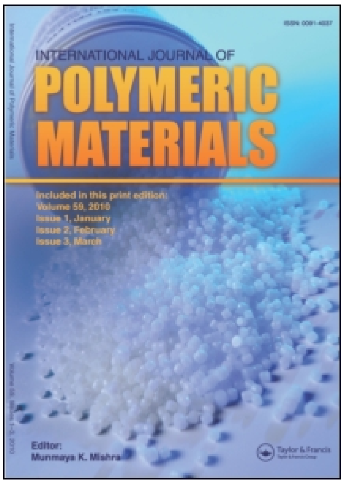

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The Role of Shrinkage Stresses in the Environmental Fracture of Adhesive Joints

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Slow interfacial crack growth occurs in epoxy-metal joints when loaded in the presence of water. Previous workers have sought to explain this on the basis of thermodynamic arguments, but this leads to inconsistencies with the results from fracture mechanics studies. A mixed mode failure criterion is proposed in this paper where the strain energy release rate contribution from shrinkage stress is included. This is found to give a more consistent model of joint failure.

INTRODUCTION

One of the most important limitations in the use of adhesive joints is their decrease in strength when exposed to the action of water.[1] When the joint is also subject to an external load, the strength decrease has been found to occur more rapidly.[2,3] Previous discussions of this phenomena have been either in terms of surface thermodynamics[4] or fracture mechanics[5,6] and there appears to be a conflict between the two approaches.

The thermodynamic arguments rely on surface energy measurements to deduce the work of adhesion, W_a. In an inert environment, W_a may be expressed as:

$$W_a = \gamma_a + \gamma_b - \gamma_{ab} \tag{1}$$

where γ_a and γ_b are the surface free energies of the substrate and adhesive and γ_{ab} is the interfacial free energy. If the joint is now immersed in water, the effective work of adhesion will change to a new value, W_{al}, calculated using the interfacial energies, γ_{al} and γ_{bl}, measured in the presence of water,

$$\text{i.e. } W_{al} = \gamma_{al} + \gamma_{bl} - \gamma_{ab} \tag{2}$$

Gledhill and Kinloch[4] measured the surface energies for dry steel and for a cured epoxy resin and determined W_a to be $+291$ mJ/m^2, whereas in water, W_{al} was -253 mJ/m^2. It was suggested that the bonded interface would therefore be expected to debond spontaneously under water and that the growth of the debonded areas would cause the observed strength decrease. Spontaneous debonding was confirmed experimentally by measuring the growth of slow interfacial cracks proceeding inwards from the exposed edges of steel-epoxy butt joints. Similar behaviour would be expected for epoxy-aluminium joints.

The fracture mechanics approach to the strength of adhesive joints has been discussed by Gurney and Amling.[7] A specific fracture surface energy, R, may be defined for crack propagation along the adhesive-substrate interface computed from the load-deflection curves obtained during quasistatic crack propagation. In general, the fracture surface energy is a function of crack propagation rate.

Mostovoy and Ripling[5,6] used double cantilever beam epoxy-aluminium specimens to measure R during slow crack growth under water in terms of the strain energy release rate, G_I. The results showed an increasing crack velocity with increasing G_I up to a critical value where the crack leaves the interface. There was some evidence for a minimum value of the strain energy release rate G_0, below which, crack propagation ceased. To establish the existence of G_0 more firmly, further work would appear to be necessary using long loading times to check for very slow crack growth. However, from Mostovoy and Ripling's data, G_0 for an anhydride cured epoxy-aluminium system may vary from 1.2 to 37 J/m^2 depending on hardener concentration and curing temperature.[6] For an amine cured system, G_0 was reported to be between 14 and 53 J/m^2.[5]

Thus it appears that the energy available for crack propagation due to the negative work of adhesion calculated from Eq. (2) is much too small to cause crack growth, and the observation of spontaneous debonding is inconsistent with the fracture mechanics results. In what follows it will be suggested that this discrepancy may arise because of insufficient consideration of the effects of shrinkage stress.

It has been shown that residual stresses are produced in epoxy adhesives by differential thermal contraction from the curing temperature[8] or from the curing reaction.[9] These stresses have been calculated to be sufficient to supply 50% of the strain energy release rate required for the fracture of epoxy joints in air[10] and this has been confirmed experimentally by Cherry and Hang.[11] Mulville and Vaishnav[12] have also shown that shrinkage stresses may make a large contribution to the critical strain energy release rate for fracture of epoxy-aluminium joints in air. With specimens loaded in water, slow crack growth can proceed at much lower G than is required in air, and hence shrinkage stress is likely to be even more important.

The experiments to be reported here were therefore designed to investigate the role of shrinkage stress in the water-induced failure of epoxy-aluminium joints by slow interfacial crack growth.

EXPERIMENTAL

A technique for reducing shrinkage stresses was developed by Cherry and Hang,[11] which involved the application of a compressive force to the polycarbonate substrate of epoxy-polycarbonate double cantilever beam fracture toughness specimens. The epoxy-aluminium system was chosen for the present work because of its industrial importance. Since large compressive forces would be required with the aluminium substrate and this would cause experimental difficulties, an alternative technique was used to that developed by Cherry and Hang.[11] With this technique the substrate was subjected to a uniaxial tension before the epoxy resin was cast on it. After the epoxy resin had been cured, release of the tensile pre-stress would allow the substrate to contract, thus balancing a predetermined portion of the resin shrinkage.

The epoxy system was Araldite D with 10 phr of a diamine hardener, HY951. This resin has a low viscosity and is easy to cast. It is transparent, which allowed the crack tip to be located, and has high stress-optical activity making it suitable for photoelastic work. Alclad 2024 aluminium alloy was used for the substrate with a surface preparation based on ASTM D2615 Method A. The specimen configuration is shown in Figure 1.

The pre-stressing load was applied using a rig with which the initial tension, applied by means of an Instron tensile testing machine could be maintained during the subsequent casting and curing operations. The resin was cast and cured in a teflon mould which was assembled around the substrate using "O" ring seals to prevent leakage of the resin. Curing took place over a period of 20 hours at 30°C.

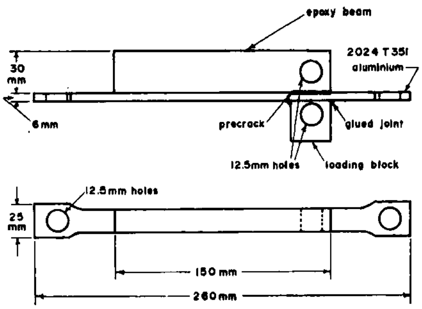

FIGURE 1 Adhesive specimen configuration.

For fracture toughness testing, the specimen was precracked with a sawcut sharpened with a razor blade. The load was applied by an Instron testing machine to 12.5 mm holes drilled in the epoxy beam and a steel loading block glued to the bottom of the substrate. For constant load tests in water, the specimen was loaded in a tank bolted to the crosshead of the testing machine; the specimen was completely immersed. Constant load was maintained by the automatic movement of the crosshead working at 0.005 cm/min.

Slow crack growth was characterized by measurement of the crack velocity as a function of the applied strain energy release rate, G_I. This was calculated from the load at crack extension and the measured variation of compliance with crack length. Since the specimens are not of constant G configuration, a small range of G values was obtained corresponding to an average crack velocity calculated from the time interval required for the measured crack extension.

Preliminary experiments were conducted to check that prestressing had the expected effect on the shrinkage stress by the use of photoelastic methods, and to measure any change in shrinkage stress due to immersion in water. Crack velocities were then measured as a function of the applied strain energy release rate for specimens manufactured at various prestress levels.

RESULTS

1 Effect of prestress

The stress distribution in the epoxy beam of the specimens was examined by observing the isochromatic patterns formed by passing circularly polarized light through the specimens in a polariscope.

Figure 2 shows the isochromatic fringe patterns for specimens with zero, 5.9 kN and 11.6 kN prestress which show a reduction in the number of fringes with increasing prestress. The average fringe order at the interface was determined for a number of specimens and plotted against prestress. This allowed an approximate value of 13.4 kN to be extrapolated for the force required to give zero residual stress. This value is in good agreement with a value deduced from the results of Cherry and Hang[11] who used the same epoxy system and similar specimen dimensions.

2 Effect of immersion on shrinkage stress

It was thought that immersion under water could possibly affect the shrinkage stress in an adhesive specimen by causing shrinkage or swelling of the polymer or by promoting stress relaxation. The significance of these phenomena was therefore investigated by directly measuring the length of an epoxy beam

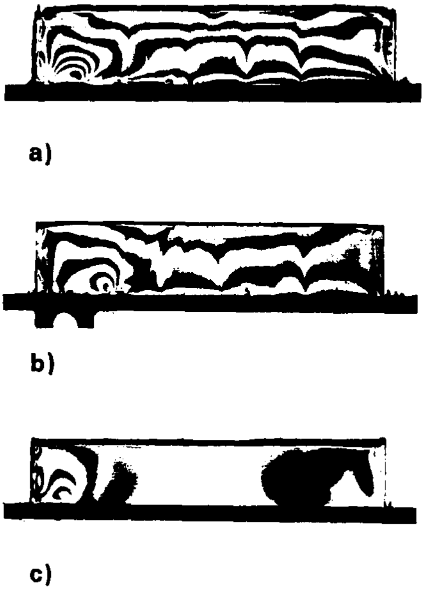

FIGURE 2 Isochromatic patterns in adhesive specimens with (a) 0 kN prestress, (b) 5.9 kN prestress, (c) 11.6 kN prestress.

during immersion and by monitoring the photoelastic fringe pattern in an adhesive specimen stored in water.

The direct measurement, using a linear variable differential transformer to measure the relative displacement between the ends of an epoxy block, detected slight shrinkage corresponding to a strain of around 1.6×10^{-5}, reaching equilibrium after an hour or two. This is negligible compared to the shrinkage during curing which corresponds to a strain of about 2×10^{-3}.

No significant change could be observed in the photoelastic fringe pattern of an adhesive specimen after more than 9 days under water. It was concluded that changes in the stress distribution in the epoxy resin due to immersion in water are insignificant compared to shrinkage during curing, for the purposes of the fracture toughness tests.

3 Fracture toughness of adhesive specimens in water

i) Unprestressed specimens Slow, interfacial crack growth was easily initiated from a blunt precrack in specimens with no prestress. The crack front moved fairly uniformly across the width of the specimen although it tended to lag behind slightly at the edges. Occasionally, a bubble trapped at the interface during pouring of the resin was encountered by the crack front, which tended

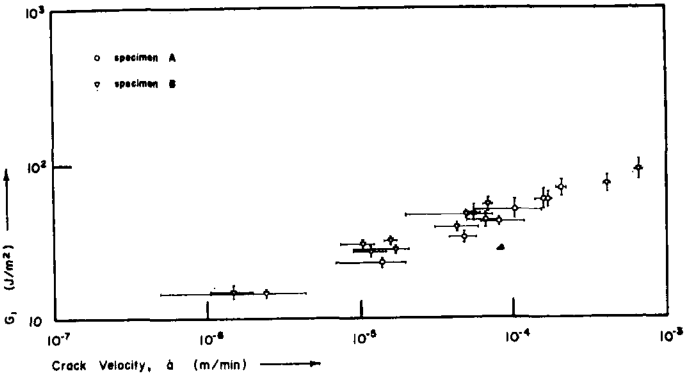

FIGURE 3 G_I versus $\dot{a}$ for adhesive specimens with 0 kN prestress in water.

to slow it down. Results where this happened were excluded from the data, as were results where the crack extended from the initial precrack.

The data from two specimens with no prestress is presented in Figure 3. Vertical error bars arise from the uncertainty in the G_I values due to scatter in the compliance calibration, uncertainties in the load and crack length measurements and the change in G_I due to crack extension under constant load with the varying G geometry. Horizontal error bars correspond to the range in crack velocities due to variable crack growth rate across the crack front.

Reproducibility between the two specimens appears to be good and a regression line of the form

$$G_I = N\dot{a}^q \tag{3}$$

has been fitted to the data with constants, $N = 9.72 \pm 2.5 \times 10^2$ (90% confidence limits) and $q = 0.32 \pm 0.02$ (90% confidence limits) using the unweighted data and treating the crack velocity, $\dot{a}$, as the dependent variable.

ii) *Prestressed specimens* One specimen at a prestress level of 2.6 kN and two specimens at 4.2 kN prestress were tested. The results (Figures 4 and 5) show a decrease in crack velocity, at a given G_I, measured from the centre of the scatter bands of over an order of magnitude between the zero prestress and 4.2 kN prestress results. Again reasonable reproducibility is obtained between the two specimens at 4.2 kN prestress. The scatter in the data is considerably worse than for the zero prestress results, largely because of the slower crack velocities and a greater tendency for non-uniform crack growth across the width of the specimen.

Regression analysis of the data for 2.6 kN gives $N = 1.57 \pm 1.1 \times 10^3$ and $q = 0.32 \pm 0.06$ (90% confidence links). For the 4.2 kN data, $N = 1.29 \pm 1.2 \times 10^3$ and $q = 0.28 \pm 0.06$ (90% confidence links). The data were

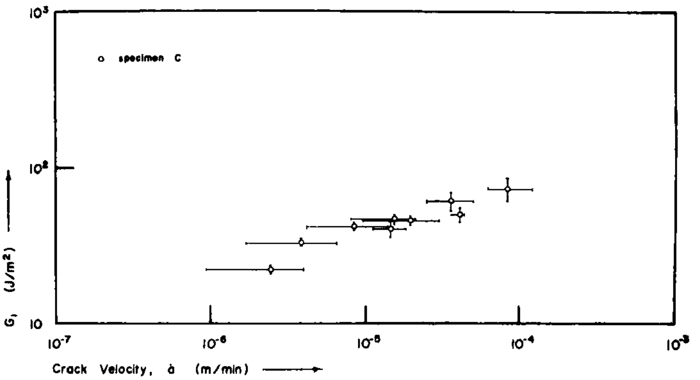

FIGURE 4 G_I versus $\dot{a}$ for an adhesive specimen with 2.6 kN prestress in water.

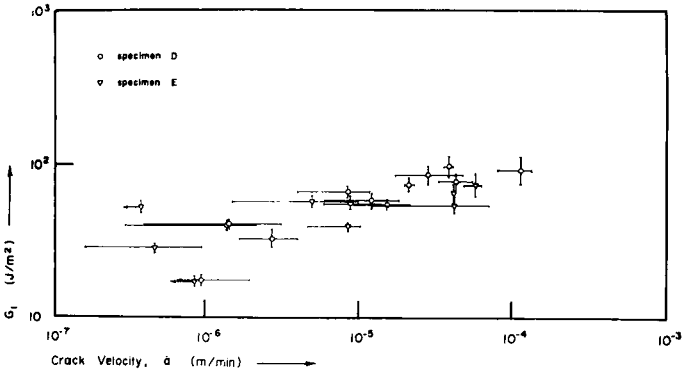

FIGURE 5 G_I versus $\dot{a}$ for adhesive specimens with 4.2 kN prestress in water.

unweighted for the regression analysis, $\dot{a}$ treated as the dependent variable and results giving only an upper limit to the crack velocity were excluded.

Attempts to obtain data at higher prestress levels were not successful. Interfacial cracks could not be started readily without causing fracture in the epoxy resin. A possible reason for this result will be discussed in a later paper.

DISCUSSION

1 Fracture behaviour of adhesive joints

Although specimens tested in air failed cohesively in the epoxy resin, those tested in water (provided G_I was below a critical value), failed by slow crack growth, at or very close to the interface. This implies that in water, the adhesive fracture surface energy is less than the cohesive fracture surface energy.

The range of fracture surface energies and crack velocity values observed during fracture in water corresponds closely to those reported by Mostovoy and Ripling[5] for an amine cured epoxy. Mostovoy and Ripling obtained fracture surface energy values from about 14 to 105 J/m^2 and crack velocities from 2.5×10^{-6} to 2×10^{-3} m/min. The present results range from about 15 to 100 J/m^2 for crack velocities of about 10^{-6} to 7×10^{-3} m/min.

2 Effect of prestressing

The effect of prestressing the substrate is to lower the interfacial shear stress as shown by the photoelasticity results. Thus the contribution to the total strain energy release rate for an interfacial crack from shrinkage stress is reduced. Figures 3, 4 and 5 show a decrease in crack velocity at a given applied strain energy release rate which is in qualitative agreement with the expected trend.

A quantitative assessment can be made by using the mixed mode failure criterion,

$$R = G_I + G_{II} \tag{4}$$

Shrinkage stress is assumed to act principally in the forward shear mode, although it may also contribute to the opening mode. Since the specimen length is ten times its width, any traverse shear mode component due to shrinkage is neglected.

The use of this mixed mode criterion has been found to be appropriate by Irwin,[13] Cherry and Hang[11] and Hartman.[14] However, it does not appear to be consistent with the common observation of much higher fracture toughness in adhesive joints loaded in pure shear mode compared to those loaded in mixed mode or tension.[14,15] Irwin[13] has pointed out that if the tensile component is insufficient to separate the crack surfaces, shear load may still be transmitted across the interface and the measured toughness will be much higher. The failure criterion, therefore, can only be applied when G_I does not approach zero.

3 Superposition of results from different prestress levels

Equation (4) may be rewritten as,

$$G = G_I + G_s \tag{5}$$

where G is the total available strain energy release rate and is equal to R, if the crack is propagating, G_I is the applied strain energy release rate and G_s is the contribution due to shrinkage stress, which is expected to act principally in the forward shear mode.

If G_s is known, the three sets of data can be replotted using G instead of G_I, and should then fall on the same curve. Cherry and Hang[11] obtained a value of 62 J/m^2 for a specimen with similar dimensions and using the same epoxy system, though with a longer curing time.

Neglecting any tensile component of G_s and using a value of 62 J/m^2 for G_s in unprestressed specimens, G_s for a prestressed specimen may be approximated by the linear function

$$G_s = 62\left(1 - \frac{F}{F_c}\right)\ \mathrm{J/m^2} \tag{6}$$

where F is the prestressing force and F_c is the force required to compensate completely for the shrinkage stress. F_c was taken to be 13.4 kN from the photoelastic results. A quadratic equation in F may be more appropriate but would not significantly reduce the scatter in the superposition. Using Eq. (6), G_s will then be about 50 and 43 J/m^2 for the 2.6 and 4.2 kN prestress levels, respectively.

Plotting G defined in Eq. (5) versus crack velocity (Figure 6) the three sets of data are found to give a good superposition considering the scatter in the original data and the approximate value for G_s. Regression analysis of the data gives an equation of the form,

$$G = N\dot{a}^q \tag{7}$$

where $N = 4.3 \pm 2.5 \times 10^2$ (90% confidence limits) and $q = 0.135 \pm 0.015$ (90% confidence limits).

Shrinkage stress therefore appears to add an extra strain energy release rate term which causes the crack to propagate faster than would be expected in the absence of shrinkage.

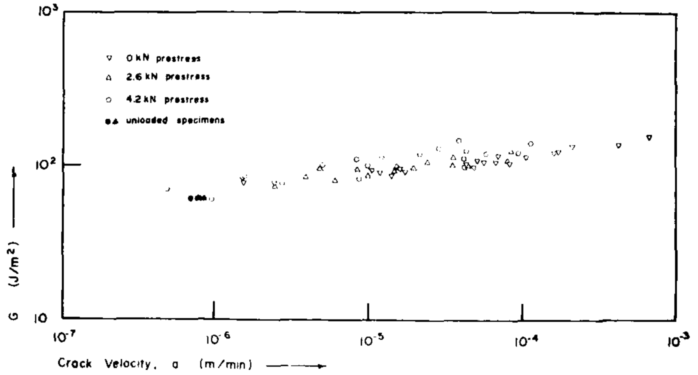

FIGURE 6 G_I versus $\dot{a}$ for adhesive specimens with various prestresses in water.

4 Limits to the crack propagation rate

The maximum crack velocity obtained approached 10^{-3} m/min and any attempt to propagate a crack at a higher velocity caused failure in the epoxy resin. The transition from adhesive to cohesive crack propagation occurs at about the same value of G_I for all specimens, although the crack velocity at which this transition occurs is much greater in the unprestressed specimens.

At propagation rates of less than 10^{-6} m/min there was a tendency for the crack to stop with no visible movement during tests lasting 48 hours. However, from Figure 6, the value of G_s contained in the unprestressed specimens (62 J/m^2) should be just sufficient to cause crack propagation at the low end of velocities observed.

5 Crack growth in unloaded specimens

To test for the possibility of interfacial crack growth under the action of shrinkage stresses alone, unprecracked and interfacially precracked adhesive specimens were immersed under water for long periods without external loading. No immediate crack growth occurred in the precracked specimens.

Two unprestressed specimens have, however, been observed to debond after long periods of immersion. Debonding began at the edges of the specimens and continued until they were almost completely debonded. In both cases, about 100 days immersion was required before debonding first began. Where the debonded area extended across the width of the specimen, velocity measurements could be made and four of these results are plotted on Figure 6. They are in reasonable agreement with the trend from externally loaded specimens.

Two specimens with prestresses sufficient to cancel almost all of the shrinkage stress showed no sign of debonding after 250 days immersion. This strongly supports the conclusion that stresses at the crack tip must be present before interfacial debonding takes place.

CONCLUSIONS

It appears that shrinkage stress may accelerate interfacial crack growth by an amount which is consistent with the change in total strain energy release rate. Shrinkage stresses may be sufficiently large to cause interfacial crack growth in the absence of external loading and the results suggest that stress must be acting at the crack tip before interfacial crack growth proceeds.

A negative work of adhesion under immersed conditions is therefore an insufficient criterion for water-induced failure by slow crack growth, and whether or not it is a necessary condition depends on the details of the mechanism operating in the fracture process zone.

We would suggest that the debonding of unloaded specimens observed by Gledhill and Kinloch[4] was activated by shrinkage stresses, which may make this result consistent with the fracture mechanics results.

Further consideration of the mechanism of fracture and the adhesive/cohesive transition will be presented in a subsequent paper.

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