of the sample, then travelled across the crack front. PS and PMMA are both relatively brittle glassy polymers that fail by crazing but the craze stress for PS is considerably lower than that for PMMA. The high interface toughness seemed to come from the PS crazes growing away from the interface. The aim of the current work was to devise a test that would discourage the crazing in the polystyrene and hence give a better value for the toughness of the interface.

2. Experimental techniques

2.1. The test

A simple way to produce a K_{II} component in a double cantilever beam test of an adhesive joint is to make the sample asymmetric. It is convenient to generate this asymmetry by bonding the sample to a substrate that

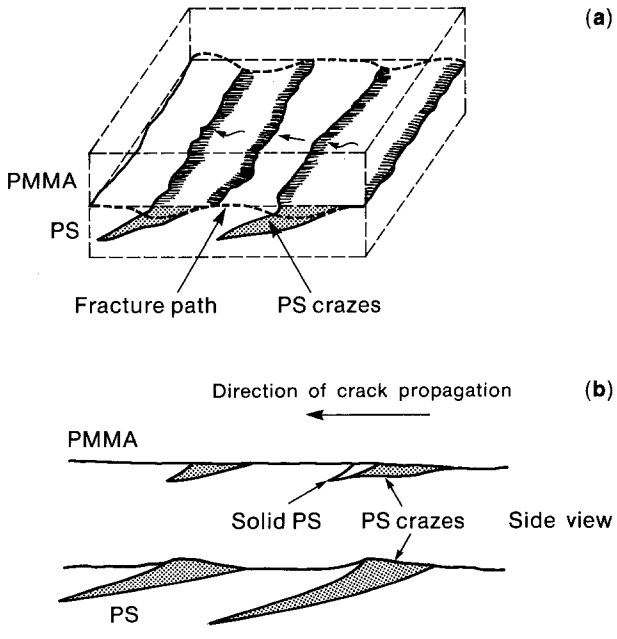

Figure 2 A sketch that shows the mode of failure of a symmetrically tested PS–PMMA joint that is consistent with Fig. 1.

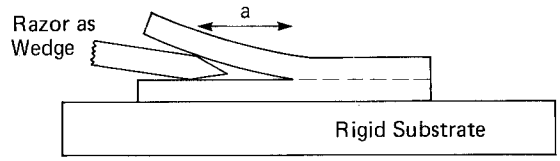

Figure 3 A sketch of the "razor" specimen.

is stiff with respect to the cantilever beams. The double cantilever beam samples used had beams of depth D of 1.7 mm, and were 50 mm long with a width B (in the plane of the crack) of about 5 mm. They were tested free-standing and also after bonding to 2 mm thick glass or 3 mm thick aluminium substrates. The samples were loaded in two different ways. In one set of tests they were wedged open using a single-edge razor blade. The crack length was measured as shown in Fig. 3. In a second set of tests the samples were loaded using a Instron testing machine. In all cases the crack lengths were measured using an optical microscope. The strain energy release rate was obtained from the equation

$$G = \frac{6P^2a^2}{EB^2D^3}\left[1 + 0.64\left(\frac{D}{a}\right)\right]^2 \quad (1)$$

for the Instron tests where P is the load, a the crack length and E the Young's modulus. The calculated compliance of the sample is given by

$$C = \frac{4a^3}{D^3EB}\left[1 + 1.92\left(\frac{D}{a}\right) + 1.22\left(\frac{D}{a}\right)^2 + 0.39\left(\frac{D}{a}\right)^3\right] \quad (2)$$

For the razor tests the fracture toughness is given by

$$G = \frac{3ED^3u^2}{8a^4[1 + (0.64D/a)]^4} \quad (3)$$

where u is the thickness of the razor blade. All these relations were derived by Kanninen [9] for a single cantilever beam on an elastic foundation. Razor tests on unbonded samples were assumed to give a G value equal to half that from Equation 3. The failure of polymeric materials is highly time-dependent and, as the insertion of a razor blade at constant speed is not convenient, the crack length in the razor tests was always measured 24 h after the razor was inserted, thereby obtaining a slow-speed or crack-arrest toughness. The high stiffness of this sample geometry meant that crack jumping was not commonly observed. The Instron tests were all done with a crosshead speed of 0.5 mm min^{-1}.

2.2. Materials

The polystyrene used was Dow Styron 685 obtained in bead form. The PMMA was Du Pont Elvacite 2021 that was obtained as a powder and the polycarbonate (PC) was Lexan 101 from General Electric. The polymers were compression-moulded into sheets 7.5 mm × 50 mm × 1.7 mm in window-frame moulds against ferrotype plates. Two sheets were joined by placing them together in their moulds and heating them to temperatures of 150 and 170° C for 2 h under light

pressure in a press. Test samples were cut from the joined sheets.

3. Results and discussion

The toughness of the PS–PMMA joint measured using the asymmetric Instron test was $13 \pm 2\,J\,m^{-2}$. This result should be compared with a value of $190 \pm 40\,J\,m^{-2}$ obtained previously using compact tension and double torsion tests [6]. The toughness of the PS–PMMA joint was also measured in three ways using the razor test, with the sample free-standing (normal double cantilever beam), with PMMA adhered to the substrate, and with PS adhered to the substrate. The free-standing sample gave a G of 60 to $100\,J\,m^{-2}$; the PMMA-adhered sample was not breakable on the interface, the crack propagated into the polystyrene upper layer and it broke off at a G of about $400\,J\,m^{-2}$; the PS-adhered sample cracked on the interface at a G of 5 to $10\,J\,m^{-2}$. Clearly the asymmetry caused by bonding the sample to a rigid substrate had a massive effect on the values of fracture toughness obtained.

Similar razor tests were done on PS–PC and PMMA–PC samples. The joint between PC and PS was expected to be weak as the polymers are thermodynamically immiscible. There is evidence that PC and PMMA are miscible [10, 11], or nearly miscible, so a strong interface is expected in this case. The PS–PC joint gave toughnesses of 14 and $30\,J\,m^{-2}$ for PS-adhered and free-standing samples, respectively. For the PMMA–PC joint the values obtained were 360 and $340\,J\,m^{-2}$ for the PMMA-adhered and free-standing samples, respectively. For neither system was it possible to propagate the crack along the interface when the PC was adhered to the rigid substrate.

Instron tests were done on a series of PS–PMMA samples where the interface had been toughened by the presence of a thin layer of block copolymer. Both the load for crack propagation and the deflection of the loading points were measured so that the toughness and sample compliance could be obtained. The compliance was measured to check that Kanninen's relations [9] apply when the sample is bonded to a rigid substrate. The mean of the ratio of measured to calculated compliance (assuming a modulus of 3.2 GPa) was 1.08 from 35 measurements which had a standard deviation of 0.11. It is evident from this result that Equation 1 can be used to obtain the toughness of bonded samples. Fig. 4 compares toughness results obtained using the Instron and razor tests. The wide range of toughness values came from varying the thickness and molecular weight of the block copolymer layer [12]. It is evident from Fig. 4 that the correlation between results obtained from the two tests was excellent. The Instron test gave values that were about a factor of 2 greater than those from the razor test. This difference could easily be caused by the differences in testing rate between the two tests.

4. Discussion

The main point of the Instron tests was to check the results obtained using the razor test. The excellent correlation between the two tests and between the calculated and measured compliances shows that the razor test, though it is very crude, can give reliable results.

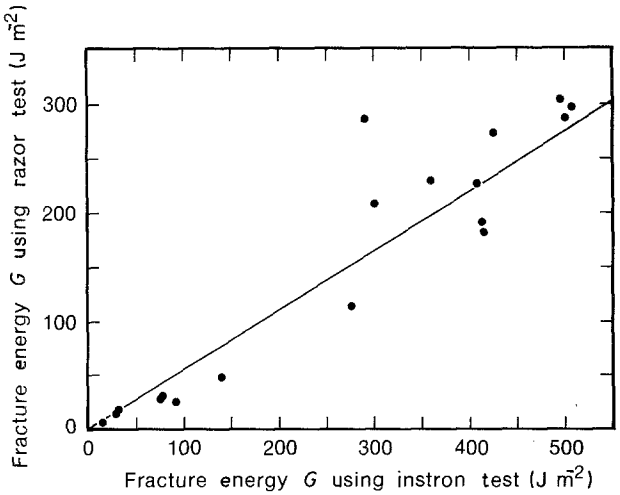

Figure 4 A plot showing the correlation of results obtained using the razor and Instron tests for a number of PS–PMMA joints that were toughened by the presence of a thin layer of PS–PMMA diblock copolymer.

The asymmetric test was developed to suppress the tendency, observed in geometrically symmetric tests, for crazes to grow away from the PS–PMMA interface into the PS and hence give a large toughness value. It was assumed that the large toughness obtained in the conventional tests was a poor representation of the "real" situation at the interface. Evidence for this point of view came from the considerable care that was required in sample handling to ensure that failure did not occur during sample preparation and mounting. The results given earlier show that the test works very well. For the PS–PMMA joint the measured fracture energy was decreased by a factor of at least 10 in changing from the symmetric to the asymmetric test. Also optical microscope observation showed that the structures that gave rise to interference fringes on the fracture surfaces were no longer present on samples that were broken using the asymmetric test. The precise stress situation in these asymmetric tests has not been evaluated, but it would appear that as long as there is sufficient K_{II} component it probably does not matter. The important thing is to suppress the tendency of crazes (which usually grow normal to the principle tensile stress [13]) to grow into the PS. The evidence for this assertion is that the Instron and razor tests gave similar results although the crack lengths were sometimes fairly different. The experiments on PS–PC and PC–PMMA suggest that the same effects occur in these systems as in the PS–PMMA system but, as PC is more craze-resistant than PMMA, in PC–PMMA joints it is the crazes in the PMMA that need to be suppressed.

There exists still the question of why crazes tend to grow away from the bond line and into the lower crazing-stress material. As mentioned in the introduction, the elastic situation at a bimaterial interface is complicated and K_{II} components are to be expected. Gautesen and Dundurs [14], following Comninou [15], have calculated the stress situation for an interface crack in a tension field that is closed at the tip.

They find a finite K_{II} component that discontinuously goes to zero as the materials become identical. Presumably this discontinuity is unphysical in the sense that bimaterial effects, for almost identical materials, are only going to occur extremely close to the crack tip. However this work does perhaps show that small elastic differences between the materials can cause significant K_{II} components. The sign of K_{II}, and hence the expected direction for the principle tensile stress, is controlled by a parameter β given by

$$\beta = \frac{\mu_2(\kappa_1 - 1) - \mu_1(\kappa_2 - 1)}{\mu_2(\kappa_1 - 1) + \mu_1(\kappa_2 - 1)}$$

where μ is the shear modulus and $\kappa = 3 - 4\nu$ where ν is the Poisson's ratio of materials 1 and 2. Material 2 is assumed to be on top so a positive K_{II} would tend to drive a craze into material 1. If the two materials have the same κ the craze will tend to grow into the material with lower shear modulus as expected. For two materials of the same modulus the craze will tend to grow into the material of lower Poisson's ratio.

Polymer glasses all have similar shear moduli and Poisson's ratio; the values of E for PS and PMMA are 3.4 and 3.2 GPa, respectively, while polycarbonate is a little lower at 2.6 GPa. Poisson's ratios are not known with sufficient accuracy to assume that they are different. These figures do not suggest that the elastic situation described above controls the craze growth direction. It could be argued that, as crazing is a dilational deformation mode, the material with lower craze resistance will show an effectively lower Poisson's ratio so the craze will turn into it. An alternative explanation could be given in terms of the different thermal contractions that the materials experience on cooling from the joining temperature. The system will start to build shear stress on the interface when the temperature cools through the lower of the two material T_g values. The material with lower T_g will contract more than the other, so it builds up an in-plane tensile stress. The crazes will then tend to grow into the material with lower T_g. This suggestion follows the correct trend but the T_g of PMMA is only about 5° C greater than that of PS so it is hard to believe that this effect is significant.

5. Conclusions

The value obtained for the fracture toughness of a joint between incompatible polymers can depend strongly on the mode of loading. Symmetrical tests, which might be expected to give nearly pure mode I loading, can give high values of the joint toughness because crazes grow away from the joint into the polymer with lower crazing resistance. These crazes can be suppressed by the use of an asymmetric fracture toughness test that tends to push the principal tensile stress into the more craze-resistance material. The toughness obtained using the asymmetric test can be lower by at least an order of magnitude than that obtained from symmetric tests. This lower value is more consistent with experience from handling the samples and so, in practical terms, is more correct. The reason why crazes grow away from the interface is not clear but is probably not explicable in terms of the elastic situation at a crack tip on a bimaterial interface.

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