Characterization of the phase structure of an amine cured rubber modified epoxy*

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The phase structure of an amine cured, rubber-modified epoxy was characterized. The sharpness of the interface between the matrix and the dispersed phase, the volume fraction of the dispersed phase, the distribution of particle sizes, and the concentration of epoxy in the dispersed phase were determined. Scanning transmission electron microscopy coupled with energy dispersive X-ray analysis revealed that the interface width is less than 500 Å. Variation in the fraction of mobile hydrogens with temperature determined by nuclear magnetic resonance indicated that a small fraction of segments participated in mixing at the interface. Differential scanning calorimetry and nuclear magnetic resonance showed that the volume fraction of the dispersed phase equalled that predicted by assuming all of the rubber plus the epoxy monomer units bonded directly to the rubber precipitates. The distribution of particles greater than 0.1 μm in diameter was measured, and the average diameter of these particles was found to be 0.8 μm. This distribution accounted for approximately 50% of the dispersed phase. The epoxy concentration in the dispersed phase was determined using ^{13}C nuclear magnetic resonance spectroscopy. This concentration was found to be less than that predicted if all the epoxy monomer units attached to the rubber molecules were present in the dispersed phase.

INTRODUCTION

The presence of microscopic rubber particles in an epoxy matrix has been shown to result in a material with enhanced toughness. Three mechanisms have been proposed to explain the improved impact resistance of rubber-toughened epoxies: crazing[1-3], shear banding[1-3], and elastic deformation of the rubber particles[4]. These mechanisms are thought either to act alone, or in combination, to produce the toughening effect. They are sensitive to the distribution of particle sizes, the composition of the dispersed phase, and possibly, the interface composition. Because these parameters are difficult to measure, their relationship to the toughening mechanism has not been thoroughly explored. In addition, the volume fraction of the dispersed phase is a critical parameter governing toughness. McGarry[16] and Bucknell and Yoshi[2] have shown that toughness varies directly with the volume fraction of the dispersed phase. The object of this work was to develop techniques which can be used to quantify these parameters. A description of the techniques developed together with the results obtained for a rubber modified epoxy are given in this paper.

This paper is divided into four sections which discuss in turn: interface sharpness, volume fraction of the dispersed phase, particle size distribution, and composition of the dispersed phase. The sharpness of the interface will be discussed first since questions of particle diameter and volume fraction of the dispersed phase depend on how the boundary between the matrix and the dispersed phase is defined. Transmission electron microscopy (*TEM*) coupled with energy dispersive X-ray analysis was used to place an upper limit on the interface width. The temperature dependence of the fraction of mobile hydrogen, as measured by ^{1}H nuclear magnetic resonance (n.m.r.), was used to show that the volume fraction of interface material is small. Scanning transmission electron photomicrographs were used to determine the volume fraction of dispersed phase. These values were compared with those determined from ^{1}H n.m.r. and differential scanning calorimetry. The particle size distribution was obtained from transmission electron photomicrographs. The composition of the dispersed phase was determined by using ^{13}C Fourier transform nuclear magnetic resonance (*FT* n.m.r.) to analyse the chemical structure of the mobile segments.

EXPERIMENTAL

Materials

The epoxy resin used in all experiments was Epon 828, a diglycidyl ether of bisphenol A with an average molecular weight of 370 g mol^{-1} manufactured by the Shell Chemical Company, Inc. The rubber was Hycar 1300X8, a carboxyl terminated butadiene acrylonitrile random copolymer manufactured by the B. F. Goodrich Chemical Company, Inc. This liquid rubber has an average molecular weight of 3500 g mol^{-1} and contains 18 wt % acrylonitrile. The rubber-modified epoxy was prepared in two steps. Firstly an adduct was formed by reacting 90 parts by weight (pbw) of epoxy with 10 pbw of the rubber (a molar ratio of 85 epoxy to 1 rubber) for 3 h at 150°C. Secondly 100 pbw of this adduct were reacted with 12 pbw of diethanol amine and allowed to cure for 16 h at 71°C.

The ^{13}C magnetic resonance experiments required the preparation of a model compound. Two mols of epoxy were reacted with 1 mol of rubber for 3 h at 150°C. Titration for acid, as well as ^{13}C magnetic resonance, revealed that essentially all of the carboxyl end groups of the rubber had reacted. The composition of the model

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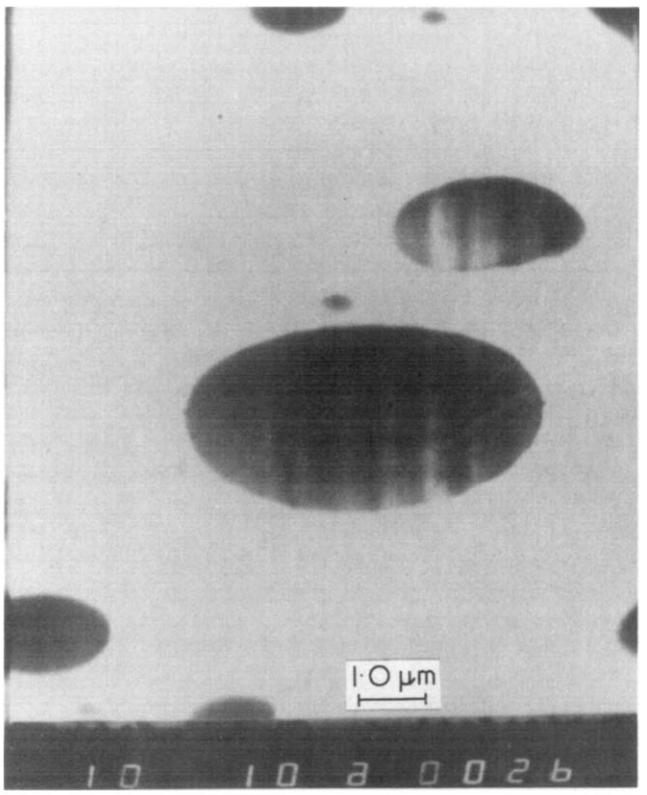

Figure 1 Transmission electron photomicrograph of rubber-modified epoxy at 10 000X magnification showing sampling location for energy dispersive X-ray analysis

compound was thus equivalent to a rubber molecule which had been endcapped with epoxy.

A pure unmodified epoxy was required for the differential scanning calorimetry experiments. This epoxy was prepared by reacting 90 pbw Epon 828 with 12 pbw diethanol amine for 16 h at 71°C. This material was therefore identical to the rubber modified epoxy except that the rubber had been omitted.

Transmission electron microscopy

Specimens for *TEM* were microtomed from material which had been cast as rods 1.1 cm in diameter. The cured samples were stained for ten mins in a tetrahydrofuran solution containing 1% osmium tetroxide as suggested by Riew and Smith[5]. Ultra-thin sections of the stained material were obtained using a Porter-Blum MT-2-B Ultra Microtome with a diamond knife at an included angle of 45°. It was found that a specimen thickness of 2000 Å was sufficiently thin to allow observation of the rubber particles and their interfaces.

The microscopy studies were done using a JEOL 100C scanning transmission electron microscope equipped with a KEVEX 5100 spectrometer for energy dispersive X-ray analysis. This combination allowed the variation in osmium concentration throughout the dispersed phase and the matrix to be investigated. A 10 Å electron beam was used in order to minimize the area being examined for each measurement. The X-ray detector is directed perpendicular to the beam axis. The samples were, therefore, rotated 40° from the plane perpendicular to the beam to increase the signal received by the X-ray detector. The $M\alpha$ osmium peak height was used as a measure of relative osmium concentration. Since osmium reacts selectively with the butadiene in the rubber[6], there is a direct correlation between the osmium concentration and the rubber concentration.

Measurements of the epoxy–rubber interface are complicated by the fact that the dispersed phase is present as spherical particles. After microtoming, the epoxy–rubber interface retains the curvature present in the bulk sample. For a 1μm particle diameter and a 2000 Å slice thickness, the departure from a straight line at the interface is less than 50 Å. Because of this small departure, the microtomed rubber particles were treated as right circular cylinders. After rotation, the particles images are elliptical. Measurement of the osmium concentration was done along the major axis of the ellipse to avoid sampling through the overlapping epoxy–rubber layer formed by tilting the sample. The location of a sampled area was apparent by a contamination spot left on the specimen by the electron beam. A typical photomicrograph of a particle that has been analysed for osmium is shown in *Figure* 1. The carbon buildup on the specimen surface at the point being analysed, together with beam scatter in the sample were estimated to broaden the 10 Å electron beam to 500 Å[7].

Nuclear magnetic resonance

The ^{1}H free induction decay measurements were made on a Bruker SXP broadband spectrometer operating at 100 MHz in the phase sensitive detection mode. The decays were captured by a Biomation 610 transient recorder. The ^{13}C spectra were taken on a system composed of the Bruker SXP spectrometer operating at 25.16 MHz and a Varian XL-100 spin decoupler operating at 100.1 MHz in the broadband mode. In each instance, the Varian V-3800-1 high-resolution magnet was stabilized by a ^{19}F external lock. The ^{1}H data reduction and the ^{13}C Fourier transforms were performed by a Digital Equipment Corp. PDP-11/34 computer. Sixteen ^{1}H free induction decays were accumulated at each temperature. A total of 6400 ^{13}C free induction decays were accumulated for the liquid materials (uncured epoxy, pure rubber, and model compound) while 64 000 decays were accumulated for the solid rubber-modified epoxy. A one second repetition rate and a 90° pulse were used for each type of measurement. The ^{1}H measurements were performed over a range of temperatures, while all ^{13}C measurements were performed at 40°C.

In a two-phase polymeric material where one phase is above and the other phase is below their respective glass transition temperatures, the ^{1}H magnetization is composed of fast- and slow-decaying components[8]. The relaxation behaviour of this material is governed by perturbations in the local magnetic field caused by neighbouring nuclear dipoles. If the polymer lattice is rigid, the nuclei experience the full effect of these interactions, and the relaxation process is rapid. The free induction decay of such a material is usually approximated by a Gaussian function

$$M(t) = M_0 \exp(-t^2 M_2/2) \quad (1)$$

where M_0 is the initial magnetization and M_2 is the second moment of the resonance line in the frequency domain. If the polymer segments are undergoing rotational or translational motions, the interaction fluctuates and begins to approach an average value of zero

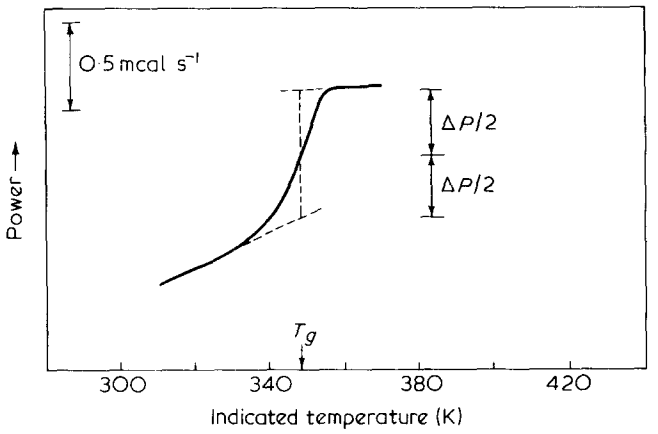

Figure 2 Scanning calorimeter output obtained with a 25 mg rubber-modified epoxy sample and a 31 mg sapphire reference material. The ordinate is the difference between the power required to heat the sample and the power required to heat the reference material, both at 20°C min^{-1}. Temperature is scanned through the glass transition range of the epoxy matrix phase

during the time span of an experiment. This is referred to as motional narrowing, and the relaxation time of the magnetization can increase by an order of magnitude. The decay for segments above their glass transition temperature can be written

$$M(t) = M_0 \exp(-t/T_2) \quad (2)$$

where T_2 is the spin–spin relaxation time. A linear combination of these decay functions, Equations (1) and (2), was used to provide a nonlinear least squares fit of the ^1H free induction decays. The pre-exponential coefficients of the two terms were then proportional to the number of hydrogens in the rigid and mobile phases respectively.

The ^{13}C *FT* spectra were taken under low power coupling conditions which eliminated only the scalar component of the dipole–dipole interaction. The intensities of the broad lines from the rigid phase were very low and could not be distinguished from baseline noise because the areas under each line, whether broad or narrow, were approximately equal to the number of carbons contributing to the peak. Thus, the composition of the mobile phase could be determined by analysing the intensities and positions of the motionally narrowed peaks.

Scanning calorimetry

A Perkin Elmer differential scanning calorimeter, model DSC-2, was operated at a heating rate of 20°C min^{-1} and a range setting of 5 mcal s^{-1}. Calorimetry was carried out on both the rubber-modified and unmodified materials. Samples of both materials were prepared in the form of 0.1 cm thick discs weighing ~25 mg. Holding both the sample thickness and heating rate constant insured that the thermal gradient in each sample was the same in all calorimetric scans. The reference material in these calorimetry experiments was a 31 mg sapphire (α–Al_2O_3) disc.

In order to analyse calorimetric measurements on a two phase polymer, its overall heat capacity, C, is expressed as the weighted sum of the individual phase heat capacities

$$C = W_d C_d + (1 - W_d) C_m \quad (3)$$

where the subscripts d and m denote the dispersed and matrix phases, respectively, and W_d is the weight fraction of dispersed phase. (It will be seen that in the rubber-modified epoxy, the dispersed phase is mostly rubber and the matrix phase is epoxy.) The rise in overall heat capacity of the polymer at the glass transition of the matrix phase is then given approximately by

$$\Delta C \approx (1 - W_d)\Delta C_m \quad (4)$$

This equation is exact only when C_d is a perfectly linear function of temperature over the glass transition range of the matrix phase.

An alternate, approximate equation for W_d could be written in terms of the corresponding heat capacity rise caused by the glass transition of the dispersed phase. Although this alternate approach has normally been adopted for determining W_d[9], the approach embodied by Equation (4) was adopted in this study. This choice was based on three considerations:

(1) Specific heat calculations carried out by one of the authors, based on a polystyrene as a model dispersed phase, showed that the W_d value obtained from Equation (4) is likely to be more reliable,

(2) Calorimetric experiments on the rubber-modified epoxy showed that ΔC could be measured more accurately at the glass transition of the matrix than at the subambient transition of the dispersed rubber phase.

(3) All the results of this paper are consistent with the assumption that the matrix phase contains little or no dissolved rubber. For this reason, the heat capacity of the matrix phase, C_m can be determined from measurements on unmodified epoxy.

Typical calorimetric output in the glass transition range of the epoxy matrix is shown in *Figure* 2. The midrange glass transition temperature T_g for the modified epoxy tended to be slightly lower (by ~1°C) than that of the unmodified epoxy. Since the heating rate was the same for the scans on both rubber modified epoxy (R) and the pure epoxy (P), the ratio of the overall heat capacity rise in these two materials could be determined as follows

$$\frac{[\Delta C]_R}{[\Delta C]_P} = \frac{[\Delta P/M]_R}{[\Delta P/M]_P} \quad (5)$$

where M is the sample mass and ΔP is the step in instrument power at T_g (*Figure* 2).

Considering Equation (4) and the fact that pure epoxy is believed to be a good model for the matrix phase, one can rewrite Equation (5) as

$$\frac{[\Delta P/M]_R}{[\Delta P/M]_P} = \frac{(1 - W_d)\Delta C_m}{\Delta C_m} = 1 - W_d \quad (6)$$

RESULTS

Characterization of the interface

Results of the X-ray analysis of the particle–matrix interfacial region are shown in *Figure* 3. The intensity of the osmium $M\alpha$ peak varies sharply, defining a distinct interface of less than 500 Å width. The interface width measurement is limited by the 500 Å diameter of the scattered electron beam. Similar results were obtained for particle sizes ranging from 0.8 to 3.0 μm.

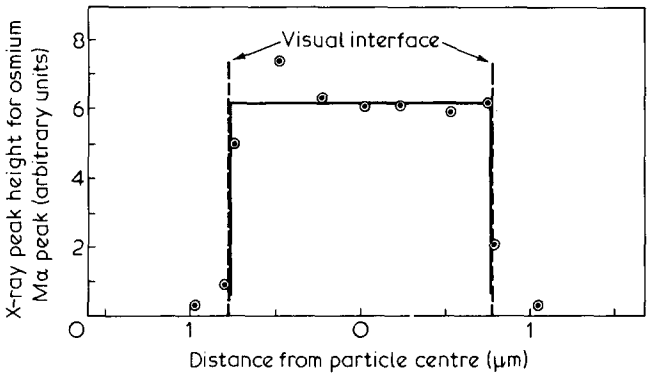

Figure 3 Concentration variation of osmium through the dispersed phase for rubber-modified epoxy

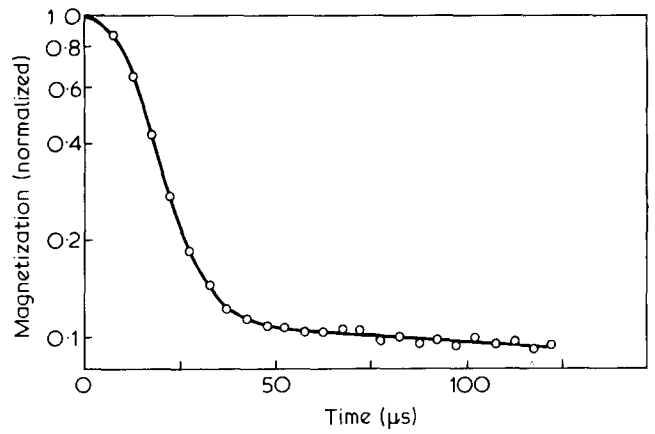

Figure 4 The ^1H free induction decay of rubber modified epoxy. The solid line is a nonlinear least squares fit of the data using a fast Gaussian and a slow exponential decay

Figure 4 shows the decay of the ^1H magnetization *versus* time for rubber modified epoxy at 28°C. The solid line is the non-linear least squares fit of the data using a linear combination of Equations (1) and (2). Every fifth data point has been shown for clarity. The decomposition assigns 87.3% of the hydrogen to the rigid epoxy phase and 12.7% of the hydrogens for the mobile rubber phase. We are confident that this decomposition is accurate to within 2%. The root-mean-square deviation of the experimental points from the theoretical fit was consistently less than 0.5% of the initial magnetization. The greatest uncertainty arises from the fact that the Gaussian decay depicted in Equation (1) is only the first term of a series expression for the decay of a generalized rigid lattice. However, not only does the Gaussian function provide an excellent fit to the initial component of the rubber modified epoxy's two component decay, but it also provides an excellent fit to the entire decay of pure epoxy in which two component behaviour does not complicate the analysis. In addition, M_2 of pure epoxy, 0.670×10^{10} s^{-2}, is in excellent agreement with the second moment of the epoxy component, 0.697×10^{10} s^{-2}, in the two phase material.

Proton free induction decays were recorded and analysed as a function of temperature. The results are shown in *Figure* 5. The decrease in percent rigid hydrogen near -10°C corresponds to the glass transition of the rubber phase, while the decrease near 110°C corresponds to the glass transition of the epoxy matrix. Note that these transitions were measured by a technique whose characteristic frequency is near 10^4 Hz, so they occur at higher temperatures than if they were measured by conventional low frequency methods. The decrease in the percent rigid hydrogen in two distinct transitions with a relative constant plateau region between transition is indicative of distinctly separated phases. Segmental mixing near the interface would result in material whose glass transition occurred at a temperature intermediate to the pure phase material transitions. This would mean that the percent rigid hydrogens would show a continual decrease with increasing temperature. Such behaviour has been observed for a polyurethane and, to some extent, a polystyrene/butadiene block copolymer in which the interface is believed to contain a significant volume of material[8]. The flatness of the plateau region for rubber modified epoxy leads to the conclusion that the number of interfacial epoxy or rubber segments is much less than the number of rubber segments in the dispersed phase.

Volume fraction of the dispersed phase

The volume fraction of dispersed phase was estimated from photomicrographs and compared to the volume fraction as determined by magnetic resonance and calorimetry. *Figure* 6 is a typical 3000× photomicrograph of an osmium stained section used to estimate the volume fraction. Examination of these micrographs revealed that less than 1% of the rubber particles contained observable phase separated islands of immobile epoxy. Since the concentration of these islands was small, they were neglected in the analysis of the micrographs. The dispersed phase was assumed to be composed of mobile segments when the area fraction was first determined by manually measuring the diameters of particles in several photographs, including only particles whose diameters were 0.1 μm and larger. The average area fraction was 7.2% with a standard deviation of 0.3%. The volume fraction was then calculated from the area fraction by taking into consideration the sample thickness and, as discussed in the next section, the distribution of particle sizes[10]. The calculated volume fraction was 6.6% in contrast to predicted values of 11.0% if only the rubber segments precipitate and 12.9% if both the rubber and the epoxy monomer units attached directly to the rubber

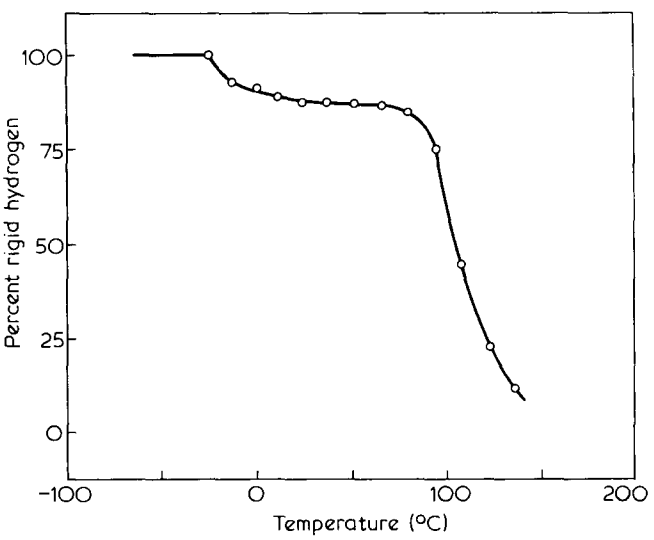

Figure 5 The percent hydrogens attributed to the glassy phase as a function of temperature

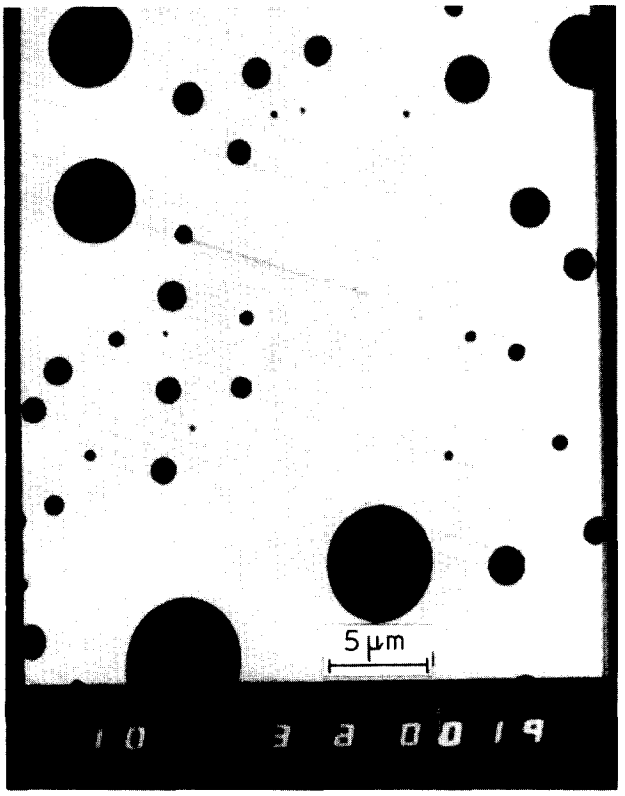

Figure 6 Transmission electron photomicrograph of rubber-modified epoxy at 3000X magnification

molecules precipitate. If the epoxy islands had not been neglected, then the discrepancy with the theoretical values would have been greater. These results imply that approximately one half of the rubber molecules either remain in the matrix or are contained in phases less than 0.1 μm in diameter. This ambiguity was resolved by calorimetry and magnetic resonance experiments.

The presence of a well-defined plateau region in the plot of percent rigid hydrogens *versus* temperature shown in *Figure* 5 permits the volume fraction of dispersed phase to be calculated. All rubber segments are assumed to be mobile as well as sufficient epoxy segments to account for the total percent of mobile hydrogens. The density of each phase was assumed to be equal to the density of material composed of only that segment (0.95 g/cc for the rubber and 1.20 g/cc for the epoxy). Based on *Figure* 5, this calculation yields $12.4 \pm 2.0\%$ by volume mobile phase, which is significantly more than the percent volume dispersed phase as measured by microscopy. This value compares favourably with the theoretical values of 11.0 and 12.9% dispersed phase, depending on whether the epoxy endcaps of the rubber molecules are assumed to be in the dispersed or matrix phase.

In order to resolve the discrepancy between the microscopy and magnetic resonance results, a calorimetry technique was employed to determine the volume fraction of the dispersed phase. Calorimetric experiments analysed by Equation (6) yielded a 95% confidence interval for W_d of $0.10 < W_d < 0.13$. This converts to a volume fraction of $14 \pm 2\%$, which compares favourably to the $12.4 \pm 2\%$ determined by the ^{1}H n.m.r. analysis.

There is a significant difference between the volume fraction of dispersed phase as determined from photomicrographs and the volume fraction of dispersed phase as determined by magnetic resonance and calorimetric techniques. The source of this difference is believed to be due to the resolution limit of the 3000 × magnification photomicrographs; only particles greater than 0.1 μm diameter were counted. *Figure*7 shows a photomicrograph taken at 15 000 × magnification; examination of this figure reveals a significant number of particles with diameters smaller than 0.1 μm. The resolution is such, however, that it is difficult to quantify the volume of small particles from a photomicrograph. From the difference in volume fractions observed using 3000 × photomicrographs and ^{1}H magnetic resonance and scanning calorimetry, it can be concluded that approximately one half of the rubber precipitates as particles whose diameters are less than 0.1 μm.

Particle size distribution

The size distribution for particles greater than 0.1 μm diameter was determined from 3000 × photomicrographs and is shown in *Figure* 8. The average particle size was found to be 0.8 μm. Estimation of particle size distribution from transmission electron photomicrographs involves two corrections when the particle diameter approaches or is larger than the sample thickness, as was true in this study. Firstly, the probability of observing a large particle is higher than for a small particle, and secondly, the probability of observing the true diameter of a particle decreases as the particle size increases. A method for converting the observed particle size distribution to the true particle size distribution was developed by J. A. Davis and C. A. Morgan[10]. A comparison of the two, shown in *Figure* 9, indicates very little difference.

A more severe correction to the observed particle size distribution is required by the fact that only particles with diameters greater than 0.1 μm were counted. As discussed

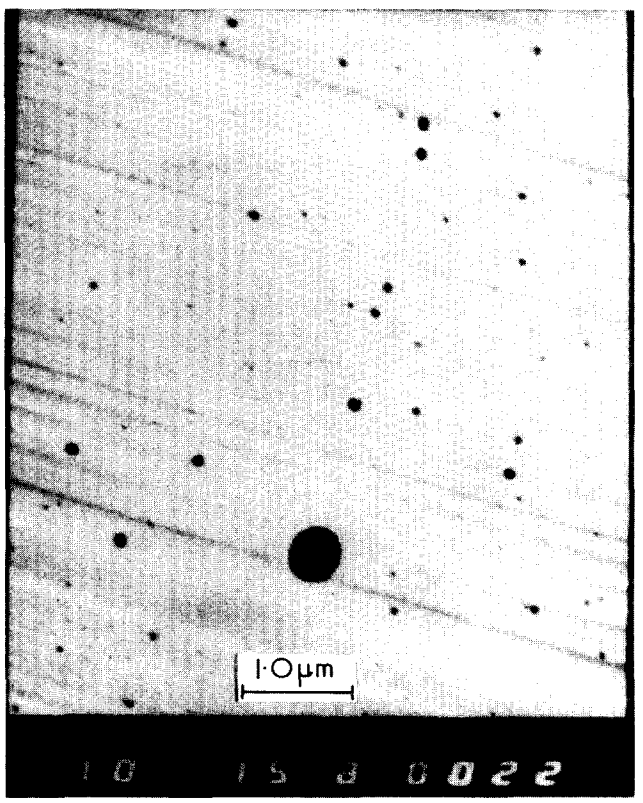

Figure 7 Transmission electron photomicrograph of rubber-modified epoxy 15 000X magnification

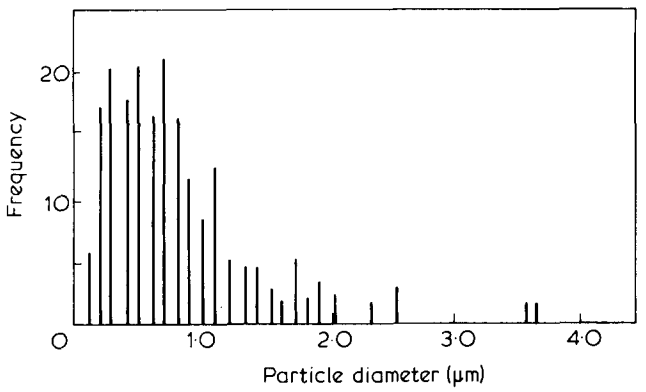

Figure 8 Particle size distribution of rubber-modified epoxy for particles whose diameters are greater than 0.1 μm

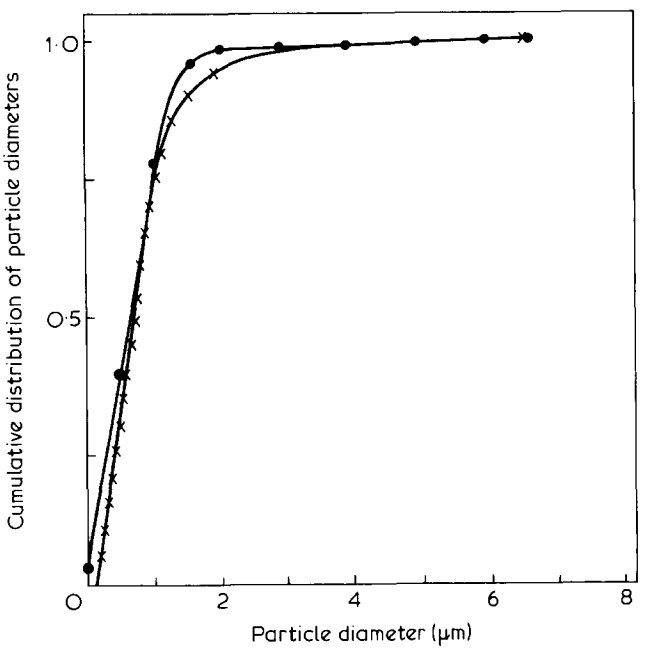

Figure 9 Observed, (x), and corrected, (•), particle size distribution for rubber-modified epoxy

previously, approximately one half of the rubber precipitates as particles with diameters less than 0.1 μm. The presence of such a large population of small particles requires that the size distribution cannot be unimodal, since any reasonable extrapolation of the observed distribution of particles with diameters greater than 0.1 μm cannot account for the volume of particles below 0.1 μm.

Composition of the dispersed phase

The composition of the dispersed rubber phase was examined by ^{13}C *FT* n.m.r. *Figure* 10 shows the ^{13}C *FT* spectra of epoxy resin and of the pure unreacted rubber. The assignments for the epoxy reference are those reported in ref 11. No attempt has been made to assign the peaks of the rubber whose spectrum is complicated by the random order of its monomer units.

Figure 11 shows the ^{13}C *FT* spectra of the model compound and the fully cured rubber modified epoxy. Each spectrum was taken under condition of low powered ^{1}H decoupling. Note that under these conditions the ^{1}H–^{13}C dipole–dipole interactions broaden the signal from any segment for which the interaction is not motionally narrowed. Spectrum 11a shows the sensitivity with which mobile epoxy segments can be detected in the presence of large amounts of rubber segments. Comparing spectrum 11a with spectra 10 and 10b, one sees that the presence of mobile epoxy segments can be clearly established by peaks at 156 ppm, the peak shoulder at 143 ppm, and the increased intensity of the peak at 114 ppm. The positions of these aromatic peaks are not affected by the rubber epoxy reaction. Peaks in the 69 and 50 ppm regions can also be seen although these peaks may shift and broaden due to the reaction. Completeness of the rubber epoxy reaction can be established by the change in position of the terminal carbon of the rubber from 175 to 171 ppm.

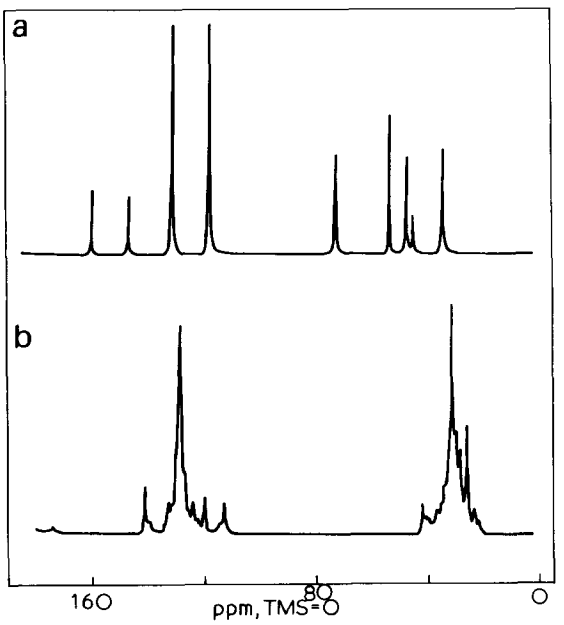

Figure 10 The ^{13}C Fourier transform spectra of (a) epoxy prepolymer and (b) rubber prepolymer

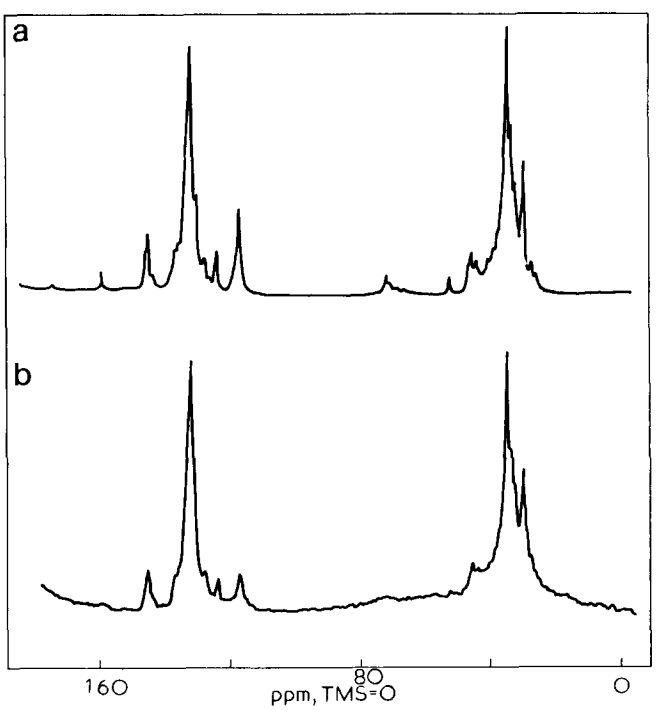

Figure 11 The ^{13}C Fourier transform spectra of (a) 2 mols epoxy to 1 mol rubber, and (b) cured rubber modified epoxy

Spectrum 11b can now be examined to determine the concentration of mobile epoxy segments in the dispersed phase. The peak at 156 ppm, the peak shoulder at 143 ppm, and the increased intensity of the peak at 114 ppm are all absent from the fully cured material. There is only a slight hint of a very broad peak at 69 ppm. Comparing spectrum 11b with spectrum 11a, it can be confidently concluded that the concentration of mobile segments in the rubber phase is less than the concentration of epoxy end caps. This means that the epoxy concentration in the dispersed phase is less than 17 wt %.

Knowledge of the composition and volume fraction of the dispersed phase coupled with knowledge of the composition of the entire material can be used to determine the composition of the matrix phase. The volume fraction of the dispersed phase was found to be $12.4 \pm 2\%$ by ^1H magnetic resonance. Assuming that the actual volume of the dispersed phase is equal to the lower limit of 10.4% and that this phase contains 17 wt % epoxy, then the matrix phase contains a maximum of 2.4% rubber by volume. The parallel calculation based on the volume fraction of dispersed phase as determined by calorimetry predicts that the matrix phase contains a maximum of 0.9% rubber by volume. Note that these calculations only predict a maximum permissible volume fraction of rubber; neither calculation should be interpreted as an argument for the presence of any rubber in the epoxy matrix.

DISCUSSION

The data presented in the results section showed that there cannot exist a unimodal distribution of particle sizes for the rubber modified epoxy examined. Two mechanisms are thought to govern the distribution of particle sizes. Visual observation of the epoxy cure reveals that precipitation of the dispersed phase is initiated by the addition of the curing agent to the epoxy/rubber solution. During the initial precipitation of the rubber molecules, very little reaction between the epoxy end caps of the rubber molecules and the bulk epoxy will have taken place. The number and size of particles formed during this precipitation will be governed by differences in the solubility parameters of the two materials, viscosity, surface tension, and nucleation sites, as in an incompatible polymer blend. The size of particles formed during this precipitation is not restricted by the molecular weight of the rubber molecules. This is evident when examining the size distribution of the dispersed phase; particles up to 6 μm are observed. These particles are several orders of magnitude larger than the mean end-to-end distance of the rubber molecule. This precipitation mechanism is felt to be responsible for the population of larger particles.

Half of the dispersed phase was found in particles 0.1 μm and less in diameter. Many of these smaller particles are thought to precipitate after appreciable epoxy cure has taken place. The epoxy end caps will then have undergone reaction with the bulk epoxy resulting in formation of an ('*AB*') segmented copolymer with the rubber molecule forming the '*B*' segments. The '*A*' blocks will be composed of network forming epoxies which limit the mobility to the copolymer. The size of the dispersed phase formed by these segmented copolymers will be governed by the rubber molecular weight in a manner analogous to that elucidated by Meier[12] for thermoplastic block copolymers. Small angle X-ray scattering (SAXS) experiments are currently being carried out with the initial goal of characterizing the size distribution of smaller particles in the cured epoxy.

In addition to determining the relationship between molecular weight and particle size for block copolymers, the factors affecting the width of interfacial zone for block copolymers have been investigated. Several equilibrium thermodynamic models have been proposed[12,13] which predict interfacial regions ranging from zones containing 40% of the dispersed phase to interfaces that are essentially sharp. Todo, *et al.*[14] using SAXS have measured the thickness of the domain boundary for a styrene–isoprene block copolymer. They found a boundary layer of 21 Å for particles ranging from 60 to 300 Å independent of particle diameter. At a particle diameter of 300 Å, this interface contains 35% of the particle volume.

Rubber modified epoxies present added complications when considering interfacial thickness. The probability of attaining equilibrium is lessened by the decreasing mobility of the segmented copolymers and the increasing viscosity of the matrix phase as the epoxy cure proceeds. Measurement of the interfacial width through SAXS is complicated for these materials because of the large distribution of particle sizes. Direct measurement of the interfacial zone is possible for large particles, as was done in this work using energy dispersive analysis with a scanning transmission electron microscope. The resolution limit on this method is 500 Å due to the electron beam spreading as it passes through the sample. In a particle of 1 μm radius, this means that interface regions containing 14% or less of the particle volume will be detected as sharp. The results, for the rubber-modified epoxy studied, indicated that the interface was sharp within the limits of the measurements. Even this limited characterization of the interface width is significant since no previous measurement of the interface has been reported on rubber-modified epoxies.

A second measure of the interfacial mixing was accomplished through the use of magnetic resonance measurement of the variation of mobile hydrogens with temperature. The amount of material undergoing transition from the glass to rubber state at temperatures intermediate to the transition temperatures of the pure materials increases as the degree of mixing at the interface increases. This broadening of the glass transition due to interfacial mixing has been observed in other two phases polymers[8]. In the rubber-modified epoxy studied, the transitions for both phases were sharp indicating that the interfacial region was small. This result applied to the entire dispersed phase and is not restricted to large particles.

In the introduction, several studies were cited that related increased volume of dispersed phase with increased toughness. The usual technique for determining the volume fraction of the dispersed phase is to measure the area fraction of the dispersed phase from micrographs taken on a scanning or transmission electron microscope. In this study, volume fraction was determined using micrographs taken on a transmission electron microscope. Because of the large distribution of particle size, the volume fraction estimated from 3000× magnification micrographs yielded a volume fraction approximately one half the true value. Both calorimetry and magnetic resonance yielded values that agreed with values predicted for complete precipitation of the dispersed phase.

Since determination of the volume fraction is critical to predicting toughness in these materials, it seems appropriate to recommend that the magnetic resonance or calorimetric methods described in this paper be used for future determination of volume fraction.

Meeks[15] and Bucknall and Yoshii[2] have found that different curing agents result in different morphologies. It is interesting to compare the results obtained in this study with results reported in literature using different curing agents. The epoxy content of the dispersed phase measured using ^{13}C magnetic resonance can be compared with qualitative estimates made by others. McGarry[16], when examining a rubber-modified epoxy cured with DMP-30, found a morphology dominated by rubber particles containing islands of phase separated epoxy. He speculated that the two phase particles are composed of rubber and epoxy rich phases that form an interprentrating network indicating a significant mobile epoxy concentration. Siebert and Riew[17] investigated a rubber–epoxy solution in which the rubber was 14% acrylonitrile. By measuring the solubility of the epoxy in rubber at room temperature, they concluded that the concentration of epoxy dissolved in the dispersed phase was 50% for a cured rubber modified epoxy. In contrast to these results, determination of the epoxy content in the dispersed phase for the rubber modified epoxy used in this study revealed that there is less than 17% epoxy by weight. Examination of an osmium stained section via microscopy showed that less than 1% of the rubber particles contained observable islands of epoxy.

STEM, ^{1}H and ^{13}C magnetic resonance, and differential scanning calorimetry have been used to characterize the phase structure of an amine cured, rubber-modified epoxy. The sharpness of the interface between the matrix and the dispersed phase, the volume fraction of the dispersed phase, the distribution of particle sizes, and the concentration of epoxy in the dispersed phase were determined. Characterization of the phase structure of rubber modified epoxies by these methods should permit greater insight into the mechanisms governing the toughness of these materials.

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