Relationship between mechanical properties of and crack progogation in epoxy resin adhesives

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Crack propagation in a series of amine-cured epoxy resin adhesives in both the bulk material and adhesive joints has been studied as a function of the formulation of the resins and the conditions of testing using a linear elastic fracture mechanics approach. In both cases propagation was found to take place in either a stick–slip (unstable) or a continuous (stable) manner; the particular type of propagation depending upon the amount and type of hardener used and the temperature and rate of testing. A constant crack opening displacement (δ) has been shown to be a unique failure criterion for continuous propagation with δ having approximately the same value in both bulk material and joints. However δ was found to increase in the stick–slip mode of propagation. These crack propagation characteristics have been related to the compressive yield behaviour of each material as determined by uniaxial compression tests performed on the epoxy resins. Possible mechanisms of crack propagation have also been discussed.

INTRODUCTION

The use of epoxy resins in structural engineering applications has increased greatly in recent years and the prediction of the strengths of components incorporating these materials is becoming vitally important. Crack propagation in epoxy resins is now generally studied using a linear elastic fracture mechanics approach[1] since they are normally brittle and general yielding does not occur. This approach has been used by several workers for bulk materials[2–8] and for adhesive joints[9–16] and a wealth of information has been accumulated. However, in spite of this no general picture has evolved and in fact much confusion has arisen concerning the propagation of cracks in epoxy resins.

It is found that crack growth may occur in one of two basic modes.

(i) In a continuous, steady manner at a constant load with the rate of crack growth being dependent upon the rate of crosshead displacement employed. This is commonly termed 'stable' crack growth and a typical load–displacement trace for a specimen exhibiting this type of behaviour is shown in *Figure 1a.*

(ii) Alternatively, crack propagation may occur intermittently in a stick–slip manner exhibiting load values appropriate to both crack initiation and crack arrest. This is termed 'unstable' crack growth and a typical load–displacement trace is shown in *Figure 1b.*

The conditions under which these two types of behaviour occur have been only identified empirically and no theories have been advanced to predict when each type of behaviour will arise. For example, Yamini and Young[17] have shown recently that the stability of crack propagation in an epoxy resin is governed by the type of hardener employed, temperature, rate of testing and environment. Gledhill and Kinloch[14] have shown that in the case of adhesive joints undergoing centre-of-bond failure different curing agents promote different types of propagation behaviour. In this paper it is the intention to show that crack propagation in both bulk and joints is related and that they may both be controlled by the same basic mechanisms.

Very little attention has been paid to the mechanisms of propagation in epoxy resins or the processes that take place at the crack tip during propagation. Since the fracture energies (typically 100 J/m^2) are at least one hundred times the energy required to break covalent bonds (less than 1 J/m^2) other energy absorbing processes, such as plastic deformation, must take place at the crack tip. In thermoplastics this deformation often manifests itself as crazing[18,19]. Although there is some evidence for crazing on a small scale in epoxy resins[20,21] there is no evidence that cracks propagate in fully cured resins with crazes at their tips as in, for example, poly(methyl methacrylate)[18–20]. It is normally thought that shear yielding occurs at crack tips in epoxy resins and we have therefore attempted to correlate the yield behaviour with crack propagation in these materials.

EXPERIMENTAL

Specimen preparation

Bulk material. The resin used for the crack propagation samples of bulk material was a commercial diglycidyl ether of bisphenol A (DGEBA) epoxy resin cured with triethylenetetramine (TETA) a mixed primary and secondary amine. The details of the preparation of the sheets of material have been given in a recent publication[17]. Different quantities of hardener were used namely 7.4, 9.8, 12.3 and 14.5 phr*. In all cases the initial hardening reaction was allowed to proceed for 23 h at room temperature followed by post-curing

* Parts by weight of hardener to 100 parts by weight of resin.

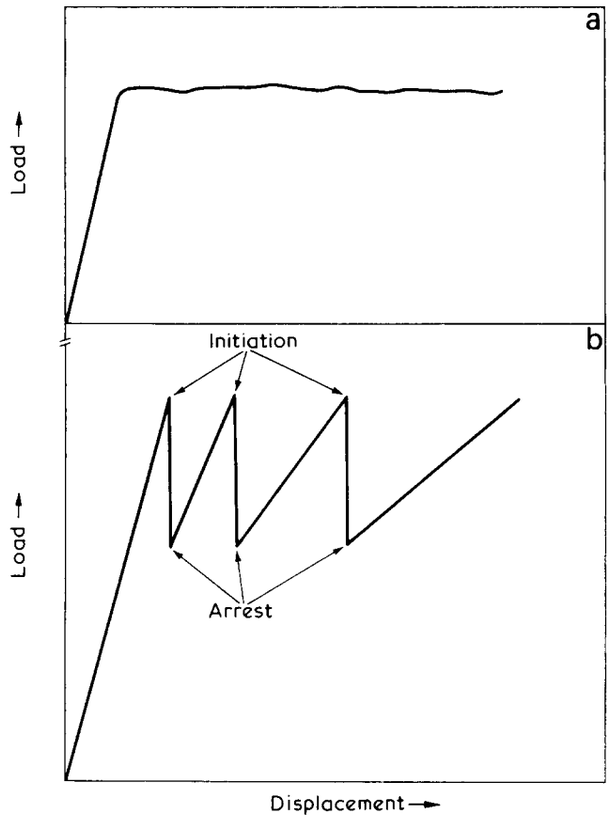

Figure 1 Typical load–displacement curves for both bulk and joints. (a) Continuous crack propagation; (b) crack jumping or stick–slip crack propagation

for 3 h at 100°C and slow cooling to room temperature.

The specimens for crack propagation experiments were cut in the form of rectangular plates 3 x 30 x 60 mm from the cast sheets. They were notched at one end and a v-shaped groove 0.5 mm deep was made along the centre of one face. To ensure that the cracks would propagate along the centre of the specimens a sharp blade was pressed into and run along the groove.

Adhesive joints. The specimen geometry employed for the adhesive joints was a tapered double cantilever beam joint. The substrate material was aluminium alloy, to specification British Standard 1474 NE4, which was machined into cantilever beams 308 mm long, 12.7 mm thick and with a height, h, varying between 16.0 and 47.8 mm. The surfaces to be bonded were first subjected to a liquid- and vapour-degreasing bath of trichloroethane, then grit blasting with 180–220 mesh alumina, then after degreasing again were finally allowed to air-dry. The epoxy adhesives employed were again based upon DGEBA resin and were formulated as shown in *Table 1*. Immediately prior to joint preparation the aluminium alloy substrates were treated, as described above, adhesive was spread on the treated faces and the two beams pressed lightly together. Small pieces of plastic sheet, previously inserted in the adhesive at the wide end of the joint, were employed to control the thickness of the epoxy resin layer to 0.50 ± 0.06 mm. Further, a piece of Teflon tape, about 30 mm long, 12.7 mm wide and 0.08 mm thick was previously placed, approximately in the centre of the adhesive and at the narrow end of the joint, to assist in propagating a 'starter' crack. Excess adhesive on the beam side was removed and the adhesive cured as indicated in *Table 1*.

Crack propagation

Bulk material. Crack propagation in the bulk material was studied using the double torsion (*DT*) test which has been described elsewhere[22]. The *DT* specimen is particularly useful for crack propagation studies since the stress intensity factor K_{Ic} is independent of crack length, c, and for an elastic material is given by:

$$K_{Ic} = P_c W_m \left[\frac{(1+\upsilon)}{Wt^3 t_n k_1}\right]^{1/2} \quad (1)$$

where P_c is the applied load, W_m is the moment arm (10.4 mm), υ is Poisson's ratio (assumed to be constant for the epoxy resins at 0.35 [17]), W is the bar width (30 mm), t is the bar thickness (3.7 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[23]. In our case $(W/2)/t$ is 4 and k_1 is 0.282.

The *DT* specimens were tested in an Instron mechanical testing machine using a constant crosshead displacement rate ($\dot{y}$) for each specimen. Under these conditions it can be shown that when propagation is stable:

$$\dot{y} = BP_c\dot{c} = \text{constant} \quad (2)$$

where B is the slope of the compliance calibration curve for the specimen and $\dot{c}$ is the crack velocity. In epoxy resins crack propagation is often unstable and occurs in a 'stick–slip' manner. In this case the crack velocity varies and is not constant. Consequently there is not a simple relationship between crack velocity and crosshead displacement rate. All experiments were carried out at 22° ± 2°C.

Adhesive joints. To obtain natural starter cracks for subsequent experiments the arms of the specimens were separated at a constant rate of 8.5 x 10^{-3} mm/sec using an Instron tensile testing machine until the crack was about 70 to 100 mm long. The specimens were then reloaded at various constant rates of displacement, $\dot{y}$, at 22° ± 2°C and 55% r.h. until crack propagation was observed.

The adhesive fracture energy, G_{Ic}, was determined from the relationship[11]:

$$G_{Ic} = \frac{4P_c^2 m}{E_s b^2} \quad (3)$$

where P_c is the applied load, E_s is the modulus of the substrate, b is the specimen thickness and m is the geometry factor given by[12]:

Table 1 Formulations and cure schedules for epoxy adhesives

Epoxy resin	Curing agent	Parts per hundred of resin used	Cure schedule
DGEBA	Triethylenetetramine (TETA)	9.8	23 h/23°C + 3 h/100°C
DGEBA	Tetraethylenepentamine (TEPA)	10.0	23 h/23°C + 8 h/80°C
DGEBA	Tri-2-ethyl hexanoate of 2,4,6-tris(dimethylamino-methyl phenol) (a 3° amine)	9.4	96 h/23°C + 1¼ h/100°C + 2½ h/180°C

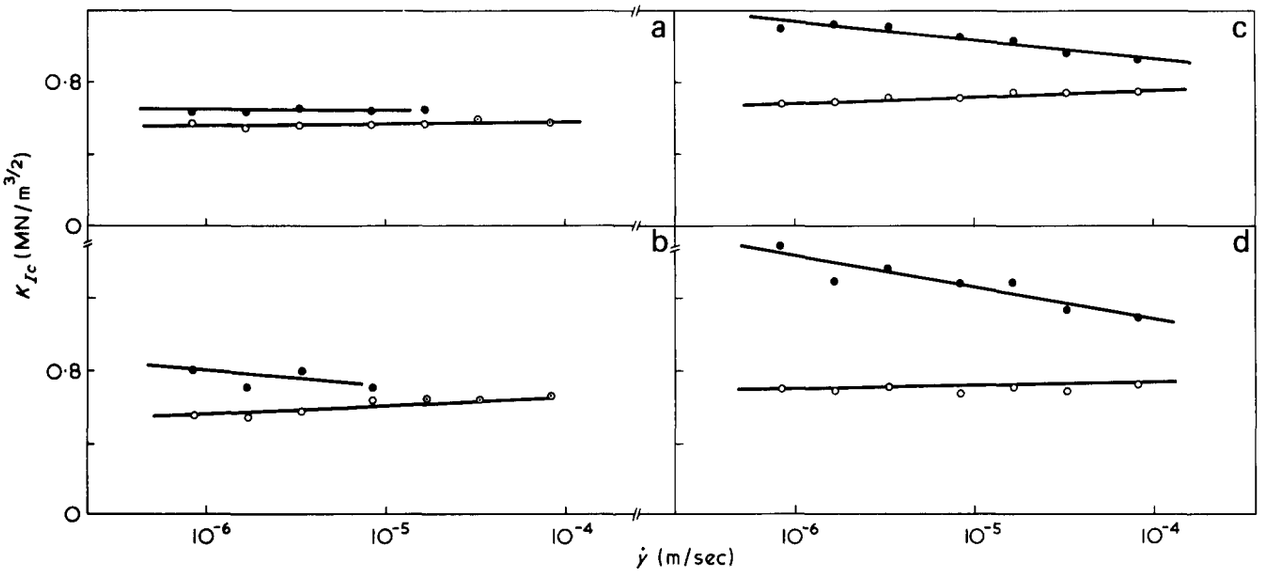

Figure 2 Variation of K_{Ic} with crosshead displacement rate, $\dot{y}$, for bulk DGEBA cured with various amounts of TETA (tested at 22° ± 2°C). ●, K_{Ici}; ○, K_{Ica}; ⊙, K_{Ic} continuous propagation. (a) 7.4 phr; (b) 9.8 phr; (c) 12.3 phr; (d) 14.7 phr.

$$m = \frac{3c^2}{h^3} + \frac{1}{h} \tag{4}$$

The corresponding value of stress intensity factor, K_{Ic}, cas calculated from[1]:

$$K_{Ic}^2 = \frac{EG_{Ic}}{(1-\upsilon^2)} \tag{5}$$

where υ is Poisson's ratio (0.35) and E taken as the compressive modulus of the adhesive.

The initial crack velocity was measured either by visual observation or, for crack velocities in excess of about 0.01 m/sec, by the crack progressively rupturing a conductive paint grid on the side of the specimen and recording the associated voltage change on an oscilloscope.

Compression testing

The resins used for crack propagation studies in both the bulk and the adhesive joints were tested in uniaxial compression. They were either machined or case into cylindrical blocks with a height to diameter ratio of 2 to 1. The blocks were deformed in a compression cage between polished steel plates, lubricated with molybdenum disulphide grease, in an Instron mechanical testing machine. A constant crosshead displacement rate, $\dot{y}$, was used for each test and this was converted to a strain rate using the specimen dimensions. The Instron had an environmental chamber which enabled some tests to be carried out either above or below room temperature. The nominal strain, e, was determined from the crosshead displacement corrected for the machine deflection using a steel blank. The load, P, was measured from the Instron chart and converted into a true stress, σ_T, using the initial specimen cross-sectional area, A_0, in the equation:

$$\sigma_T = \frac{P}{A_0}(1-e) \tag{6}$$

which assumes constant volume deformation.

RESULTS

Crack propagation in bulk

Effect of hardener content. Crack propagation in the DGEBA resin cured with TETA was studied at 22° ± 2°C using a range of crosshead displacement rates and different amounts of curing agent. The effect of changing these variables is shown in *Figure 2*. K_{Ici} and K_{Ica} are the stress intensity factors for initiation and arrest, respectively and the differences between them characterizes the amount of jumping which has taken place. When the difference is large, propagation occurs by means of large jumps, whereas when it is small the jumps are small and when K_{Ici} is equal to K_{Ica} propagation is continuous. In all cases it was found that the tendency for cracks to jump increased with increasing hardener content and with decreasing crosshead displacement rate, $\dot{y}$.

Effect of temperature. The effect of changing the temperature upon crack propagation in the DGEBA/9.8 phr TETA resin has been reported in a recent publication[17] where the results are given for a fixed $\dot{y}$ of 8.3×10^{-6} m/sec. *Figure 3* shows the effect of changing $\dot{y}$ upon crack propagation at different temperatures. At room temperature there is a transition between crack jumping and continuous propagation at a value of $\dot{y}$ of about 10^{-5} m/sec. At −40°C propagation appears to be entirely continuous and the value of K_{Ic} required for crack propagation increases slightly with increasing $\dot{y}$. On the other hand at + 67°C propagation is by jumping and the value of K_{Ic} required to initiate propagation decreases with increasing $\dot{y}$. At this temperature the jumps are so large that the cracks are not able to arrest before reaching the end of the specimens.

Crack propagation in joints

Effect of hardener type. The adhesive fracture energy, G_{Ic}, and crack velocity, $\dot{c}$, were measured over a range of constant displacement rates, $\dot{y}$, for joints bonded with either the DGEBA/10 phr TEPA or DGEBA/9.8 phr TETA adhesives. Those data, together with the values of true compressive yield stress, σ_y, and compressive modulus, E, as a function

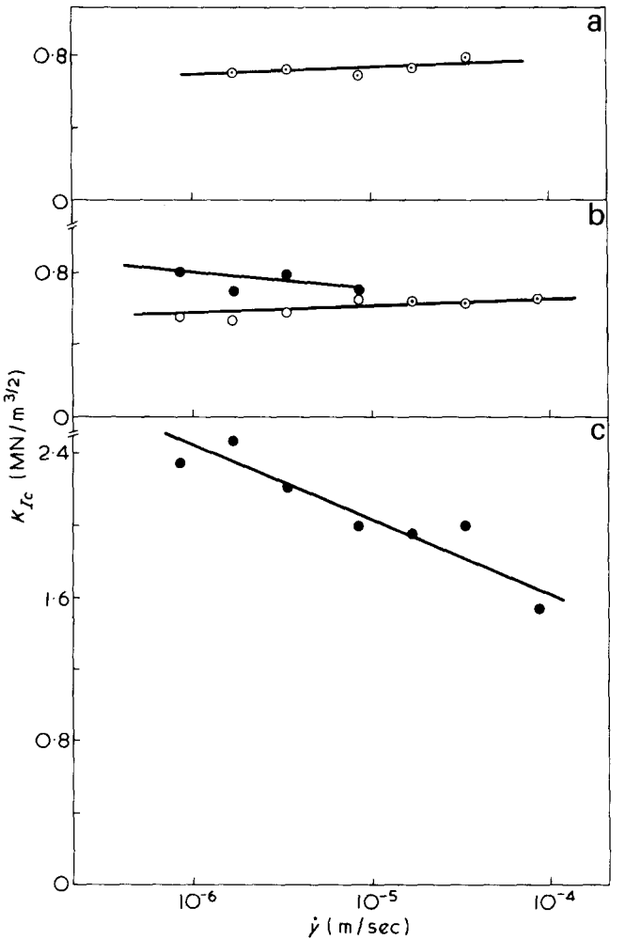

Figure 3 Variation of K_{Ic} with crosshead displacement rate, $\dot{y}$, for bulk DGEBA/9.8 phr TETA at different temperatures. ●, K_{Ici}; ○, K_{Ica}; ⊙, K_{Ic} continuous propagation. (a) –40°C; (b) 22°C; (c) 67°C

of strain rate, $\dot{e}$, for these epoxy resins are shown in *Tables 2* and *3*, respectively. The values of stress intensity factor, K_{Ic}, for joint failure were calculated using equation (5) and are plotted as a function of $\dot{y}$ in *Figure 4*.

In the case of the DGEBA/10 phr TEPA Joints continuous crack growth was observed over the complete range of displacement rates employed and K_{Ic} increased slightly as the rate was increased. For the DGEBA/9.8 phr TETA joints stick–slip growth was observed below displacement rates of about 10^{-5} m/sec while above this value continuous crack growth occurred. For both of these adhesives centre-of-bond failure occurred and when continuous crack growth resulted, the crack velocity was found to be directly proportional to the displacement rate employed and the relationship between these parameters was in good agreement with that previously established[14] for other DGEBA/polyamine cured adhesives.

However, previous work[14] has shown that if the hardener employed is the tertiary (3°) amine only stick–slip crack growth is observed and the initial crack velocity was always greater than about 20 m/sec. For these unstable cracks values of K_{Ic} for crack initiation and arrest could be identified and the results have been presented previously elsewhere[14].

Uniaxial compression tests

Effect of type and amount of hardener. Compressive stress- strain curves were obtained for the DGEBA resins cured with different types of hardener and the results are shown in *Figure 5* for an initial strain rate of 6×10^{-4} sec^{-1} at room temperature (22° ± 2°C). The two resins cured with the polyamines (TETA and TEPA) had yield stresses in excess of 100 MPa and yielded at strains of less than 0.08. In contrast the tertiary amine cured material had a yield stress of the order of 85 MPa and yielded at a strain of 0.08. It also flowed to a higher strain before finally fracturing.

The amount of TETA hardener in the DGEBA resin was

Table 2 Fracture data for joints and uniaxial compressive properties of epoxy resin for DGEBA/10 phr TEPA adhesive (Tests conducted at 22° ± 2° C)

$\text{Log}_{10}\dot{y}$ (m/sec)	$\text{Log}_{10}\dot{c}$ (m/sec)	G_{Ic} (kJ/m^2)	K_{Ic} (MN/m$^{3/2}$)	$\text{Log}_{10}\dot{e}$ (sec^{-1})	σ_y (MPa)	E (GPa)	δ (μm)
–6.07	–3.71	0.064	0.45	–4.84	109	2.75	0.67
–5.67	–3.38	0.050	0.40	–4.44	111	2.81	0.51
–5.67	–3.41	0.052	0.41				0.53
–5.67	–3.56	0.051	0.40				0.52
–5.37	–3.25	0.055	0.42	–4.14	112	2.86	0.56
–5.07	–2.74	0.054	0.42	–3.84	114	2.90	0.54
–5.07	–2.72	0.069	0.48				0.69
–4.67	–2.34	0.052	0.42	–3.44	116	2.96	0.51
–4.67	–2.39	0.053	0.42				0.52
–4.67	–2.85	0.050	0.41				0.49
–4.37	–2.08	0.054	0.43	–3.14	117	3.00	0.48
–4.37	–1.95	0.052	0.42				0.51
–3.67	–0.93	0.058	0.45	–2.44	120	3.11	0.58
–3.37	–1.29	0.055	0.44	–2.14	121	3.15	0.52
–3.07	–0.60	0.055	0.45	–1.04	123	3.20	0.51
–2.37	0.60	0.059	0.47	–1.14	126	3.31	0.53
–2.07	0.90	0.065	0.50	–0.84	127	3.35	0.58

Table 3 Fracture data for joints and bulk specimens and uniaxial compressive properties of epoxy resin for DGEBA/9.8 phr TETA materials. (Tests conducted at 22° ± 2°C)

				Joints				Bulk specimens		
Log $\dot{y}$ (m/sec)	Log $\dot{e}$ (sec^{-1})	σ_Y (MPa)	E (GPa)	G_{Ic} (kJ/m^2)	K_{Ic} ($MN/m^{3/2}$)	Log $\dot{c}$ (m/sec)	δ (μm)	K_{Ic} ($MN/m^{3/2}$)	Log $\dot{c}$ (m/sec)	δ (μm)
−6.07	−4.84	101	2.91	0.112(i) 0.070(a)	0.61(i) 0.48(a)	S/S	1.26(i) 0.79(a)	0.80(i) 0.55(a)	S/S	2.18(i) 1.03(a)
−5.07	−3.84	106	3.11	0.074(i) 0.070(a)	0.51(i) 0.50(a)	S/S	0.80(i) 0.75(a)	0.62(i) 0.60(a)	S/S	1.40(i) 1.17(a)
−4.78	−3.55	108	3.17	–	–	–	–	0.63	−3.15	1.16
−4.67	−3.44	108	3.19	0.079	0.54	−2.40	0.83	–	–	–
−4.47	−3.24	110	3.23	–	–	–	–	0.61	−2.76	1.05
−4.07	−2.84	112	3.31	0.079	0.55	−1.80	0.80	0.64	−2.46	1.10
−3.07	−1.84	118	3.51	0.089	0.60	−0.60	0.86	–	–	–
−2.67	−1.44	120	3.59	0.084	0.59	−0.20	0.80	–	–	–

(i) = initiation; (a) = arrest

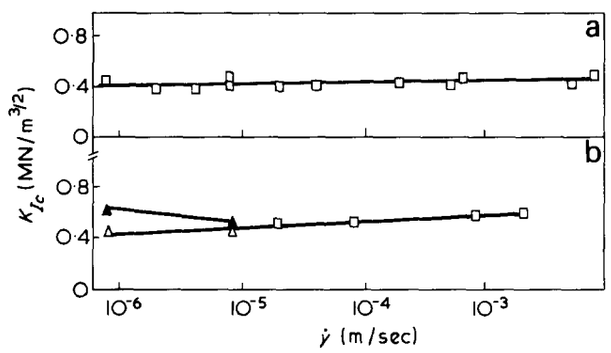

Figure 4 Variation of K_{Ic} with crosshead displacement, $\dot{y}$, for joints bonded with either (a) DGEBA/10 phr TEPA or (b) DGEBA/9.8 phr TETA. ▲, K_{Ici}; △, K_{Ica}; ◬, K_{Ic} continuous propagation

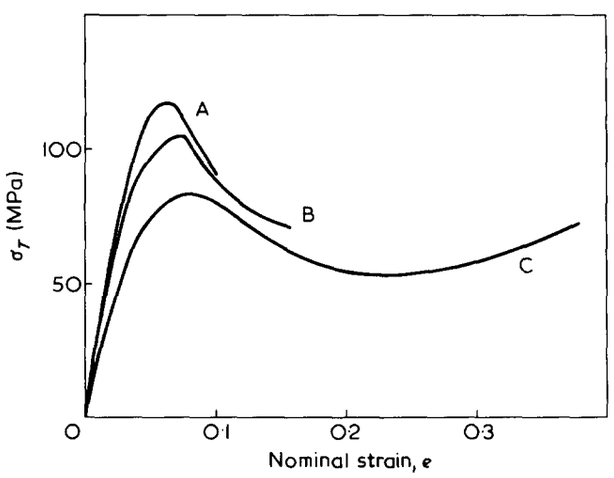

Figure 5 True compressive stress/nominal strain curves for various DGEBA based epoxy resins at 22° ± 2°C. ($\dot{e} = 6 \times 10^{-4}$ sec^{-1}). A, DGEBA/10 phr TEPA; B, DGEBA/9.8 phr TETA; C, DGEBA/9.4 phr 3° amine

varied between 7.4 and 14.5 phr to observe the effect of hardener content upon a particular resin/hardener system and to obtain compressive data upon the same formulations as used for the crack propagation studies. The resulting compressive stress–strain curves are given in *Figure 6*. It can be seen that the yield stress and compressive modulus fall with increasing hardener content over the range of hardener content investigated. The yield strain on the other hand increases with increasing hardener content from about 0.05 for the 7.4 phr TETA resin to about 0.09 for the 14.5 phr TETA material.

Effect of testing rate and temperature. For all the materials it was found that both the yield stress and modulus increased with increasing crosshead displacement rate. The results are given in detail in *Tables 2* and *3*. The strain rate, $\dot{e}$, is the initial strain rate calculated by dividing $\dot{y}$ by the initial specimen height. Some values at very low and high strain rates have been extrapolated so that they can be used to calculate the parameters of interest. *Figure 7* shows the measured variation of yield stress with strain rate for the polyamine (9.8 phr TETA) and tertiary amine cured materials over several decades of strain rate.

The effect of testing temperature upon the compressive deformation of the DGEBA/9.8 phr TETA resin was also investigated. The yield stress, yield strain and compressive modulus increased as the temperature of testing was decreased. Stress–strain curves obtained at four different temperatures are given in *Figure 8* for an initial strain rate of 6×10^{-4} sec^{-1}.

DISCUSSION

Comparison of bulk and joint fracture

Comparison of *Figures 2* and *4* clearly reveals that the fracture of bulk specimens and joints has the same general characteristics, i.e. stick–slip crack growth being favoured at lower crosshead displacement rates while continuous crack propagation occurs at higher displacement rates.

A detailed comparison is given for the DGEBA/9.8 phr TETA epoxy resin in *Table 3*. There are several points of

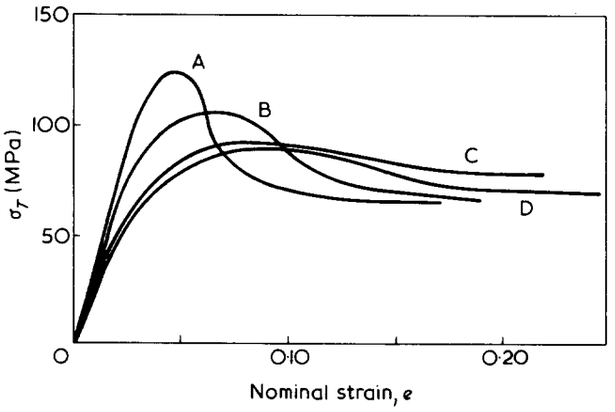

Figure 6 True compressive stress/nominal strain curves for DGEBA cured with various amounts of TETA (tested at 22° ± 2°C) ($\dot{e}$ = 6 X 10^{-4} sec^{-1}). A, 7.4 phr; B, 9.8 phr; C, 12.3 phr; D, 14.7 phr

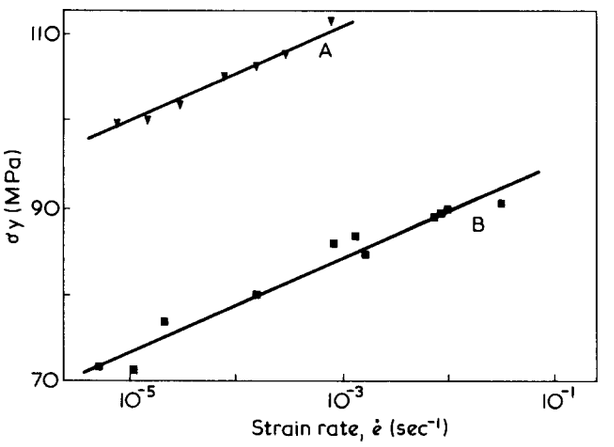

Figure 7 True compressive yield stress as a function of initial strain rate for A, DGEBA/9.8 phr TETA and B, DGEBA/3° amine

interest that should be noted. First of all, the value of $\dot{y}$ at which the transition from stick–slip to continuous crack growth occurs is approximately the same in both joints and bulk specimens, namely about 10^{-5} m/sec. Secondly, for continuous crack propagation at a given displacement rate the crack velocity in the particular geometry of specimens chosen is of the same order for the epoxy resin in either the bulk or joint forms. Thirdly, the values of K_{Ic} are within about 20% and this discrepancy may simply arise from the K_{Ic} (joint) values being deduced from equation (5) which requires a value of modulus, E, for the epoxy resin to be selected. In *Tables 2* and *3* the uniaxial compressive data, measured over a range of strain rates, has been related to the fracture data, measured over a range of displacement rates, by arbitrarily assigning a convenient strain rate, $\dot{e}$, of 1.4 x 10^{-5} sec^{-1} to a displacement rate, $\dot{y}$, of 8.5 x 10^{-7} m/sec. However, a more appropriate strain rate for volume elements close to the crack tip may be deduced by considering the strain rate near the tip, $\dot{e}_{tip}$, which is given by:

$$\dot{e}_{tip} \sim \frac{e_y}{t} \tag{7}$$

where t is the time-scale of the deformation of such a volume element and e_y the yield strain. In a period of time, t, the crack will have travelled a distance of the order of the plastic zone size $2r_{Iyc}$ and so:

$$t \sim \frac{2r_{Iyc}}{\dot{c}} \tag{8}$$

Thus combining equation (7) and (8):

$$\dot{e}_{tip} \sim \frac{e_y \dot{c}}{2r_{Iyc}} \tag{9}$$

Taking e_y as about 0.05 and r_{Iyc} as 20 μm[15] then for the range of continuous crack velocities measured in the present experiments the value of $\dot{e}_{tip}$ lies between about 10^{-1} and 10^4 sec^{-1}. Strain rates of this magnitude are not readily accessible in uniaxial compression experiments but the values of modulus, E, appropriate to such strain rates would be expected to be somewhat higher than those used to deduce K_{Ic} (joint). Indeed a rough extrapolation of the modulus–strain rate data given in *Table 3* to obtain values of E at these high strain rates reveals that such values of E, together with the appropriate values of G_{Ic}, would result in values of K_{Ic} (joint) virtually identical with K_{Ic} (bulk).

Fracture criterion

Recently a constant crack opening displacement has been suggested as a unique failure criterion for several different polymers under certain test conditions[15,24,25]. The crack opening displacement, δ, is given by:

$$\delta = \frac{K_{Ic}^2}{\sigma_y E} \tag{10}$$

and the usefulness of this parameter to describe the fracture of epoxy resins, both in bulk and in joints, will now be examined.

The crack opening displacement, δ, is shown as a function of crack velocity in *Figure 9* for joints bonded with either the DGEBA/10 phr TEPA or the DGEBA/3° amine adhesives. The values of K_{Ic}, σ_y, E and δ are detailed in *Table 2* for the former adhesive and the fracture data for the latter adhesive has been published previously[14]. The DGEBA/10 phr TEPA joints exhibit continuous crack growth and the value of δ is

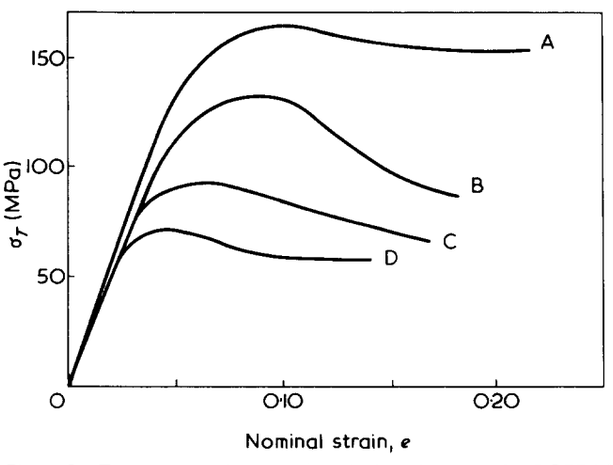

Figure 8 True compressive-stress/nominal-strain curves for DGEBA/9.8 phr TETA at various temperatures. ($\dot{e}$ = 6 X 10^{-4} sec^{-1}). A, −40°C B, 0°C; C, 40°C; D, 80°C

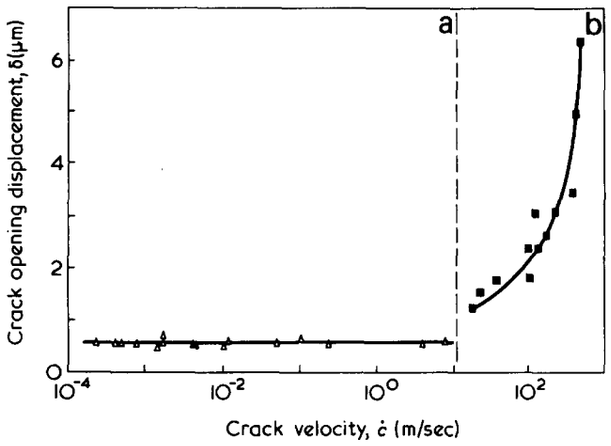

Figure 9 Crack opening displacement, δ, as a function of crack velocity, ċ, for joints bonded with (a) DGEBA/TEPA (△) or (b) DGEBA/3° amine (■) (test temperature 22° ± 2°C)

constant over five decades of crack velocity with a mean value of δ of 0.54 ± 0.06 μm. However, for the DGEBA/3° amine joints the mode of crack growth was entirely stick–slip and δ increases as the initial crack velocity rises. In this case δ does not provide a unique criterion.

The values of δ for the DGEBA/9.8 phr TETA epoxy resin tested in both bulk and joint form are shown in *Table 3* for a range of crosshead displacement rates. Again the value of δ is only constant when continuous crack propagation occurs. The mean value for bulk fracture is 1.10 μm and that for joint fracture is 0.82 μm. Considering the assumptions made in deducing the value of the parameters used in equation (10) to calculate δ, the near agreement of these values of δ suggests that continuous crack propagation in both bulk specimens and joints may be governed by the attainment of a unique value of δ of about 0.9 μm.

The crack opening displacement, δ, is shown as a function of temperature for the bulk fracture of DGEBA/9.8 phr TETA in *Figure 10*. These results confirm that a constant δ provides a fracture criterion only when continuous crack propagation occurs. The value of δ in this case (below 10°C) is about 0.95 μm and is in very good agreement with the values for different crosshead displacement rates in the bulk and joint cases at room temperature.

Mechanisms of crack propagation

As we now have a semiquantitative idea of the fracture criterion in epoxy resin adhesives it would be useful to consider the mechanisms of crack propagation. It is clear that two mechanisms probably exist. Continuous propagation takes place with a constant δ criterion and this can imply one particular mechanism. On the other hand stick–slip propagation does not obey a constant δ criterion and probably takes place through a different mechanism.

Continuous crack propagation in the epoxy resins bears a strong similarity to isothermal crack propagation in poly(methyl methacrylate) (PMMA) which also occurs by means of a constant δ criterion[24]. In PMMA continuous propagation takes place through a region of crazed material at the tip of the crack which can be accurately modelled by a Dugdale line plastic zone[26,27]. However, there is little direct evidence for crazing in epoxy resins. Lilley and Holloway[21] have reported seeing crazes in the vicinity of crack tips in similar epoxy resin systems to those used in this work and the crazes were found to be arranged in a similar way as those around the tips of cracks in polystyrene (PS). However, this particular geometry of crazing in PS tends to blunt the cracks and promote unstable rather than stable propagation[28]. Van den Boogaart[20] has observed crazes at the tips of moving cracks in under-cured epoxy resins and reported that these crazes were identical to those in PMMA although no micrographs were shown of the epoxy resin crazes. In fully cured resins the crazes were not present[20]. At room temperature, in this present work crack propagation was found to be more stable in formulations containing lower amounts of curing agents. This points to the possibility of continuous propagation taking place in the epoxy resins through crazes at the crack tip but more work is required before this suggestion can be confirmed.

The epoxy resin formulations which have been found to give rise to stable propagation at room temperature also show larger load drops at yield than those which undergo stick–slip propagation (*Figures 2* and *4–6*). Haward, Murphy and White[29] have shown that thermoplastics which have large load drops when tested in compression also tend to craze more readily. Thus, this also points to the possibility of crazing taking place in the epoxy resins exhibiting continuous propagation.

Figure 10 shows that the crack opening displacement, δ, rises rapidly when a material undergoes a transition between stable and stick–slip propagation. This is a clear indication that blunting of the crack is taking place when stick–slip propagation occurs. The exact reason for this is at the mo-

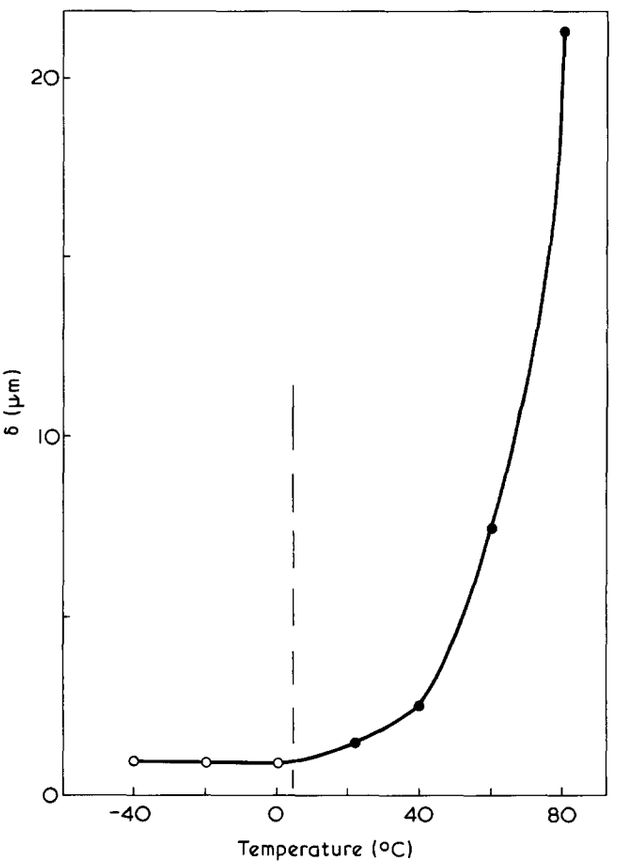

Figure 10 Crack opening displacement, δ, as a function of test temperature for bulk DGEBA/9.8 phr TETA. ○, Continuous; ●, stick–slip

ment not fully understood and it is possible to put forward several explanations for consideration. In the DGEBA/9.8 phr TETA resin, at low crosshead displacement rates, propagation tends to be stick–slip whereas at higher rates propagation is continuous (*Figure 2*). The yield stress of this material decreases as the strain rate is reduced (*Figure 7*) which means that plastic deformation will be easier at low rates of testing. The formation of a plastic zone should therefore be easier at lower crosshead displacement rates. Similarly, the reduction in yield stress as the temperature is increased (*Figure 8*) will also promote easier plastic zone formation which is again consistent with a greater tendency for crack blunting and, hence, for stick–slip behaviour is this material as the temperature is increased (*Figure 3*). Although this mechanism gives a good qualitative explanation of the experimental observations it does not explain why there is a transition between the two types of propagation behaviour at particular temperatures for specific formulations of resin and hardener. This has been explained in a previous publication[17] in terms of $dG_{Ic}/d\dot{c}$ or $dK_{Ic}/d\dot{c}$ becoming negative and so leading to stick–slip propagation. However, this is more likely to be a consequence of the transition rather than a reason for it. It is now apparent that there must be slight and subtle changes in the structure and properties of the material at different testing rates and temperatures, and with different amounts and types of hardener, which lead to the different types of crack propagation taking place.

Implications for static fatigue

In service conditions epoxy resins are often subjected to static loading and so the prediction of the static fatigue characteristics of these materials is of immense importance.

In one material which shows pronounced stick–slip behaviour in constant $\dot{y}$ tests it has been shown[15] that the logarithm of the time-to-failure, during static loading, is linearly dependent upon the applied adhesive fracture energy. The failure time was found to be controlled by an incubation period since when crack propagation did occur the crack velocity was extremely high (i.e. about 20 m/sec) and thus the time during which the crack was actually propagating prior to complete failure was very small (of the order of milliseconds).

However, recent work has shown that epoxy resins, both in the bulk[30] and in joints[31], do not always show this type of static fatigue behaviour. Some resins, especially those which usually exhibit continuous crack propagation behaviour in constant $\dot{y}$ tests, do not appear to suffer from time-dependent failure during a reasonable time scale even when loaded to about 95% of the short-term K_{Ic} value. It has been further shown[31] that if the static fatigue behaviour of such a material is interrupted and a constant $\dot{y}$ test performed, the epoxy resin shows stick–slip crack propagation rather than continuous propagation for the initial crack movement. This occurs at a much higher K_{Ic} value (up to about 100% higher) than for continuous propagation in the material before being subjected to static loading. However, after the first jump propagation takes place in a continuous manner at the original level of K_{Ic}.

Using the model proposed in the previous section static fatigue loading is equivalent to a very low strain rate test. Thus, the yield stress of the material is reduced, local crack blunting occurs and the apparent toughness of the material is increased and stick–slip propagation occurs. However, once the crack has propagated through the blunting region further propagation occurs in a stable continuous manner.

Further, this tendency for the cracks to blunt and hence cause an increase in the apparent K_{Ic} after a short time under static load means that although the static load applied may initially represent about 95% of that required for fracture this percentage rapidly diminishes as the experiment proceeds. This explains why fracture is not observed within the expected time scale (i.e. several months).

CONCLUSIONS

Crack propagation in amine-cured epoxy resin adhesives in both bulk and joint specimens has been shown to take place in either a continuous or stick–slip manner depending upon the formulation of the resin and the experimental conditions. When propagation is continuous it has been shown that a constant crack opening displacement is a unique failure criterion. Crack propagation in the adhesive joints has been shown to be completely analogous to that in the bulk material. In both cases the transition between stick–slip and continuous propagation takes place at approximately the same rate of testing and both types of propagation occur at about the same values of stress intensity factor and crack opening displacement. The resins used in the crack propagation studies have also been tested in uniaxial compression. It has been shown that the formulation which have the highest yield stresses tend to fail by continuous propagation whereas the materials with lower yield stresses undergo stick–slip crack propagation.

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