

# Deformation and fracture behaviour of a rubber-toughened epoxy: 2. Failure criteria

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(Received 9 March 1983)

In part 1 the microstructure and fracture characteristics of a rubber-modified epoxy, and for comparison that of the unmodified epoxy, were examined in detail. Based on this analysis a qualitative mechanism involving cavitation, shear yielding and plastic flow was proposed. As an extension of this work, the present paper considers the yield behaviour of the epoxy material and uses the data determined, together with the previously reported fracture results, to calculate values of the crack opening displacement. The rate/temperature dependence of the crack opening displacement and the correlations established between stress intensity factor,  $K_{Ic}$ , yield stress and type of crack growth suggest that the extent of crack tip blunting largely governs the relative toughness of the epoxy materials and induces transitions in the types of crack growth observed. A quantitative expression is then presented which successfully describes the fracture toughness values over a wide range of temperatures and rates. The two parameters in this expression are shown to be material constants and therefore provide a unique failure criterion. They can be viewed simply as curve-fitting parameters but they may also have some significance in terms of a critical stress that must act over a critical distance ahead of the crack tip to produce crack growth.

**Keywords** Epoxy resins; crack modelling; fracture; liquid rubbers; toughening; yield

## INTRODUCTION

The new generation of rubber-toughened epoxies are two-phase materials essentially consisting of relatively small rubbery particles dispersed in, and bonded to, a matrix of epoxy. This microstructure results in a considerably enhanced toughness compared to the unmodified epoxy but without appreciable losses in other important properties, such as modulus and high-temperature performance. For these reasons rubber-toughened epoxies are being increasingly employed as the basis for adhesive compositions and as the matrix material for fibre composites.

In a previous paper<sup>1</sup> (Part 1) the microstructure and fracture characteristics of a model rubber-modified epoxy, and for comparison that of the unmodified epoxy, were examined in detail. As might be expected, the stress intensity factor,  $K_{Ic}$ , (or fracture toughness) for the onset of crack growth was shown to be appreciably greater for the rubber-modified epoxy and to be more dependent upon test rate and temperature. Over the wide range of test temperatures and rates, however, some important similarities between the two materials were observed. For example, with both materials three basic types of crack growth could be identified. These were:

(i) Brittle stable crack growth occurred where the crack grew in a steady controlled manner with the rate of crack propagation being dependent upon the displacement rate,  $\dot{y}$ , of the testing machine employed. This type of crack

growth was termed 'type C'. It was generally favoured by very high displacement rates and/or low test temperatures and under these conditions the value of  $K_{Ic}$  for crack growth was comparatively low and almost independent of test temperature and rate.

(ii) A second type of crack growth could be identified when crack propagation occurred intermittently in a stick/slip manner exhibiting load values appropriate to both crack initiation and arrest. This brittle, unstable crack growth was termed 'type B' and was generally favoured by lower displacement rates or higher test temperatures compared to the conditions under which brittle, stable crack growth (type C) was observed. The stress intensity factor,  $K_{Ic}$ , for crack extension was rate/temperature dependent and greater than the value for crack arrest which was virtually rate/temperature independent.

(iii) At higher test temperatures stable crack growth was again observed. However, unlike the brittle stable crack growth discussed in (i), a relatively high value of  $K_{Ic}$  was now required and examination of the fracture surfaces clearly revealed that a highly ductile fracture had occurred. This ductile stable crack growth was termed 'type A' and the associated value of  $K_{Ic}$  was highly dependent upon rate and temperature, again in contrast to brittle stable (type C) crack growth.

Another common feature of the behaviour for both materials is that the transition between one type of crack

growth and another generally occurred over a range of temperatures and rates and was characterized by a combination of both growth modes. This combination consisted of a short region of stable slow crack growth during the latter stages of loading followed by unstable growth which produced a rapid drop in the load. The one exception to this behaviour was the transition between type B and type A growth in the unmodified epoxy which was sharp without any region of intermediate behaviour.

Many other similarities and differences between the behaviour of the two materials were discussed in part 1<sup>1</sup> and this discussion concluded that these characteristics could be rationalized by the proposal that shear yielding and plastic flow are the pertinent deformation mechanisms in both materials. It was suggested, however, that the extent of this yielding and flow is controlled by different factors in the two materials. In the unmodified epoxy the normal crack tip stress field is the dominant factor, but in the modified epoxy the rubber particles also play a major role. In the latter case the stress concentrations around the particles near the crack tip augment the crack tip stress field and act as multiple initiation points for shear yielding in the matrix. The material also undergoes dilatation which leads to microvoid formation either in the rubber particle or at the particle/epoxy-matrix interface. This further facilitates shear yielding in the matrix by lowering the degree of constraint in the vicinity of the voids. Thus, both the fracture toughness and the rate/temperature sensitivity of the rubber-modified epoxy are greatly enhanced.

The toughening mechanism outlined above, and discussed in detail in part 1<sup>1</sup>, highlights the importance of investigating the yield behaviour of the epoxy materials and determining the extent of localized plastic deformations and accompanying crack tip blunting. The present paper first considers both these aspects and then describes a quantitative expression for the failure behaviour. It will be shown that this model leads to an understanding of the different types of crack growth occurring over particular test rate/temperature regimes and the rate/temperature dependence of the measured  $K_{Ic}$  values. This model enables failure criteria for both the unmodified and rubber-modified epoxies to be identified.

EXPERIMENTAL

The materials

The materials, their preparation and characterization were described in detail in the previous paper<sup>1</sup>. The epoxy resin employed was basically a diglycidyl ether of bisphenol A and was cured using piperidine. The rubber used was a carboxyl-terminated, random copolymer of butadiene and acrylonitrile. The formulations of the epoxy materials are shown in Table 1 and specimens were

Table 1 Formulations of epoxy materials

	Unmodified epoxy	Rubber-modified epoxy
Epoxy resin	100 (phr*)	100 (phr)
Piperidine	5	5
Carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber	—	15

\* phr = parts per hundred resin by weight

prepared by casting the material into a mould and then curing at 120°C for 16 h and allowing to cool slowly.

Uniaxial compression studies

Since the epoxy materials under study fracture when tested in uniaxial tension prior to plastic yielding, their yield behaviour was examined by testing in uniaxial compression. Cylindrical rods of the cured epoxies were cast as described above and then machined to give test specimens with a height-to-diameter ratio of about 2:1. The specimens were deformed in a compression cage between polished steel plates lubricated with molybdenum disulphide grease. A constant displacement rate,  $\dot{y}$ , was used for each test and this was converted to a strain rate,  $\dot{\epsilon}$ , using the specimen dimensions. 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 load-displacement record and converted into a true stress,  $\sigma$ , using the initial specimen cross-sectional area,  $A_0$ , in the equation:

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

which assumes constant-volume deformation. The true compressive modulus,  $E$ , true compressive yield stress,  $\sigma_{yc}$ , and the yield strain  $e_y$ , were also determined.

Fracture experiments

The experimental results in this study suggested that crack tip blunting was an important feature in the failure mechanism. In an effort to examine this effect directly a series of fracture experiments was performed in which a blunt crack tip was produced by drilling a small hole at the end of the pre-crack of the compact-tension test specimen and determining the value of the stress intensity factor for crack initiation as described previously<sup>1</sup>. In this way fracture data could be obtained for a range of different, known crack tip radii.

RESULTS AND DISCUSSION

Modulus and yield data

The true compressive modulus,  $E$ , and yield stress,  $\sigma_{yc}$ , determined as described above are shown as a function of strain rate,  $\dot{\epsilon}$ , and temperature,  $T$ , in Figures 1 and 2 for the

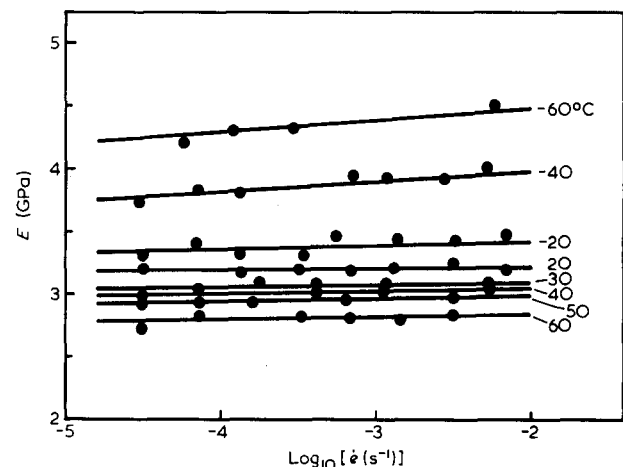


Figure 1 True compressive modulus,  $E$ , versus logarithm of strain rate,  $\dot{\epsilon}$ , for the unmodified epoxy

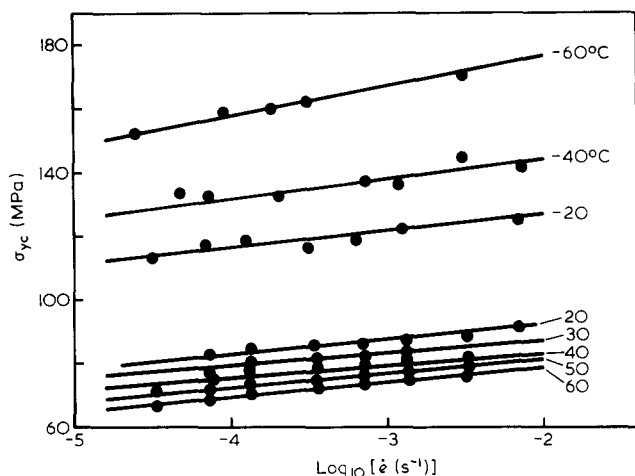


Figure 2 True compressive yield stress,  $\sigma_{yc}$ , versus logarithm of strain rate,  $\dot{\epsilon}$ , for the unmodified epoxy

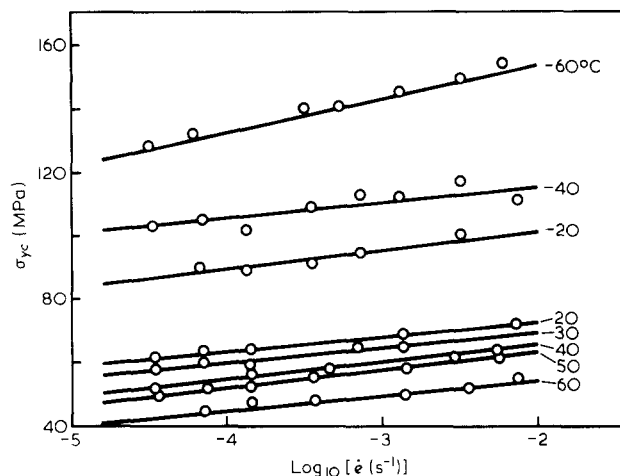


Figure 4 True compressive yield stress,  $\sigma_{yc}$ , versus logarithm of strain rate,  $\dot{\epsilon}$ , for the rubber-modified epoxy

unmodified epoxy and Figures 3 and 4 for the rubber-modified epoxy respectively.

Considering first the modulus values, then as expected for viscoelastic polymeric materials, the value of  $E$  decreases as the test temperature increases or the rate decreases. The presence of the rubbery second phase in the rubber-modified epoxy results in the value of  $E$  for this material being somewhat lower than for the unmodified epoxy and being slightly more rate/temperature dependent; again these observations are exactly as expected.

The values of true compressive yield stress,  $\sigma_{yc}$ , are plotted against the logarithm of the strain rate,  $\dot{\epsilon}$ , in Figures 2 and 4 for the unmodified and rubber-modified epoxies respectively. The latter material has a two-phase microstructure (see part 1<sup>1</sup>) and the rubbery second phase possesses a low shear modulus compared to the epoxy matrix, which means that the rubbery particles are unable to support a significant share of the stress. This is reflected in the values of  $\sigma_{yc}$  for the rubber-modified epoxy being somewhat lower than for the unmodified epoxy. The ratio of the yield stress of the rubber-modified to the unmodified material varies from about 0.9 at low test temperatures to about 0.6 at high temperatures. It is of

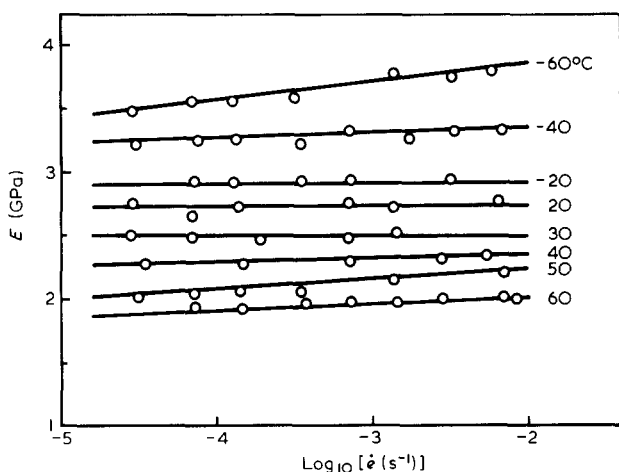


Figure 3 True compressive modulus,  $E$ , versus logarithm of strain rate,  $\dot{\epsilon}$ , for the rubber-modified epoxy

interest to note that the variation of this ratio with temperature, or indeed with rate, implies that any model which attempts to describe the dependence of the yield stress of a material upon the concentration of a second particulate phase must not simply be based upon the microstructural geometry, which is invariant with test conditions. The effective area model<sup>2,3</sup> is one such simplistic idea which assumes no adhesion between spherical filler particles and the matrix. Thus, the load is sustained only by the matrix and, from elementary geometrical considerations, an average stress borne by the matrix in those regions where yielding is occurring is deduced. The relation between the yield stress of the two-phase material and the volume fraction,  $v_f$ , of the spherical second-phase is given by:

$$\sigma_{yc}(\text{two-phase material}) = \sigma_{yc}(\text{matrix})(1 - 1.21v_f^{2/3}) \quad (2)$$

This model has recently been examined<sup>4</sup> in connection with rubber-toughened thermoplastics and found to result in only moderate agreement when predicting the yield stress behaviour as a function of the volume fraction of the rubbery phase present. The present work reinforces the inapplicability of the effective area model. In the case of the epoxy materials, a yield stress ratio for the rubber-modified to the unmodified material of about 0.7 is predicted from equation (2). Now, whilst the model may be modified to take into account the presence of good adhesion across the rubber/matrix interface, the model would still not predict the rate/temperature dependence of the yield stress ratio. Obviously, the load-sharing ability of the rubbery particles, particularly at low temperatures when their moduli are relatively high, must be taken into account if any model is successfully to predict the effect of the rubbery phase on the material's yield behaviour.

The data in Figures 2 and 4 clearly demonstrate the viscoelastic nature of the yield behaviour of both materials. The values of  $\sigma_{yc}$  decrease as the temperature is increased or the rate decreased. This dependence may be modelled using the Eyring theory of viscosity. The Eyring theory<sup>5,6</sup> assumes an activated rate process, i.e. one involving the surmounting of a potential energy barrier of height  $\Delta E^*$ . The energy barrier may be surmounted because random thermal fluctuations ensure that the

thermal or kinetic energy of an atom or molecular segment varies in time with a finite probability of exceeding the potential barrier. The model envisages that the effect of an applied stress is to reduce the height of the barrier for a jump in the forward direction and to increase it for a jump in the reverse direction. It is further assumed that the macroscopic strain rate of the sample is proportional to the net jump rate of the segments in the forward direction. Thus in the high-stress region where yield occurs the Eyring theory gives the relationship between strain rate,  $\dot{\epsilon}$ , and yield stress,  $\sigma_{yc}$ , as:

$$\dot{\epsilon} = A_E \exp\left(-\frac{\Delta E^* - v^*|\sigma_{yc}|}{RT}\right) \quad (3)$$

where  $A_E$  is a constant,  $R$  is the gas constant and  $v^*$  is the activation volume. This equation has been used by several workers<sup>7-11</sup> to describe the rate and temperature dependence of the yield behaviour of glassy thermoplastic polymers such as poly(methyl methacrylate), polyvinylchloride and polycarbonate. It may be conveniently rearranged so that:

$$|\sigma_{yc}| = \frac{\Delta E^*}{v^*} + \frac{2.303RT}{v^*} \log\left(\frac{\dot{\epsilon}}{A_E}\right) \quad (4)$$

The yield data shown in *Figures 2* and *4* for the unmodified and rubber-modified epoxies respectively are indeed such that  $\sigma_{yc}$  versus  $\log \dot{\epsilon}$  plots are linear over the complete temperature range studied. Equation (4), however, predicts that the slope should decrease with decreasing temperature, but the figures clearly show an increase in slope at  $-60^\circ\text{C}$ . One possible explanation for this is that the  $\beta_r$  transition of the epoxy and the glass transition of the rubber particles occur in this general time/temperature region<sup>1</sup>. These transitions may complicate the yielding mechanisms in this range. At higher temperatures, however, the viscoelastic nature of the yield behaviour for these materials may be modelled by equation (4). An inspection of the data using a correlation analysis gives best-fit values for the activation energy,  $\Delta E^*$ , and the activation volume,  $v^*$ , which are  $350 \text{ kJ mol}^{-1}$  and  $2.0 \text{ nm}^3$  per molecule respectively for the unmodified epoxy and  $290 \text{ kJ mol}^{-1}$  and  $1.9 \text{ nm}^3$  per molecule respectively for the rubber-modified epoxy. The correlation coefficients associated with these values over the range of test rates and temperatures are 0.97 and 0.99 for the unmodified and rubber-modified epoxies.

It is evident, therefore, that the viscoelastic nature of the yield process in thermoset epoxies and many glassy thermoplastics may be described by an activated rate model, such as equation (4). This is in agreement with the results of Sultan and McGarry<sup>12</sup> who studied similar materials and found the same result but with a somewhat lower activation energy of  $240 \text{ kJ mol}^{-1}$ . Further, it has been found<sup>7,8</sup> that for polycarbonate, which is also a derivative of bisphenol A and has a somewhat similar backbone structure to an epoxy, the yield behaviour *above* about  $-50^\circ\text{C}$  could be modelled by equation (4) with values of  $\Delta E^*$  and  $v^*$  of  $335 \text{ kJ mol}^{-1}$  and  $2.8 \text{ nm}^3$  respectively. These values are obviously very similar to those obtained for the thermoset epoxies. Thus, the current studies strongly support recent work reported by Yamini and Young<sup>13</sup>. These authors examined the extension of the Argon<sup>14</sup> and Bowden<sup>15</sup> theories of yielding in

glassy thermoplastics to crosslinked thermoset polymers. They concluded that the plastic deformation of epoxy materials below their glass transition temperature is in many respects similar to that of glassy amorphous thermoplastics.

However, whilst the above discussions have illustrated the usefulness of an activated rate model, the physical significance of the parameters  $\Delta E^*$  and  $v^*$ , if any, is obscure. The value of  $\Delta E^*$  cannot usually be directly correlated to any molecular relaxation process. It has been suggested<sup>16</sup> that the activation volume represents the volume of the polymer segment which has to move as a whole in order for flow to occur. Alternatively, it has been argued<sup>17</sup> that although  $v^*$  has the dimensions of volume, it is not in fact a volume: the quantity  $v^*\sigma_{yc}$  has the dimensions of energy and is the work done on a mobile segment during a jump. Thus, it is extremely difficult to interpret the values of  $\Delta E^*$  and  $v^*$  calculated for the unmodified and rubber-modified epoxies in terms of molecular structural parameters and they are probably best thought of as fitting parameters which indicate the stress and temperature dependence of the process.

#### Crack opening displacement

The various models<sup>7</sup> such as those of Irwin<sup>18</sup> and Dugdale<sup>19</sup> have been proposed to describe the extent and shape of the localized plastic deformation zone at a crack tip. From these models one may define a parameter known as the crack opening displacement,  $\delta_1$  (see *Figure 8*) and the value of  $\delta_{ic}$  for the onset of crack growth is given by:

$$\delta_{ic} = \left(\frac{K_{Ic}}{\sigma_{yt}}\right)^2 e_y \quad (5)$$

where  $K_{Ic}$  is the measured stress intensity factor at the onset of crack growth,  $\sigma_{yt}$  is the tensile yield stress and  $e_y$  is the yield strain.

The value of  $\delta_{ic}$  obviously reflects the degree of crack tip blunting and values were therefore calculated for the unmodified and rubber-modified epoxies. The relevant value of  $K_{Ic}$  was taken from the results presented in part 1<sup>1</sup> and values of  $\sigma_{yc}$  and  $e_y$  were determined from the uniaxial compression tests, as described above. Now in polymers the yield stress is usually dependent upon both the hydrostatic and deviatoric components of the stress tensor and a consequence of this is that the true yield stress is invariably higher in uniaxial compression than in tension. Various workers<sup>7,12,20,21</sup> have investigated the applicability of different yield criteria which embody a hydrostatic stress component and in the case of epoxies these criteria reveal that the ratio of the tensile to the compressive yield stress ( $\sigma_{yt}:\sigma_{yc}$ ) is about 0.75. This ratio has been used in the present work to deduce the values of the true tensile yield stress,  $\sigma_{yt}$ . The fracture data were related to the yield data by approximately equating the time-to-failure in the former tests to the time-to-yield in the latter. This resulted in a displacement rate,  $\dot{y}$ , of say  $8.3 \times 10^{-7} \text{ m s}^{-1}$  being equivalent to a strain rate,  $\dot{\epsilon}$ , of  $8.3 \times 10^{-5} \text{ s}^{-1}$ , i.e. a two decade difference.

Values of the crack opening displacement,  $\delta_{ic}$ , at the onset of crack growth are shown as a function of test temperature, at three different test rates, for the unmodified and rubber-modified epoxies in *Figures 5* and *6* respectively. The main types of crack growth initially

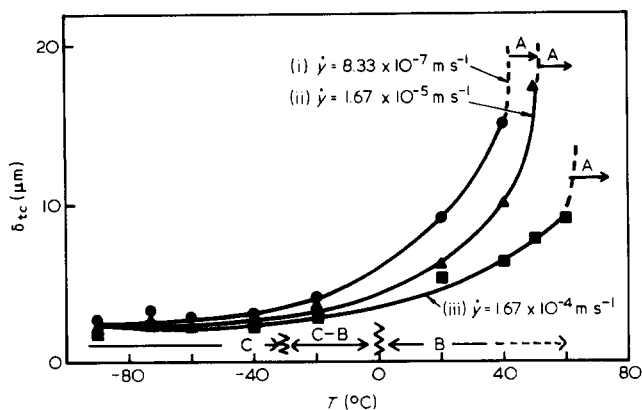


Figure 5 Crack opening displacement,  $\delta_{ic}$ , as a function of test temperature for the unmodified epoxy: type A, ductile stable crack growth; type B, brittle unstable crack growth; type C, brittle stable crack growth; type C→B, combination of types

observed in the fracture tests at the different temperatures and rates are also indicated.

Several interesting aspects arise from these data. Firstly, it was noted in part 1<sup>1</sup> that the values of  $K_{Ic}$  exhibited a slight increase when going from  $-60^\circ$  to  $-90^\circ\text{C}$ . In Figures 5 and 6, however, no such trend is seen for  $\delta_{ic}$ . This suggests that the low-temperature increase in  $K_{Ic}$  reflects a relatively small decrease in  $\delta_{ic}$  at low temperatures combined with a larger increase in  $\sigma_{yt}$  over the same range. Secondly, the values of  $\delta_{ic}$  increase with increasing temperature and decreasing rate. This suggests that the extent of localized plastic deformations at the crack tip, and the associated crack tip blunting, increases steadily as the temperature is increased or rate decreased, i.e. as the material's yield stress steadily falls. Thirdly, accompanying this increase in crack tip blunting, transitions in the type of crack growth are observed: type C to type B

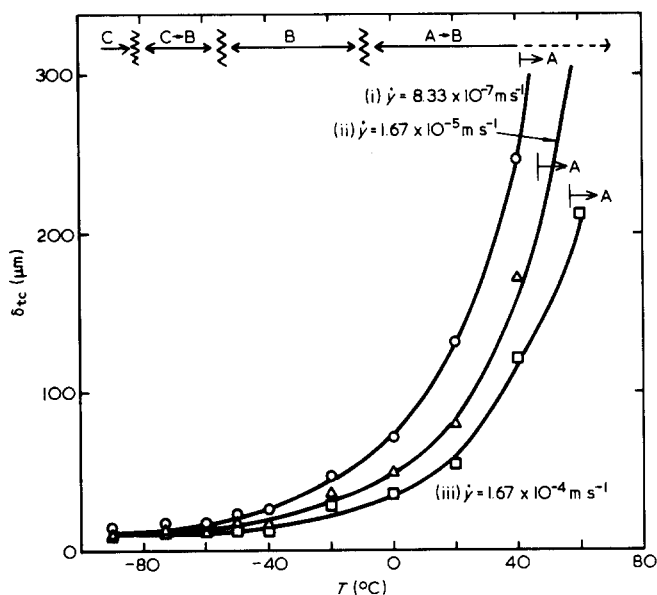


Figure 6 Crack opening displacement,  $\delta_{ic}$ , as a function of test temperature for the rubber-modified epoxy: type A, ductile stable crack growth; type B, brittle unstable crack growth; type C, brittle stable crack growth; type C→B and type A→B, combination of types

type A as the crack becomes progressively blunter prior to propagation. It is noteworthy that when brittle stable crack growth initiates (i.e. types C or C→B) then the value of  $\delta_{ic}$  is far less rate/temperature dependent than when types B or A growth initiate. However, the value of  $\delta_{ic}$  for brittle stable crack growth is still not invariant with test temperature or rate. This is in contrast to some glassy thermoplastics<sup>22,23</sup> and indeed even some other unmodified epoxies<sup>24,25</sup> where a constant value of  $\delta_{ic}$  has been found to govern the fracture behaviour during this type of crack growth. In the case of the thermoplastics this difference may arise because a different energy-dissipating mechanism is involved: localized crazing at the crack tip for the thermoplastics but localized shear yielding for the present epoxy formulations. Further, the apparent differences in behaviour of the present and previously studied epoxies may actually be non-existent. Careful examination of the previous work reveals that a far more limited temperature range was employed and any small but systematic variation in the value of  $\delta_{ic}$  could have been obscured by the experimental scatter. In any event, it is obvious that for the unmodified and rubber-modified epoxies currently under investigation a constant crack opening displacement does not provide a valid failure criterion over any significant part of the rate/temperature spectrum studied.

#### Relation between fracture and yield behaviour

The above observations do however enable a qualitative relation, based upon the role of crack tip blunting, to be postulated between the fracture behaviour and the viscoelastic yield behaviour of the materials. The basis for this relationship is the idea that crack tip blunting decreases the local crack tip stress concentration and thus higher applied loads are required to cause failure.

Considering the relations in detail, then crack opening displacement increasing with increasing temperature and decreasing rate is obviously a clear indication that the extent of crack tip blunting, resulting from localized plastic deformation at the crack tip, is increasing under these conditions. Furthermore, the results suggest that this rate/temperature dependence arises from the viscoelastic nature of the yield processes in these materials: the yield stress decreasing with increasing temperature and decreasing rate.

Therefore, turning to the rate/temperature dependence of the fracture behaviour, at low temperatures (or very high loading rates) crack initiation will involve a minimum of crack tip yielding and so the crack is relatively sharp and the stress intensity factor low. This is also the case for crack arrest which is associated with very short deceleration times (i.e. very high crack tip strain rates). Thus at low temperatures, both initiation and arrest involve relatively sharp cracks and similar loads, so stable crack growth results. As the temperature is increased (or the loading rate decreased) the yield stress declines (and the time during which plastic flow can occur increases) so more crack tip yielding is possible. This results in higher failure loads (larger  $K_{Ic}$  values). Once the crack begins to grow, however, the crack tip sharpens because the time period during which the material at the crack tip can yield is reduced. Consequently, the load required to propagate this sharp crack is less than that required to initiate crack growth. Only when the load falls to that associated with crack arrest will the growth stop. This of course produces

unstable crack growth. Eventually when the temperature is high enough (at a given loading rate) a ductile or tearing failure mode is achieved and stable crack growth is observed once again. The interdependence of rate and temperature in affecting the transition to ductile stable (type A) crack growth may be clearly seen in Figures 5 and 6. As the test rate is increased, which results in less crack tip blunting at a given temperature, a higher transition temperature is observed. Interestingly enough, although this transition behaviour is very different for the modified and unmodified epoxy (the latter showing a very dramatic increase in  $\delta_{ic}$  and  $K_{Ic}$ ) the transitions occur at similar rates and temperatures.

The arguments outlined above may also be readily employed to explain results from previous experiments where epoxy resins were: (i) subjected to a constant load just below the short-term fracture load for a few days prior to testing<sup>26,27</sup> or (ii) exposed to high humidity or water for a short period prior to testing<sup>28,29</sup>. These experiments showed that such test conditions can cause both an increase in toughness and a change from brittle stable to unstable crack growth. These changes can be explained in terms of the arguments presented above since such conditions would be expected to increase the ability of the material to undergo relatively greater deformation in the vicinity of the crack tip due to a lowering of the strain rate or plasticization, respectively.

Now these relations between fracture toughness, type of crack growth and yield behaviour may be expressed in a more quantitative manner by normalizing the measured values of the stress intensity factors at the onset of crack growth by  $K_{Ics}$ . The values of  $K_{Ics}$  were taken to be the stress intensity factors measured at the lowest test temperatures where the yield stresses were high and the crack tip relatively sharp as indicated by the low values of  $\delta_{ic}$  shown in Figures 5 and 6. Thus, for the unmodified and rubber-modified epoxies, values for  $K_{Ics}$  of  $0.85 \text{ MN m}^{-3/2}$  and  $1.6 \text{ MN m}^{-3/2}$  were deduced<sup>1</sup>, respectively. The ratio  $K_{Ic}/K_{Ics}$  then reflects the change in toughness due to crack blunting. This ratio is shown plotted against the corresponding tensile yield stress,  $\sigma_{yt}$ , for the epoxies in Figure 7. The results in this figure show a general correlation between toughening, the type of crack growth, and the yield stress. A close examination, however, reveals that the correlation is not quantitative especially for describing the behaviour of modified versus unmodified epoxy in the region between type B and type A crack growth. The unmodified epoxy shows a sudden increase in  $K_{Ic}$  and a sudden shift from type B to type A crack growth for  $\sigma_{yt}$  values below 60 MPa. There is no intermediate type A→B growth. The modified epoxy, on the other hand, shows a gradual increase in  $K_{Ic}$  with decreasing  $\sigma_{yt}$  and a wide range of type A→B growth.

ANALYSIS OF CRACK TIP BLUNTING

Theory

In light of the observation above, it is of interest to examine models which combine yield behaviour with various failure criteria to see if any such theory can describe the fracture results for these materials. One model which has shown some success in the past for certain epoxy systems<sup>30</sup> was examined and although it contains only a very simplistic picture of the crack tip deformation zone, the results were promising. This model

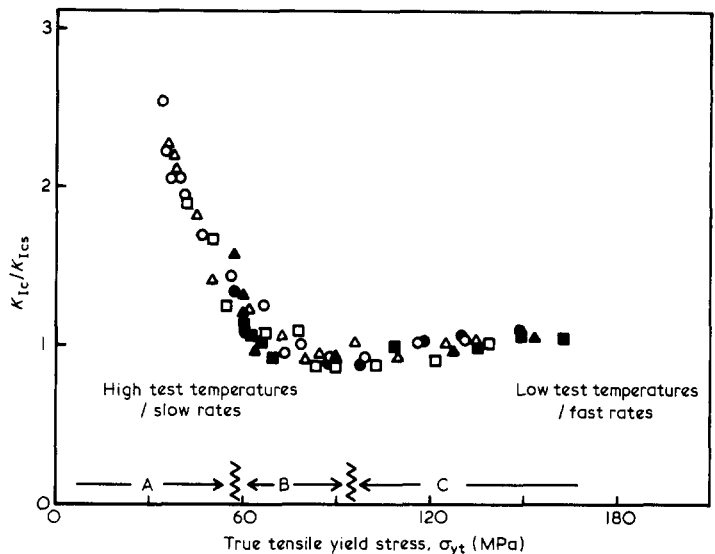


Figure 7 Relation between  $K_{Ic}/K_{Ics}$  ratio, true tensile yield stress,  $\sigma_{yt}$ , and type of crack growth:  $\circ, \bullet, \dot{\gamma}=8.33 \times 10^{-7} \text{ m s}^{-1}$ ;  $\triangle, \blacktriangle, \dot{\gamma}=1.67 \times 10^{-5} \text{ m s}^{-1}$ ;  $\square, \blacksquare, \dot{\gamma}=1.67 \times 10^{-4} \text{ m s}^{-1}$ ; open symbols, rubber-modified epoxy; filled symbols, unmodified epoxy. Crack initiation via: type A, ductile stable crack growth; type B, brittle unstable crack growth; type C, brittle stable crack growth

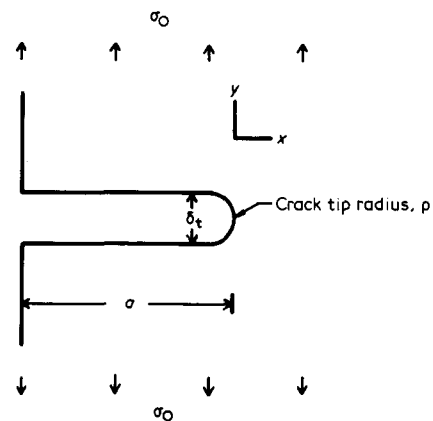


Figure 8 Crack tip geometry

can be formulated by noting that, for a crack tip radius,  $\rho$ , and length,  $a$ , then the stress,  $\sigma_{yy}$ , normal to the axis of the crack at a small distance,  $r$ , ahead of the tip (Figure 8) is given by<sup>31</sup>:

$$\sigma_{yy} = \frac{\sigma_0 \sqrt{a}}{\sqrt{(2r)}} \frac{1 + \rho/r}{(1 + \rho/2r)^{3/2}} \tag{6}$$

where  $\sigma_0$  is the applied stress. Now it has been postulated<sup>30,32</sup> that fracture occurs when a critical stress,  $\sigma_{tc}$ , is attained at a certain distance,  $c$ , ahead of the crack tip; then  $\sigma_{yy} = \sigma_{tc}$  and  $r = c$  and equation (6) becomes:

$$\sigma_{tc} = \frac{\sigma_0 \sqrt{a}}{\sqrt{(2c)}} \frac{1 + \rho/c}{(1 + \rho/2c)^{3/2}} \tag{7}$$

The measured stress intensity factor,  $K_{Ic}$ , at the onset of

crack growth is related to the applied stress,  $\sigma_0$ , by:

$$K_{Ic} = \sigma_0 \sqrt{\pi a} \quad (8)$$

and the propagation of a 'sharp' crack at a value of  $K_{Ics}$  may be interpreted as requiring the critical stress,  $\sigma_{Ic}$ , to be attained at the distance,  $c$ , such that:

$$K_{Ics} = \sigma_{Ic} \sqrt{2\pi c} \quad (9)$$

Thus, by rearranging equation (7) so that:

$$\frac{\sigma_0 \sqrt{\pi a}}{\sigma_{Ic} \sqrt{2\pi c}} = \frac{(1 + \rho/2c)^{3/2}}{1 + \rho/c} \quad (10)$$

and substituting for equations (8) and (9) yields:

$$\frac{K_{Ic}}{K_{Ics}} = \frac{(1 + \rho/2c)^{3/2}}{1 + \rho/c} \quad (11)$$

Hence the ratio  $K_{Ic}/K_{Ics}$  may be directly and quantitatively related to the crack tip radius,  $\rho$ , at the onset of crack growth by assuming a failure criterion based upon the attainment of a critical stress acting at a certain distance ahead of the tip. A brief examination of equation (11) shows that it exhibits the same general trends with regard to rate and temperature dependence that were used successfully in the yield stress discussion to explain in a qualitative way the observed fracture behaviour. The important question therefore is whether this expression can provide a quantitative description.

#### Fracture results

To examine this question experimentally, values of  $K_{Ic}/K_{Ics}$  are plotted against  $\sqrt{\rho}$  for the unmodified and rubber-modified epoxies in Figures 9 and 10 respectively. The values of the crack tip radius,  $\rho$ , at failure were determined by two different methods. Firstly, previous experimental studies by Kinloch and Williams<sup>30</sup> and theoretical analysis by McMeeking<sup>33</sup> have indicated that the value of  $\rho$  may be taken to be equivalent to the crack opening displacement,  $\delta_{Ic}$ . The open data points in Figures 9 and 10 represent results from the fracture

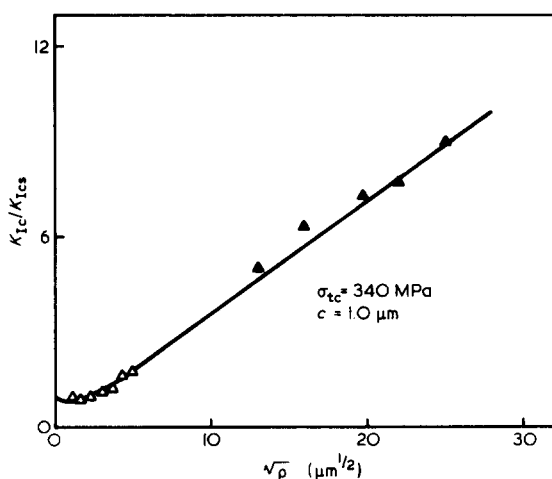


Figure 9  $K_{Ic}/K_{Ics}$  ratio versus  $\sqrt{\rho}$  for the unmodified epoxy:  $\Delta$ , values of  $\rho$  deduced from equation (5);  $\blacktriangle$ , measured values of  $\rho$ ; full curve, theoretical relation from equation (11)

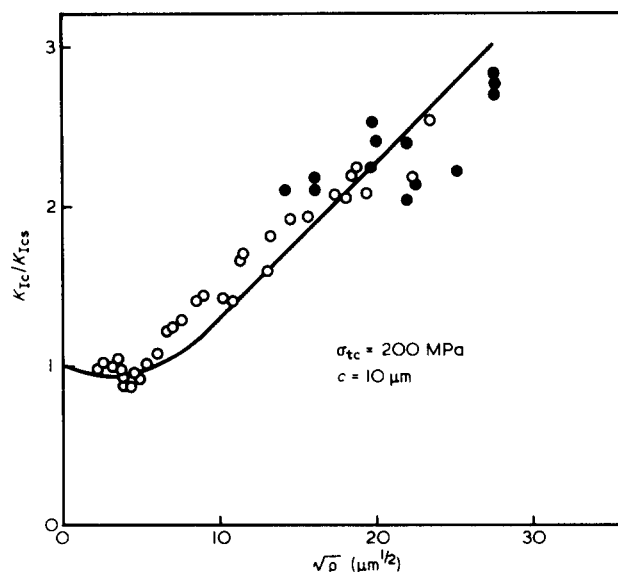


Figure 10  $K_{Ic}/K_{Ics}$  ratio versus  $\sqrt{\rho}$  for the rubber-modified epoxy:  $\circ$ , values of  $\rho$  deduced from equation (5);  $\bullet$ , measured values of  $\rho$ ; full curve, theoretical relation from equation (11)

experiments reported in part 1<sup>1</sup> where the degrees of blunting developed naturally during the test and in these instances the values of  $\rho$  were calculated from equation (5). Secondly, the filled data points represent the results of the experiments where a blunt crack tip was formed by drilling a hole at the end of the crack so the values of  $\rho$  in these cases were known. Finally, the full curves drawn in these figures are the theoretical relations deduced from equation (11), using the value of  $c$  indicated.

The data shown in Figures 9 and 10 convincingly demonstrate that the results obtained from both types of experimentally induced blunting, where the values of  $\rho$  were either calculated or measured directly, are in good agreement. Furthermore, for both epoxy materials both types of induced blunting are in accord with the theoretical relation predicted from equation (11).

#### Failure criterion

Equations (5) and (11) therefore provide a description of  $K_{Ic}$  based upon a knowledge of the yield behaviour ( $\sigma_{yt}$  and  $e_y$ ) and two adjustable parameters, namely  $c$  and  $K_{Ics}$  (or  $\sigma_{Ic}$ ). By applying an appropriate analysis the experimental data were fitted to equation (11) and the best values of  $c$  and hence  $\sigma_{Ic}$  obtained. The results give values of  $\sigma_{Ic}$  and  $c$  of 340 MPa and 1.0  $\mu\text{m}$  for the unmodified epoxy and 200 MPa and 10  $\mu\text{m}$  for the rubber-modified epoxy. Since these parameters are indeed constants for each material, they provide unique failure criterion over the complete range of test conditions.

The two constants,  $c$  and  $\sigma_{Ic}$ , may be interpreted simply as empirical fitting parameters in a set of equations which provide a good first-order fit of the data over a wide range of conditions. It is intriguing, however, to speculate about the possible implications that these parameters may have when interpreted in terms of a critical stress level acting over a critical distance ahead of the crack tip. Firstly, the toughened rubber-modified epoxy has a lower value of  $\sigma_{Ic}$  but a higher value of  $c$  than does the unmodified epoxy. Secondly, the values obtained for  $\sigma_{Ic}$  suggest that a stress of roughly 2–4 times the uniaxial tensile yield stress must

be reached in the plastic zone. Consequently, it is tempting to interpret the critical stress,  $\sigma_{ic}$ , as a constrained yield stress. Such values would be in agreement with the analyses of crack tip stress distributions reported by McMeeking<sup>33</sup>, Rice and Rosengren<sup>34</sup> and Rice and Johnson<sup>35</sup>, especially if a degree of post-yield strain hardening occurs as has been reported for epoxy materials<sup>25</sup>. Also, the values of  $\sigma_{ic}$  calculated from the present analysis, which is based upon linear elastic fracture mechanics, are in good agreement with values of the maximum stress,  $\sigma_{yy}$ , ahead of a crack preceded by a plastic zone recently deduced by Narisawa *et al.*<sup>36</sup> who used a slip-line field solution for perfectly plastic bodies. They calculated values of  $\sigma_{yy}(\max)$  which represented the stresses necessary for yielding under the constrained conditions at a crack tip and, for three different simple epoxy formulations, reported values of the order of several hundred megapascals. If this interpretation of  $\sigma_{ic}$  as a constrained yield stress is correct, then it does reveal that the degree of constraint is obviously significantly less for the rubber-modified epoxy than for the unmodified material (c.f.  $\sigma_{ic}$  values). However, the value of  $\sigma_{ic}$  of 200 MPa for the toughened epoxy does imply that cavitation of the rubber particles cannot have fully relieved the constraint close to the crack tip, at least in the initial stages of crack growth. This may reflect the fact that the distance over which the critical stress acts is very much smaller than the shear yield deformation zone or that the stress field ahead of the crack never does completely attain a state of simple extension. Thirdly, although a detailed physical interpretation of the critical stress,  $\sigma_{ic}$ , is possible the significance of the critical distance is not yet clear. For example, it does not appear to correlate with any of the microstructural features of the epoxy materials which were discussed previously in part 1<sup>1</sup>. However, recent work<sup>37</sup> on crack growth in mild steel suggests that there may be no simple physical significance to the critical distance. Knott *et al.*<sup>37,38</sup> have determined critical distances for various mild steels but employed a different analysis to that described in the present paper. Despite some initial tentative correlations, they have concluded that the most satisfactory interpretation of the value of  $c$  is a statistical one. The argument is essentially based upon the likelihood of there being a 'weak region' some distance ahead of the crack but within the high stress intensification region, which will act as a site for microcrack initiation.

At the present time, however, it must be concluded that further work is needed to determine what physical significance may be attached to the values of the parameters  $\sigma_{ic}$  and  $c$ . In this respect it is suggested that systematically varying the microstructure of the rubber-modified epoxy, by for example changing the cure conditions<sup>39</sup>, and determining the values of  $\sigma_{ic}$  and  $c$  for this range of materials would be extremely interesting, and possibly most rewarding.

## CONCLUSIONS

The viscoelastic nature of the compressive yield behaviour in an unmodified and a rubber-modified epoxy has been investigated and the rate and temperature dependence of the yield stress shown to follow a stress-activated rate process. This model involves the surmounting of a potential energy barrier for which an

applied stress lowers the barrier for a jump in the forward direction and increases the barrier for a jump in the reverse direction. The predictions from this model are in good agreement with the experimental results and values for the activation energy and volume have been determined. The values of these parameters are similar to those which have been reported for yielding in glassy amorphous thermoplastics, which emphasizes the similar nature of shear yielding mechanisms in both crosslinked thermoset and glassy thermoplastic polymers.

These data have been used, together with the fracture data reported previously in part 1<sup>1</sup>, to calculate the crack opening displacement,  $\delta_{ic}$ , at the onset of crack growth. The value of this parameter has been found to increase with increasing temperature and decreasing rate and thus does not provide a unique failure criterion. This is in contrast to the situation in some glassy thermoplastics where brittle stable crack growth initiates at a constant  $\delta_{ic}$  value. Possible reasons for this difference in behaviour, based upon the presence of different localized energy-dissipating mechanisms, have been discussed. It has been argued that the rate/temperature dependence of  $\delta_{ic}$  for the epoxies suggests that the localized plastic yield behaviour at the crack tip leads to an increasing degree of crack tip blunting with increasing temperature and decreasing rate, i.e. as the yield stress falls. This, in turn, increases the relative toughness of the epoxy material and induces transitions in the types of crack growth. The relationships that have been found to exist between the toughness and the yield stress, as well as the type of crack growth, offer strong support for this proposal.

Finally, a quantitative expression has been employed in an effort to obtain a slightly more realistic failure model by including the effect of a finite crack tip radius on toughness. This expression fits the fracture data over a wide range of temperatures and yields two parameters which provide a unique failure criterion for the epoxy materials. Although they may be regarded simply as curve-fitting constants, it is suggested that they are material constants representing a critical stress that must be reached at a critical distance ahead of the crack tip in order to cause crack growth.

## ACKNOWLEDGEMENTS

The authors would like to thank Dr W. D. Bascom (Hercules), Mr J. R. Rushford (NBS), Dr D. A. Tod (PERME), Professor J. G. Williams (Imperial College) and Dr R. J. Young (Queen Mary College) for many helpful discussions and comments during the course of the present studies.

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