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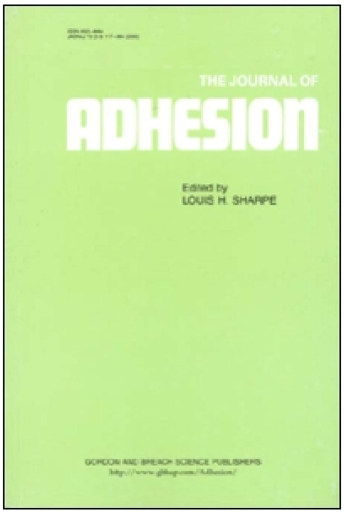

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Viscoelastic Fracture of Structural Adhesives

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Viscoelastic Fracture of Structural Adhesives

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Experiments conducted on several different elastomer-modified epoxy systems indicated that the high fracture energy of most structural adhesives is achieved through crack-tip deformation processes that are viscoelastic. It is essential therefore that the fracture behavior of such materials be determined as a function of temperature and loading history. The linear viscoelastic properties of the model systems were functions of formulation and thermal history but when these parameters were controlled the behavior was thermo-rheologically simple over a wide range of conditions. The fracture behavior was also dependent on formulation and thermal history although the effects of history were quite small in the range of conditions studied here. The fracture behavior at various temperatures and loading rates could be characterized to a first approximation by a master curve of fracture energy *vs.* reduced time-to-failure. This characterization makes it possible to compare the properties of different formulations and to predict their fracture behavior over a wide range of conditions.

INTRODUCTION

In recent years there has been a great effort to increase the operational efficiency of aerospace and other vehicles by reducing their weight through the use of adhesives and composites in primary and secondary structures. This has placed a heavy burden on the present state of adhesive bonding technology in terms of both producing new materials that meet the rigorous demand of these applications and developing the failure models required for efficient design with such materials. The polymers used in structural adhesives and composites

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are generally highly cross-linked so that they will have the high modulus and low long time creep that are usually desirable in these applications. Unfortunately, high cross-linking inevitably leads to brittle materials and thus it is necessary to toughen them if they are to be used in structural applications. One of the most successful methods to toughen cross-linked epoxy systems is the addition of an elastomer. The curing reactions are controlled so that the final material is a matrix of epoxy with small elastomer particles dispersed in and bonded to the matrix. The two phases are never pure materials, however, since the matrix usually contains some elastomer and the particles often contain a good deal of epoxy (the epoxy may even be phase separated within the elastomer particle). The type of phase separation that occurs and the distribution of particle sizes depend on the cure chemistry that is utilized.[1,2,3] Although these factors largely determine the properties of the material, it is not yet possible to completely control the composition or to relate it to the material's performance.

The reason for utilizing this type of two phase system can be explained as follows. It is not difficult to generate materials that are highly resistant to the growth of cracks. In doing this, however, it is usually necessary to make sacrifices in other properties such as modulus. The advantage of the elastomer-modified material is that the two phase nature of the system makes possible toughening mechanisms that do not occur in a single phase material. These mechanisms can greatly increase the resistance to crack growth in the material. Equally important is the fact that these toughening processes can be restricted to localized regions at the tips of cracks, flaws and other stress risers so that the bulk properties are relatively unaffected. Since the matrix itself is almost pure epoxy polymer, the bulk properties such as modulus are close to those of a simple epoxy. Consequently, it is possible to increase the resistance to crack growth with a minimum sacrifice in other properties. For this reason most commercial structural adhesives are based on a technology of this type.

Although a great deal is known about the elastomer-modified epoxies, there are still several areas where important questions remain unanswered. First, there is a need to develop methods and models to characterize the resistance of these materials to crack growth as a function of variables, such as temperature and loading history, so that these materials can be used efficiently in the design of high performance vehicles. Second, once reliable characterization techniques have been developed, it will be possible to study the relationship between the composition/formulation of various polymer systems and their performance so that optimum materials can be developed. The purpose of this paper is to show how the behavior of these systems might be characterized for one particular type of loading history and then illustrate the importance of such a characterization by considering the data for samples made using two different formulations.

BACKGROUND

Although elastomer-modified epoxies have been available commercially for some time, it was not until about 1970 that results began to appear in the literature.[4,5] Since that time a number of studies [1–3,6–10] have been performed and many of these have sought to elucidate the mechanisms responsible for the high resistance to crack growth in these materials. A hypothesis[11,12] which is consistent with the available data is that localized deformation processes can occur in these materials at the tips of cracks, flaws, and other stress raisers. These processes produce a blunting of the crack tips thereby reducing the high local stresses resulting from the stress intensifying effect of these defects. The net result is that a higher external load can be applied to the specimen without the crack-tip stress reaching the critical value for initiation of crack growth.

Although this hypothesis provides a first step toward understanding the behavior of these systems, a detailed explanation requires more specific information about the nature of the deformation processes involved and a means to assess their effect. A number of mechanisms have been suggested based on observations of the samples during fracture tests and on examinations of the fracture surfaces after failure. When fracture tests are performed, the region ahead the tip of the precrack shows a marked stress-whitening prior to failure. Examination of the fracture surface in this region with a scanning electron microscope (SEM) gives a picture such as that shown in Figure 1. The

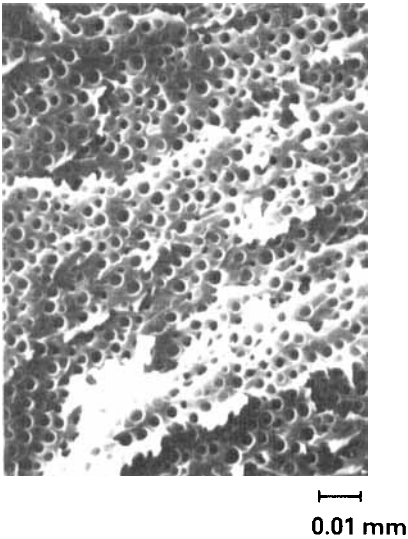

FIGURE 1 SEM picture of the fracture surface in the deformation zone region for 17.5 pphr CTBN-epoxy specimen.

surface is covered with holes where rupture has occurred either within the rubber particle or between the particle and the matrix leading to collapse of the rubber back against the epoxy. This observation suggests a possible deformation mechanism.[9] This mechanism asserts that the particle rupture occurs prior to the initiation of crack growth and thus contributes to the observed stress - whitening. Once the holes are present, the epoxy in the regions between the holes may yield and undergo plastic flow by a localized drawing process. This leads to crack blunting. A second possible deformation mechanism[6,7,13] that has been proposed arises from the observation that there is a dilation of the matrix and that this is probably associated with microvoid formation. This would not only produce crack blunting but also contribute to the stress-whitening. A third possible deformation process[6,7] involves general yield and plastic flow (see Figure 1). In some samples there is evidence for crack-tip plastic flow via shear banding while the fracture surface of other samples show the results of crack-tip yielding but with no clear pattern of shear bands. In either case the yielding can contribute to crack blunting. Two other deformation processes have also been suggested. One[14] involves the stretching and tearing of the rubber particles as the crack faces part while the other[13] involves the formation of crazes. In addition to these five possible mechanisms, a number of other processes may also occur. At present, however, the evidence suggests that the first three hypotheses are the most likely source of the high crack growth resistance in these materials.

Although the exact details of the crack-tip deformation processes are not yet fully understood, several research groups have had considerable success in modelling the fracture behavior of these materials by considering the size of the crack-tip deformation zone[7,9,10] as the critical parameter. These groups characterized the resistance to crack growth in mode-I failure (tensile loading perpendicular to plane of the precrack) by the critical strain energy release rate or fracture energy $\mathcal{G}_{IC}$. The size of the deformation zone, Δ, at the point of failure can then be related to $\mathcal{G}_{IC}$ via various models. In all cases this leads to the conclusion that a larger Δ corresponds to a larger $\mathcal{G}_{IC}$, and thus it is beneficial to maximize Δ. There is, however, usually a limit on Δ because it is desirable to localize the deformation zone to the crack-tip region so that global yielding of the sample does not occur. Consequently there is a trade-off that must be considered.

When elastomer-modified epoxies are utilized in adhesives (or composites), there are additional considerations involving the deformation zone size. In a pioneering study several years ago Bascom *et al.*,[7,8] studied adhesive specimens and measured the dependence of $\mathcal{G}_{IC}$ values on the bond thickness, h. They found that $\mathcal{G}_{IC}$ varied dramatically with h as shown in Figure 2. Their explanation for this effect is illustrated schematically in Figure 3. For very thin bonds h is less than the normal value of Δ, *i.e.*, that corresponding to the

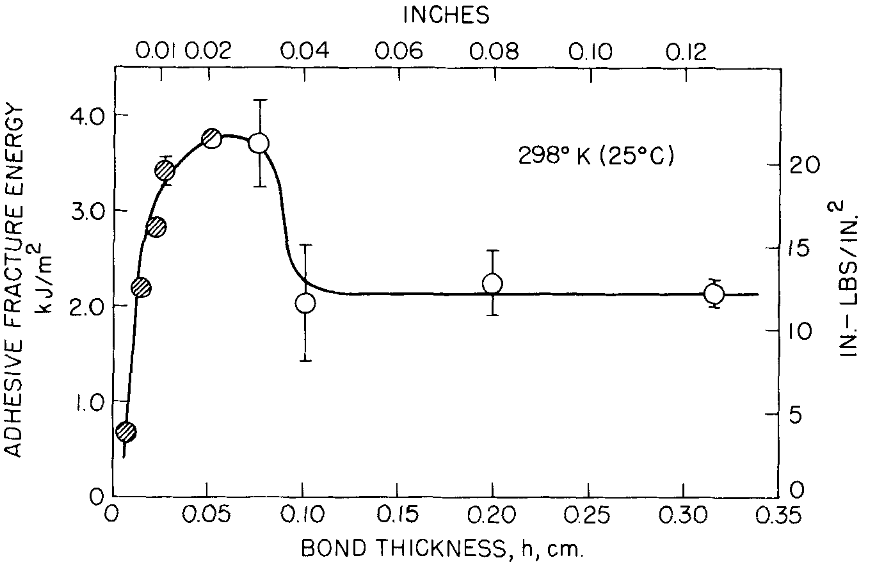

FIGURE 2 Fracture energy *vs.* adhesive bond thickness measured at room temperature and a cross-head speed of 0.02 mm/sec for adhesive specimens made with 17.5 pphr CTBN-epoxy (ref. 7).

equivalent bulk specimen. As a result the deformation zone size in the adhesive specimen is restricted and therefore the measured value of $\mathscr{G}_{IC}$ for bonded samples decreases with decreasing *h*. For bonds where *h* is approximately equal to the Δ for bulk samples, the adhesive $\mathscr{G}_{IC}$ reaches a maximum value since the deformation zone is not restricted.

Up to this point the trends in the experimental results are in agreement with the qualitative model shown in Figure 3. At larger values for *h*, however, the experimental results show that $\mathscr{G}_{IC}$ decreases to a plateau value that is less than the maximum adhesive $\mathscr{G}_{IC}$. Until recently this effect at high bond thicknesses was not understood. During the last six months, however, a joint program with Prof. Wang at the University of Illinois has shown that the bond thickness effect in adhesive joints can be predicted quantitatively when the

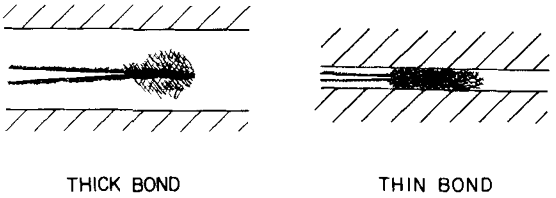

FIGURE 3 Schematic representation of the crack-tip deformation zone in adhesive bonds.

unusual stress field generated in an adhesive bond is taken into consideration. A complete discussion of these results will be published in a future paper.

Although a complete prediction of the bond thickness effect requires a detailed analysis of the stress field, Bascom *et al.*,[7,8] have shown that the optimum bond thickness (*i.e.*, that corresponding to the maximum adhesive $\mathscr{G}_{IC}$) can be estimated. Based on the picture shown in Figure 3, they proposed that the optimum bond thickness would correspond to the size of the deformation zone estimated from measurements on a bulk sample at the appropriate temperature and loading rate. As a crude method to estimate Δ, they used the elastic-plastic model which relates $\mathscr{G}_{IC}$ to the yield stress, σ_y, the yield strain, ε_y, Poisson's ratio, v, and the radius of the deformation zone, r_c, for plane strain conditions (Figure 4).

$$\mathscr{G}_{IC} = 6\pi(1-v^2)\sigma_y\varepsilon_y r_c \tag{1}$$

They measured $\mathscr{G}_{IC}$, σ_y, and ε_y at the appropriate conditions and calculated r_c. The resulting value of $2r_c$ was in good agreement with the optimum bond thickness.

It is well known that the fracture energy of adhesive bonds is temperature dependent. If only a single bond thickness is studied, however, it is very difficult to understand the temperature effect because it is coupled with a bond thickness effect. As a result, Bascom *et al.*,[7] have studied both the bond thickness and temperature effects. They found that the major role of temperature was to shift the optimum bond thickness value with only a small change in the maximum $\mathscr{G}_{IC}$. Their results are shown in Figure 5. As will be shown later, the $\mathscr{G}_{IC}$ for bulk specimens changes dramatically over this temperature range and thus these materials show the surprising behavior in that the maximum adhesive $\mathscr{G}_{IC}$ can be much greater than or less than the corresponding bulk $\mathscr{G}_{IC}$. What makes this particularly interesting is that Bascom *et al.*,[7] have shown that at all but the lowest temperature there is a good correlation between the optimum bond thickness and the calculated value of $2r_c$ based on bulk sample measurements. Consequently, there is good agreement between bulk and adhesive specimens for the size of the deformation zone measured perpendicular to the crack plane even though the $\mathscr{G}_{IC}$

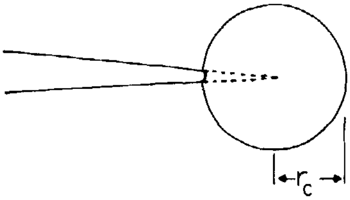

FIGURE 4 Schematic representation of crack-tip deformation zone for elastic-plastic model.

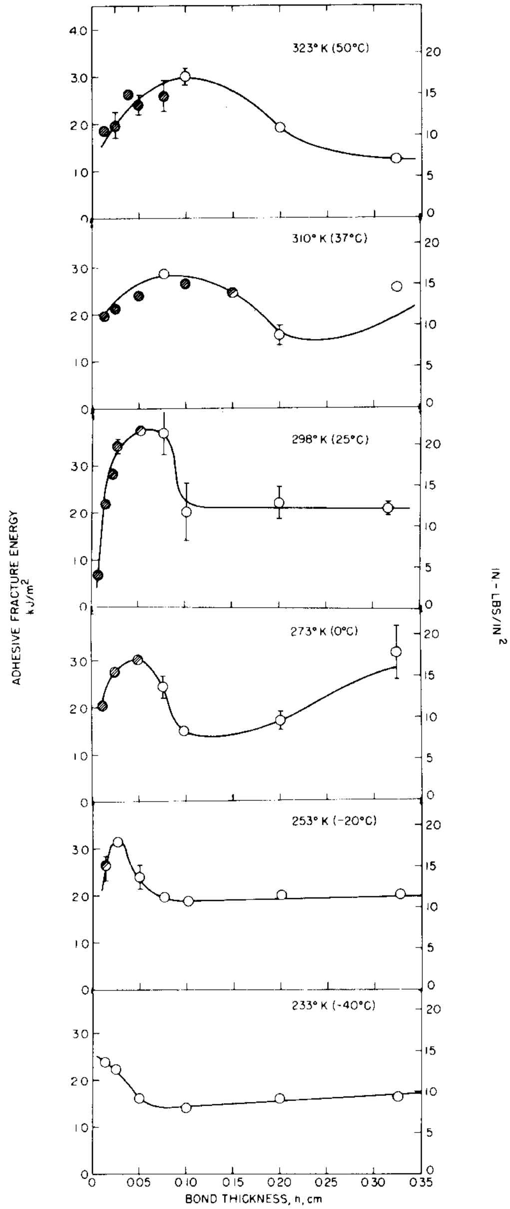

FIGURE 5 Fracture energy *vs.* adhesive bond thickness measured at a cross-head speed of 0.02 mm/sec at a series of different temperatures for adhesive specimens made with 17.5 pphr CTBN-epoxy (ref. 7).

values can be quite different. Wang, Hunston, and Rushford[15] have shown that at least part of the difference between bulk and adhesive $\mathscr{G}_{IC}$ can be attributed to the fact that the deformation zone extends down the bond line by a length that is different than what would be expected from the results of bulk sample tests. The reason for this difference is the unusual stress field in adhesive bonds. A complete discussion of this work will be published later.

In a recent series of studies, Shaw and Kinloch[10] have repeated the experiments of Bascom *et al.*,[7] and found a similar result. In their work however both the plane stress and the plane strain assumptions to calculate r_c were tried and they concluded that a better correlation is obtained with the former. Using the plane stress r_c, they obtained good correlations even at low temperatures where the study by Bascom *et al.*, had found only qualitative agreement. Consequently, for the type of loading conditions examined in the studies by these two groups, it is possible to estimate the optimum bond thickness and how it changes with temperature by measuring the properties of bulk samples.

An examination of the toughening mechanisms that have been proposed together with the observation that $\mathscr{G}_{IC}$ is a strong function of temperature suggests that the fracture behavior of these materials may be controlled by viscoelastic processes. If this is true, then $\mathscr{G}_{IC}$ should depend on the loading history as well as temperature. Since it is easier to make large changes in temperature than in loading rate, this latter variable has usually been ignored in adhesive bond studies. Recent papers,[9,16] however, have demonstrated that the effects of loading history are at least as crucial as those of temperature since the variations in $\mathscr{G}_{IC}$ are just as large and the range of loading histories encountered in practical applications (from impact to long term durability) may be much greater than the range of temperatures encountered. These investigations[9,16] measured $\mathscr{G}_{IC}$ for adhesive bond specimens at three different constant cross-head displacement speeds and a series of different temperatures. The studies demonstrated that results for different loading rates are difficult to understand unless the bond thickness effects are also studied. Figure 6, for example, indicates that $\mathscr{G}_{IC}$ can increase, decrease, or remain unchanged with increasing loading rate depending on the conditions of the tests. The explanation for these results can be understood by noting that for a property controlled by viscoelastic processes the effect of changing the loading rate is the reverse of that for changing the temperature. This combined with the results shown in Figure 5 indicates that increasing the loading rate will decrease the optimum bond thickness. As a result $\mathscr{G}_{IC}$ for adhesive bonds of a particular thickness will increase, decrease, or remain relatively constant with increasing loading rate when the bond thickness is less than, greater than, or approximately equal to the optimum values for h. This model provides a clear and simple explanation for experimental results such as those shown in Figure

6. In a more recent set of experiments Shaw and Kinloch[8] have investigated the bond thickness dependence of $\mathcal{G}_{IC}$ at three loading rates and have thereby generated detailed curves showing a decrease in optimum bond thickness with increasing loading rate. Their results indicate not only that the viscoelastic relationship between rate and temperature is followed but also that the optimum bond thickness can be estimated from measurements on bulk specimens.

The results described above suggest a two step approach to understanding the failure of adhesive joints. First, the viscoelastic fracture of bulk samples must be studied as a function of temperature and loading history so that models can be developed to predict the failure behavior. Second, the modifying influence of the adhesive bond geometry on the bulk behavior must be considered. This influence includes not only the restricting effect of the bond thickness on the deformation zone size but also the more complex way in which the difference in properties of the adhesive and adherend alter the crack-tip stress field. This paper addresses the first of these two areas by studying the failure of bulk specimens as a function of temperature and loading rate.

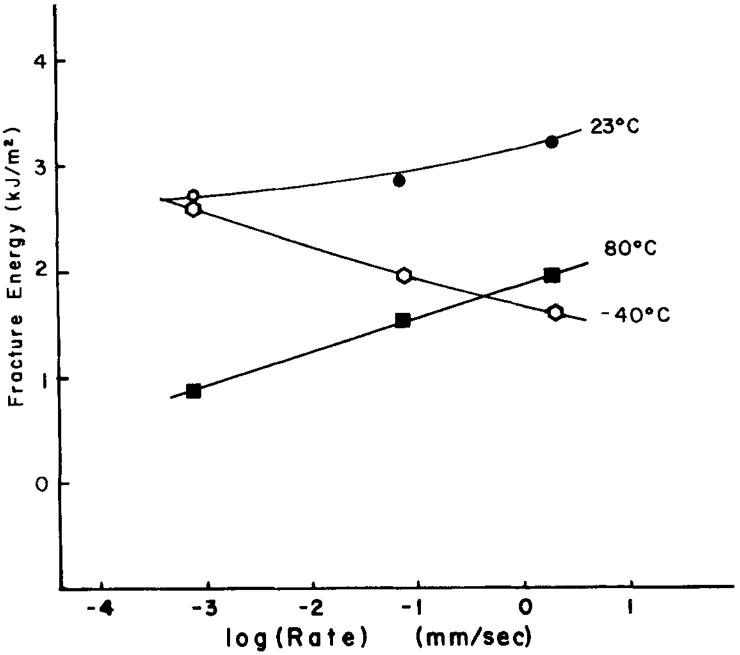

FIGURE 6 Fracture energy *vs.* cross-head speed for adhesive specimens (17.5 pphr CTBN-epoxy) with a bond thickness of 0.25 mm measured at 3 temperatures (ref. 9).

EXPERIMENTAL SECTION

Experiments were performed using a simple unmodified epoxy and two different types of elastomer-modified epoxies. All materials were cured with piperidine (5 parts per hundred resin, pphr) at 120°C for 16 h. Samples of the first type of modified-epoxy were formulated by adding various amounts (0, 5, 11.7, and 17.5 pphr) of a liquid elastomer (carboxyl-terminated polybutadiene acrylonitrile: B. F. Goodrich, Hycar CTBN) to the epoxy resin (diglycidyl either of bisphenol-A: Dow Chemical Co., DER-332) before adding the piperidine. For the second type of modified system 24 pphr of bisphenol-A (BPA) was added to the epoxy together with 5 pphr of CTBN prior to the addition of piperidine. In all cases the ingredients were thoroughly mixed, poured into a metal mold that had been coated with silicone rubber, and then cured into plates with dimensions of 22 cm × 22 cm × 1.25 cm. Various specimens were then cut from these plates.

The reactions that occur during the curing of the elastomer-modified systems are quite complex and not all of the details have been established. A discussion of the chemistry of these materials is given elsewhere[1,3] but two particular points are worth noting here. First, the elastomer does not self-polymerize but copolymerizes with the epoxy. As the molecular weights of the epoxy and the rubber-epoxy copolymer increase, the mutual solubility decreases until eventually phase separation occurs. The reactions then continue until ultimately a material with rubber particles dispersed in and covalently bonded to the matrix is produced. At the present time the extent of the bonding between the matrix and the particles is not known.

Based on this picture it is clear why the rubber particles always contain at least a little epoxy. Moreover, in some cases the volume of the rubber phase is much larger than what would be expected based on the concentration of CTBN and thus substantial quantities of epoxy are present in the particles. This may be very important because it has been suggested that the volume fraction of the elastomer phase plays a crucial role in determining the fracture energy of the material.[2] In addition to the epoxy in the rubber phase, there may be some CTBN in the epoxy matrix. This has the expected effect of slightly degrading the desired bulk properties, but its effect on the fracture energy is not entirely known.

A second important observation about the curing reactions is that for CTBN concentrations less than about 20 pphr the modified system mentioned first (epoxy-CTBN mixture cured with piperidine) will produce a distribution of particle sizes that centers around a particle diameter of 2 to 5 micron (see Figure 1, for example). With the second modified-epoxy system (containing BPA), however, the cure chemistry is such that a different final product is

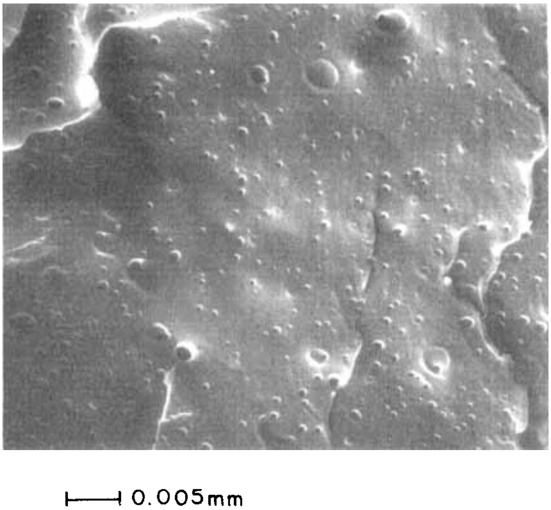

FIGURE 7 Fracture surface in rapid crack growth region for 5 pphr CTBN-BPA-epoxy specimen.

obtained. This material probably differs in many ways from that made without BPA but one change is particularly noticeable. When the fracture surface is examined with an SEM, the material is found to contain particles in two different size ranges. The large particles have diameters of a few micron and are therefore similar in size to the particles seen in the simpler system. In addition to this, however, there are many small particles with diameters of 0.2 micron and less. This situation has given rise to the term "bimodal" to describe the distribution of particle sizes. An example of this type of material is shown in Figure 7 which is an SEM picture of the fracture surface.

The modified-epoxy systems described here represent only two of the many formulations that are possible. In this work experiments were performed with an unmodified epoxy, three different examples of the simple CTBN system, and one example of the CTBN-BPA material in an effort to illustrate the type of variations that can be obtained. Descriptions of the samples are given in Table I.

A detailed study of the linear viscoelastic properties of these formulations was performed using a specially modified Rheogoniometer.[17] Most viscoelastic testing performed on solids is isochronal, *i.e.*, at a single time (or frequency) or over such a small range that meaningful time dependent data cannot be deduced. This limits the information that can be obtained. The device used here was designed to measure properties over a 5.5 decade range of frequencies and temperatures between −200°C and 400°C. It can also be used to perform

TABLE I

Formulation and properties of the various modified-epoxy samples†

	Concentrations					
Sample designation	CTBN (pphr)	BPA (pphr)	Fracture energy (kJ/m^2)	T_α (1 Hz) (°C)	Δ_{SF}	Δ_T
A	0	0	0.12	98.9	0	0
B	5	0	1.08	97.8	+0.7	−1.1
C	11.7	0	2.49	96.1		
D	17.5	0	3.80	93.5	—	—
E	5	24	2.18	99.0	−0.1	+0.1

† Fracture energy values for 30°C and M cross-head speed.

stress relaxation experiments and this expands the range of direct measurement with a single instrument and sample to almost 8 decades of time. On-line computer data acquisition and analysis makes it possible to perform the experiments accurately and analyze the results in a reasonable time period.

For many polymeric materials it has been shown that, in the measurement of mechanical properties, changing the test temperature has approximately the same effect as shifting the time (or frequency) scale of the measurement.[18] The size of the shift is usually designated as log (a_T). If the extent to which this approximate relationship is valid for a given material can be established, then the data can be extrapolated by time-temperature superposition[18] to give a general description of the behavior of the material over a significantly wider range of experimental conditions that can be conveniently measured in the laboratory. To establish the limits on this approximation, however, requires the direct measurement of properties over at least a one-and-a-half decade range of time (or frequency) scales and in most cases a minimum of three decades is highly desirable. Since this type of measurement has not been extensively applied to glassy polymers, the applicability of time-temperature superposition techniques to such systems must be established for each new material. In the present work, the ability to measure properties over a wide range of frequencies makes it possible to evaluate these techniques critically.

In addition to the linear viscoelastic experiments, bulk samples of each type of epoxy were tested for fracture behavior at 30°C and a cross-head displacement rate of 0.08 mm/sec using the compact tension geometry. The specimens were loaded to failure, and the critical strain energy release rates or fracture energies, $\mathscr{G}_{IC}$, were calculated using standard equations.[19] In addition to determining $\mathscr{G}_{IC}$, each fracture experiment was also characterized by measuring a value for the time to failure, t_f, *i.e.* the total elapsed time between the initial application of the load and the onset of rapid crack growth. Since these materials are viscoelastic, it is important to measure the effect of loading history. An examination of all possible loading histories would be impossible, therefore, the present study was restricted to a particular type of loading history, *i.e.* constant cross-head speed tests, as a first step. In this regard three particular systems (the unmodified-epoxy, the 17.5 pphr CTBN-epoxy, and the 5 pphr CTBN-BPA-epoxy) were extensively characterized by measuring the fracture behavior at temperatures between −60°C and 75°C and at cross-head displacement rates of 0.0008, 0.08, and 2.0 mm/sec (designated hereafter as S, M, and F respectively). Here again the time to failure was determined for each test.

It is well known that the linear viscoelastic properties of glassy polymers depend on the thermal history of the sample.[20–23] As a result, it is important to determine if the so-called physical aging effect also influences the fracture energy. This question is particularly important since there is evidence that high stresses, such as those encountered in fracture experiments, can accelerate aging effects.[22] For most of the experiments described in this paper a standard thermal history was used so that any variations due to physical aging could be minimized. One particular set of fracture experiments, however, was performed on samples of the 17.5 pphr CTBN-epoxy which had been prepared with two different thermal histories.

In the standard thermal history plates of the material were cured as described previously and, after slow cooling in the oven, they were cut into samples with the appropriate dimension. A vacuum oven was then preheated to 120°C, and the samples were placed in the oven and allowed to equilibrate for 30 minutes. The oven was then turned off and allowed to cool slowly over an 18 h period. This slow cooling provided samples that gave reproducible results. The samples with non-standard thermal histories were prepared in the same way up to and including the 30 min equilibration in the oven. At that point, however, one set of samples was removed from the oven and rapidly cooled by placing them on a large stone counter top. A second set of samples was removed from the oven and quenched in ice water. This produced test specimens with two different non-standard thermal histories. With these specimens the fracture experiments were performed as soon as possible so that there was a minimum of physical aging prior to testing. The experiments were performed at 0.42 mm/sec cross-head speed at various temperatures.

In measuring fracture behavior, it is important to have a sharp precrack in the sample if reproducible results are to be obtained. Since heating the sample to 120°C might have a blunting effect, the fracture specimens were not precracked until after the thermal treatment. The precracks were inserted by cooling a small region where the precracks were to be initiated with liquid nitrogen and tapping that region with a knife edge to generate a propagating crack. When the propagating crack grew beyond the brittle cold region, it arrested and thereby gave a specimen with a sharp precrack. It is well known that the crack-tip radius of the precrack must be less than a critical value if the fracture results are to be reproducible and independent of the precrack insertion technique. Generally speaking, the higher the fracture energy, the larger the critical radius so that precrack insertion is most difficult in the unmodified epoxy. Experiments performed on modified and unmodified samples given the standard thermal history and tested at room temperature have indicated that the precracking procedure described above gives good results. It is likely that this observation can be extended to the other conditions and thermal histories tested in this work. To minimize any variations that might arise if this assumption is not completely valid, however, an effort was made to keep the precracking procedure as constant as possible in all of the tests.

RESULTS AND DISCUSSION

Table I lists the fracture energies for the unmodified epoxy, for CTBN-epoxy samples with three different elastomer concentrations, and for the modified epoxy with bisphenol-A. The results show a rapid increase in $\mathscr{G}_{IC}$ with added elastomer. As has been pointed out previously,[7,8] however, in the CTBN-epoxy-piperidine system the fracture energy reaches a maximum at a CTBN concentration of about 20 pphr and decreases if more CTBN is added because the resulting material no longer has the rubber particle—glassy matrix morphology. Moreover, the bulk properties such as modulus rapidly degrade as the CTBN concentration is increased above 20 pphr because they depend critically on the presence of a glassy matrix. Consequently, there is an optimum concentration of CTBN in systems of this type.

Table I also indicates that the addition of BPA to the system substantially increases the fracture energy at least for the 5 pphr CTBN system. As will be shown later, the BPA system also has bulk properties that are superior to the simple CTBN-epoxy system because the phase separation is better. This would suggest that optimizing the CTBN concentration in the BPA-epoxy system would produce a superior material. To a degree, the data in the present study support this idea; however, they also indicate that comparisons of the fracture behavior for different formulations based on data such as that in Table I can be dangerous. All of the elastomer-modified specimens developed large regions of localized deformation (stress-whitening) at the tip of the precrack prior to failure. This suggests that viscoelastic effects are involved and, if so, measurements made at one set of conditions provide only a very limited view of the complete fracture behaviour. As a result it is essential to consider the effects of loading rate and temperature before drawing any firm conclusions.

In recent studies by Gledhill and Kinloch,[24] static fatigue experiments were performed on unmodified epoxies, and they found that, within certain time-temperature ranges, the fracture energies could be correlated by a simple fracture model. Although this model involves non-linear viscoelastic considerations, the time dependence is introduced by way of a creep modulus that in a number of cases is in the range of linear viscoelastic response. To study this correlation further, the linear viscoelastic behavior of modified and unmodified epoxies was measured in addition to the fracture data.

The dynamic shear modulus in the linear viscoelastic range was measured over 4 to 5 decades of frequency, ω, and a temperature range of 80°C. The results were then examined for the applicability of time-temperature superposition. Despite the rather complex nature of the modified epoxies, it was found that data for both the modified and unmodified materials superimposed quite well in the range from room temperature to somewhat above the glass transition temperature. Master curves were constructed and normalized to 90°C. Figures 8 and 9 show the results for the unmodified epoxy, the 5 pphr

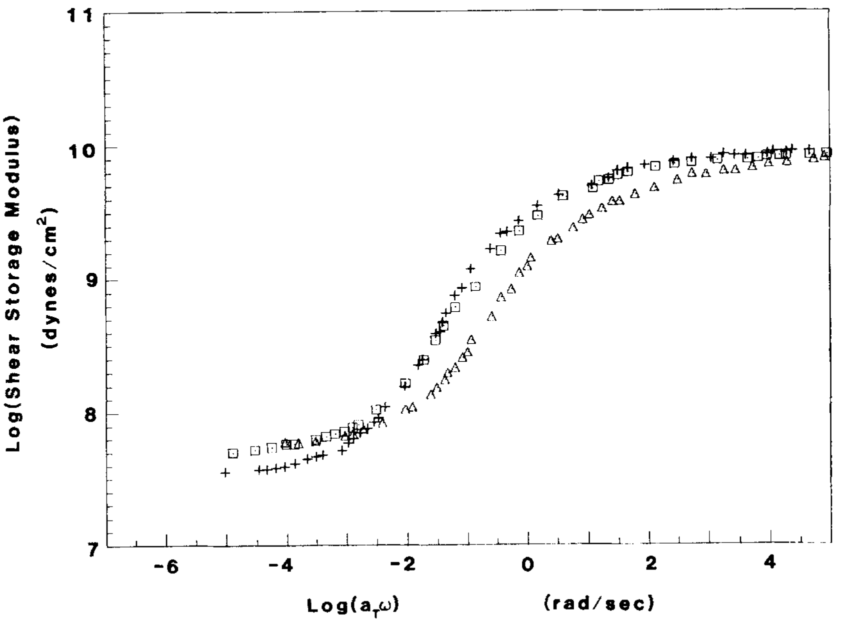

FIGURE 8 Dynamic shear storage modulus *vs.* reduced frequency at a reference temperature of 90°C: □ for unmodified epoxy, △ for 5 pphr CTBN-epoxy, and + for 5 pphr CTBN-BPA-epoxy.

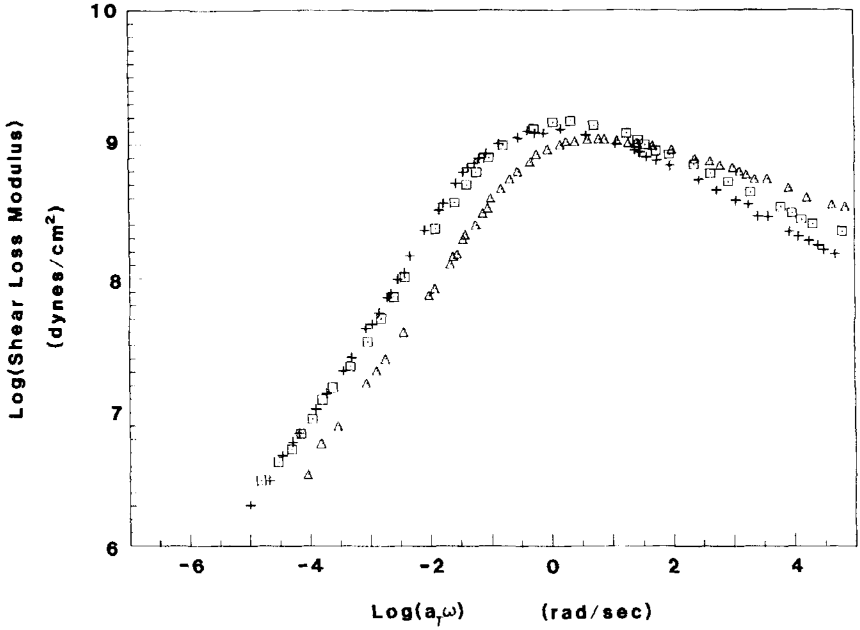

FIGURE 9 Dynamic shear loss modulus *vs.* reduced frequency at a reference temperature of 90°C: □ for unmodified epoxy, △ for 5 pphr CTBN-epoxy, + for 5 pphr CTBN-BPA-epoxy.

CTBN epoxy, and the 5 pphr CTBN epoxy with BPA. Despite the considerable differences in composition, these curves are remarkably similar. The 5 pphr CTBN sample exhibits a shift to higher frequencies corresponding to a small decrease in the glass transition temperature, T_g. The curves are quite sensitive to changes in T_g since a three degree decrease in T_g shifts the curves by about one order of magnitude on the frequency axis. Since the mechanical properties in this temperature-frequency range are dominated by the matrix the shift can probably be attributed to the presence of some CTBN in the epoxy matrix, and as a result, the change in T_g provides a crude measure of the extent to which the phase separation is incomplete. In support of this proposition is the observation that BPA is thought to promote phase separation, and the sample with BPA shows no shift in the transition. Moreover, the bulk properties of the BPA material are almost identical to those of the simple epoxy in the glassy range. This suggests that better phase separation generally leads to better bulk properties.

With larger concentrations of CTBN, the indications of incomplete phase separations in the CTBN-epoxy system increase. This is shown in Table I where the temperatures corresponding to the peak in the loss tangent, tan δ curves measured at 1 Hz, T_α (1 Hz), are listed. The 11.7 and 17.5 pphr CTBN samples show significant shifts in T_α; however, the magnitude of the shifts cannot be considered unique since there are significant batch to batch variations. This is because the degree of phase separation depends on cure conditions that are not completely controlled. When phase separation is incomplete, the transition is not only shifted to higher frequencies, but it is also broadened. Figure 10 compares the data for the unmodified epoxy with that for the 17.5 pphr CTBN epoxy. As shown in this figure, there is a substantial broadening of the transition indicating that the material now has a wider distribution of relaxation times.

Figure 11 plots the shift factors, a_T, used in generating the master curves shown in Figures 8 and 9 as a function of temperature. In the temperature range studied here, little or no vertical shift was required for superposition. When these curves are normalized (see Table I) with respect to the unmodified epoxy by shifting the temperature an amount, Δ_T, corresponding to the difference in the glass transition temperatures and shifting the frequency by an amount, Δ_{SF}, equal to the frequency change corresponding to the shift in T_g, the data for all three samples falls along a single curve (Figure 11). The shape of shift factor curve below T_g is related to the thermal history of the sample.[17] In the present experiments great care was taken to give each sample the same thermal history, and the results in Figure 11 indicate that this effort was successful.

Perhaps the most important result of the viscoelastic experiments, however, is that the application of the time-temperature superposition procedure to the data produced well-defined master curves for all of the samples. Even though the direct measurements were performed over a 4 to 5 decade frequency range, there are no significant departures from superposition. This means that deviations from "thermo-rheologically simple" behavior are relatively small

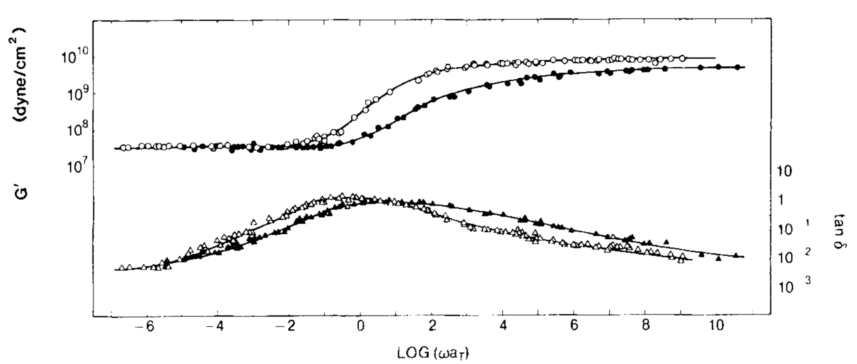

FIGURE 10 Dynamic shear storage modulus and loss tangent *vs.* reduced frequency at a reference temperature of 95°C open symbols for unmodified epoxy, and filled symbols for 17.5 pphr CTBN-epoxy.

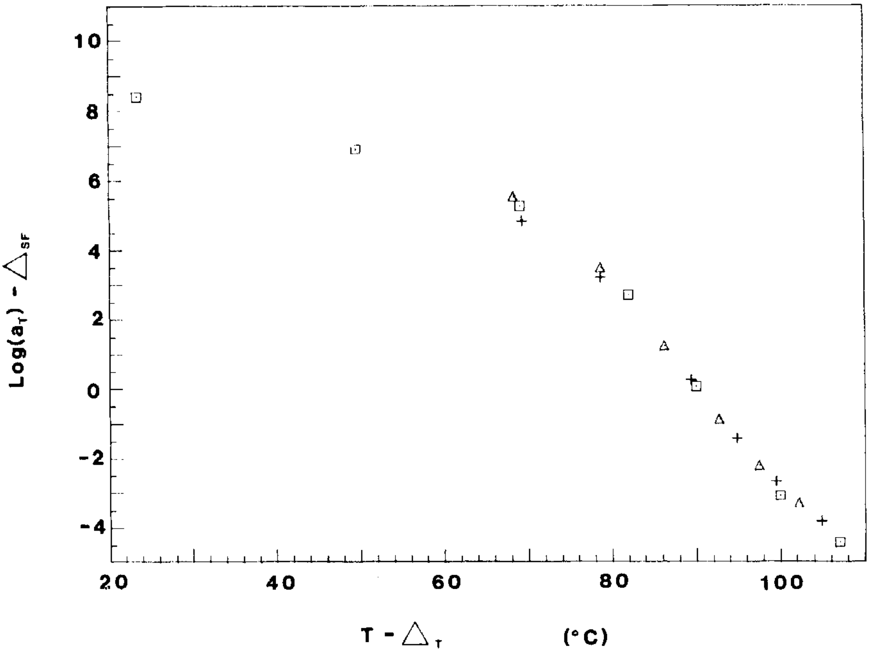

FIGURE 11 Log (shift factor) *vs.* temperature data adjusted to compensate for differences in the glass transition temperature: □ for unmodified, △ for 5 pphr CTBN-epoxy, and + for 5 pphr CTBN-BPA-epoxy.

over this range. It is of interest, therefore, to see if the fracture energy exhibits similar trends.

Figure 12 shows the fracture data for the unmodified epoxy as a function of temperature at three cross-head speeds. For this brittle material the loading rate and temperature dependences are very small over most of its useful range. The upper temperature limit on this region of behavior is marked by a sudden change from brittle to ductile behavior. This transition point, however, is a strong function of loading rate with decreasing rates shifting the transition to lower temperatures. This behavior for $\mathcal{G}_{IC}$ is qualitatively similar to that observed for the linear viscoelastic shear modulus in that both show relatively little change with time and temperature over most of the range of interest and both exhibit sharp transitions with a similar time-temperature dependence.

Figure 13 depicts the fracture energy for the 17.5 pphr CTBN-epoxy as a function of temperature at three cross-head speeds (open symbols and solid lines). The fracture behavior of the modified epoxy is very different than that for the unmodified epoxy or the linear viscoelastic behavior of either material. There is no distinct brittle-to-ductile transition but rather a large and

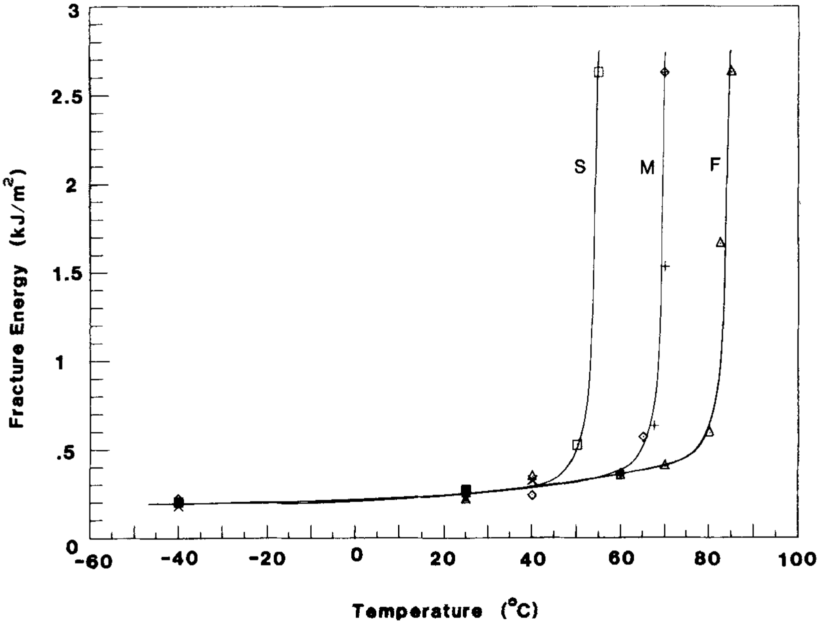

FIGURE 12 Fracture energy *vs.* temperature at 3 cross-head speeds for bulk specimens of unmodified epoxy.

continuous increase in $\mathscr{G}_{IC}$ with increasing temperature that begins at low temperatures and extends over at least a 100°C temperature range. Some differences in behavior are expected for the modified epoxy since the failure processes involved are not the same as those for the unmodified epoxy. Nevertheless, it is perhaps surprising that the differences are so great. These results suggest that a more complex model may be necessary to describe the failure of the modified material, and it may be necessary to formulate this model with a more explicit dependence on nonlinear properties. It is interesting to note, however, that the results show a consistent variation with rate. Such a variation indicates that an examination of the data for rate and temperature dependence is required if the results are to be fully understood.

If the fracture data at each temperature are plotted as a function of a variable related to loading rate, the applicability of the reduced variables method can be tested. It is not clear, however, what variables should be used to characterize loading rate. Ideally, the parameter should be a measure of the stress or strain rates in the crack-tip region since that is where the crucial events take place. Unfortunately, the crack-tip parameters vary with position and for a non-linear viscoelastic material the precise values of these parameters are unknown. Consequently, a number of non-crack-tip quantities

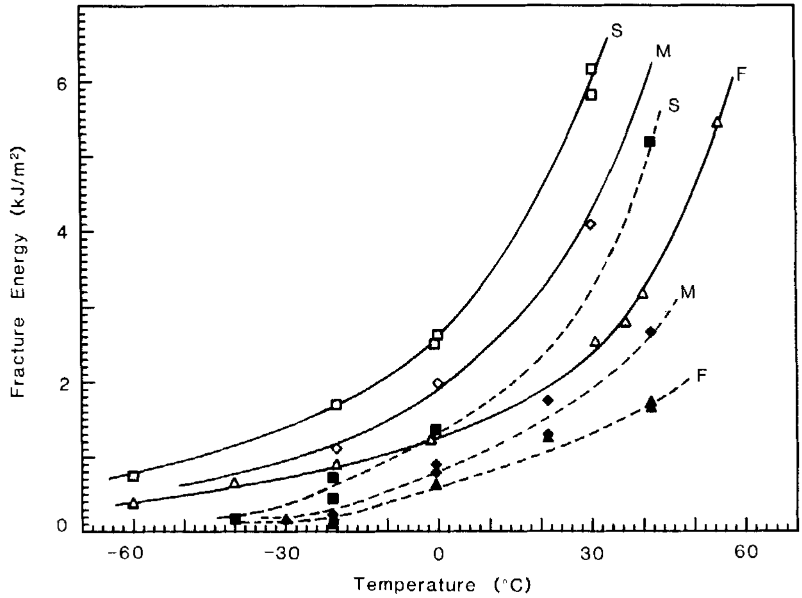

FIGURE 13 Fracture energy *vs.* temperature at 3 cross-head speeds for bulk specimens of 17.5 pphr CTBN-epoxy: open symbols, solid lines; and of 5 pphr CTBN-BPA-epoxy: filled symbols, dotted lines.

have been or might be used to assess the effects of changing the cross-head speed. The present study employed time-to-failure, t_f, for this purpose based largely on the fact that in linear viscoelasticity time is the critical variable. This is not however a unique choice and thus failure to get superposition with this parameter would not rule out other possibilities.

The fracture data for the 17.5 pphr CTBN-epoxy was plotted against t_f at various temperatures and then shifted horizontally to see if superposition would be obtained (the data scatter was large enough that vertical shifts were not considered). The shifted data (reference temperature 20°C) are shown in Figure 14, and although the superposition of the data in this graph is not perfect, it strongly suggests the existence of a qualitative correlation between temperature and loading rate. This is what would be expected if the behavior were dominated by linear viscoelastic effects, but it is interesting to note that a similar relationship seems to exist even though nonlinear properties appear to be important. This is not totally unexpected however since similar results have been obtained by a number of workers for propagating cracks in elastomers.[25,26]

Since viscoelastic effects play a major role in the fracture of these materials, it is important to determine if physical aging also occurs. Figure 15 shows the

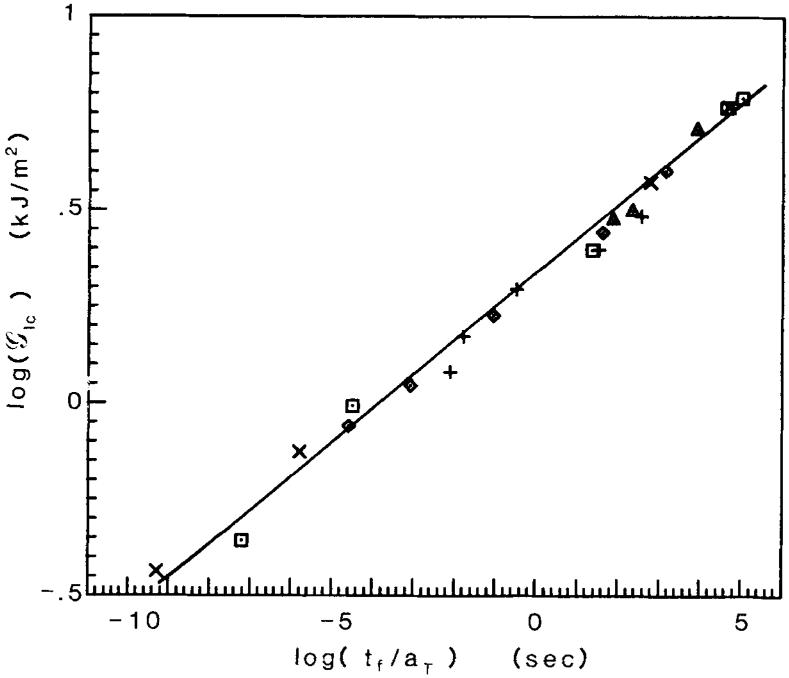

FIGURE 14 Master curve of fracture energy *vs.* reduced time-to-failure at a reference temperature of 20°C for the 17.5 pphr CTBN-epoxy: × = −60°C, □ = −40°C, ◇ = −20°C, + = 0°C, △ = 15°C, × = 23°C, □ = 30°C, ◇ = 36°C, + = 40°C, △ = 50°C, and × = 60°C.

data for samples subjected to the three different thermal histories. To verify the reliability of the comparisons, there were a number of cases where samples with the standard thermal history were prepared simultaneously with those having the alternative histories. The ×'s in Figure 15 give the data for these standard history comparison samples while the line represents the average of all data for the tests performed at 0.08 mm/sec cross-head speed on samples with the standard history. The agreement between these two sets of results is good. Data for the samples that were rapidly cooled and quenched are also shown in the figure and for these samples the fracture energy is slightly higher than that for the specimens with a standard history. In view of the normal experimental scatter in fracture tests, however, the effects of thermal history were apparent only when a number of experiments were performed at each set of conditions. When this is done, the results indicate that within the range of parameters studied here, and this includes the range utilized in most fracture work, thermal history is not a significant source of error in fracture experiments so long as extreme histories are avoided. There is however a slight shift in behavior that is in the direction expected for physical aging effects.

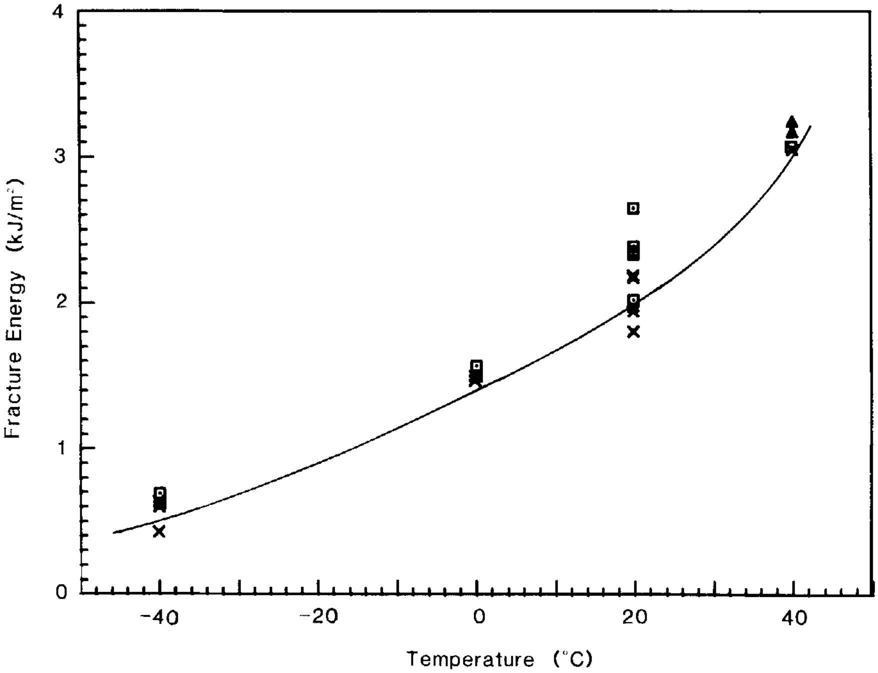

FIGURE 15 Fracture energy *vs.* temperature for bulk samples of 17.5 pphr CTBN-epoxy with different thermal histories measured at a cross-head speed of 0.42 mm/sec. Curve represents all data with standard thermal history, × represents data for comparison samples with standard history while □ and △ are data for rapid cooled and quenched samples respectively.

There are three additional features of the aging data that should be noted. First, all of the experiments here were conducted well below the glass transition temperature and thus the aging rates were slow. As a result the aging times studied may not have been long enough to produce large effects. Second, the test might be expected to show the largest effect, *i.e.*, the quenched samples tested at 39°C, was complicated by the fact that it required a significant period of time at 39°C for the sample to reach temperature equilibrium and, during that period, aging occurred. At the time of the fracture tests, therefore, the sample could not accurately be described as quenched. Finally, if aging effects do influence the fracture behavior of these materials, the critical question from a practical point of view would be the extent to which the materials become more brittle with long term aging, *i.e.* after months or years. This question cannot be answered based on the experiments performed here. There is, however, one very important assertion that can be drawn from the present results. Previous work[21] has shown that the major effect of physical aging is to shift the characteristic time scales for the response of the material to longer times. Although vertical shifts may also be present, they are usually small.[21] As a result physical aging produces large changes in the linear viscoelastic modulus only in regions relatively close to the glass-to-rubber transition. Over most of the glassy region the modulus behavior is fairly flat and thus a time scale shift has relatively little effect.[20] The fracture behavior of the modified epoxies, on the other hand, varies dramatically over a very wide range of time (rate) and temperature, and consequently, a shift in the characteristic time scales for the material would produce major changes in $\mathcal{G}_{Ic}$ over an extremely large range of conditions. As a result, if long term physical aging effects are significant in fracture, important changes in $\mathcal{G}_{Ic}$ would be observed even well below the glass-to-rubber transition region. Based on this result, it is clear that additional studies to determine if long term aging effects do influence fracture behavior are badly needed.

In addition to examining the rate and temperature dependence of fracture for the 17.5 pphr CTBN-epoxy, a detailed study was performed with the CTBN-BPA-epoxy material for comparison. Data for this system are shown in Figure 13 as filled symbols and dotted lines. These results were also

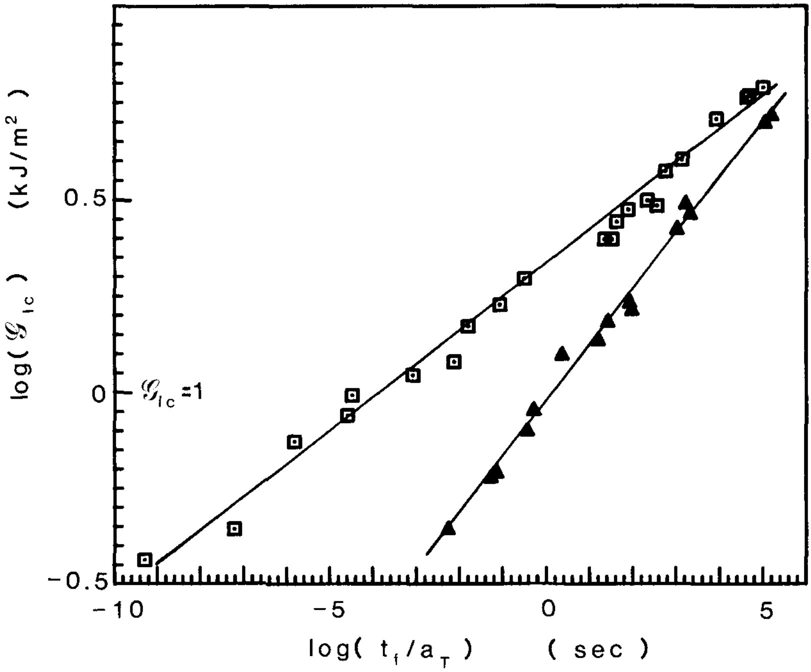

FIGURE 16 Master curves for fracture energy *vs.* reduced time-to-failure at a reference temperature of 20°C: □ for the 17.5 pphr CTBN-epoxy, and ▲ for the 5 pphr CTBN-BPA-epoxy.

examined for the applicability of superposition techniques. Just as with the previous material, the data were plotted against t_f and shifted. The resulting curve is shown in Figure 16 together with the data for the 17.5 pphr CTBN-epoxy system. Here again there is a clear correlation between temperature and loading history. What is particularly interesting, however, is that the resulting master curves indicate that the two modified materials have very different rate dependences.

The results in Figure 16 clearly illustrate why judgements regarding the fracture behavior of a elastomer-modified material can be very dangerous when based on measurements made at a single set of conditions. For example, at very low loading rates or slightly elevated temperatures the 17.5 pphr CTBN and the CTBN-BPA systems are very similar. At low temperatures or impact type loading conditions, however, the 17.5 pphr CTBN-epoxy is much more resistant to crack growth than the CTBN-BPA material. Consequently, without determining the effects of loading rate and temperature on the fracture behavior, it is impossible to take advantage of the full potential of elastomer-modified materials in practical applications. The method of data analysis discussed here may provide a useful technique for characterizing the fracture behavior of such materials. Such a characterization would then provide both a means to estimate fracture behavior over a wide range of conditions and a basis on which performance-composition relationships could be developed for a large variety of elastomer-modified epoxy formulations.

CONCLUSIONS

The fracture behavior of adhesively bonded joints fabricated with elastomer-modified epoxies is dependent on: (1) the fracture energy of the bulk adhesive itself and (2) the degree to which the geometry of the bonded joint restricts the toughening processes normally present in the bulk adhesive. The rudimentary understanding that has been developed for the second factor leads to the conclusion that more must be learned about the first factor before adhesive bond failure can be understood. The results presented here demonstrate that like other high fracture energy polymers the elastomer-modified epoxies achieve their very good fracture properties through viscoelastic processes that vary substantially with temperature and loading history. As a result fracture tests performed at a single set of conditions provide only a very limited picture of the overall fracture behavior and thus predictions based on such data can over or underestimate the fracture energy for a different set of conditions by a very large factor. In practical applications this could have disastrous consequences.

Experiments designed to examine the effects of physical aging on fracture energy showed that for toughened–epoxies $\mathcal{G}_{IC}$ changes relatively little over the limited range of histories normally used in the laboratory. The small changes that were found, however, are in the direction expected for physical aging effects. Moreover, the data indicate that if long term physical aging does influence $\mathcal{G}_{IC}$, the consequences would be very important because the fracture behavior would be altered over an extremely wide range of temperatures and loading histories.

Fracture experiments performed on specimens of the toughened–epoxies suggest that in constant cross-head speed tests there is a correlation between temperature and time-to-failure that makes it possible to apply time-temperature superposition techniques to help characterize the fracture behavior of these materials. This characterization provides a means to estimate the properties of the materials over a wide range of conditions. Moreover, since the behavior of modified–epoxies changes substantially when the formulation is altered, the techniques discussed here may provide a basis on which to establish structure-property relationships that will help in the development of optimized materials. Finally, the present results can serve as a useful tool in future studies designed to extend the considerations discussed here to improve the understanding of adhesive bond fracture.

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