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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 $K > K_c$.

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.
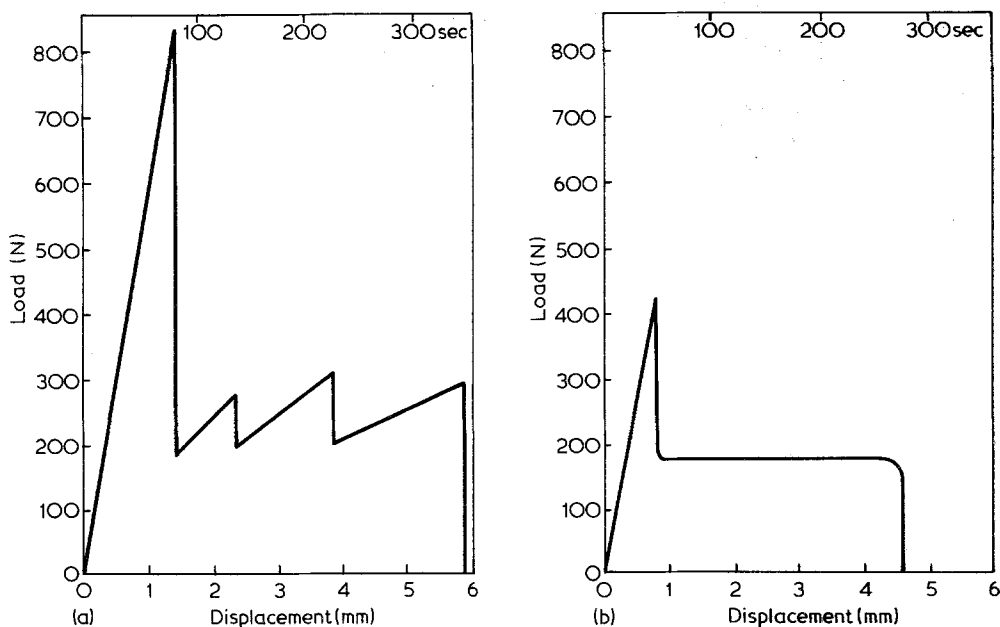
Figure 1 (a) Load–deflection curve for double torsion test PMMA in methanol. Cross-head speed 1.0 mm min^{-1}. (b) Load–deflection curve for double torsion test. PMMA in air. Cross-head speed 1.0 mm min^{-1}.

80 mm wide, with central grooves 1 mm deep × 0.1 mm wide to contain the crack. To control initiation of the crack a Vee notch was milled at one end of the sample and a scalpel blade was pressed into the root using an attachment fitted to a Vickers hardness testing machine [13]. The moment arm employed to bend the sample was 27 mm and the bulk of tests so far have used a cross-head speed of 1 mm min^{-1} in an Instron testing machine. Prior to immersion in a bath of methanol, samples were coated with grease to prevent surface crazing. Under these conditions very consistent crack-jumping behaviour has been observed. Fig. 1a shows a representative load–deflection curve. The initial peak varies markedly in height from sample to sample, and evidently reflects the quality of the pre-formed crack. Thereafter the second and subsequent peaks show only slight variation. For twenty-four peaks observed over eight samples representing three orientations with respect to the long direction of a single cast sheet, the mean value of K_{Ii} was 1.96 ± 0.2 MN m$^{-3/2}$. Variance analysis showed the absence of any trend in K_{Ii} with sample orientation or with successive peaks in the same test. With respect to K_{Ia}, the mean value was 1.27 ± 0.16 MN m$^{-3/2}$, again with no significant effect of orientation, but with a tendency for the higher

values to be observed after second or third peaks in the same test.

PMMA is of course widely recognized as a material which exhibits stable crack propagation in air [13–15]. In our own tests on dry PMMA, performed with a view to establishing our technique, cracking was indeed stable, (Fig. 1b) and the value of K_c obtained, 1.11 ± 0.04 MN m$^{-3/2}$ for a crack speed of (0.95 ± 0.04) × 10^{-3} m sec^{-1} is in very good agreement with published values [12, 15]. Variables shown by these tests to be non-significant in relation to K_c are orientation (see above) and the presence or absence of a coating of petroleum jelly on the specimen. It will be noted that in agreement with Yamini and Young [2] we find K_c for stable crack propagation in air to be comparable with K_{Ia} for unstable crack propagation, while K_{Ii} is appreciably higher.

Investigations into the effect of cross-head speed are at a very early stage, but we have observed at a speed of 20 mm min^{-1} a significant reduction in the value of K_{Ii} to 1.76 ± 0.14 MN m$^{-3/2}$. The corresponding value of K_{Ia} is 1.29 ± 0.08 MN m$^{-3/2}$, not distinguishable from the figure at lower speed. Again, comparison with [2] is invited. It is appropriate at this point to remark a further very close similarity between the behaviour of our PMMA/methanol samples and

epoxy resin samples as reported in an earlier paper of R. J. Young [1]. The fracture appearance of samples which exhibited crack-jumping is virtually indistinguishable between the two systems. (See Fig. 3a of [1]). A similar mechanism is therefore strongly implied.

Concerning the general problem of unstable crack propagation, points for discussion are; first, the similarity in behaviour between PMMA in contact with methanol, and epoxy resin in contact with air, water or vacuum [2]; and second, the apparent difference in behaviour between PMMA/methanol reported here and, for example, PMMA/ethanol in other work [10].

The basic requirement for unstable crack propagation is stated to be [4] that the specific work of fracture, R, decrease with increasing crack speed $\dot{a}$, i.e. $\mathrm{d}R/\mathrm{d}\dot{a}$ shall be negative. In equivalent terms, $\dfrac{\mathrm{d}}{\mathrm{d}\dot{a}}(K_c)$ must be negative.

Epoxy resins, it is argued, fulfil this requirement by their inherent chemical characteristics, and any effect of environment is marginal [4]. PMMA is reliably reported to show an increase in K_c with crack speed, at least up to $0.1\,\mathrm{m\,sec^{-1}}$ [12] so that $\dfrac{\mathrm{d}}{\mathrm{d}\dot{a}}(K_c)$ must be inherently positive. It would seem that the observation of crack-jumping behaviour in such a material must be attributed exclusively to the effect of environment, probably through some such mechanism as has been described above [11]. We should thus re-examine the possibility that epoxy resins show crack-jumping behaviour because of an environmental effect. The idea is supported by the remarkably similar fracture appearance in the two types of system, and by the similar relationships of parameters K_c, K_{Ii} and K_{Ia}. It will be further supported if tests confirm the initial indication that K_{Ii} for PMMA in methanol decreases at higher cross-head speeds in the double-torsion test. At the same time, the evidence against an environmental mechanism presented by fracture tests on epoxies in a vacuum chamber [2] is not conclusive. A polymer at room temperature would be expected to carry an appreciable quantity of adsorbed water. While continuous pumping may hold the chamber pressure at 2×10^{-2} Torr, the presence of localized regions of higher moisture concentration on the specimen cannot be ruled out. Small surface cavities or cracks would be ideal sites for such traps, and the residue of liquid could promote the observed crack jumping.

One point from the work of Yamini and Young which has not been discussed is their observation that, at a fixed cross-head speed, unstable cracking sets in when the temperature is raised. This might be difficult to explain by an environmental mechanism, and we do not wish to speculate, but we suggest that on a basis of the other evidence, such a mechanism should be further considered.

Concerning our second point for discussion, the apparent discrepancy between our work on PMMA/methanol and that of Mai on closely similar systems, there seem to be two possibilities. One is that methanol is anomalous in its behaviour towards PMMA, and other evidence [16] suggests that this may be so. The other possible explanation lies in the different cross-head speeds used in the two investigations, which were otherwise geometrically similar. We have said that in Mai's work K_{Ii} increased very rapidly with cross-head speed, whereas K_c for tests in air changes quite slowly. A fivefold increase in cross-head speed could easily cause the inversion from $K_{Ii} < K_c$ (Mai, $0.2\,\mathrm{mm\,sec^{-1}}$) to $K_{Ii} > K_c$ (this work, $1\,\mathrm{mm\,sec^{-1}}$). We should like to return to this point when more evidence has been accumulated.

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Comments on "Effect of environment on stability of cracking in brittle polymers"

We would like to take this opportunity to comment upon the recent letter of Hakeem and Phillips [1] concerning the stability of crack propagation in brittle polymers. They have rightly pointed out the similarity between this phenomenon in poly-methylmethacrylate (PMMA) in methanol and epoxy resins. They suggested that since these two phenomena are apparently very similar that they could possibly be due to a similar mechanism. They have noted in both cases the tendency for crack propagation to become more stable at high cross-head speeds and suggested that this might be because of environmental attack; in the case of PMMA by methanol and in epoxy resins possibly by water vapour in the air or adsorbed by the sample. We would agree with their conclusions from the evidence they have cited and in fact one of us [2] came to a similar conclusion several years ago. However, further investigation of this hypothesis does not confirm the environmental mechanism that the evidence seems to suggest at first sight.

The critical experiment is to look at the propagation of cracks in epoxy resins in a completely dry environment. It was expected that, for example, under vacuum if environmental water vapour was causing jumping that in this case propagation should be continuous as for example in PMMA in air. To the disappointment of the authors it was found that when epoxy resins were tested under vacuum (0.02 Torr) that crack propagation was by a stick-slip mechanism at slow cross-head speeds and so indistinguishable from propagation was by a stick–slip mechanism at slow fore left with no option but to modify our hypothesis and conclude that the instability was an inherent property of the material and not

dependent upon environmental water vapour. Hakeem and Phillips [1] have rightly pointed out that the test in vacuum is not conclusive. Adsorbed water in the specimen may lead to localized regions of high moisture concentration in the specimen. Having done our critical experiment and obtained a negative result we were still not absolutely sure that the environmental mechanism
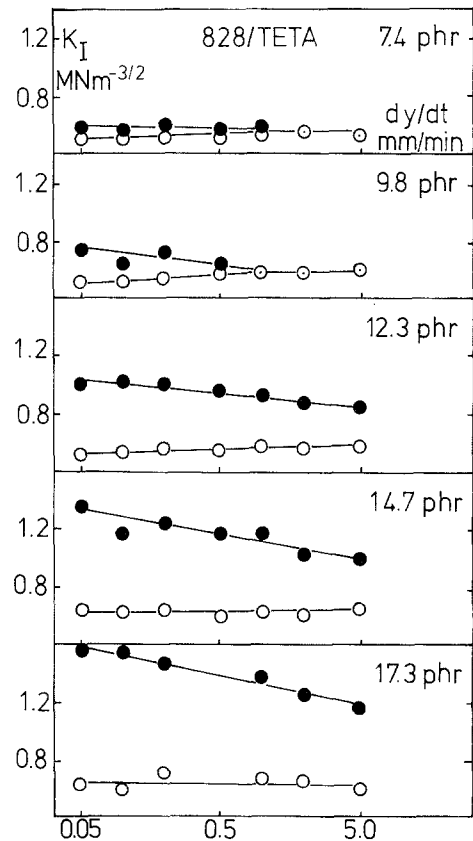

Figure 1 Variation of K_{Ii} and K_{Ia} with cross-head speed in resins cured for 3 h at 100° C with different stated amounts of hardener. ● K_{Ii}; ○ K_{Ia}; ◉ K_{I} continuous (phr means parts of hardener by weight per hundred parts of resin).