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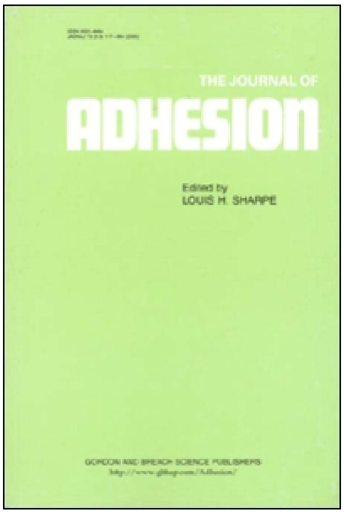

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The Use of Time-Temperature Superpositioning in Studying the Fracture Properties of Rubber-Toughened Epoxy Polymers

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The Use of Time-Temperature Superpositioning in Studying the Fracture Properties of Rubber-Toughened Epoxy Polymers*

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The fracture energies, G_{Ic}, of an unmodified and a rubber-modified epoxy have been ascertained as a function of test temperature and rate. A time-temperature superpositioning technique has been adopted in order to produce a master curve of the fracture energy, G_{Ic}, *versus* the reduced rate of test, t_f/a_T; where t_f is the time-to-failure and a_T is the time-temperature shift factor. The value of the shift factor, a_T, as a function of test temperature has been determined from time-temperature shifting the yield stress and the modulus data for the materials. The master curve of G_{Ic} *versus* t_f/a_T has been modelled and the values of the constants employed in the model have been deduced. The values of the constants so determined are discussed with respect to the microstructures of the epoxy polymers.

KEY WORDS fracture mechanics; modelling; rubber-modified epoxies; time-temperature superpositioning; yield behaviour.

INTRODUCTION

In recent years several studies[1–8] have revealed important information on the relationship between the crosslink density and the fracture properties for both unmodified and rubber-modified thermosetting epoxy polymers. These studies have shown that sharp increases in the fracture energies for both the unmodified and the rubber-modified epoxies at room temperature may result by increasing the segmental molecular mass, M_c, between crosslinks.

However, little work has been published concerning how the fracture properties ascertained as a function of M_c would also be affected by using different test rates

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and temperatures. This information is of interest for many reasons. For example, any change in the crosslink density will invariably lead to changes in the glass transition temperature of the material, which can be demonstrated by the following empirical equation which was proposed by Nielsen:[9]

$$T_g = T_{g0} + 3.9 \cdot 10^4 / M_c \qquad (1)$$

where T_g is the glass transition temperature of the crosslinked epoxy polymer which has a molecular mass between crosslinks of M_c and T_{g0} is the glass transition temperature of the uncrosslinked epoxy polymer. Now, apart from any effects on the measured toughness which are directly attributable to the crosslink density, the changing of glass transition temperature may well affect the fracture properties measured at room temperature. This is because the important term in this respect is the value of $(T_g - T)$, where T is the test temperature, and the value of the term $(T_g - T)$ may obviously be changed by either selecting a different test temperature or by changing the glass transition temperature.

Previous work has shown that the fracture properties of epoxy polymers measured over a wide range of test temperatures and rates may be expressed in terms of the reduced time of test, t_f/a_T, where t_f is the time-to-failure and a_T is the time-temperature shift factor. This time-temperature superpositioning technique is based[10–13] on the time-temperature equivalence of the viscoelastic properties of polymers. It has been previously employed by Bitner *et al.*,[14] Huntson *et al.*,[15] and Hunston and Bullman[16] to study the fracture properties of a range of unmodified and rubber-modified epoxy polymers. These workers suggested that the master curve for the fracture energy, G_{Ic}, as a function of test rate and temperature could be represented by the following equation:

$$G_{Ic} = G_{Ics} + C^* t_f^m e^{-\frac{m\Delta E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \qquad (2)$$

In the above equation, G_{Ics} is the minimum value of the fracture energy (typically measured at very low test temperatures), R is the gas constant and T_0 is a reference temperature (which was usually taken as $T_g - 80°C$). The terms C^*, m and ΔE (an activation energy) are constants which characterise the toughening magnitude, rate dependence and temperature dependence of G_{Ic}, respectively.

In the present study, the effects of the crosslink density of the epoxy matrix polymer on the fracture properties will be studied by employing two rubber-toughened epoxy polymers which possess different crosslink densities for the epoxy matrix, hence somewhat different glass transition temperatures for the epoxy matrix. However, previous work[1] employed electron microscopy to demonstrate that they possess identical rubbery phase microstructures. The values of the fracture toughness, K_{Ic}, and fracture energy, G_{Ic}, measured at room temperature for these materials have also been determined by Kinloch *et al.*[1] and are presented in Table I. Obviously, an increase in the value of M_c results in dramatic improvements in the fracture energies for both the unmodified and rubber-toughened epoxy materials. The aims of the present study are: (i) to investigate the effects of using a wide range of test rates and temperatures, (ii) to see how simply a decrease of about 12°C in the glass transition temperature of the epoxy matrix affects the observed increase in the toughness, (iii) to obtain a master curve for the fracture energy for the epoxy

TABLE I
Properties of the rubber-toughened and untoughened materials cured under different conditions (after Kinloch *et al.*[1])

Material	M_c (g/mole)	T_g (epoxy) (°C)	V_f (%)	K_{Ic} ($MPa.m^{0.5}$)	G_{Ic} (kJ/m^2)
UME16hr&120C	590	100	—	0.88	0.21
RME16hr&120C	630	101	18	2.64	2.23
UME6hr&160C	4900	87	—	1.29	0.46
RME6hr&160C	4370	89	19	4.23	5.90

Note: V_f = volume fraction of dispersed rubbery particles

polymer having the higher value of M_c (previous work[15] has obtained such relationships for the other epoxy polymers), and (iv) to investigate the use of equation (2) to model the time-temperature relationships which are ascertained.

EXPERIMENTAL

Materials

The epoxy polymers examined in the present study were model materials based upon a simple unmodified and a rubber-toughened epoxy resin. The epoxy resin employed was derived from the reaction of bisphenol A and epichlorohydrin and was largely composed of the diglycidyl ether of bisphenol A (DGEBA). The curing agent was piperidine. The rubber used to prepare the multiphase, rubber-modified epoxy polymer was a carboxyl-terminated, random copolymer of butadiene and acrylonitrile (CTBN rubber: carboxyl content 2.37 wt/wt%; molecular mass 3500 g/mole). The formulations of the epoxy polymers are shown in Table II.

To prepare sheets of the rubber-modified epoxy the CTBN rubber was added to the epoxy resin and hand-mixed for approximately 5 to 10 minutes. This mixture was heated to 65 ± 5°C in a water bath and mixed for 5 min using an electric stirrer, then degassed in a vacuum oven at 60°C until frothing stopped. When the mixture had cooled to below 30°C the piperidine was mixed in gently to minimise air entrapment. To make sheets of the materials for testing, the rubber-epoxy mixture was then poured into a preheated mould and cured at either (i) 16 hours at 120°C or (ii) 6 hours at 160°C, and allowed to cool slowly. These two different curing schedules lead to materials having different crosslink densities of the epoxy matrix but with

TABLE II
Formulations of epoxy polymers

	Unmodified epoxy (phr*)	Rubber-modified epoxy (phr)
DGEBA epoxy resin	100	100
Piperidine	5	5
CTBN rubber	—	15

*phr = parts per hundred of resin

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the same rubbery phase microstructures. Sheets of the unmodified epoxy were prepared in the same manner but without the addition of rubber.

For simplicity, the two rubber-modified epoxies, together with their unmodified counterparts, are coded as "UME16hr&120C" and "RME16hr&120C" and as "UME6hr&160C" and "RME6hr&160C"; the terms "UME" and "RME" refer to "unmodified epoxy" and "rubber-modified epoxy," respectively, and the terms "16hr&120C" and "6hr&160C" refer to the curing condition which was used.

Mechanical Properties

The dynamic mechanical properties of the materials were studied by conducting dynamic mechanical thermal analysis (DMTA). The storage modulus was measured over a temperature range between −80°C and 160°C at different frequencies.

Plane-strain compression tests were performed to determine the elastic modulus and yield stress of the materials over a temperature range from −80°C to 40°C. Details of the test method have been described by Williams and Ford.[17] The fracture toughness was determined by using the compact-tension specimen and the crack tip was formed by lightly tapping a sharp razor blade into the specimen and thereby growing a natural crack ahead of the razor blade. The fracture tests were conducted over the temperature range between −60°C and 40°C and at three different rates of test, *i.e.* 0.2mm/min, 2mm/min and 20mm/min. The value of the fracture toughness at the onset of crack growth was assessed by visual observation of the crack or by using the 5% compliance offset method as described in the relevant standard.[18] Linear elastic fracture mechanics was assumed to be appropriate and the validity of the results was ensured by using the procedures described in the relevant ASTM fracture mechanics specification.[18] Impact tests were also conducted to measure the fracture energy under high test rates. An instrumented Charpy impact test was employed and the procedures outlined by Plati and Williams[19] were followed.

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RESULTS AND DISCUSSIONS

DMTA Tests

Figure 1 shows the storage shear moduli for both the "UME6hr&160C" and "RME6hr&160C" materials as a function of test frequency and at different test temperatures. For both materials, the shear modulus increases with increasing frequency or decreasing temperature, due to the viscoelastic nature of the materials. Straight lines have been drawn through the data points but the results obtained at −60°C do suggest that the points may lie on a curve; this is especially apparent in Figure 1a. This might well be the case and would arise from the presence of a β-relaxation peak for the materials at around −70°C.

Plane-strain Compression Tests

The compressive modulus and yield stress were measured at various test temperatures and rates of displacement. The results for the compressive modulus are presented in Figures 2a and 2b for the "UME6hr&160C" and "RME6hr&160C"

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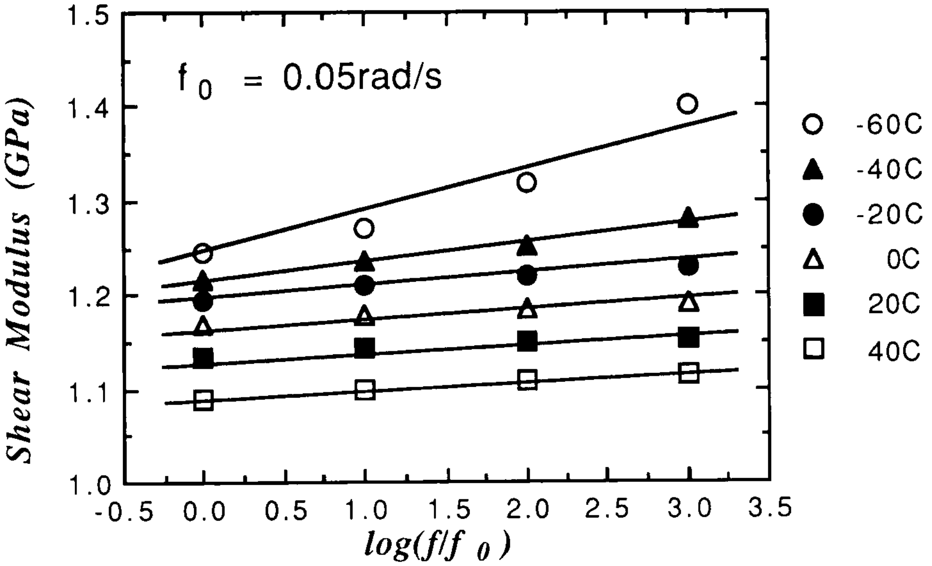
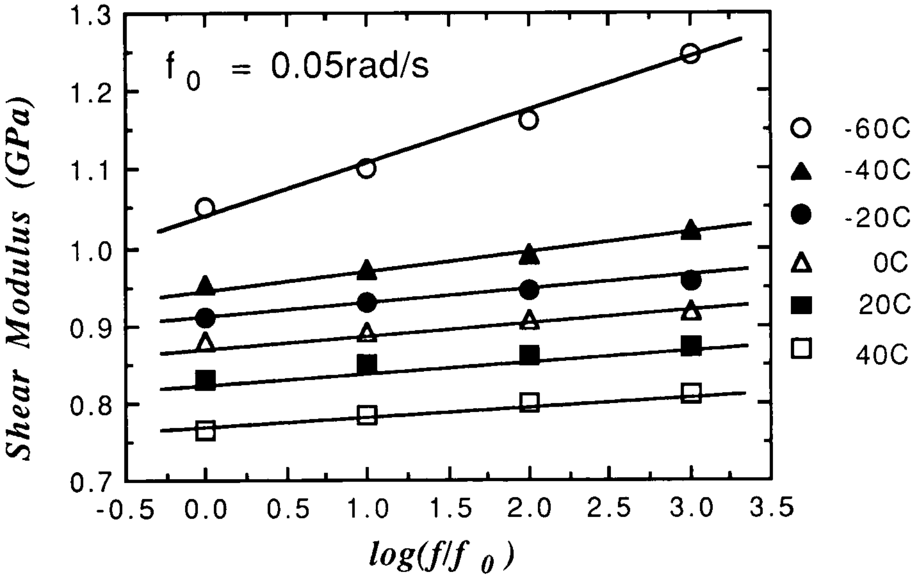


(a)



(b)

FIGURE 1 Values of the storage shear moduli measured using DMTA at different test temperatures and frequencies. (a) "UME6hr&160C" material. (b) "RME6hr&160C" material. (f is the test frequency and f_0 is a reference test frequency)

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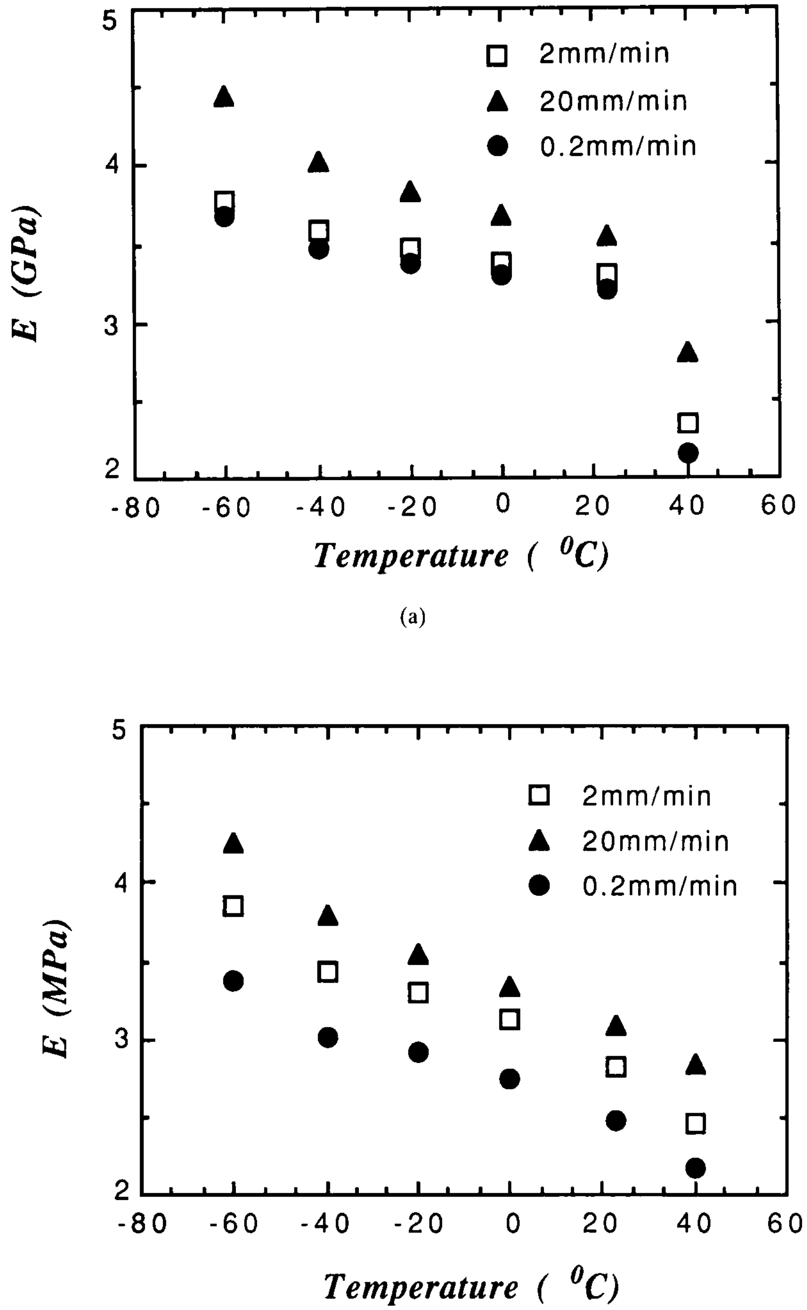

(a)

(b)

FIGURE 2 Values of the compressive modulus measured at different test temperatures and rates. (a) "UME6hr&160C" material. (b) "RME6hr&160C" material.

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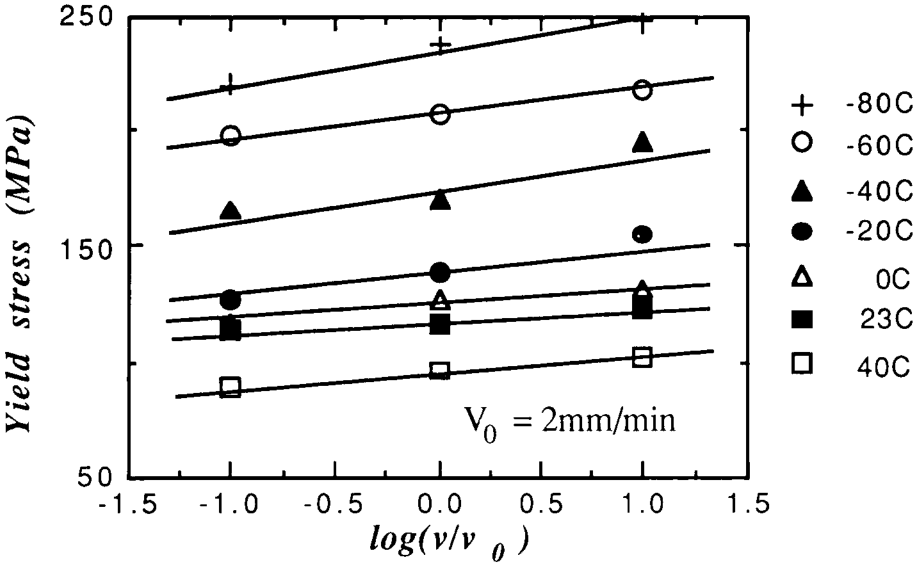
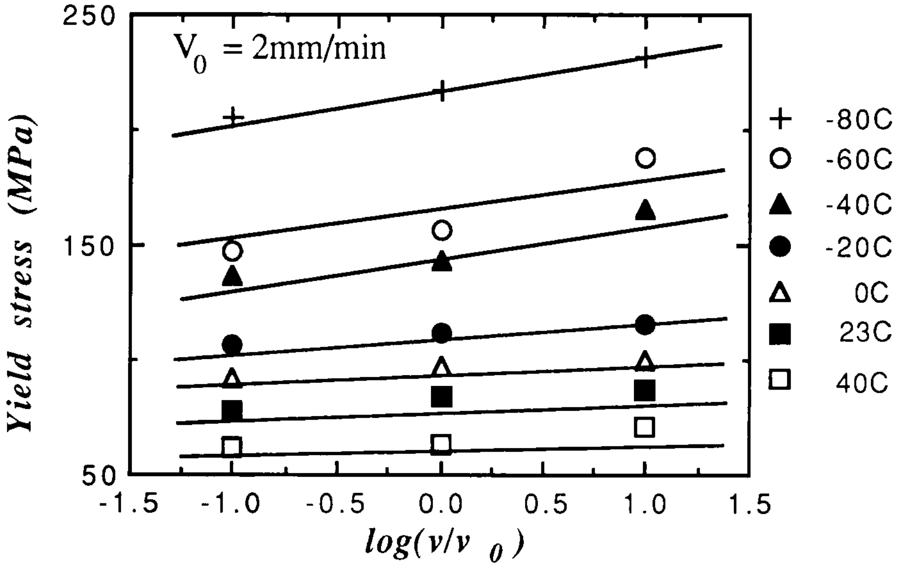


(a)



(b)

FIGURE 3 Values of the yield stress measured at different test temperatures and rates. (a) "UME6hr&160C" material. (b) "RME6hr&160C" material. (v is the displacement test rate and v_0 is a reference displacement test rate) materials, respectively. In general, the compressive modulus decreases rapidly in value with increasing temperature, and also decreases with decreasing test rate. Except at the highest test temperature of 40°C, the modulus of the unmodified epoxy was significantly higher than that of the rubber-modified epoxy.

From Figure 3, it is clear that, for both the "UME6hr&160C" and the "RME6hr&160C" materials, the value of the yield stress decreases with increasing temperature, and also decreases with decreasing test rate.

Fracture Tests

The stress intensity factor, K_{Ic}, at the onset of crack growth was determined from the compact tension tests. The K_{Ic} values for both the unmodified and the rubber-modified epoxies cured for 6 hours at 160°C were measured over a range of temperatures and test rates. The results are presented in Figure 4. For the unmodified epoxy, below about 0°C, the values of K_{Ic} are relatively independent of rate and temperature. At higher temperatures, the K_{Ic} value increases somewhat with increasing temperature and/or decreasing test rate. By contrast, the rubber-modified epoxy gave higher values of K_{Ic} over the entire rate/temperature range, reflecting the enhanced toughness of the multiphase material. The values of K_{Ic} were also far more dependent on the test rate and temperature than those for the unmodified epoxy.

The fracture energy, G_{Ic}, was calculated using the following equation:

$$G_{Ic} = K_{Ic}^2 (1 - \nu^2) / E \tag{3}$$

where ν is Poisson's ratio, which was taken as 0.35. The value of the Young's

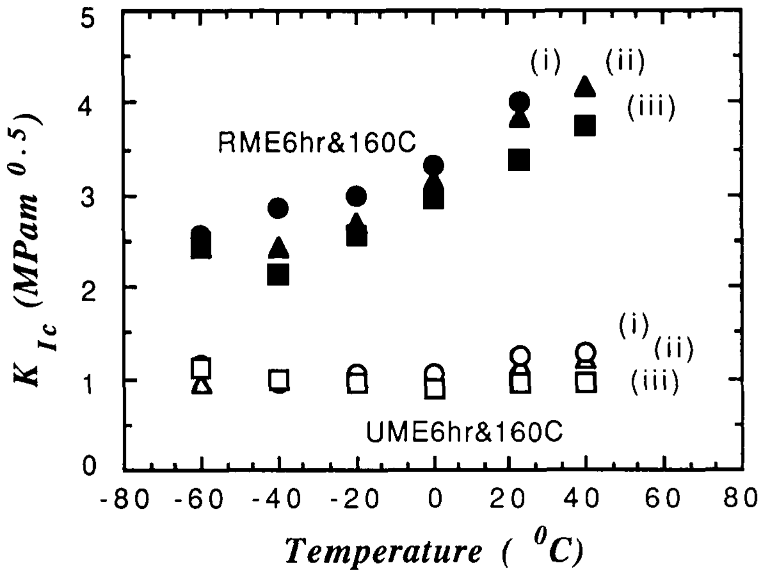


FIGURE 4 Values of the fracture toughness for both the "UME6hr&160C" and the "RME6hr&160C" materials measured at different test temperatures at rates of: (i) 0.2mm/min; (ii) 2mm/min; (iii) 20mm/min.

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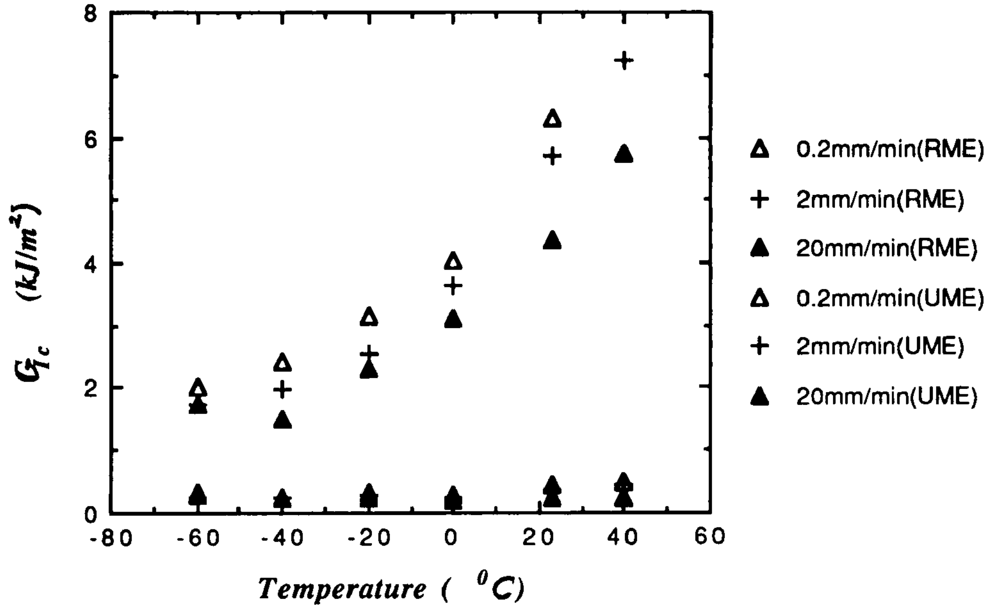

FIGURE 5 Values of the fracture energy for both the "UME6hr&160C" and the "RME6hr&160C" materials measured at different test temperatures at rates of: (i) 0.2mm/min; (ii) 2mm/min; (iii) 20mm/min.

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modulus, E, was determined from the plane-strain compression tests. The value of K_{Ic} and the corresponding value of E used in equation (3), to calculate the values of G_{Ic}, were taken at the same rate of displacement. Figure 5 shows the relationship between the fracture energy and temperature at the three different test rates. As may be seen, for the unmodified epoxy the fracture energy is not greatly affected by the test temperature and rate. However, in the case of the rubber-modified epoxy, the value of G_{Ic} is very dependent upon the test temperature and rate and the toughness increases with increasing temperature and with decreasing test rate. The increase in toughness induced by the presence of the rubber particles is very effective over the entire rate/temperature range, as demonstrated by the significantly higher fracture energies of the rubber-toughened epoxy compared with those of the unmodified epoxy.

The fracture properties of the rubber-modified epoxy ("RME6hr&160C") were also studied under dynamic impact conditions at room temperature at two different impact rates. Figure 6 plots the measured absorbed impact energy against the product BDΦ, where Φ is the geometry factor[19] and B and D are the width and depth of the specimen, respectively. The plots are linear, as predicted by the theoretical expressions,[19] and the slopes give the values of the fracture energies. The fracture energies for the "RME6hr&160C" material were determined to be 3.89kJ/m^2 and 4.10kJ/m^2, corresponding to the two Charpy hammer velocities of 0.99m/s and 0.83m/s respectively. There is not considered to be any significant difference in the values of these two fracture energies, which reflects the fact that the two impact velocities are very close in value.

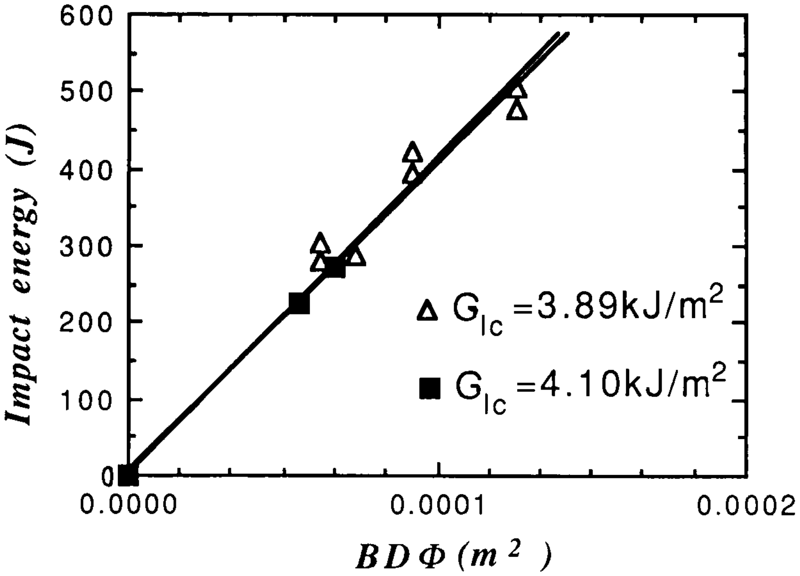

FIGURE 6 Results from impact tests conducted on the "RME6hr&160C" material at two impact velocities.

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Time-temperature Superpositioning

As discussed earlier, for viscoelastic polymers, it is possible to superimpose the data measured under different rate and temperature conditions onto a single master curve. In the case of epoxy polymers, examples of such master curves have been previously given by Hunston and co-workers[15,16] in studying the fracture properties of the "UME16hr&120C" and "RME16hr&120C" materials.

The principles of time-temperature superpositioning may also be applied to the mechanical properties of the "UME6hr&160C" and the "RME6hr&160C" materials. For example, the curves for the storage shear moduli (see Figure 1) may be shifted along the frequency axis by a shift factor of a_T to form a single master curve for each of the two materials, taking the curve of the shear moduli at 0°C as a reference temperature, T_{0r}. These two master curves are shown in Figure 7 and the data superimpose very well. Similarly, in the case of the yield stress, a single master curve was constructed for each of the two materials by shifting the curves for the yield stress (see Figure 3) along the time axis, again taking the curves at 0°C as the reference temperature, T_{0r}. The two master curves are shown in Figure 8 and a very good superpositioning of the data is again evident.

Four sets of shift factors may, therefore, be obtained from constructing these master curves (for the two materials and the modulus and yield stress data) and the values of the shift factors, a_T, so obtained may be plotted against the inverse of the test temperature, as shown in Figure 9. It may be seen that these different sets of shift factors agree well with each other, especially when it is recalled that different mechanical property data have been measured to obtain these values and that both the unmodified and rubber-modified materials have been tested over a wide range

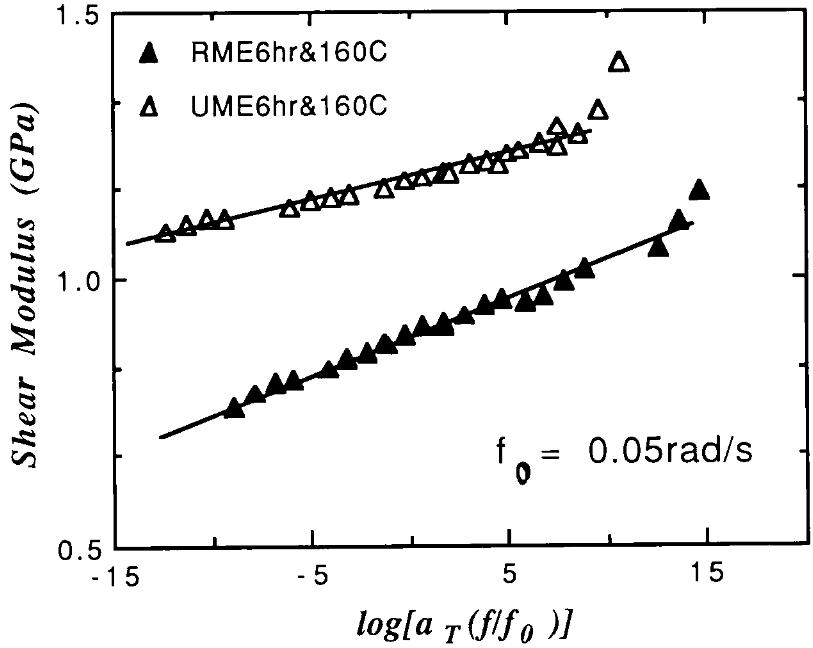

FIGURE 7 Master curves obtained by shifting the individual curves in Figure 1 for the two materials along the frequency axis by a factor of a_T; reference temperature, $T_{0r}=0°C$.

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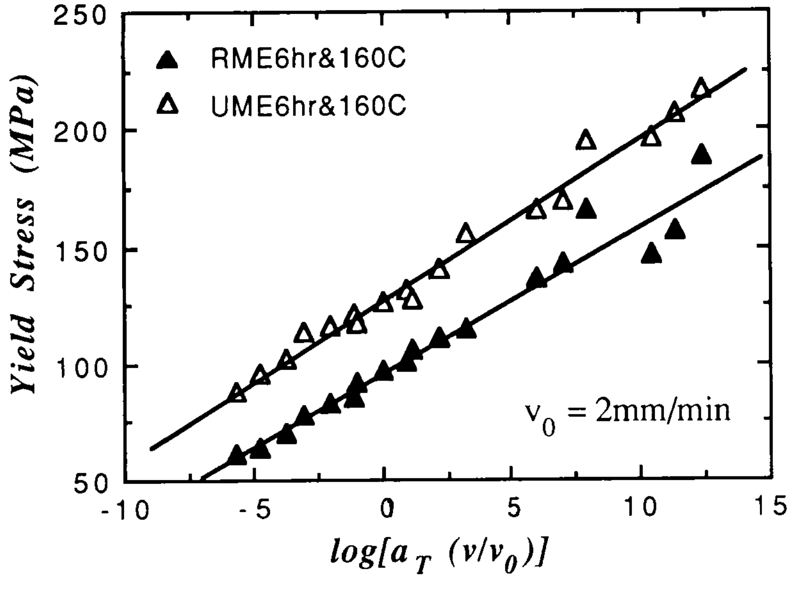

FIGURE 8 Master curves obtained by shifting the individual curves in Figure 3 for the two materials along the time (rate) axis by a factor of a_T; reference temperature, $T_{0r}=0°C$.

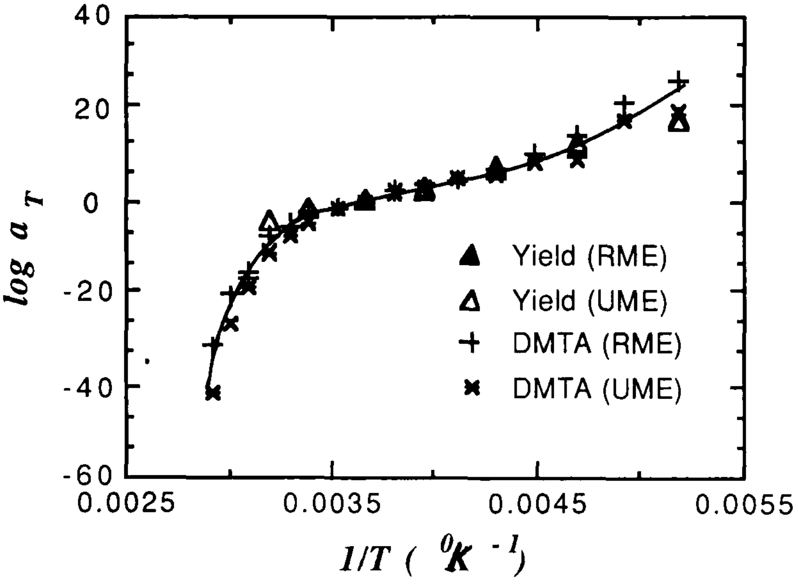

FIGURE 9 The shift factor, a_T, determined from the yield and shear moduli (DMTA) data (see Figures 7 and 8) for both the "UME6hr&160C" and the "RME6hr&160C" materials.

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of temperatures. Further, in the plot of log a_T *versus* T^{-1} there exists an approximately linear portion, as shown in detail in Figure 10, which may be described by the expression:

$$a_T = Be^{\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \tag{4}$$

where R is the gas constant, B is another constant and T_0 is a reference temperature. The reference temperature T_0 does not have to be the same as the reference temperature, T_{0r}, which was used in constructing the master curves in Figure 7 and Figure 8. The choice of T_0 only affects the value of B, since the values of B at two different reference temperatures, T_{01} and T_{02}, are related to each other by the following equation:

$$B_{T_{02}} = B_{T_{01}} e^{\frac{\Delta E}{R}\left(\frac{1}{T_{02}}-\frac{1}{T_{01}}\right)} \tag{5}$$

Now, as discussed earlier, any meaningful comparison between different materials should be undertaken with reference to their respective glass transition temperatures. Indeed, in previous work[15,16,20] a fixed reference test temperature equal to $T_g - 80°C$ was taken. Therefore, in the present studies the actual value of the reference temperature, T_0, was taken to be 8°C, such that the value of $T_g - T_0$ was again 80°C. (The average value for the T_g of the epoxy matrix was taken as 88°C, see Table I.) From Figure 10, using a least squares statistical method, the value of B and ΔE at this reference temperature were calculated to be:

$$B = 38.54 \tag{6}$$

$$\Delta E = 239.3\,\text{kJ/mol} \tag{7}$$

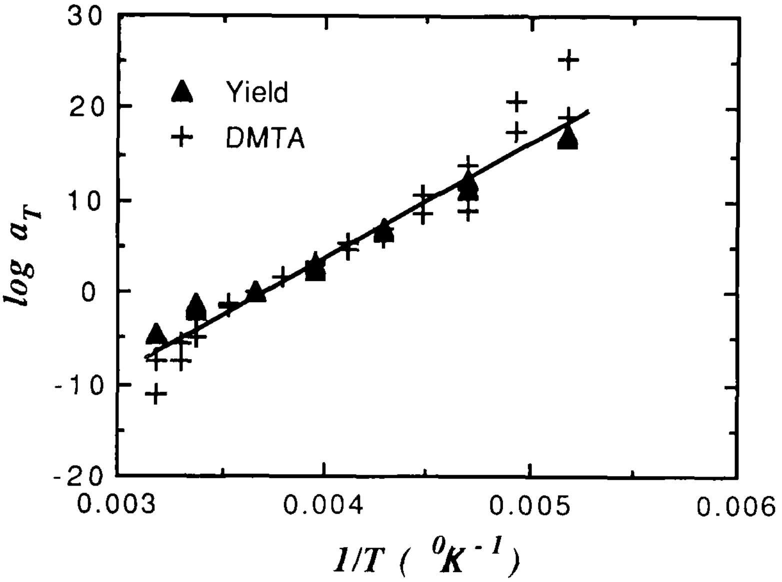

FIGURE 10 The linear portion of the relationship shown in Figure 9.

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As discussed by Ferry,[10] to establish fully the validity of the time-temperature superposition approach in a specific study, the shift factors from one set of data should equally be applicable to another set of properties. If this is the case, then the shift factors described above which were obtained from shear modulus and yield experiments should also permit the fracture energy data to be superimposed to give a master curve. Thus, the shift factors deduced from the modulus and yield experiments (shown in Figures 9 and 10) were next used in an attempt to superimpose the fracture energy, G_{Ic}, measurements. (In order to compare the results with the previous work[15,16,20] the same time-scale was selected, *i.e.* the time-to-failure, t_f, which is the time from the application of the load to that of the onset of crack growth in a fracture test. Obviously, other parameters, such as the loading rate, are related to the time-to-failure and could also be selected, as previously commented by Hunston and Bullman.[16]) The values of the respective fracture energies for the two materials, normalised by reference to an arbitrary fracture energy, G_o, were therefore plotted against $\log[t_f/(t_0\, a_T)]$, as shown in Figure 11; where the appropriate value of a_T is taken from Figure 9. In Figure 11 the value of t_0 is an arbitrary reference time scale which was introduced to normalise the values of the time-to-failure, t_f. The introduction of G_o and t_0 in the presentation of Figure 11 is necessary as the parameters G_{Ic} and t_f, with their associated units, cannot strictly be used directly as variables in a logarithmic function. For convenience, the values of G_o and t_0 were taken to be:

$$G_o \equiv 1\text{kJ/m}^2 \text{ and } t_0 \equiv 1\text{s} \tag{8}$$

From Figure 11 it may be seen that, within experimental scatter, all the values of G_{Ic} measured at the different test temperatures and rates may indeed be fitted to

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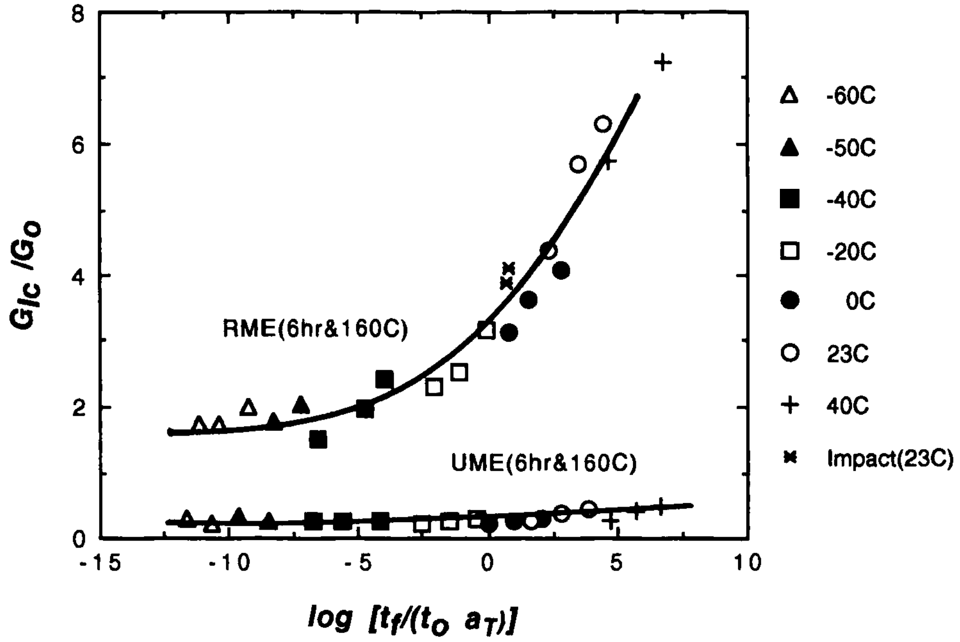

FIGURE 11 Master curves of the fracture energy *versus* the reduced time-to-failure for the "UME6hr&160C" and the "RME6hr&160C" materials. Reference temperature, T_0, is ($T_g - 80°C$).

two master curves. The master curve for the unmodified epoxy shows very little rate/temperature dependence, whilst that for the rubber-modified material shows a strong dependence upon the testing conditions.

In order to determine the constants which reflect the rate dependence (m) and toughening magnitude (C*) for the rubber-modified epoxy, a plot of $\log(G_{Ic} - G_{Ics})/G_o]$ *versus* $\log[t_f/(a_T t_0)]$ was constructed from the data shown in Figure 11, taking G_{Ics} as the lowest value of the fracture energy which was measured within the studied rate/temperature range. A linear relationship was obtained, as shown in Figure 12, and a least squares statistical method gave the following equation:

$$\log[(G_{Ic} - G_{Ics})/G_o] = 0.489 + 0.10\log[t_f/(a_T t_0)] \qquad (9)$$

Using the values given in equation (9), and those previously quoted in equations (4) and (6), to substitute into equation (2) leads to:

$$G_{Ic} = G_{Ics} + C^* G_o \left[\frac{t_f}{t_0}\right]^m e^{\frac{-m\Delta E}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]} \qquad (10)$$

where:

$$G_{Ics} = 1.68\,\mathrm{kJ/m^2} \qquad (11)$$

$$m = 0.1 \qquad (12)$$

$$C^* = 2.14 \qquad (13)$$

It should be noted that equation (10) only differs from equation (2) due to the introduction of G_o and t_0. However, the values of G_o and t_0 have been chosen in

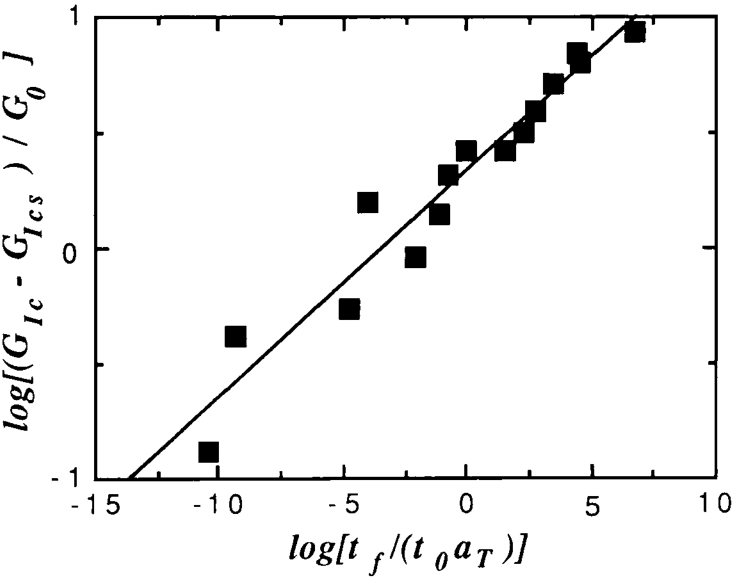

FIGURE 12 The relationship between the fracture energy *versus* the reduced time-to-failure, shown as a double logarithmic plot.

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the present study such that the parameters C*, m and ΔE are equal in value, whether calculated *via* equation (2) or (10).

Interpretation of the Model

The physical meanings of the parameters introduced in equations (7) to (13) may be described as follows. The term G_{Ics} is the limiting toughness at low temperatures and high loading rates. The values of m and ΔE represent the dependence of the fracture properties on the test rate and temperature, respectively. The term C* scales the magnitude of the increase in toughness, within the range of test temperatures and rates which were studied. Now these parameters can be used for quantitative comparisons of the mechanical properties of the different formulations, when they are obtained at a comparable reference temperature. Such a comparison is made in Table III for the two rubber-modified epoxies which differ with respect to the value of M_c for the epoxy matrix. In both cases the reference temperature is taken to be $T_g - 80°C$.

Obviously, when the curing condition is changed from 120°C for 16 hours to 160°C for 6 hours, this has the effect of increasing the molecular mass, M_c, between crosslinks of the epoxy matrix. This results in the epoxy matrix being able to undergo more extensive plastic deformation.[1] Since plastic yielding of the matrix is an essential feature of the toughening mechanisms[21,22] induced by the presence of the dispersed rubbery phase, an increase in M_c is reflected in the limiting toughness G_{Ics} being higher for the "RME6hr&160C" material. The dependence of the fracture properties on the test temperature is also higher for the "RME6hr&160C" material,

TABLE III
Comparison of the rubber-modified epoxy polymers

Material	M_c (g/mole)	G_{Ic} (kJ/m^2)	G_{Ics} (kJ/m^2)	C*	m	ΔE (kJ/mol)
RME16hr&120C	630	2.23	0.6	1.14	0.12	160.5
RME6hr&160C	4370	5.90	1.68	2.14	0.10	239.3

Note: (1) G_{Ic} values were measured at room temperature at a rate of 2mm/min
(2) Reference temperature, $T_0 = T_g - 80°C$

as represented by the increase in the value of the activation energy, ΔE. There was only a small, if any significant, change in the value of m, indicating that there was little, if any, change in the rate sensitivity of the rubber-modified epoxy due to the different curing conditions.

The term C* scales the magnitude of the increase in toughness observed at the higher test temperatures and lower test rates. Comparing the "RME16hr&120C" with the "RME6hr&160C" material, this parameter increased in value from 1.14 to 2.14 due to the change in the cure conditions, which represents an increase of 88%. However, the value of the fracture energy, G_{Ic}, measured at room temperature increased from 2.23kJ/m^2 to 5.90kJ/m^2; namely, an increase of about 160%. (If the different values of G_{Ics} for the two formulations are taken into account, see Table III, then the increase is still about 160%.) As discussed earlier, this relatively large increase in the fracture energy at room temperature is partly due to the decrease in the glass transition temperature. When tested at room temperature, the "RME6hr&160C" material was effectively tested at a temperature nearer to its T_g than the "RME16hr&120C" material. Therefore, the increase in the fracture energy by a factor of 160% is due to the combined effects of both a lower crosslink density and a lower glass transition temperature of the tougher "RME6hr&160C" material. In contrast, the values for C* were obtained at a reference temperature of $T_g - 80°C$ for both the respective materials. Hence, the increase in the value of C* for the "RME6hr&160C" material is a more direct measure of the improvement in toughening which is attributable to increasing the segmental molecular mass, M_c, between crosslinks in the rubber-toughened epoxies, after allowing for the effects of changes in the glass transition temperature which accompany this change in the crosslink density.

Hunston and Bullman[16] also calculated the values of C* for other formulations and the results are presented in Figure 13, together with the values deduced in the present investigation. For the standard formulations of rubber-toughened epoxies cured at 120°C for 16 hours, when a unimodal distribution of rubber particles was attained, the values of C* increase linearly with the rubbery volume fraction. It should be noted, however, that the value of C* is somewhat higher than expected from this linear relation in the case of the formulation which gave a bimodal distribution of rubber particles. This employed bisphenol A in its preparation which was thought to change the crosslink density of the epoxy, as well as giving a bimodal distribution of rubber particles.[20] Thus, it is of interest to note that the two formulations which gave an increased molecular mass, M_c, between crosslinks also gave an

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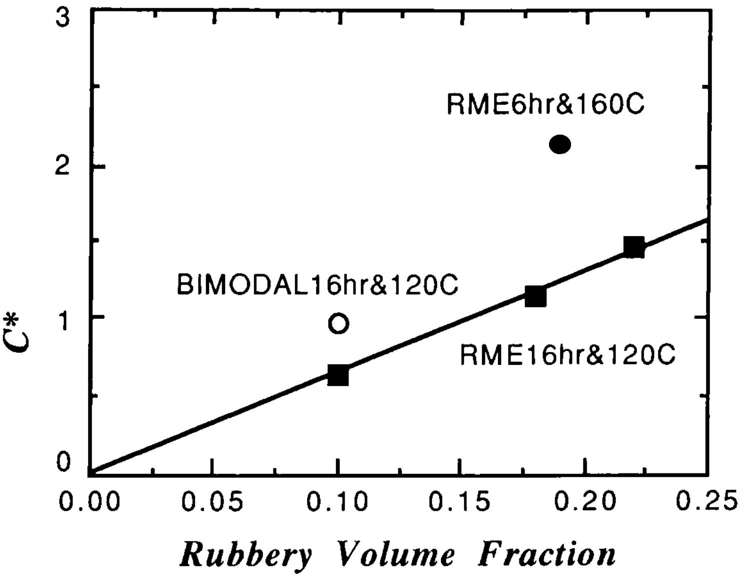

FIGURE 13 The toughening magnitude, C*, as a function of the volume fraction of rubber particles for the various formulations of rubber-modified epoxies. (The filled square points are for the material cured for 16hr at 120°C which gave a unimodal distribution of rubber particles.)

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additional improvement in the values of C* (and hence G_{Ic} value), compared with the standard "RME16hr&120C" material. Thus, the relationships between C* and rubbery volume fraction might possibly be considered to be a series of linear relationships, the slopes of which are governed by the value of M_c of the matrix, with higher values of M_c giving a greater slope.

CONCLUSIONS

The fracture energies, G_{Ic}, of an unmodified and a rubber-modified epoxy have been ascertained as a function of test temperature and rate. In particular, the effect of changing the molecular mass, M_c, between crosslinks has been examined. A time-temperature superpositioning technique has been adopted in order to produce a master curve of the fracture energy, G_{Ic}, *versus* the reduced rate of test, t_f/a_T; where t_f is the time-to-failure and a_T is the time-temperature shift factor. The value of the shift factor, a_T, as a function of test temperature has been determined from time-temperature shifting the yield stress and the modulus data for the materials. The master curve of G_{Ic} *versus* t_f/a_T has been modelled and the values of the constants employed in the model have been deduced. A toughening parameter, termed C*, has been derived from the study which provides an objective and quantitative parameter which may be used to relate the magnitude of toughening recorded to the microstructural features of the epoxy polymer.

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