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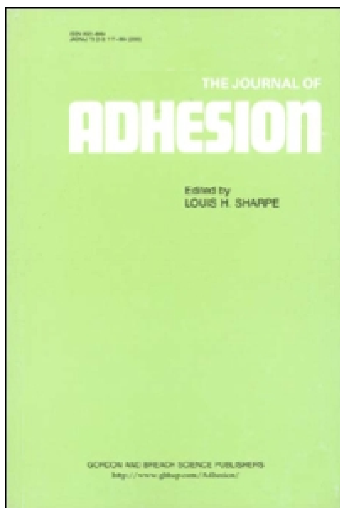

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Willard D. Bascom[a]; Robert L. Cottington[a]
[a] Naval Research Laboratory, Washington, D.C., U.S.A.

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Effect of Temperature on the Adhesive Fracture Behavior of an Elastomer-Epoxy Resin

WILLARD D. BASCOM and ROBERT L. COTTINGTON
Naval Research Laboratory, Washington, D.C. 20375, U.S.A.

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The bulk and adhesive fracture behavior of a diglycidyl ether bisphenol-A epoxy modified with 15% carboxy-terminated butadiene acrylonitrile was determined as a function of temperature. The bulk fracture toughness increased sharply near the resin T_g in a manner similar to unmodified epoxy resins. The adhesive fracture energy exhibited a maximum with respect to bond thickness and this maximum broadened and shifted to larger bond thicknesses with increasing temperature. These results are discussed in terms of the size and stress condition of the crack tip deformation zone.

INTRODUCTION

The large improvements in epoxy resin fracture energy that can be achieved by the incorporation of carboxy-terminated butadiene acrylonitrile (CTBN) elastomers have been described by Sultan, Laible and McGarry,[1-3] Riew, Rowe, Siebert and Drake[4,5] and Bascom, Cottington, Jones and Peyser.[6] Increases in the cleavage (opening-mode or mode-I) fracture energy ($\mathscr{G}_{Ic}$) of forty-fold over the unmodified epoxy resin have been reported.[2,6] It has been established that the CTBN elastomers copolymerize with the liquid epoxy resin to form micron size elastomeric particles within the crosslinked epoxy resin matrix.[4,5] McGarry *et al.*[1] and Bascom *et al.*[6] have demonstrated that the increased fracture energy is associated with an enlargement of the crack tip deformation zone diameter by the elastomer particles, analogous to the mechanism for the improved toughness of high-impact polystyrene described by Bucknall and Smith.[7]

The adhesive fracture energy (mode-I) of epoxy resins is also considerably improved by the addition of CTBN elastomer except that the effect is

strongly dependent on bond thickness. Bascom *et al.*[6] have shown that the adhesive $\mathscr{G}_{Ic}$ is a maximum and equal to the bulk value when the crack tip deformation zone diameter, $2r_c$, and the bond thickness are equal. As the bond thickness is reduced to less than $2r_c$ there is a precipitous decrease in fracture toughness. There is also a decline in adhesive $\mathscr{G}_{Ic}$ when the bond thickness is increased above $2r_c$.

The effect of temperature on the adhesive fracture of epoxy resins has been reported by Mostovoy and Ripling.[8,9] Their results for unmodified epoxy resins had a relatively simple and consistent pattern which can be explained in terms of the temperature-strain rate response of the polymer. Their results for commercial, modified epoxy resin adhesives indicated a complex temperature dependence which can be explained by a superposition of bond thickness effects on the temperature dependence of the resin fracture energy.

EXPERIMENTAL

Materials

The elastomer-epoxy resin system was the same as previously described[6]; a piperidine-cured bisphenol A diglycidyl ether (DGEBA; Dow Chemical Co., DER-332) containing a carboxy-terminated butadiene-acrylonitrile (CTBN, B. F. Goodrich Co., Hycar 1300X8, 17–18% acrylonitrile). The 15 wt.% CTBN-epoxy resin was used in this work since this composition had been found to give maximum fracture toughness with respect to elastomer concentration. The resin composition and cure conditions are listed in Table I. The aluminum adherends were cut from 1.3 cm thick 5086-alloy plates. They were machined and then cleaned by acid chromate etching.[6]

TABLE I

Elastomer-modified eposy resin

	Percent by weight
Bisphenol A diglycidyl ether	81
Carboxy-terminated butadiene-acrylonitrile	15
Piperidine (reagent grade)	4

Cured at 120° for 16 hours; $T_g = 341°K$.

Methods

Bulk and adhesive fracture energies were determined using constant compliance, tapered double cantilever beam specimens as described by Mostovoy and Ripling.[10] The specimen configuration, shown in Figure 1, is for

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opening mode fracture energy (mode-I) as given by,

$$\mathscr{G}_{Ic} = \frac{4P_c^2}{b^2 E_b} m \tag{1}$$

where P_c is the load at crack propagation, b is the specimen thickness (~ 1.0 cm), E_b the bending modulus of the resin for bulk fracture specimens or of the aluminum for adhesive fracture specimens. The value of m is determined by the specimen taper.[10]

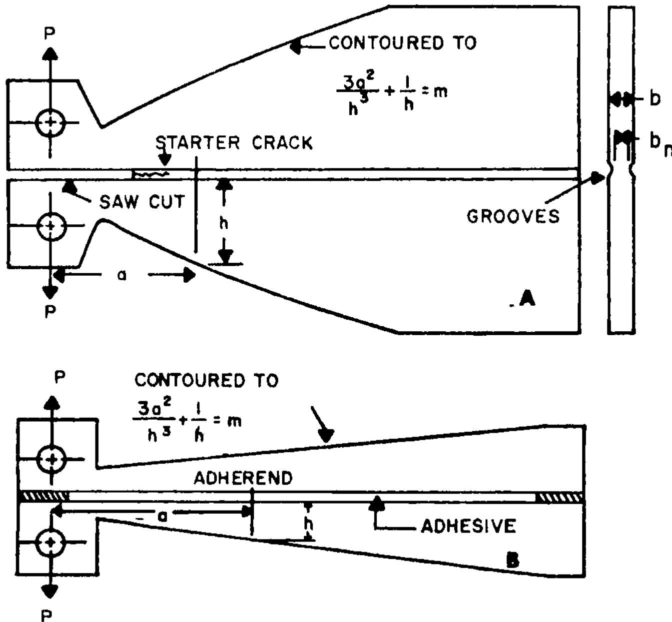

FIGURE 1 Constant compliance test specimen for mode-I fracture; A-bulk specimen, B-adhesive specimen.

The load-displacement ($P - \delta$) curves obtained from the tapered-DCB tests generally show a series of peaks due to the crack alternately propagating and arresting as it is driven through the specimen. The peak heights are taken as the load for the initiation of crack propagation ($\mathscr{G}_{Ic}$) and the valleys give the load for crack arrest ($\mathscr{G}_{Ic}^a$). In the case of stable propagation the $P - \delta$ chart is a continuous horizontal line.

Tensile strengths and moduli were determined using ASTM Method D638-64T and the bending moduli were determined using the four-point loading method.[10] All mechanical tests were performed on an Instron TT-B at 0.05 in/min (0.13 cm/min) strain rate in a constant temperature chamber controlled to ± 1°C.

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RESULTS

The tensile strength, modulus and bulk fracture energy of the 15% CTBN-DGEBA resin were determined over the temperature range of 233–323°K (−40 to +50°C) and the results are presented graphically in Figures 2 and 3. The adhesive fracture energies of these resins were determined in the same temperature range as a function of bond thickness and the results are given in Figures 4–10. Note the maximum in adhesive $\mathscr{G}_{Ic}$ with respect to bond

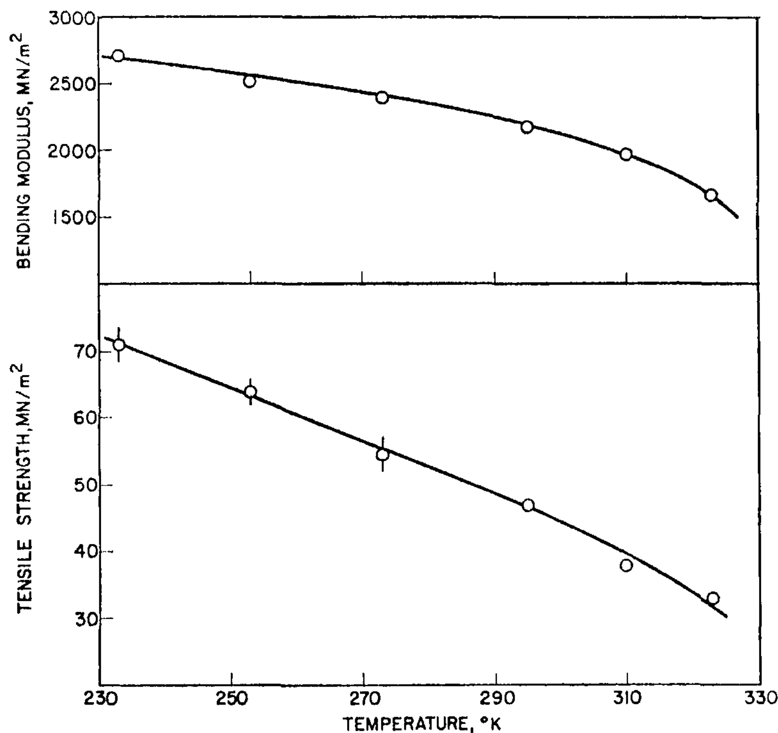

FIGURE 2 Tensile strength and bending modulus *vs* temperature of the 15% CTBN-DGEBA resin.

thickness and that this maximum undergoes a systematic shift toward greater bond thicknesses with increasing temperature and at each maximum there is a transition from unstable propagation in the thicker bond specimens to stable propagation for the thin bond specimens. As a convenience for discussion purposes the maximum adhesive fracture energy will be designated as $\mathscr{G}_{Ic}$(max) and the corresponding bond thickness as h_{max}.

The arrest energies could not be obtained for the bulk specimens since the high strain energy at crack initiation in the tough elastomer-epoxy

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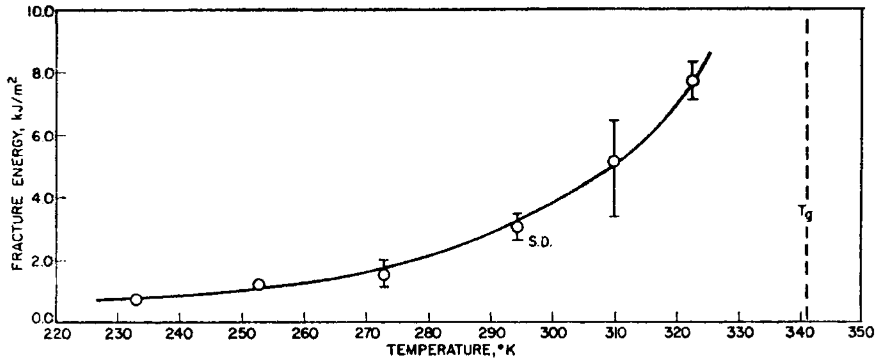

FIGURE 3 Bulk fracture energy, $\mathscr{G}_{Ic}$, *vs* temperature of the 15% CTBN-DGEBA resin.

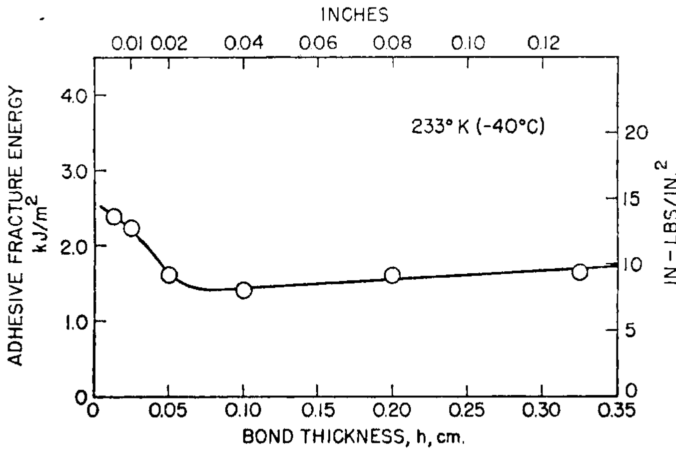

FIGURE 4 Adhesive fracture energy *vs* bond thickness at 233°K; ○, unstable propagation, ●, stable propagation.

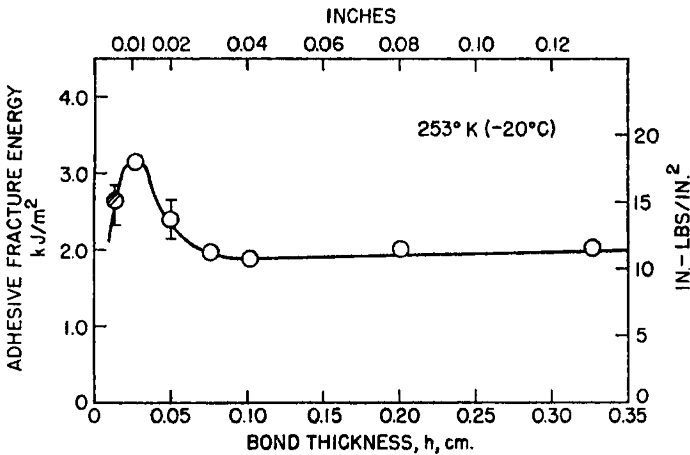

FIGURE 5 Adhesive fracture energy *vs* bond thickness at 253°K; ○, unstable propagation, ⊘, stable propagation.

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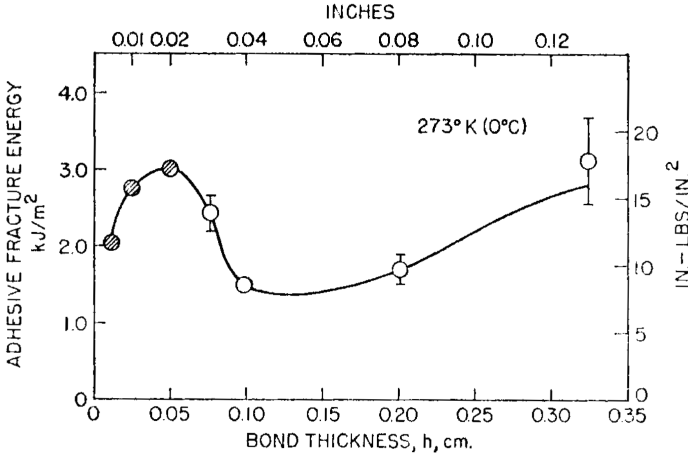

FIGURE 6 Adhesive fracture energy *vs* bond thickness at 273°K; ○, unstable propagation, ●, stable propagation.

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cannot be dissipated in the relatively short (23 cm) specimen length.[6] However, arrests were observed in the adhesive fracture tests and typical data are plotted in Figure 7 as a function of bond thickness at constant temperature (298°K) and as a function of temperature at constant bond thickness (0.20 cm) in Figure 10. Note that $\mathscr{G}^a_{Ic}$ was insensitive to temperature and to bond thickness.

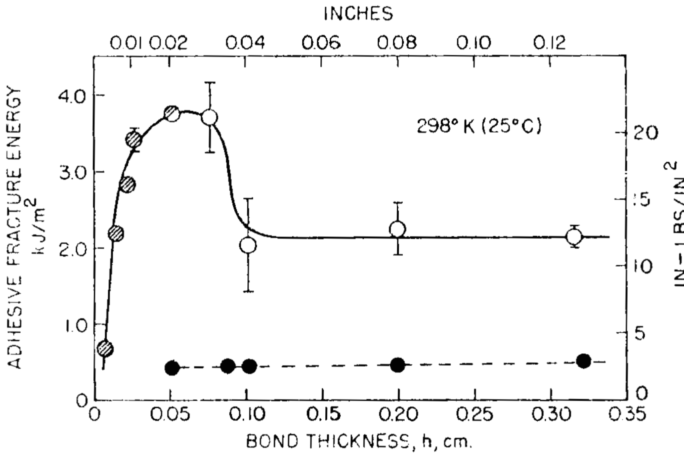

FIGURE 7 Adhesive fracture energy *vs* bond thickness at 298°K; ○, unstable propagation, ●, stable propagation, ●, arrest energy.

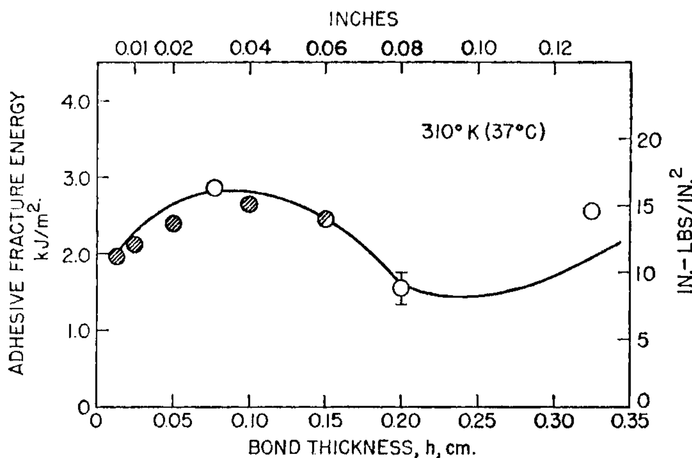

FIGURE 8 Adhesive fracture energy *vs* bond thickness at 310°K; ○, unstable propagation, ●, stable propagation.

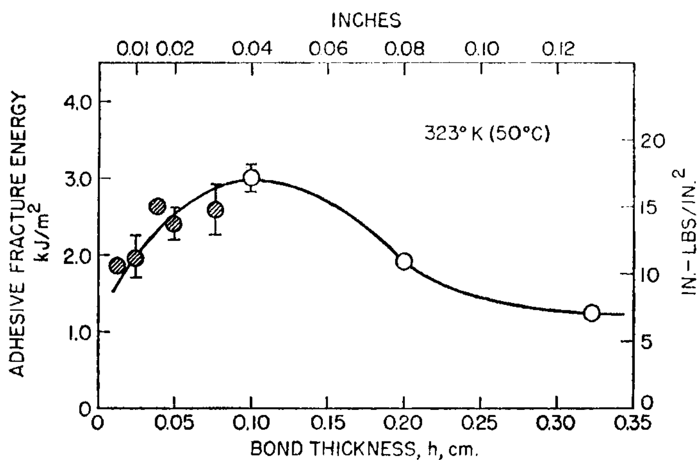

FIGURE 9 Adhesive fracture energy *vs* bond thickness at 323°K; ○, unstable propagation, ●, stable propagation.

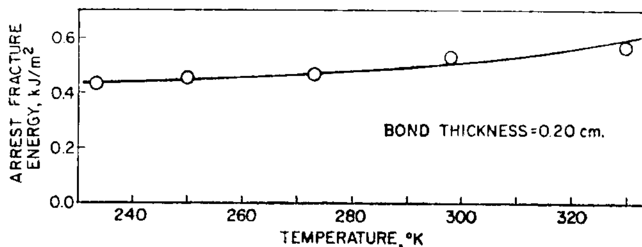

FIGURE 10 Arrest fracture energy *vs* temperature at 0.20 cm. bond thickness.

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DISCUSSION

Bulk fracture

Before discussing the results of this work it is instructive to consider the work of Mostovoy and Ripling[8,9] on the effect of temperature on the adhesive fracture energy of unmodified, amine and anhydride cured epoxy resins. The general trend of their data is illustrated in Figure 11 and is characterized by a steep rise in $\mathscr{G}_{Ic}$ at both ends of the temperature range. Although their study did not include the piperidine-DGEBA resin, there is no reason to believe its behavior with respect to temperature would be significantly different, especially since the room temperature fracture behavior was similar in all respects to the room temperature fracture behavior of the epoxy resins studied by Mostovoy and Ripling.

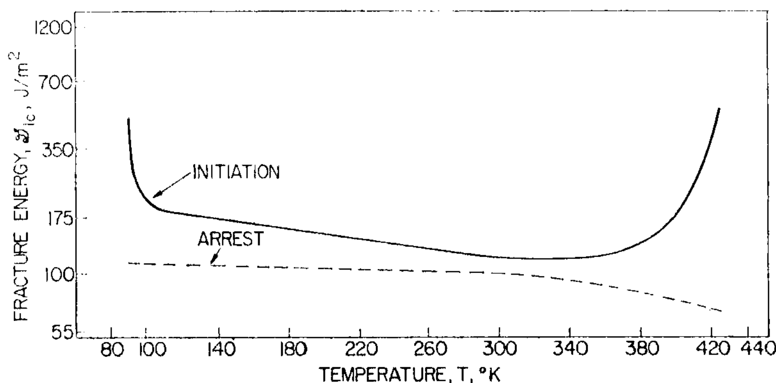

FIGURE 11 Adhesive fracture energy *vs* temperature for unmodified epoxy resins.

The T *vs* $\mathscr{G}_{Ic}$ curve in Figure 11 was drawn from the data for a hexahydrophthalic anhydride (HHPA)-DGEBA resin.[9] Note the steep rise in fracture energy at both the low and high ends of the temperature range. The increase in $\mathscr{G}_{Ic}$ near 400°K can be reasonably attributed to the approach to the glass transition temperature (T_g) of the HHPA-DGEBA resin.[11] An increase in fracture energy near T_g is associated with an increase in molecular mobility allowing greater plastic deformation at the crack tip during crack initiation. Maxima in the $\mathscr{G}_c$ of polymers near second order transitions have been discussed by Williams, Radon, Turner and Johnson.[12,13]

At the lower end of the temperature spectrum (~90°K) the steep rise in $\mathscr{G}_{Ic}$ may be related to some second order structural transition although this seems unlikely at such a low temperature and since there are distinct β-transitions at higher temperatures (~200°K, Ref. 11, p. 6–29) which did

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not affect $\mathscr{G}_{Ic}$. Alternatively, the rise in $\mathscr{G}_{Ic}$ at 90°K may be related to the limiting crack velocity observed for these and other polymers at 298°K.[14,15] Peretz and DiBennedetto have reported the limiting velocity for unmodified epoxy resins as $\sim 3 \times 10^4$ cm/sec[15] which would, by time-temperature superposition, correspond to a low temperature phenomenon. Actually, the high toughness at the low temperature may be an artifact resulting from plasticization of the resin by the LN_2 coolant as described by Olf and Peterling[16] for the fracture of thermoplastic resins.

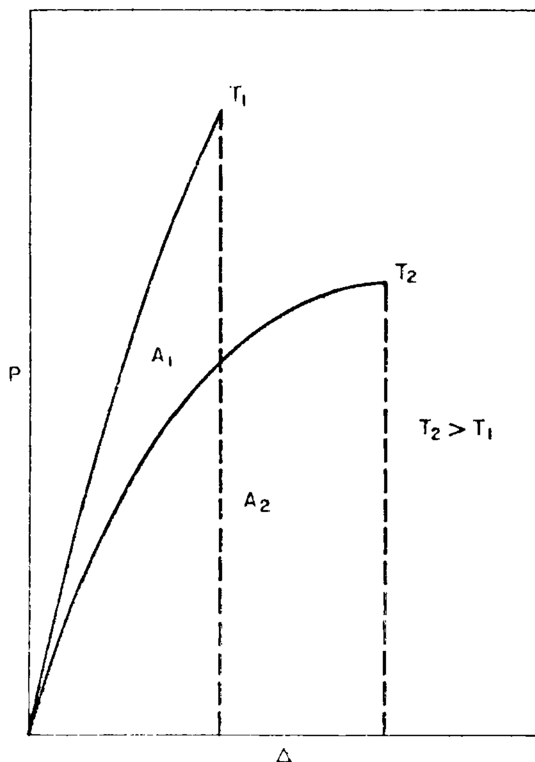

FIGURE 12 Schematic tensile load-displacement graphs.

The arrest energies are also given in Figure 11 but they do not show abrupt changes at high or low temperatures. The physical significance of crack arrest is problematical. However, it is clear that unstable propagation arises because of the strain rate sensitivity of the resin, i.e., $\mathscr{G}_{Ic}$ decreases with increasing crack velocity. Therefore, it is reasonable that the arrest of a moving crack, where the strain rate is orders of magnitude greater than the strain rate at crack initiation, would not be especially sensitive to temperature

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effects on the rheological response of the resin which so strongly affect crack initiation.

The effect of temperature on the bulk fracture energy of the 15% CTBN-DGEBA resin given in Figure 3 indicates a rise in $\mathcal{G}_{Ic}$ as the temperature approaches the T_g characteristic of the epoxy matrix ($T_g = 341°K$ is slightly lower than the 344°K of the unmodified epoxy due to a small amount of molecularly dissolved elastomer).[6] The fact that it is the matrix T_g that dictates this thermal-mechanical response is evidence that despite the extensive deformation of the elastomer particles[6] it is the visco-elastic (plastic) response of the matrix that governs energy dissipation at the crack tip. The function of the elastomer particles is to enlarge the volume in which this dissipation occurs relative to the unmodified epoxy. The bulk fracture behavior at low temperature will be the subject of a later investigation.

The decrease in tensile yield strength with increasing temperature despite the parallel increase in resin toughness is symptomatic of the increasing rubber-like behavior in approaching T_g. Load displacement curves for the tensile tests at 50°C and −20°C are shown schematically in Figure 12. The increase in the area under the curves can sometimes be associated with toughness and is consistent with the increase in $\mathcal{G}_{Ic}$ observed here.

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Adhesive fracture

The adhesive $\mathcal{G}_{Ic}$ values exhibited a much more complex dependence on temperatures than did the bulk $\mathcal{G}_{Ic}$, which from Figures 4 to 10, is clearly related to bond thickness. The relationship between bond thickness, h, and adhesive $\mathcal{G}_{Ic}$ established earlier[6] at 25°C had four characteristics:

a) A maximum in $\mathcal{G}_{Ic}$.

b) A transition from stable to unstable propagation with increasing h at h_{max}.

c) A precipitous decline in $\mathcal{G}_{Ic}$ as the bond thickness was reduced below h_{max}.

d) A decline to a more-or-less constant value of $\mathcal{G}_{Ic}$ when the bond thickness was increased above h_{max}.

These same characteristics are evident for the data taken at the temperatures of this study with the additional observations that h_{max} increases with temperature and that there is a broadening of the maximum in $\mathcal{G}_{Ic}$ with increasing temperature.

It has been shown[6] that there is an approximate correspondence between h_{max} and the diameter of the crack tip deformation zone, $2r_c$. From the elastic-plastic model of fracture the zone radius is related to the bulk fracture energy by:

$$\mathcal{G}_{Ic} \approx 6\pi\sigma_y\varepsilon_y r_c \tag{2}$$

where σ_y and ε_y are the tensile yield stress and strain respectively. Taking data from Figures 2 to 3 and estimating ε_y from σ_y/E, the values of $2r_c$ were computed from Eq. (2) and are listed in Table II along with the values of h_{max}. The correspondence is nearly quantitative at the higher temperatures but becomes less satisfactory even at 25°C. Part of this discrepancy can be attributed to the fact that the tensile strength obtained from Figure 2 increasingly underestimates the true yield strength as the temperature decreases and the error is aggravated by the use of σ_y^2 in computing r_c. Nonetheless, the shift in $\mathscr{G}_{Ic}$ (max) and the transition from unstable to stable propagation toward smaller bond thicknesses is clearly associated with a decrease in $2r_c$. The transition in mode of propagation, i.e., unstable to stable, was shown to be the result of a change from center-of-bond failure in thick bonds ($h > h_{max}$) to a shear failure near the metal/resin boundary when the plastic zone fills the bond ($h < h_{max}$).[6]

TABLE II

Comparison of h_{max} and crack tip deformation zone diameter, $2r_c$

Temp, °K	h_{max} (cm)	$2r_c$ (cm)
323	0.10	0.12
310	0.075	0.078
298	0.060	0.033
273	0.050	0.013
253	0.025	0.008
233	$\ll$0.01	0.004

It is evident from the data in Figures 4 to 10 that a comprehensive picture of the effect of temperature on $\mathscr{G}_{Ic}$ requires fracture measurements as a function of bond thickness. To illustrate this point a plot of adhesive $\mathscr{G}_{Ic}$ *vs* temperature is given in Figure 13 for 0.025 cm (10 mil) bond thickness. Plotted in the same figure (broken line) are the data of Mostovoy and Ripling[9] for a commercial "rubber-modified epoxy" structural adhesive that had also been tested at 10 mil bond thickness. Note that in both cases the toughness was maximum at room temperature. In a study of six other commercial "modified-epoxy" adhesives including a nylon-epoxy composition, Mostovoy and Ripling found that the optimum toughness was at or very near room temperature. Clearly, the CTBN-epoxy resin serves as a first order model for structural adhesives in the magnitude and temperature dependence of adhesive $\mathscr{G}_{Ic}$. A closer simulation of commercial adhesive would require resin compositions having multiple size distributions of elastomer particles. In addition, other modifiers might be included such as inorganic fillers or thixotropic agents used to control resin flow.

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The decrease in $\mathscr{G}_{Ic}$ above and below room temperature when measured at constant bond thickness can be understood in terms of Eq. (2). At temperatures below 25°C the decline in adhesive toughness can be attributed to a decline in the deformation zone size, r_c since in Eq. (2) the yield strength actually increases as the temperature is lowered. The decrease in adhesive $\mathscr{G}_{Ic}$ with temperature is precipitous compared to the change in bulk $\mathscr{G}_{Ic}$ over the same temperature range (25°C to −40°C). This is a little difficult to understand since the parameters in Eq. (2) are the same for both adhesive

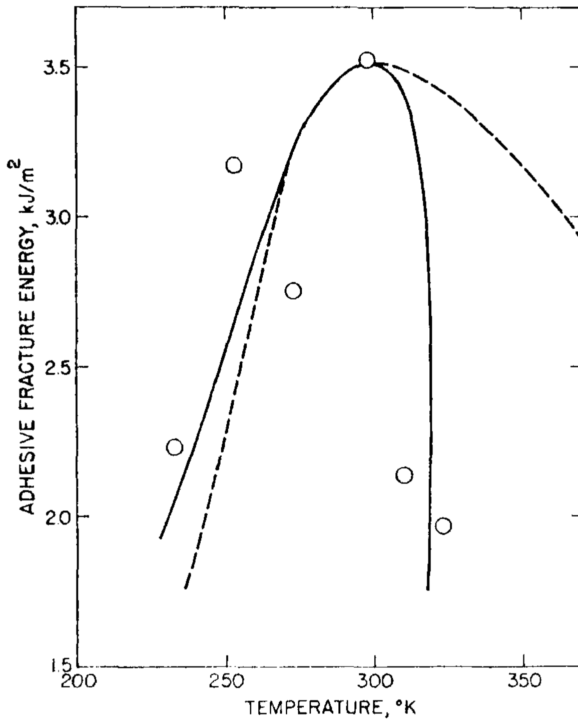

FIGURE 13 Adhesive fracture energy of the 15% CTBN–DGEBA epoxy, ○, and a commercial adhesive (- - -, Ref. 9) as a function of temperature at constant bond thickness (0.025 cm).

and bulk fracture. The difference may be due to a deviation from plane-strain conditions in the adhesive specimen when $2r_c$ is significantly smaller than the bond thickness. This effect is discussed in the next section.

Above room temperature the decline in toughness with increasing temperature (Figure 13) is due to the fact that at constant bond thickness the r_c term in Eq. (2) cannot increase and so as yield strength is lost with increasing temperature the adhesive $\mathscr{G}_{Ic}$ decreases. This trend is in distinct contrast

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with the bulk toughness for which there is no constraint on development of the deformation zone and $\mathscr{G}_{Ic}$ increases progressively toward T_g.

$\mathscr{G}_{Ic}$ at $h > h_{max}$

In the earlier study of modified-epoxy adhesive fracture[6] it was suggested that the decrease in $\mathscr{G}_{Ic}$ at bond thicknesses greater than h_{max} was the result of a deviation from plane-strain conditions at the crack tip. Observations made in the present study tend to confirm this suggestion. In Figure 14 sketches are given of the stress-whitened regions of crack initiation observed on the fracture surfaces in post-failure examination. This whitening of the resin is the result of the dilation of the epoxy-matrix and the elastomer particles in the triaxial stress field of the crack tip that prevails under plane-strain conditions. The dark line in each of the sketches in Figure 14 represent the region of greatest deformation (most intense stress whitening) with an advance region of less deformed resin that increases in area as the bond thickness is reduced.

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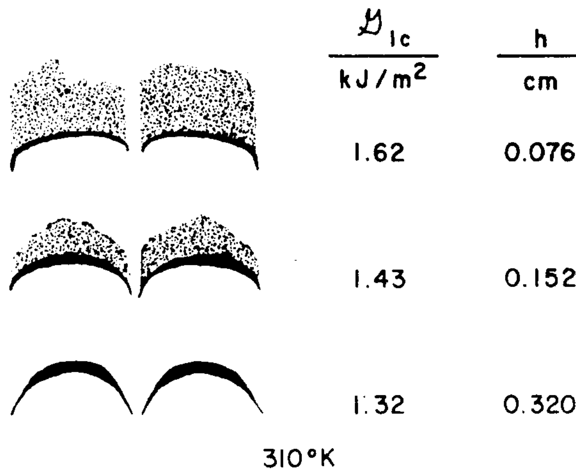

FIGURE 14 Sketches of "fingernail" markings on adhesive fracture surfaces produced by stress-whitening at crack initiation.

The features in Figure 14 of greatest interest to the present discussion are (a) the narrowing of the more intense stress-whitened band near the bond edges and (b) the increase in the curvature of the bands as the bond thickness was increased. These features are attributed to a deviation from the plane-strain condition at the crack tip near the bond edges where there is no lateral constraint and a condition of plane-stress exists. The change in curvature of the whitened zone suggests that the region of plane-stress increases with increasing bond thickness. Usually, such a change in stress

condition leads to a higher fracture energy since $\mathscr{G}_c$ is generally greater in plane-stress than in plane-strain.[17] However, the high toughness of these epoxy-elastomer resins and other multiphase polymers is associated with the triaxial dilatation of the elastomer particles. Evidently, the toughness is reduced to the extent of deviation from the triaxial stress condition at the bond edges as the resin layer is thickened.

Although a similar situation with respect to plane-strain/plane-stress must exist for bulk fracture of the elastomer–epoxy resin, the magnitude of the effect on $\mathscr{G}_{Ic}$ is probably not as great due to the much lower stress intensity factor, K, in the bulk compared to adhesive resin. Even though the $\mathscr{G}_{Ic}$ values are comparable, K, which is given by,

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

is determined by the modulus, E, which is 10^5 psi for the bulk resin but 10^7 psi for the aluminum adherends. Thus, the stress level at the crack tip is much less severe and less likely to cause lateral contraction in bulk than in an adhesive layer.

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