Crack propagation in an amine-cured epoxide resin

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Crack propagation has been studied in a DGEBA epoxide resin cured with two different series of amine hardeners. Both series produced a cured resin in which cracks propagated in a stick–slip manner in a series of jumps. With a primary diamine hardener, the initiation energy depended on the molecular weight of the hardener, but with a mixed amine hardener the initiation energy was independent of molecular weight. There were also significant differences in fracture surface morphologies between the two series. The effect of temperature and testing rate on the fracture energy and fracture surface morphology of ethylene diamine cured resin has also been studied. The fracture initiation energy increased with increasing temperature and decreasing testing rate and there is some indication of a peak occurring in the 22° C data. Long term static loading experiments have failed to show the occurrence of a static fatigue effect. Different batches of nominally identical resin produced different results, leading to problems of irreproducibility of behaviour.

1. Introduction

Epoxide resins are among the few plastics which are used as structural engineering materials. As matrices for high performance composites, as adhesives in aerospace and other technologies, and as insulators for large magnets in accelerator and fusion technology, they are required to withstand high static and dynamic stresses. Their resistance to fracture is thus of considerable practical importance.

Although a good deal of work has been carried out to attempt to characterize the fracture behaviour of epoxides, most of these studies have been *ad hoc* investigations of the effect of varying curing agents and curing conditions, without attempting to understand how the structural changes at the molecular level affect the initiation and propagation of cracks. One reason for this, which also inhibits interpretation of much of the earlier work, is that a very wide range of epoxide resins and curing agents exists, and their chemistry and resulting network structure are in most cases not clearly understood. The increasing body of published work on the fracture of simpler plastics,

such as for example polymethylmethacrylate and polystyrene, has provided a better understanding of fracture phenomena in plastics generally. This, combined with the increasing engineering importance of epoxides, has provided the impetus for a more detailed understanding of their fracture behaviour, which has been the subject of several recent and continuing studies [1–10].

The present work on an amine-cured epoxide developed out of an earlier study of an anhydride-cured epoxide [7, 11]. The objectives of the earlier work were to determine the applicability of a linear elastic fracture mechanics approach to the prediction of failure, with particular regard to the prediction of static fatigue lifetimes. Static fatigue is the phenomenon whereby a material which has been stressed under a steady load for a period of time suddenly fractures without the load being increased. This can occur either by a slow growth of a stable crack to a size where instability occurs, due possibly to the assistance of the environment, or else by processes occurring in the vicinity of the crack tip which alter the structure of the material and effectively reduce its toughness.

Considerable difficulties due to irreproducibility of behaviour became apparent in the earlier work. Apparently identical specimens obtained from the same plate of cast resin could be tested under identical conditions of strain rate and temperature yet fail in different modes, cracks propagating unpredictably sometimes in a stick-slip manner and sometimes in a continuous manner. Although the effects of moisture, strain rate and temperature were briefly studied, reproducibility could not be obtained and it was learned that other workers had experienced similar problems [12]. The reasons for the lack of reproducibility are not known. It is known, however, that the reaction of anhydrides with epoxide resins is complex, several chemical reactions occurring simultaneously, and this may have been a contributing factor. Consequently it was decided to explore amine-cured epoxides, systems whose chemistry is rather better understood than anhydride-cured epoxides, and determine the effect of cross-link density, testing rate and temperature on the mode of crack propagation and the fracture energy.

2. Experimental

The epoxide resin used throughout was Ciba-Geigy "Araldite" MY750, a liquid diglycidyl ether of bisphenol A with a molecular weight of approximately 360 and an epoxide content of 5.05 to 5.30 equiv. kg^{-1}. During the course of the work three different batches of MY750 were used. These were supplied at different times but were otherwise nominally identical. Rather different results were obtained with the three batches as will be described later. Most of the work was carried out on the first batch and unless specifically stated, any results described were obtained from that source. Six aliphatic amine curing agents were employed, three primary diamines and three polyamines containing primary and secondary amine groups, and are shown in Table I. Primary amines form the terminal groups of all the curing agents and the secondary amine groups in the polyamines are separated from each other and from terminal groups by ethylene groups. Stoichiometric amounts of curing agent were used with the exception of the triethylene tetramine where a slight excess of resin was employed to enable closer comparison with other published work [9].

To manufacture plates the resin was degassed for 20 min and, with the exception of hexamethylene diamine, the liquid amine was added and stirred for 5 min. The solid hexamethylene diamine has a melting point of 42° C and was raised to this temperature before addition to the resin at the same temperature. The stirred mixtures were further degassed but degassing was terminated when there was any indication of boiling of the more volatile amine fraction. The mixture was cast in a steel mould which had been coated and baked with a release agent. The mould dimensions were 255 mm × 160 mm × 3 mm. Electrical heaters in contact with the steel moulds were used to give a more uniform and controllable temperature distribution than was obtainable in ovens. The heaters, with temperature feedback controllers, gave a cure schedule for the diamine systems of one hour at 60° C followed by 1 h at 160° C, and for the polyamines of 2 h at 60° C after 2 h precure at 20° C.

Fracture energies were measured by means of the double torsion test which has been described in detail elsewhere and is shown schematically in Fig. 1 [7, 13]. The essential feature of this technique is that the compliance C of the specimen increases linearly with increasing crack length a. The fracture energy G is given by the load P at which the crack propagates by

$$G = \frac{P^2}{2b} \frac{\partial C}{\partial a}$$

where b is the specimen thickness, and since $\partial C/\partial a$ is independent of crack length the fracture energy may easily be calculated from the crack propagation

TABLE I The curing agents

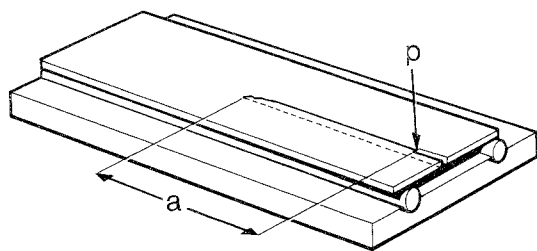| Curing Agent	Quantity (weight %)	Supplier
Ethylene diamine (EDA)	8.3	British Drug Houses Ltd.
Tetramethylene diamine (TDA)	12.2	Cambrian Chemicals Ltd.
Hexamethylene diamine (HDA)	16.1	B.D.H. Ltd.
Diethylene triamine (DETA)	11.5	B.D.H. Ltd.
Triethylene tetramine (TETA)	11.0	Ciba-Geigy (UK) Ltd.
Tetraethylene pentamine (TEPA)	15.0	B.D.H. Ltd.

Figure 1 The double torsion test. Specimen dimensions were 75 mm × 25 mm × 3 mm.

Curing agent	Initiation energy G_i ($J m^{-2}$)	Arrest energy G_a ($J m^{-2}$)
Ethylene diamine	329 ± 38	164 ± 19
Tetramethylene diamine	489 ± 83	160 ± 20
Hemamethylene diamine	575 ± 50	155 ± 14
Diethylene triamine	130 ± 20	113 ± 15
Triethylene tetramine	141 ± 29	105 ± 23
Tetraethylene pentamine	136 ± 20	114 ± 15

load after a prior calibration has been carried out. For most materials tested in this way, cracks propagate continuously under constant load. However epoxides and some other plastics are peculiar in that cracks can propagate in a series of jumps. The crack remains stationary until the load is increased to some level P_i at which the crack suddenly moves rapidly until it arrests at a lower load P_a. Where such "stick–slip" behaviour occurs, two fracture energies can be defined, a so-called initiation energy G_i and a so-called arrest energy G_a.

Measurements were carried out on an Instron machine at constant crosshead speeds at temperatures between 0 and 70° C. In addition static fatigue tests were carried out on a battery of double torsion machines, which could each be dead-weight loaded individually, in a laboratory with a controlled temperature of 20° C.

Fracture surfaces were studied by reflected light optical microscopy. In addition crack tip deformation was observed during initiation and propagation at low crack velocities by means of a microtesting machine. This was a small double torsion test rig which could be mounted on the stage of a Vickers 55 microscope on which the optics and stage are inverted. The double torsion test machine consisted of a depth micrometer driven by a stepping motor through a fixed barrel so that the tip of the micrometer acted as the moving load point. Tests were carried out on specimens which had polished surfaces to facilitate observation of surface features during crack growth.

3. Results
3.1. Effect of curing agent
Table II shows the values of G_i and G_a obtained at 22° C at a cross-head speed of 0.05 cm min^{-1} for the six different systems. In almost every test the materials failed by stick-slip crack propagation.

For both series G_a is apparently unaffected by curing agent. G_i varies with curing agent in the primary amine series but does not vary in the mixed amine series. Measurements were also carried out on TETA-cured material which had been post-cured for 1 h at 160° C. The effect of post-curing was to increase the fracture energies to $G_i =$ 240 Jm^{-2} and $G_a = 160$ Jm^{-2} with consequently larger crack jumps.

The mode of crack propagation, and the appearance of the fracture surfaces, differed between the primary amine-cured system and the mixed amine-cured system.

The primary amine-cured system exhibited completely stick-slip behaviour with no tendency for continuous crack propagation, the load-displacement record consisting of sharp peaks and troughs as shown in Fig. 2a. The fracture surfaces typically exhibited the features shown in Fig. 2b. Prior to AB the surface was smooth, glassy and featureless even at magnifications of up to × 1000. At AB there was a sharp transition to the rough surface ABCD. At CD there was a sharp transition to a hackle. The hackle finally disappeared into the following glassy surface with a less well-defined transition at EF. The features between AB and EF are a result of events occurring during the arrest and re-initiation of crack propagation. AB, CD and EF are successive positions of the crack front, their curved shape resulting from the stress distribution occurring in the double torsion test. In Section 3.2 it will be shown that the sizes of the rough surfaces ABCD depend on the temperature of testing. This fact has been used to determine at which stage of arrest and re-initiation they occur. From measurements carried out after propagating cracks at different temperatures, it was possible to calibrate the surface feature size and temperature
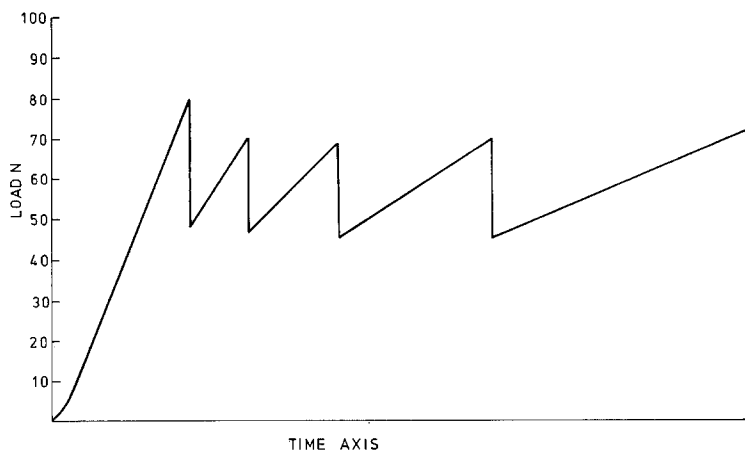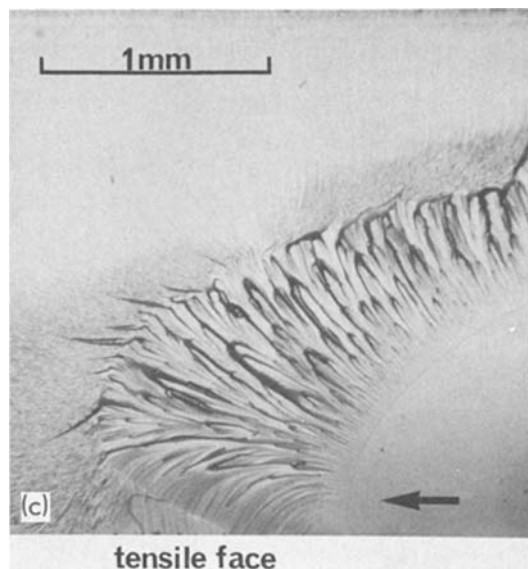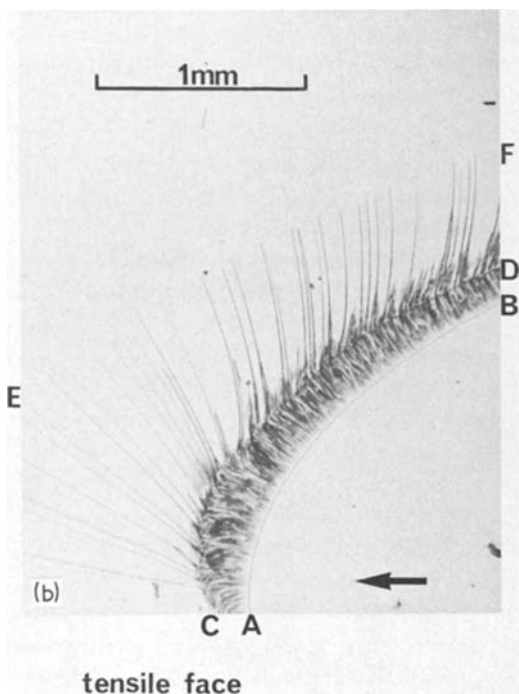
tensile face

tensile face

of test. Then, by propagating a crack at a given temperature, halting the test when the crack arrested and continuing the test at a different temperature, it was possible from an examination of the fracture faces to conclude that AB is the position of crack arrest. The profile of the crack surfaces have also been examined. Prior to AB and after EF the crack propagates along a planar surface. At AB it often moves out of the plane to CD and then returns to the plane at EF, as shown in Fig. 3. The crack tip profile was also examined during loading using the microtesting machine and the observed events are shown in Fig. 4. Initially, the crack is "sharp"; on loading, crack opening occurs as the crack tip blunts; surface features similar to slip lines begin to form; a secondary crack initiates and is observed to accelerate until it moves too rapidly to be seen. Hence the surface features in Fig. 2b may be interpreted as indicating that the crack moves rapidly until it abruptly arrests at AB. On re-loading the crack slowly grows from its arrest position AB accelerating through CD and EF.
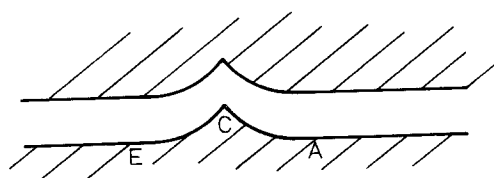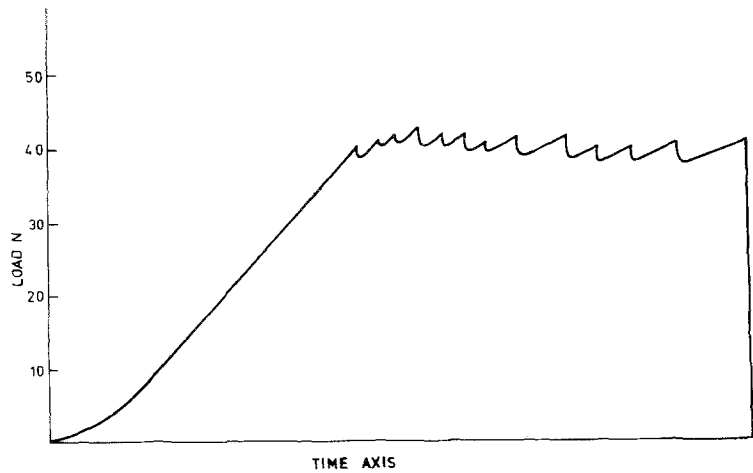
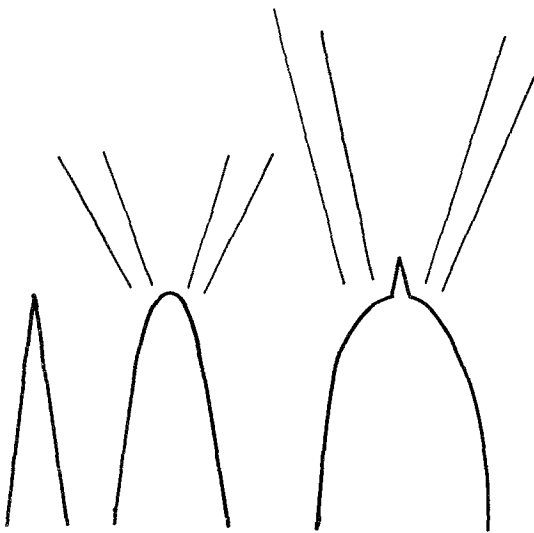*Figure 3* Profile of the crack arrest.

(a)

Figure 4 Successive states of crack blunting and initiation of a sharp crack in the primary amine-cured epoxide resin.
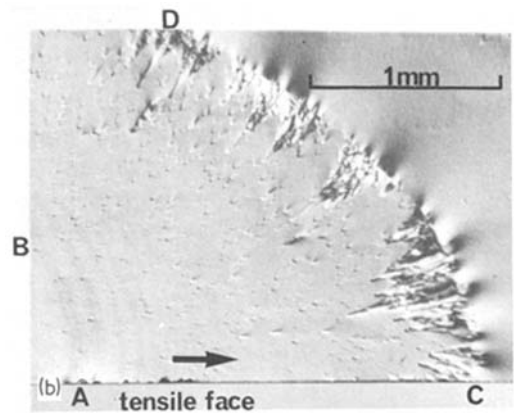

Figure 5 Fracture of the mixed amine-cured epoxide resin. (a) A load–displacement record. (b) Fracture surface features occurring in TETA-cured material at 20° C and 0.2 cm min^{-1}. The arrow shows direction of crack movement.

The mixed amine-cured systems also exhibited primarily stick-slip behaviour, although there was frequently a tendency for some continuous crack propagation at 22° C and 0.05 cm min^{-1}, resulting in a load–deflection curve with rounded troughs and an irregular load versus time trace, as shown in Fig. 5a. Typical features of the fracture surfaces are shown in Fig. 5b. Prior to AB the fracture surface is smooth, glassy and featureless. At AB there occurs a poorly defined transition after which pock-marks occur on the surface, increasing in density as the crack approaches CD. At CD there is either a very thin, featureless arrest line, or triangular features as shown. After CD there is a glassy featureless surface. Observation of the crack surface profile during propagation, using the micro-testing machine, showed the features in Fig. 6. As
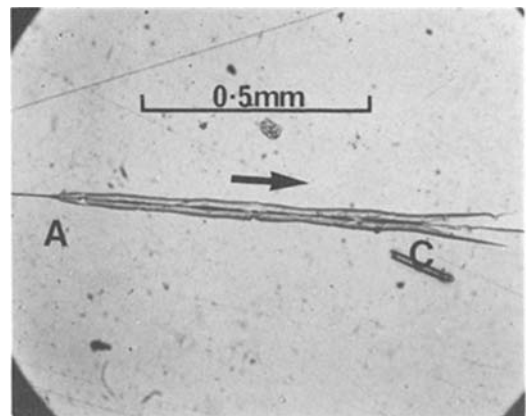

Figure 6 Plastic shear during the slowing (A) and arrest (B) of a crack in a mixed amine cured resin. The arrow shows direction of crack movement.

TABLE III The fracture data of EDA-cured MY750 (Uncertainties are standard deviations of a mean calculated from 5 to 10 measurements)

Cross-head speed (cm min^{-1})		Temperature					
		Batch 1					Batch 3
		0° C	22° C	35° C	50° C	70° C	22° C
0.005	G_i	264 ± 16	296 ± 16	361 ± 12	503 ± 29	536 ± 83	380 ± 31
	G_a	148 ± 4	146 ± 8	148 ± 3	163 ± 14	124 ± 14	164 ± 7
0.02	G_i		375 ± 19				327 ± 30
	G_a		169 ± 8				167 ± 10
0.05	G_i	233 ± 4	329 ± 38	331 ± 78	429 ± 92	446 ± 34	
	G_a	152 ± 4	164 ± 19	135 ± 21	164 ± 47	154 ± 12	
0.1	G_i						290 ± 21
	G_a						158 ± 10
0.2	G_i		274 ± 32				
	G_a		143 ± 24				
0.5	G_i	187 ± 26	269 ± 51	286 ± 63	293 ± 13	308 ± 73	263 ± 15
	G_a	141 ± 10	165 ± 28	158 ± 26	163 ± 9	149 ± 38	169 ± 12

the crack slows, a sunken region appears, adjacent to the crack face, similar to the region of plastic shear occurring in metals. It appears that, in contrast to the primary amine system, the crack decelerates over a distance rather than arresting abruptly. It then re-initiates abruptly at CD, rather than accelerating over a distance as in the primary amine system.

3.2. Effect of temperature and testing rate

The effects of temperature and testing rate on the fracture energy of EDA-cured epoxide resin were first determined on the first batch of epoxide resin. The G_i and G_a data obtained are presented in Table III, and in Fig 7 the G_i data are plotted without error bars for clarity. G_a is unaffected by testing conditions, but G_i varies substantially tending to increase with increasing temperature and decreasing testing rate but exhibiting a peak in the 22° C data.

After these measurements were completed, it was intended to carry out measurements at lower temperatures. At that stage all of the first resin batch had been used and measurements were commenced on a second batch. This second batch differed slightly in colour from the first batch and preliminary measurements at ambient temperature gave very different fracture energies from the first batch. Consequently a third batch was obtained. This had the same colour as the first batch and preliminary measurements indicated similar fracture energies to the first batch. However, in order to be

certain of the identical nature of batches 1 and 3, the measurements at different testing rates at ambient temperature were repeated. The results for batch 3 are shown in Fig. 8. Comparison with Fig. 7 shows that the behaviour of batches 1 and 3 were very different, batch 3 not exhibiting the peak at 22° C exhibited by batch 1.

The fracture surfaces obtained after testing at different temperatures have been studied. Similar features were observed in both EDA-cured and HDA-cured materials, but were more pronounced in the latter and therefore micrographs of those, rather than of the former, are shown here. Fig. 2b showed a typical fracture surface of HDA-cured epoxide obtained at 22° C at 0.05 cm min^{-1}, and in Section 3.1 the procedure for identifying the positions of crack arrest and reinitiation was outlined. The size of the rough zone corresponding to crack reinitiation varies with temperature and testing rate, increasing in area with increasing temperature and decreasing testing rate, indicating a correlation between G_i and the size of the initiation zone. For example, Fig. 2c shows a fracture surface obtained at 50° C at 0.05 cm min^{-1} for comparison with Fig. 2b.

3.3 Static fatigue experiments

Some measurements were carried out to determine the susceptibility of amine-cured epoxides to static fatigue under ambient conditions. Several specimens of both EDA- and TEPA-cured material were tested by the same procedure. The TEPA-cured
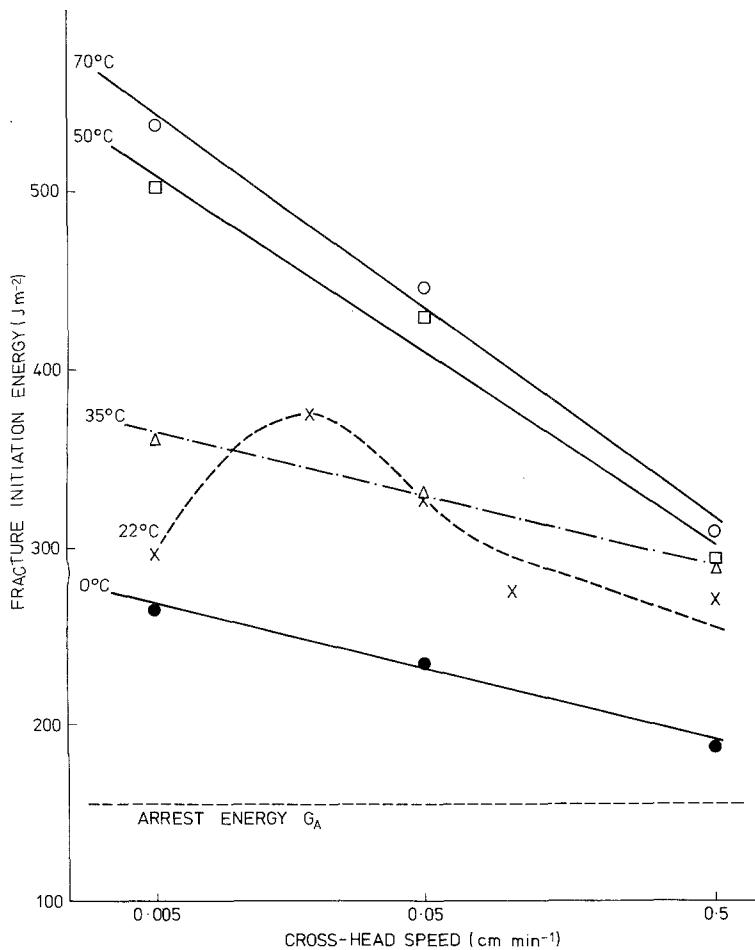
Figure 7 The variation of G_i with testing rate and temperature of batch 1 of epoxide resin cured with EDA.
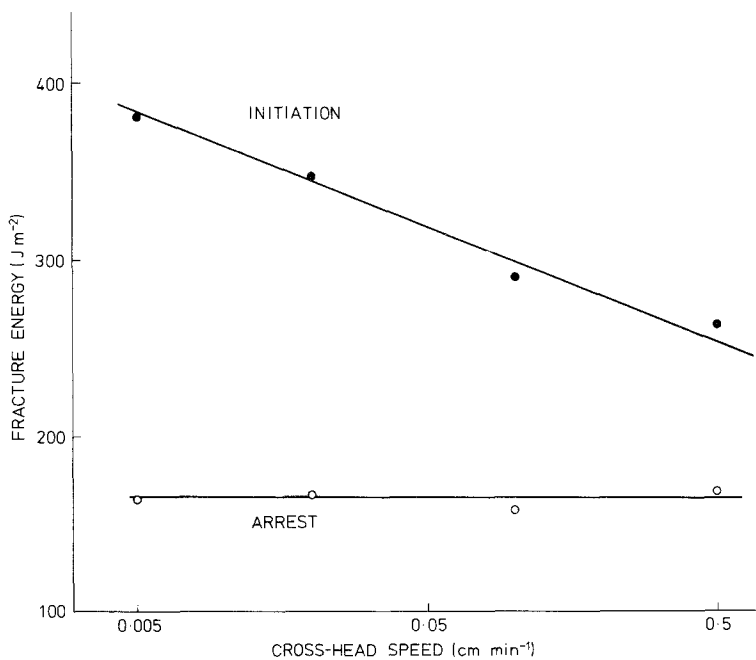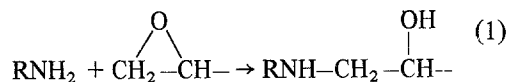

Figure 8 The variation of G_i with testing rate at 22° C, of batch 3 of epoxide resin cured with EDA.

317

material was selected because it exhibited the closest approximation to continuous crack propagation, under ambient conditions, of the amine-cured epoxides studied in this work. Each specimen was first pre-cracked on an Instron machine so that several crack jumps occurred and the loads for crack initiation and arrest for the individual specimens were determined. They were then mounted in a series of static fatigue rigs and subjected to constant dead-weight loads ranging from 70% to 95% of the initiation load. The lengths of the cracks were measured at regular intervals and after a period in excess of 4 months at ambient temperature and humidity none of the cracks had grown any longer than at the beginning of the test. A few of the specimens were removed from the static fatigue rigs and tested in an Instron machine at a strain rate of $0.05 \, cm \, min^{-1}$. The load required to cause the rested crack to propagate was in-increased by approximately 20% but successive crack jumps occurred at the same loads as in the original setting-up procedure.
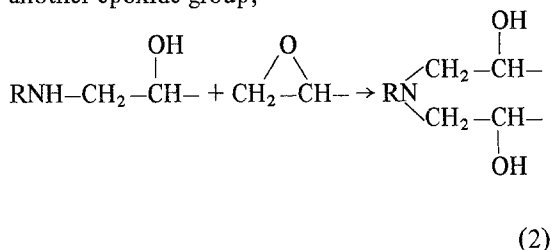
4. Discussion

Table II shows that for the same conditions of testing rate and temperature G_i is independent of curing agent in the mixed amine series, but varies with curing agent in the primary amine series. This behaviour is qualitatively in agreement with what would be expected. The curing agents belonged to two different series. Their structure and that of the resin are represented in Fig. 9. One series of curing agent consisted of ethylene diamine (EDA), tetramethylene diamine (TDA), and hexamethylene diamine (HDA) for which $n = 2, 4, 6$ respectively. The other consisted of diethylene triamine (DETA), triethylene tetramine (TETA) and tetra-ethylene pentamine (TEPA) for which $n = 1, 2, 3$ respectively. The first series contained only primary amine groups, while the second contained primary and secondary amine groups. When an epoxide resin and an amine react, an active hydrogen atom
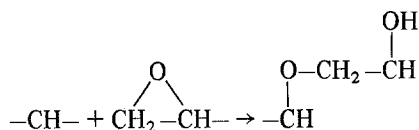
in the amine molecule reacts with the oxygen atom in the epoxide group. Thus, for a primary amine, [14, 15]

$$RNH_2 + CH_2-CH- \rightarrow RNH-CH_2-CH-- \quad (1)$$

The resulting secondary amine then reacts with another epoxide group,

$$RNH-CH_2-CH- + CH_2-CH- \rightarrow RN\begin{matrix} CH_2-CH- \\ CH_2-CH- \end{matrix} \quad (2)$$

When the starting amine is secondary, only Reaction 2 takes place. Etherification can also occur to a very limited extent,

$$-CH- + CH_2-CH- \rightarrow -CH\begin{matrix} O-CH_2-CH \end{matrix}$$

but Reactions 1 and 2 predominate. Hence, when curing agents of the ethylene diamine series are employed, it would be expected that a network structure would develop of the general fom shown in Fig. 10a, while for the DETA series the structure in Fig. 10b would form. The difference between these being that in Fig. 10a the molecular links are spaced by $(CH_2)_n$, the number n depending on the curing agent, while in Fig. 10b the links are spaced by C_2H_4, independent of the value of n. Hence, at least to an approximation, it would be expected that different members of the ethylene diamine series would lead to different cross-link densities in the fully cured state, while in the DETA series there would be little variation in cross-linking density. In accordance with this simple argument,
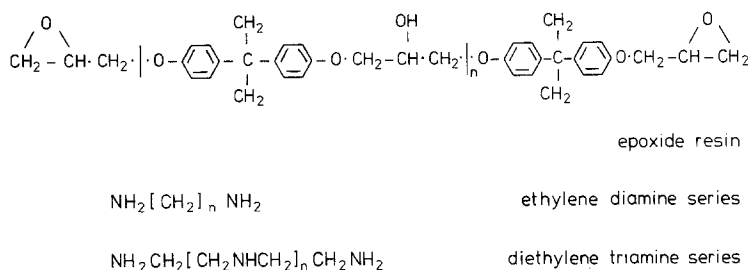
epoxide resin

$$NH_2[CH_2]_n NH_2$$

ethylene diamine series

$$NH_2CH_2[CH_2NHCH_2]_n CH_2NH_2$$

diethylene triamine series

Figure 9 The structure of the resin and curing agents.

R - CH₂ / N [CH₂]ₙ N / CH₂ - R structure...

$$\begin{array}{ccc} R-CH_2 & & CH_2-R \\ \diagdown & & \diagup \\ & N[CH_2]_n N & \\ \diagup & & \diagdown \\ R-CH_2 & & CH_2-R \end{array}$$

A

$$\begin{array}{ccccc} R-CH_2 & & CH_2-R & & CH_2-R \\ \diagdown & & | & & \diagup \\ & NCH_2[CH_2NCH_2]_n\,CH_2\,N & & \\ \diagup & & & & \diagdown \\ R-CH_2 & & & & CH_2-R \end{array}$$
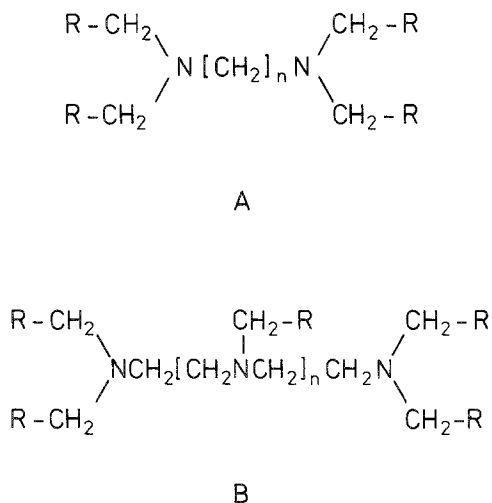
B

Figure 10 The network structures.

G_i of the primary amine series increases with molecular weight of the curing agent, tetramethylene diamine, the intermediate of the three, producing a cured epoxide whose G_i values lies midway between the other two cured systems, while G_i of the mixed amine series is independent of molecular ·weight. These results suggest that as the cross-link density increases (i.e. n decreases) G_i decreases. Again, qualitatively, this might be expected as G_i appears to be controlled by the ability of the material to deform plastically, as discussed below, and the more tightly bound structure of ethylene diamine-cured material would be expected to deform less easily than the more open structure of hexamethylene diamine-cured material. However, when the effect of varied curing conditions is also considered, an anomaly in this simple picture arises. The mixed amine series in Table II were all essentially under-cured, and the effect of post-curing was to increase G_i, that of TETA cured epoxide increasing from 140 to $240\,Jm^{-2}$. Post-curing would be expected to yield a structure which has an increased cross-link density, and thus the variation· of G_i with cross-link density is different in this case than was obtained by varying the molecular weight of the amine. In addition to this anomaly it is not clear why the mode of crack propagation and the morphology of fracture surfaces should differ so markedly between the primary amine series and the mixed amine series. The effect of molecular structure and cross-link density on the initiation energy is clearly more complex than indicated by our simple argument.

On varying the temperature and testing rate of the EDA-cured system, G_a remains fairly constant, but G_i varies quite substantially, as shown in Figs. 7 and 8. Apart from the peak at 22° C in batch 1 data, G_i decreases with increasing testing rate and decreasing temperature. Observations of the fracture surfaces, as described in Section 3.1 and shown in Figs. 2 and 4, have revealed that prior to the rapid propagation of the crack there is a period of slower growth which results in a rough and hackled surface region. The size of this rough and hackled zone also decreases with increasing testing rate and decreasing temperature, clearly indicating a correlation between G_i and the deformation and slow crack growth prior to unstable crack propagation. Marshall *et al* [16] and Atkins *et al* [17] have carried out similar measurements to these on polymethylmethacrylate and it is instructive to compare their results and conclusions with those obtained here on epoxides. One of the objectives of the present work was to determine an activation energy for the molecular process controlling the fracture energy of the cured epoxide resin, from measurements of G_i at different temperatures and testing rates, in order that the controlling process might be identified. Marshall *et al* and Atkins *et al* have independently obtained the activation energy of the molecular process in PMMA from their measurements. The data which they obtained were very similar, and the activation energies which they calculated agreed, but the arguments that they used in their calculations were rather different. Atkins *et al* made use of an empirical relationship between the time to failure t_f and stress σ which was discovered by Zhurkov to be satisfied by many solids

$$t_f = A_0 \exp\left(\frac{U - \phi\sigma}{kT}\right)$$

where A_0 and ϕ are constants, U is the activation energy, k is Boltzmann's constant and T is absolute temperature. Then, arguing that crack speed is inversely proportional to the fracture time of molecules, and that the stress at the crack tip is proportional to fracture toughness G by $\sigma = G/u_c$ where u_c is the displacement at the crack tip, they obtained a toughness-biased Ree-Eyring equation

$$\dot{a} = A_1 \exp\left\{-\frac{[U - \lambda G]}{kT}\right\}$$

where $\dot{a}$ is crack velocity, λ is a constant. Marshall *et al*, on the other hand, started from the Dugdale

model of deformation processes at a crack tip and took into account the empirical observation that the yield strain ϵ_y of PMMA is largely independent of testing rate and temperature so that

$$G = E \, \epsilon_y u_c$$

where E is Young's modulus and u_c is the crack opening displacement. They then assumed that the crack opening displacement is a constant, independent of temperature and strain rate, and introduced a temperature and strain rate dependence to G through a temperature and strain rate dependence of Young's modulus. For PMMA in the temperature and testing rate regimes describable by these equations, G increases with testing rate and decreasing temperature. It must be emphasized that both Marshall *et al*, and Atkins *et al* were considering a situation where PMMA undergoes continuous crack propagation as opposed to stick-slip propagation. However, since we are here considering G_i, it is not unreasonable to compare this with the behaviour of the continuous crack propagation energy G in their work. In EDA-cured epoxide, G_i varies with temperature and strain rate in a manner completely opposite to that exhibited by PMMA and the molecular processes controlling the fracture energies of the two materials must be quite different and the equations employed successfully to evaluate activation energies for PMMA cannot be used for this material. Although both are glassy plastics, PMMA is not cross-linked and is capable of crazing and it is probably this process which controls the fracture energy. Epoxides, however, are cross-linked, and are generally not capable of crazing, and the process which controls the fracture initiation energy is probably the yielding and flow of the material at the crack tip. It is instructive to consider whether G_i can be related to the yielding and flow processes, and how they are affected by the conditions of test. A crack tip deformation model such as the Dugdale line plastic zone is clearly a physically reasonable starting point for a solution, i.e.

$$G_i = \sigma_y u_c \qquad (1)$$

where σ_y is the yield stress and u_c is the crack opening displacement, a quantity which is sometimes assumed in fracture studies to be independent of temperature and testing rate. The flow of epoxides during yielding can be treated as a viscous flow mechanism and described by a rate

process [18]

$$\dot{\gamma} = A \left(\frac{kT}{h} \right) \exp \left\{ -\frac{Q}{kT} \right\} \sinh \left(\frac{S \lambda_1 \lambda_2 \lambda_0}{2kT} \right)$$

where $\dot{\gamma}$ is the strain rate, k is Boltzmann's constant, h is Planck's constant, T is temperature, S is the mean shear stress, and λ_1, λ_2, λ_0 are interatomic, intermolecular and jump distances. Under the conditions of these experiments, this reduces to a first approximation to

$$\dot{\gamma} = A \exp \left[\frac{\phi \sigma_y - U}{kT} \right]$$

and on this basis, and empirically, the yield stress of an epoxide decreases with increasing temperature and decreasing strain rate. Thus, yield stress varies in an inverse fashion to G_i and Equation 1 therefore implies that for this epoxide system at least the critical crack opening displacement is not independent of temperature and strain rate but must vary more rapidly than yield stress.

The peak which was observed in the variation of G_i with strain rate at $22°$ C from the first batch of resin, was not repeated with the third batch. There is no reason to suppose that this peak was not a real effect and its absence from the batch 3 data is an indication of the variability of properties of commercially available resins and curing agents. Irreproducibility of behaviour has been observed by other workers and is discussed below. It is tempting to speculate that the peak was due to a molecular relaxation which modified the yield and flow. If this is correct the most likely relaxation is that which causes the γ loss peak in the dynamic mechanical spectrum due to mobility of the $-CH_2-CH(OH)-CH_2-O-$ segment [19]. Further work is required however to define the effect.

Static fatigue has not been observed to occur in any of the experiments reported here. After loading pre-cracked specimens within a few per cent of their failure load for several months, not one has spontaneously failed. This behaviour is in complete contrast to that observed by Gledhill and Kinloch [10] who have studied a very similar epoxide resin (Shell 828), but cured with a different, tertiary amine. Their system also failed in a stick-slip manner on loading at a constant crosshead speed, in the same way as our systems. But on loading under constant load for periods of time, their specimens failed in times ranging from a few

minutes up to several months on loading at loads greater than about one half of the crack initiation load. The published work of Gledhill and Kinloch differs from the present work in that they studied crack propagation in the adhesive layer between two metal adherends. However, in their experiments the cracks propagated along the centre of the epoxide layer and not along the interface. They were thus studying cohesive failure rather than adhesive failure. Fracture energies obtained from thin films of low toughness adhesives which fail cohesively rather than adhesively tend to be very similar to those obtained from bulk resin specimens [25, 26] because the plastic deformation zone associated with the crack tip is smaller than the glue-line thickness and therefore largely unaffected by the presence of the adherends [10]. It therefore appears that the behaviour of their system was a reflection of the epoxide resin properties. In the present work, the effect of loading both EDA- and TEPA-cured materials for long periods of time is to cause an opening and consequent rounding of the crack tip due to creep. To some extent the dead-weight loading experiment may therefore be regarded as a slow strain-rate experiment, with a strain-rate determined by the creep rate. Since G_i, and by implication the crack propagation load, of these materials increases with decreasing strain rate, the dead-weight loading experiment is qualitatively in agreement with the constant strain-rate experiments reported here. It is interesting, and important, that two different types of static fatigue behaviour have been observed, that reported here and that observed by Gledhill and Kinloch. Clearly in engineering applications, all other things being equal it would be preferable to use a system which does not exhibit static fatigue, and the reasons for the differences in behaviour need to be understood.

A problem, fundamental to understanding crack propagation in epoxide resins, is why in some resins cracks propagate in a stick-slip manner, while in others they propagate continuously. Several suggestions have been made to explain why stick-slip propagation occurs and this behaviour is at least qualitatively understood. Cracks sometimes propagate in a stick-slip manner when the fracture energy of the material decreases with increasing crack velocity, i.e. $dG/d\dot{a}$ is negative [20]. Certain combined conditions of specimen geometry and negative $dG/d\dot{a}$ can lead to crack jumping and

these have been discussed extensively by Mai, Atkins and their co-workers [21]. Various suggestions have been made to explain why $dG/d\dot{a}$ can be negative. For example, in PMMA [22] and in rubber modified acrylic polymers [23], it has been suggested that the effect is due to molecular relaxation processes and the variation of G with $\dot{a}$ corresponds to the internal friction, tan δ, peak. An alternative explanation postulated for PMMA is that instability occurs due to the onset of significant thermal softening in the crack tip region as deformation changes from an isothermal process at low crack speeds to adiabatic at high speeds [16]. A third possibility is that if the flow of the material is particularly sensitive to strain-rate, at high rates corresponding to large crack velocities there will be less irreversible deformation and thus absorbed energy, than at low crack velocities. It is, however, worth mentioning that there is no evidence that the fracture energy of a running crack in these epoxies varies with crack velocity. Gledhill and Kinloch [9] have carried out measurements of G as a function of crack velocity in an apparently identical material to the TETA-cured resin used in this work. Their results showed that G was independent of crack velocity over a wide range. Their results should be compared with the results presented here with caution, as in their material cracks propagated in a continuous manner rather than in a stick-slip mode – this will be discussed further later. For the observations reported here of the crack profile and behaviour, it is probable that the explanation of crack jumping in this work is rather different and is as follows. The load at which a crack propagates, and thus in the double torsion test the critical stress intensity factor K_{IC} and the critical rate of release of strain energy G_{IC}, depend on the crack tip radius. On loading at a constant relatively low rate, an initally sharp crack in an epoxide resin gradually blunts as the material at the tip deforms. As the load continues to increase, blunting continues until eventually a new, sharp crack is initiated at the tip of the blunt crack. At its formation this new sharp crack has a small crack tip radius and is thus subjected to a stress intensity factor K_I much greater than the critical stress intensity factor K_{IC} appropriate to its propagation. The overstressed crack is therefore in a grossly unstable state and very rapidly accelerates to a high velocity with a substantially constant crack tip radius. These events are shown in

Fig. 4. A similar sequence of events in metals has been described by Broberg [24] discussing work by Broek and Tetelman.

Although stick-slip behaviour is qualitatively understood in general terms, the way in which the structure at the molecular level controls the behaviour and determines the way cracks propagate is not at all understood. In this laboratory, in support of our engineering problems, ad hoc measurements have been made of cracks propagating in a variety of epoxide systems. It has been observed that under ambient conditions, cracks propagating in the amine-cured MY750 epoxide resin described in this paper have almost invariably propagated in a stick-slip manner. Gledhill and Kinloch, however, have propagated cracks in a system (Shell 828 cured with TETA) which is very similar to one of ours and have observed them to propagate continuously, although more recently after changing from one batch of curing agent to another batch of nominally identical curing agent they too have obtained stick-slip propagation and have been unable to repeat the earlier continous crack propagation [25]. As in their earlier work [9, 10] they studied cracks propagating in adhesive layers, but in both cases failure was cohesive rather than adhesive and the change in behaviour was not the result of a transition from cohesive to adhesive failure. In earlier work [7, 11] on MY750 cured with an anhydride, cracks were obsered to propagate unpredictably sometimes in one mode and sometimes another, while in other anhydride-cured epoxides, which have been studied for large magnet insulations, cracks invariably propagated continuously. The unravelling of this problem is of scientific and technological interest. Its solution is made difficult by the apparent variability of commercially available resins and curing agents which has led to the irreproducibility of some of the data in this and other people's work. This is well demonstrated by the differences reported here between the three different batches of nominally identical resin which were employed. The behaviour of the cured epoxide resin appears to be extremely sensitive to what must be assumed to be relatively minor changes in its structure, and a detailed understanding of the way in which the structure at the molecular level affects the initiation and propagation of cracks will require very careful characterization of the starting materials and their cross-linked structure.

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