

Rubber-Modified Epoxies. II. Morphology and Mechanical Properties

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Synopsis

A wide range in morphology paralleling a spectrum of phase separated and dissolved rubber, can be developed in rubber-modified epoxies through control of rubber-epoxy compatibility and cure conditions. These morphologies result in different stress response mechanisms. Dissolved rubber promotes plastic deformation and necking at low strain rates that provide large increases in the elongation to break. Dissolved rubber is ineffective in providing improvement at impact rates. Phase separated rubber domains can also increase the elongation to break since cavitation is promoted at the interfacial boundary. The elongation is limited to the extent of cavitation and therefore large increases in the energy to break are not found. The presence of rubber domains was found to be a necessary but not sufficient condition for impact energy improvement. Optimum materials contained a relatively large amount of dissolved rubber and a low volume fraction of phase separated rubber. These combine high elongations at low strain rates with improved impact properties.

INTRODUCTION

The addition of a low molecular weight reactive liquid rubber can improve the low strain rate toughness and impact strength of cured epoxy resins.¹⁻³ This improvement can often be achieved without significant degradation of thermal and mechanical properties. *In situ* phase separation produces rubber-rich domains (0.1 to 5.0 μm in diameter) that can promote toughening by different mechanisms. Rubber that does not phase separate remains in the epoxy matrix and enhances ductility.

The elastomers used in the present study are carboxyl-terminated copolymers of butadiene and acrylonitrile (CTBN). The carboxyl endgroups react with a bis epoxide to form a low molecular weight intermediate of epoxy-terminated rubber.⁴ This intermediate promotes interfacial bonding in two phase systems.

Increased acrylonitrile content of the rubber enhances its compatibility with diglycidyl ether of bisphenol-A (DGEBA) epoxy resin. Compatibility can also be increased by increasing the temperature of cure.

Gelation is a macroscopic phenomenon that occurs during the cure of a thermoset polymer. The gel point reflects the onset of formation of a three-dimensional network structure which occurs at a fixed chemical conversion that can be predicted from the functionality of the starting resin.⁵ It has been demonstrated^{6,7} that domain growth in a rubber-modified epoxy is terminated at gelation. If gelation occurs prior to phase separation no domains appear.

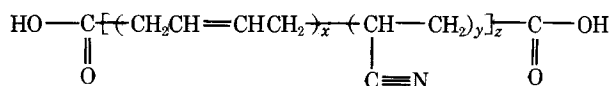
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The objective of this study was to control the development of morphology and then relate the mechanical properties to the morphologies developed. The first part of the study is reported separately.⁸

MATERIALS

The elastomers employed are low molecular weight copolymers of butadiene and acrylonitrile produced by the B. F. Goodrich Co. and marketed under the trade name Hycar CTBN. The idealized structure of Hycar CTBN is



where $x = 5$, $y = 1$ and $z = 10$ for a typical copolymer [CTBN($\times 8$)]. (Properties of CTBN rubbers are found in ref. 8.) Two rubber modifiers, CTBN($\times 13$) and CTBN($\times 8$), with 27 and 17 wt % acrylonitrile were examined. CTBN($\times 13$) contains the higher acrylonitrile content and is the more compatible modifier. Three cure temperatures were employed to widen the compatibility range of each copolymer.

The base resin was Epon 828, a low molecular weight liquid DGEBA resin manufactured by Shell Chemical Co. Epoxy and rubber were prereacted at 150°C in the presence of triphenylphosphine. Prereaction insures the formation of the epoxy-rubber intermediate and promotes blending of epoxy and rubber prior to cure. Chain-extended solid resins were produced by reaction of the epoxy-terminated rubber with bisphenol-A (BPA).

Dicyandiamide, a multifunctional curing agent, was used. Monuron, 3-(p-chlorophenyl)-1,1-dimethylurea (duPont), was used as an accelerator. The curing agent and accelerator were incorporated by coextrusion with the epoxy resin.

Previous work,^{6,7} and results from the present study⁸ indicate that morphology development is arrested at gelation. It is therefore only necessary to gel at a prescribed temperature to develop the intended morphology. The resin can then be cured at a second cure temperature to develop optimum matrix properties. All the formulations, modified and unmodified, were gelled at a gel temperature and then postcured at 210°C. The formulations are presented in Table I. Curing conditions are presented in Table II.

TABLE I
Composition and Notation for Model Resins

Chemicals	Composition		
	241 (U)	242 (13)	243 (8)
Epon 828	69.1	60.0	60.0
Bisphenol-A	30.9	25.0	25.0
CTBN	0	15.0 (CTBN $\times 13$)	15.0 (CTBN $\times 8$)
Dicyandiamide (phr)	1.5	1.5	1.5
Monuron (phr)	0.75	0.75	0.75

TABLE II
Cure Conditions and Notation

Resin	Modifier	Gel temperature/time		
		210°C/40 min ^a	170°C/30 min ^b	130°C/1 hr ^b
241 (U)	none	241/210 ^c	241/170	241/130
242 (13)	CTBN (1300 × 13)	242/210	242/170	242/130
243 (8)	CTBN (1300 × 8)	243/210	243/170	243/130

^a Gel and cure at 210°C/40 min.

^b Post-cured 40 min at 210°C.

^c 241/20 represents composition 241 cured and gelled at 210°C.

EXPERIMENTAL

Thermomechanical analysis (TMA) was used to determine glass transition temperatures. The increase in the coefficient of thermal expansion above T_g is detected as a break in the displacement of the probe that rests on the specimen.

A fully automated torsional braid analyzer (TBA) was used to obtain dynamic mechanical spectra (~1 Hz) which provided information on phase separation. A review of the technique and application has been published.⁹ An automated TBA system is commercially available from Plastics Analysis Instruments, Inc., Princeton, NJ.

Low strain rate tensile testing (ASTM D638) was conducted on an Instron model TM-S mechanical tester. The crosshead speed of 0.254 cm/min provided a strain rate of 0.113 min⁻¹. All testing was conducted at ambient conditions of 25°C and 50% relative humidity (RH) in an environmentally controlled room.

The notched Izod impact test (ASTM D256) was employed to obtain the high strain rate response of cured epoxy resins.

Scanning electron micrographs (SEM) of rubber-modified epoxy resins were obtained on an AMR 1000 SEM instrument. The specimen was fractured immediately after removal from liquid nitrogen. The fracture surface was coated with a thin layer of gold using a high-vacuum gold sputterer.

Transmission electron micrographs (TEM) were obtained on ultrathin microtomed sections. Each specimen was stained with osmium tetroxide prior to sectioning. The stained rubber-rich domains appear as darkened areas in the transmission electron micrographs. The epoxy phase appears white.

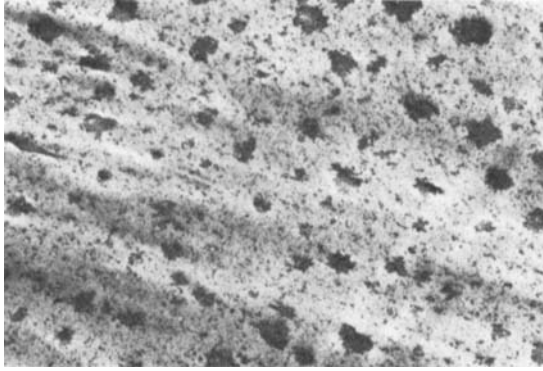
Specimen preparation techniques were developed to obtain defect-free test coupons from the powdered epoxy resin formulations. Tensile testing (the elongation to break in particular) is highly defect dependent. Successful specimen preparation consisted of fusing the powders under moderate vacuum prior to cure.

RESULTS AND DISCUSSION

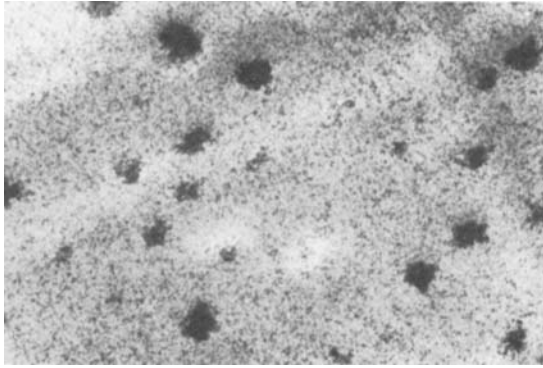
Reports^{1,3} and microscopy results from the current work^{2,8} indicated that the more compatible formulations provide smaller rubber domains.

The volume fraction of phase separated rubber may be less than that expected from the amount of rubber added. This was detected by several techniques.

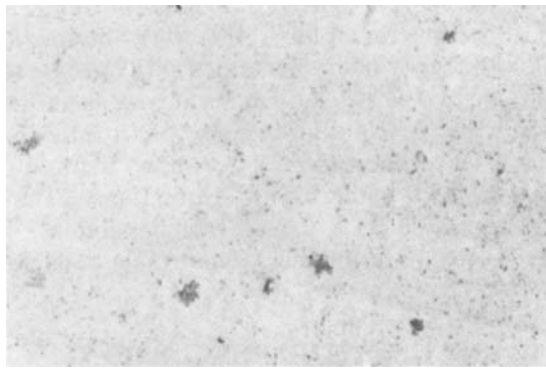
Transmission electron micrographs of OsO₄-stained thin sections are pre-



1 μ
(a)

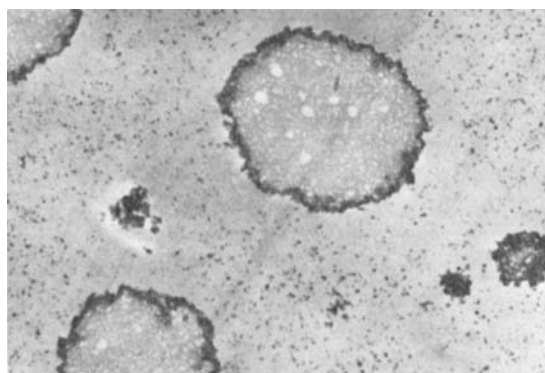


1 μ
(b)

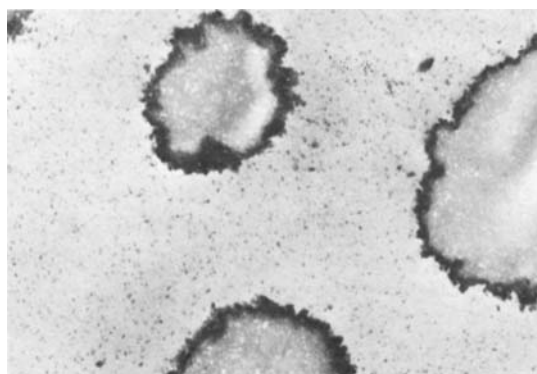


1 μ
(c)

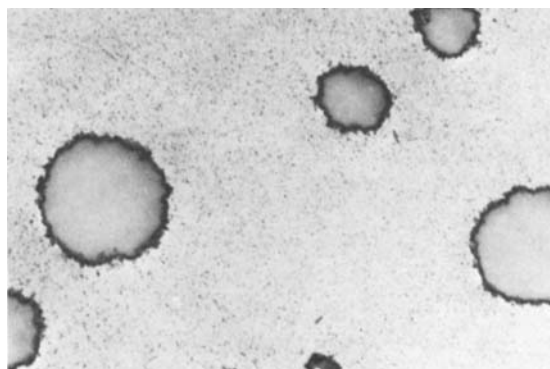
Fig. 1. TEM micrographs of rubber-modified epoxies: (A) 242/130, (B) 242/170, (C) 242/210, (D) 243/130, (E) 243/170, (F) 243/210.



1 μ
(d)



1 μ
(e)



1 μ
(f)

Fig. 1. (Continued from previous page.)

sented in Figure 1. Quantitative microscopic analysis¹⁰ was conducted using the set of TEM micrographs; the average domain size, volume fraction, and number of domains/area of phase separated rubber were determined (Table III).

Greater acrylonitrile content of the copolymer and higher cure temperature

TABLE III
 Morphological Data

Material	D^a	ϕ_2^b	$N/100 \mu\text{m}^2^c$
242/210	—	0.000	0
242/170	0.2	0.035	230
242/130	0.2	0.070	190
243/210	1.0	0.100	20
243/170	1.0	0.130	24
243/130	1.0	0.182	30

^a Average domain size (μm).

^b Volume fraction of phase separated rubber.

^c Number of domains on $100 \mu\text{m}^2$ of test plane.

both promote dissolution of rubber rather than precipitation. Sample 242/210 is the extreme case where all the rubber appears to have remained in solution. This material is clear and the large rubber domains evident in samples 242/170 and 242/130 could not be detected with electron microscopy or with TBA. The TBA spectrum of this rubber-modified epoxy is presented in Figure 2. The absence of a distinct damping peak, associated with phase separated rubber,⁸ and the optical clarity indicate either complete phase blending¹¹ or the absence of particles above a small critical size.

Rubber dissolved in the epoxy matrix phase plasticizes the epoxy glass transition temperature (${}_E T_g$). In principle, the fraction of dissolved rubber can be predicted from the Gordon-Taylor copolymer equation¹²

$$\frac{1}{T_g} = \frac{1}{W_1 + KW_2} \left(\frac{W_1}{T_{g1}} + \frac{KW_2}{T_{g2}} \right) \quad (1)$$

where W_1 and W_2 are weight fractions of epoxy and rubber; T_{g1} and T_{g2} are the T_g 's of unplasticized epoxy and pure rubber⁸; T_g is the glass transition temperature of the homogeneous epoxy-rich matrix phase; and K is the normalization constant. The glass transition temperatures for the series of rubber-modified

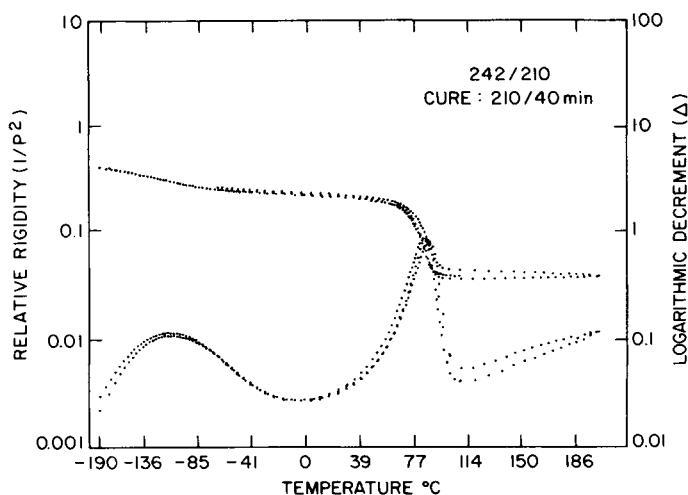


Fig. 2. TBA spectrum of 242/210. Note the absence of a rubber relaxation at about -30°C .

TABLE IV
Glass Transition Temperatures of Model Resins Determined at 10°C/min by TMA

Resin	Gel temperature		
	130°C ^a	170°C ^a	210°C ^b
241 (U)	101	103	100
243 (8)	91	83	79
242 (13)	85	83	75

^a Post-cured 210°/40 min.

^b Gel and cure at 210°/40 min.

and unmodified cured epoxies are shown in Table IV. The normalization constant (K) can be evaluated from 242/210. This resin does not contain phase separated rubber, hence $W_2 = 0.15$ and $W_1 = 0.85$. K was determined to be 0.88. The weight fraction of dissolved rubber can then be calculated from the plasticized epoxy T_g of each resin (see Table V).

The volume fraction of phase separated rubber measured by TEM may appear to exceed the amount of elastomer added (Table III). Prereaction of epoxy and CTBN insures copolymer formation. CTBN and epoxy must then be incorporated in the domains since the domain size is larger than the molecular length of CTBN. TEM analysis has shown that epoxy is present as phase segregated

TABLE V
Weight Fraction of Dissolved Rubber Determined from the Gordon-Taylor Equation and Plasticization of Epoxy Glass Transition Temperature

Resin	Gel temperature		
	130°C	170°C	210°C
241 (U)	0.00	0.00	0.00
243 (8)	0.041	0.082	0.088
242 (13)	0.076	0.095	0.150

TABLE VI
Tensile Test Data and Morphological Results^a

Material	ϕ_2	D	E ^b	E_r^c	σ_y^d	σ_{yr}^e	ϵ_b^f	T_g^g
241 (U)/210	—	—	1256	1.00	63.11	1.00	22.8	9.65
242 (13)/210	0.00	—	1265	1.01	58.97	0.93	41.1	19.22
243 (8)/210	0.100	1.0	1136	0.90	45.06	0.71	16.9	6.00
241 (U)/170	—	—	1218	1.00	61.66	1.00	33.7	14.33
242 (13)/170	0.035	0.20	1138	0.93	51.74	0.84	53.1	21.08
243 (8)/170	0.130	1.0	1000	0.82	40.37	0.65	21.5	7.16
241 (U)/130	—	—	1211	1.00	60.56	1.00	20.3	8.20
242 (13)/130	0.070	0.20	1063	0.88	47.61	0.79	45.3	16.88
243 (8)/130	0.182	1.0	935	0.77	38.30	0.63	24.8	7.78

^a Strain rate: 0.113 min⁻¹; conditions: 25°C and 50% relative humidity.

^b Young's modulus (MPa).

^c Relative Young's modulus.

^d Yield stress (MPa).

^e Relative yield stress.

^f Elongation to break (%).

^g Toughness (MPa).

inclusions within the larger rubber domains. These epoxy inclusions are evident in TEM micrographs of 243/130 and 243/170 (see Fig. 1). The composition of the domains can be obtained from a material balance of dissolved rubber determined from the Gordon-Taylor equation and the volume fraction of phase separated domains obtained with quantitative microscopy.

Tensile properties for the series of modified and unmodified cured epoxy resins are presented in Table VI. Morphological data discussed earlier are also presented in this table.

The relative modulus decreases with increasing volume fraction of phase separated rubber. The same maximum value is found in the 241 unmodified resins and 242/210. They are all single phase polymers. The 242/210 resin is rubber modified but the rubber is not phase separated. It is interesting to note that dissolved rubber is not as detrimental to the tensile modulus as phase separated rubber.

The generalized Kerner equation^{13,14} can be used to predict the relative modulus as a function of the volume fraction of the dispersed phase (ϕ_2)

$$\frac{M}{M_1} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2} \quad (2)$$

where M is the modulus (shear, Young's, or bulk) of the composite and M_1 is the modulus of the matrix phase. The parameters A and B account for Poisson's ratio of the matrix (ν), which is assumed to be 0.35, and the relative moduli of filler and matrix phases

$$A = (7 - 5\nu)/(8 - 10\nu) \quad (3)$$

$$B = \frac{M_2/M_1 - 1}{M_2/M_1 + A} \quad (4)$$

Since $M_1 \gg M_2$, $B = -1/A = 0.86$. ψ depends on the volume fraction and the maximum packing fraction of the filler (ϕ_m):

$$\psi = 1 + [(1 - \phi_m)/\phi_m^2]\phi_2 \quad (5)$$

The final expression for the relative tensile modulus of a rubber-modified epoxy is

$$\frac{E}{E_1} = \frac{1 - \phi_2}{1 + 0.86(1 + 1.1\phi_2)\phi_2} \quad (6)$$

The tensile moduli of the unmodified 241(U) resins were used as E_1 . This is not entirely correct since the matrix in rubber-modified epoxy may contain up to 15% of dissolved CTBN. Sample 242/210 has demonstrated, however, that low levels (15%) of dissolved rubber do not change the modulus of the epoxy to an appreciable extent. It is therefore acceptable to use 241(U) resin properties to represent the matrix material in rubber-modified formulations. Equation (6) and the tensile modulus data are plotted against the morphological data in Figure 3.

Toughness, the area beneath the low strain rate stress-strain curve, and elongation to break data are also presented in Table VI. Toughness is plotted as a function of gel temperature in Figure 4. The error bars for each data point

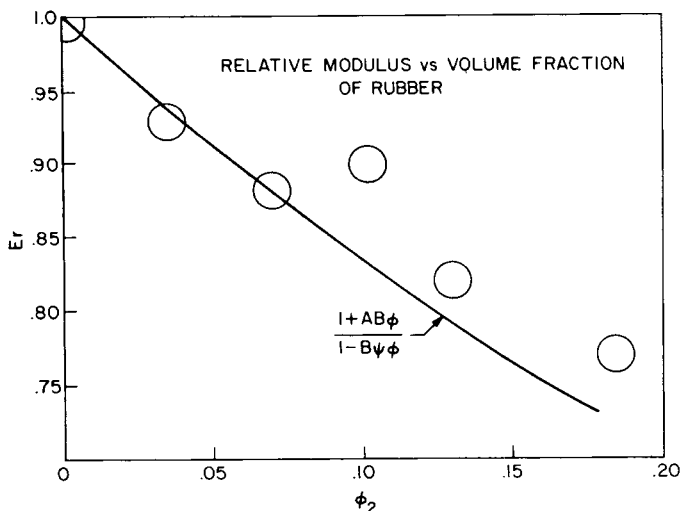


Fig. 3. Relative modulus plotted against volume fraction of phase separated rubber. Line represents the generalized Kerner equation.

represent the standard deviation over 8–12 specimens. The improved formulations were only those which contained X13 rubber. The improved X13 formulations were able to yield by volume-conserving plastic deformation. The X8 resins were predominantly stress whitened and showed deterioration in low strain rate toughness in comparison with the unmodified formulations. SEM micrographs of the failure surface of 243/170 showed considerable debonding at the domain interface (Fig. 5). Cavitation has also been found in other reports.³

TOUGHNESS VS. GEL TEMPERATURE

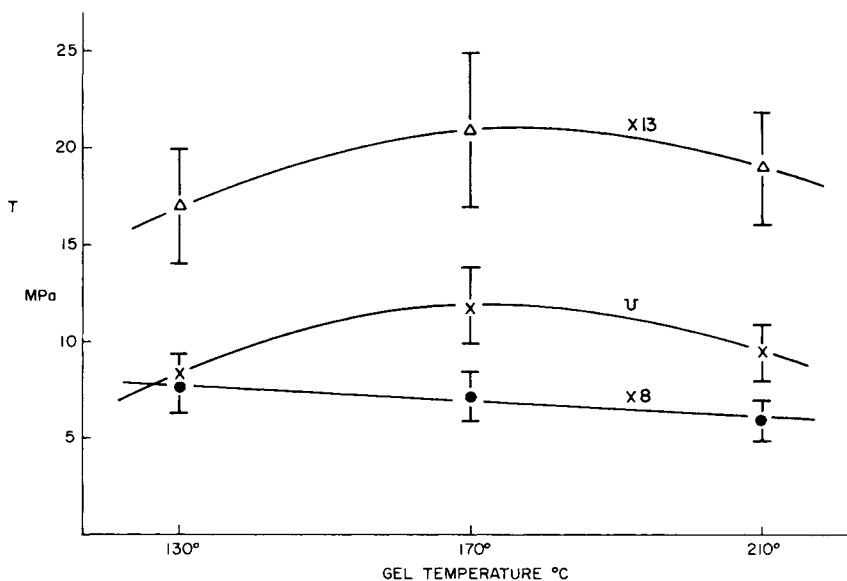


Fig. 4. Toughness plotted as a function of gel temperature. Error bars represent standard deviation.

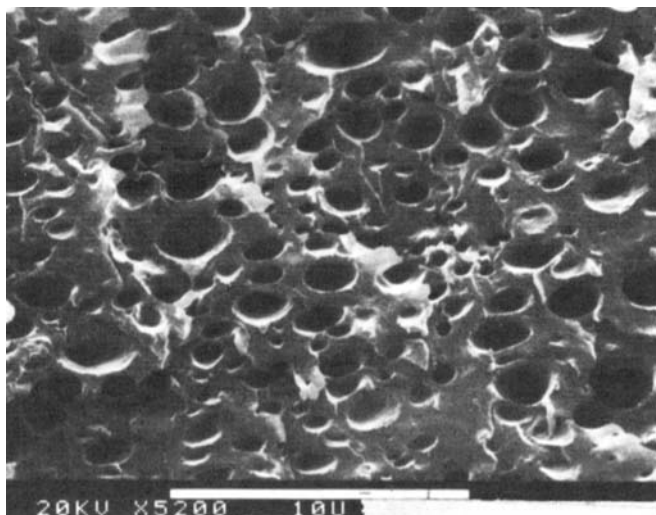


Fig. 5. SEM micrograph of tensile failure surface of 243/170.

Stress whitening is an energy dissipation mechanism but the elongation is limited, since the cavities quickly coalesce to produce catastrophic failure. Cavitation presumably involves the sequence of particle debonding and cavity enlargement.

Plastic deformation, which is promoted by dissolved rubber, is a more effective toughening mechanism than stress whitening at low strain rates. Specimens that contained only a small fraction of phase separated rubber were able to display both necking and stress whitening.

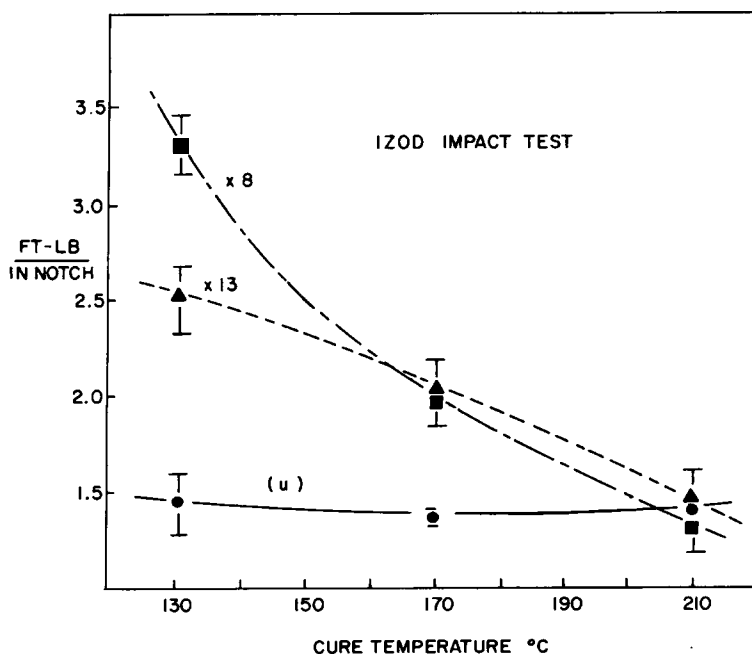


Fig. 6. Izod impact energy plotted against gel temperature. Error bars represent standard deviation.

The Izod impact test was employed to obtain the high strain rate response of modified and unmodified epoxy materials. The Izod impact energy is plotted as a function of gel temperature in Figure 6. Each data point is the average of 10–12 specimens. The single phase unmodified materials all show equally poor impact energies. The single phase rubber-modified material, 242/210, has the same impact energy (and modulus) as unmodified epoxy material. There is improvement in 242/170 and 242/130. Both of these are two phase systems. The 243(8) materials show a similar behavior. There is a significant improvement in impact energy in 243/170 and 243/130. The 243/210 material is unusual since it is phase segregated yet does not provide impact energy improvement. This system shows the same impact energy as 241/210 and 242/210, both single phase polymers. The domains in the TEM micrograph for 243/210 (Fig. 1) did not display the epoxy inclusions that were evident in 243/130 and 243/170. This indicates a larger extent of phase blending. The domains may be mechanically indistinguishable from the matrix at the high strain rate of the impact test and are therefore ineffective in promoting toughening. The impact energy results indicate that the presence of a dispersed rubbery second phase is a necessary but not sufficient condition for impact energy improvement.

STRESS RESPONSE MODEL

The mechanical property data can be fitted to a concise model that is an extension of the Ludwik–Davidenkow–Orowan hypothesis.^{15,16} Brittle fracture and plastic deformation are independent processes that can be represented by separate characteristic curves. (Crazing is not discussed here since it does not appear to occur in these epoxy systems.) The intersection of the two lines is the brittle–ductile transition. The yield stress involves a viscous dissipation mechanism and is assumed to show the greater temperature sensitivity. The response mechanism is decided by arguing that whichever process will occur at the lower stress will be the operative one. This will be either brittle failure or yield for a single phase material. There are other response mechanisms that

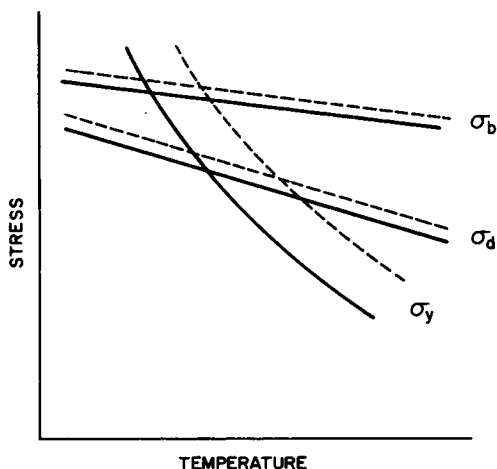


Fig. 7. Stress response model for rubber-modified epoxies. (—) Low deformation rate; (---) high deformation rate; σ_y , yield stress; σ_d , debonding/cavitation stress; σ_b , brittle failure stress.

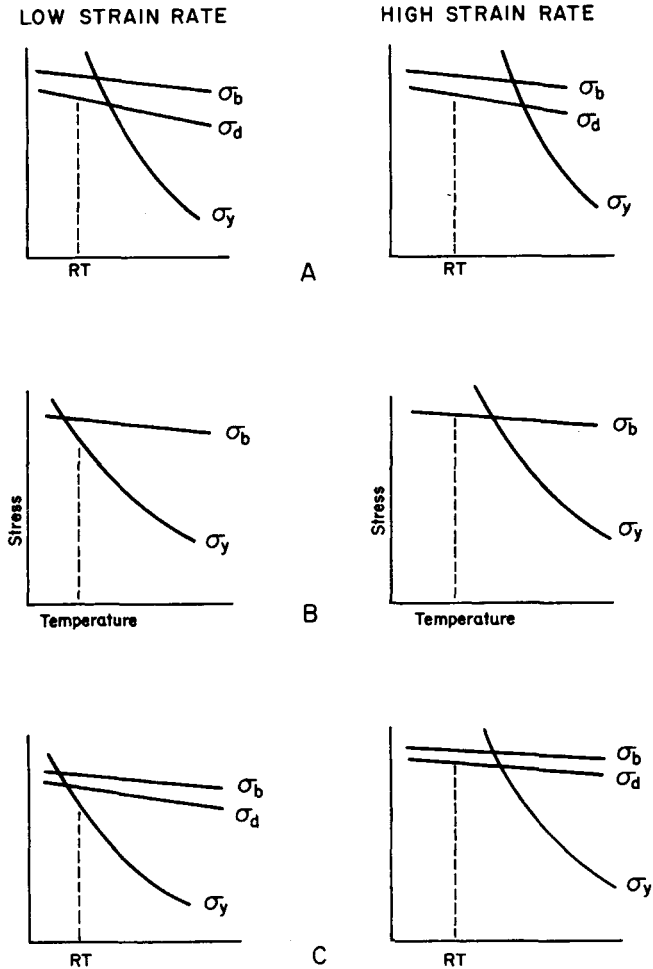


Fig. 8. Stress response model for rubber-modified epoxies with different amounts of dissolved and phase separated rubber: (A) two-phase system with a large volume fraction of phase separated rubber; (B) single phase, rubber-modified epoxy with all rubber dissolved; (C) two phase system containing both phase separated and dissolved rubber.

may operate in a two phase system. The presence of domains in a rubber-modified epoxy introduces debonding and cavitation as a stress response mechanism. This introduces a new line on the stress response diagram.

Changing the strain rate will produce a shift in the curves. The viscous element is the most rate dependent and the yield stress will be shifted to higher temperature at a higher strain rate. This model is summarized in Figure 7.

The mechanical response of a phase separated, modified epoxy that contains little dissolved rubber is explained in the following manner [Fig. 8(A)]. During low strain rate tensile testing, the stress builds until it reaches a line that represents a response mechanism. The first line reached is the debonding/cavitation line. A yield stress is noticed as the specimen stress whitens. It fails soon afterward since the cavities coalesce quickly to provide catastrophic failure. At higher strain rates, the first line reached is again the cavitation stress. The impact energy can be increased because of the presence of rubbery domains in

the fracture plane. High levels of phase separated rubber do not usually improve the impact energy since the domains decrease the effective area of the hard-phase epoxy in the fracture plane.

In a single phase, rubber-modified epoxy [Fig. 8(B)], the yield stress has been shifted to lower temperatures as a result of the dissolved rubber in the epoxy matrix. The debonding/cavitation line is absent, since this resin is single phase. The first line reached at low strain rates is the yield stress. The material can exhibit high elongation to break and good toughness through plastic deformation. At the higher strain rates associated with the Izod impact test, the yield stress line has been shifted to higher temperature. The first line to be reached at room temperature is now the brittle failure stress since there is no debonding/cavitation line to screen it out. The material fails in a brittle manner and the impact energy is poor.

Optimum properties result from the correct combination of phase separated and dissolved rubber [Fig. 8(C)]. When the rubber and epoxy are relatively compatible, the interfacial bonding is good and the debonding stress is high. The yield stress line is again shifted to lower temperature since there is a large amount of dissolved rubber in the epoxy matrix. The system is able to reach its yield stress at room temperature at low strain rates. The yield stress is unattainable at impact rates but the debonding/cavitation line is available. The material can then exhibit improved impact properties since the brittle failure line is again blocked out. This material has both improved low strain rate toughness and improved impact properties.

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