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Low-temperature behaviour of epoxy-rubber particulate composites

S. C. KUNZ
Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

P. W. R. BEAUMONT
Department of Engineering, University of Cambridge, Cambridge, UK

Toughness and mechanical property data are presented for a carboxyl-terminated acrylonitrile butadiene (CTBN) rubber-modified epoxy resin in the temperature range 20 to − 110° C. A toughening model based on ultimate strain capability and tear energy dissipation of the rubber, present as dispersed microscopic particles in an epoxy matrix, is used to explain the suppression of composite toughness (G_{Ic}) below − 20° C. The toughness loss is attributed to a glass transition in the rubber particles, and to a secondary transition in the epoxy resin, both occurring in the range − 40 to − 80° C. Strain-to-failure and modulus measurements on bulk rubber–epoxy compounds, formulated to simulate rubber particle compositions, confirm a decrease in rubber ductility coincident with the onset of composite toughness loss. An increase in rubber tear energy associated with its transition to a rigid state can explain the observation that even at low temperatures composite toughness generally remains significantly higher than that of pure epoxy. Although the low-temperature epoxy transition reduces molecular mobility in the matrix phase, residual ductility in, and energy dissipation by, the rubber particles determine the extent of composite toughness suppression. The low-temperature data bear out the particle stretching–tearing model for toughening.

1. Introduction

The toughening effect of microscopic rubber particles dispersed in an epoxy resin matrix is widely recognized and has been measured for a variety of resin/curing agent/rubber systems. At room temperature the toughness of an unmodified epoxy can be increased by more than a factor of ten depending on variables such as the curing agent used, and the type and concentration of rubber added (see for example [1–6]). Studies which have included measurements at temperatures in the 0 to − 110° C range show a significant, monotonic decrease in the toughness values from 20° C [1, 6, 7].

Theories currently used to account for the effect of the rubber particles, at both ambient and low temperatures, have evolved from earlier studies of toughened thermoplastics. Specifically, matrix-deforming processes such as cold-drawing, multiple crazing and shear yielding [1, 2, 4, 5, 8–10] are widely thought to be induced by the stress-concentrating particles and are considered the dominant toughening mechanisms. In contrast, a recently proposed toughening model [6] emphasizes the role of the particles themselves during crack propagation: the rubber particles bridging the opening crack surfaces are capable of very large extensions during which elastic energy is stored and later dissipated during tearing of the rubber. This mechanism for toughening is particularly relevant to rubber-modified cross-linked, thermosetting polymers in which crazing and yielding processes are highly uncharacteristic. The model is supported by microscopic observations and measurements of particle failure and, furthermore, gives a quantitative prediction for the toughness dependence on particle volume-fraction and tearing energy.

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TABLE I Properties of CTBN rubbers

Property	A (CTBN 1300 × 13)	B (CTBN 1300 × 8)	C (CTBN 1300 × 15)
Acrylonitrile content (%)	27	18	10
Molecular weight	3400	3500	3600
Carboxyl (%)	2.40	2.37	2.47
Functionality	1.85	1.85	1.9
Specific gravity at 25° C	0.960	0.948	0.924
EPHR*	0.059	0.053	0.057
	0.056	0.052	

*Equivalents per hundred of rubber.

The particle stretching–tearing model for toughening is further examined in this paper to explain the suppression of toughening at low temperatures. A ductile–brittle transition temperature is estimated for the rubber particles from elastic modulus and strain-to-failure measurements on bulk rubber–epoxy compounds simulating the rubber particle compositions. The transition temperature is shown to coincide with that at which toughness values of the particulate composites drop and their elastic mechanical properties undergo marked changes. These observations are used to substantiate the proposed theory that a loss in toughness of the composites at low temperatures is due to the reduced strain capability of the rubber particles below their glass transition temperature.

2. Experimental procedure

2.1. Materials

The epoxy resin and rubber additives used in this study are the same as described previously [6]: MY 750, a diglycidyl ether of bisphenol A (DGEBA), cured with 4,4′-diaminodiphenylmethane (DDM), an aromatic amine and three carboxyl-terminated acrylonitrile-butadiene (CTBN) rubbers with a range of molecular weights and acrylonitrile contents summarized in Table I. Castings of pure epoxy resin were made from 100 parts by weight (pbw) of resin and 27 pbw of hardener. CTBN–epoxy composites ("Type II", [6]) were fabricated using the preceding resin and hardener amounts with 7, 14.5 and 23 pbw of rubber to give concentrations of 5, 10 and 15 wt %, respectively. Both unmodified and modified materials were cured for 2 h at 80° C, 1 h at 120° C and 2 h at 180° C. Each of the three CTBN rubbers, designated A, B and C in order of decreasing acrylonitrile content, produces a range of particle sizes (mean diameter, $\bar{d}$, and standard deviation, STD) in the composites shown in Table II. Also listed in Table II are the volume fractions (V_R) and of particles (V_P) for the given weight fractions (W_R) of rubber added [6].

TABLE II Composition and morphology of composites

CTBN rubber	W_R (%)	V_R (%)	V_P (%)	$\bar{d}$ STD (× 10^6 m)
A	5.25	6.43	8.13	0.18 ± 0.1
	10.02	12.13	12.81	0.26 ± 0.2
	15.59	18.63	18.50	0.43 ± 0.3
B	5.25	6.50	6.42	1.86 ± 1.3
	10.02	12.26	13.91	2.36 ± 1.3
	15.56	18.78	28.94	3.33 ± 3.1
C	5.25	6.66	7.77	3.60 ± 4.2
	10.02	13.26	18.10	8.40 ± 9.5
	15.57	19.19	30.18	21.10 ± 22.4

Mixtures of primarily CTBN rubber and small amounts of epoxy resin were fabricated to simulate the rubbery phase of the composite materials. The liquid elastomers can be polymerized by adding epoxy resin as a curing agent where the minimum amount of resin necessary to cure 100 pbw of rubber is calculated from the product of the number of equivalents per hundred of rubber (EPHR) and the equivalent weight of the epoxy (in this case, 192.31) [11]. A range of rubber–resin compositions were produced by varying the equivalent ratios of epoxy-to-CTBN, from the most rubbery formulation (equivalent ratio of 1 : 1), to more rigid ones where a stoichiometric amount of hardener is added to cure the excess resin. The formulations shown in Table III to achieve equivalent ratios of 1 : 1, 2 : 1, 3 : 1 and 4 : 1 were used to simulate a range of possible particle compositions [12]. To fabricate the compounds, the resin and CTBN were mixed, heated to 80° C before stirring in the melted hardener and cured as thin sheets (~ 5 mm thick) using the same schedule as for the pure resin and composites.

TABLE III Formulation of rubber–epoxy compounds

Epoxy to CTBN equivalent ratio	CTBN rubber	CTBN (pbw)	Epoxy resin (pbw)	Hardener (pbw)
1:1	A	100	10.77	0
	B	100	10.00	0
	C	100	10.96	0
2:1	A	100	21.54	2.91
	B	100	20.00	2.70
	C	100	21.92	2.96
3:1	A	100	32.31	5.82
4:1	B	100	40.00	8.10
	C	100	43.84	8.88

2.2. Test methods

Double torsion tests [13, 14] were used to determine the fracture energy (toughness), G_{Ic}, as well as the critical stress intensity factor (fracture toughness), K_{Ic}. Measurements were made on both unmodified resin and CTBN–epoxy composites in the temperature range 23 to $-110°$ C, at the approximate intervals -20, -80 and $-110°$ C. The elastic modulus, E, and unnotched fracture strength, σ_f, were obtained from conventional three-point bend tests [13] at the same low temperatures.

Tensile samples cut from the cast rubber–epoxy compounds (cross-sectional area $\simeq 2$ to $5\,mm^2$; $\simeq 4$ cm long) were tested at an extension rate of $300\,cm\,min^{-1}$ to obtain Young's modulus and maximum strain-to-failure [13]. These tests for simulating particle stretching and failure were carried out at the approximate temperature intervals 23, 20, -30, -40 and $-50°$ C.

Tear tests were also performed on the bulk rubbers to determine their characteristic tearing energy according to the theory and methods of Rivlin and Thomas [15]. The so-called "trousers tear" experiments, in which the energy for initiation and stable growth of a tear is measured in a relatively large volume of rubber (sample size of approximately 3 mm thick, 1 to 3 cm wide, 6 to 15 cm long), were conducted at room temperature only [13].

All the low-temperature mechanical tests were performed in an environmental chamber cooled with liquid nitrogen spray and controlled to within ± 2° C.

3. Results

3.1. Composites

Toughness values of the various CTBN–epoxy composites and the unmodified resin are compared over the decreasing temperature range in Fig. 1. At approximately $-20°$ C, G_{Ic} of pure epoxy falls to 50% of its room-temperature value and remains relatively constant at all lower temperatures. The composites also undergo a decrease in G_{Ic} at $-20°$ C, but in general retain a level of toughness significantly greater than that of the unmodified resin between -20 and $-80°$ C. Rubber A modified material, which has both the smallest

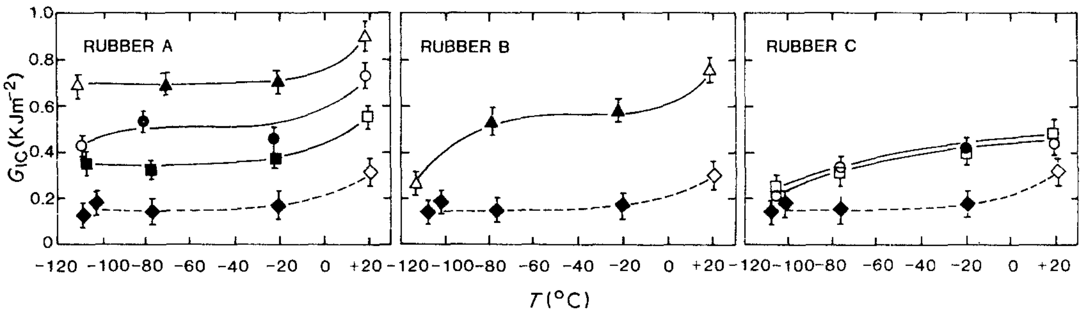


Figure 1 Toughness dependence on temperature of epoxy–rubber composites; shaded data points refer to continuous cracking, open points refer to stick–slip cracking. For △, $V_R = 0.18$; ○, $V_R = 0.12$; □, $V_R = 0.06$; and ---◇--- represents 100% epoxy.

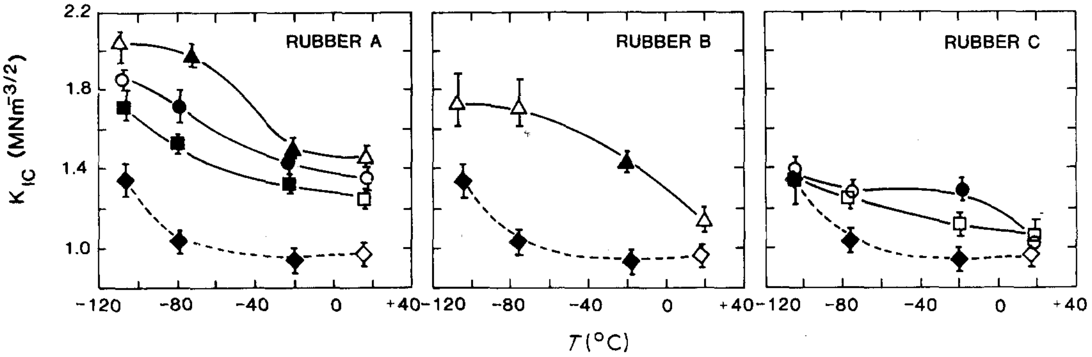


Figure 2 Critical stress intensity factor as a function of temperature for epoxy–rubber composites. For △, $V_R = 0.18$; ○, $V_R = 0.12$; □, $V_R = 0.06$; and ---◇--- represents 100% epoxy.

particles (Table II) and the highest toughness at room temperature, generally shows no further reduction in G_{Ic} at temperatures below − 80° C. For materials containing Rubbers B and C, however, the G_{Ic} values continue to drop significantly below − 80° C, and at − 110° C approach the level of pure epoxy.

A transition in fracture mode also occurs at − 20° C (Fig. 1). Contrary to the normal stick–slip fracture (alternating crack propagation and arrest) of all the materials at room temperature, continuous cracking (stable propagation) is observed in the unmodified resin and most of the composites at low temperatures. Composites with high volume fractions of rubber revert back to stick–slip behaviour near − 110° C.

In contrast to the drop in fracture energy at low temperatures, K_{Ic} of the composites increases over the same temperature range as shown in Fig. 2. K_{Ic} of the unmodified resin remains constant between + 20 and − 80° C and subsequently rises by 40% between − 80 and − 110° C. The fracture toughness values of Rubber A containing materials are also 40% higher between − 80 and − 110° C than at + 20° C. Similarly, for composites with larger particles (Rubbers B and C), K_{Ic} increases below − 20° C but more gradually. Rubber C material in particular shows the smallest variation with temperature; its values at − 110° C coincide with those of the unmodified resin.

Fig. 3 shows the low-temperature dependence of elastic modulus. The unmodified resin begins to increase significantly below − 20° C and rises to three times its ambient value at − 110° C. This behaviour is indicative of a secondary transition which has been reported by others [16, 17] between − 40 and − 80° C, depending on frequency and cure conditions. All composites follow a

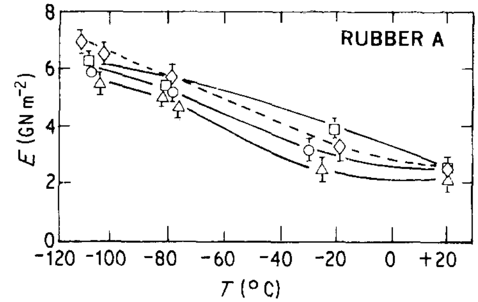
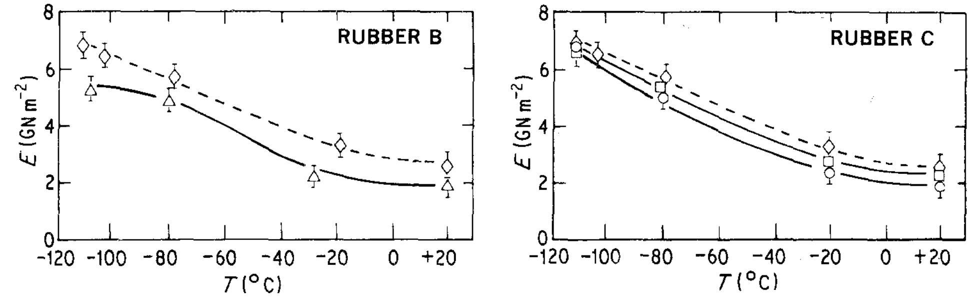


Figure 3 Young's modulus dependence on temperature for epoxy–rubber composites. For △, $V_R = 0.18$; ○, $V_R = 0.12$; □, $V_R = 0.06$; and ---◇--- represents 100% epoxy.



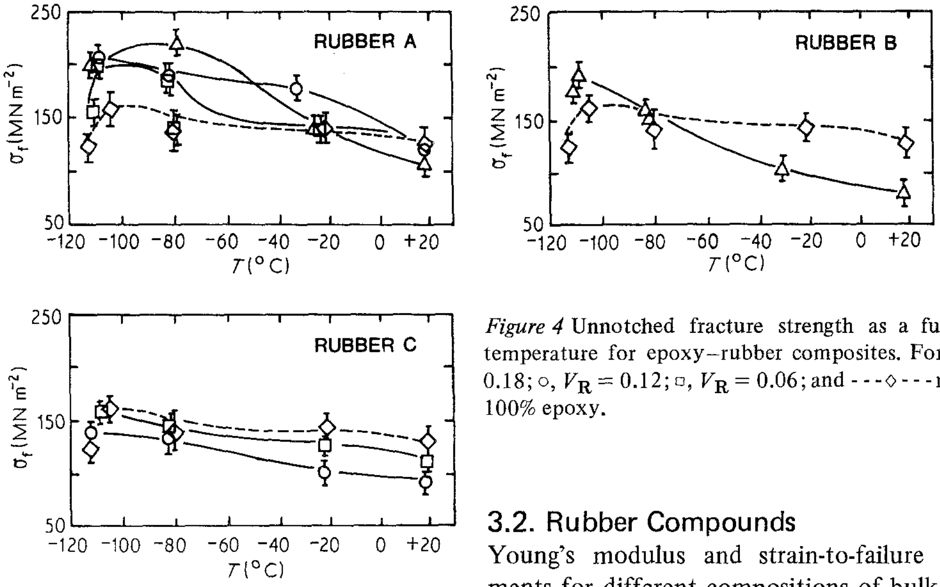


Figure 4 Unnotched fracture strength as a function of temperature for epoxy–rubber composites. For △, $V_R = 0.18$; ○, $V_R = 0.12$; □, $V_R = 0.06$; and - - -◇- - - represents 100% epoxy.

similar curve with modulus values for large volume fractions of rubber falling below those for smaller concentrations as expected. At − 110° C the composite moduli approach or coincide with that of pure epoxy.

The effect of low temperature on unnotched fracture strength is illustrated in Fig. 4. σ_f of the pure resin increases slightly down to − 80° C and reaches a maximum at approximately − 104° C before dropping to its initial ambient value at − 110° C. In general the composites start to show a marked increase in strength at approximately − 30° C, coincident with the onset of modulus increase, which leads to a peak in the σ_f–T curves between − 80 and − 110° C. In this temperature range, the σ_f values are nearly twice those measured at + 20° C.

3.2. Rubber Compounds

Young's modulus and strain-to-failure measurements for different compositions of bulk rubber–epoxy are summarized in Tables IV and V. Using rubber elasticity theory [18], E was obtained by measuring the tangent of a nominal stress (σ_N)–extension ratio (λ) curve, exemplified in Fig. 5, at $\lambda = 1$ where λ is related to the nominal strain, e, by $\lambda = e + 1$. Hooke's law is obeyed only at strains less than approximately 1%; beyond this extension, up to about 400% ($\lambda = 5$), the properties of rubber are defined in terms of the shear modulus G, where

$$\sigma_N = G\left(\lambda - \frac{1}{\lambda^2}\right). \tag{1}$$

This equation is described by the theoretical curve in Fig. 5. At even greater extensions, the stress rises steeply due to strain-induced crystallization and bond-stretching of the rubber molecules [18], and the modulus increases rapidly to a limiting

TABLE IV Young's modulus, E, of rubber compounds at 23° C

CTBN rubber	Composition (epoxy to CTBN equivalent ratio)	E (MN m^{-2})
A	1:1	1.32 ± 0.6
	2:1	3.81 ± 2.0
	3:1*	3.25 ± 0.3
B	1:1	1.98 ± 0.5
	2:1	1.3 ± 0.5
	4:1*	3.0 ± 1.0
C	2:1	2.62 ± 1.0
	4:1	2.32 ± 0.3

*Porous casting.

TABLE V Strain-to-failure of rubber compounds at 23° C

CTBN rubber	Composition (epoxy to CTBN equivalent ratio)	e_f
A	1:1	⩾ 9.5 ± 0.5
	2:1	6.1 ± 1.5
	3:1*	5.0 ± 1.0
B	1:1	⩾ 10.0
	2:1	⩾ 10.0
	4:1*	7.1 ± 1.1
C	2:1	⩾ 10.0
	4:1	⩾ 10.0

*Porous casting.

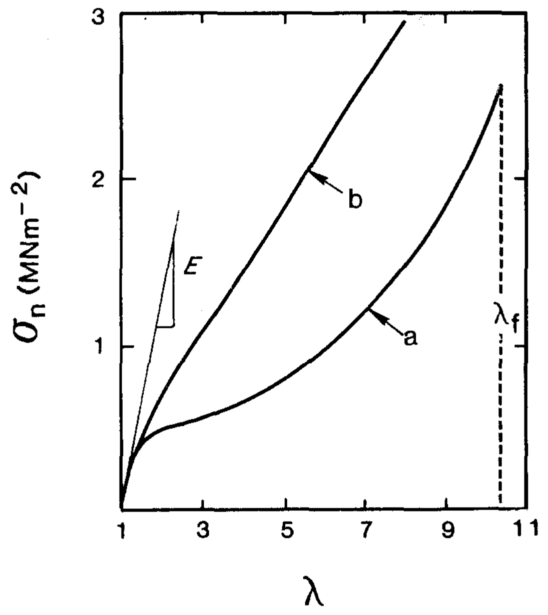


Figure 5 Nominal stress–extension ratio curve: (a) obtained for typical rubber–epoxy compound; (b) theoretical (Equation 1).

value before rupture occurs. Failure is indicated in Fig. 5 by the extension ratio λ_f, and the nominal failure strain e_f is then $(\lambda_f - 1)$.

The E values in Table IV increase by factors of 1.5 to 3 as the epoxy concentration in the rubber compound is raised, with the exception of Rubber C which appears insensitive to composition. No consistent trend favouring acrylonitrile content of the rubber is seen, however. In general, Young's modulus of the compounds lies between 1.0 and 3.0 MN m^{-2} over the range of compositions, and it follows from the relation $E = 3G$ [18] that the shear moduli are of the order of 0.3 to 1.0 MN m^{-2}.

The nominal failure strains in Table V indicate that the maximum extensibility of A and B rubber compounds decreases by up to 50% as the epoxide content is trebled or quadrupled. Rubber C is again insensitive to compositional changes and, with typical e_f values between 10 and 15, has the largest strain capacity of all the rubbers. At the lowest epoxide concentration (1 : 1), all the compounds can undergo strains greater than 900%; at higher epoxide concentrations the minimum measured strain is 500%. A trend is apparent where the lowest acrylonitrile content rubbers, B and C, undergo larger strains-to-failure than Rubber A, for a given composition.

Low-temperature effects on tensile modulus for the three rubbers are shown in Fig. 6. For all compositions of A and C, a decrease in temperature from 23 to − 40° C produces a nearly two-fold, monotonic increase in modulus. The lowest epoxy content Rubber B compound behaves identically. For higher epoxy concentrations in Rubber B, peaks in the E values which occur at approximately − 20 and − 30° C are followed unexpectedly by a sharp decrease as the temperature approaches − 50° C. This behaviour is not fully understood but may be due to porosity in the sample (Table IV) or to effects of epoxide inclusions in the rubber (described later).

Fig. 7 illustrates the dependence of e_f on tem-

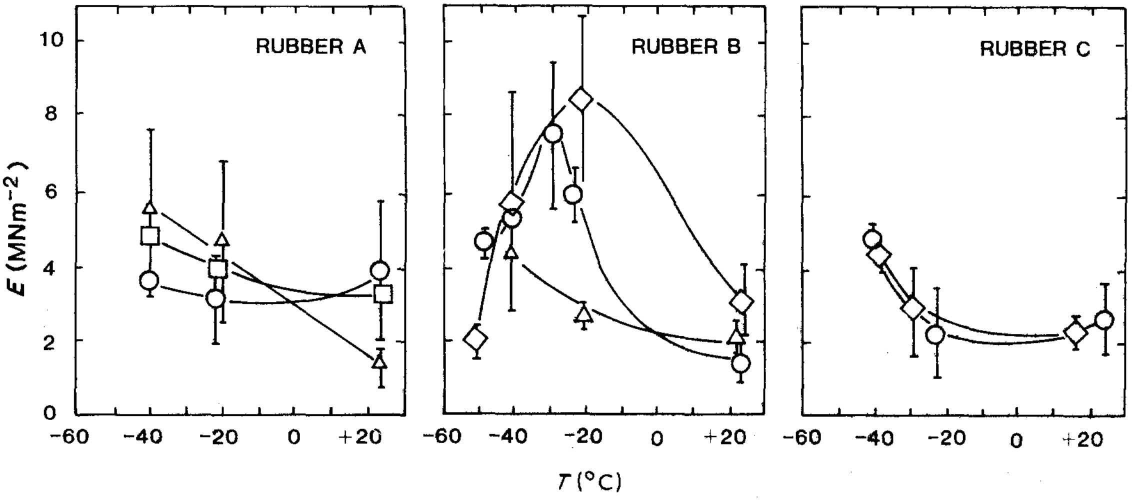


Figure 6 Young's modulus for CTBN–epoxy compounds from simple extension tests, as a function of temperature. Epoxy to CTBN equivalent ratio: △, 1 : 1; ○, 2 : 1; □, 3 : 1; and ◇, 4 : 1.

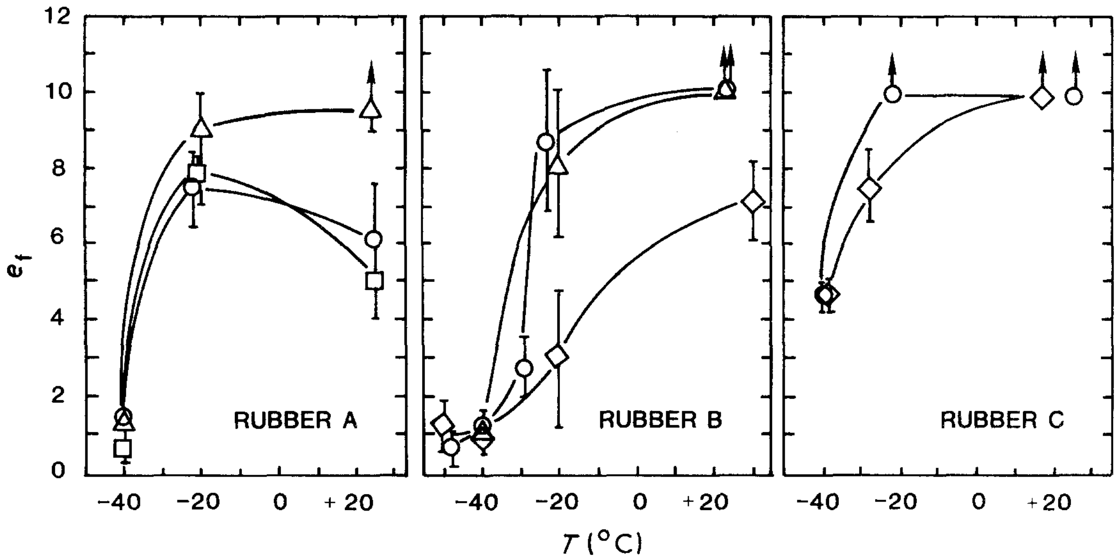


Figure 7 Strain-to-failure of CTBN–epoxy compounds from simple extension tests, as a function of temperature. Epoxy to CTBN equivalent ratio: △, 1 : 1; ○, 2 : 1, □, 3 : 1; and ◇, 4 : 1.

perature. In general, all three rubber types and their compounds undergo 700 to 1000% strains at temperatures above − 20° C; the largest strains occurs in the lowest acrylonitrile content rubbers. Below − 20° C, e_f decreases to approximately 1 for Rubbers A and B, and 5 for Rubber C. The transition temperature at which extensibility decreases sharply to its minimum value depends on composition of the compounds. Rubbers containing low levels of epoxy retain a greater capacity for large elongations at low temperatures than those with high concentrations. Fig. 7 indicates a shift in transition temperature from approximately − 20 to − 30° C as the acrylonitrile content decreases, i.e. from Rubber A to C.

The room-temperature tearing energies, Γ_t, of the rubber compounds, summarized in Table VI, depend on type and composition of the rubbers as well as on width of the specimen. Typical values of Γ_t range between 3 and 25 kJ m^{-2} which are representative of a vulcanized rubber [15] for example. Γ_t is highest for Rubber A compounds and follows a decreasing trend in order of lower acrylonitrile contents from B to C. In general, increasing the epoxide concentration of a given rubber results in higher tear energies except for Rubber C where the opposite effect is found. The decrease in Γ_t for 3 : 1 and 4 : 1 ratios in Rubbers A and B is attributed to porosity. Also, reducing the specimen width generally results in a lower tear energy. For example, Γ_t for a 1 cm wide sample of Rubber A is between 20 and 60% less than for the 3 cm wide sample, depending on composition.

TABLE VI Tear energies of rubber compounds at 23° C

CTBN rubber	Composition (epoxy to CTBN equivalent ratio)	Γ_t (kJ m^{-2}) at specimen width, *w*	
		3 cm	1 cm
A	1 : 1	10.3 ± 0.6	–
	2 : 1	22.3 ± 2.7	8.6 ± 0.9
	3 : 1*	16.9 ± 2.1	12.9 ± 1.0
B	1 : 1	–	–
	2 : 1	13.0 ± 1.0	9.7 ± 0.3
	4 : 1*	9.8 ± 0.2	11.5 ± 0.3
C	2 : 1	6.1 ± 0.1	–
	4 : 1	3.3 ± 0.7	–

*Porous casting.

4. Discussion

4.1. Toughening model

The microfracture processes observed in rubber-modified epoxy and described in detail elsewhere [6] can be summarized as follows. A crack in the composite propagates through the brittle epoxy matrix and leaves rubber particles bridging the crack as it opens. The particles stretch to large strains and ultimately fail by tearing. A model for particle failure based on dissipation of the stored elastic strain energy in tearing of the rubber leads to an expression for the critical extension ratio for particle failure, Γ_t,

$$\lambda_t^2 - \frac{4}{\lambda_t} + 3 = \frac{4\Gamma_t}{\bar{G}\bar{r}}. \qquad (2)$$

The failure strain depends directly on the rubber tear energy, Γ_t, and varies inversely with the particle size, $\bar{r}$, and effective rubber shear modulus, $\bar{G}$. Referring again to the strain energy storage and tearing characteristic of the rubber particles, an independent expression can be derived for their toughening contribution to the composite, ΔG_{Ic},

$$\Delta G_{Ic} = \bar{G}\left(\lambda_t^2 + \frac{2}{\lambda_t} - 3\right) V_p \bar{r}. \qquad (3)$$

This equation predicts a linear dependence of the toughness increase on the volume fraction and size of rubber particles. By combining the condition for particle failure in Equation 2 with Equation 3 the predicted toughness increase takes the final form

$$\Delta G_{Ic} = \left(1 - \frac{6}{\lambda_t^2 + \lambda_t + 4}\right) 4\Gamma_t V_p. \qquad (4)$$

The toughness of the composite as a whole can be expressed using a simple rule of mixtures

$$G_{Ic} = G_{Ic}^{E}(1 - V_p) + \Delta G_{Ic}, \qquad (5)$$

where the superscript "E" refers to the epoxy matrix. Referring to Equation 4, the toughness increase converges to

$$\Delta G_{Ic} \simeq 4\Gamma_t V_p \qquad (6)$$

for large tearing strains ($\lambda_t > 4$), and decreases towards an approximate average value

$$\Delta G_{Ic} \simeq 2\Gamma_t V_p \qquad (7)$$

for larger particles ($\lambda_t = 2, 3$).

4.2. Applicability of the model at low temperatures

Fig. 1 illustrates the toughness decrease of both unmodified and rubber-modified epoxy resin as the temperature is lowered from 20 to − 110° C. According to Equation 5, this reflects a loss in the energy-absorbing capability of either the matrix (G_{Ic}^{E}) or of the rubber particles (ΔG_{Ic}) or both. The toughness of the pure resin decreases to a constant value between − 20 and − 110° C which is 50% lower than at room temperature. G_{Ic} of the composites follows a similar trend but remains significantly greater than that of the epoxy resin. The shape of the curves in Fig. 1 suggests that the loss in toughness of the composites may be controlled by the low-temperature transition in the epoxy matrix phase: however, an appreciable toughness contribution of the rubber particles themselves is apparent from the magnitude of the composite G_{Ic} values.

According to the model described by Equation 4, the toughening contribution of the particles depends on their strain capability and tear energy. A first approximation to these properties at low temperatures can be arrived at from the bulk rubber compounds. Both the increase in modulus (Fig. 6) and the decrease in failure strain (Fig. 7) between − 20 and − 40° C reflect the onset of a glass transition (T_g) in that temperature range. A T_g near − 40° C was observed by other investigators [19] for compounds of Rubber B having identical epoxy–CTBN compositions to those used in this study. Similarly, loss-factor, tan δ, studies [16] showed transition behaviour ranging from distinct epoxy and rubber peaks at − 81 and − 55° C, respectively, to overlapping peaks at − 50° C over two decades of frequency. Pure CTBN rubbers undergo a glass transition between approximately − 50 and − 80° C the lower temperatures corresponding to low acrylonitrile contents [11]. For the epoxy–amine system used in this study, a secondary transition has been reported between − 46 and − 74° C depending on cure conditions. Unknown variables such as particle strain rate (frequency) during composite fracture and particle composition preclude precise evaluation of particle glass transition temperatures. Furthermore, the particle T_g is dependent upon its morphology: for a two-phase polymer, two discrete glass transitions corresponding to those of the pure constituents are expected, whereas an immiscible polymer blend exhibits a weighted average of the latter two transitions [20]. Although a two-phase microstructure consisting of discrete spherical epoxide inclusions up to 1 μm in diameter dispersed in a rubbery matrix has been observed in the rubber compounds [13], the nature of the inclusions and matrix and their effect on the particle T_g is not known.

These observations suggest two conclusions regarding particle behaviour at low temperature. First, rubber particles in the composites should lose ductility, resulting in decreased tearing strains, at temperatures below − 40° C. Second, the tear energy of the particles should increase as the temperature is lowered towards the T_g due to an increase in internal viscosity which hinders molecular mobility [18, 21]. For example, Γ_t of a butadiene–acrylonitrile elastomer with a $T_g = -38°$ C, increases by an order of magnitude

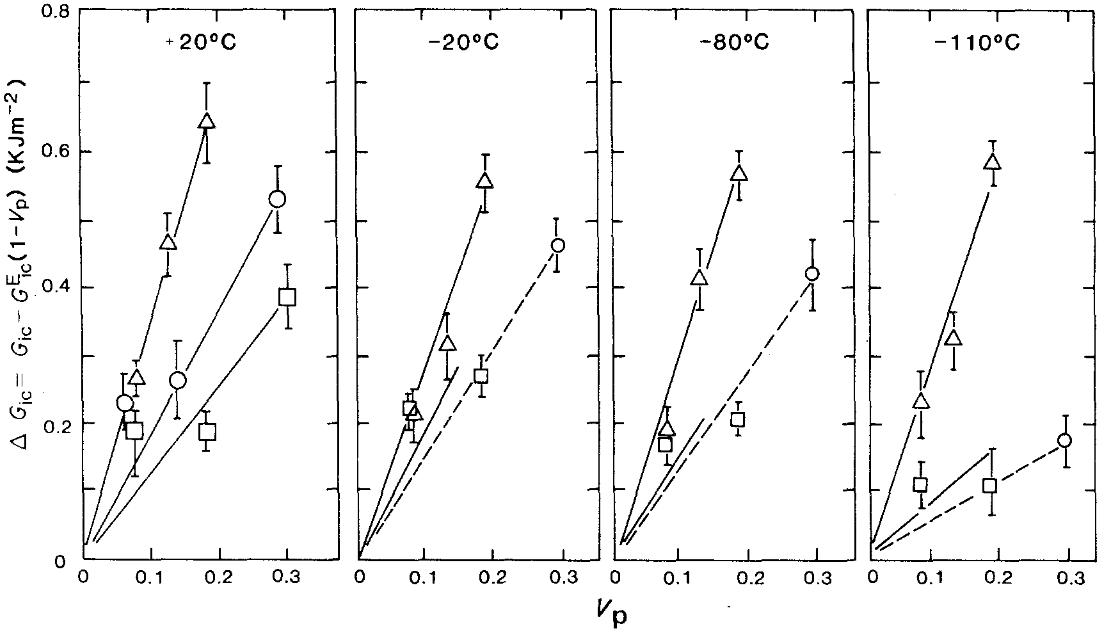


Figure 8 Increase in composite toughness as a function of particle volume fraction at various low temperatures. Rubber A, △, Rubber B, ○; and Rubber C, □.

as the temperature is lowered from 20 to − 20° C [21]. A decrease in λ_t and an increase in Γ_t of the rubber particles at low temperature have opposite effects on ΔG_{Ic} according to the model's predictions (Equation 4). If the tear strain decreases more rapidly than the tear energy increases, then an overall decrease in the particle toughening contribution is expected. This condition is illustrated by the low-temperature data in Fig. 1 showing a toughness loss of the composites: G_{Ic} decreases as the particles lose their ability to stretch, but remains significantly higher than $G_{\mathrm{Ic}}^{\mathrm{E}}$ as long as the energy required to tear the particles (Γ_t) is greater than the fracture energy of the matrix, at temperatures above the glass transition of the rubber.

An approximation of rubber particle properties can be made using the toughness data of Fig. 1. Values of ΔG_{Ic} calculated using Equation 5 are plotted in Fig. 8 as a function of the volume fraction of particles. The data can be adequately described by a linear dependence which follows the model's prediction (Equation 4). A previously described method is then used to calculate apparent tear energies of the particles from the slopes of the experimental lines [6]. Based on the strain-to-failure measurements for the bulk rubbers (Fig. 7), λ_t of a particle at − 20° C is taken as similar to its 20° C value. Thus, at − 20° C, Γ_t is estimated by the ratio ($\Delta G_{\mathrm{Ic}}/4V_{\mathrm{p}}$) for particles of Rubbers A and B ($\lambda_t > 4$), and by ($\Delta G_{\mathrm{Ic}}/2V_{\mathrm{p}}$) for particles of Rubber C ($\lambda_t \approx 2$), according to Equations 6 and 7, respectively. As a first approximation, the tearing strain of particles of all sizes at temperatures below − 40° C is assumed to be less than 4 (e.g. $\lambda_t \approx 2$, $e_f \approx 1$; see Fig. 7), and Γ_t is again approximated by the quantity ($\Delta G_{\mathrm{Ic}}/2V_{\mathrm{p}}$). These estimations of − 80 and − 110° C particulate tear energies are shown in Table VII together with those for 20 and − 20° C. If, instead, λ_t is assumed to have decreased significantly at temperatures below − 40° C and is taken as 1.1 ($e_f = 0.1$), then the Γ_t values in Table VII at − 80 and − 110° C

TABLE VII

Rubber	Γ_t (kJ m^{-2})			
	20° C	− 20° C	− 80° C	− 110° C
A	0.88 ± 0.10	0.73 ± 0.05	1.57 ± 0.06	1.51 ± 0.08
B	0.46 ± 0.05	0.40 ± 0.05	0.72 ± 0.10	0.29 ± 0.08
C	0.64 ± 0.13	1.00 ± 0.30	0.78 ± 0.20	0.42 ± 0.12

would be ten times higher. Similarly, for $\lambda_t = 1.01$ ($e_f = 0.01$), the -80 and $-110°$ C tear energies would be a hundred times higher than shown.

For the estimated values shown in Table VII, the particle tear energy of a given rubber increases by up to a factor of two between 20 and $-80°$ C and then decreases between -80 and $-110°$ C. In the cases where λ_t was assumed to be of the order of 1.1 and then 1.01, at temperatures below $-40°$ C, the magnitude of Γ_t values would range from 3 to $16\,\text{kJ m}^{-2}$ and 30 to $160\,\text{kJ m}^{-2}$, respectively. The former range in tear energy values (for $\lambda_t = 1.1$) is typical of that obtained for bulk rubber [15] and particularly of those measured for bulk CTBN rubber compounds shown in Table VI. Those Γ_t values obtained for $\lambda_t = 1.01$, however, are considered to be unrealistically high. Thus, a value of λ_t between 1.1 and 2 is estimated to be likely at temperatures between -40 and $-110°$ C. The unavailability of an optical microscope with a cold-stage precluded direct verification of particle failure strains at low temperatures.

In general, a glass transition in the particles can account for a rise in Γ_t between ambient temperature and -40 to $-80°$ C. A decrease in Γ_t in the vicinity of $-80°$ C is also consistent with the fact that below the T_g of the pure rubber, the particles becomes glassy as molecular flow ceases and the tear energy approaches the surface energy [18, 22]. Although the tear energies of the particles in Table VII follow the general trend expected from lowering the temperature, they do not increase as much as expected from typical bulk rubbers. If those estimated values are indeed representative of the rubber particles (i.e. $\lambda_t \approx 2$), then the difference in low-temperature behaviour can be attributed in part to a volume effect on Γ_t: the energy dissipated in molecular flow in a large volume of rubber should be significantly greater than that in a microscopic particle [22]. This is supported by the tear energy values in Table VI which decrease as the specimen width is reduced. Another consideration is the effect of low temperature on the adhesion between the rubber particles and the resin matrix. The thermal expansion coefficient of rubber is an order of magnitude greater than that of epoxy resin, and a particle in a composite will attempt to contract away from the matrix as the temperature is lowered. Consequently, a well-bonded particle is subject to a triaxial tension [23, 24] which, if sufficiently high, could induce premature failure of the rubber at the particle–matrix interface. This in turn would reduce the strain capacity and tear energy of the particle during fracture. Cavities surrounding the particles in a composite tested at $-80°$ C, shown in Fig. 9, may be illustrations of this effect observed, however, only at temperatures of $-80°$ C and below.

As previously discussed in detail [6], ΔG_{Ic} depends on particle size only insofar as it reflects the chemical nature of the rubber (% acrylonitrile), and, hence, tear energy and tear strain of the

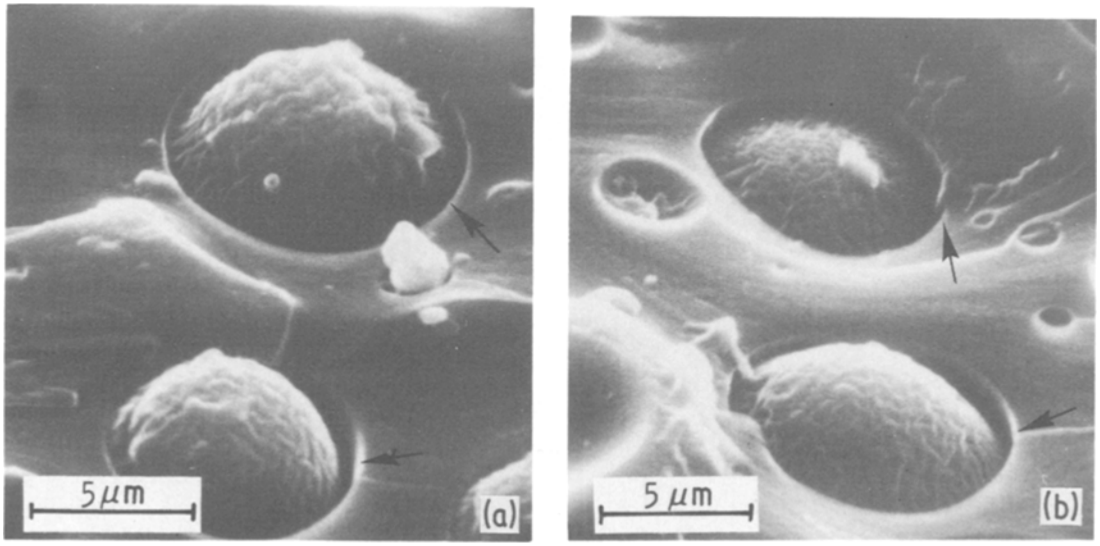


Figure 9 Torn rubber particles in a composite tested at $-80°$ C. The cavities surrounding the particles are an indication of interfacial failure due to thermal contraction of the rubber.

particles. This is expected also at low temperatures, based on bulk rubber data. For example, Tables IV and VI show trends of increasing E and Γ_t with increasing acrylonitrile content (from A to C), while Table V and Fig. 7 indicate a corresponding rise in T_g and decrease in e_f.

Other low-temperature data for CTBN-modified epoxy [1, 7], where the lowest test temperature was − 55° C, show the same trend of decreasing toughness as observed in this study. In particular, McGarry *et al.* [1] report a drop in the ambient G_{Ic} value of pure epoxy to a nearly ten-fold lower, constant value at − 20° C. Similarly, both rubber-modified epoxy/hardener systems examined lose the majority of their toughness between 20 and 0° C, attaining fairly constant lower values at − 20° C, which are nevertheless between 4 and 10 times higher than that of the pure epoxy. The investigators maintain that at low temperatures the rubber phase is not sufficiently elastomeric to induce significant molecular orientation at the crack tip which, by presenting an obstacle to crack growth, is the postulated mechanism of increasing fracture energy. The fact that the composite toughness is markedly higher than that of the pure epoxy at low temperature argues, however, that sufficient molecular mobility does exist in the rubber particles, to temperatures as low as − 80° C, to provide a significant toughening contribution through particle tear energy. This observation cannot be explained by other theories which attribute rubber particle toughening exclusively to matrix flow processes since these are suppressed below the epoxy resin T_g. Thus, the particle stretching–tearing mechanism can account for toughness contributions at low temperature even when particle ductility is reduced, which lends further support to its role toughening potential at ambient temperature.

5. Conclusions

The particle–stretching model is used to explain the suppression of rubber toughening at low temperatures. A glass transition between − 40 and − 80° C is estimated for the rubber particles, based on elastic modulus and failure strain measurements on bulk rubber–epoxy compounds. This transition produces both a reduction in failure strain and an increase in tear energy of the particles. The observed coincident loss in composite toughness bears out the prediction that tear strain decreases more rapidly than tear energy increases. A significant tear energy contribution of the rubber particles to overall fracture energy is reflected by the composites retaining higher toughness values than the unmodified epoxy at low temperatures. Direct measurements of particulate parameters at low temperature are difficult but desirable to obtain a more quantitative corroboration of the model.

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