Partially Miscible Blends of Epoxy Resin and Epoxidized Rubber: Structural Characterization of the Epoxidized Rubber and Mechanical Properties of the Blends

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SYNOPSIS

The cure process and the mechanical properties of blends of diglycidyl ether of bisphenol-A–based epoxy resin and hydroxyl terminated, internally epoxidized polybutadiene rubber have been studied. Internal oxirane groups are characterized by a main absorption at 885 cm^{-1} in the infrared spectrum while the terminal oxirane groups of the diepoxide monomer absorb at 913 cm^{-1}. In the absence of prereaction of the rubber, gelation of the epoxy matrix occurs much faster than any reaction involving the internal oxirane groups or the terminal hydroxyl groups. Therefore, only weak chemical bonding between the rubber particles and the epoxy matrix exists and the fracture toughness of the blends does not show any significant improvement. Upon prereaction of the rubber with an excess diepoxide monomers, a 40% improvement in the value of the critical stress intensity factor is obtained. However, dynamic mechanical spectra of these blends acquired in the rubbery plateau region uniquely demonstrate that this improvement is due to the incorporation of the rubber into the epoxy network rather than to the presence of phase-separated rubber particles. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that a small amount of rubber can greatly improve the fracture toughness of epoxy resins by forming discrete rubbery particles that are chemically bonded to the matrix. The toughening effect is generally accompanied by a relatively small loss of thermomechanical properties. A review of the literature indicates that both chemistry[1,2] and thermodynamics[3,4] play an essential role in determining the final properties of these rubber/epoxy blends. Thermodynamics include issues of miscibility and phase separation. Initially, the rubber must be able to dissolve in the monomer/curing agent/catalyst mixture. However, miscibility must not be too great because phase separation of the rubber before gelation of the epoxy matrix is also required for

efficient toughening. Too good of a miscibility leads to a diluent effect rather than a toughening effect. The balance between phase separation and polymerization depends on the solubility of the rubber in the epoxy resin, the initial fraction of rubber, and the cure conditions. This balance, in turn, determines the particle size distribution and the composition of the epoxy-rich and rubber-rich phases and, thus, directly influences the mechanical properties. Chemistry of the rubber includes issues of selectivity and reactivity. Functional groups must be present on the rubber backbone in order to selectively react with the epoxy matrix. Indeed, chemical bonding between the rubber particles and the epoxy matrix is necessary for efficient stress transfer. It has been proposed[1] that the rubbery particles are composed of a mixture of linear rubber–epoxy copolymers and crosslinked epoxy resin. In the absence of chemical bonding or curing, only van der Waals attractive and/or hydrogen bonding type of forces are present and not much toughening is expected. If, on the other hand, the reactivity of the functional

groups is too high, the rubber reacts rapidly with the epoxy matrix. In this case, the system is flexibilized rather than toughened. In this article, the term flexibilized will be used when the ductility of the system is increased by incorporating a flexible rubbery molecule as part of the polymer network. On the other hand, the term toughened will be used when the toughness of the system is improved without major changes in the molecular structure of the brittle phase.

The morphology and mechanical properties of these systems have been studied extensively in the literature.[5,6] Most often fracture toughness measurements are correlated with parameters such as the epoxy resin cure temperature, volume fraction of dispersed phase, average rubber particle diameter, strain rate of the test, test temperature, etc. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are then used to determine the mechanisms of failure. It has been shown that enhanced plastic shear yielding of the matrix is the main source of increased toughness. This enhancement is brought about by the stress concentration effect due to the presence of the rubbery particles.

However, the overwhelming majority of the studies have used a carboxylic acid-terminated butadiene acrylonitrile copolymer (CTBN) as the toughening agent. In this study, an epoxidized, hydroxyl-terminated polybutadiene rubber (E-HTB) was used. The epoxidized rubber is characterized by various spectroscopic techniques and its reactivity studied. Its potential as a rubber-toughening agent is then evaluated through mechanical testing. The dynamic mechanical properties and the morphology of the blends are presented in detail elsewhere.[7-9]

EXPERIMENTAL

Materials

The epoxy system chosen for this study, diglycidyl ether of bisphenol-A (DGEBA)/bisphenol-A, catalyzed by a tertiary amine (Lewis Base), is a very versatile material. Depending on the reaction conditions and on the initial stoichiometry, the material can exhibit a thermoset or thermoplastic character.[10] The crosslink density and the degree of branching can be controlled to promote either stiffness or toughness. An excess bisphenol-A favors linear growth of the chains, whereas an excess diepoxide promotes branching and crosslinking. The bisphenol-A to DGEBA stoichiometric ratio, s, used in

the industry is generally about 0.6. Bisphenol-A is often used in rubber-toughening application because it appears to enhance the toughening effect.[11,12] In both rubber-toughened and nontoughened systems, it acts as a chain extender. The glass transition of such a system is about 100–103°C when ideal curing conditions are used (slow initial cure followed by postcure). The DGEBA resins, EPON 825 for spectroscopic study, Epon 828 for sample molding, and the bisphenol-A were obtained from Shell Chemical Corporation. The catalyst, p-chlorophenyl-1,1 dimethylurea (trade name Monuron) is manufactured by DuPont and is used at 2% of the total weight. Three different grades of epoxidized, hydroxyl-terminated polybutadiene (E-HTB) resins were evaluated in this study. These resins (trade name Poly bd) were provided by Elf-Atochem. They have the following general structure:

$$HO-[(CH_2-CH=CH-CH_2-)_l$$
$$-(CH_2-CH-)_m-$$
$$|$$
$$CH=CH_2$$
$$O$$
$$/\backslash$$
$$(CH_2-CH-CH-CH_2-)_n]_x-OH$$
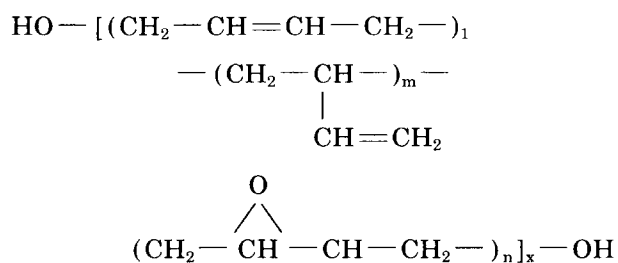
and some of their properties are presented in Table I. Poly bd 600 and Poly bd 605 resins are hereafter described as low-epoxidized and medium-epoxidized rubber, respectively. The nonepoxidized rubber, R20LM, cannot be used for sample molding because it is too immiscible with the epoxy resin. It is mentioned here as the precursor to the low-epoxidized and medium-epoxidized rubber. All materials used in this study were used as received without further purification. However, bisphenol-A was dried in a vacuum oven at 110°C for 12 h prior to use, as water content can influence the kinetic of the diepoxide/bisphenol-A reaction.

Apparatus and Sample Preparation

Sample Preparation

Epoxy resin/epoxidized rubber blends were prepared in the following typical manner. A proper amount of Epon 828 (290 g) is first degassed for 30 min in a vacuum oven at 80°C. The epoxidized rubber is degassed separately under the same conditions. The catalyst (2% total weight of the mixture) is then added as a finely ground powder to the diepoxide and the mixture is stirred for about 5 min to

Table I   Physico-Chemical Properties of the E-HTB Resins Used in This Study

	Poly bd R20LM	Poly bd 600	Poly bd 605
Oxirane oxygen (wt %)	0	3.5	6.1
Viscosity at 23°C (mPa·s)	1500	5500	23,000
Solubility parameter (MPa$^{1/2}$)	17.2	17.7	18.2
Molecular weight, Mn (g/mol)	2750	2940	3270
Polydispersity	2.3	2.4	2.8
Specific gravity at 23°C	0.90	1.01	1.01
Glass transition temperature, T_g (°C)	−75	−60	−47

ensure proper dispersion of the catalyst. The rubber is then added to the diepoxide/catalyst and the resulting homogeneous mixture is stirred for 5 min before being degassed by steps for 45 min. At this point the mixture is clear and has a very low viscosity. Meanwhile, bisphenol-A (100 g) is molten in a separate oven at 160–170°C. It is then quickly added to the rubber/diepoxide mixture and stirred vigorously for 15 s. The content of the beaker is then poured in preheated vertical mold consisting of a silicon rubber spacer between two glass plates treated with a silicon-based mold release agent. Typical cure cycles are 7 h at 100°C followed by an immediate postcure at 125°C for 4 h. The molded sheet (270 × 120 × 10 mm) is then slowly cooled down to room temperature. Rubber content is typically reported in terms of initial weight fraction of rubber, w_R^0.

Prereaction of the Rubber

In order to improve the mechanical properties of the blends, the epoxidized rubber was prereacted with an excess diepoxide to achieve better bonding between the rubber particles and the epoxy continuous phase. The medium-epoxidized rubber and EPON 825 were reacted in the bulk in a flask blanketed with argon. The flask was placed in an oil bath at constant temperature and its content stirred mechanically for a total reaction time of 4 to 6 h. An excess of EPON 825 (molar ratio of epoxide to hydroxyl groups equal to 10) was used to ensure complete reaction. The catalyst, p-chlorophenyl-1,1 dimethylurea, was used at 0.7% of the total weight. For analysis, a small amount of the reaction mixture is taken out of the reaction flask. The rubber-epoxy adduct is separated from the excess diepoxide by two reprecipitations in methanol. This procedure results into an adduct with 98–99% purity, as determined by size exclusion chromatography. The purified material is used to determine the extent of

reaction by size exclusion chromatography. The remaining material is added to the appropriate amount of diepoxide and bisphenol-A to mold samples with a known rubber content.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR study was conducted on a Bomem Michelson MB, single-beam Fourier transform infrared spectrometer with variable resolution. The spectrometer is equipped with a liquid nitrogen-cooled, mercury-cadmium-telluride (MCT) detector for data collection in the region 500–4000 cm^{-1}. Two different infrared techniques were used in this study. For the microstructure characterization of the polybutadiene resins, samples were spin coated onto a KBr disk from a solution of the polymer dissolved in tetrahydrofuran (10% by weight). The thickness of the homogeneous film was adjusted to avoid overabsorption in the range of interest. Spectra were collected at 4 cm^{-1} resolution after purging the sample chamber with dry nitrogen for 20 min. Spectral analysis was conducted on a Digital Microvax II computer.

Attenuated total reflection (ATR) spectroscopy was the technique of choice when studying reaction kinetics. A custom-made single-reflection cell designed for reaction injection molding was used in this study and has been described in detail elsewhere.[13] The cell temperature can be varied up to 200°C and is monitored by a proportional integral derivative PID temperature controller. ATR is particularly suited to monitor reactions where large amount of flow can occur due to low initial viscosity of the components and/or slow crosslinking. Both the horizontal geometry of the cell and the constant, wavelength-dependent, probing depth of ATR ensure that the changes in the intensity of reference bands will be minimal. Samples for the kinetic study were prepared by dissolving the medium-epoxidized polybutadiene and a mixture of the bisphenol-A and

the catalyst in two ethyl acetate solutions. The concentration of the catalyst was maintained at 2% of the total weight of the reactants. These solutions were prepared stoichiometrically at low concentration. Before each experiment, equal volume of the reactants was pipetted into a vial. The content of the vial was then injected in the ATR cell. The cell was thermally equilibrated at the chosen reaction temperature between 110°C and 170°C. Spectral collection was initiated 2 min after injection, but the cell temperature was back to equilibrium within 1 min. At each temperature, coadded spectra (20 scans) were acquired automatically with appropriate time delay (from 2 to 5 min for the initial step of the reaction). The initial concentration of internal epoxide groups is obtained by extrapolation to zero time of the first few data points.

Raman Spectroscopy

Raman spectra were collected on a Bomem DA3 Fourier Transform Raman Spectrometer, equipped with a Nd : YAG lasing at 1.064 μm. Five thousand scans were collected at a resolution of 4 cm^{-1} in order to obtain appropriate signal-to-noise ratio for the weak epoxy Raman lines.

Nuclear Magnetic Resonance (NMR)

^{1}H FT-NMR was performed on a Varian XL-200 spectrometer tuned to 200 MHz. Samples were dissolved in deuterated chloroform at a concentration of 2×10^{-2} g/mL. Thirty-two transients were averaged for each sample.

Size Exclusion Chromatography (SEC)

SEC was performed on a Waters 800 system with ultrastyragel columns having pore size of 50, 100, and 1000 nm, operated with tetrahydrofuran at 1.0 mL/min. An ultraviolet (UV) absorbance detector set at 254 nm and a differential refractive index (RI) detector were used for data acquisition. Typical sample concentration was 0.2% by weight. The instrument is calibrated with polystyrene standards.

Scanning Electron Microscopy (SEM)

Fracture surfaces of rubber/epoxy blends were studied with a JEOL JSM-35CF scanning electron microscope, after coating with a thin layer of gold. The average number of particles per unit area, $\bar{N}$(particles/μm^2), the average particle diameter, $\bar{D}$(SEM), and the volume fraction of dispersed phase, V_D(SEM), can be determined from a statistical analysis conducted on magnified micrographs.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical spectra were obtained on a Rheometrics Dynamic Mechanical Spectrometer RMS-800 with a temperature capability ranging from −150 to 600°C. A force rebalance transducer with 2000 g-cm torque was used with a rectangular sample torsion fixture. Measurements were collected at 2°C intervals with a heating rate of 2°C/min. The reported glass transition temperature is obtained from the maxima in the loss modulus spectrum, G'' vs. temperature.

Mechanical Property Measurements

Tensile tests were performed according to ASTM D638. For each composition, at least four dogbone specimens (150 × 18 × 7 mm) were machined from a 10 mm molded sheet. An Instron machine was used at a constant crosshead speed of 1 mm/min. The true sample strain was recorded by a longitudinal extensometer. Tests were performed at room temperature (25°C). The Young's modulus, E, was obtained from the experimental load–strain curves. The yield stress, σ_y, is taken as the maximum in the engineering stress.

Fracture toughness measurements were conducted in a three-points bending, and single-edge notch (SEN) set-up, according to ASTM E 399. The SEN test is preferred over the IZOD impact test because of the higher reliability of the results. At least four three-point bending specimens (110 × 18 × 10 mm) per composition were tested. These dimensions ensure plane strain conditions. Tests were conducted at room temperature on an Instron machine at a crosshead speed of 1 mm/min and for a
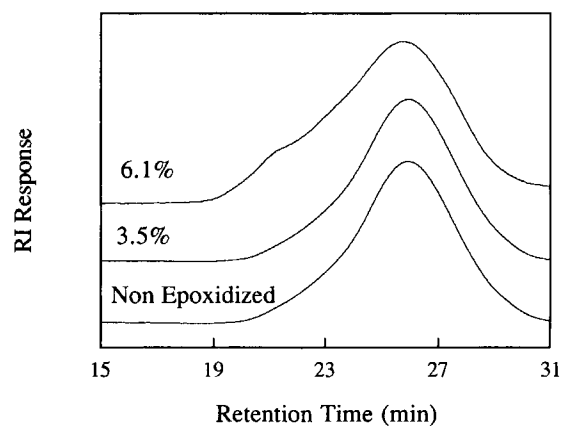

Figure 1 SEC Chromatograms (RI response) for the nonepoxidized, low-epoxidized, and medium-epoxidized rubber.

span, S, of 72 mm. A prenotch was first introduced with a saw. A sharp crack is then initiated by tapping with a small hammer on a razor blade. From SEN measurements, the value of the critical stress intensity factor, K_{Ic}, is obtained (K_{Ic} in MPa·m$^{1/2}$):

$$K_{Ic} = \frac{P_f S}{B W^{3/2}} \cdot f(a/W) \qquad (1)$$

where P_f is the load at failure, B is the specimen thickness, and W is the specimen width. The specimen shape factor, f, is a function of the dimensionless parameter, $r = a/W$:

$$
\begin{aligned}
&f(r = a/W) \\
&= \frac{3r^{1/2}[1.99 - r(1 - r)(2.15 - 3.93r + 2.7r^2)]}{2(1 + 2r)(1 - r)^{3/2}}
\end{aligned}
$$

$$(2)$$

where a is the crack length.

RESULTS AND DISCUSSION

Microstructure Characterization

The epoxidation reaction of polybutadiene is well documented.[14,15] An organic peracid such as peracetic acid, reacts with a double bond to yield an internal oxirane:

$$CH_3COOOH + \text{—CH}\text{=}\text{CH—} \rightarrow$$

$$\underset{\text{—C H— CH—}}{\overset{O}{\diagup\diagdown}} + CH_3COOH$$
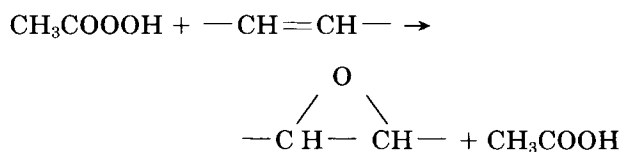
In principle, the epoxidation reaction should conserve molecular weight distribution. This is true for the most part as the main retention time remains constant at 25.2 min (RI response) for all three polymers (Fig. 1). However, the SEC chromatograms also indicate that some higher molecular weight material is formed, as evidenced by the presence of a broad shoulder centered at 21 min in the chromatogram of the medium-epoxidized rubber. This suggests that interchain reaction occurs, possibly through ether linkage formation via polymerization of oxirane groups.[16,17]

The effect of the epoxidation reaction on the microstructure of the Poly bd resin chains was studied by FTIR spectroscopy, FT Raman spectroscopy, and ^{1}H NMR. Figure 2 compares the infrared spectrum
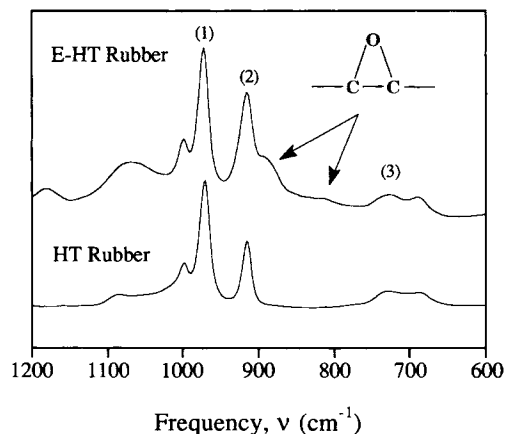

Figure 2 Effect of the reaction of epoxidation on the infrared spectrum. Modes (1), (2) and (3) are characteristic of the *trans*, vinyl and *cis* units on the polybutadiene backbone.

of the starting polybutadiene in the 600–1200 cm^{-1} region with that of the medium-epoxidized rubber. The *internal* oxirane exhibits two characteristic absorption frequencies in this region, a broad, weak, symmetric in-plane ring deformation (I) at 816 cm^{-1} and a stronger antisymmetric mode (II) at 885 cm^{-1}. In the Raman spectrum, (II) is observed at 887 cm^{-1} but (I) is too weak to be clearly detected. A third mode (III), assigned to the oxirane ring "breathing" vibration, appears at 1239 cm^{-1} in the Raman spectrum and at 1268 cm^{-1} in the infrared spectrum, where it is seen as a very weak band. In the case of the epoxy monomer (EPON 825), which contains two *terminal* oxiranes, (II) is observed at 913 cm^{-1} in the infrared spectrum and at 918 cm^{-1} in the Raman spectrum. These results are summarized in Table II. For comparison, the corresponding frequencies for terminally and internally epoxidized butane compounds (1,2 and 2,3-epoxybutane) are also reported.[18-21] Notice the similarities in absorptions between 2,3-epoxybutane and epoxidized polybutadiene. Table II also shows that, in general, (I) and (II) appear at lower frequency for an internal oxirane than for a terminal oxirane (compare 1,2-epoxybutane and 2,3-epoxybutane).

The position of the lower frequency band has been used in the past[22,23] to distinguish between monosubstituted (here epoxidized *vinyl* unsaturation), disubstituted (here epoxidized *cis* or *trans* unsaturation), and trisubstituted oxirane. The medium range location of this band at 810 cm^{-1} for epoxidized polybutadiene is a first indication of the probable absence of epoxidized *vinyl* units in this resin. A more direct confirmation is obtained by comparing

Table II **Characteristic Raman and IR Absorptions for the Internally Epoxidized Rubber and the Terminally Epoxidized Diepoxide Monomer**

	Poly db 605 (This Article)		EPON 825 (This Article)		2,3-epoxybutane[18–20]		1,2-epoxybutane[18,21]	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman
(I)	816	—[d]	—[b]	811	777 (cis) 812 (trans)	779 (cis) 812 (trans)	830	830
(II)	885	887	913	918	886 (cis) 887 (trans)	886 (cis) 887 (trans)	908	903
(III)	1268	(1260)[a] 1239	—[c]	1257	1279 (cis) —[d] (trans)	1277 (cis) 1255 (trans)	1259	1259

The results for 1,2-epoxybutane and 2,3-epoxybutane are shown for comparison.
(I) Symmetric in-plane ring deformation.
(II) Asymmetric in-plane ring deformation.
(III) Ring breathing vibration.
[a] Very weak shoulder at 1260 cm^{-1} might be due to cis oxirane units while more distinct mode at 1239 cm^{-1} is tentatively assigned to trans oxirane units.
[b] Masked by strong aromatic CH wag of bisphenol-A unit (observed at 837 cm^{-1} for 1,2-epoxy-3-phenoxypropane, a model compound for DGEBA).
[c] Masked by strong aromatic asymmetric O—O—C stretch of bisphenol-A unit (observed at 1236 cm^{-1} for 1,2-epoxy-3-phenoxypropane).
[d] Absent or too weak to be observed.

the distribution of double bond configurations before and after epoxidation. This distribution is derived from the changes in relative intensity of characteristic trans (969 cm^{-1}, trans CH wag), cis (726 cm^{-1}, cis CH wag), and vinyl (912 cm^{-1}, CH$_2$ wag) bands for polybutadiene. The respective specific absorptivities were taken from a review article on the subject.[24] Curve resolving of the spectra in Figure 2 was performed in the 600–1050 cm^{-1} region to obtain the intensity of the bands of interest. The infrared results are summarized in Table III, along with the data obtained from ^{1}H NMR. There is a good agreement between the two techniques. The table shows that the relative percentage of vinyl groups increases as a result of epoxidation. This indicates unambiguously that only cis and trans units undergo epoxidation while vinyl units remains unaffected. The relative increase of the vinyl content results from

the decrease of the total number of unsaturations. Thus, there are no pendant oxirane groups on the polybutadiene backbone. This is important for the interpretation of the kinetic study for the reaction with bisphenol-A, because pendant monosubstituted, oxiranes are less hindered than internal, disubstituted oxiranes and, thus, are expected to react faster.

Evidences in the infrared and ^{1}H NMR spectra indicate that both the cis and trans oxirane configurations are possible in epoxidized polybutadiene. Taking 2,3-epoxybutane as an example, one would expect a broad band for mode (I) if both cis and trans are present. Indeed, for the medium-epoxidized rubber, this mode is rather broad, although weak (Figure 2). Moreover, when the medium-epoxidized rubber is further reacted with bisphenol-A at elevated temperature (130°C), two components can

Table III **Distribution of unsaturations before and after epoxidation, by FTIR and ^{1}H NMR**

	FTIR			^{1}H NMR[a]	
	trans (%)	cis (%)	vinyl (%)	trans + cis (%)	vinyl
Poly bd R20LM	54	24	22	78	22
Poly bd 600	50	26	24	74	26
Poly bd 605	46	25	29	70	30

[a] Based on the following assignments (shifts in ppm from TMS): vinyl: 4.99 and 5.66, cis and trans: 5.41.

be distinguished in mode (II) (tentative assignments: *cis* oxirane at 879 cm^{-1} and *trans* oxirane at 889 cm^{-1}), suggesting also that the reactivity of the *cis* and *trans* configurations may be slightly different. ^{1}H NMR confirms the presence of two configurations [*trans*: δ = 2.60 ppm (68%), *cis*: δ = 2.80 ppm (32%)] as well as the absence of *vinyl* oxirane. These shifts have been observed by others[25] at 2.65 (*trans*) and 2.92 ppm (*cis*) in highly epoxidized polybutadiene (60%). In DGEBA, the characteristic shift due to the methylene group of the terminal oxirane is seen at 2.89 ppm.

Last, the oxirane groups were found to be thermally stable. At an elevated temperature, 160°C, and over a period of 2 h, no change in the intensity of mode (II) was observed, although there are various indications that the olefinic part of the medium-epoxidized rubber main chain undergoes oxidative degradation, as reflected in the appearance of three new carbonyl modes at 1697, 1723, and 1774 cm^{-1} and possibly isomerization, which leads to the changes in the C — H stretching region. The carbonyl modes have been observed by others[26] and assigned to α-β unsaturated aldehydes, saturated aldehydes, and five-membered lactone structure. Thus, the changes in the intensity of mode (II) recorded during the kinetic experiment are real and not due to thermal degradation.

Kinetic Study

Reactivity of the Internal Oxirane Groups

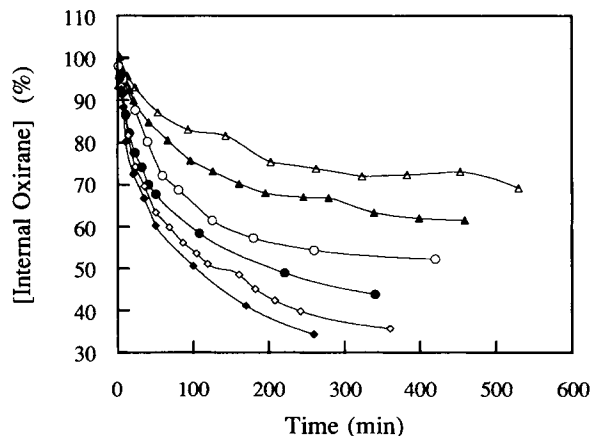The kinetic of the catalyzed reaction of the medium-epoxidized rubber and bisphenol-A under stoichio-
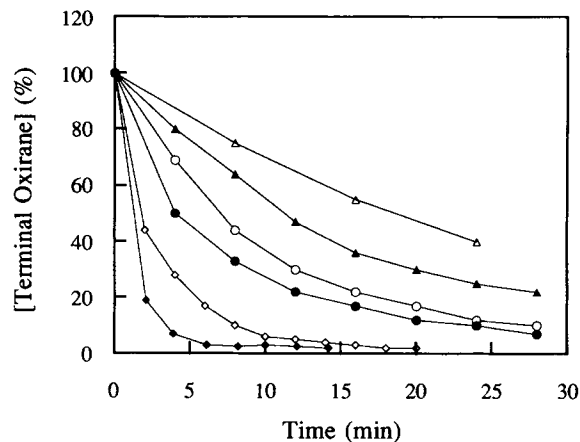
Figure 4 Kinetic of the terminal oxirane (DGEBA)/ bisphenol-A reaction (after Ishida and Smith[10]). ($\triangle$), 110°C, ($\blacktriangle$), 120°C, (O), 130°C, ($\bullet$), 140°C, ($\diamond$), 150°C, and ($\blacklozenge$), 160°C.

metric conditions was followed by FTIR-ATR spectroscopy in the 110–170°C temperature range. The results are shown in Figure 3 and are compared to similar data obtained by Ishida and Smith[10] for the EPON 825/bisphenol-A reaction (Fig. 4). In Figure 3, the intensity of the 885 cm^{-1} oxirane band has been scaled based on the 912 cm^{-1} *vinyl* polybutadiene band which is used as an internal standard, and normalized with respect to the initial intensity. The reaction of the internal oxirane groups is much slower than that of the terminal groups. Under the reasonable assumption of a random coil conformation of the polybutadiene chain, some oxirane groups are buried inside the coil, and the probability of contact between the curing agent and such internal oxirane is low. Thus, the reaction proceeds very slowly. The time necessary to reach 50% oxirane conversion at 150°C is about 130 min for the epoxidized polybutadiene/bisphenol-A reaction while it is only about 2 min for the EPON 825/bisphenol-A reaction. The conformational hindrance also explains why total conversion of the oxiranes is not reached. The ultimate conversion rate was found to be a function of the reaction temperature. Two regimes have been observed for this reaction (Fig. 5). First, a chemical regime, where only the reactivity of the oxirane sites matters, followed by a diffusion regime, where the accessibility of the oxirane sites becomes the important factor. At longer time, crosslinking of the rubber through the difunctional bisphenol-A is also expected to bring a change in mechanism. The time at which the transition between these two regimes occurs decreases almost linearly with reaction temperature (Fig. 6). The kinetic data was
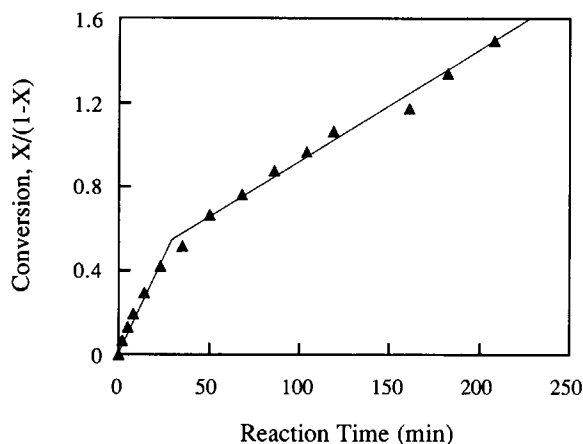
Figure 3 Kinetic of the internal oxirane/bisphenol-A reaction. ($\triangle$), 110°C, ($\blacktriangle$), 120°C, (O), 130°C, ($\bullet$), 140°C, ($\diamond$), 150°C, and ($\blacklozenge$), 160°C.

Figure 5 Change in regime for the reaction of internal oxirane groups and bisphenol-A (reaction temperature, 150°C). X is the fractional oxirane conversion.

Figure 7 Arrhenius plot for the reaction of internal oxirane groups and bisphenol-A for the chemical regime (▲) and the diffusion regime (△).

analyzed assuming an overall second-order reaction, i.e., first order with respect to the oxirane and bisphenol-A concentration, respectively. Assuming Arrhenius behavior is followed, the activation energy, ΔEa, of the reaction can be determined from the following equation:

$$\ln k = \ln A - (\Delta Ea/RT) \qquad (3)$$

where A is a constant, R is the gas constant (1.987 cal/mol·K), and T is the temperature (K). Figure 7 is a plot of eq. (3) for the two regimes discussed previously. The activation energy was found to be 15.8 kcal/mol for the chemical regime and 22.1 kcal/mol for the diffusion regime. The higher value for
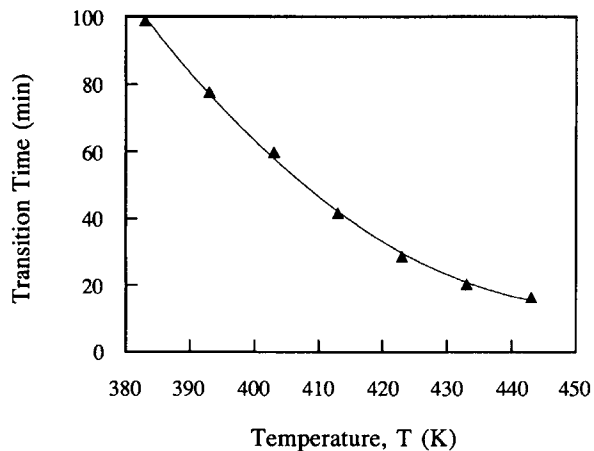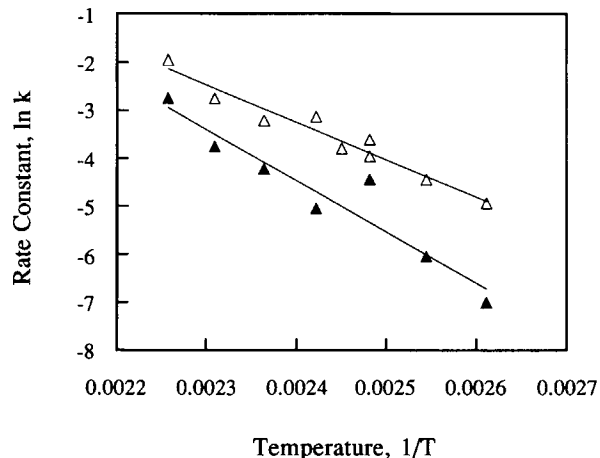
the diffusion regime is expected because of the limited availability of the oxiranes for reaction. The value of 15.8 kcal/mol can be compared with the 19 kcal/mol found by Ishida and Smith[10] for the reaction of a terminal oxirane with bisphenol-A. The lower activation energy actually suggests that internal oxiranes are more reactive than terminal groups when subject to an acidic attack.

The present kinetic study indicates that chemical bonding between the rubber particles and the epoxy matrix through the internal oxirane groups is unlikely because bisphenol-A reacts preferentially with DGEBA. Thus, the role of the internal oxirane groups is essentially to increase miscibility as the nonepoxidized rubber is very immiscible with the diepoxide monomer.

Reactivity of the Terminal Hydroxyl Groups

Riew and co-workers[1,2] have shown that the rubber must first form an epoxy-rubber adduct in the initial stage of the reaction so as to ensure chemical bonding. They also observed that terminal reactive groups are more effective than pendant groups in toughening epoxy resins. More importantly, they found that the selectivity of the terminal group toward the epoxy group is more important than its reactivity. Specifically, they reported that carboxylic acid end groups are more selective than phenol end groups which, in turn, are more selective than terminal hydroxyl groups; however, the order of reactivity is reversed. For the present system this would indicate that gelation of the matrix in the EPON 825/bis-

Figure 6 Transition time (▲) between chemical and diffusion regime as a function of reaction temperature.

phenol-A reaction occurs before chain extension of the rubber proceeds.

Therefore, the kinetic of the reaction between the terminal groups of the medium-epoxidized rubber and EPON 825 was investigated by FTIR and SEC. Additionally, this reactivity study was also undertaken to clarify the prereaction conditions. Indeed, there exist large differences in the literature[27,28] for the recommended time and temperature of treatment (from 4 h at 85°C to 4 h at 150°C for a CTBN rubber). The extent of reaction was followed for the purified rubber-epoxy adduct from the increase in UV absorption due to the presence of the aromatic rings on the epoxy-rubber adduct.[28] The pure rubber does not show any absorption at 254 nm. The area under the UV absorption was referenced to that under the RI response and the resulting quantity is followed as a function of time, as shown in Figure 8. Figure 8 shows that the reaction does not reach a plateau within the time frame of the experiment. The reaction is found to proceed rapidly at first, but slows down at a longer reaction time. The initial rapid increase might be attributed to the reaction of the hydroxyl end groups while the slow increase observed at the longer reaction time is due presumably to the side reaction of the secondary hydroxyl groups with the diepoxide. Secondary hydroxyl groups are present initially on the polybutadiene backbone but are also created each time a terminal hydroxyl group reacts with a diepoxide. Thus, the reaction can always proceed further and it becomes difficult to observe a well-defined plateau. This suggests that the adduct becomes increasingly branched
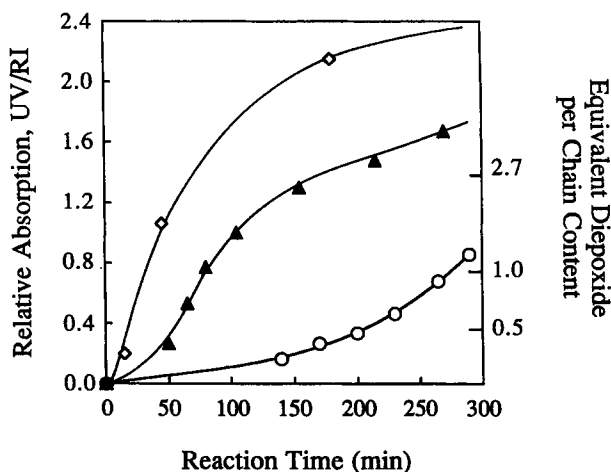

Frequency, ν (cm⁻¹)

Figure 9 Infrared spectrum of a model mixture (two diepoxide molecules per polybutadiene chain) and spectrum of a fraction collected after 155 min at 104°C. (1) Characteristic band of the polybutadiene backbone (C═C stretch), (2) Characteristic band of the diepoxide molecule (aromatic ring breathing vibration).

at higher reaction time. Indeed, after about 9 h at 104°C the reaction mixture forms a gel and cannot be used any more to mold samples. For practical application it is, therefore, desirable to let the reaction proceed only until the end of the first stage.

FTIR spectra of the purified fractions of reacted material were obtained and compared to the spectrum of a model mixture of medium-epoxidized rubber and diepoxide (Fig. 9). The model mixture sim-

Reaction Time (min)

Figure 8 Kinetic of the reaction between the epoxidized rubber (Poly bd 605) and the diepoxide (EPON 825) followed by UV-SEC. (O) 81°C, (▲) 104°C, and (◇) 113°C.
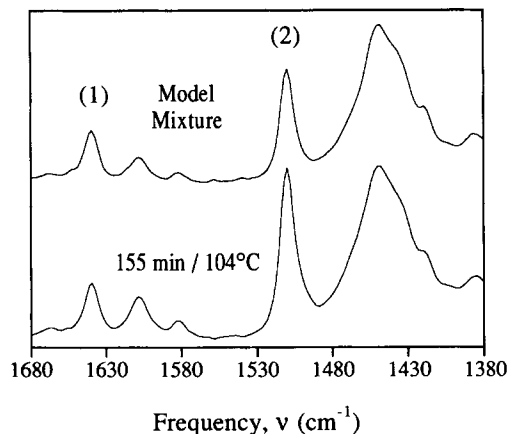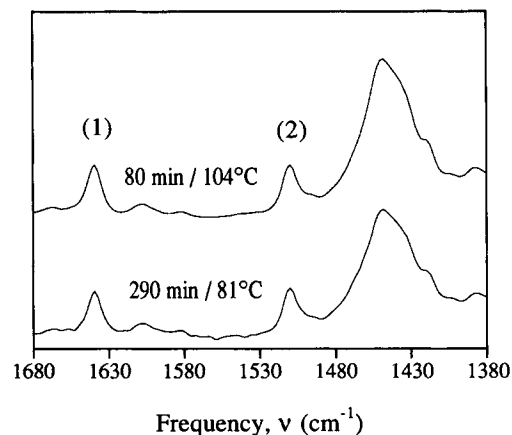

Frequency, ν (cm⁻¹)

Figure 10 Infrared spectrum of a fraction collected after 80 min at 104°C and spectrum of a fraction collected after 290 min at 81°C. (1) Characteristic band of the polybutadiene backbone (C═C stretch), (2) Characteristic band of the diepoxide molecule (aromatic ring breathing vibration).
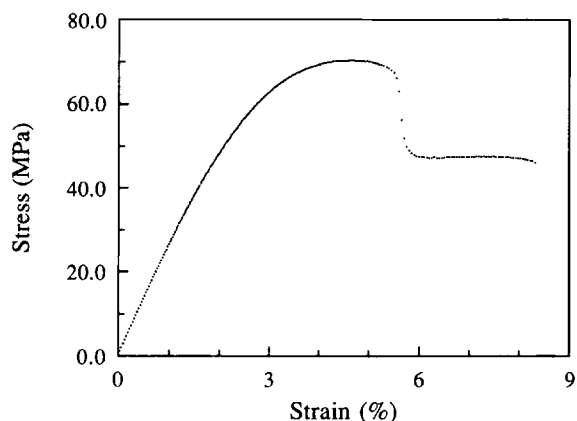
Figure 11   Typical stress–strain curve for the pure epoxy resin.

Figure 13   Tensile yield stress, σ_y, as a function of initial rubber content, w_R^0. (●) Medium-epoxidized rubber and (○) low-epoxidized rubber.

ulates a rubber chain end-capped by two diepoxide molecules. The extent of reaction in terms of a number of epoxy molecules grafted per chain can be estimated by comparing the ratio between the intensity of the aromatic ring breathing vibration (1509 cm^{-1}) and the 1640 cm^{-1} reference band of the polybutadiene (C=C stretching mode) for the reacted material and the model mixture. This way, the relative area under the UV absorption can be converted to an average number of grafted diepoxide molecules per chain (Fig. 8). Notice in Figure 8 that this conversion becomes nonlinear at larger values of the relative UV absorption. As an example, Figure 9 indicates that a fraction collected after 155 min at 104°C contains about 2.7 diepoxide molecules per
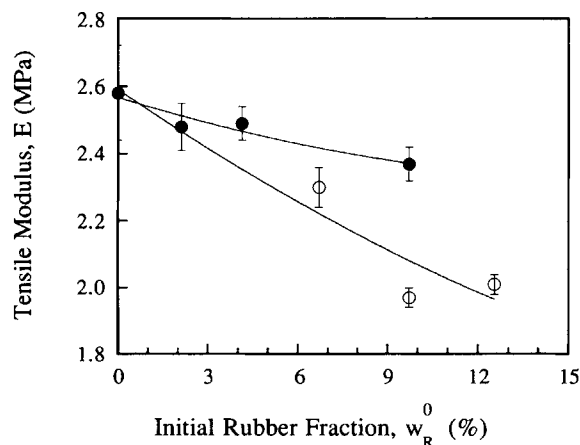
rubber chain. That UV-SEC and FTIR are complementary techniques is further illustrated in Figure 10. Indeed, the IR spectrum for a sample reacted for 80 min at 104°C is virtually identical to that for a sample reacted for 290 min at 81°C, as expected from the fact that these two samples also exhibit a very similar relative UV absorption (Fig. 8).

Finally, Figure 9 indicates that the reaction between the hydroxyl end groups and the diepoxide is faster than that between the internal oxirane and bisphenol-A but it is still substantially slower than the curing reaction of the epoxy matrix. Thus, for the molding conditions adopted, chemical bonding between the rubber particles and the epoxy matrix is weak and little toughening should be expected with the as-received material.

Mechanical Properties

Tensile Properties

Figure 11 is a typical stress–strain curve for the pure epoxy resin. Unlike most other epoxy resins, the DGEBA/bisphenol-A resin exhibits a ductile tensile behavior characterized by a high elongation at break (8.5% ± 0.2%). At higher strain, yielding is accompanied by the formation of a neck. The dependence of the modulus and yield stress on rubber content is illustrated in Figure 12 and Figure 13, for samples containing unreacted rubber. Two types of behavior are observed, depending on the oxirane content of the rubber. For the medium-epoxidized rubber, both modulus and yield stress are relatively independent on rubber content. This is especially true at low

Figure 12   Tensile modulus, E, as a function of initial rubber content, w_R^0. (●) Medium-epoxidized rubber and (○) low-epoxidized rubber.

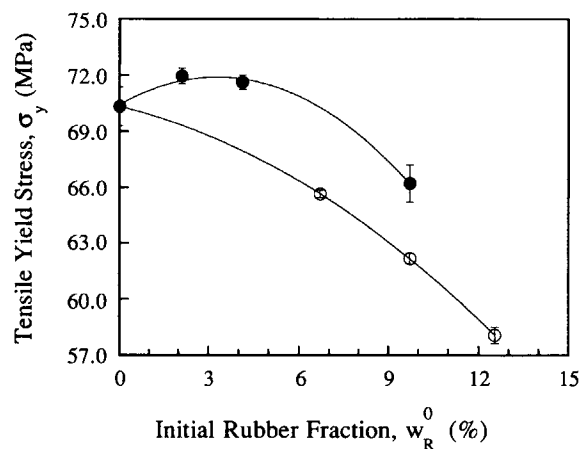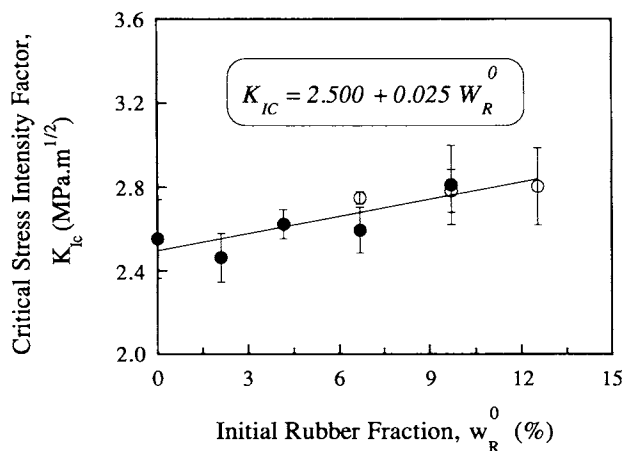**Figure 14** Critical stress intensity factor, K_{IC}, as a function of initial rubber content, w_R^0, for nonprereacted rubber. (●) Medium-epoxidized rubber and (○) low-epoxidized rubber.

rubber content ($w_R^0 < 6\%$), where there is little phase separation. For these samples, dynamic mechanical analysis shows that most of the medium-epoxidized rubber just dissolves into the epoxy continuous phase.[7] Therefore, the tensile test results seem to indicate that dissolved rubber does not affect significantly the properties of the epoxy continuous phase. This was also confirmed by dynamic mechanical analysis.[9] On the other hand, for the low-epoxidized rubber, modulus and yield stress decrease continuously with rubber content. This rubber is less compatible with the epoxy resin because of its lower internal oxirane content. In this case, the volume fraction of dispersed phase becomes significant.

Fracture Properties

Figure 14 shows that, in the absence of prereaction of the rubber, almost no improvement in the value of the critical stress intensity factor, K_{Ic}, is observed. For both the low- and medium-epoxidized rubber, K_{Ic} varies between 2.5 and 2.8 MPa·m$^{1/2}$. This result is expected because the reactivity study has shown that chemical bonding between the rubber and the epoxy is unlikely because gelation of the matrix occurs before any substantial reaction of the rubber can take place. The rubber particles act merely as voids in this case. One would, therefore, expect a slight decrease of K_{Ic} with rubber content. However, it is possible that dissolved rubber counterbalances the negative effect of the rubber "voids" by enhancing the shear yielding ability of the matrix. Last, one should note that K_{Ic} for the pure epoxy

resin is fairly high. Indeed, for most epoxy resins, values below 1.5 MPa·m$^{1/2}$ are generally reported. However, Figure 11 has shown that this particular DGEBA/bisphenol-A system is ductile, whereas most epoxy resins exhibits brittle tensile behavior. This indicates a tough material and might explain the high value of K_{Ic} reported here. Note that this value is not an artifact because thinner specimens (4 mm), for which plane strain conditions might be challenged, also yielded a similar value of K_{Ic}.

The previous results have shown the necessity of prereacting the rubber to increase the interactions between the rubber particles and the matrix. Changes in the value of the critical stress intensity factor were investigated as a function of prereaction time at a given rubber content ($w_R^0 = 12.5\%$). Figure 15 shows that K_{Ic} increases continuously with prereaction time to about 3.4 MPa·m$^{1/2}$. This represents a modest improvement (36%) upon the value obtained for the pure epoxy sample (2.5 MPa·m$^{1/2}$). Also, this improvement does not seem to depend very much on rubber content as a similar value, 3.4 MPa·m$^{1/2}$, was also obtained for a sample containing 9.7% of prereacted rubber (3 h at 113°C). It should be noted that the relatively small improvement in K_{Ic} is likely due to the selection of the particular epoxy system which is already much tougher than ordinary, highly crosslinked epoxy systems whose strain to failure ranges from 1.5 to 3%.

At this point it is necessary to discuss the origin of this improvement in toughness. According to Kinloch,[29] the rubber particles enhance shear localization by acting as stress concentrators. Hydrostatic tension ahead of the crack tip causes rapid cavitation of the rubber. The voided damage zone then blunts the crack, which behaves as if it had a much larger crack tip radius. In effect, there is a much larger plastic zone associated with this crack, which is the source of the toughening effect. Well-bonded rubber particles differ from simple voids because, unlike voids, they can bear their share of the load in triaxial tension. Therefore, it is desirable to ensure chemical bonding between the rubber particles and the epoxy matrix. Prereaction of the rubber is one possible way to promote interfacial bonding.

However, prereaction of the rubber also enhances its miscibility and reactivity with the diepoxide monomers. Upon curing, one would then expect the rubber-epoxy adduct to dissolve more easily into the epoxy continuous phase than the nonprereacted rubber. In this case, the rubber acts as a plasticizer. If its reactivity is sufficient, the adduct might even
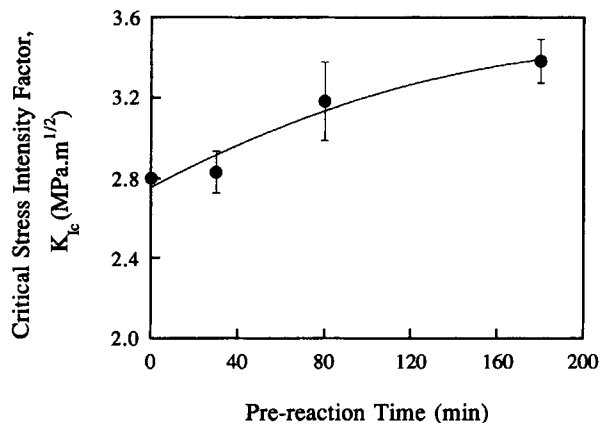
Figure 15 Critical stress intensity factor, K_{IC}, as a function of prereaction time for samples containing 12.5% of prereacted medium-epoxidized rubber (prereaction temperature = 104°C).

Figure 17 Typical fracture surface of a sample containing 10.3% of as received medium-epoxidized rubber. Volume fraction of dispersed phase, V_D = 0.089. Average particle diameter, $\bar{D}$ = 0.33 ± 0.09 μm.

be incorporated to some extent in the epoxy network. In this case, it acts as a flexibilizer. Both effects (plasticizer/flexibilizer) are important because they increase the ability of the matrix to deform under shear. Like crack tip blunting, enhanced matrix shear deformation also results in increased toughness.

Dynamic Mechanical Properties

To investigate the toughening mechanism, dynamic mechanical spectra of samples containing similar
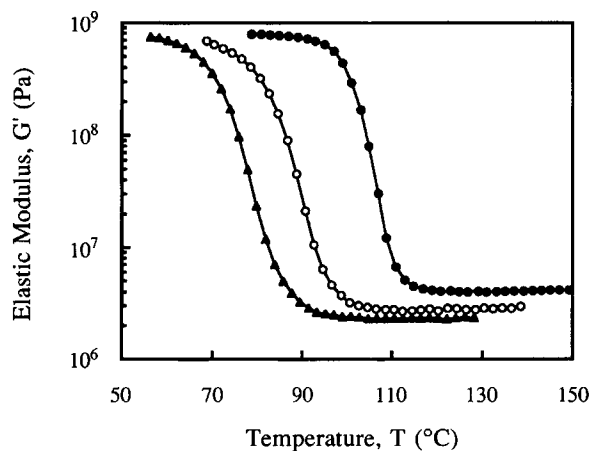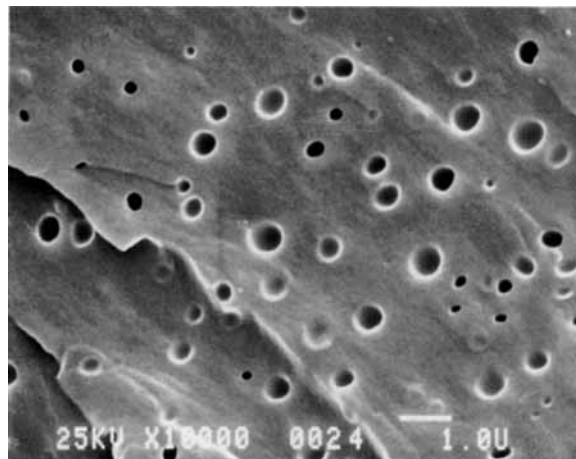

Figure 16 Dynamic mechanical spectra of epoxidized rubber/epoxy resin blends in the glass transition region of the epoxy continuous phase and in the rubbery plateau region. (●) Pure epoxy resin, T_g = 103°C, (○) blend containing 10.3% of as received medium-epoxidized rubber, T_g = 80°C, and (▲) blend containing 9.7% of prereacted medium-epoxidized rubber, T_g = 74°C.

amount, 9.7% and 10.3%, respectively, of prereacted and as received rubber were obtained and compared to the spectrum of the pure epoxy resin. As noted previously, the sample containing the prereacted rubber exhibits a larger value of the critical stress intensity factor, K_{Ic} = 3.4 MPa $\cdot$ m$^{1/2}$, than the sample containing the unmodified rubber, K_{Ic} = 2.8 MPa $\cdot$ m$^{1/2}$. The results of the DMA study are shown in Figure 16, where two main effects are observed. First, there is a large decrease in the glass transition temperature, T_g, of the epoxy continuous phase for both blends. Second, a drop in the value of the rubbery plateau modulus is also observed. The decrease in T_g is well understood in terms of the Gordon-Taylor Equation[7,9,30] and is observed whether the rubber acts as a plasticizer or flexibilizer. However, the fact that the sample containing the prereacted rubber exhibits an even lower T_g than the sample containing the unmodified rubber only indicates that the miscibility of the rubber with the epoxy matrix has been greatly improved by the prereaction. This effect is quite substantial because the additional drop in T_g is about 6°C. Enhanced miscibility means that very little rubber phase separates upon curing. Indeed, SEM reveals that the volume fraction of dispersed phase, V_D, is less than 2% in this case. On the other hand, the sample containing the unmodified rubber exhibits clear phase separation (Fig. 17). The volume fraction of dispersed phase is about 9% with a mean particle diameter of about 0.3 μm. The presence of a dispersed phase explains the drop in elastic modulus observed in the rubbery plateau re-

gion for the sample containing the unmodified rubber. This drop can be accurately modeled by the Kerner Equation.[9] However, the important fact here is that the sample containing the prereacted rubber exhibits an even lower elastic modulus, whereas there is almost no significant amount of dispersed phase in this case. This decrease can then only be explained if the prereacted rubber acts as a flexibilizer for the epoxy matrix. Copolymerization of the rubber with the epoxy matrix results in a much looser epoxy network. The theory of rubber elasticity indicates that the drop in modulus is inversely proportional to the average molecular weight between crosslinks.

Dynamic mechanical analysis is, therefore, able to show that the toughening effect observed here is probably due entirely to the flexibilizing action of the prereacted rubber. With the unmodified rubber, part of the rubber phase separates while the remaining part dissolves in the epoxy continuous phase where it acts as a plasticizer. Thus, the improvement is modest in this last case.

CONCLUSIONS

In this article, the microstructure and the reactivity of hydroxyl terminated, epoxidized polybutadiene rubber has been studied. Spectroscopic techniques show that only *cis* and *trans* unsaturations are epoxidized. Internal oxirane groups are characterized mainly by a strong absorption at 885 cm^{-1} in the infrared spectrum and 887 cm^{-1} in the Raman spectrum. When the epoxidized rubber is added to a DGEBA/bisphenol-A epoxy resin, several reactions can take place upon curing. ATR spectroscopy and SEC show that, at 100°C, the terminal oxirane (DGEBA)/bisphenol-A reaction is substantially faster than the terminal hydroxyl/DGEBA reaction, and much faster than the internal oxirane/bisphenol-A reaction.

Thus, prereaction of the rubber with an excess DGEBA is necessary if chemical bonding between the rubber particles and the epoxy matrix is desired. Blends containing 9 to 12% of prereacted rubber exhibit a value of the critical stress intensity factor higher by about 40% than that for the pure epoxy sample. This modest improvement may be due to the fact that the starting epoxy is already ductile (8–9% elongation at failure).

Finally, dynamic mechanical analysis shows that this improvement is mostly due to the flexibilizing effect of the prereacted rubber rather than due to

the presence of a second phase. This result suggests that the possibility of changes in the network structure of the epoxy continuous phase should be considered when reviewing reports of toughness improvement in the literature. Indeed, toughness gain from the flexibilizing effect might become very substantial, especially if the starting epoxy is a brittle resin.

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