13. G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, *Plastics Polymers* (1969) 75.
14. J. G. WILLIAMS, J. C. RADON and C. E. TURNER, *Polymer Eng. Sci.* (1968) 130.
15. P. W. R. BEAUMONT and R. J. YOUNG, *J. Mater. Sci.* **10** (1975) 1334.
16. M. G. PHILLIPS, unpublished research, Bath University (1976).

Received 31 January
and accepted 3 March 1978.

M. I. HAKEEM
M. G. PHILLIPS
School of Materials Science,
The University,
Bath, UK

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 polymethylmethacrylate (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

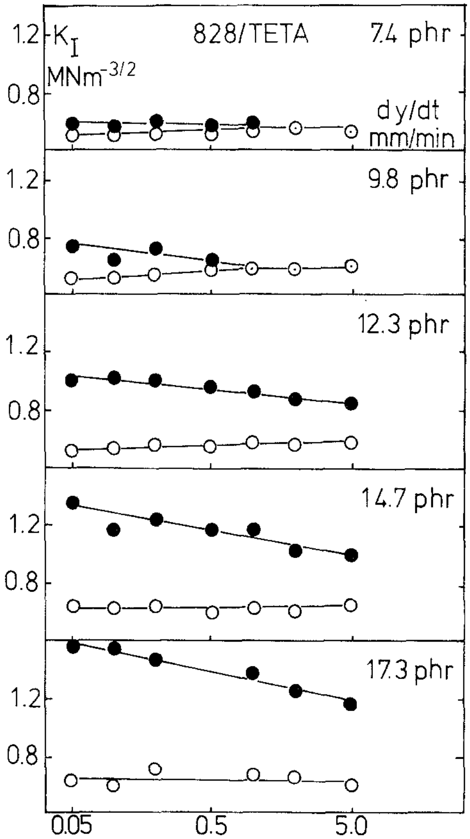

Figure 1 Variation of K_{Ii} and K_{Ia} with cross-head speed in resins cured for 3 h at 100° C with different stated amounts of hardener. ● K_{Ii}; ○ K_{Ia}; ⊙ K_I continuous (phr means parts of hardener by weight per hundred parts of resin).

was incorrect, and so we pursued another course to try to tie down the mechanism. More recently we have looked at the effect of temperature, the amount of curing agent and effect of curing conditions upon the stability of crack propagation in epoxy resins [4, 5].

From these recent investigations we feel more confident that the stability of crack propagation is a material property but still we cannot entirely rule out the environmental mechanism. Of course, water does have at least a secondary effect in that propagation in liquid water tends to be more unstable than in laboratory air. This work will be reported more fully later but we think that it would be worthwhile to present some of the more significant results at this stage. All the crack propagation tests have been done using the double torsion geometry [3] and the resin used was Epikote 828 with triethylene tetramine as hardener. We have looked at the effect of altering several variables and the results are given below.

(1) Effect of variation of amount of curing agent with constant curing conditions (3 h at 100° C): Fig. 1 shows the effect of the amount of hardener upon the stability of crack propagation. It can be seen that at a given cross-head speed the difference between K_{Ii} and K_{Ia} increases as the amount of hardener is increased. This can be due to the environmental mechanism if the amount of hardener present affects the susceptibility to environmental attack.

(2) Effect of variation of curing temperature with a constant amount of curing agent (9.8 phr)* and a constant curing time (3 h): Fig. 2 shows the effect of curing temperature upon the stability of crack propagation. It can be seen that at a given cross-head speed the difference between K_{Ii} and K_{Ia} increases as the temperature of curing increases. This is even more difficult to reconcile with the environmental mechanism since in each case the amount of hardener and curing time are the same. Unless the different curing temperatures produce different structures which have a different susceptibility to environmental attack we find it difficult to see how an environmental mechanism would work.

In this letter it is not possible to present any more results but we have shown [3] for instance that by testing at different temperatures the tendency for unstable propagation becomes more pronounced as the glass transition temperature is approached. Hakeem and Phillips have admitted that this is difficult to explain by an environmental mechanism. Also we have examined the comprehensive yield behaviour of different formulations of resin and hardener and found large variations in the comprehensive yield stress which appear to follow variations in the crack propagation characteristics. It is extremely unlikely that the environment would have any effect upon the yield mechanisms.

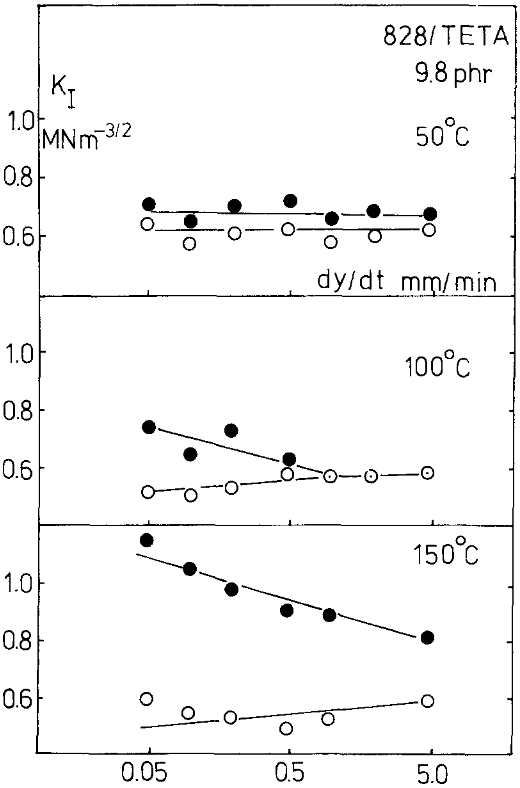

Figure 2 Variations of K_{Ii} and K_{Ia} with cross-head speed in resins with 9.8 phr of hardener cured for 3 h at different stated temperatures. ● K_{Ii}; ○ K_{Ia}; ⊙ K_I continuous.

In conclusion we would like to state that we feel that crack propagation in epoxy resins is controlled principally by the structure of the material and that water vapour in the environment has very little effect. We agree with Hakeem and Phillips that at first sight the stability of crack propagation would appear to be environmentally

---

*phr = parts of hardener by weight per hundred parts of resin.

controlled, as for example with PMMA in methanol. However, tests of this hypothesis do not appear to bear this out. Another example of unstable crack propagation in the absence of any environmental effects is with polystyrene [6]. Crack propagation is unstable when specimens are pre-cracked in a "normal" way. However, when a high frequency fatigue crack is put in the specimen as a starter crack, propagation is found to be continuous. The reason for this is thought to be the presence of branched crazes in the ordinary pre-cracked specimens and a sharp single craze at the tip of the fatigued crack. It may be that similar processes are taking place at the crack tip in epoxy resins although there is little evidence for crazing [4]. The phenomenon of crack propagation in epoxy resins is still not fully understood and we feel that there is still a great deal to be done before we have a complete answer to all the questions that can be raised.

References

1. M. I. HAKEEM and M. G. PHILLIPS, *J. Mater. Sci* **13** (1978) 2284.
2. R. J. YOUNG and P. W. R. BEAUMONT, *ibid.* **11** (1976) 776.
3. S. YAMINI and R. J. YOUNG, *Polymer* **18** (1977) 1075.
4. R. A. GLEDHILL, A. J. KINLOCH, S. YAMINI and R. J. YOUNG, *ibid*, **19** (1978) 574.
5. S. YAMINI and R. J. YOUNG, to be published.
6. G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, *Int. J. Fract.* 9 (1973) 295.

Received 15 March
and accepted 20 March 1978.

S. YAMINI
R. J. YOUNG
Department of Materials,
Queen Mary College,
University of London, UK

The combined effects of Fe and H_2 on the kinetics of silicon nitridation

Mechanisms have recently been proposed to explain how Fe additions to silicon influence the nitriding reaction [1, 2]. It has been shown that Fe promotes the removal of the silica layer covering the silicon particles and, through liquid phase reactions, encourages the growth of β-Si_3N_4; it also promotes α-Si_3N_4 growth, and it was suggested that this occurs because the formation of Fe/Si liquid, at the reaction temperature, suppresses the development of the reaction-inhibiting coherent layers of nitride.

It is known that additions of H_2 to the nitriding atmosphere increase the nitriding rate [3] and influence growth morphology [4], and in this brief note we report some preliminary data relating to the combined effects of Fe and H_2 on the reaction.

Compacts were formed by isostatically pressing ($210\,MN\,m^{-2}$) specially prepared high purity silicon powder (particle size $<8\,\mu m$) [5]; where required, 0.5 wt% iron powder, having similar particle size, was well mixed with the silicon. The compacts were nitrided at 1360° C in a system described previously [5], the weight changes being monitored continuously to provide the kinetic data in Fig. 1.

The forms of the curves for pure and Fe-contaminated silicon, reacted in pure nitrogen (Curves A and B respectively) have been discussed previously [6]. The addition of 5 vol% H_2 to the nitriding gas (Curve C) leads to the expected marked increase on the overall reaction rate. The point we would like to stress here is the very fast kinetics for the iron-contaminated silicon, nitrided in N_2/H_2 atmospheres (Curve D).

A consideration of the rate of evaporation of Si at the reaction temperature and the observed rates of nitride formation, leads us to believe that the dominant nitriding reaction with pure N_2 is the vapour phase nitridation of silicon. This is contrary to a long-held view [7, 8] that the nitridation of silicon monoxide according to [1] is the major reaction.

$$3SiO(g) + 2N_2(g) = Si_3N_4(s) + \tfrac{3}{2}O_2(g) \quad (1)$$

Although the stated objection to Reaction 1 on thermodynamic grounds is invalid [9, 10], it can be excluded on kinetic grounds, since the rate of removal of oxygen from the Si_3N_4 formation site is many orders of magnitude too low to sustain the observed reaction rates.