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MORPHOLOGY OF RUBBER MODIFIED EPOXY ENCAPSULANTS*

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ABSTRACT

Examination of rubber modified epoxy, cured with diethanol amine, via the transmission electron microscope has shown that a broad distribution of rubber particle sizes exists. The average particle size for particles greater than .1 μm was found to be .8 μm. A significant population of particles was found whose diameters are less than .1 μm. Examination of the particle interface showed that the interface between the dispersed phase and the epoxy matrix was sharp within the accuracy of the method used. The morphology observed was compared against morphologies which have been purported to result in toughening via shear banding and crazing. It was found that the observed particle size distribution did not preclude toughening by these mechanisms.

INTRODUCTION

Incorporation of rubber spheres into an epoxy matrix has resulted in encapsulants that have greater impact resistance and the capability to withstand·more severe thermal cycling without an appreciable loss in physical properties. For these reasons, rubber modified epoxies have become the encapsulants of choice for neutron generators during the past several years. The rubber modified epoxy is used without fillers, with aluminum oxide, or with glass microspheres depending upon the properties which are most critical.

The rubber used at Sandia Laboratories is a butadiene/ acrylonitrile copolymer produced by the B. F. Goodrich Chemical Company, Inc., containing approximately 18% acrylonitrile. A carboxylic acid group terminates each end of the molecule. The average molecular weight is 3500 g/mole. The Goodrich designation for this product is CTBN 1300X8. Prior to curing the epoxy, each rubber molecule is chemically attached to two epoxy molecules through reaction of the carboxylic acid end groups with the oxirane ring of the epoxy molecule. During cure of the epoxy, the rubber precipitates to form a second phase of spherical particles whose average diameter is ~ 1 μm. Typically the ratio of epoxy to rubber is 9:1.

It has been shown that the particle size and distribution of the rubber particles has a great effect on the toughness of cured resin.[1,2] Particle size is generally controlled through the choice of rubber acrylonitrile content, amount of rubber, curing agent, and cure schedule. This has led to the proposal of several mechanisms through which the rubber toughening of epoxies occurs. The rubber particles have been proposed as sites for stress concentration that result in crazes which dissipate energy.[1-3] The rubber spheres are also proposed as sites around which plastic flow occurs resulting in shear banding.[1-3] The rubber spheres are generally assumed to be chemically attached to the matrix through the epoxy linkages of each rubber molecule. When a stress is applied and a crack formed, toughening is proposed to result from the dissipation of energy through the elastic deformation of the rubber particles.[4] It has been proposed by Sultan & McGary[1] that crazing predominates when particles are > 1 μm in diameter and that shear banding occurs when the particles are smaller.

Since particle size and distribution and the interface between the rubber spheres and the matrix, are thought to be the governing parameters for increased toughness in the rubber modified epoxies, a method was needed to define these variables. The method chosen was examination of osmium stained samples in a transmission electron microscope. This technique allows observation of submicron particles and also allows observation of a randomly picked sample instead of a fracture surface which are the major objections to using optical and scanning electron microscopy.

SAMPLE PREPARATION

Specimens for examination in the transmission electron microscope may be cut from bulk samples or from specimens cured in molds designed for compatibility with the microtome. The standard sample used in these experiments was a rubber modified Epon 828 epoxy sample cured with diethanol amine. The cure schedule was 16 hours at 71°C.

The cured samples were then stained in an osmium tetraoxide (OsO_4) solution using the method of Riew and Smith.[6] A 1% osmium in tetrahydrofuran solution was used with a staining time of 10 minutes. The tetrahydrofuran allows greater penetration of the osmium in the epoxy matrix. Osmium tetraoxide reacts with the carbon/carbon double bonds to give a rigid material[6] which allows microtoming. The reaction is shown below:
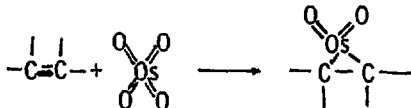
Since carbon/carbon double bonds are present in the butadiene portion of the rubber molecules and absent in the epoxy, the rubber molecules are selectively stained. The osmium atom has a high electron scatter cross section which provides contrast between the stained rubber particles and the epoxy matrix in the electron microscope, with the rubber appearing opaque and the epoxy transparent.

Microtoming of the stained specimen was accomplished using a Porter-Blum MT-2-B Ultra Microtome and a diamond knife with an included angle of 45°. It was found that a slice thickness of 2000Å was sufficiently thin to allow observation of the rubber particles and their interface. Staining times of ten minutes were sufficient to obtain staining to a depth of 20 to 50 μm which allows several sections to be taken from a specimen. No particle distortion occurred during microtoming of the samples cured with diethanol amine. Some distortion was observed in a sample cured with Shell curing agent Z.

INTERFACE EXAMINATION

All transmission electron microscopy was done in a JEOL 100C electron microscope equipped for scanning transmission operation and using a KEVEX 5100 spectrometer for energy dispersive x-ray analysis. This combination allowed investigation of the variation of osmium concentration through the dispersed phase into the matrix. A 100Å electron beam was used for the
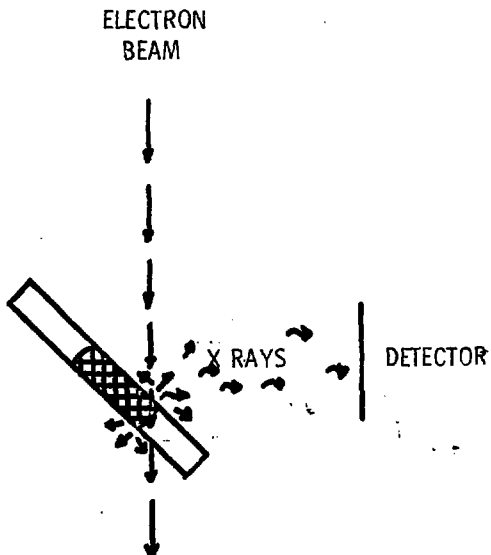
ELECTRON BEAM

X RAYS

DETECTOR

Figure 2. Schematic of epoxy/rubber section illustrating
sampling error introduced through sampling per-
pendicular to the axis of rotation for energy
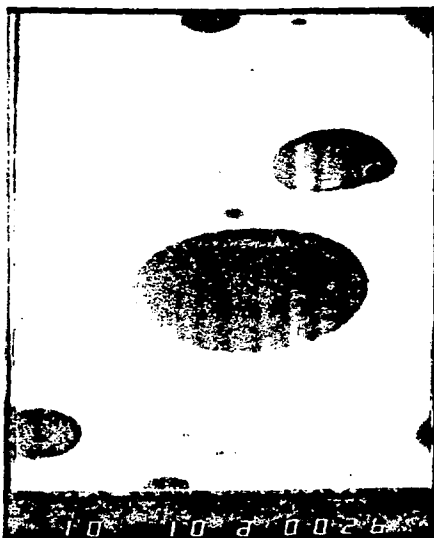dispersive x-ray analysis.

Figure 2. Transmission electron photomicrograph of Epon
828/rubber/diethanol amine at 10,000x magnifi-
cation showing sampling location for energy
dispersive x-ray analysis.

analysis to minimize the area sampled with each measurement. The sample was rotated 40° from horizontal to increase the signal received by the x-ray detector. The M∝osmium peak height was used as a measure of relative osmium concentration. Since the osmium reacts only with the butadiene, there is a direct correspondence between the osmium concentration and the rubber concentration. Th.. measurements were taken on a line parallel to the axis of rotation. This minimizes errors introduced from sampling at an interface as shown in Figure 1. Location of the area sampled was accomplished through location of the contamination spot left by the electron beam. A typical photomicrograph of a particle that has been analyzed for osmium is shown in Figure 2. The carbon build up on the surface at the point being analyzed together with beam scatter in the sample has been estimated to broaden the electron beam from 100Å to 500Å.[7] Particles analyzed were all large relative to the thickness of the sample to minimize errors introduced through particle curvature at the interface.

Figure 3 shows a typical result for Epon 828/rubber/ diethanol amine. The interface is perfectly sharp within experimental error. Similar results were obtained for particle sizes ranging from .8 to 3 μm. This indicates that precipation of the rubber occurs early in the epoxy cure and that little or no reaction has occurred between the epoxy attached to the rubber molecules and the remaining epoxy. If appreciable reaction had occurred, a diffused interface would be seen corresponding to differing degrees of crosslinking. This observation fits with what is visually observed during the epoxy cure. When no rubber is present, addition of the curing agent causes the solution to cloud, but as the curing agent reacts, the solution regains its clarity. Five minutes after the addition of the curing agent, the epoxy solution is again clear. When rubber is present in the epoxy solution, addition of the curing agent also causes clouding, but the solution never clears. This suggests that the rubber starts precipitating during the first five minutes of the epoxy cure before the epoxies attached to the rubber molecules have had time to react. During subsequent cure of the epoxy matrix, it seems reasonable to assume that the epoxy attached to the rubber molecule which is on the interface undergoes reaction with the epoxy matrix. Thus even with a sharp interface the rubber is probably still chemically bound to the matrix. This speculation means that the toughening mechanism involving elastic deformation of the rubber particle is available but that the energy required to pull the particle from the matrix may be lower than the ultimate strength of the rubber.

PARTICLE SIZE DISTRIBUTION AND VOLUME FRACTION

Figure 4 shows a typical transmission electron photomicrograph of osmium stained sections of Epon 828/rubber/ diethanol amine. Particle size distribution was measured from these photomicrographs. Examination of Figure 4 shows that the
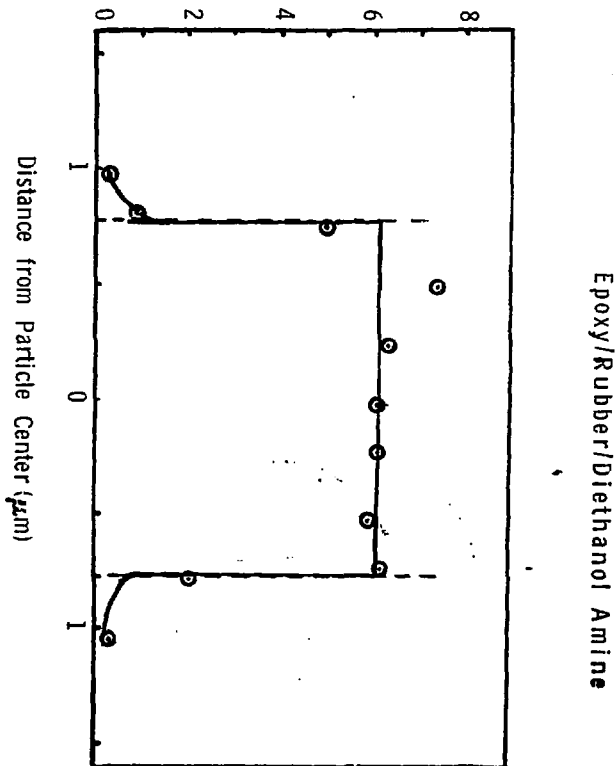
Figure 3. Concentration variation of osmium through the dispersed phase for Epon 828/rubber/diethanol amine.

particle size distribution is large. Particle size distribution measurements were limited to particles whose diameters were .1 µm or greater because of resolution limitations of the photomicrographs taken at 3000X magnification. The average particle size was found to be .8 µm. The distribution of particle sizes is shown in Figure 5.

Estimation of particle size distribution from transmission electron photomicrographs results in some bias errors when the particle diameter approaches or is bigger than the slice thickness, as is the case in this study. Two sources of bias are that the probability of observing a large particle is higher than for a smaller particle and 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 true particle size distribution was developed by J. A. Davis and C. A. Morgan.[8] A comparison of the observed and true particle size distribution is shown in Figure 6. There is very little difference between the two, indicating that the bias errors are offsetting.

A more severe error is introduced through the restriction of counting only particles whose diameters are greater than .1 µm. Figure 7 shows a photomicrograph of Epon 828/rubber/ diethanol amine at 15,000X magnification. It is apparent from this photomicrograph that a great number of particles exist whose diameters are less than .1 µm. A method is being sought to include these in the particle count for determination of particle distribution. Examination of the particle size distribution shown by Figure 5 and the presence of smaller particles as shown by Figure 7 leads to the conclusion that toughening by both shear banding and crazing can occur in Epon 828/rubber/diethanol amine if the observation of Sultan and McGary[1] is correct.

The weight fraction of rubber is 10% of the uncured resin. When difference in density and the addition of curing agent are considered, however, a rubber volume fraction of 11% is predicted if all the rubber precipitates. Calculation of volume fraction from the observed area fraction in the photomicrographs gives approximately 7%. The difference between the theoretical 11% volume fraction and the observed 7% volume fraction must be accounted for in one of two ways. The rubber may be present as small particles, or it must be dissolved in the matrix. Measurements at Sandia Laboratories by R. A. Assink and R. R. Lagasse, using nuclear magnetic resonance and differential scanning calorimetry respectively, have found that the volume fraction of the dispersed phase is 11%. This indicates that substantially all the rubber precipitates and that the 4% unaccounted for by the particles whose diameters are greater than .1 µm must be present as particles whose diameters are less than .1 µm.
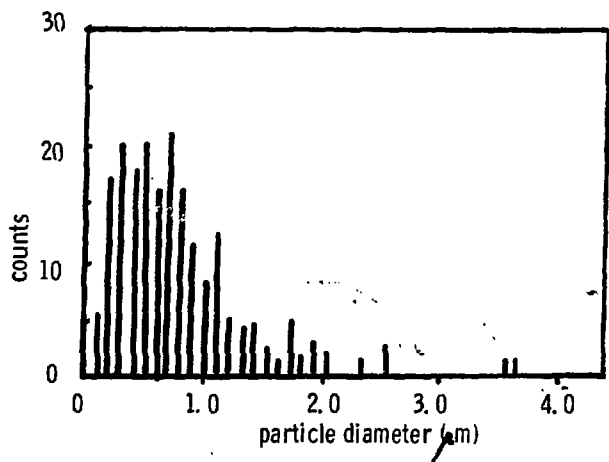
Figure 5. Particle size distribution for Epon 828/rubber/
diethanol amine for particles whose diameters
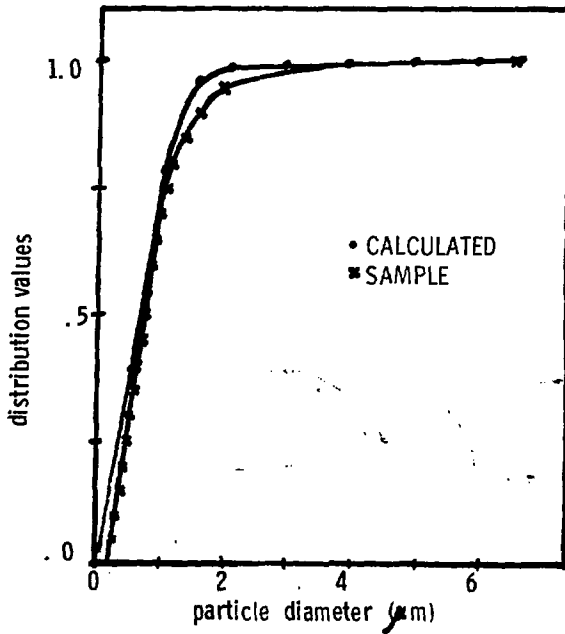are greater than .1 μm.

Figure 6. Observed and calculated particle size distribution for Epon 828/rubber/diethanol amine.
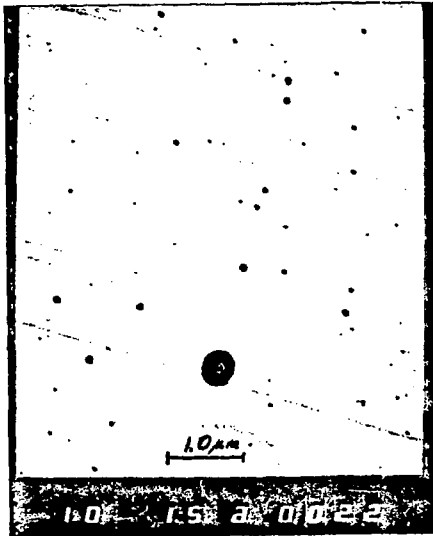
Figure 7. Transmission electron photomicrograph of Epon
828/rubber/diethanol amine at 15,000x magnifi-
cation.

SUMMARY

Examination of rubber modified epoxies via transmission electron microscopy of osmium stained sections has led to a clearer understanding of the morphology of the rubber modified epoxy. Distribution of the dispersed phase particle size for particles greater than .1 μm has been found, and the presence of a second population of particles whose diameters are less than .1 μm shown. This result indicates that the toughness mechanisms of shear banding for particles less th n .1 μm diameters and crazing for particle diameters approximately 1 μm are available for toughening the rubber modified epoxies used in neutron generators. Interface studies have suggested that the epoxies attached to the ends of the rubber molecule undergo very little reaction prior to precipitation, leading to speculation that the bond between the epoxy matrix and the rubber phase fail before the rubber reaches its ultimate strength when it is deformed. The interface was found to be very sharp. The width of the interface was within the experimental error of the measurement which is $\pm$ 300A.

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