

# Thermal Behavior and Morphology of Rubber-Modified Epoxies

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## SYNOPSIS

Rubber-modified epoxies of tetraglycidyl-4,4'-diaminodiphenyl methane and a carboxyl-terminated copolymer of butadiene-acrylonitrile (CTBN) have been investigated by differential scanning calorimetry, scanning electron microscopy, and micrograph image analysis. Bisphenol-A (BPA) was used to produce chain-extended resins by reaction with the epoxy-terminated rubber. Diaminodiphenyl sulfone was used as a hardener. Partially cured resins were prepared with different amounts of added CTBN and cured in an oven for different cure times at 448 K. From the measured heat of reaction of the samples, a fast curing reaction was observed when BPA was present in the resin formulation. In the study of the morphology, the average size of the domains was seen to increase with the CTBN content. These CTBN-rich domains appear to include substantial amounts of epoxy material, as indicated by the measured glass transition temperature of the CTBN-rich phase. The size of domains was observed to range mostly from 0.1 to 5  $\mu\text{m}$  in diameter and to show a slightly bimodal distribution, with modes around 1  $\mu\text{m}$  and 3–4  $\mu\text{m}$  when 15 and 20 phr CTBN was added. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

To improve the impact resistance and fracture toughness of thermoset epoxy resins, low molecular weight liquid rubber-modified epoxies have been studied by many investigators.<sup>1–12</sup> Sultan and McGarry<sup>1</sup> studied rubber-modified epoxies of the diglycidyl ether of bisphenol-A (DGEBA) with a carboxyl-terminated copolymer of butadiene-acrylonitrile (CTBN) and suggested that the observed enhancement in fracture toughness of the rubber-modified epoxy is derived from crazing and band formation. Riew et al.<sup>2</sup> showed that the addition of bisphenol-A (BPA) to the formulation of the DGEBA/CTBN resin increased the toughening effect of the rubber. In the study of rubber-modified epoxies of DGEBA/CTBN with BPA added to the resin formulation by Manzione et al.,<sup>5,6</sup> they concluded that the dissolved rubber promotes plastic

deformation and necking at low strain rates, providing large increases in the elongation at break.

For the rubber-modified epoxy resins of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and CTBN,<sup>13–16</sup> Lee et al.<sup>13</sup> studied the transition phenomena and the morphology for resins with different amounts of CTBN added. Choe and Oh<sup>16</sup> studied the TGDDM/CTBN blend with the addition of BPA and observed the size of domains using scanning electron microscopy.

Recently, investigators have studied the modification of epoxies with thermoplastics such as poly(ether sulfone)<sup>17,18</sup> and poly(ether imide)<sup>19</sup> to reduce the lowering of the glass transition temperature while enhancing the fracture toughness of brittle epoxy resins.

In our present study, we examined the thermal behavior of rubber-modified epoxies of the TGDDM/CTBN type with added BPA by determining experimentally the heat of reaction ( $\Delta H$ ) and the glass transition temperature ( $T_g$ ) by differential scanning calorimetry (DSC). The morphology of the rubber-modified epoxies was examined by

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scanning electron microscopy (SEM) and image analysis of the photomicrographs.

## EXPERIMENTAL

### Materials

The epoxy resin used in this work was Ciba-Geigy MY720 resin, which consists essentially of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM). The elastomer used as a rubber-modifier was carboxyl-terminated butadiene-acrylonitrile (CTBN) copolymer produced by the B. F. Goodrich Co. under the name of Hycar CTBN 1300 × 13. The characteristics of CTBN are shown in Table I, and the structures of the materials used in this study are shown in Figure 1.

Epoxy and CTBN were prereacted at 353 K in the presence of triphenylphosphine catalyst.<sup>15</sup> Pre-reaction insures the formation of the epoxy-rubber intermediate and promotes blending of the epoxy and the rubber prior to the cure.<sup>6</sup> Bisphenol-A (BPA) was used to produce chain-extended solid resins by reaction with the epoxy-terminated rubber.<sup>1,2,6,12,14</sup>

The resin was cured with diaminodiphenyl sulfone (DDS) that was supplied by Ciba-Geigy under the name of hardener HT 976. Methyl ethyl ketone (MEK), 150 parts per hundred resin by weight (phr), was used as a solvent to decrease the viscosity of the resin. The resin formulations with different amounts of CTBN are presented in Table II.

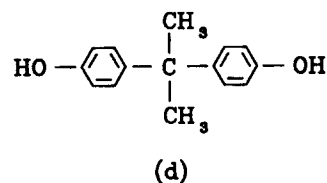
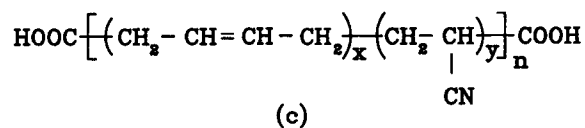
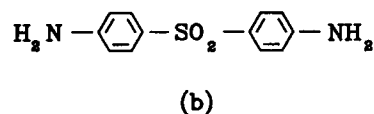
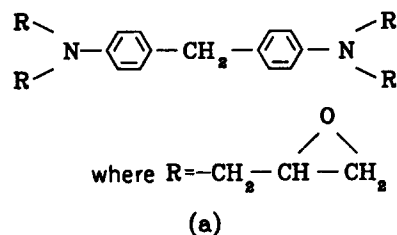
After MEK was eliminated from the resins, partially cured resins were prepared in a vacuum drying oven. For curing, the samples were heated from 298 to 448 K at a heating rate of 2–3 K min<sup>-1</sup> in the oven. After reaching 448 K, further curing was conducted in the oven at 30 min increments from 0 to

**Table I** Characteristics of Carboxyl-terminated Butadiene Acrylonitrile Rubber<sup>a</sup>

Properties	CTBN (1300 × 13)
Molecular weight	3,500
Acrylonitrile content (wt %)	27
Viscosity, Brookfield, cp (300 K)	570,000
Specific gravity	0.960
Solubility parameter	9.14
$T_g^b$ (K)	215

<sup>a</sup> Material and data supplied by B.F. Goodrich Co.

<sup>b</sup> Glass transition temperature determined by DSC in our laboratories.



**Figure 1** Molecular structure of the materials used in this study: (a) tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM); (b) diaminodiphenyl sulfone (DDS); (c) carboxyl-terminated copolymers of butadiene-acrylonitrile (CTBN); (d) bisphenol-A (BPA).

300 min. Using the samples prepared according to the above procedure, the morphology of the epoxies was studied.

### Differential Scanning Calorimetry

The thermal properties of all samples were measured calorimetrically<sup>20</sup> using a Perkin-Elmer differential

**Table II** Composition of Resins Used in This Study

Chemicals	Resins					
	A	B	C	D	E	F
TGDDM <sup>a</sup>	100	100	100	100	100	100
CTBN (phr) <sup>b</sup>	0	0	5	10	15	20
BPA (phr) <sup>c</sup>	0	24	24	24	24	24
DDS (phr) <sup>a</sup>	52	44	44	44	44	44

<sup>a</sup> Supplied by Ciba-Geigy Co.

<sup>b</sup> Supplied by B.F. Goodrich Co.

<sup>c</sup> Supplied by Junsei Chemical Co.

scanning calorimeter, Model DSC-7, with a Perkin-Elmer thermal analysis data station Model Delta. For the partially cured resins, samples were initially heated from 313 to 573 K at a heating rate of 10 K min<sup>-1</sup> to measure the residual heat of reaction ( $\Delta H_{\text{resid}}$ ).<sup>21</sup> To measure the glass transition temperature ( $T_g$ ) of the epoxy-rich phase for the mixture, the samples were cured at 448 K for 5 h and then postcured at 473 K for 10 h. The sample size was between 10 and 12 mg, and the samples were surrounded by a nitrogen atmosphere. A temperature range of 173–323 K using liquid nitrogen cooling was used to measure the  $T_g$  of the CTBN-rich phase.

For the neat (unreacted) resins, the samples were initially heated from 313 to 573 K at a heating rate of 10 K min<sup>-1</sup> to measure the heat of reaction ( $\Delta H_{\text{RXN}}$ ) of the mixture (Fig. 2). The sample size used for the neat resin was about 2 mg.

### Scanning Electron Microscopy

The morphology of the cross-section surfaces of partially cured resins was examined by SEM in a Cambridge Model 250-MK3 instrument at 15 kV accelerating voltage after gold sputter coating (50

nm). The fractured surface of the samples was prepared by cryogenic fracturing.<sup>22</sup> The particle size, its distribution, and the area fraction of the domains were measured using an image analyzer, Model Luzex 500.

## RESULTS AND DISCUSSION

### Thermal Behavior of Rubber-modified Epoxies

In Figure 2 are presented the DSC thermograms of the neat resins containing different amounts of CTBN. From Figure 2, we can see that the curing reaction is faster in resin B than in resin A. This behavior is due to the presence of BPA in resin B. The addition of BPA to resin B likely results in a condensation reaction between BPA and the epoxy resin.<sup>4</sup> The thermograms for resins C and D, which in addition to BPA contain 5 and 10 phr CTBN, respectively, show an exothermic peak no different from that of resin B. Therefore, we can say that the addition of BPA to the epoxy formulation results in a faster curing reaction because of the condensation reaction between BPA and the epoxy.

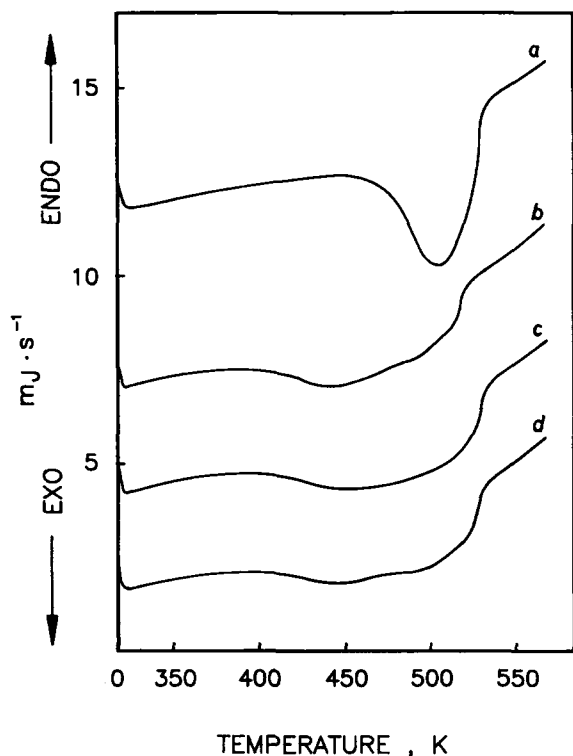
In Figures 3 and 4 are presented the DSC thermograms of the partially cured resins A and C, respectively. The resins were cured in the oven from 298 to 448 K with a heating rate of 2–3 K min<sup>-1</sup>. Then, the resins were further cured at 448 K at 30 min increments from 0 to 300 min. The thermograms in Figures 3 and 4 show the residual heat of reaction ( $\Delta H_{\text{resid}}$ ) after the resins were cured in the oven. From Figures 3 and 4, we can see that the  $\Delta H_{\text{resid}}$  decreases with increasing cure time for both resins without CTBN and BPA and the resin containing CTBN and BPA, respectively.

In Figure 5 is presented the degree of cure ( $\alpha$ ) with cure time for the partially cured resins with different amounts of CTBN added. The degree of cure was calculated by eq. (1)<sup>23</sup>:

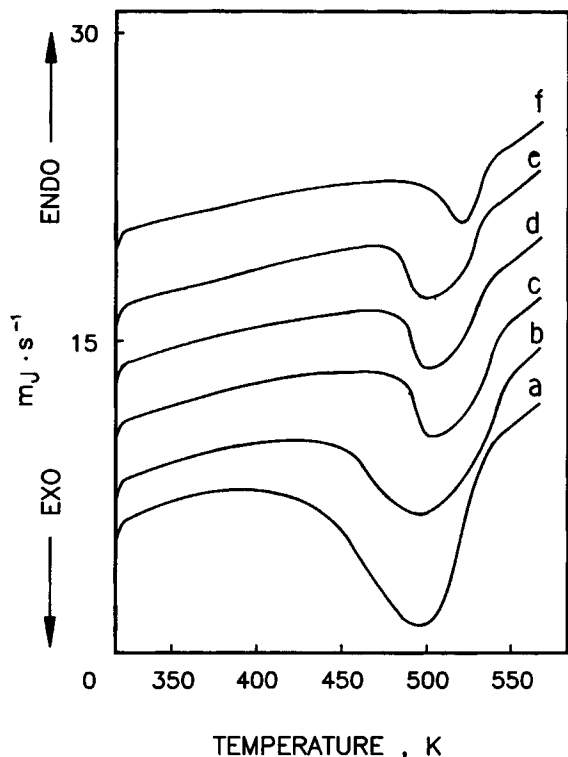
$$\alpha_t = \frac{\Delta H_{\text{RXN}} - \Delta H_{t,\text{resid}}}{\Delta H_{\text{RXN}}} \equiv \frac{\Delta H_t}{\Delta H_{\text{RXN}}} \quad (1)$$

where  $\alpha_t$  is the degree of cure at time  $t$ ;  $\Delta H_{\text{RXN}}$ , the heat of reaction at  $\alpha = 1.0$  for the neat resin;  $\Delta H_{t,\text{resid}}$ , the residual heat of reaction at time  $t$ ; and  $\Delta H_t$ , the heat of reaction at time  $t$ . To calculate  $\alpha$  from eq. (1), the  $\Delta H_{\text{RXN}}$  of the neat resins was measured using DSC (Fig. 2) and has been found to be -604.8, -592.0, -587.2, -587.0, -598.9, and -600.3 J g<sup>-1</sup> for resins A, B, C, D, E, and F, respectively.

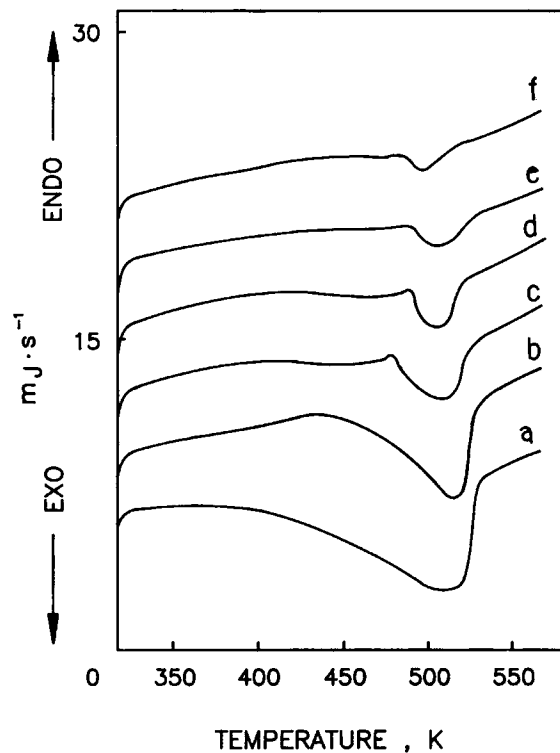
In Figure 5, we can see that  $\alpha$  increases rapidly



**Figure 2** Thermograms showing the exotherm of the neat resins: (a) resin A; (b) resin B; (c) resin C; (d) resin D. Compositions are given in Table II.



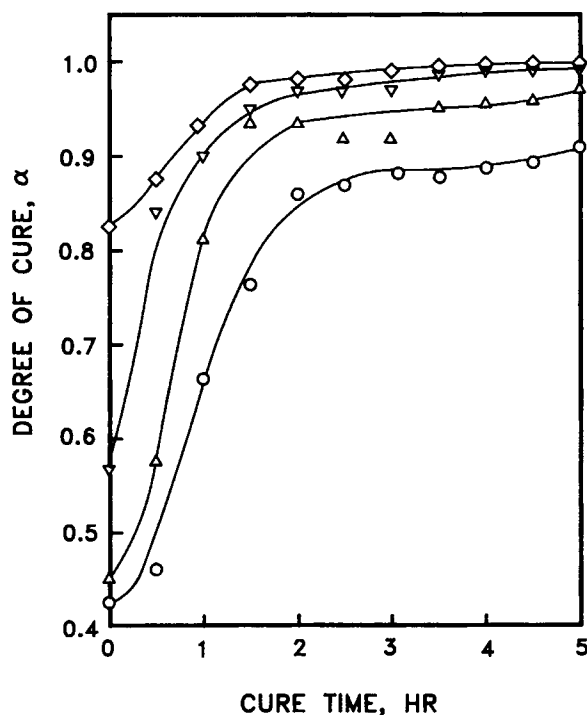
**Figure 3** Thermograms showing the residual exotherm of resin A (0 phr BPA, 0 phr CTBN) with the following cure times at 448 K: (a) 0 h; (b) 1 h; (c) 2 h; (d) 3 h; (e) 4 h; (f) 5 h.



**Figure 4** Thermograms showing the residual exotherm of resin C (24 phr PBA, 5 phr CTBN) with the following cure times at 448 K: (a) 0 h; (b) 1 h; (c) 2 h; (d) 3 h; (e) 4 h; (f) 5 h.

with cure time until 1 h, after which  $\alpha$  increases slowly. Also, for the same cure time,  $\alpha$  increases with the increase in CTBN content. From the degree of cure, it appears that most of the phase separation stops and the morphology is determined within about 1 h at 433 K. This behavior will be discussed later in interpreting the micrographs obtained using scanning electron microscopy (SEM). In this study, we have not measured gelation time and temperature directly, but, from the study of rubber-modified epoxies in the DGEBA/CTBN system, Manzione et al.<sup>5</sup> concluded that gelation halts phase separation and seals the morphology.

For all the resins, the values of  $T_g$  of the epoxy-rich phase are shown in Table III. From Table III, we can see that the  $T_g$  of resin B is 22 K below that of resin A. The only difference in resin formulation between A and resin B is that BPA is added in resin B. Therefore, we propose that the BPA and the rubber-modified epoxies have reacted and that this reaction resulted in the reduction of  $T_g$  of the epoxy-rich phase by chain extension of the TGDDM by the BPA, by addition of the more flexible CTBN to the TGDDM epoxy, and by plasticization of the epoxy-rich phase by unreacted BPA and dissolved



**Figure 5** Effect of cure time on the degree of the cure ( $\alpha$ ) for the resins cured in the oven at 448 K: (O) resin A; ( $\Delta$ ) resin C; ( $\nabla$ ) resin D; ( $\diamond$ ) resin F.

**Table III Glass Transition Temperature ( $T_g$ ) of Epoxy-rich Phase**

	Resin						CTBN
	A	B	C	D	E	F	
$T_g$ (K)	515	493	494	493	492	492	215

CTBN rubber. The  $T_g$ 's of resins C, D, E, and F to which were added 5, 10, 15, and 20 phr CTBN, respectively, were found to be similar to the  $T_g$  of resin B. From this result, it appears that most of the CTBN has formed phase-separated rubber phases rather than extending the epoxy chains or remaining unreacted in the epoxy-rich phase as a plasticizer.

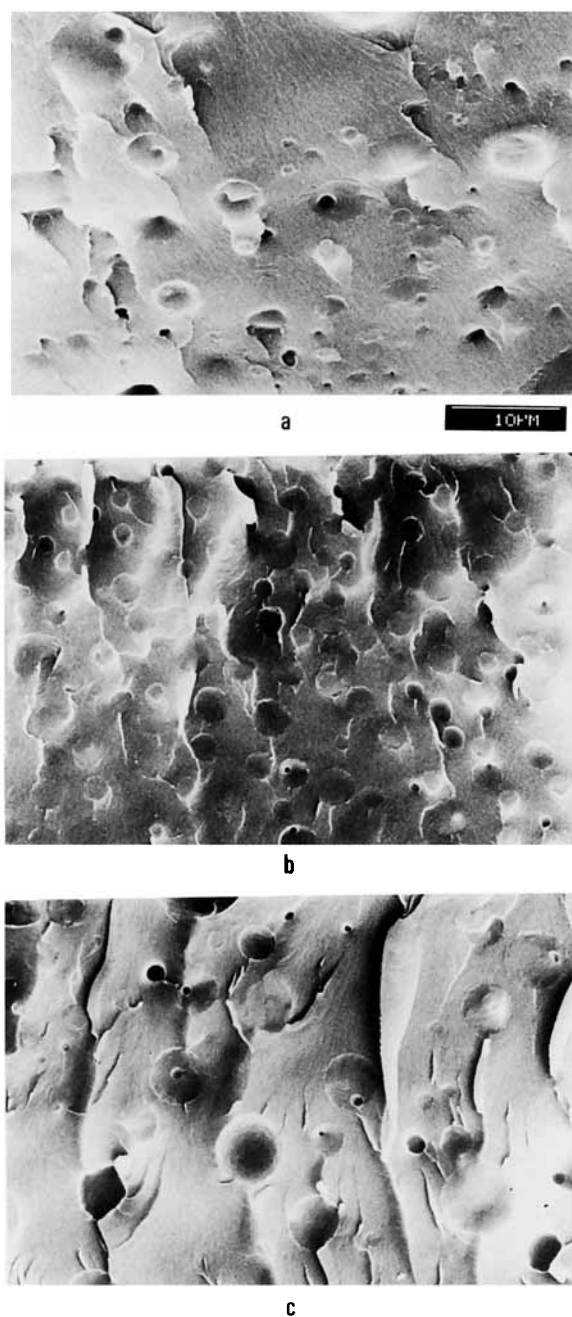
For resin F to which was added 20 phr CTBN, the  $T_g$  of the CTBN-rich phase was measured and found to be 234 K, which appeared to be 19 K higher than the  $T_g$  of the CTBN homopolymer. This increase in  $T_g$  of the CTBN-rich phase may be due to the presence in the CTBN-rich phase of epoxies that have reacted with the CTBN.

### Scanning Electron Microscopy of Rubber-modified Epoxies

The morphology of the rubber-modified epoxies was studied using scanning electron microscopy (SEM) and image analysis. In Figure 6 are presented micrographs of resin F containing 20 phr CTBN. The samples were cured in the oven at 448 K with different cure times. We can see in Figure 6(a) some rubber domains, but phase separation is not completed. At the longer times in Figure 6(b) and (c), we can see that phase separation between the CTBN and the epoxy stops and the size of domains does not change appreciably with cure time. For the other resins C, D, and E containing 5, 10, and 15 phr, similar behavior is observed. From the above morphological features and the thermal behavior of the epoxies, we conclude that the phase separation between CTBN and epoxy stops and the morphology is fixed within 1 h at 448 K.

The cross-sectional areas of the domains shown in Figure 6 were measured using an image analyzer. In Table IV are presented the average size and area fraction of domains for the resins with different amounts of CTBN. Both the diameter and the area fraction of the domains are seen to increase with increasing amounts of CTBN in the mixtures. The data shown in Table IV and Figures 7 and 8 are obtained from five different micrographs, equivalent to an area of  $480 \mu\text{m}^2$  for each sample, with annealing

times of 1–5 h at 448 K. From the above results, we can see that the average diameter of the domains is increasing and the distribution of the domain size becomes broad with an increase in the amount of CTBN added. The fraction of domains with diameters less than or equal to  $1 \mu\text{m}$  was calculated and found to be 55.0, 32.1, 16.0, and 13.7% for resins C, D, E, and F, respectively.



**Figure 6** Scanning electron micrographs obtained from cryogenically fractured cross-section surfaces of resin F cured at 448 K for the following times: (a) 0 h; (b) 1 h; (c) 5 h.

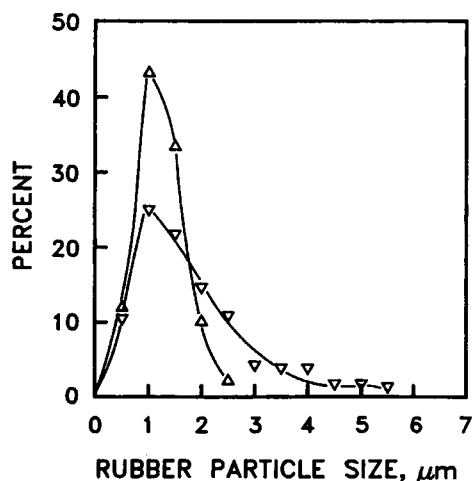
**Table IV** Average Size and Area Fraction of Domains Dispersed in the Epoxy Matrix

Sample (CTBN content)	Domain Size <sup>a</sup>	Area Fraction <sup>b</sup>
Resin C (5 phr)	1.52	7.42
Resin D (10 phr)	2.08	12.62
Resin E (15 phr)	2.27	15.15
Resin F (20 phr)	2.55	18.57

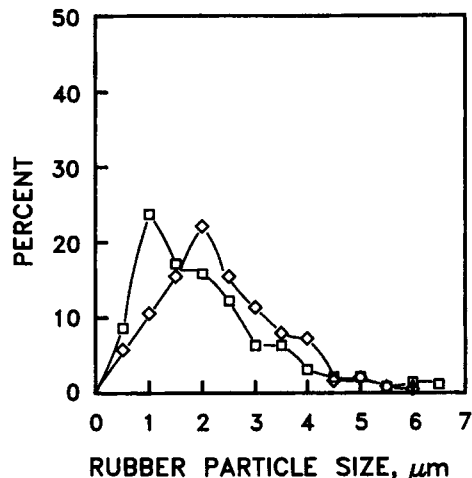
<sup>a</sup> Average domain diameter in  $\mu\text{m}$ .<sup>b</sup> Average area fraction of domains in percent.

In the study of a rubber-modified epoxy of DGEBA/CTBN by Sultan and McGarry,<sup>1</sup> enhancement in fracture toughness of rubber-modified epoxy is derived from crazing and shear band formation. They suggested that large particles are responsible for crazing and small particles cause shear banding in a CTBN-toughened epoxy resin. Riew et al.<sup>2,3</sup> showed that the addition of BPA to the DGEBA/CTBN resin formulation increased the toughening effect of the rubber and observed bimodal distributions of particle size with a wide distribution of CTBN molecular weight during the early stage of curing.

In a study of the TGDDM/CTBN (10 phr) system without added BPA, Lee et al.<sup>13</sup> reported the particle diameter distribution to be in the range of 3–15  $\mu\text{m}$ . From the study of the TGDDM/CTBN



**Figure 7** Distribution of the domains obtained from micrographs for the resins cured at 448 K for various cure times from 1 to 5 h: ( $\Delta$ ) for resin C; ( $\nabla$ ) for resin D. The area percentage of domains having diameters in the range of  $x \pm 0.25 \mu\text{m}$  is plotted vs. the diameter  $x$  in  $0.5 \mu\text{m}$  increments.



**Figure 8** Distribution of the domains obtained from micrographs for the resins cured at 448 K with various cure times from 1 to 5 h: ( $\square$ ) for resin E; ( $\diamond$ ) for resin F. The area percentage of domains having diameters in the range of  $x \pm 0.25 \mu\text{m}$  is plotted vs. the diameter  $x$  in  $0.5 \mu\text{m}$  increments.

(10 phr) system with BPA, Choe and Oh<sup>16</sup> observed the diameter of domains to be in the range of 0.25–5  $\mu\text{m}$ .

In our present study of TGDDM/CTBN with BPA, the size of the domains was observed to range mostly from 0.1 to 5  $\mu\text{m}$  in diameter and to show a slightly bimodal distribution, with modes around 1  $\mu\text{m}$  and 3–4  $\mu\text{m}$ , as seen in Figures 7 and 8. When 10 phr CTBN was added, the average size of the domains was found to be 2.08  $\mu\text{m}$  and 87% of the domains were less than or equal to 3  $\mu\text{m}$ , as seen in Figure 7. The mode at 3–4  $\mu\text{m}$  was just beginning. At 15 and 20 phr CTBN (Fig. 8), the mode at 3–4  $\mu\text{m}$  is more developed, and the prevalent size of the smaller domains increased with increasing CTBN concentration.

## CONCLUSIONS

In the study of rubber-modified epoxies of TGDDM and CTBN, the curing reaction was observed to be faster when BPA was present in the resin formulation. The faster reaction may be due to a condensation reaction between the BPA and the epoxy resin.

The glass transition temperature ( $T_g$ ) of the rubber-modified epoxies with different amounts of CTBN has been determined by DSC. The epoxies with different CTBN contents showed similar  $T_g$ 's, from which we can conclude that most of the CTBN

has reacted and formed phase-separated rubber domains. When BPA was added, the BPA reacted, bringing about a reduction of the  $T_g$  of the epoxy-rich phase.

In the study of the morphology by scanning electron microscopy and image analysis, phase separation between the CTBN and the epoxy stops, and the morphology is fixed, within 1 h at 448 K. The average diameter of the domains increases with an increase of CTBN content and has been found to range up to 2.25  $\mu\text{m}$  when 20 phr CTBN is added to the resin formulation. The area fraction of domains less than or equal to 1  $\mu\text{m}$  in diameter diminished with increasing amounts of CTBN in the resin formulation. The size of domains was observed to range mostly from 0.1 to 5  $\mu\text{m}$  in diameter and to show a slightly bimodal distribution, with modes around 1  $\mu\text{m}$  and 3–4  $\mu\text{m}$  when 15 and 20 phr CTBN was added.

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