Stability of crack propagation in epoxy resins

S. Yamini and R. J. Young
Department of Materials, Queen Mary College, Mile End Road, London E1 4NS, UK
(Received 23 May 1977)

The propagation of cracks in epoxy resins has been studied using a linear elastic fracture mechanics approach and a double torsion testing geometry. Under constant crosshead displacement rate conditions cracks are found to propagate in an unstable 'stick–slip' manner at high temperatures and with low rates of testing whereas at lower temperatures and using higher rates of loading propagation is more stable and cracks propagate in a continuous manner. The presence of liquid water tends to cause a transition from stable to unstable propagation at room temperature. The influence of specimen geometry upon crack stability is also discussed.

INTRODUCTION

Epoxy resins are now widely used in structural applications. They are often used as adhesives or matrix materials for composites and because of the structural applications the prediction of the strength of such components is vitally important. Such predictions are normally made using linear elastic fracture mechanics[1]. This approach has been used to investigate crack propagation in brittle polymers such as poly(methyl methacrylate)[2–4]. However, as far as epoxy resins are concerned much of the effort has been concerned with crack propagation in adhesive test pieces[5–10] and until recently crack propagation in the resin alone had not received so much attention[11–15]. It is now becoming apparent that before crack propagation in the adhesive case can be understood, crack propagation in the resin alone must be fully characterized.

Crack propagation in epoxy resins has in the past been rather difficult to control and many investigators have produced results which have appeared to be inconsistent in themselves[14] and to contradict the work of others[15–17]. Many of these problems have stemmed from the widely reported observation that epoxy resins are prone to crack propagation sometimes by means of a continuous (stable) mode and at other times by means of a crack jumping (unstable or 'stick–slip') mode[11–15]. The different types of load–displacement curves which arise from these different modes of crack propagation are illustrated schematically in *Figure 1*.

The stability of cracking in epoxy resins has been shown to vary with type and amount of curing agent and heat treatment, environment and testing rate[11]. In addition it has recently become clear that the specimen geometry can exert an influence on crack propagation in materials that are prone to unstable crack propagation[9,16]. Although the phenomenon of crack propagation in these materials is at least partly understood there have been no successful attempts at explaining why the variation in crack propagation behaviour occurs and no successful explanations of the underlying mechanism. The reason for this is probably that the conditions under which each type of crack propagation occur have not been properly identified which makes any formulation of a theoretical explanation difficult. It is the purpose of this investigation by concentrating upon one particular resin system to identify at least some of the variables which control the crack propagation behaviour. In particular we have varied the testing rate, temperature and environment. Also under a specific set of testing conditions the effect of different curing agents and composition have been investigated.

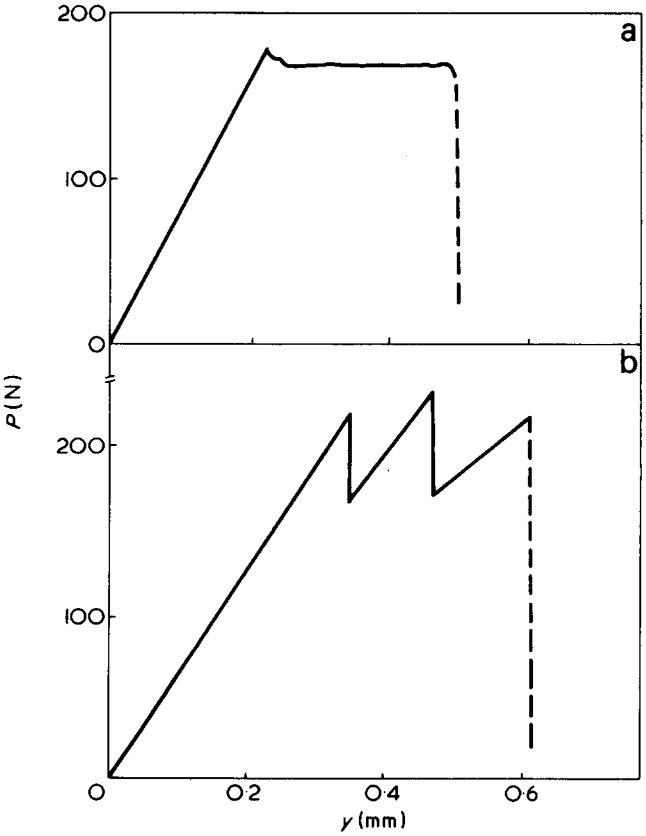

Figure 1 Typical curves of load P against displacement y for epoxy resin DT specimens during crack propagation[11]. (a) Continuous stable cracking; (b) crack jumping or stick–slip behaviour

Table 1 Curing agents used with Epikote 828 epoxy resin

Curing agent	Abbreviated name
Diethylenetriamine	DETA
Triethylenetetramine	TETA
Tetraethylenepentamine	TEPA
Piperidine	–
Triethylamine	TEA

Table 2 Values of K_{Ii} and K_{Ia} for *DT* specimens (6 mm thick) of Epikote 828 cured with different hardeners. All specimens were post-cured for 3 h at 100°C. The values of K_I were measured in air at a crosshead displacement rate of 0.5 mm/min and a temperature of 22° ± 2°C. The amounts of hardener in the resins are not necessarily to stoichiometric concentrations but are typical suggested formulations[24]

Curing agent	phr	K_{Ii} (MN/m$^{3/2}$)	K_{Ia} (MN/m$^{3/2}$)
DETA	9.5	0.71 ± 0.04	0.61 ± 0.03
TETA	9.8	0.70 ± 0.05	0.63 ± 0.05
TETA	13.0	1.09 ± 0.05	0.64 ± 0.05
TEPA	10.0	0.64 ± 0.07	0.55 ± 0.05
Piperidine	4.3	0.83 ± 0.07	0.59 ± 0.07
TEA	7.5	0.94 ± 0.06	0.53 ± 0.03

EXPERIMENTAL

Moulding and specimen preparation

The epoxy resins were cast between glass plates (200 mm square), clipped together and held at the correct separation (6 or 3.7 mm) by means of a PTFE extruded rod spacer. Ambersil (supplied by Ambersil Ltd) polyurethane release agent was used to stop the resin sticking to the glass. The resin (Epikote 828) was weighed into a beaker and degassed in an oven at 70°C for about 45 min. A measured amount of the required curing agent was added to the resin while still warm. The mixture was then stirred for several minutes and poured into the mould.

The initial hardening reaction was allowed to proceed at room temperature for at least 24 h prior to post curing. In order to reduce the possibility of inducing internal stress the castings were heated slowly(~1°C/min) to the post-cure temperature (100°C) and they were held at this temperature for 3 h before they were allowed to cool gradually to room temperature again.

The different amine curing agent used along with their abbreviations are listed in *Table 1*. The principle material studied was the Epikote 828 hardened with 9.8 phr* TETA. The same resin with DETA (9.5 phr) was also used. Other hardeners and formulations were also investigated and they have been listed in *Table 2*. Experiments were also carried out on moulded sheet (6 mm) supplied by Ciba–Geigy (UK) Ltd. This was CT200 resin cured with 30 phr HT901 phthalic anhydride curing agent for 16 h at 135°C.

The cast sheets were cut into rectangular plates approximately 60 by 30 mm. They were notched at one end and a V-shaped groove 0.5 mm deep was made along the centre of one face. Finally a sharp razor blade was pressed and run very gently along the groove to ensure that the cracks would propagate along the centres of the specimens.

Crack propagation

Crack propagation in the epoxy resins was studied using the double-torsion (*DT*) test which has been described elsewhere for use with brittle polymers[3]. The *DT* specimen is particularly useful for crack propagation studies since the stress intensity factor K_I is independent of crack length a and for an elastic material is given by[18]:

$$K_I = PW_m \left[\frac{(1+v)}{Wt^3 t_n k_1} \right]^{1/2} \tag{1}$$

where P is the applied load, W_m is the moment arm (10.4 mm), v is Poissons ratio (assumed to be constant for the epoxy resins at 0.35), W is the bar width (30 mm), t the bar thickness (3.7 or 6 mm) and t_n the plate thickness in the plane of the crack. k_1 is a constant which depends upon the ratio $(W/2)/t$ and is 1/3 when this ratio is infinity. The variation of k_1 with $(W/2)/t$ for the *DT* specimen is given elsewhere[18].

The *DT* specimens were deformed in an Instron mechanical testing machine at a constant displacement rate (dy/dt). Under these conditions when crack propagation is stable it can be shown[3] that:

$$\left(\frac{dy}{dt}\right) = BPV = \text{constant} \tag{2}$$

where B is the slope of the compliance calibration curve for the specimen and V is the crack velocity (da/dt). When propagation takes place by means of crack jumping there is not a simple relationship between crack velocity and displacement rate.

Crack propagation was carried out in laboratory air at 22° ± 2°C and in distilled water at the same temperature. It was also studied in an Instron environmental chamber with the temperature thermostatically controlled to ±2°C. Above room temperature the temperature was controlled by electrical heating and below room temperature cold CO_2 vapour was blown over the specimen in the chamber during testing.

Some experiments were carried out under vacuum in apparatus designed by and described elsewhere by Dr P. E. Reed[19]. The vacuum chamber is a glass Dewar and the specimens are deformed by a screw driven crosshead. The vacuum was maintained by a rotary pump to a pressure of 2×10^{-2} Torr and before testing under vacuum the chamber was flushed out three times with dry argon gas. Because of size restrictions the *DT* geometry could not be used in the vacuum chamber and compact tension (*CT*) specimens were used instead. The specimens were similar in design to those of poly(methyl methacrylate) used by Atkins *et al.*[20] but smaller by a factor of 2. They were precracked by machining a narrow slit which ended with a swallow-tail[20]. No values of K_I or fracture energy were determined from these specimens and they were used only to examine propagation behaviour. All experiments on the *CT* specimens were carried out at a temperature of 20° ± 2°C with a displacement rate of 0.08 mm/min.

CRACK PROPAGATION

Under laboratory conditions

The effect of displacement rate upon crack propagation in air at 22° ± 2°C is illustrated in *Figure 2* for two thicknesses

---

* phr represents parts by wt of hardener to 100 parts by wt of resin

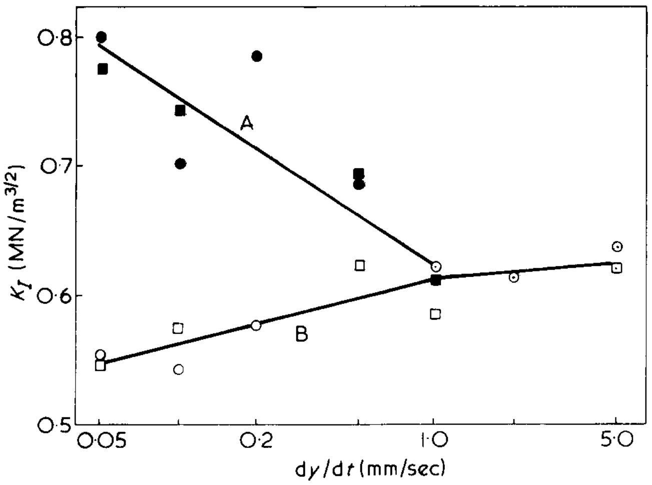

Figure 2 Variation of K_I with crosshead displacement rate (dy/dt) for *DT* specimens of Epikote 828 cured with 9.8 phr TETA. ■, □, ⊡, 6 mm thick specimens; ●, ○, ⊙, 3.7 mm thick specimens. ■, ●, K_{Ii}; □, ○, K_{Ia}; ⊡, ⊙, K_I continuous propagation. A, K_{Ii}; B, K_{Ia}

of *DT* specimens of TETA (9.8 phr) cured resin. The difference between K_{Ii} and K_{Ia} characterizes the amount of jumping. When the difference is large such as at low crosshead speeds the crack propagates by means of large jumps. When K_{Ii} and K_{Ia} have the same value propagation is continuous. The height of the jumps becomes smaller as the displacement rate is increased until a crosshead displacement rate of 1 mm/min is reached when propagation becomes continuous.

Similar behaviour was found using the same resin with another hardener and with another system. This is illustrated in *Figure 3*. A transition between crack jumping and continuous propagation with increasing displacement rate occurs for Epikote 828 cured with DETA (9.5 phr) as shown in *Figure 3b*. The results from an earlier study by Young and Beaumont[11] upon crack propagation in CT 200 cured with HT901 are given in *Figure 3c*. Although only three crosshead speeds were used the same trend as for the other two resins is clearly apparent.

The effect of varying curing agents with Epikote 828 was also examined and to minimize the number of variables crack propagation was studied only in air at a crosshead displacement rate of 0.5 mm/min. The values of K_{Ii} and K_{Ia} are given in *Table 2*. In all cases under the conditions used crack propagation was unstable and propagation took place by crack jumping. However, the values of K_{Ia} were roughly constant whereas there was considerable variation with K_{Ii} indicating a large difference in the size of the jumps. For the three amines which contained a mixture of primary and secondary amine groups DETA, TETA, TEPA, when similar amounts of curing agent were used the values of K_{Ii} and K_{Ia} were similar. However, when a larger amount of curing agent was used with TETA the value of K_{Ii} was significantly increased.

Effect of water

The effect of water upon crack propagation in the TETA (9.8 phr) cured resin was investigated. The variation of K_{Ii} and K_{Ia} with crosshead displacement rate in distilled water for this system is given in *Figure 4*. The broken lines represent the values of K_{Ii} and K_{Ia} for propagation in laboratory air. The effect of water can be clearly seen as to suppress continuous propagation and cause cracks to jump over the entire range of crosshead displacement rates used. However, there is a tendency for the heights of the jumps (indicated by the difference between K_{Ii} and K_{Ia}) to decrease as the crosshead displacement rate is increased.

Because of the tendency of water to cause crack jumping an attempt was made to see if the absence of water would promote stable crack propagation. The *CT* specimen was used in this case and for this type of specimen with the TETA (9.8 phr) cured resin crack propagation was found to be stable in air at crosshead displacement rates in excess of about 10 mm/min. Also unlike the *DT* specimen at a constant crosshead speed continuous crack propagation does not take place in constant load but the load decreases as the crack becomes longer. For crack propagation under vacuum (2×10^{-2} Torr) a crosshead displacement rate of 0.08 mm/min was used. Under these conditions crack propagation was unstable in laboratory air. Load–displacement curves for the *CT* specimens of TETA cured resin in laboratory air and under vacuum at 20° ± 2°C are given in *Figure 5*. It can be seen that the two curves are very similar and it appears that crack jumping is *not* suppressed by the absence of air con-

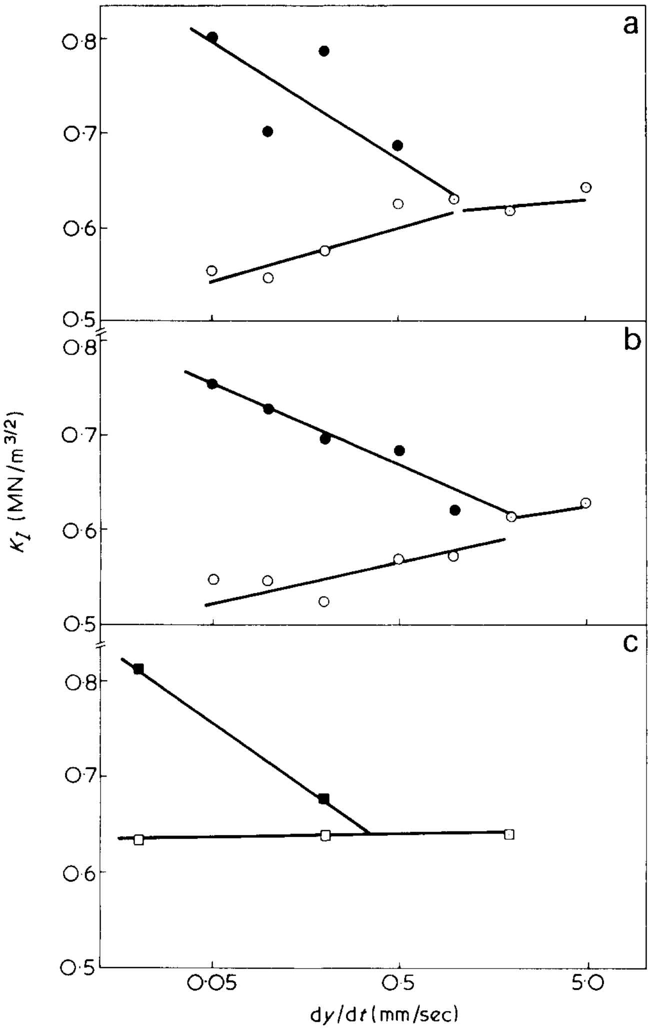

Figure 3 Variation of K_I with crosshead displacement rate for *DT* specimens of different cured epoxy resin systems. (a) Epikote 828 with 9.8 phr TETA; (b) Epikote 828 with 9.5 phr DETA; (c) CT200 with 30 phr HT901. ■, □, ⊡, 6.3 mm specimens; ●, ○, ⊙, 3 mm specimens. ■, ● K_{Ii}; □, ○ K_{Ia}; ⊡, ⊙ K_I continuous propagation

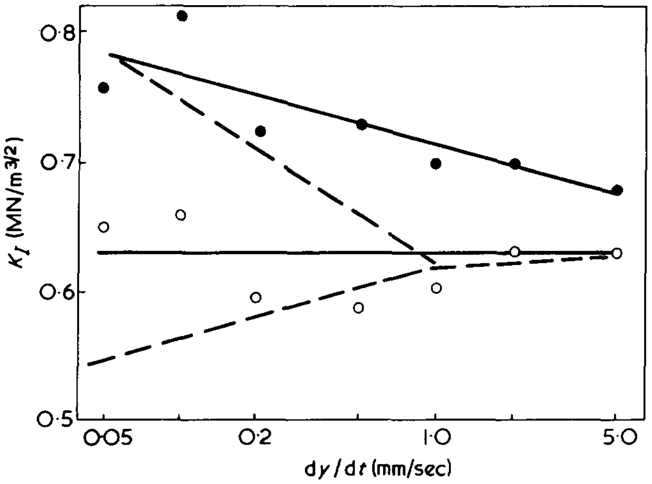

Figure 4 Variation of K_I with crosshead displacement rate for 3.7 mm thick *DT* plates of Epikote 828 cured with 9.8 phr TETA tested in distilled water at 22° ± 2°C. ●, K_{Ii}; ○, K_{Ia}

taining water vapour. The small jumps before maximum load in *Figure 5* are due to crack growth through the initial swallow-tail region of the *CT* specimens.

Effect of temperature

The effect of testing temperature upon crack propagation in the TETA (9.8 phr) cured resin was also studied. A displacement rate of 0.5 mm/min was used exclusively and the variation of K_{Ii} and K_{Ia} with temperature is given in *Figure 6*. At the crosshead displacement rate employed crack propagation is continuous below about 10°C (283K) whereas above this temperature crack jumping occurs. The jumping becomes more marked as the glass transition temperature (93° ± 2°C) of the material is approached. At high temperatures the jumps were so large that it was not possible to measure values of K_{Ia} as the cracks could not be arrested within the specimens. All the specimens had been precracked at room temperature so that they contained sharp cracks before they were tested at elevated temperatures.

DISCUSSION

It can be seen from the experimental results that several factors affect the stability of crack propagation in epoxy resins. In this discussion it is intended that the Epikote 828 cured with TETA should be used as the reference material as it appears to be typical of amine cured epoxy resins. For this material it is clear that high rates of testing, low temperatures and the absence of water promote stable crack propagation. It was also clear that no curing agents could be found which when used in conjunction with Epikote 828 could promote entirely stable crack propagation in *DT* specimens at room temperature in air.

Before the stability of crack propagation in the material can be considered in detail it is essential to establish how the geometry of the *DT* specimens affects crack propagation. It has been demonstrated by Mai and coworkers[9,16] that when the tapered double-cantilever beam (TDCB) is used for crack propagation studies in materials which are prone to crack jumping the stability of crack propagation depends upon both the properties of the material and the specimen geometry. The general criterion for stability has been given by Mai and Atkins[16] for displacement controlled machines as:

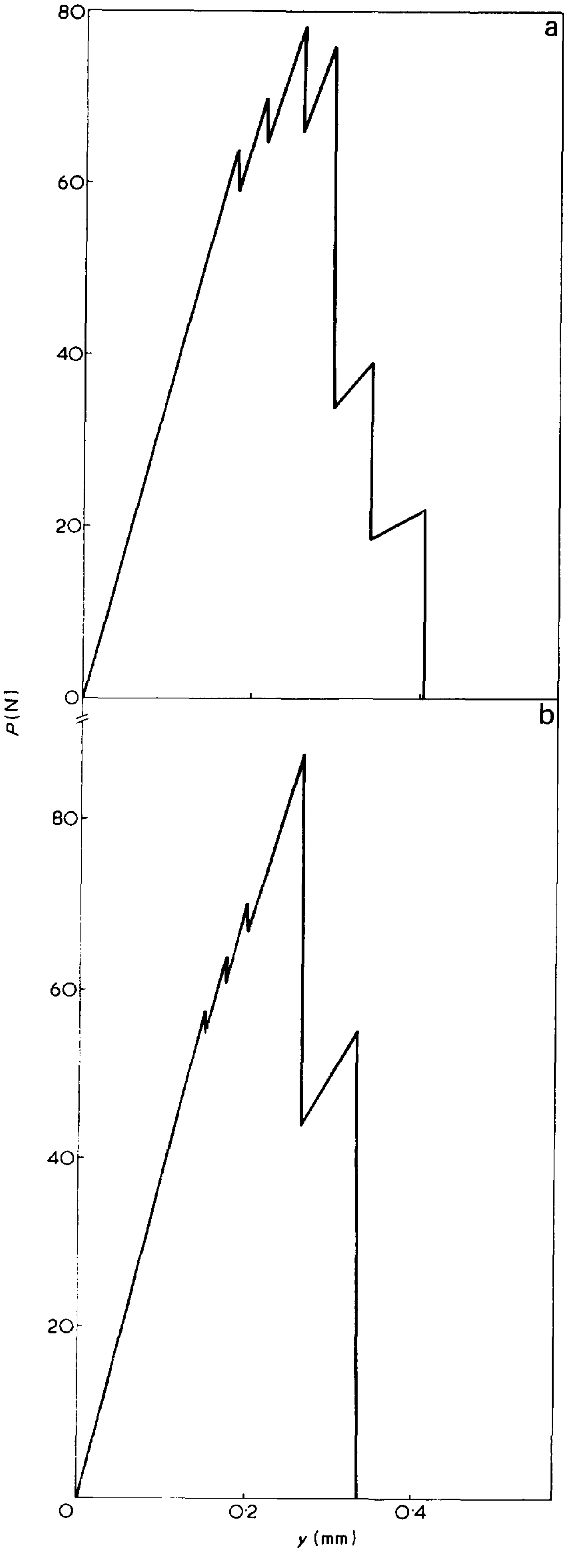

Figure 5 Plots of load *P versus* displacement for *CT* specimens of Epikote 828 cured with 9.8 phr TETA tested at a crosshead displacement rate of 0.08 mm/min. (a) In laboratory air at 20° ± 2°C. (b) under vacuum of 2 X 10^{-2} Torr at 20° ± 2°C

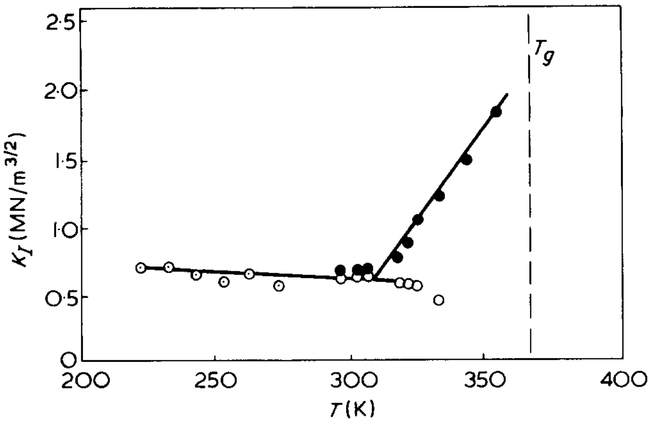

Figure 6 Variation of K_I with temperature for 3.7 mm thick specimen of Epikote 828 cured with 9.8 phr TETA tested at 0.5 mm/min. ●, K_{Ii}; ○, K_{Ia}; ⊙, K_I continuous

$$\frac{1}{G_I}\frac{\mathrm{d}G_I}{\mathrm{d}a} \geqslant \frac{\mathrm{d}^2(y/P)}{\mathrm{d}a^2}\bigg/\frac{\mathrm{d}(y/P)}{\mathrm{d}a} - \frac{2\mathrm{d}(y/P)}{\mathrm{d}a}\bigg/(y/P) = \frac{n_u}{a} \qquad (1)$$

where y is the crosshead displacement rate, P the applied load and a the crack length. G_I is the fracture toughness or strain energy release rate. It is related to K_I through the general relation:

$$K_I^2 \simeq EG \qquad (2)$$

where E is the modulus. For the DT specimen the slope of the compliance calibration curve is constant (B) i.e.:

$$\frac{\mathrm{d}(y/P)}{\mathrm{d}a} = B \text{ and } \frac{\mathrm{d}^2(y/P)}{\mathrm{d}a^2} = 0$$

The right hand side of the inequality in equation (1) is known as the 'geometric stability factor' (*gsf*) and is therefore given by:

$$\frac{n_u}{a} = \frac{-2B}{(y/P)}$$

for the DT specimen. Experimentally determined values of n_u as a function of crack length are given in *Figure 7*. The curves show that the *gsf* is negative when the DT specimen is used in displacement-controlled machines. However, it is not particularly negative when compared with for example the TDCB loaded from the wide end[9,16]. Since the *gsf* is not very negative for the DT specimen this means that materials that are prone to unstable crack propagation should normally exhibit crack jumping when used in DT specimens. This makes it particularly useful for the study of the stable and unstable behaviour. It also follows that any material for which $\mathrm{d}G_I/\mathrm{d}\dot{a}$ is positive will exhibit stable crack propagation when used for DT specimens. This has been clearly demonstrated for the case of poly(methyl methacrylate) by one of the authors[3]. Unstable crack propagation in the DT specimen therefore shows that the material has negative $\mathrm{d}G_I/\mathrm{d}\dot{a}$ (or $\mathrm{d}G_I/\mathrm{d}a$)[16] characteristics when this occurs.

Having established that the transition from unstable to stable crack propagation in the epoxy resin specimens is due to a change in the materials properties the question arises of the mechanism which causes the transition. There are two possibilities. One is that water vapour from the atmosphere is absorbed at the crack tip as the specimen is loaded and the material is plasticized locally at the crack tip. When the value of K_I or G_I is large enough the crack can then burst through the water-affected region and go through virgin material which should have a lower toughness[16]. The observation that water increases K_{Ii} (*Figure 4*) but leaves K_{Ia} virtually unchanged would appear to support this suggestion. Unstable propagation still occurs in the absence of water vapour (i.e. in vacuum *Figure 5*) and so it appears that water has the effect of making unstable propagation occur more readily whereas the action of water vapour alone is not the main reason for crack jumping. It appears that this is principally a material property and not an environmental effect. The second and most likely reason for unstable crack propagation in the epoxy resins is that they possess negative $\mathrm{d}G_I/\mathrm{d}\dot{a}$ (or $\mathrm{d}K_I/\mathrm{d}\dot{a}$) characteristics[21]. Indeed Mai[16] using stabilized test pieces has shown this to be true for an epoxy system. It is also implied by the increase in K_{Ii} with decreasing testing rate that is observed in *Figures 2* and *3*. Although this explains the phenomenon of unstable propagation the reason for the transition to stable behaviour and the underlying mechanisms are not explained. The phenomenon of crack propagation in these materials bears a strong similarity to the propagation of cracks at different rates in strain-crystallizing and filled elastomers which has been reviewed by Andrews[22]. In these materials both stick–slip and continuous propagation are found at different temperatures and under different rates of testing. It has been possible to explain stick–slip behaviour for example in reinforced rubbers as being due to a 'stationary stress distribution' at the crack tip caused by the material having high mechanical hysteresis[23].

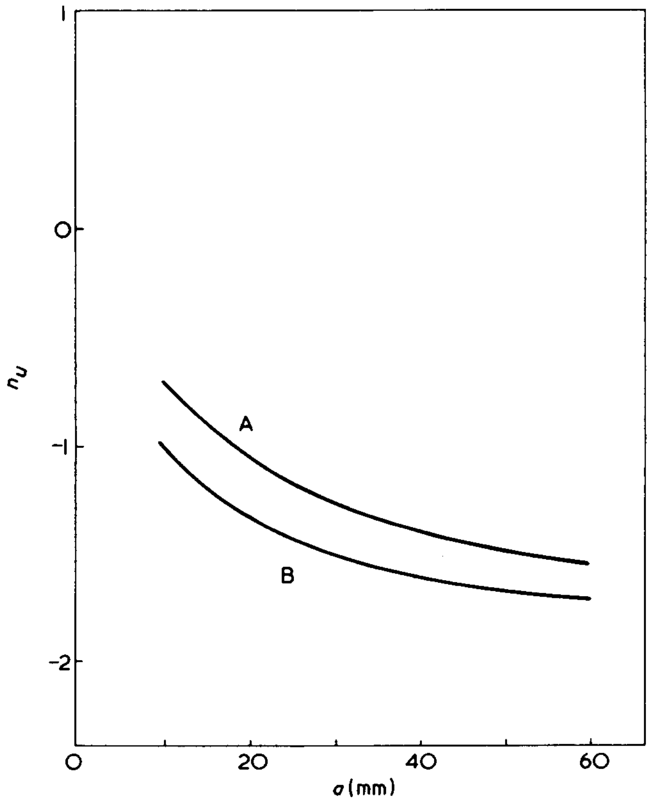

Figure 7 Variation of geometric stability factor n_u with crack length a for DT specimens of different thickness. A, 6.0 mm; B, 3.7 mm

With the knowledge of the crack propagation behaviour and the indentification of the conditions under which the different types of propagation occur it is hoped that we will now be in a position to establish the mechanisms that control the stability of crack propagation in epoxy resins.

CONCLUSIONS

The stability of crack propagation in an epoxy resin cured with different hardeners has been studied and in general it is found that cracks can propagate in either a stable or an unstable manner. At high rates of strain and at low temperatures propagation tends to be stable and crack growth is continuous. At higher temperatures, low rates of strain and in liquid water propagation is unstable and occurs by means of a 'stick–slip' mode. Possible reasons for this type of behaviour have been discussed and it is clear that although the phenomenon is understood there is need for an explanation of the behaviour in terms of the micromechanisms of crack propagation.

ACKNOWLEDGEMENTS

The authors would like to thank Dr P. E. Reed of Queen Mary College Materials Department for use of the vacuum testing facility.

REFERENCES

1 Knott, J. F. 'Fundamentals of Fracture Mechanics', Butterworths, London, 1973
2 Marshall, G. P., Coutts, L. H. and Williams, J. G. *J. Mater. Sci.* 1974, 9, 1409
3 Beaumont, P. W. R. and Young, R. J. *J. Mater. Sci.* 1975, **10**, 1334
4 Young, R. J. and Beaumont, P. W. R. *Polymer* 1976. **17**, 717
5 Mostovoy, S. and Ripling, E. J. *J. Appl. Polym. Sci.* 1966, **10**, 1351
6 Mostovoy, S. and Ripling, E. J. *J. Appl. Polym. Sci.* 1969, **13**, 1083
7 Mostovoy, S. and Ripling, E. J. *J. Appl. Polym. Sci.* 1971, **15**, 641
8 Mostovoy, S. and Ripling, E. J. *Appl. Polym. Symp.* 1972, **19**, 395
9 Mai, Y. W., Atkins, A. G. and Caddell, R. M. *Int. J. Fract.* 1975, **11**, 939
10 Gledhill, R. A. and Kinloch, A. J. *Polymer* 1976, **17**, 727
11 Young, R. J. and Beaumont, P. W. R. *J. Mater. Sci.* 1976, **11**, 779
12 Evans, W. T. and Barr, B. I. G. *J. Strain Anal.* 1974, **9**, 166
13 Diggwa, A. D. S. *Polymer* 1974, **15**, 101
14 Phillips, D. C. and Scott, J. M. *J. Mater. Sci.* 1974, **9**, 1202
15 Selby, K. and Miller, L. E. *J. Mater. Sci.* 1975, **10**, 12
16 Mai, Y. W. and Atkins, A. G. *J. Mater. Sci.* 1975, **10**, 2000
17 Selby, K. and Miller, L. E. *J. Mater. Sci.* 1975, **10**, 2003
18 Young, R. J. and Beaumont, P. W. R. *J. Mater. Sci.* 1977, **12**, 684
19 Reed, P. E. results to be published
20 Atkins, A. G., Lee, C. S. and Caddell, R. M. *J. Mater. Sci.* 1975, **10**, 1394
21 Corten, H. T. 'Fracture, An Advanced Treatise Vol. 7', (Ed. H. Liebowitz), Academic Press, New York, 1972
22 Andrews, E. H. 'Fracture in Polymers', Oliver and Boyd, London, 1968
23 Andrews, E. H. *J. Mech. Phys. Solids* 1963, **11**, 231
24 Brydson, J. A. 'Plastics Materials', Newnes–Butterworth, London, 1975