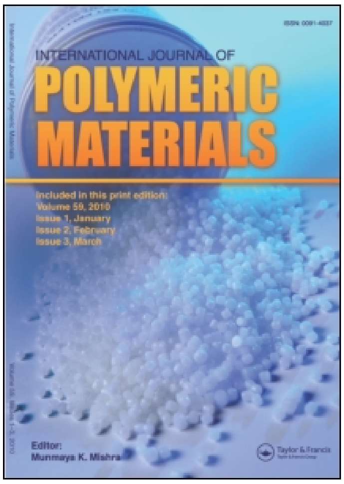

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Crack Tip Processes and the Adhesive-Cohesive Transition in the Environmental Fracture of Adhesive Joints

B. W. Cherry[a]; K. W. Thomson[a]
[a] Department of Materials Engineering, Monash University, Clayton, Victoria

To cite this Article Cherry, B. W. and Thomson, K. W.(1980) 'Crack Tip Processes and the Adhesive-Cohesive Transition in the Environmental Fracture of Adhesive Joints', International Journal of Polymeric Materials, 8: 1, 13 — 24

To link to this Article: DOI: 10.1080/00914038008077931

URL: http://dx.doi.org/10.1080/00914038008077931

Intern. J. Polymeric Mater., 1980, Vol. 8, pp. 13–24
0091–4037/80/0801–0013 $04.50/0

Printed in Great Britain

Crack Tip Processes and the Adhesive-Cohesive Transition in the Environmental Fracture of Adhesive Joints

B. W. CHERRY and K. W. THOMSON

Department of Materials Engineering, Monash University,
Clayton, Victoria 3168

(*Received November 20, 1978*)

Following an earlier paper concerning the role of shrinkage stress on the environmental fracture of adhesive joints, further work has been carried out to investigate the factors which control and limit the rate of interfacial crack growth. The fracture surfaces have been examined using scanning electron microscopy and data from bulk epoxy resin specimens has been obtained for comparison with the results from adhesive specimens. This has allowed a model for slow, water induced crack growth to be proposed.

1. INTRODUCTION

An investigation of the environmental failure of epoxy–aluminium joints was reported in an earlier paper.[1] In this paper it was shown that slow crack growth may proceed at or close to the epoxy–aluminium interface (adhesive cracking) when the joint is loaded under water, but that it proceeds through the bulk epoxy (cohesive cracking) when loaded in air. It was also observed that for joints immersed in water, as the crack velocity was increased, it eventually left the interface and became a cohesive crack in the epoxy resin. This transition has been observed by other workers[2] but has not been fully explained. Similarly the factors controlling the rate of interfacial crack growth have not been widely discussed. Since an understanding of the factors that define the crack speed and limit the speed of an adhesive crack should provide important information about the mechanism of fracture, the work reported in this paper is primarily concerned with the adhesive–cohesive transition in epoxy–aluminium systems.

A wide variety of mechanisms have been proposed for water induced interfacial crack growth. The proposed mechanisms include, the thermodynamic instability of the epoxy–aluminium interface in the presence of water,[3] the disruption of polymer–polymer bonds,[4,5] hydration of the oxide layer[6] or corrosion[7] and preferential absorption of water to the oxide, displacing the adhesive.[3,8] Each of these mechanisms may have associated with it a different explanation of the adhesive–cohesive transition and so the various mechanisms must be examined in more detail.

Gledhill and Kinloch[3] have suggested that the diffusion rate of water through the bulk epoxy is important in determining the rate of crack growth. If the crack is loaded to travel faster than the diffusion rate of water will allow, then a transition to cohesive fracture may occur. Gledhill and Kinloch favour an explanation of the adhesive–cohesive transition which is diffusion controlled on the grounds that the activation energies for crack propagation and aqueous diffusion through the resin are similar.[3]

Williams and Marshall[9] have presented a model for environmental crack growth in bulk polymers where the propagation velocity is assumed to be controlled either by molecular relaxation processes at the crack tip or by the rate of entry of the environmental fluid into the crack tip region. At low crack speeds, molecular relaxation processes in the plasticized polymer control crack propagation and the crack speed varies slowly with the stress intensity factor. At intermediate crack speeds the flow of the environmental liquid controls crack propagation and the crack speed rises sharply with the stress intensity factor. At high crack speeds molecular relaxation processes in the unplasticized polymer control crack propagation and again the crack speed varies slowly with the stress intensity factor. Results with poly-methylmethacrylate and polyethylene conformed well to this model. The model may also be applicable to adhesive joints provided certain differences between monolithic polymers and joints can be taken into account. In particular, the shrinkage stresses developed across the interface must be considered[1] as well as chemical processes which may influence the rate of crack growth. The adhesive–cohesive transition may then result from the flow control condition where the strain energy release rate necessary to accelerate the crack increases rapidly and may exceed that required for cohesive fracture. The rate of adhesive crack growth may then be associated with the relaxation of the plasticized polymer in the crack tip region.

If the supply of water to the crack tip region is adequate up to moderate speeds, other factors must cause the observed transition to the bulk epoxy. If the mechanism of fracture depends on stress activated hydrolysis of either polymer–metal or polymer–polymer bonds,[5] then the reaction rate may be significantly limited by the temperature and the local stress in the crack tip region. The strain energy release rate required to increase the crack speed may then rise steeply if this limiting condition is exceeded, until the local stress becomes sufficiently high to break polymer–polymer bonds by a different mechanism and thus initiate cohesive fracture.

In the experiments to be described in this paper, a determination of the form of the dependence of crack velocity on stress intensity factor and of the effect of varying immersion time on crack propagation characteristics will help to elucidate which of the above mechanisms is applicable to the epoxy–aluminium system.

2. EXPERIMENTAL

The adhesive specimens used in this investigation were identical to those described in an earlier paper.[1] Basically, they consisted of a 6 mm 2024 Alclad aluminium substrate with surface preparation based on ASTM D2651 Method A, and a 30 mm thick epoxy beam cast on top of the substrate to form a double cantilever beam specimen. Fracture under water was induced by mode I loading of the specimen in an Instron testing machine. The specimen was originally designed so that shrinkage stresses could be controlled by prestressing the substrate before casting and curing the epoxy resin. The epoxy system was Araldite D with HY951 diamine hardener at 10 phr. Curing time was 20 hours at 30°C.

The major requirements for the cohesive fracture toughness specimens were stability of cracking and maintenance of the crack in the required direction. Crack stability is generally dependent on the geometry of the test specimen and the compliance of the loading mechanism.[10] If a stiff testing machine is used, stable crack growth is expected, provided the strain energy release rate decreases sufficiently rapidly with increasing crack length under conditions of fixed displacement between the loading points.

Two basic configurations are available for measuring the cohesive toughness of the epoxy resin. Mostovoy and Ripling,[2] for example, used a layer of adhesive sandwiched between two shaped beams made from aluminium. During rising load tests, fast fracture occurred in the adhesive layer. This approach, however, may be subject to complications arising from shrinkage stresses contributing to the strain energy release rate which would be difficult to quantify. The alternative approach is to use monolithic specimens manufactured from cast blocks of epoxy.

Initial experiments with tapered double cantilever beam specimens[12] were unsuccessful since failure occurred by unstable fracture extending down the centre line without arrest. The specimen geometry finally adopted was a double cantilever beam configuration with wide beams and deep side grooves on both sides (Figure 1). Crack arrest could be reliably achieved about half-way down the specimen during testing in air. The specimens were cast from the same epoxy system as used for the adhesive specimens and also cured at 30°C for 20 hours. They were then milled to shape, grooved and drilled. The precrack was cut with a fine saw, then sharpened with a razor blade immediately before testing.

Strain energy release rate versus crack velocity data had already been obtained for adhesive specimens in an earlier part of this investigation.[1] To examine the importance of diffusion of water through the polymer in determining the rate of crack growth, an adhesive specimen was tested after immersion in water for relatively long periods.

Crack growth rates in the bulk epoxy resin were studied using cohesive specimens under water. These were loaded until a crack initiated and grew unstably, usually arresting about half-way down the specimen. Loading was continued at various crosshead speeds and stable crack growth could then be obtained, allowing velocity measurements. Strain energy release rates could be calculated using an experimental compliance calibration and the measured load and crack length.[1]

The fracture surface of adhesive and cohesive specimens was examined using scanning electron microscopy. In the case of adhesive specimens the locus of failure is relevant to determining details of the fracture mechanism.

3. RESULTS

3.1. Effect of long-term immersion

Adhesive specimens were tested under water by taking a set of measurements of crack velocity, $\dot{a}$, at various applied strain energy release rates, G_I, over about 2 cm of crack growth. They were then stored under water for 335 hours and tested for a further 2 cm. Finally, a third set of results were obtained after storing under water until the total immersion time was 1011 hours. The G_I versus $\dot{a}$ curves obtained after long-term immersion could then be compared with the initial curve.

This experiment was performed with three specimens, but the uncertainty in velocity measurements was in general larger than any difference between the curves. The data in Figure 2 was obtained from a specimen which gave exceptionally good results since the crack front was particularly uniform across the width of the specimen.

The results indicate a small shift towards lower crack velocities, at a given G_I, between the first set of points and the second and third sets. No significant change is apparent between the latter sets of data. The G_I values plotted in

Figure 2 were calculated using a separate experimental compliance calibration for each of the three sets of results. It should be noted that if the G_I values are calculated using the combined compliance calibration data from all the results obtained at all the different immersion times, then the scatter in the G_I versus $\dot{a}$ curve is increased and the shift to slower crack velocities is no longer apparent.

The compliance calibration curve showed a definite change in gradient after the first period of long term immersion and computing separate calibrations for each set of results should be more accurate. The change in gradient of the compliance curve is probably a result of saturation of the polymer with water, and a consequent change in the bulk deformation characteristics.

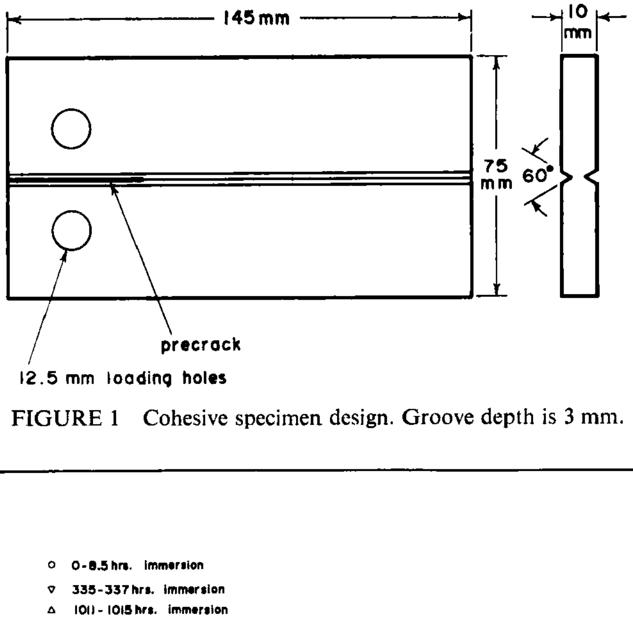

FIGURE 1 Cohesive specimen design. Groove depth is 3 mm.

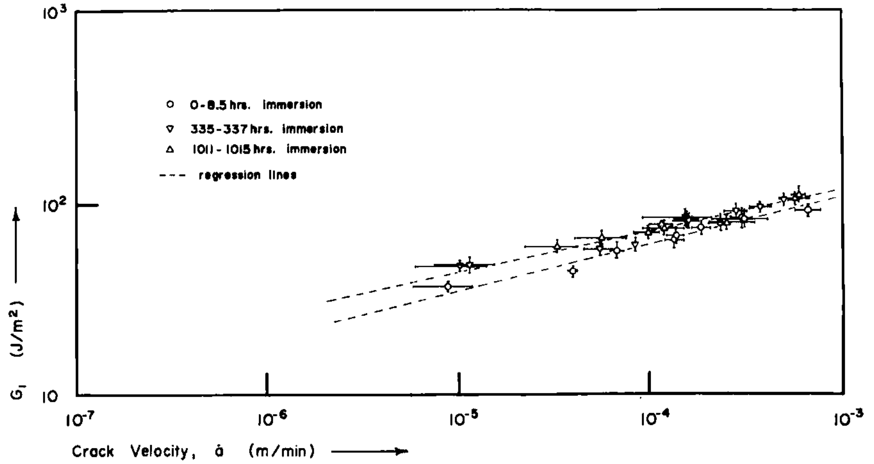

FIGURE 2 G_I versus $\dot{a}$ for an adhesive specimen after long-term immersion.

The position of the crack front during each period of long term immersion was clearly visible on the aluminium fracture surface at the conclusion of the test due to deposits left on the surface, apparently by corrosion processes (Figure 3).

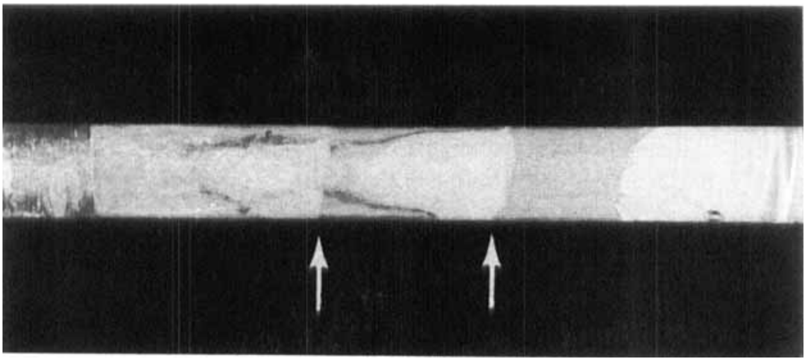

FIGURE 3 Aluminium fracture surface after long-term immersion. Positions where the crack was stationary during immersion are marked.

3.2. Fracture of bulk epoxy resin

When tested in air, unstable crack growth was always observed in bulk epoxy specimens with the critical fracture toughness depending on the crosshead speed of the testing machine.[12] In water, however, stable crack growth could be obtained allowing measurements of G_I as a function of crack velocity.

The results from four cohesive specimens where stable crack growth was obtained are shown in Figure 4. Unfortunately, it is difficult to discern any clear trend in the data. Some difficulty was experienced in trying to increase the range of observed velocities. Crack velocities less than 4×10^{-3} m/min could not be obtained; any attempts to achieve a lower velocity resulted in the crack stopping completely. Subsequent loading then caused unstable fracture. The measurement of crack speeds above about 2×10^{-2} m/min was not possible using these techniques, although faster cracking did appear to be possible.

3.3. Fracture surface of adhesive and cohesive specimens

i) *Adhesive specimens*

Scanning electron microscopy of the etched aluminium surface (Figure 5) shows evidence of longitudinal scratching resulting from the abrasion during initial surface preparation. A large number of etch pits are also visible, some of which are up to 10 μm across and probably 5 μm deep. The aluminium fracture surface from an adhesive specimen debonded by slow crack growth under water (Figure 6) appears to be virtually identical to the unbonded surface. There is no evidence of any widespread epoxy residue.

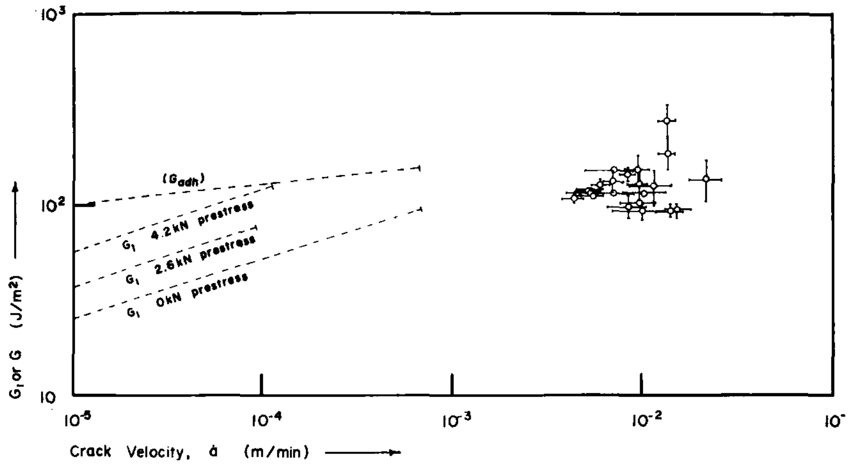

FIGURE 4 G_I versus $\dot{a}$ for cohesive specimens in water. Lines of best fit to adhesive data are also shown.

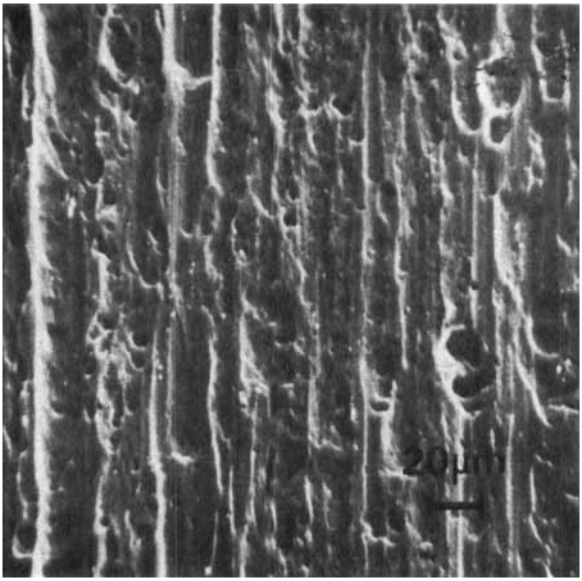

FIGURE 5 Etched surface of an aluminium substrate.

FIGURE 6 Aluminium fracture surface.

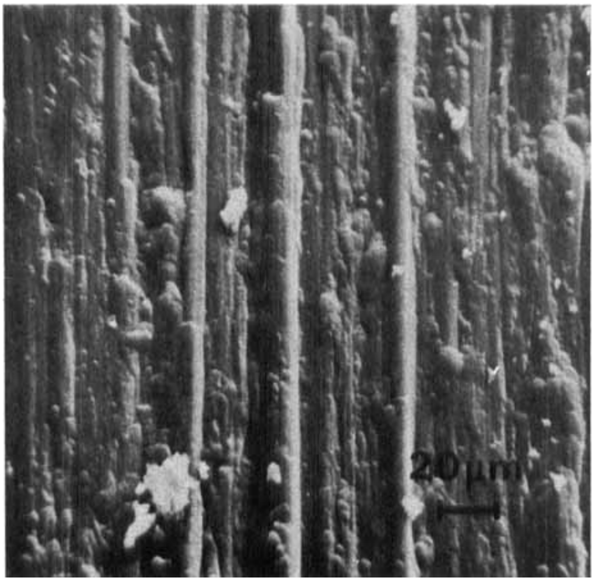

FIGURE 7 Epoxy fracture surface from an adhesive specimen.

The epoxy fracture surface was coated with a thin layer of gold by vacuum deposition. The surface replicates most of the features on the aluminium fracture surface (Figure 7) although there is possibly less fine detail and no large protrusions which may be expected from material embedded in the deeper etch pits as were observed by Patrick *et al.*[13] This may indicate that wetting is incomplete and small air spaces remain in some of the etch pits. The slight loss of detail may indicate plastic deformation during the debonding process. A few light coloured particles are visible on the epoxy surface in Figure 7 which may be dust picked up during specimen preparation.

ii) *Cohesive specimens*

Regions of stable crack growth in the fracture surface of epoxy specimens loaded under water appeared more diffuse than the smooth, glassy areas of unstable crack growth. Scanning electron microscopy of the gold coated fracture surface showed an essentially featureless surface with some indistinct striations parallel to the direction of propagation.

4. DISCUSSION

4.1. Rate controlling processes

The results of the long term immersion experiment in Section 3.1 show that the crack speed at a given G_I for an adhesive specimen loaded under water is not noticeably increased after 4 weeks immersion. If the rate of diffusion of water through the bulk polymer and accumulation at the interface is a factor in determining the rate of debonding, as has been suggested by Gledhill and Kinloch,[3] then some effect would be expected.

No evidence for corrosion during the debonding process was obtained during examination of the fracture surfaces of the adhesive specimens. Corrosion was observed, however, on the surface of interfacially cracked specimens subjected to long term immersion. However this corrosion only occurred on the surfaces of pre-existing cracks and since crack propagation did not occur in these specimens while they were stored under water corrosion is unlikely to be a cause of debonding, but appears to occur in immersed specimens once an interfacial crack has been formed.

If relaxation processes in the epoxy resin control the rate of crack growth in the manner proposed for bulk polymers by Williams and Marshall,[9] then since this model predicts a gradient of about 0.1 in the log G versus log $\dot{a}$ curve for relaxation controlled crack growth, the same gradient would be expected of an adhesive specimen.

In an earlier paper[1] the gradient of the log G_I versus log $\dot{a}$ curve was found to be around 0.3. However, when shrinkage stress was considered and the results replotted using the total strain energy release rate, G, the gradient became 0.135 ± 0.015 which is in reasonable agreement with the Williams and Marshall model.

It is suggested that the existence of a minimum strain energy release rate, below which crack growth ceases, and the failure of a pre-existing interfacial crack to extend under the action of shrinkage stress alone, are both due to crack blunting by relaxation processes causing a reduction in the intensity of the crack tip stress field.[12]

4.2. The adhesive–cohesive transition

The measurements of the adhesive and cohesive fracture surface energies in water suggest that the locus of failure changes to minimize the energy required for the formation of new fracture surfaces.

The rate of entry of water seems unlikely to be a cause of the transition. Williams and Marshall's model[9] predicts that a region with a gradient of 1.0 would occur near the transition velocity if flow control became important. The data from cohesive specimens shows no sign of such a region and if flow control does not occur in cohesive specimens near the transition velocity, it would be unlikely to do so in the adhesive specimens.

Furthermore, the earlier data[1] from adhesive specimens with various amounts of shrinkage stress showed that the transition occurred at about the same G_I value in specimens with different shrinkage stress and consequently, with the maximum interfacial crack propagation velocity varying by nearly an order of magnitude. If the rate of entry of water was a limiting factor, the transition velocity would be expected to be constant and essentially independent of shrinkage stress.

Another possible explanation for the adhesive to cohesive transition is that a stress activated reaction operating in the fracture process zone may eventually limit the crack growth rate. The kinetics of the reaction would be controlled by the stresses near the crack tip and the temperature. At low speeds the mechanism may proceed fast enough so that the propagation rate is limited by other factors, probably relaxation processes. Eventually, however, the reaction kinetics may be insufficient and a new fracture mechanism would become operative. Since no large difference is observed between the adhesive and cohesive fracture surface energies in water, on either side of the transition, it seems more likely that the same kind of stress activated reaction operates in both cases. Also since stable cracking occurs in both the epoxy resin and at the interface in adhesive specimens, only in the presence of water, it seems probable that the same process is involved in both cases. A change in reaction mechanism therefore seems unlikely to be the cause of the adhesive to cohesive transition.

4.3. The fracture surface

The scanning electron microscopy results were consistent with failure along the actual interface between the aluminium oxide and the epoxy resin as no residue could be observed.

The observation of replication on the epoxy surface cannot be taken as conclusive evidence that the locus of failure is at the interface. Bascom *et al.*,[14] has shown that this may be observed with mixed mode fracture of aluminium–epoxy specimens even though a residue of epoxy several tens of nanometers thick could be detected by ^{14}C labelling and Auger spectroscopy. However, recent work by Gettings *et al.*[15] has shown that epoxy–steel joints fractured after immersion in water had failed exactly at the interface between the adhesive and the hydrated oxide layer. This was established by the use of Auger and X-ray photoelectron spectroscopy and a similar result may be expected for joints which fail by slow crack growth.

5. CONCLUSIONS

Interfacial crack growth can occur only in the presence of both stress and water as shown previously.[1] The rate controlling process does not appear to be the diffusion rate of water into the polymer or the flow of water into the crack tip region. The observed dependence of crack velocity on the total strain energy release rate is, however, reasonably consistent with rate control by relaxation processes operating in the epoxy resin.

The mechanism of failure, on the molecular level, has not been unambiguously determined. It is unlikely that corrosion is important in forming a debonded area. Similarly the preferential adsorption theory has been found to be inadequate. Since stress and water are both required it seems probable that stress activated hydrolysis of metal oxide–polymer bonds is involved.

The following model of interfacial crack growth appears to be consistent with the available data, however it should be noted that the model proposed is speculative and that further work is required to provide firmer experimental support.

A stress concentrator is initially required at the interface to intensify the stress field established by the external loads in combination with shrinkage stresses. Water must also be available at the site of the stress concentration as would be the case for a small debonded area extending from an exposed edge.

The simultaneous presence of water and the stress field then allows a stress activated reaction to proceed at the tip of the initial flaw. The reaction preferentially severs bonds near the interface rather than those more distant from it and thus, the fracture process zone at the tip of the slowly moving crack is formed.

However, movement of the fracture process zone must be accompanied by movement of the fracture surfaces and by redistribution of the stress field. Plastic deformation of the polymer is therefore required and a plastic zone is set up extending into the polymer beyond the fracture process zone, where bond breaking is occurring. Relaxation processes in the plastic zone will operate and its size will reach equilibrium with the available strain energy release rate. Hence, the bond severing mechanism depending on the conjoint action of stress and water at the crack tip defines the locus of failure, though the rate of crack propagation is determined by the relaxation processes in the plastic zone.

If the available strain energy release rate is too small, the crack tip will deform, reducing the stress concentration and preventing crack growth. If it is too high, cohesive fracture is initiated.

Acknowledgement

Financial support to K. W. Thomson from the Electrical Research Board through Wilson Electric Transformer Co. is gratefully acknowledged.

References

1. B. W. Cherry and K. W. Thomson, *Intern. J. Polymeric Mater.* **7**, 191-201 (1979).
2. S. Mostovoy and E. J. Ripling, *J. App. Poly. Sci.* **13**, 1083–1111 (1969).
3. R. A. Gledhill and A. J. Kinloch, *J. Adhesion* **6**, 315–330 (1974).
4. C. Kerr and S. Orman, *Brit. Poly. J.* **2**, 97–103 (1970).
5. C. Kerr, N. C. MacDonald and S. Orman, *Brit. Poly. J.* **2**, 67–70 (1970).
6. D. D. Eley and R. Rudham, *Adhesion—Fundamentals and Practice*, MoT, Elsevier, pp. 92–102 (1969).
7. J. E. McCarty, AIAA paper no. 76–340, 15th Structures, Structural Dynamics and Materials Conference, Las Vegas (1974).
8. N. J. DeLollis, Handbook of Adhesive Bonding, ed. C. V. Cagle, McGraw-Hill, N.Y., pp. 2.1–2.16 (1973).
9. J. G. Williams and G. P. Marshall, *Proc. Roy. Soc.* **A342**, 55–77 (1975).
10. C. Gurney and J. Hunt, *Proc. Roy. Soc.* **A299**, 508–524 (1967).
11. S. Mostovoy, P. B. Crosley and E. J. Ripling, *J. Mat.* **2**, 661–681 (1967).
12. B. W. Cherry and K. W. Thomson, *Int. J. Frac.*, **14**, R17–R19 (1978).
13. R. L. Patrick, J. A. Brown, L. E. Verhoeven, E. J. Ripling and S. Mostovoy, *J. Adhesion* **1**, 136–141 (1969).
14. W. D. Bascom, C. O. Timmons and R. L. Jones, *J. Mat. Sci.* **10**, 1037–1048 (1975).
15. M. Gettings, F. S. Baker and A. J. Kinloch, *J. Appl. Poly. Sci.* **21**, 2375–2392 (1977).