

Viscoelastic fracture behaviour for different rubber-modified epoxy adhesive formulations

D.L. Hunston and G.W. Bullman

(National Bureau of Standards, USA)

The viscoelastic fracture behaviour of various rubber-modified epoxy formulations was analysed using a time-temperature superposition approach. The shift factors for all of these systems were quite similar. In addition, an equivalent analysis of yield stress data was performed for one of the samples; it gave shift factors similar to those from the fracture experiments thus indicating a close correlation between yield and toughening. A simple empirical equation was found to describe the fracture data for all the materials and, consequently, the parameters in this equation provide a good method to characterize the fracture behaviour and to compare different materials.

Key words: adhesives; fracture behaviour; viscoelasticity; rubber-modified epoxies; time-temperature superposition

Many modern structural adhesives are based on rubber-modified epoxies because these systems combine a high crack growth resistance with good elevated temperature performance and a high modulus. Many different rubber-modified epoxy formulations have been developed, and these produce a wide variety of morphologies and fracture behaviours¹⁻⁵. Unfortunately, the fracture behaviours of these systems are complicated by the fact that they vary dramatically with changes in test temperature and/or loading rate (or loading history)¹⁻⁴. This is illustrated in Fig. 1, which shows the results for fracture tests on bulk specimens of a model rubber-modified epoxy system². Since other formulations exhibit very different fracture properties, there is a need to develop methods to analyse behaviour such as that shown in Fig. 1. Only with this approach will it be possible to characterize these materials, to compare different formulations and to develop the relationships between formulation and performance that are needed to optimize the materials.

Previous work has suggested that these rate and temperature effects are a reflection of viscoelasticity and that time-temperature superposition methods might be useful for developing models for the data^{1,2,6}. A possible approach for such an analysis was suggested by these previous studies^{2,7}. In this approach, the time-to-failure was used to characterize the rate dependence and, based on this parameter, a time-temperature superposition analysis was found to be useful for evaluating a number of model systems. The purpose of this paper is to refine this

procedure and apply it to analyse the data from a number of different formulations.

Experimental details

Materials

The data evaluated in this work were obtained from previous studies^{2,7} on a model unmodified epoxy and a variety of rubber-modified epoxy formulations. The unmodified epoxy samples were made by curing the diglycidyl ether of bisphenol A with 5 phr (parts by weight per hundred parts by weight of epoxy) piperidine at 120°C for 16 h in moulds coated with release agent.

Two types of rubber-modified epoxies have been studied. Both formulations give the conventional morphology, *ie* elastomer particles dispersed in and bonded to a predominantly epoxy matrix. The first type was prepared by adding different concentrations (5, 15 and 18.5 phr) of an elastomer (carboxyl-terminated polybutadiene-acrylonitrile) to the epoxy and curing as described above. This produces a simple distribution⁸ of particle sizes centred around 1 μm , although some studies⁹ have suggested that very small particles ($\sim 0.05 \mu\text{m}$) may also be present. The average particle size increases as the rubber concentration is increased, and the distribution of particle sizes broadens slightly but is generally similar in shape⁸. The second type of rubber-modified epoxy involves a much different distribution of

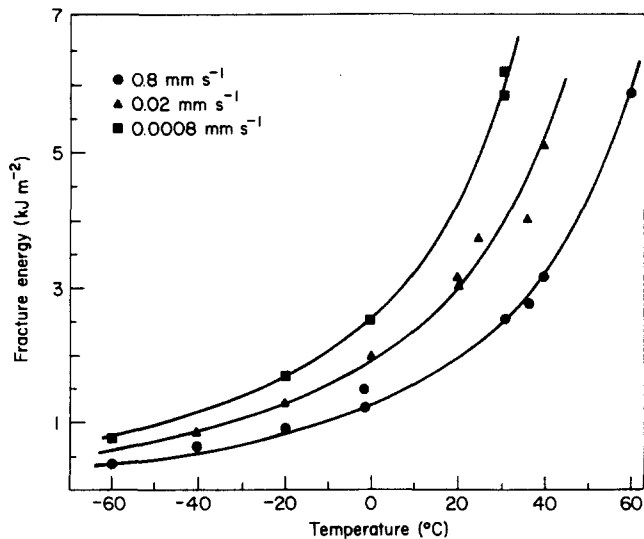


Fig. 1 Fracture energy for formulation D measured as a function of temperature at three cross-head speeds

particle sizes. In this case bisphenol-A (24 phr) is added to the epoxy-elastomer mixture (5 phr elastomer) and then cured as described above. For this formulation the morphology consists of small particles ($< 0.5 \mu\text{m}$) as well as larger particles similar to those in the previous systems⁸. For this reason it has sometimes been called a

bimodal system although this may not be a completely accurate description of the distribution. The morphologies for the four rubber-modified epoxy materials are shown in Fig. 2. A list of the five samples and their composition is given in Table 1. More details on the materials and their cure chemistry can be found in previous publications^{2, 5, 7, 10}.

Although these model systems represent a variety of morphologies, one potentially important limitation is that all of these materials have very similar epoxy matrices. For example, the glass transition temperatures (T_g s) are within $\pm 3^\circ\text{C}$. This is illustrated in Table 1 which lists one measure of the T_g designated T_α . This is the temperature corresponding to the peak in the loss tangent curve measured at 1 Hz. The values given in this table are the results of a number of tests at two different laboratories, but in general the primary experiments involve increasing the temperature in steps with long equilibration times after each step and frequency scans at each temperature. Details can be found in References 11 and 12. The similarity in the matrices is of interest since studies have shown that the matrix plays a major role in the fracture behaviour¹³.

Recently, data have been published^{14, 15} for several systems with higher T_g s. These data provide an opportunity for a brief look at the effects of the matrix on the analysis method. These materials employ a similar epoxy,

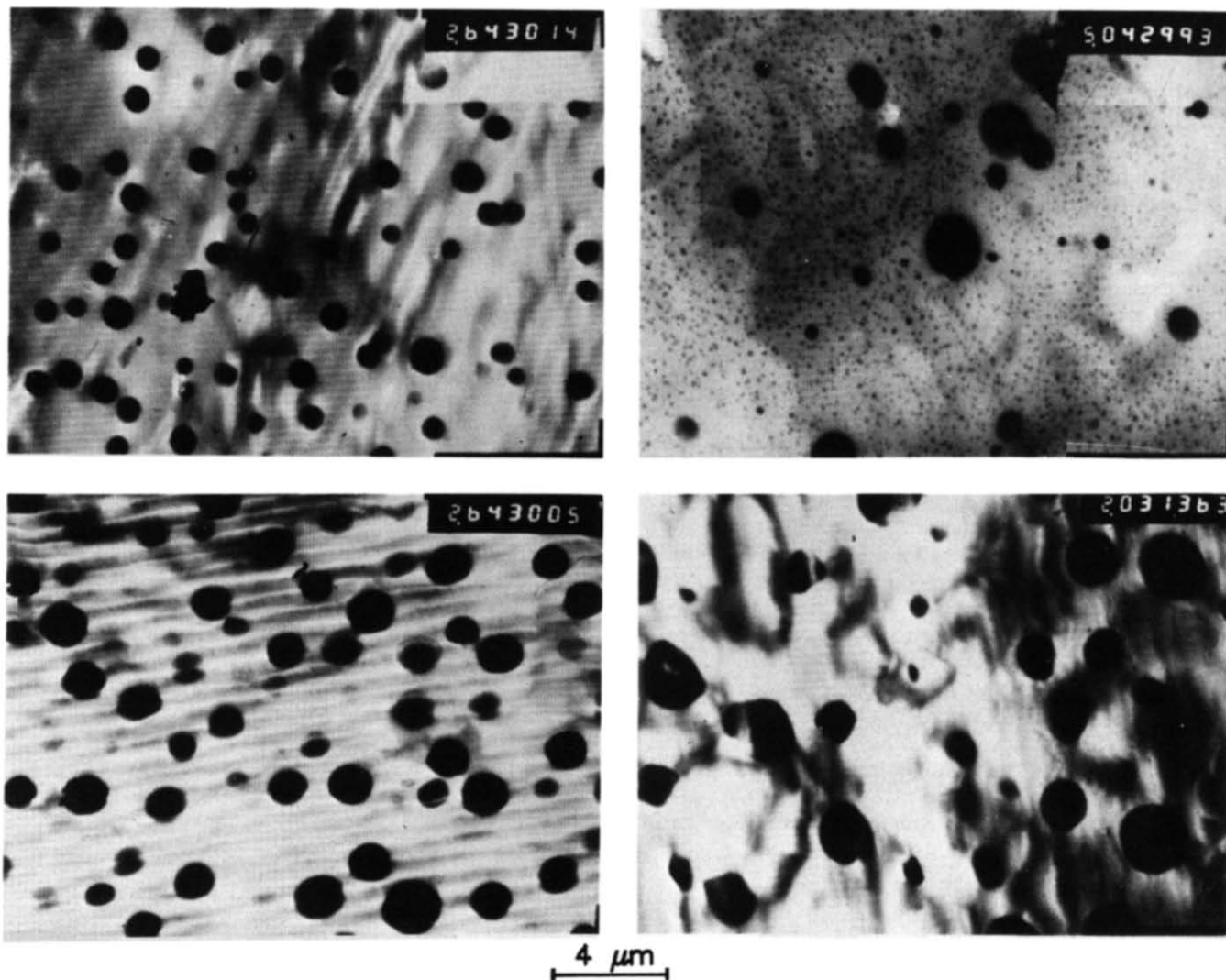


Fig. 2 Transmission electron microscope pictures for formulations B to D (counter-clockwise starting top left) with rubber stained using osmium tetroxide⁸

Table 1. Composition of model epoxy materials

Designation	Concentration (parts by weight)				T_g (°C)
	Epoxy	Elastomer	Piperidine	BPA	
A	100	0	5	0	101
B	100	5	5	0	100
C	100	15	5	0	103
D	100	18.5	5	0	98
E	100	5	5	24	104

BPA — Bisphenol A

a related elastomer (amino-terminated polybutadiene-acrylonitrile), but are cured with trimethylene glycol di-p-aminobenzoate (TMAB) rather than piperidine. Their T_g s depend on cure time and temperature as well as formulation. The particular data analysed here are for one formulation with two different cure histories. These two materials are described in Table 2, which also gives their reported T_g s.

Characterization

The fracture data analysed in this paper and other background information on the materials involved can be found in previous publications^{1-4, 6, 7, 16}. The fracture experiments were performed using compact tension specimens cut from the moulded plates. After being precracked, these specimens were pulled to failure in a tensile test machine using a variety of temperatures (-60°C to 60°C) and cross-head speeds (2 mm s⁻¹ to 0.0008 mm s⁻¹). The four formulations shown in Fig. 2 were characterized for both temperature and rate dependence. The high T_g formulations, however, were tested only as a function of temperature so the data available are more limited. The fracture energies for all of the samples and load-temperature histories were calculated using standard ASTM equations.

Results and discussion

Based on suggestions from previous studies^{1, 2, 6}, the data for the fracture experiments (see Fig. 1, for example) were analysed using the time-temperature superposition. To do this, it was first necessary to select an appropriate parameter to characterize the time or rate dependence. The previous research^{1, 2, 6} suggested time-to-failure, t_f (the time from the initial load application until failure), as a possible parameter and demonstrated that superposition could be obtained with this choice. There are, however, a number of other parameters which could have been used without affecting the results since, in all the tests

conducted, the precrack lengths and moduli changed very little over the range of conditions used. Consequently, t_f is directly related to other possible choices such as loading rate. The analysis conducted here will follow the suggestion of the previous work and use time-to-failure.

To perform the superposition, the data were first plotted as fracture energy, G_{IC} , against t_f at various temperatures. The curves were then shifted along the t_f axis to obtain the best overlap (the scatter made it impossible to identify any small vertical shifts that might be present). Fig. 3 shows the results of this process for three of the four model rubber-modified epoxy formulations. As shown in this figure, the procedure consolidated the data around a single curve for each formulation. The superposition process also generated the shift factors, $\log(a_T)$, necessary for superposition, and these are shown in Fig. 4 plotted against reciprocal temperature. Surprisingly, the shift factor data for all three formulations fall along a single curve.

For comparison, a similar superposition process was applied to yield stress data for a rubber-modified epoxy containing 15 phr elastomer⁷. Data from the work of Kinloch and Shaw⁴ were obtained for compressive yield behaviour measured as a function of temperature and cross-head speed. The data were plotted as yield stress vs time-to-yield at a series of temperatures. The data were then shifted to give master curves and shift factors. The shift factors obtained in this way were then added to the graph as shown in Fig. 4. The agreement was excellent⁷. This suggests that the shift factors are not particularly dependent on formulation and that yielding is a major factor in the toughening mechanisms for these materials.

When comparing different formulations, it is useful to have a simple empirical equation to model the data. The following²⁻⁷ represents one possibility. The data in Fig. 3 were fit to a simple power-law equation (solid curves). Although this equation has some obvious shortcomings (in terms of extrapolation, for example, the long time-to-failure fracture energy is predicted to be unlimited), the curves do provide reasonable first approximations to the

Table 2. Composition and cure conditions for additional epoxy samples*

Designation	Concentration (parts by weight)			Cure	
	Epoxy	Elastomer	TMAB	Temperature (°C)/ time (h)	T_g (°C)
F	100	15	39.9	100/40	125
G	100	15	39.9	200/3	148

*Data from References 14 and 15

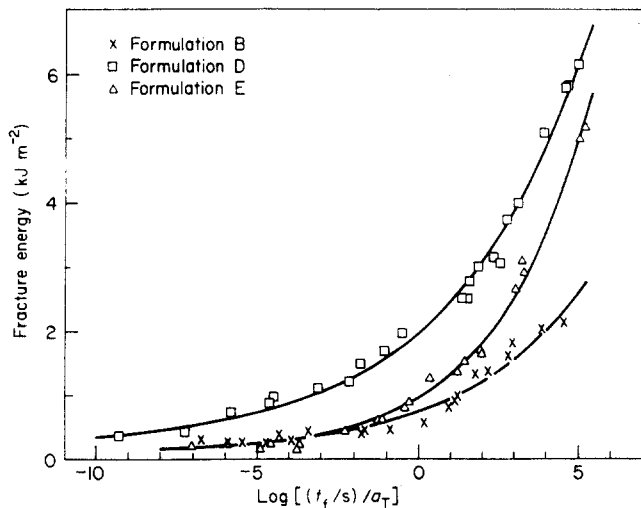


Fig. 3 Master curves for fracture energy vs normalized time-to-failure for formulations B, D and E at a reference temperature of 20°C. Curves from Equation (1)

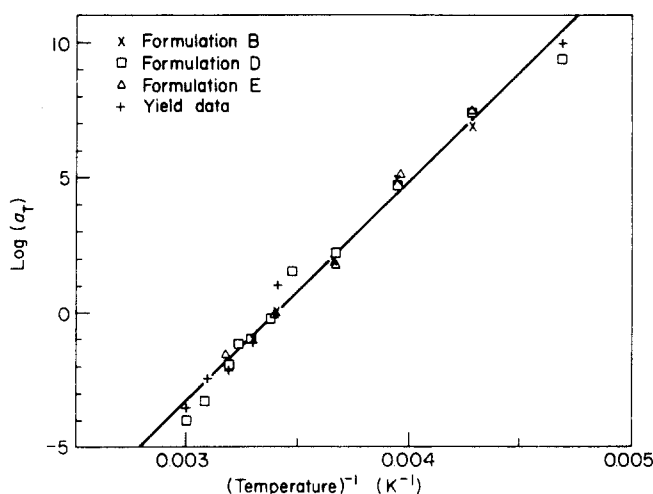


Fig. 4 Shift factors for data in Fig. 3 and yield data. Line from Equation (1)

data over the range of conditions actually measured. In the case of the shift factors, a simple straight line provides a reasonable fit of the data, as plotted in Fig. 4. Although the data can be fitted to this Arrhenius-type relationship, there are other equations which also fit the data. Consequently, the Arrhenius-type relationship shown in Fig. 4 may have basic significance or may simply be an empirical equation for fitting the data.

Implicit in this treatment of fracture data is the use of a reference temperature. The best way to illustrate this is by writing the equation described above in the following form:

$$G_{IC} = A(t_f/a_T)^m + G_{ICB} \quad (1a)$$

$$a_T = e^{\Delta E/R[1/T - 1/T_0]} \quad (1b)$$

where a_T is the time-temperature shift factor, A , m , ΔE and G_{ICB} are empirically determined parameters, R is the gas constant and T_0 is the reference temperature. As long as Equation (1) is applicable, the choice of a reference temperature affects only the value of A . If A is determined at one reference temperature, T_{01} , conversion to a different reference temperature, T_{02} , can be made as follows:

$$A_{T_{02}} = A_{T_{01}} e^{m\Delta E/R[1/T_{01} - 1/T_{02}]} \quad (2)$$

By using these equations it is possible to determine the values of the parameters for the four rubber-toughened epoxies described in Table 1 at a reference temperature of 20°C. The results are given in Table 3.

Previous studies^{1-4, 6, 7} have shown that the toughening in elastomer-modified epoxies is related to yielding and plastic flow and through this connection to the T_g . Any comparison between different materials, therefore, is most meaningful when referred to their T_g s. Although T_0 in Equation (1) can be taken as T_g , it is more useful to select a lower value such as $T_0 = T_g - 80^\circ\text{C}$ since this places the reference temperature in the range where the fracture measurements were made. By using this approach with $T_0 = T_g - 80^\circ\text{C} = T_R$, new values can be calculated for A and these values are also given in Table 3.

Although Equation (1) is empirical, it is useful in that the parameters have significance in terms of behaviour: G_{ICB} measures the limiting toughness at low temperatures and high loading rates; A reveals the magnitude of the toughening; m assesses the rate sensitivity of the fracture energy; and ΔE measures the temperature dependence of the failure process. Once sufficient data become available for a variety of formulations, the relationships between these parameters and the morphologies can be determined.

Although the present data are too limited to draw definitive morphology-property correlations, it is tempting to offer some speculation as a guide for future study. Since the temperature dependence is similar for all four formulations, the important morphological feature in this regard may be the matrix composition since it also shows little variation among these samples. This is indicated by their similar T_g s. The rate dependence, as characterized by the value of m in the equation, appears to be a function of particle size distribution since m is similar for all three examples of type one rubber-modified epoxy but quite different for type two. This speculation is somewhat risky, however, since morphology is the most obvious but not the only difference between type one and type two formulations. For example, the addition of bisphenol-A to the epoxy without the elastomer is known to increase the fracture energy somewhat¹⁷. The coefficient A is clearly a strong function of rubber content but also depends on other factors such as morphology. This is consistent with previous studies¹⁸ that show the volume fraction of phase-separated elastomer to be a critical parameter in toughening. It is interesting to note that, although formulation D has the highest toughening, a small portion of this may be due to its slightly lower T_g . In this connection, A_{T_R} should represent a better parameter for comparisons.

Although the results in Table 3 form the basis for some interesting speculation, they also illustrate the limitation inherent in the similarity of the epoxy matrices. Consequently, it is of interest to analyse the data for the higher T_g systems. This can be done in a similar way except that for these systems the data were determined only as a function of temperature. Since the variation in time-to-failure was small over a large portion of the range of test conditions, Equation (1) can be rewritten in the following form:

$$G_{IC} = A' e^{-m\Delta E/RT} + G_{ICB} \quad (3a)$$

where

$$A' = A t_f^m e^{m\Delta E/RT_0} \quad (3b)$$

If relationship (1) is valid for these new materials, then

Table 3. Values of parameters in Equation (1)

Designation	m	ΔE (kJ mol ⁻¹)	G_{ICB} (kJ m ⁻²)	A_{20} (kJ m ⁻²)	A_{T_R} (kJ m ⁻²)
B	0.118	160	0.15	0.65	0.65
C	0.121	160	0.50	1.05	1.14
D	0.116	160	0.38	1.55	1.47
E	0.151	160	0.15	0.86	0.98

A_{20} — Reference temperature 20°C; A_{T_R} — Reference temperature T_R — 80°C

Equation (3) should be applicable and A' should be a constant. To test this proposition the fracture data for the high T_g materials are plotted in Fig. 5, and the best fit curves from Equation (3) are also shown. In addition this figure contains selected data (data with similar time-to-failure values) for the formulation designated C from Reference 15. In viewing the data for the higher T_g materials, it must be noted that the experimental uncertainty is significantly higher than with the other model systems. There are two reasons for this. First, the times-to-failure are not constant for the data on formulations F and G but vary somewhat as a function of fracture energy. Second, the data points for formulations B to E represent averages of three to 10 separate tests while formulations F and G have not been subjected to such extensive study. Under these conditions the curves in Fig. 5 represent reasonable fits to the data.

Nevertheless, more experiments are clearly needed for a critical test of Equations (1) and (3).

The data for the high T_g material raises some interesting questions about the effects of the matrix on the parameters in Equation (1). Unfortunately, as can be seen from Equation (3), it is not possible to evaluate any of the parameters when only the temperature dependence is measured. This reinforces the need for further experiments in this area.

Conclusions

The results presented here indicate that the fracture behaviour of rubber-modified epoxies is viscoelastic in nature and that this is responsible for the strong rate and temperature effects. By using time-temperature superposition techniques, however, the data can be modelled,

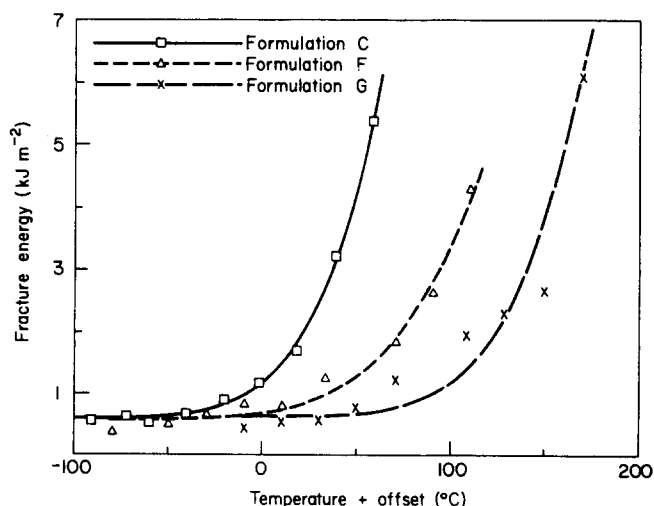


Fig. 5 Fracture data for formulations C, F and G. Curves from Equation (3). The results for formulations F and G are shifted to the right by 10°C and 50°C, respectively, so the curves can be seen more easily

at least to a first approximation, with simple empirical relationships. The equation used in this work is particularly useful for comparing results for different formulations because the parameters involved can be related to physically meaningful effects: A measures the magnitude of the toughening; m assesses the rate sensitivity; ΔE indicates the temperature sensitivity; and G_{ICB} measures the lower limit of G_{IC} at low temperatures and high rates. Future work should make it possible to use these parameters to establish valuable structure/property relationships for these very useful rubber-modified epoxy materials.

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Authors

The authors are with the Polymers Division of the National Bureau of Standards, Gaithersburg, MD 20899, USA. Inquiries should be directed to Dr Hunston in the first instance.