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

In a recent communication, Hakeem and Phillips [1] have commented on two very interesting problems concerning the effect of environment on stability of cracking in brittle polymers. The first problem deals with stick–slip crack propagation in epoxy resins. Because of the close resemblance between their experimental observations on cracking of PMMA in methanol and those by Yamini and Young [2] on epoxy resins, they suggested that the yet unresolved cause of crack instability in epoxy resins might be just an environmental effect. In replying, however, Yamini and Young [3] based on their most recent experimental findings felt that crack propagation in epoxy resins was principally controlled by the structure of the material and that any environmental effect was negligible. We do not wish to add anything further here at present but agree that much more work is needed to pin down the exact mechanisms of crack instability in epoxy resins. Although it has been suggested by Gledhill *et al.* [4] that the decrease of the specific work of fracture, R, with crack speed $\dot{a}$; i.e. $\mathrm{d}R/\mathrm{d}\dot{a}$ negative [5], is not the cause but rather the consequence of stick–slip cracking, from the crack mechanics viewpoint, we wish to stress that $\mathrm{d}R/\mathrm{d}\dot{a}$ or $\mathrm{d}R/\mathrm{d}a$ negative is a neccessary condition for crack instability [5, 6]. In conclusion, Yamini and Young mention that polystyrene is an example where unstable cracking occurs in the absence of an environmental effect. While this is so, the implication that similar processes are taking place at the crack tip in epoxy resins as in polystyrene to give stick–slip fracture seems questionable. Our initial experience [7] with double torsion polystyrene specimens pre-notched in the "normal" way with a razor blade show that in the cross-head speed range of 0.05 mm min^{-1} to 50 mm min^{-1} in the Instron machine the transition speed between stable continuous and unstable stick–slip cracking increases with increasing temperature (e.g. 0.5, 2 and 10 mm min^{-1} for 40, 60 and 80° C respectively) and that at a given temperature stable cracking occurs below this transition cross-head speed and stick–slip fracture occurs above. This latter behaviour is opposite to that in epoxy resins and the reason is not fully understood. A better example which gives stick–slip fracture in the absence of an environmental effect is TPX (poly(4-methyl-*l*-pentane)) [6]. The cause of instability has not been studied in details yet but it is probably due to crack tip blunting as a result of its very large fracture toughness value. A parallel study on TPX may thus give new insight into the mechanisms of fracture instability in epoxy resins.

The second problem that Hakeem and Phillips discussed concerns the apparently different fracture behaviour between PMMA–methanol and PMMA–ethanol systems. They found that the crack initiation (K_i) values of PMMA at 1 and 20 mm min^{-1} cross-head rates in methanol were always greater than the corresponding K_c values in air and that the K_i value was larger for the slower cross-head speed. However for the PMMA–ethanol experiments reported in [8], K_i was found to be less than K_c in air. They suggested that therefore it was possible that methanol was anomalous in its behaviour towards PMMA and that a five-fold increase in the corss-head rate of the Instron machine could cause an inversion from $K_\mathrm{i} < K_\mathrm{c}$ to $K_\mathrm{i} > K_\mathrm{c}$ (since K_i increased very rapidly with cross-head speed [8]). We have just finished an experimental investigation on the environmental

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stress cracking of PMMA in some twenty organic solvents [9] including a series of primary alcohols using the solubility parameter approach. We feel that we cannot entirely agree with the explanations of Hakeem and Phillips [1] and we think that the discrepancy is probably caused by the different definitions of K_i used in their work and in [8]. Certain aspects of this investigation [9] which are relevant to the discussion on stability of cracking in liquid environments are given presently in this communication.

Plasticization of the crack tip material by absorption of environment produces two effects competing against each other. The reduction of the polymer glass transition temperature together with the presence of a dilatant stress make crazing at the crack tip easier to occur. However, plasticization and subsequent crazing also effectively blunt the crack tip so that the stress concentration factor is markedly reduced. The sequence of events in a fracture experiment under monotonic increasing displacement conditions (such as in an Instron machine) are as follows. The onset of craze–crack growth as a result of the first effect of plasticization commences at a very small load thus giving a low K_i value, much smaller than K_c in air. This occurs very early on the linear part of the load–displacement curve since the steady craze–crack growth is usually about 0.25–2 mm, which is not enough to cause marked changes in the compliance. K_i is independent of specimen geometry but is strongly dependent on strain rate [8]. As crazes are gradually developed the crack tip becomes blunted, so to cause further crack growth, a larger load is needed. Eventually, softening of the locally plasticized crack tip material gives $(\partial R/\partial a) < (\partial G/\partial a)$ so that unstable cracking occurs.* Note that G is the strain energy release rate. The magnitude of this instability load gives the unstable K_c value, which we believe has been defined by Hakeem and Phillips [1] as their K_i. If this is so, the apparent discrepancy between their work and ours [8] can be explained. It should however be noted that this instability K_c value is mainly affected by the specimen geometry which in turn determines the pattern of crazes at the crack tip. Usually, K_c is much larger in the liquid environment than in air as measured by Hakeem and Phillips due to a much sharper crack tip in the latter condition. Our preliminary experiments conducted on razor notched single edge tension PMMA specimens immersed in methanol show that the instability K_c value decreases with cross-head speed as illustrated schematically in Fig. 1. For example, in methanol, mean instability K_c values from three tests are 2.93, 3.30 and 3.95 MPa $m^{1/2}$ at cross-head speeds of 20, 10 and 1 mm min^{-1} respectively. These K_c values at 1 and 20 mm min^{-1} are obviously much larger than those reported by Hakeem and Phillips [1], probably because they have used double torsion specimens in which the grooves would have severely limited the size and confined the development of the crazes at the crack tip. It is not easy to measure optically K_i at high corss-head rates and it is probable that under these extreme conditions K_c (air) $= K_i$ (environment) $=$ K_c (environment). Note that instability K_c (air) values are invariant with cross-head rate. Depending on which one of the two possible K_i loci shown in Fig. 1 is really taking place and until such experimental results are obtained, it is unwise to conclude whether $K_i > K_c$ (air) can happen.

At very high strain rates, such as under impact conditions, one tends to think that since the time scale of liquid absorption would greatly exceed that required to fracture, environmental effects, if any, could be neglected. Fig. 2 shows some recent experimental impact data of razor notched PMMA Charpy specimens in air and in methanol. The

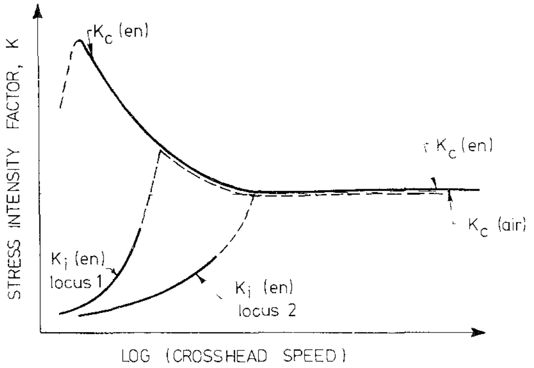

Figure 1 Schematic showing variation of K_i and K_c in liquid environments and K_c in air with cross-head rate.

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*It has been shown however in [8] that depending on the specimen geometry continuous stable cracking can take place by an appropriate choice of cross-head rates so that a newly created craze zone is always ahead of the propagating crack-front.

TABLE I Experimental results for PMMA immersed in primary alcohols* [9]

Environment	Flory–Huggins interaction parameter [9] (χ_H)	Critical strain (ϵ_c)(%)	Stress intensity factors (MPa m$^{1/2}$)	
			Initiation (K_i)	Instability (K_c)
Methanol	2.75	0.50(0.31)†	0.027	1.49
Ethanol	3.08	0.34	0.030	1.54
Propanol	3.85	0.33	0.107	2.15
Butanol	4.91	0.35	0.164	2.39
Pentanol	6.26	0.41	0.187	2.40
Hexanol	7.18	0.44	0.149	2.19
Octanol	12.08	0.58	0.206	2.30

*Experiments were performed at 23° C and 50% r.h. Cross-head speed for K-testing was ~ 2×10^{-1} mm min^{-1}.

†Value from Vincent and Raha [12].

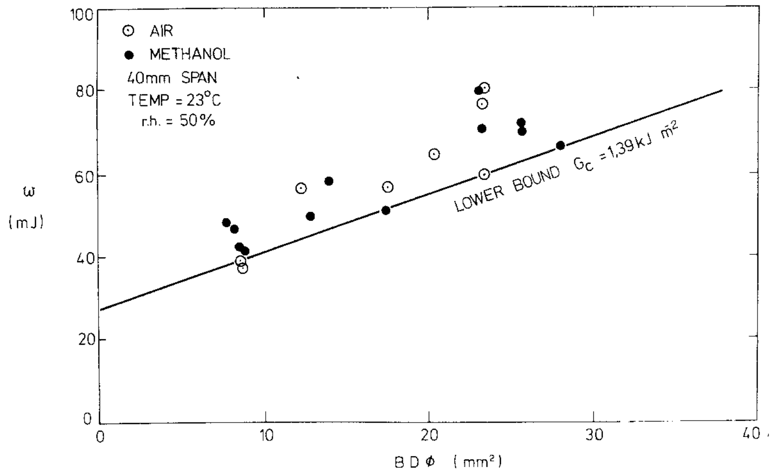

Figure 2 Data of PMMA in air and in methanol.

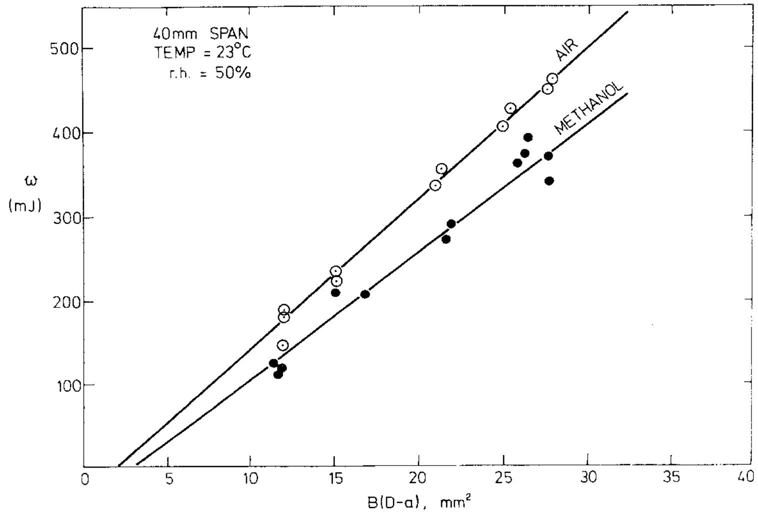

Figure 3 Charpy impact data of ABS in air and in methanol.

striking velocity is 3.3 m sec^{-1}. Analysis of these data using linear elastic fracture mechanics [10] shows that $G_c \simeq 1.39\,\text{kJ}\,\text{m}^{-2}$ (i.e. $K_c \simeq 1.94$ MPa m$^{1/2}$) in both air and methanol thus confirming the absence of an environmental effect at these extremely high strain rates. It is however worth mentioning that similar impact experiments performed on a more ductile polymer, ABS, give lower impact energy values (ω) in methanol than in air at equivalent ligament areas, $B(D-a)$, as shown in Fig. 3. This suggests that the picture is more complicated than is originally thought and assessment of impact fracture resistance of polymers in liquid environments should be a subject of technological importance which requires further studies in the future.

Table I summarizes our recent experimental results obtained in a series of primary alcohols. It is shown that in general terms both ϵ_c and K_i increase with the Flory–Huggins interaction parameter (χ_H). The instability K_c values although show a similar trend their magnitudes are determined principally by the relative sizes of the crack tip craze bundles prior to unstable fracture. From methanol to pentanol, the craze size increases as the molar volume increases. It is also noted that in the course of the critical strain measurement experiments [9] we have observed, as Phillips does, that methanol (AR grade) behaves somewhat differently to PMMA than the other alcohols. Compared with say ethanol which produces many fine crazes in PMMA the crazes created in methanol are relatively few in number but larger in size. A full discussion on this subject will be contained in a future publication [11].

Note added in proof

Although the cause of "stick–slip" fracture is not fully known, reanalysis of Mai and Atkins' data [5] shows that for the particular epoxy resin they studied "stick–slip" may be due to an isothermal –adiabatic transition. Using Equations 12 and 13 in [13] the instability crack velocity is calculated to be some 0.2 m sec^{-1} when $T = 298\,\text{K}$ and the crack tip temperature rise is approximately 8° C. These calculated results are in good agreement with the experimental data presented in [5].

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Discussion of "Microstructural characterization of 'REFEL' (reaction-bonded) silicon carbides"

Sawyer and Page [1], in studying the microstructure of "REFEL" reaction-sintered SiC, claim that, "... in contrast to previous descriptions of the microstructure, it has been found that the newly-formed SiC is deposited from the supersaturated solution of carbon in molten silicon both epitaxially on the original SiC grains, maintaining the same α-polytypic stacking sequences, and by nucleation of fine cubic β-SiC elsewhere". The main thrust of their argument is that, while the SiC that

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