preferential formation of β-Si_3N_4 at reaction temperatures above the silicon melting point.)

(5) α-Si_3N_4 cannot be directly converted to β-, at least under readily accessible conditions of temperature and pressure: the usual "transformations" observed involve a liquid phase in which β-Si_3N_4 precipitates following solution of α-Si_3N_4 [11, 12].

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On the opening and edge-sliding fracture toughness of aluminium–epoxy adhesive joints

Much work has already been done on the fracture mechanics and mechanisms of aluminium–epoxy adhesive joints for the opening fracture mode [1–4]. The critical strain energy release rate (G_{IC}) is usually used to characterize their crack propagation resistance. This follows from an energy balance approach of the fracture process which gives [5]

$$G_{IC} = \frac{P_c^2}{2B}\frac{dC}{da} \qquad (1)$$

where P_c is the fracture load, B the specimen thickness, a the crack length and C the compliance. In the evaluation of G_{IC}, C is experimentally determined and hence includes all compliance contributions due to the adherend, the adhesive and any crack tip plasticity effects.

Little work however has been reported to date on the critical stress intensity factor, or equivalently the fracture toughness (K_{IC}) [6, 7], for these aluminium–epoxy adhesive joints, even though it is a much more useful design parameter from the stress analysis viewpoint. In homogeneous isotropic materials, K-expressions for a wide range of test-piece geometries and loading configurations have been computed and are readily available in published literatures [8, 9]. Thus, in the most general form,

$$K = \sigma\sqrt{a}\phi \qquad (2)$$

where σ is the applied stress and ϕ is the shape correction factor. Equation 2 is however not directly applicable to two-phase materials such as aluminium–epoxy adhesive joints, and this explains why relatively few K_{IC} data exist. However, through some strenuous efforts and laborious finite element analyses, Trantina [6] and Stone *et al.* [7] have independently obtained an approximate K-expression for adhesive joints with very thin bond line thickness, which is related to the one-material solution of Equation 2. Thus,

$$\left(\frac{K_{al-ep}}{K_{al}}\right)^2 = \left(\frac{\phi_{al-ep}}{\phi_{al}}\right)^2 = \frac{E_{ep}\,G_{al-ep}}{E_{al}\,G_{al}}\ . \qquad (3)$$

Trantina [6] has also shown that the strain energy release rates G_{al} and G_{al-ep} are equal* so that Equation 3 is reduced to

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*Without going through the finite element analysis one can easily obtain that for a very thin bond line the compliance contribution due to the adhesive is negligible. It follows from Equation 1 therefore that $G_{al} = G_{al-ep}$.

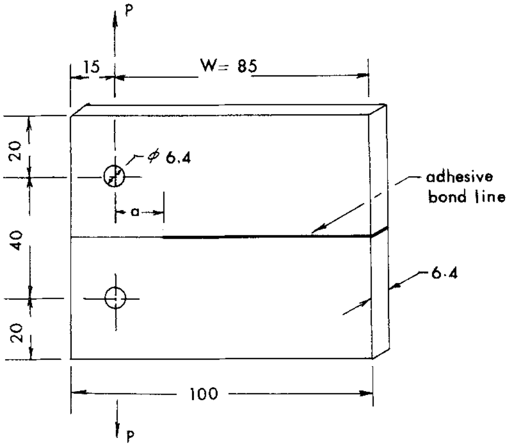

Figure 1 Mode I compact tension specimen. All dimensions in mm.

$$\left(\frac{K_{\text{al-ep}}}{K_{\text{al}}}\right)^2 = \left(\frac{\phi_{\text{al-ep}}}{\phi_{\text{al}}}\right)^2 = \frac{E_{\text{ep}}}{E_{\text{al}}}. \qquad (4)$$

This allows the critical stress intensity factor of the aluminium–epoxy adhesive joints to be determined from

$$K_{\text{IC}} = \sigma\sqrt{a}\,\phi\left(\frac{E_{\text{ep}}}{E_{\text{al}}}\right)^{1/2} = \sigma\sqrt{a}\,\phi^* \qquad (5)$$

where $\phi^* = \phi(E_{\text{ep}}/E_{\text{al}})^{1/2}$ is the equivalent shape correction factor taking into account the bond line effect. In Equations 3 to 5, E is the Young's modulus and the subscripts (al) and (ep) denote aluminium and epoxy resin respectively.

Since the opening fracture mode in aluminium–epoxy adhesive joints is the main concern in most previous studies little work has been conducted to date on the potentially significant edge-sliding fracture mode. Obviously, many more investigations are called for in order to understand the mechanics and mechanisms of the actual shear fracture process. Stone *et al.* [7] made the first effort, albeit unsuccessful, to study mode II shear fracture in aluminium–epoxy adhesive joints. Tapered double-cantilever-beam (DCB) specimens with two bond lines under apparently pure shear forces were used. However, as shown by their finite element analysis and subsequently proven by their experiments, Stone *et al.* found that the fracture process was actually mixed mode rather than purely edge-sliding. There is consequently a need to search for a better edge-sliding fracture specimen geometry. One such possibility (to be used in this work) is the compact shear test-piece developed by Chisholm and Jones [10] which is originally used for mode II shear fracture is homogeneous materials. From independent photo-elastic stress analysis experiments it has been proven [10] that the $K_{\text{I}}/K_{\text{II}}$ ratio is very small (~0.01) so that fracture is predominantly edge-sliding. Using boundary collocation techniques Chisholm and Jones have also computed values of the shape correction factor ϕ[†] for this compact shear test-piece. In order to allow for the anisotropy of the aluminium–epoxy adhesive specimens, the same modification as needed for the opening mode case is considered sufficient [11]. Thus, the critical stress intensity factor for shear fracture (K_{IIC}) is given by

$$K_{\text{IIC}} = \sigma\sqrt{a}\,\phi\left(\frac{E_{\text{ep}}}{E_{\text{al}}}\right)^{1/2} = \sigma\sqrt{a}\,\phi^* \qquad (6)$$

The present note reports some experimental results on both K_{IC} and K_{IIC} values of two 2024-aluminium–epoxy (Araldite GY250) adhesive systems, one cured with a primary amine (HY951) and the other with a tertiary amine (HY960). Compact tension specimens, Fig. 1, were used for the mode I tests and compact shear specimens, Fig. 2, were used for the mode II experiments. A special test rig for the compact shear specimens

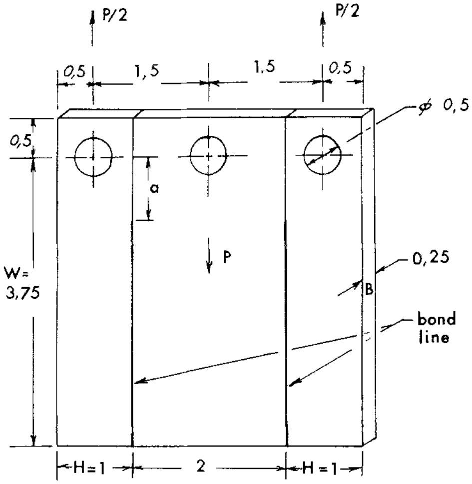

Figure 2 Mode II compact shear specimen. All dimensions in inches.

[†] Note that the mathematical expressions of the shape correction factors, ϕ and ϕ^*, in Equations 5 and 6 are entirely different. For consistencies in symbols however they have been used the same in these two equations.

TABLE I Adhesives employed and their cure schedules

Epoxy resin	Araldite GY250	Araldite GY250
Curing agent	Primary amine HY951 (triethylene tetramine)	Tertiary amine HY960 (dimethylamino-methyl phenol)
Parts per hundred of resin used	11.0	9.4
Cure schedule	2 h/23° C + 2 h/60° C	96 h/23° C + $1\frac{1}{4}$ h/100° C + $2\frac{1}{4}$ h/180° C
Young's modulus (Gpa)	3.0	3.0

was manufactured according to Chisholm and Jones [10] and the test set-up was shown in Fig. 3. The specimens were prepared as described below. The aluminium bonding surfaces were first milled using a sharp fly cutter, followed by wet sanding with 600 grit silicon carbide sandpaper on a rotatry surface grinder. A line designating the length of the adhesive to be used was then scribed faintly across the bonding surfaces which were subsequently degreased with acetone and rinsed thoroughly with tap water. The adhesive mixture was prepared with a hardener/resin composition as given in Table I. To control the length of the adhesive bond, a thin layer of petroleum jelly was spread up to the incribed line and the already prepared adhesive mixture was spread adjacent on the other side of the line. The aluminium adherends were then pressed together slightly and put into the oven for curing according to the schedules shown in Table I. This method of preparing adhesive specimens was found to be more effective than using teflon tapes as spacers. The average bond line thickness for all mode I and II specimens was 0.001 in. Petroleum jelly was found to have negligible effects on the fracture toughness of the adhesive joints by some other independent experiments. A total of more than 50 specimens for each fracture mode were prepared and tested with a Hounsfield Tensometer in this investigation. As a result of the relatively compliant testing machine all fracture experiments were remarkably unstable. Fracture loads (P_c) were recorded against the corresponding crack lengths (a). These measurements were subsequently used to calculate the critical stress intensity factors K_{IC} and K_{IIC} from Equations 5 and 6. Thus, for the opening fracture mode [8, 9],

$$K_{IC} = \frac{P_c}{BW^{1/2}} \left(\frac{E_{ep}}{E_{al}}\right)^{1/2} \times \left[29.6\,(a/W)^{1/2} - 185.5\,(a/W)^{3/2} + 655.7\,(a/W)^{5/2} - 1017\,(a/W)^{7/2} + 638.9\,(a/W)^{9/2}\right] \quad (7)$$

where $B = 6.35$ mm, $W = 85$ mm, $E_{al} = 70$ GPa and $E_{ep} = 3.0$ GPa. For the edge-sliding fracture mode [10],

$$K_{IIC} = \frac{P_c}{BH} \sqrt{a} \left(\frac{E_{ep}}{E_{al}}\right)^{1/2} \quad (8)$$

Since ϕ is unity for $H = 25.4$ mm and $W = 95$ mm over the range of $a/W = 0.2$ to 0.7 [10].

Fig. 4 shows the K_{IC} and K_{IIC} results for the aluminium–epoxy adhesive joints cured respectively with the primary (HY951) and the tertiary (HY960) amines. These results were also obtained as a function of (a/W) between 0.2 and 0.7. At least five tests were conducted at each crack length. The scatter in K_{IC} is found to be much smaller than that in K_{IIC}. In fact in the mode II shear fracture tests, occasionally an unusual low fracture load was obtained thus giving a very low

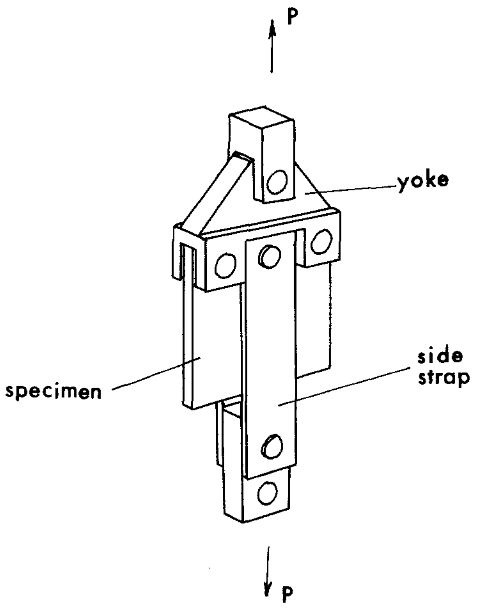

Figure 3 Test set-up for mode II shear fracture experiments.

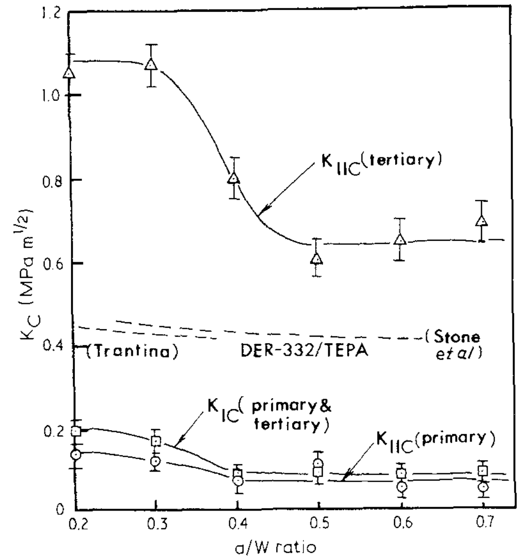

Figure 4 Mean fracture toughness (± 1 standard deviation) versus a/W for aluminium–epoxy adhesive joints.

K_{IIC} value. This is thought to be a consequence of the applied loading which incidentally is not in pure shear, since only a slight relative opening at the crack tip will cause the fracture load to drop remarkably. Such results have not been included in Fig. 4. It is highly desirable that other mode II fracture specimen geometries be developed in future investigations to validate these K_{IIC} results obtained with the compact-shear specimens. Work towards this direction is presently in progress.

Returning to Fig. 4 it should be noted that for the adhesive joints cured with the primary amine, K_{IC} and K_{IIC} are of the same order of magnitude over the entire a/W range. The mean fracture toughness value remains constant at 0.07 MPa m$^{1/2}$ for $0.4 < a/W < 0.7$ and then increases to 0.14 MPa m$^{1/2}$ at $a/W = 0.2$. The tertiary amine cured adhesive joints have K_{IC} values close to those obtained for the primary amine cured joints. It is not possible to show these minimal differences in Fig. 4. However, the K_{IIC} values are obviously very much larger than the K_{IC} values at corresponding a/W ratios. K_{IIC} is approximately constant at 0.64 MPa m$^{1/2}$ for $0.5 < a/W < 0.7$ and then rises to 1.05 MPa m$^{1/2}$ at $a/W = 0.2$*. This fracture behaviour is very different from the primary amine cured adhesive joints where both K_{IC} and K_{IIC} values are nearly equal. Physically this means that tertiary amine-cured adhesive joints are more resistant to edge-sliding fracture than opening fracture. It is suspected that the ability of the large spherical nodules (~410 Å) in tertiary amine adhesives to sustain considerable plastic shear deformations before eventual fracture [12] is the main cause of these large K_{IIC} values. Obviously more thorough investigations are needed to confirm this proposition.

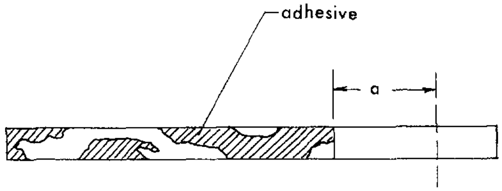

Figure 5 Typical mode I and mode II fractured surfaces.

The K_{IC} results for the aluminium–epoxy (DER-332/TEPA) adhesive joints obtained by Trantina [6] and Stone *et al.* [7] are also shown in dotted lines in Fig. 4. Both single edge notched and tapered DCB specimens were employed in their studies. It may be seen that the K_{IC} results of the present work are much lower than their average K_{IC} value of 0.42 MPa m$^{1/2}$. This is probably due primarily to the difference in the quality of surface preparation. Alumina grit blasting and chromic acid etching of surfaces to be bonded were not used in this investigation.

Detailed examinations of the fracture surfaces have not been performed in this preliminary work. However, the surface features were similar for both the opening and edge-sliding fractured specimens. Intermittent fracture close to the interfaces and shear fracture across the adhesive have been recorded (see Fig. 5). It is also noted that fracture always occurs along one bond line rather than on both bond lines in the mode II shear fracture experiments.

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*It seems necessary in future investigations to understand whether this variation of K_{IC} and K_{IIC} and a/W is a geometric or a genuine effect.

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Effect of environment on stability of cracking in brittle polymers

We have recently commenced an investigation of environmental stress cracking in polymers by performing double torsion tests on PMMA in methanol. We were impressed by the close resemblance between our observations and work which has been reported on epoxy resin systems during the last few months both in this Journal [1] and elsewhere [2]. This leads us to offer some comments on the question of unstable crack propagation.

S. Yamini and R. J. Young [2] studying epoxy resins, used double-torsion specimens and an Instron testing machine. In tests at room temperature in air, cracking was found to be stable at high cross-head speeds, of about 1 mm min^{-1}. That is to say, crack speed and load remained constant over several centimetres of crack growth (cf. Fig. 1b, from the present work). It follows from the geometry of the double torsion test that stress intensity, K, similarly remained constant. At lower cross-head speeds a region of unstable or "stick–slip" cracking was encountered (cf. Fig. 1a). With progressive decrease in cross-head speed, the stress intensity for crack jump initiation, K_{Ii}, increased markedly, while K_{Ia}, for the crack arrest condition, changed very little. Tests performed to study the influence of environment showed that immersion in distilled water caused crack jumping to set in earlier (i.e. with less decrease in cross-head speed) but that testing under vacuum did not suppress unstable cracking. Yamini and Young concluded that although environment may influence the matter, crack-jumping is an intrinsic property of the epoxy resin material. This viewpoint is shared by other workers. A. D. S. Diggwa [3] showed that crack-jumping could be observed in the presence or in the absence of a water environment, but was unable to distinguish clearly environmental effects from inherent chemical effects. Other workers have taken inherent crack-jumping behaviour as a starting point and discussed its analysis and interpretation [4–7].

Previous work on PMMA in liquid environments has either not been concerned with unstable crack propagation [8, 15], or has involved different experimental techniques [9]. An important exception is the work of Y. W. Mai [10] who observed crack-jumping in double-torsion tests on PMMA in several environments, not including methanol. For our purpose, the relevant points from Mai's wide-ranging study are: first, immersion in a liquid environment gives values of K_{Ii} lower than K_{c} for stable crack propagation in air. Second, increasing cross-head speed causes K_{Ii} to increase for all PMMA/environment systems studied; in some cases this rate of increase is very rapid. Third, a crack growing in dry PMMA under stable (constant K) conditions is arrested by the introduction of a liquid at the crack tip. This causes the load to increase, and propagation to become unstable. Finally, these observations are rationalized by a theory attributed to Gurney and Hunt [11] whereby the crack is arrested by blunting of the tip in material plasticized by the environment; crack-jumping involves the breaking-out of the crack into virgin material, under conditions where $K > K_{\mathrm{c}}$.

In our experiments, samples were cut from 6.25 mm "Perspex" sheet to the same dimensions as those used by G. P. Marshall *et al.* [12] i.e.