

# Room Temperature Curing of CTBN-Toughened Epoxy Adhesive with Elevated Temperature Service Capability

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## Synopsis

The adhesive joint strengths at room temperature (25°C) and at 120°C for an epoxy resin cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol and containing varying amounts of a carboxyl-terminated polybutadiene-acrylonitrile copolymer (CTBN) were investigated and reported. It was observed that as CTBN content increased, lap shear strength and T-peel strength increased significantly and passed through a maximum at about 10 parts CTBN content per 100 parts epoxy resin and then decreased. To explain the observed results, the effect of CTBN content on the bulk tensile strength, impact energy, glass transition temperature ( $ET_g$ ), and morphology were also evaluated. SEM observations showed microphase separation between CTBN and epoxy matrix for the composition containing 10 parts CTBN per 100 parts epoxy resin, and this composition exhibited maximum bulk tensile strength and impact energy. The enhancement of bulk mechanical properties, hence the adhesive joint strength, was attributed to the higher toughness produced by the dispersed rubber particles. At higher CTBN content, the rubber phase became continuous, and the system exhibited a fall in mechanical properties, hence in adhesive joint strength, which was attributed to the flexibilization effect. The glass transition temperature of the cured epoxy resin was little influenced by CTBN incorporation up to 10 parts per 100 parts epoxy resin. Higher levels of CTBN content due to the flexibilization effect, decreased the  $ET_g$ , hence the elevated temperature capability. The results of this study demonstrate that epoxy resins containing low levels of CTBN, cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol can be used to formulate structural adhesives for use in elevated temperature environments.

## INTRODUCTION

Epoxy resins have been used for formulating structural adhesives because of such properties as good wetting and formation of strong bonds with many polar high-energy substrates, low cure shrinkage without evolution of low molecular weight substances, superior mechanical properties, and environmental stability. For structural adhesives with good elevated temperature capability, high glass transition temperature is an essential requirement to retain the adhesive strength at high temperature. All unmodified cured epoxy resins with relatively high  $T_g$  have one drawback, i.e., their brittleness, which can produce catastrophic failure of the adhesive joint. Therefore, it is necessary to toughen epoxy resins without reduction in thermal and mechanical properties, if they are to be used as structural adhesives with good elevated temperature properties. Extensive studies have been reported on enhancement of toughness of cured epoxy resins without significant reduction in thermal and mechanical properties, by the addition of low levels of a reactive liquid rubber such as carboxyl-ter-

minated butadiene-acrylonitrile copolymer.<sup>1-3</sup> The theory<sup>4</sup> is that during the initial stage, the reactive liquid rubber is compatible with the epoxy-hardner mixture. As curing proceeds, molecular weight increases and phase separation occurs. This two-phase microstructure consisting of small rubber particles dispersed and bonded to the epoxy matrix results in higher toughness because the mechanical energy is uniformly distributed by the rubber particles, thereby reducing the local stress concentration. The result is that higher external loads need to be applied for breaking the specimens. This improvement is achieved without significant reduction of thermal and mechanical properties of the crosslinked epoxy resin since the epoxy matrix contains very little or no rubber.

There have been several recent publications detailing heat-cured CTBN-toughened epoxy structural adhesives,<sup>5</sup> but only scanty reports are available on room temperature curing elastomer-toughened epoxy adhesive formulations. Heat-cured epoxy adhesives produce high joint strength with elevated temperature service capability. But fabrication of structures with these adhesives is difficult or impractical because of heat curing. Recently, considerable interest has been aroused for epoxy adhesives that cure at ambient with elevated temperature capability.<sup>6</sup> Such adhesives would aid many industries like aerospace, automotive, and electronics by facilitating low cost fabrication and rework. As a part of the development program on a room temperature curing epoxy adhesive with elevated temperature service capability, we studied the effect of CTBN concentration on the room temperature and elevated temperature (120°C) adhesive joint strengths of an epoxy resin cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol. The results are discussed in the present work. Tris(*N,N*-dimethyl aminomethyl) phenol has three tertiary amino groups, and generally tertiary amine cured epoxy resins have better elevated temperature properties.<sup>7</sup> To explain the observed results, the effect of CTBN concentration on glass transition temperature ( $E T_g$ ), stress-strain properties and impact energy were also measured. Morphology of the CTBN-modified epoxy formulations was examined by scanning electron microscopy (SEM).

## EXPERIMENTAL

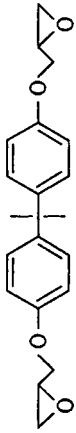
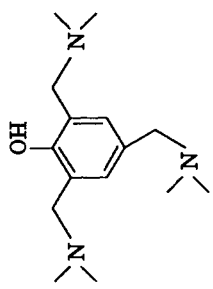
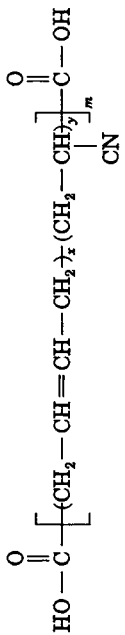
### Materials

Chemical structure, characteristics and source of epoxy resin, hardner, and toughening agent used in the present work are given in Table I.

### Procedures

CTBN was end capped with epoxy resin by an alkyl hydroxy esterification reaction.<sup>9</sup> One hundred parts by weight CTBN was added to 100 parts by weight epoxy resin containing 0.25 parts by weight triphenyl phosphine and mixed with a mechanical stirrer under N<sub>2</sub> atmosphere at 80°C until carboxyl group was completely reacted. The conversion of carboxyl group was determined by titration in a toluene-methanol (1 : 1) mixture with 0.05 *N* alcoholic potassium hydroxide. The epoxy-terminated rubber was then diluted with appropriate amount of epoxy resin to get various concentration of rubber in the formulations.

TABLE I  
Chemical Structure and Source of Epoxy Resin, Hardner, and Toughening Agent

Materials	Chemical structure	Source
1. Epoxy resin	 <p>(Also small amount of higher mol. wt. polymer. Epoxy value 5.5 g eq/kg)</p>	Hindustan Ciba Geigy Ltd., Bombay. Trade name: Araldite GY 250
2. Tris( <i>N,N</i> -dimethyl amino methyl) phenol (epoxy hardner)	 <p>(Nitrogen content obtained 15.3%)</p>	Hindustan Ciba Geigy Ltd., Bombay. Trade name: Hardner HY 960
3. Liquid carboxyl-terminated butadiene-acrylonitrile random copolymer <sup>8</sup> (toughening agent)	 <p>where <math>x = 5</math>, <math>y = 1</math>, and <math>m = 10</math> (Acrylonitrile content = 18% mol. wt. - 3500 g/mol)</p>	B. F. Goodrich Co., USA. Trade name: CTBN (Hycar 1300 × 8)

All the formulations were mixed with 6 phr tris(*N,N*-dimethyl amino methyl) phenol and cured under ambient conditions for seven days.

Single lap shear bond strength and T-peel strength specimens were made as per ASTM-D-1002 and ASTM-D-1876. The substrate used was B51 SWP aluminum alloy containing 0.4% Fe, 0.6% Mn, 1% Si, and 0.8% Mg. The aluminum specimens were abraded and treated with  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  etchant. The adhesive formulation was applied on both sides over the area to be bonded and mated using contact pressure. The strength of the jointed specimens were measured after curing at room temperature for a week. Instron model 4202 was employed for the measurement of joint strength using a crosshead speed of 10 mm/min. Five specimens for each formulations were tested. Lap shear strength at 120°C was determined after soaking the specimens for 10 min at that temperature.

To study the mechanical properties (ultimate bulk tensile strength and percentage of elongation at break), dumbbells were cast directly in a silicone mold. The dumbbells were permitted to cure for seven days at room temperature and tensile testing was conducted in Instron 4202 at a crosshead speed of 10 mm/min with a gauge length of 45 mm.

The Charpy unnotched impact test was employed to obtain impact energy. The impact test specimens in all cases were  $125 \times 10 \times 10$  mm. The impact test was carried out at room temperature and impact energy reported in joules/centimeter.

Differential scanning calorimetry (DSC) was used to determine glass transition temperature ( $ET_g$ ). The  $ET_g$  of the sample cured at room temperature for seven days was determined using DSC-20-Mettler TA 3000 instrument at a heating rate of 10°C/min. The DSC curves indicated residual cure exotherm; therefore  $ET_g$  of the sample, after curing for seven days at room temperature followed by 10 min at 120°C was also determined.

Morphology of the cured resin was studied by SEM observation of fractured surface. SEM micrographs of the fractured surface of the tensile test specimens were obtained using stereoscan 250 MK-3 Cambridge instrument at 5000× magnification. The specimen was cut and mounted on an aluminum stub using a conductive paint and was sputter coated with gold before taking SEM, for obtaining a conductive surface.

## RESULTS AND DISCUSSION

CTBN molecules, if not chemically bound to epoxy resin, can deteriorate the mechanical performance of the bulk epoxy resin. Moreover, collection of free CTBN molecules at the metal interface can act as a weak boundary layer in the adhesive joint. For this reason, before mixing with the hardner, CTBN was prereacted with epoxy resin till no carboxyl group was found by titration. The product is epoxy-terminated CTBN (Fig. 1), which promotes blending of epoxy resin and rubber prior to cure and is capable of reacting with hardner in the same manner as epoxy resin. The CTBN-epoxy prereacted intermediate was mixed with appropriate amounts of epoxy resin, and the combination was cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol. The curing mechanism<sup>10</sup> (Fig. 2) involves attack of tertiary amine on epoxy, resulting in crosslinked thermoset polymer.

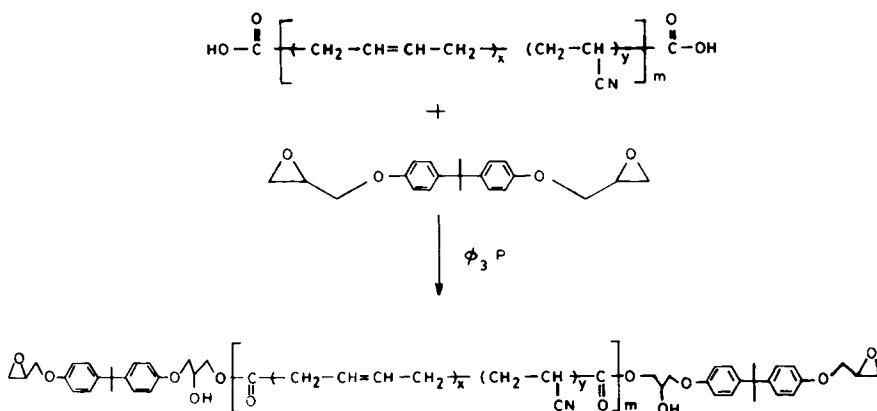


Fig. 1. Reaction of CTBN with epoxy resin producing epoxy-terminated rubber.

Figure 3 shows development of shear bond strength and bulk tensile strength of a CTBN-modified epoxy formulation with cure time at ambient. After approximately seven days at room temperature the shear strength and bulk tensile strength reached maximum values. This time was taken as the cure time for all the adhesive formulations. The DSC curve (Fig. 4) of one-week room temperature cured sample indicated  $ET_g$  and residual cure exotherm (RCE). It could be predicted from the DSC trace that cure reaction is not completed after one week at ambient, even though shear bond strength and bulk tensile strength reached their optimum value. Another DSC curve is also shown in Figure 4 for the same sample, which was postcured at 120°C for 10 min. This curve showed no RCE peak, and the  $ET_g$  shifted to higher temperature.

Figure 5 illustrates the influence of CTBN concentration on the adhesive joint strength of epoxy resin cured at room temperature with tris (*N,N*-dimethylaminomethyl) phenol for one week. The T-peel strength values and the lap shear strength values at room temperature and at 120°C increase at low levels of CTBN concentration, show a maximum, then decrease with the rubber con-

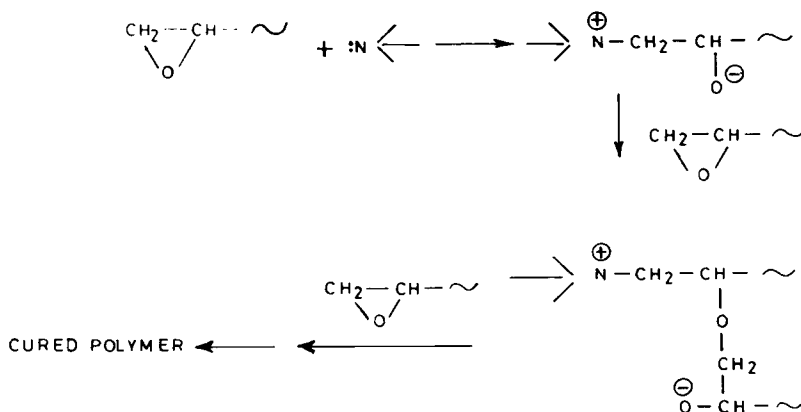


Fig. 2. Cure reaction of epoxy resin with *t*-amine.

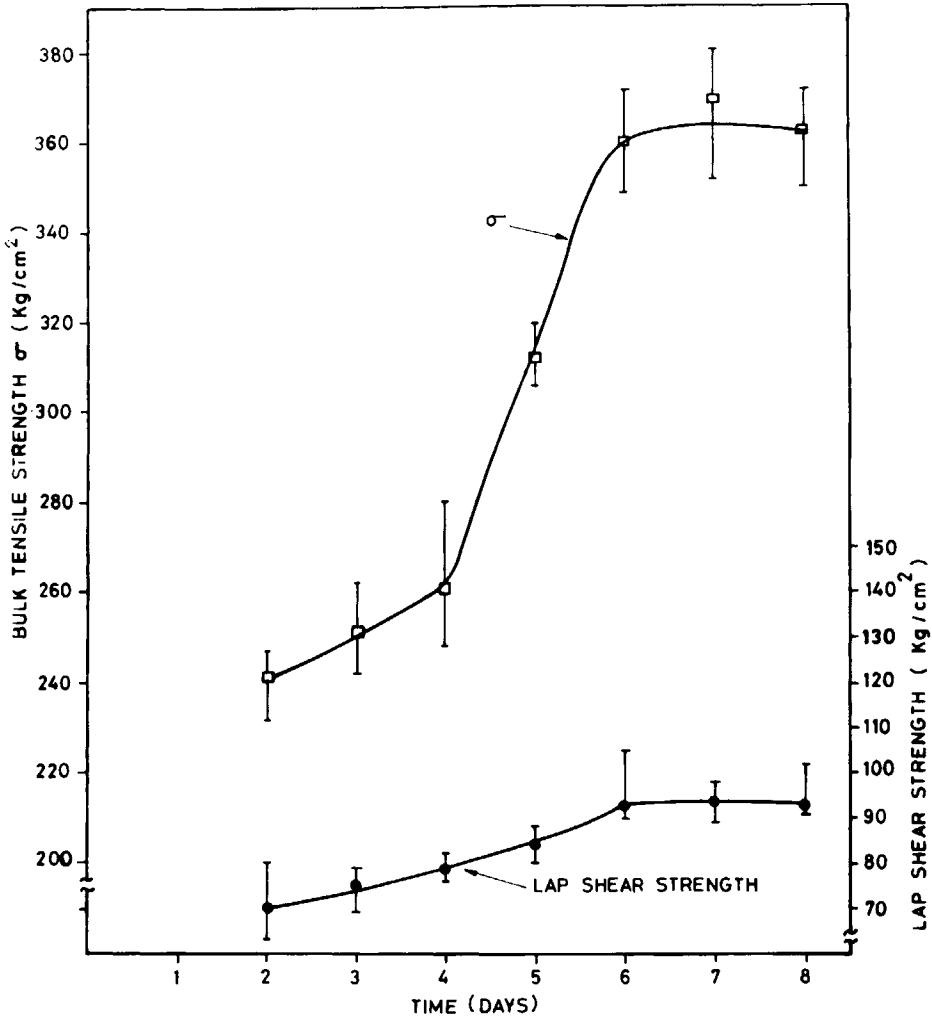


Fig. 3. Strength development of CTBN-modified epoxy adhesive with cure time at ambient temperature (CTBN content 15 parts per 100 parts epoxy resin).

tent. The maximum appears in the vicinity of 10 parts CTBN per 100 parts by weight epoxy resin. The maximum value of room temperature shear strength is about three times, and the maximum peel strength value is about five times the values of unmodified epoxy resin. It may be noted that maximum shear strength value at 120°C is increased 1.6 times than that of unmodified resin.

These results can be explained by the toughening and flexibilizing effects by the addition of CTBN to epoxy resin. The toughening effect of the cured epoxy resin by the incorporation of CTBN is evidenced by the Charpy impact test (Fig. 6). Beyond ten parts CTBN per hundred parts epoxy resin, we do not observe an improvement in impact energy but a fall. This may be explained considering the change in morphology of the fractured surface of the cured epoxy resin by the addition of CTBN. Unmodified cured epoxy failed in a brittle manner [Fig. 7(A)]. For the CTBN-modified formulation containing

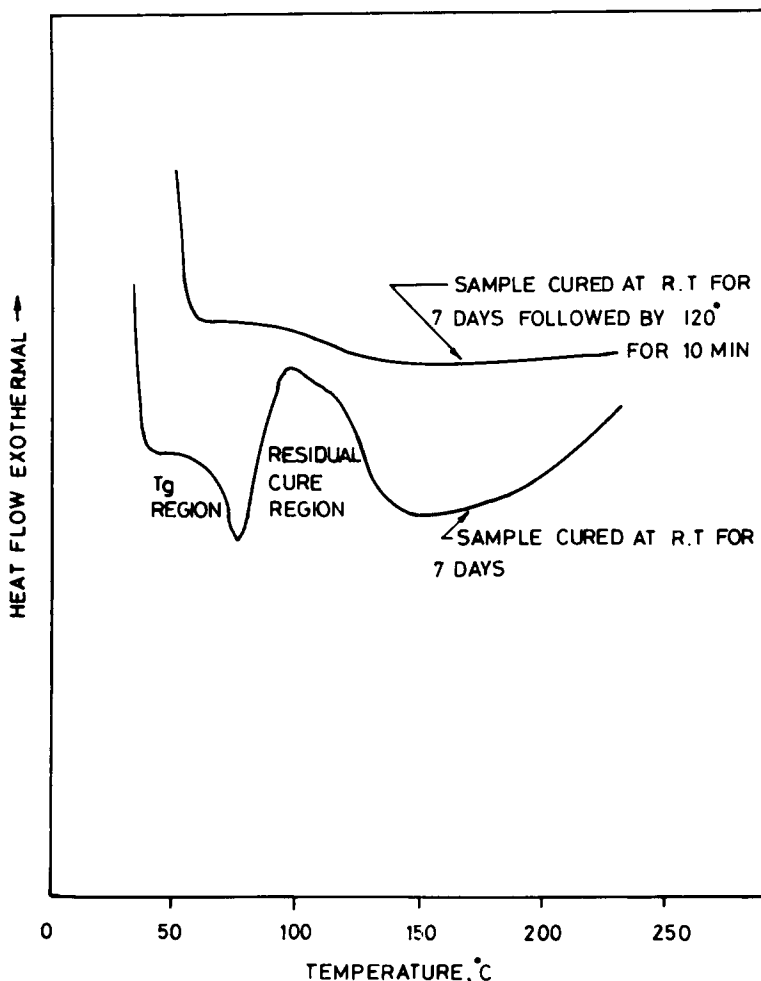


Fig. 4. DSC scan of CTBN-modified epoxy adhesive in  $N_2$  atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ .

ten parts CTBN per hundred parts epoxy resin, the morphology is a two-phase microstructure consisting of relatively small rubber particles dispersed in the epoxy matrix [Fig. 7(B)]. In Figure 7(B) we can see the cavities of the broken rubber particles. This two-phase microstructure is believed to increase the breaking strength by means of a crack terminating mechanism, and the fractured surface appears cavitated. On increasing the concentration of CTBN, the second phase became indistinguishable from the matrix due to aggregation [Figs. 7(C) and (D)]. The rubber that does not phase separate can lead to flexibilization of cured epoxy resin and hence can decrease the rigidity. The modification of epoxy resin with CTBN has no effect on  $T_g$  of the cured epoxy resin up to 10 parts CTBN per 100 parts epoxy resin, but results in a reduction in  $T_g$  beyond 15 parts per 100 parts epoxy (Table II).

This illustrates that at low levels of CTBN there is phase separation and little CTBN in the epoxy matrix. Since the epoxy matrix contains relatively

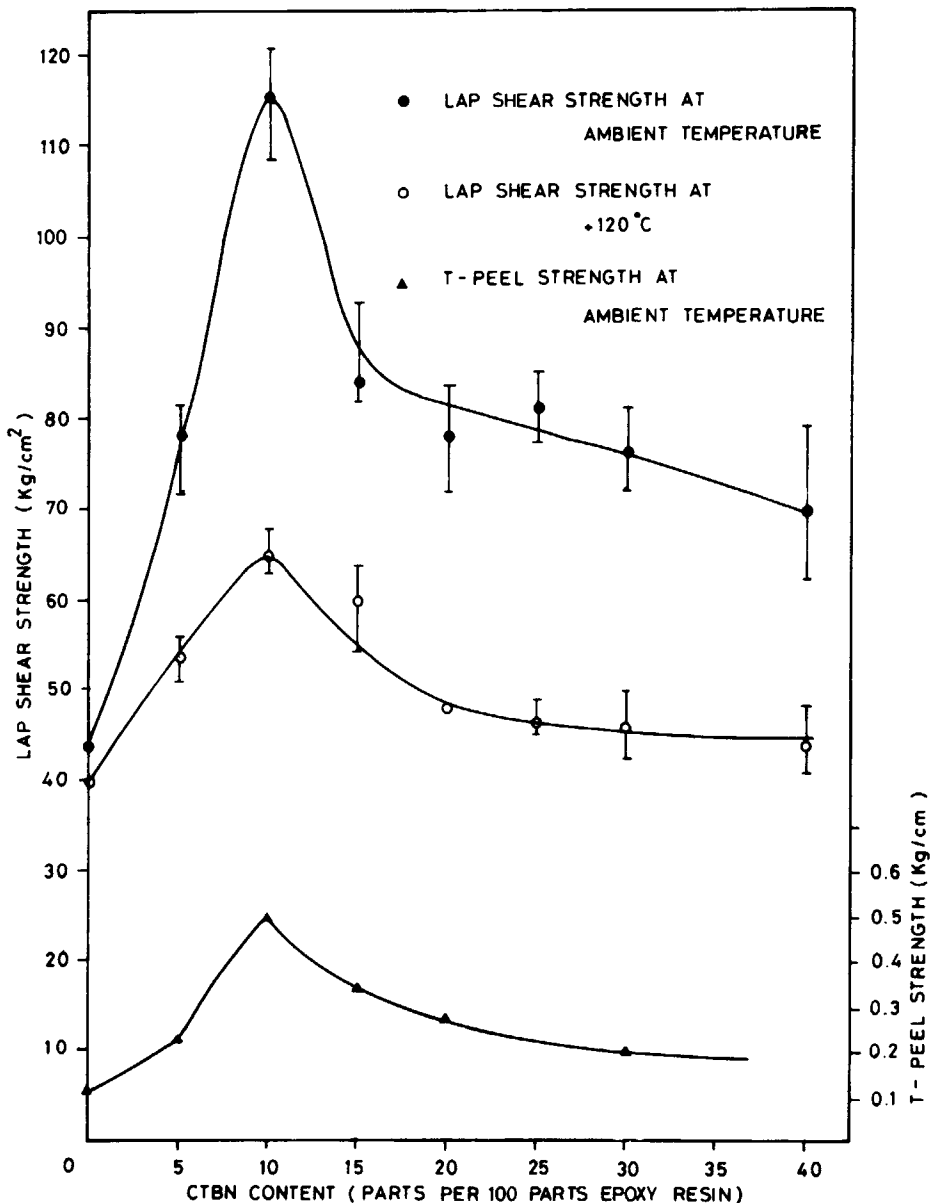


Fig. 5. Lap shear and T-peel strength as a function of CTBN concentration in epoxy resin.

little elastomer, the thermal properties ( $ET_g$ ) are close to that of unmodified epoxy. Above 10 parts CTBN per 100 parts epoxy resin,  $ET_g$  values decrease due to the flexibilization of epoxy resin by CTBN.

The toughening and flexibilizing effects by the addition of CTBN to epoxy resin is further illustrated from the plots of ultimate bulk tensile strength ( $\sigma$ ) and the ultimate percentage of elongation (eb%) as a function of CTBN concentration (Fig. 8). Above 10 parts CTBN content per 100 parts epoxy resin, cured epoxy compositions lose bulk tensile strength, and the percentage of



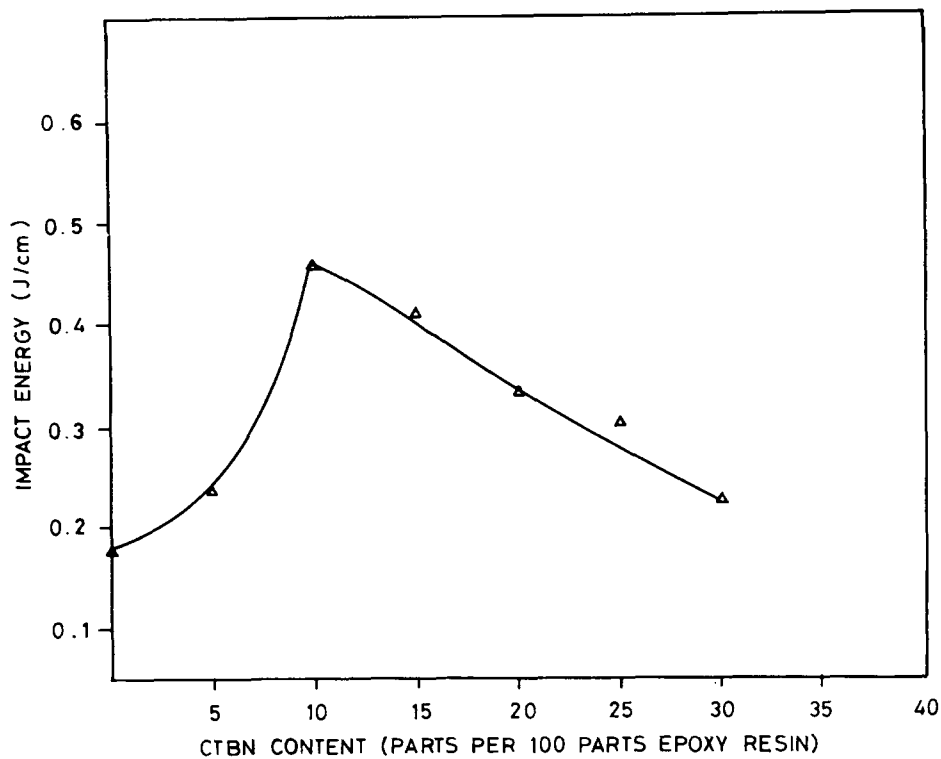


Fig. 6. Impact energy as a function of CTBN concentration in epoxy resin.

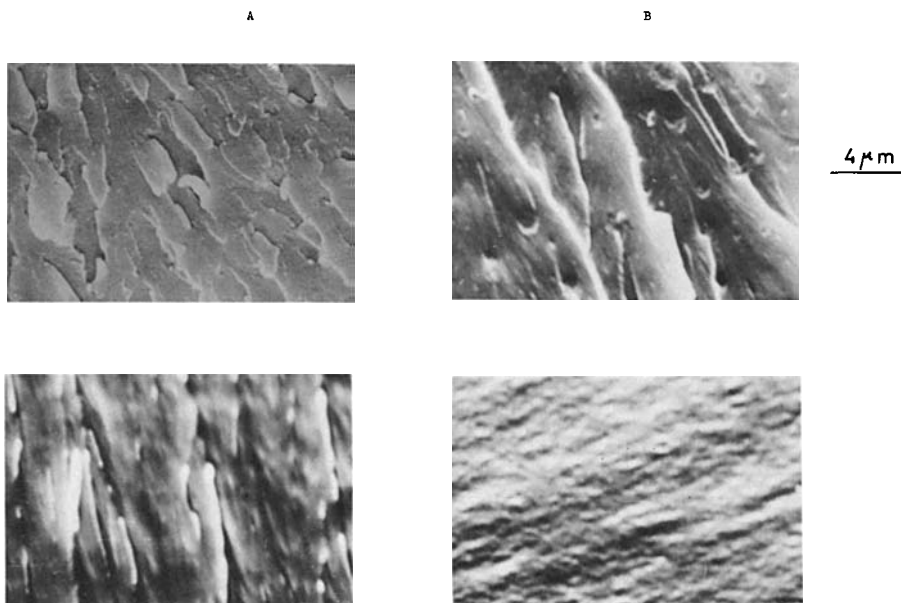


Fig. 7. SEMs of the tensile fractured surfaces of epoxy resin cured at ambient temperature with tris(*N,N*-dimethylaminomethyl) phenol. (A) Without CTBN, (B, C, D) containing 10, 20, 30 parts CTBN content per 100 parts epoxy resin, respectively.

TABLE II  
Effect of CTBN Concentration on  $T_g$  of Cured Epoxy Resin

CTBN content in epoxy resin <sup>a</sup>	$ET_g$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$ET_g$ ( $^{\circ}\text{C}$ ) <sup>c</sup>
0	74	116
5	72	116
10	72	115
15	71	112
20	68	102
25	66	100
30	67	99
40	66	94

<sup>a</sup> Parts are per 100 parts by weight of epoxy resin.

<sup>b</sup> After seven days room temperature curing.

<sup>c</sup> After seven days room temperature curing followed by 10 min soaking at  $120^{\circ}\text{C}$ .

elongation increases. Even though the direct relationship between the mechanical properties of the bulk adhesive and adhesive joint strength is not well established, it is recognized at least qualitatively, that if a satisfactory interfacial state of adhesion is achieved, the mechanical properties of the adhesive material control the adhesive joint strength.<sup>11-13</sup> Epoxy adhesives have great affinity to aluminum alloys and attach to the oxide layers formed by the surface preparation.<sup>14</sup> For CTBN-modified epoxy composition, due to the strong physical and chemical interactions of epoxy resin with aluminum surface, the required

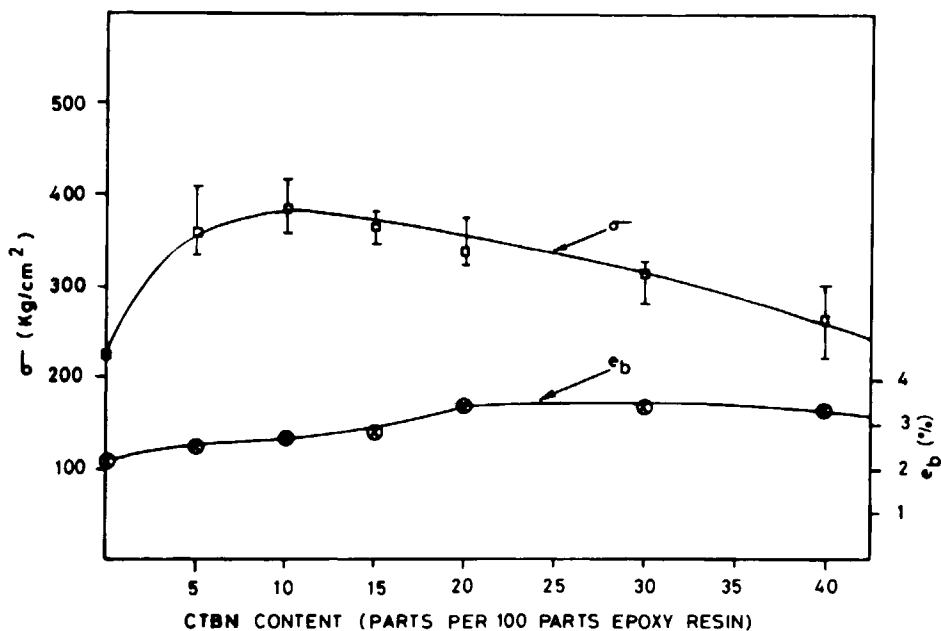


Fig. 8. Bulk tensile strength ( $\sigma$ ) and breaking elongation ( $e_b$ ) as a function of CTBN content in epoxy resin.

interfacial attachment might be achieved, and some correlation between adhesive joint strength and bulk mechanical properties can be expected. Adhesive joint strength maximum was found in the range where bulk tensile strength and impact energy are maximum. Moreover this optimum composition was found to have better elevated temperature (120°C) lap shear strength. The high-temperature capability of the system might be due to the shifting of  $ET_g$  to higher values due to the postcuring taking place when the specimen is soaked at the test temperature (Table II). The postcuring is also found to improve the room temperature shear strength of the adhesive composition.

### SUMMARY AND CONCLUSIONS

Our effort was aimed toward the development of a room temperature curing epoxy adhesive with high-temperature service capability. As a part of the development program, the effect of CTBN concentration on the room temperature and elevated temperature (120°C) adhesive joint strength of an epoxy resin cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol hardener was investigated. CTBN was incorporated into epoxy resin before the addition of hardener by prereacting with epoxy resin until no carboxyl group was found by titration. The effect of CTBN concentrations on bulk mechanical properties,  $ET_g$ , and morphology were also evaluated. The results of this study led to the following conclusions.

1. Low levels of CTBN addition in an epoxy resin cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol showed improved joint strength at ambient and elevated temperature conditions, over the unmodified epoxy resin. The maximum adhesive joint strength was obtained at a level of 10 parts CTBN per 100 parts epoxy resin. This composition also was found to exhibit appreciably improved bulk tensile strength and impact energy. Because of the increase in bulk mechanical properties of the cured epoxy resin by the addition of CTBN, we believe the adhesive joint strength was also improved.
2. From SEM studies of the fractured surface, a relationship between strength and the morphology of the fractured surface was found. The fractured surface of unmodified epoxy resin cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol showed brittle fracture, and this exhibited low adhesive and mechanical strength. For CTBN-modified composition containing 10 parts of CTBN per 100 parts of epoxy resin, a two-phase microstructure consisting of small rubber particles dispersed in epoxy matrix was found by SEM observation. The phase-separated rubber particles are believed to retard the crack propagation and produce high bulk mechanical strength, hence improved adhesive joint strengths. At higher levels of CTBN concentrations, the rubber phase became indistinguishable from the epoxy matrix, and no phase-separated rubber particles were seen in the SEM micrograph. The rubber that is not phase separated can lead to softening of cured epoxy resin, which decreases the bulk mechanical properties and hence the adhesive joint strengths.
3. Epoxy formulation cured at room temperature with tris(*N,N*-dimethyl-

aminomethyl) phenol was found to exhibit good elevated temperature capability. The  $ET_g$  was shifted to higher values when the specimen was soaked at elevated temperature, due to postcuring. Incorporation of low levels of CTBN (up to 10 parts CTBN per 100 parts epoxy resin) had no deteriorating effect on  $ET_g$  and exhibited better elevated temperature properties. Higher levels of CTBN concentration decreased the  $ET_g$  and hence the elevated temperature capability due to the flexibilization effect.

- Overall, it was shown that incorporation of low levels of CTBN serve as an easy method to increase the adhesive joint strength of an epoxy cured at room temperature with tris(*N,N*-dimethylaminomethyl) phenol hardener, retaining its high-temperature service capability. We believe CTBN-modified polyfunctional epoxies such as epoxy novalac cured with tris(*N,N*-dimethylaminomethyl) phenol can improve the  $ET_g$  further and hence the high-temperature performance. Therefore further work is recommended with high functional epoxies.

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