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Fracture energy of epoxy resins above T_g

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Measurements were made of the fracture suface energy of epoxy resins above their glass transition temperatures as a function of temperature, crack velocity and resin composition. The fracture energy, $\mathscr{T}$, obeys the WLF time–temperature superposition principle in the same way as in more conventional elastomers. Measurements also indicate a lower limit to $\mathscr{T}$, designated $\mathscr{T}_0$, which is independent of time and temperature. A theoretical calculation of $\mathscr{T}_0$ agrees well with the experimental data.

1. Introduction

In the previous work of Andrews and King [1], a fracture mechanics approach was employed to study the adhesion of epoxy resins to metal substrates. This work was carried out above the glass transition temperature of the resin to facilitate determination of the "intrinsic failure energy", θ_0, of the adhesive bond. This parameter has previously been shown to reflect the chemical or physical character of the interfacial bonding and thus to illuminate the mechanism of adhesion.

In order to evaluate θ_0 from adhesive failure tests, it is necessary to know the *cohesive* fracture properties of the resin [2]. The present paper is thus concerned with the determination of these cohesive properties.

The generalized fracture mechanics theory of Andrews [3] gives the cohesive fracture energy, $\mathscr{T}$, per unit area of crack surface and the adhesive fracture energy, θ, per unit area of interfacial crack plane, thus,

$$2\mathscr{T} = 2\mathscr{T}_0\,\Phi(\dot{c}, T, \epsilon_0) \qquad (1)$$

$$\theta = \theta_0\,\Phi(\dot{c}, T, \epsilon_0) \qquad (2)$$

where $\mathscr{T}_0$, θ_0 are the appropriate intrinsic failure energies and Φ is the loss function dependent on crack velocity, temperature and applied strain. Provided the adhering substrate is rigid, Φ is the same quantity in Equations 1 and 2. Note that $2\mathscr{T}$ is comparable to θ since $\mathscr{T}$ is referred to unit area of crack surface and θ to unit area of crack plane (two surfaces to the plane).

The particular fracture properties investigated in this paper are the loss function Φ, being the time and temperature dependent part of $\mathscr{T}$, and the intrinsic fracture energy $\mathscr{T}_0$, being the independent part. Both parameters are studied experimentally in the regime $T > T_g$ for epoxy resins of various compositions and, additionally, $\mathscr{T}_0$ is calculated theoretically using a modification of the Lake and Thomas theory [4] for elastomer networks.

The results obtained in this paper have previously been used [1] to evaluate θ_0 for a series of epoxy to metal adhesive bonds, using the simple formula, derived from Equations 1 and 2.

$$\theta_0 = \frac{\theta\,\mathscr{T}_0}{\mathscr{T}} \qquad (3)$$

2. Experimental

2.1. Materials and specimen preparation

The epoxy resin used was a diglycidyl ether of bisphenol A of molecular mass ~370 (Shell "828"). The hardener ("Shell 114") was a blend of two cycloaliphatic amines with added benzyl alchohol as an accelerator. The stoichiometric mixture of these components is obtained using a mass ratio of resin to hardener of 5 to 2. Other mass ratios, 5/1, 5/1.25 and 5/3 were also prepared and tested.

To investigate the cohesive fracture of the epoxy resin, rectangular specimens of the simple extension type, of dimensions 14.4 cm × 5.5 cm ×

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0.3 cm containing an edge crack of length c, were used. The resin and hardener were outgassed and heated at 70° C in a vacuum oven. The hardener was added to the resin, mixed and the mixture finally poured into open top moulds. The rectangular test pieces were left to gel at ambient temperature for 4 h, then postcured for $15\frac{1}{2}$ h at 120° C. The specimens were cooled at a rate of approximately $15°\mathrm{C\,h^{-1}}$.

The edge crack was produced by insertion of a sharp razor blade into the cured epoxy after heating for a few minutes at a temperature approximately 30° C above that of its glass-to-rubber transition.

2.2. Testing procedures

The experimental results reported in this paper were obtained at temperatures above the T_g of the epoxy resin and testing was carried out in the temperature control cabinet of an Instron testing machine. The tip of the edge crack was observed by means of a cathetometer containing an eyepiece graticule. When the crack propagated, its growth could be timed over a fixed distance (usually 1 mm) on the graticule scale, providing an average initial crack velocity $\dot{c}$.

The specimen was extended in tension at a selected cross-head speed until crack propagation was observed. The load–deflection curve was recorded meanwhile and the onset of crack propagation was noted on the curve by manual operation of an "event marker". The area under the load–deflection curve, divided by the volume of the epoxy sheet, gives the average input strain energy density. Strictly speaking this quantity only equals the input energy density, W_0, remote from the crack, when no crack is present. However, the load–deflection curves for specimens containing cracks and for uncracked specimens are indistinguishable in practice, so that W_0, and its critical value W_{0c} for the onset of crack propagation, can be deduced directly in each experiment.

Cross-head speeds ranging from 0.01 to 0.5 cm $\mathrm{min^{-1}}$ were employed, the higher speeds normally giving larger initial growth rates $\dot{c}$ at a given temperature. The procedure described for measuring $\dot{c}$ is adequate for tests above T_g. For tests below T_g, crack propagation is often too rapid for visual measurement of $\dot{c}$ and in these cases an electrical resistance method was used instead. This will be described elsewhere [5].

3. Characterization of materials

3.1. Degree of cross-linking

Above its T_g the epoxy resin is a highly cross-linked elastomer and, in principle, the cross-link density or the relative molecular mass M_c between cross-links can be obtained from stress–strain data using the theory of rubber-like elasticity. In particular,

$$\left.\begin{aligned} f[2A_0(\lambda-\lambda^{-2})]^{-1} &= C_1 + C_2\lambda^{-1} \\ C_1 &= \rho RT/2M_c \end{aligned}\right\} \qquad (4)$$

where f is the force in simple extension to produce an extension ratio λ in a specimen of unstrained cross-sectional area A_0; C_1, C_2 are the Mooney–Rivlin constants, ρ the density, T the temperature and R the gas constant.

Thus a plot of $f[2A_0(\lambda-\lambda^{-2})]^{-1}$ against λ^{-1} should give a straight line from which C_1 is obtained as an intercept and C_2 as the slope. Fig. 1 confirms that this behaviour is obtained for the epoxy resins employed in this study, with $C_2 = 0$. The values of C_1 and thence of M_c, were as follows:

Resin/hardener ratio	5/1	5/1.25	5/2	5/3
$C_1\,(\mathrm{MN\,m^{-2}})$	0.38	0.97	2.06	1.22
$C_2\,(\mathrm{MN\,m^{-2}})$	0	0	0	0
M_c	5150	2000	900	1420

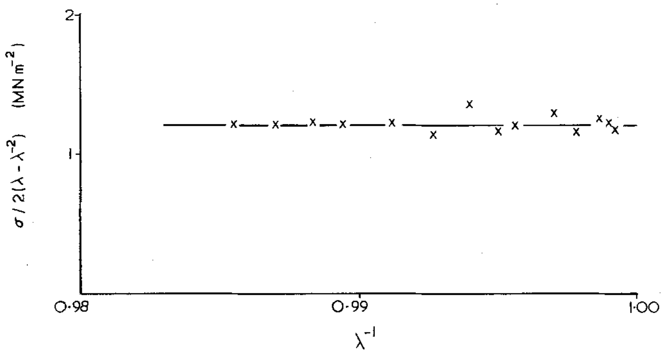

Figure 1 Mooney–Rivlin plot for the 5/3 epoxy at 370 K.

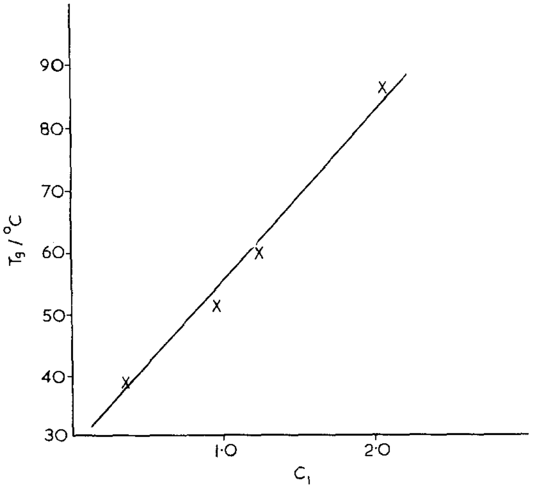

Figure 2 Relationship between glass transition temperature and the Mooney–Rivlin constant C_1 for a series of epoxy resins.

The value of C_1 is a maximum at the stoichiometric ratio, as is the T_g. Fig. 2 shows C_1 plotted against T_g, where an almost linear dependence results.

In spite of the agreement of our data with Equations 4, caution is required because these equations are based on the assumption of random coiling of the molecules which is unlikely to occur in such highly cross-linked systems as the epoxy resins.

Treloar [6] has given a series expansion for the force f in which the first term is identical to the prediction of the kinetic theory of rubber-like elasticity (i.e. Equations 4 with $C_2 = 0$) but which includes higher terms to take account of the finite extensibility of network chains. If this equation is used [7] the following conclusions can be drawn.

Taking 3 to 4 as a reasonable estimate for the number of bonds per statistical link in the epoxy, gives a value of approximately 30 statistical links between junction points for the 5/1 epoxy. This gives a deviation from the rubber-like elasticity theory of approximately 3% at a strain of 0.1. For the 5/2 epoxy the number of statistical links between cross-links will be lower. Taking this number to be 5, which is probably an underestimate, give a deviation of approximately 22% from the theory at 0.1 strain. This value of strain is in excess of the fracture strains obtained in testing and so 22% may be considered to be the worst possible deviation of the epoxy from rubber-like elasticity theory, due to finite extensibility effects. Thus application of Equation 3 to the epoxy resin is justified, although the value of M_c obtained for the 5/2 epoxy may be an underestimate due to non-Gaussian behaviour.

3.2. The network structure of the epoxy

The hardener, Epikure 114, is a blend of two cycloaliphatic primary diamines with an accelerator, benzyl alcohol. Three reactions which may occur in such an epoxy–hardener system are the opening of the epoxide ring by (1) a primary amine, (2) a secondary amine, or (3) a hydroxyl group [8]. Although the last reaction can occur, the first two predominate [9].

The molecular mass of the epoxy monomer unit is 340 and that of the hardener is in the range 100 to 150 as estimated from mass spectrometer data [10]. Using these figures together with the M_c values derived earlier, certain conclusions can be drawn about the way the network structure varies with hardener content (Fig. 3). The 5/2 epoxy having the stoichiometric ratio of constituents, is highly cross-linked with an M_c of 900, producing a relatively rigid, inflexible network. It is presumed that virtually all of the epoxy and hardner molecules are fully incorporated into the network, i.e. are integral parts of the main chain segments. As the proportion of hardener is increased (5/3 epoxy) to produce an excess of

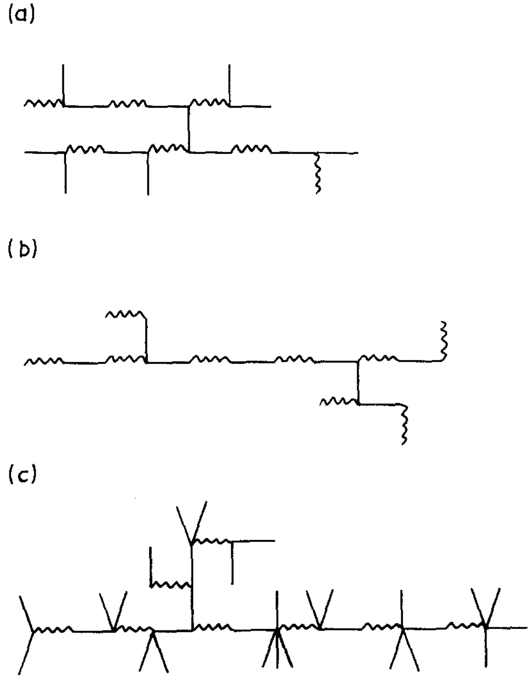

Figure 3 Postulated network structures of the cured epoxy resins; (a) 5/2 epoxy, (b) 5/3 epoxy, (c) 5/1 epoxy. (——) epoxy molecule (〰) amine molecule.

amine, M_c increases to approximately 1400. All of the epoxy groups are consumed by the amine molecules and a more linear molecule is produced. The network structure should be more flexible but of the same kind as that of the 5/2. As the proportion of hardener is decreased, however, a different type of structure is likely to emerge. For the 5/1 epoxy there is a definite excess of epoxy groups so the amine groups will quickly be used up, probably producing an essentially linear polymer. There will still be a large proportion of unreacted epoxy molecules. It is expected that reaction (3) will then become important. Whenever an active hydrogen of the amine reacts with an epoxide ring, a pendant – OH group is produced. Once all of the amine hardener has reacted with the epoxy resin the – OH groups produced by these reactions can themselves open up the epoxide rings of unreacted epoxy molecules. It is expected therefore that at points where a molecule of hardener has reacted with a molecule of resin, there will be a number of pendant epoxy molecules as shown in Fig. 3. Most of these pendant epoxy molecules will have one unreacted epoxide ring. The 5/1 epoxy thus differs from the 5/2 and 5/3 epoxy in two ways. First, it has a considerably lower cross-link density, indicated by an M_c value of 5150. Secondly, it is expected to have a significantly different network structure, due to the presence of pendant epoxy molecules. The 5/1.25 epoxy, with an M_c value of approximately 2000, also has an excess of epoxy and is assumed to possess a network structure similar to the 5/1 epoxy, but with a higher cross-link density and smaller number of pendant epoxy molecules.

The 5/1 epoxy differs from the 5/2 and 5/3 compositions in its adhesive properties. The unreacted epoxide group in the "cilia" of the 5/1 epoxy can react with metallic oxide surfaces to form strong chemical bonds [1].

4. Results

4.1. Analysis

The cohesive failure energy, $\mathscr{T}$, per unit area of fracture surface was calculated using the formula [11]:

$$\mathscr{T} = kcW_{oc} \tag{5}$$

The strain in the epoxy resin at which crack propagation occurred was always less than 5% and under these conditions, $k \sim \pi$. Fig. 4 shows typical plots of W_{oc} versus c^{-1}, confirming the validity of Equation 5 and providing slopes from which $\mathscr{T}$ is immediately deducible.

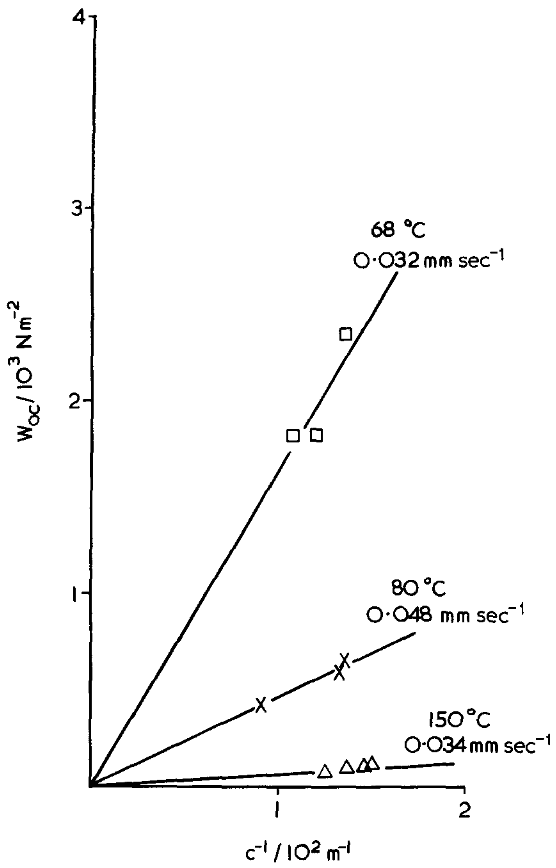

Figure 4 Critical energy density versus reciprocal crack length. Typical results for the 5/1 epoxy under various conditions.

Since the T_g of the epoxy resin depends on the hardener content (Fig. 2), it is meaningless to compare $\mathscr{T}$ for different resin/hardener compositions at the same temperature. Hence the data obtained for each composition was shifted to the T_g of a particular composition by applying the WLF transform,

$$\log a_T = \frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{6}$$

where a_T is the "shift factor". The conventional "universal" values of the WLF constants $C_1 = 17.4$ and $C_2 = 51.6$ K, were employed.

4.2 Reduced-rate dependence of $\mathscr{T}$

Figs. 5 to 8 show log 2 $\mathscr{T}$ as a function of log $\dot{c}\,a_T$ for the epoxy resin with different compositions. Each of the curves reflect the response of the material at the T_g and demonstrates the viscoelas-

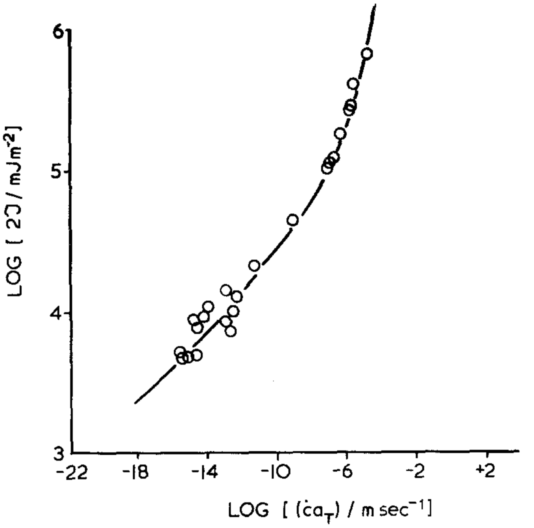

Figure 5 Logarithmic plot of fracture energy ($2\mathscr{T}$) against "reduced" crack velocity, using T_g as the reference temperature. Data for the 5/2 epoxy resin.

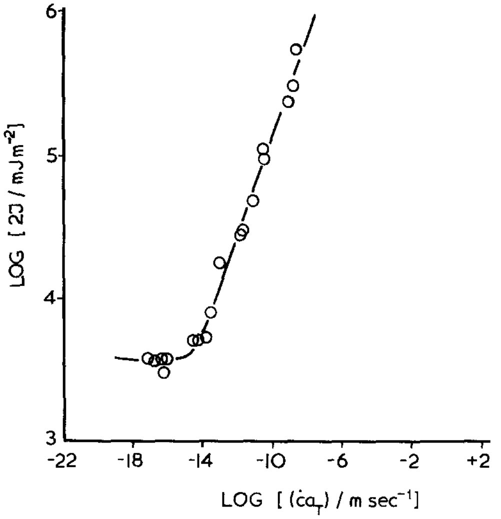

Figure 6 As Fig. 5 but for the 5/1 epoxy.

tic nature of the epoxy resin. The curves in fact reflect the effect on $\mathscr{T}$ of the loss function Φ, which is dependent on rate and temperature.

Fig. 6 indicates that, for the 5/1 epoxy at low values of reduced rate, an abrupt transition occurs, producing a constant value of $\mathscr{T}$ which is independent of crack velocity and temperature. This appears to be the onset of a truly elastic regime for which $\Phi \rightarrow 1$ and the constant value of $2\mathscr{T}$ obtained (3700 mJ m^{-2}) should be equal to $2\mathscr{T}_0$. This value compares well with the theoretically determined value of $2\mathscr{T}_0$ discussed later in the paper.

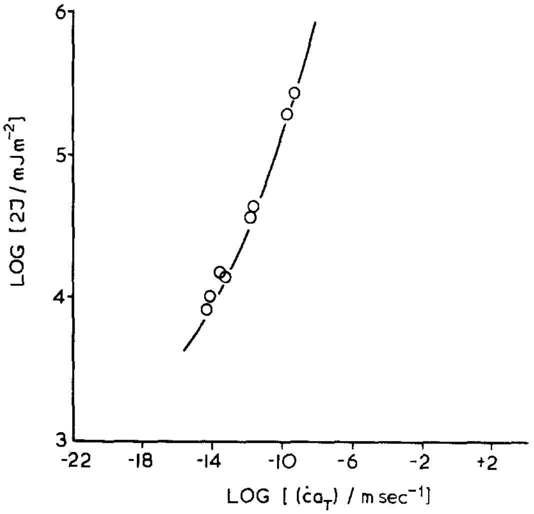

Figure 7 As Fig. 5 but for the 5/1.25 epoxy.

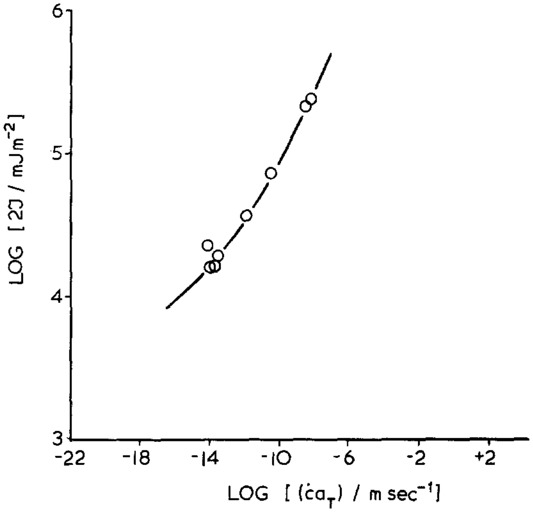

Figure 8 As Fig. 5 but for the 5/3 epoxy.

4.3. Effect of the WLF constants

The curves of log $\mathscr{T}$ versus log $\dot{c}\, a_T$ for the four resin/hardener compositions are shown together, for comparison, in Fig. 9. The curves have been extrapolated to the theoretically determined values of $\mathscr{T}_0$ (see later).

It can be seen that the curves have different shapes and slopes and this is probably due to changes in the loss function Φ. It is possible, however, that these differences are due to variation of the WLF constants, C_1 and C_2 used in Equation 6. The so-called "universal" values of 17.4 and 51.6 K for C_1 and C_2 respectively (when the T_g is the reference temperature), are only averages and the values of the constants do in fact vary from one polymer to another [12]. The only variable

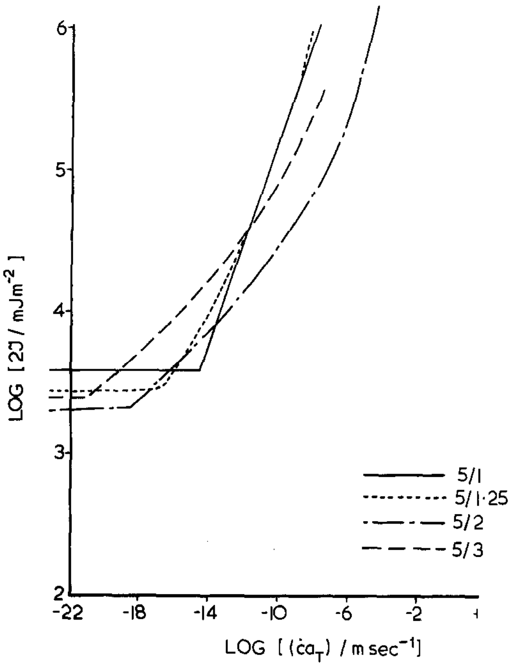

Figure 9 Data of Figs. 5 to 8 with calculated lower limits (2 $\mathcal{T}_0$) added.

affecting $\mathbf{C}_1$ is the fractional free volume, f_0, at the reference temperature (T_g), which should not vary significantly from one polymer to another, and in fact experimental values of $\mathbf{C}_1$ are reasonably constant. The constant, $\mathbf{C}_2$, however, depends not just on f_0, but also on α_f, the thermal expansion coefficient of the free volume relative to the total volume, and shows quite considerable variation from one polymer to another [12].

The data shown in Fig. 9 was replotted using different values of $\mathbf{C}_1$ and $\mathbf{C}_2$ to investigate the effect of these constants on the shape and slope of the curves. As expected, variation of $\mathbf{C}_1$ had a negligible effect. Variation of $\mathbf{C}_2$ produced a small, but not very significant change in the slope and shape of the curves. Values of $\mathbf{C}_2$ ranging from 10 up to 200 were used in order to try to make the 5/3 epoxy curve coincident with, or at least run parallel to (in the sense of a vertical shift), the 5/2 epoxy curve. The optimum value was found to be $\mathbf{C}_2$ = 40 K, but although the curve is slightly more parallel to the 5/2 curve, the effect is small and generally the only significant result of varying the $\mathbf{C}_2$ value is to shift the curve along the abscissa. Hence the variation of slope and shape of the curves in Fig. 9 seems to be a genuine reflection of different relaxational responses within the epoxy and not an artifact due to use of the wrong values for the WLF constants.

4.4 Effect of hardener content on Φ

Having established that the curves shown in Fig. 9 genuinely reflect the dependence of the loss function, Φ (and hence $\mathcal{T}$) on the reduced rate of crack propagation, the reason for the different shapes and slopes can now be considered. The curves for the 5/2 and 5/3 epoxies, with values for the molecular weight between cross-links, M_c, of 900 and 1420, respectively, are not parallel but are of similar shape. These curves differ from those obtained for the 5/1 and 5/1.25 epoxies, which, with M_c values of 5150 and 2000, respectively, are much steeper and less curved. There thus appears to be a difference in the relaxational response of the epoxy as M_c increases above 2000. If there were no such differences one would expect four curves of approximately the same shape, the slope increasing with M_c (as the material becomes more "lossy"). The curves would not be expected to cross one another. There appears to be a mechanism operating in the epoxy compositions with low hardener content (large M_c value) which has the effect of reducing the energy losses at relatively low rates. At high rates, the energy losses approach and possibly exceed the values for a "normal" network in which the losses are simply dependent on M_c. (By "normal" we mean "without pendant groups").

Fig. 9 also shows that the rate of deformation at which $\mathcal{T}$ reaches its lower limit of $\mathcal{T}_0$ is higher for the low hardener content epoxies (5/1 and 5/1.25) than for the 5/2 epoxy. For a "normal" network, one would expect this value of rate to be *reduced* with increasing M_c, as indeed is shown by the 5/3 epoxy relative to the 5/2 epoxy.

These effects are probably due to the different network structure which is believed to occur in the epoxy at low hardener contents. At low rates of deformation the pendant epoxy molecules (Fig. 3) or "cilia" can separate the main chain segments and act as a plasticizer. This plasticizing action facilitates molecular segmental motion and reduces the energy dissipated viscoelastically, resulting in a decrease in Φ and hence of $\mathcal{T}$. On the other hand, as the rate of deformation is increased, and the time scale involved is less than that required for relaxation of the cilia, segmental motion may be hindered by the cilia acting as bulky side groups. The overall effect of the existence of network "cilia" would therefore be to produce a much faster rise of mechanical losses (and thus of Φ and $\mathcal{T}$) with increasing rate than is encountered in "normal" networks not containing pendant epoxy chains.

5. Determination of $\mathcal{T}_0$

Figs. 5 to 8, in which data has been shifted using the WLF equation, show that the cohesive failure energy, $\mathcal{T}$ (because of the loss function Φ) is very dependent on the rate and temperature of testing. At very low rates a point is reached at which all of the segmental relaxation times are within the time scale of the experiment and hence no energy is dissipated in frictional processes between molecular segments. A constant value of failure energy, $\mathcal{T}_0$, is reached (obtained in normal testing with only the 5/1 epoxy – Fig. 6) which is independent of rate; $\mathcal{T}_0$ is the minimum energy required to produce crack growth, i.e. in the absence of viscoelastic losses. It is basically the energy required to break C–C bonds in the polymer backbone, although, as we shall see, other aspects such as chain flexibility and degree of cross-linking have a great effect on its value.

Two approaches have been previously employed for the determination of $\mathcal{T}_0$ in other elastomeric systems, these being experimental [13, 14] and theoretical [4] respectively. These two methods were applied in the present work, as will be described below. The experimental approach afforded only limited success.

5.1. Experimental method for $\mathcal{T}_0$

Attempts were made to measure $\mathcal{T}_0$ directly using two techniques; fatigue tests and static loading tests.

Fatigue tests were carried out to determine $\mathcal{T}_0$ as described by Lake and Lindley [13]. The crack growth rate (crack length per cycle) in sheet specimes of epoxy resin was shown to be a linear function of $\mathcal{T}$, at slow rates. Extrapolation to zero crack growth rate should give $\mathcal{T}_0$. Using this method, values of $2\mathcal{T}_0$ for the 5/2 epoxy of 1.9×10^4, 1.65×10^4 and 6.6×10^3 mJ m^{-2} were obtained. These values are very inconsistent and are, moreover, greater than the lowest value obtained from dynamic testing of this epoxy (4.6×10^3 mJ m^{-2} – see Fig. 5). These values cannot therefore be correct $\mathcal{T}_0$ values and must include considerable contributions from energy dissipated viscoelastically.

Static loading tests were carried out on pre-cracked specimens loaded in an oven. The crack was monitored in order to determine the crack growth rate (crack length per time) as a function of $\mathcal{T}$. Extrapolation to zero velocity gave two separate estimates for $2\mathcal{T}_0$ of 3.8×10^3 and 4.5×10^3 mJ m^{-2} for the 5/2 epoxy, and one of 5.7×10^3 mJ m^{-2} for the 5/1 epoxy. These values are however, probably overestimates of $\mathcal{T}_0$ due to the large extrapolation required.

5.2. The theory of Lake and Thomas

The theoretical determination of $\mathcal{T}_0$ has been based on the approach of Lake and Thomas [4]. Modifications to the theory are necessary to enable determination of $\mathcal{T}_0$ without recourse to parameters such as chain flexibility, which are as yet unknown for the epoxy resin. We must first consider the theory of Lake and Thomas. Crack propagation involves the rupture of C–C bonds in the sections of polymer backbone between cross-links, which will be termed "chains". All of the chains are considered to contain the same number of monomer units, $\bar{n}$, and have the same displacement length, $\bar{L}$, between cross-links. The energy required to rupture the chain is not the dissociation energy of the weakest bond but is in fact this quantity multiplied by the number of bonds which can store this energy. The Lake and Thomas approach considers monomer units (which can contain several bonds) rather than individual bonds. Thus the energy required to rupture the chain is given by $\bar{n}\,U$, where U is the fracture energy of one monomer unit. Thus $2\mathcal{T}_0$ is obtained by multiplying the energy needed to rupture one chain ($\bar{n}\,U$) by the number of chains crossing unit area, which is given by $\frac{1}{2}\bar{L}\,N$, where N is the number of chains per unit volume. The factor of $\frac{1}{2}$ appears because some of the chains actually lie in the fracture plane and not across it. Thus:

$$2\mathcal{T}_0 = \tfrac{1}{2}\bar{L}N\bar{n}U \qquad (7)$$

From rubber elasticity theory, the mean displacement length of a chain is given by:

$$\bar{L} = \left(\frac{8\bar{n}}{3\pi}\right)^{1/2}\gamma l \qquad (8)$$

where l is the length of the monomer unit and γ is a factor determined by the freedom of rotation of the bonds in the chain. In fact γ^2 is defined as the number of monomer units per equivalent statistical (completely freely jointed) link. Thus a high degree of chain flexibility is shown by a low value of γ, and hence a small value for the displacement length. Elimination of $\bar{L}$ from Equations 7 and 8 gives:

$$2\mathscr{T}_0 = \left(\frac{2}{3\pi}\right)^{1/2} \gamma\, l\, U N(\bar{n})^{3/2} \qquad (9)$$

This equation assumes a constant displacement length ($\bar{L}$), and a uniform number of monomer units per chain ($\bar{n}$). Lake and Thomas modified this equation by assuming that displacement lengths follow a Gaussian distribution and that the number of monomer units per chain is determined by random cross-linking, to give:

$$2\mathscr{T}_0 = (\tfrac{3}{8})^{1/2} \gamma\, l\, U N(\bar{n})^{3/2} \qquad (10)$$

5.3. Modification of the theory of Lake and Thomas

The epoxy resin has a monomeric molecular weight of 340 and the number of monomer units between crosslinks varies between two and ten, depending on the proportion of hardener. Thus the equivalent statistical link (which is assumed to be completely freely jointed) will probably be less than one epoxy monomer unit and hence Equations 9 and 10 are not very useful in their present form. Also the parameter γ is unknown for the epoxy resin. An alternative approach has been developed, though many of the assumptions are basically the same.

The first difference is to consider the energy required to rupture a chain in terms of the bond dissociation energy, denoted here by E_b, and not by the energy needed to rupture a monomer unit, U. The energy necessary for chain rupture is now almost nE_b, where n is the number of bonds which are capable of storing the energy required to break the weakest bond, E_b.

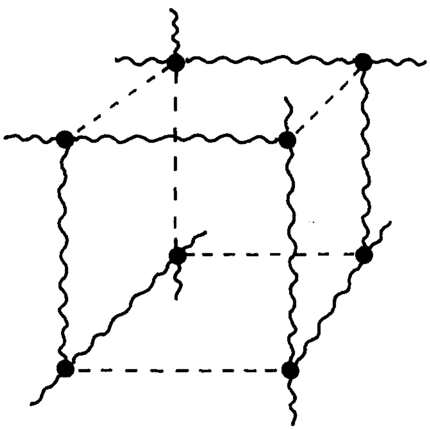

Figure 10 Simple cubic array of cross-links.

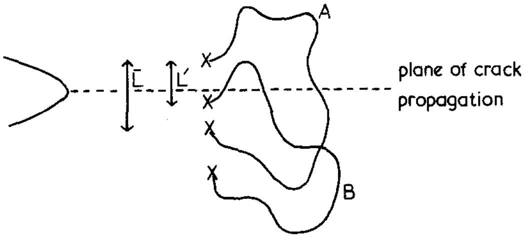

Figure 11 Schematic diagram of two network chains (see text). Broken line shows plane of crack propagation.

The cross-link junctions are assumed to be arranged in a simple cubic structure (Fig. 10). It is assumed that L', the distance between nearest cross-links is equivalent to the mean displacement length, $\bar{L}$, of the chains, i.e. that adjacent cross-links lie on the same chain. This is the important difference between this approach and that of Lake and Thomas. The difference is made clear by consideration of Fig. 11. In this schematic diagram the distance between nearest cross-links is less than the mean displacement length, i.e. $L' < \bar{L}$. Thus when the crack passes along the plane indicated, chain B will experience no stress as both of its cross-link junctions lie on one side of the fracture plane. It is only the chains which actually cross this plane which contribute to $\mathscr{T}_0$. Thus the number of chains crossing unit area should, in the simple theory, be equal to $\frac{1}{2} N\bar{L}$ (as used by Lake and Thomas) and not $\frac{1}{2} NL'$. It is, however, expected that in the highly cross-linked epoxy network the adjacent junction points will in fact lie on the same chain. Approximate calculations support this assumption. A molecular model of the epoxy molecule shows this to be relatively flexible and a random statistical link of between 2 and 4 bonds is a reasonable assumption. Taking $\bar{L}$ to be approximately $(n_s)^{1/2}\, l_s$ where l_s is the length of the random statistical link and n_s is the number of these links per chain, an estimation of $\bar{L}$ is possible, knowing M_c and the average bond length. Thus values of $\bar{L}$ for the 5/2 epoxy are approximately 8 to 12 Å and for the 5/1 vary between 18 and 28 Å. Values of L', the distance between nearest cross-links are given approximately by $\nu^{-1/3}$, where ν is the cross-link density. Each cross-link corresponds to 2 chains and so ν can be replaced by $(N/2)$, which is calculated using rubber elasticity theory (see later). Values obtained for L' are approximately 15 Å for the 5/2 and 25 Å for the 5/1 epoxy. These L' values correspond closely to those determined for $\bar{L}$ and although these are only approximate calculations, they demonstrate that the assumption $L' \simeq \bar{L}$ is reasonable.

The cube shown in Fig. 10 is of unit volume and hence contains N chains. The number of chains contained in one of the molecular segments which lies parallel to one axis of the cube is $(\bar{L})^{-1}$ (since $\bar{L}$ is approximated to L'). Hence:

$$N = \frac{1}{(\bar{L})^3} \qquad (11)$$

is the number of chains in the cube of unit volume. Now, the number of chains crossing a plane of unit area is $\frac{1}{2} N\bar{L}$, as obtained by Lake and Thomas. The factor $\frac{1}{2}$ appears because every chain crossing a plane which is perpendicular to it will have, on average, one chain cross-linked to it which is parallel to the plane. Chains which are parallel to the plane of crack propagation should not be considered in the calculation of $\mathcal{T}_0$. Now, $\bar{L}$ and N are inter-related (Equation (11)) so the number of chains crossing unit area of plane is given by $\frac{1}{2} N^{2/3}$. The difference between this approach and that of Lake and Thomas [4], is that the latter used the substitution for $\bar{L}$, given by Equation 8. This equation involves the parameter γ which is unknown for the epoxy resin. The approach adopted here, where $\bar{L}$ is given by Equation 1 does not assume anything about the flexibility of the chain between the cross-links. The only assumption made is that adjacent cross-links belong to the same chain. 2 $\mathcal{T}_0$ is now given by the energy to rupture one chain (nE_b) multiplied by the number of chains per unit area ($\frac{1}{2} N^{2/3}$):

$$2\mathcal{T}_0 = \tfrac{1}{2} N^{2/3} nE_b \qquad (12)$$

This equation is furthermore of greater application to epoxy resins than that of Lake and Thomas, because it involves the number and strength of individual bonds and not monomer units.

TABLE I Values of N and n for different resin/hardener compositions

Epoxy	N $\times 10^{-26}$ (m^{-3})	n
5/2	7.60	20
5/3	4.78	30
5/1.25	3.48	40
5/1	1.35	100

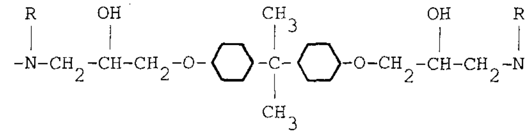

Figure 12 An epoxy molecule after reaction with two molecules of amine hardener.

5.4. Determination of the parameters

C_1 (Equation 3) is related to the density of network chains, N, by the theory of rubber elasticity:

$$C_1 = \tfrac{1}{2} NkT \qquad (13)$$

where k is Boltzmann's constant and T is the absolute temperature. Values of N were determined using this equation and are given in Table I. It was shown earlier that application of the theory of rubber-like elasticity to epoxy resin, above the T_g, is justifiable.

In order to determine n, the number of bonds per chain which are capable of storing energy, it is first necessary to know how many monomer units there are per chain. This can be estimated from the calculated values of M_c and the molecular weights of the epoxy monomer unit and the hardener. Values of n can then be calculated and are given in Table I. The benzene rings and the resonant oxygen–benzene ring bond (Fig. 12) are strong and should store very little energy. For this reason they have not been included in the calculation of n.

E_b is the energy required to rupture the weakest bond in the main chain. The C–C bond in the (–CH(OH)–CH_2–O– benzene ring) section of the main chain (Fig. 12) is probably the weakest bond since it experiences two separate weakening effects. One is due to the presence of the pendant –OH group which displaces neighbouring electron cloud distributions. An example of this effect is given by the difference in dissociation energy of the C–H bond in methyl alcohol and the same bond in methane. The bond energy [15] in methane (CH_3–H) is 101 kcal mol^{-1}, while in methyl alcohol ($HOCH_2$–H) it is only 92 kcal mol^{-1}. This amounts to a reduction in energy of approximately 9% due to the presence of the –OH group.

The second weakening effect arises from the proximity of the oxygen–benzene ring resonance. Once this C–C bond is ruptured, one of the freed electrons can readily enter into this resonance producing a relatively stable radical. An example of this effect can be seen by comparing the dissociation energy of the C–H bond in benzene and toluene. In benzene, the freed electron cannot

TABLE II Values of $2\mathscr{T}_0$ for the four resin/hardener compositions

$2\mathscr{T}_0$ (mJ m^{-2})			
5/2	5/3	5/1.25	5/1
*2590	2830	3050	4050
†3200	3580	3890	5160

*Using Equation 12.
†Using Equation 18.

enter the resonance of the benzene ring, while in toluene it can. The bond energy [15] in benzene (C_6H_5–H) is 102 kcal mol^{-1} while in toluene ($C_6H_5CH_2$–H) it is only 77.5 kcal mol^{-1}. This amounts to a reduction in energy of approximately 24%.

It is assumed that the C–C bond in the (–CH (OH)–CH_2–O– benzene ring) sequence ruptures first with an energy which is less than that of a normal C–C bond by approximately 10% due to the effect of the polar –OH group and approximately 25% due to the proximity of the oxygen–benzene ring resonance. Lake and Thomas [4] took the general value for the C–C bond to be 4.6×10^{-19} J (obtained from the data of Cottrell [15]). Because of the two effects experienced by the C–C bond discussed above, the value of its bond energy is reduced from 4.6×10^{-19} J to 3.1×10^{-19} J. This latter value is thus taken to be the value of E_b for the epoxy resin. Having determined values for N, n and E_b, $2\mathscr{T}_0$ is calculated using Equation 12 and the values obtained are given in Table II. The results follow the expected trend in that an increase in the molecular weight between cross-links M_c results in a larger $2\mathscr{T}_0$. As discussed earlier, the cohesive failure energy curve for the 5/1 epoxy (Fig. 6) has a cut-off point at a value of approximately 3700 mJ m^{-2}. This compares very well with the value of 4050 mJ m^{-2} determined using our modified theory, and suggests that the cut-off in Fig. 6 does in fact locate $\mathscr{T}_0$. The theoretically determined value of $2\mathscr{T}_0$ for the 5/2 epoxy also agrees well with the lowest value obtained from the static loading tests (3800 mJ m^{-2}). The theoretically determined $2\mathscr{T}_0$ values have been marked in Fig. 9 and the cohesive failure energy curves extrapolated to these points.

5.5. Alternative theory

Lake and Thomas [4] also proposed an alternative, approximate, theoretical approach to the determination of $\mathscr{T}_0$. Thomas [16] has demonstrated an approximate relationship between tearing energy, the unstrained diameter, d, of the tip of a crack, and the strain energy density at the tip, W_t:

$$2\mathscr{T}_0 \simeq W_t d \qquad (14)$$

Lake and Thomas [4] assumed that the smallest possible tip diameter in the unstrained state must be comparable with the distance between cross-links i.e. $d \simeq \bar{L}$. They took the value of W_t to be the energy stored in each monomer unit (U) multiplied by the number of monomer units per unit volume ($N\bar{n}$). Substitution for $\bar{L}$ from Equation 8 gives an expression for $2\mathscr{T}_0$ which is exactly twice that given by Equation 10, the result of their main theory. It is considered here that this difference of a factor of 2 should not arise. When using a value for N, the number of chains per unit volume, account should be taken of the fact that on average half of the chains are actually parallel to the plane of crack propagation and hence cannot store any energy during the fracture process. It is thus considered that the equation used by Lake and Thomas should have been:

$$2\mathscr{T}_0 \simeq \tfrac{1}{2} W_t d \qquad (15)$$

Now, when substitution is made for W_t and d, a relationship for $2\mathscr{T}_0$ is obtained which is identical to that of Equation 9.

In order to apply Equation 15 to epoxy resin, substitution for W_t must be made in terms of bonds rather than monomer units, and d cannot be approximated by $\bar{L}$ as this parameter required knowledge of the chain flexibility of the epoxy (Equation 8). Thus W_t is equal to the maximum energy which can be stored in a bond, E_b, multiplied by the number of bonds per unit volume, Nn. Assuming that the minimum, crack tip diameter, d, is approximately equal to $\bar{L}$, which is equivalent to L', the distance between nearest cross-links then d can be approximated by $\nu^{-1/3}$. The cross-link density, ν, is equivalent to $N/2$ and so Equation 15 gives:

$$2\mathscr{T}_0 \simeq \frac{1}{2^{2/3}} N^{2/3} n E_b \qquad (16)$$

This equation gives values of $2\mathscr{T}_0$ (Table II) which differ by only a small numerical factor from those obtained using the theory developed here (Equation 12).

5.6. Comparison of $\mathscr{T}_0$ values in elastomers and epoxy resins

Why are the $2\mathscr{T}_0$ values for the epoxy an order of magnitude lower than those for rubbers? Values obtained for $2\mathscr{T}_0$ for rubbers both experimentally and theoretically are generally of the order of $5 \times 10^4\ \mathrm{mJ\,m^{-2}}$. The highest value obtained here for epoxy is $4.05 \times 10^3\ \mathrm{mJ\,m^{-2}}$. It was thought that this difference merely reflected the much greater M_c in the case of the rubbers, i.e. the epoxy has a much higher cross-link density so that the chains cannot store as much energy in the fracture process. However, Ahagon and Gent [14] obtained experimental $\mathscr{T}_0$ values for polybutadiene, with a low value of M_c, of the same order of magnitude as those reported by Lake and Thomas [4]. For instance, Gent reports a $2\mathscr{T}_0$ of $3.7 \times 10^4\ \mathrm{mJ\,m^{-2}}$ for unswollen polybutadiene with M_c equal to 2000 (before correction for entanglements and free ends). The corresponding epoxy with this M_c value (5/1.25 epoxy) has $2\mathscr{T}_0$ equal to $3.05 \times 10^3\ \mathrm{mJ\,m^{-2}}$.

One possible explanation for this difference is that the equation used to calculate $2\mathscr{T}_0$ (Equation 14) takes no account of the chain flexibility (as described by the parameter γ) of the epoxy, which may be considerably different from that of the rubbers.

Using molecular models, it can be shown that polybutadiene is more flexible than epoxy resin. Polybutadiene should thus have a lower value of γ and $\mathscr{T}_0$ (Equation 9). Thus differences in chain flexibility do not explain the differences in $\mathscr{T}_0$ values.

One reason for the discrepancy in $\mathscr{T}_0$ values must be the relatively low bond energy in the epoxy (3.1×10^{-19} J compared with 4.6×10^{-19} J for the general C–C bond). This amounts to a reduction of approximately 30%. A more significant explanation, however, lies in the value of n. Approximately half of the molecular weight of the epoxy unit lies in the 2 benzene rings. Thus for the same M_c, the value of n for the epoxy is considerably less than it is for most rubbers. At M_c equal to 2000 polybutadiene [14] has n equal to 111 while the 5/1.25 epoxy has n (bonds storing energy) equal to 40 and n (bonds which can rotate) equal to 32. This produces a reduction in $2\mathscr{T}_0$ of approximately 80%. Hence if E_b and n were raised to 4.6×10^{-19} J and 111 respectively, then the value of $2\mathscr{T}_0$ for the 5/1.25 epoxy would increase from $3050\ \mathrm{mJ\,m^{-2}}$ to approximately $26\,000\ \mathrm{mJ\,m^{-2}}$. This is certainly approaching the value ($3.7 \times 10^4\ \mathrm{mJ\,m^{-2}}$) quoted by Gent [14] for polybutadiene with an M_c value of 2000.

Thus it appears that the low $\mathscr{T}_0$ values of the epoxy are mainly a result of the small number of bonds which store significant amounts of energy and also the relatively low energy required to rupture the weakest bond. The former has the greatest effect.

6. Conclusion

Andrews' equation for cohesive fracture (Equation 2) has been successfully applied to the failure of epoxy resin above the T_g. This equation states that the cohesive failure energy, $\mathscr{T}$, is the product of the intrinsic cohesive failure energy, $\mathscr{T}_0$, and the loss function Φ.

The variation of Φ as a function of hardener content has been investigated. Two effects were noted. First, as expected, Φ increases with increasing M_c, the molecular weight between cross-links. Another effect occurs at low proportions of hardener, where the energy losses within the material are considerably reduced at low rates of crack propagation. This is believed to be due to the plasticizing mechanism of the "cilia" (epoxy molecules attached to the main chain at one end only) resulting from the depletion of hardener.

The theoretical determination of $2\mathscr{T}_0$ for rubbers, proposed by Lake and Thomas, has been modified and applied to epoxy resins above the T_g. Values of $2\mathscr{T}_0$ have been calculated for different resin/hardener compositions. With one of these compositions values were determined from normal dynamic and static loading tests which correlated very closely with the theoretically calculated value.

Values for $2\mathscr{T}_0$ were found to be an order of magnitude lower than those of rubbers. This appears to be mainly due to the smaller number of bonds in the epoxy, which are capable of storing significant amounts of energy when the main chain is subjected to stress.

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