

# Studies on the Conductivity Properties of a Family of Cyanoethylated Amine Cured Epoxy Resin Matrices

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**ABSTRACT:** A group of epoxy matrices having a varied amount of crosslink densities have been prepared by curing diglycidyl ether of bisphenol A (DGEBA)–epoxy resin with the help of a family of cyanoethylated amine hardeners based on the adducts of 1 mole of triethylenetetramine and  $x$  moles of acrylonitrile, where  $x = 1, 2,$  and  $3,$  to effect increasing level of cyanoethylation of triethylenetetramine. The electrical conductivities of such epoxy matrices having increasing crosslink densities were evaluated by a two-probe a.c. technique in the frequency range of 100 Hz to 13 MHz using an impedance analyzer in the temperature range

from 299 to 495 K. It was observed that the conductivity increased with an increased level of cyanoethyl ( $-\text{CH}_2\text{CH}_2\text{CN}$ ) moiety in the matrix resin, while the activation energy ( $E_a$ ) of conductivity in the elastomeric region above  $T_g$  generally showed a reversed trend with respect to  $E_a$  from 1.11 to 0.83 eV, where  $T_g$  is defined by  $T_g = (T_g + \Delta T)$ , the  $(\Delta T)$  for this family of matrix resin being 44.83°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1627–1631, 2003

**Key words:** thermal properties; conductivity; resins; glass transition; polyamines

## INTRODUCTION

Critical circuit components are nowadays coated or encased in dielectric materials to isolate them from adverse environmental and operational effects like electrical flashover and current leakage.<sup>1</sup> The unique properties of epoxy resin systems have made them the predominant thermosetting resin for potting and encapsulation of a variety of optoelectronic items, coils, capacitors, resistors, transistors, semiconductors, integrated circuits (ICs), and LSI devices.<sup>2</sup> Progress in electronics is becoming critically dependent on electronic packaging and interconnections. And selection of a proper packaging material is one of the key requirements to achieve fast clock rates, uniform and appropriate electrical impedance, etc.<sup>1–3</sup>

Many important electronic industries need electrically conductive adhesives. Such high performance conductive products are prepared today by incorporation of high loading of precious metal powders like silver or gold into an epoxy system.<sup>2,4</sup> In most cases, these epoxy resins are crosslinked by hardeners like amines.<sup>2,4</sup> Die-attach adhesives<sup>2,4</sup> are one such electrically conductive material used worldwide to bond dies to the substrates of hybrid and monolithic ICs, light emitting diodes (LEDs), and other devices. And

amine-cured epoxy resins find application in such die-attach adhesives.<sup>2</sup>

It therefore would be of interest to examine the electrical conductivity properties of different epoxy matrices resulting from curing using different amine hardeners to effect varying crosslink densities through incorporation of different levels of cyanoethyl moiety into the matrix resin. In this article, the conductivity properties of such epoxy matrices due to a family of cyanoethylated triethylenetetramine<sup>5,6</sup> hardeners is reported.

## EXPERIMENTAL

### Materials

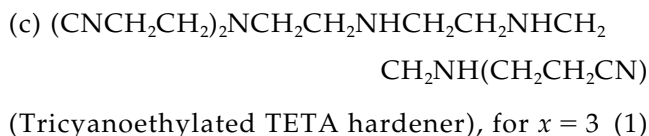
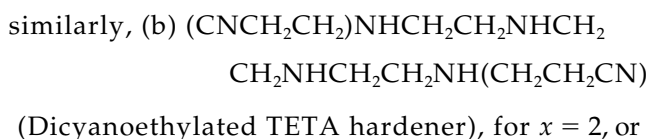
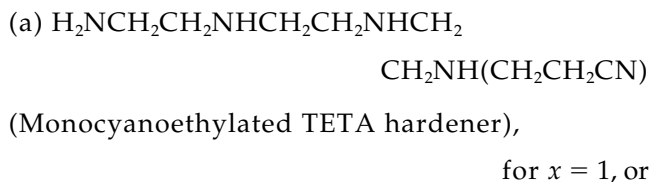
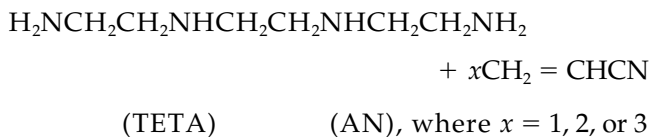
In this investigation, the epoxy resin used was a DGEBA (diglycidyl ether of bisphenol A)–epoxy resin (LY 556, Hindustan Ciba-Geigy Ltd.). And the hardeners [or, crosslinker, i.e., the products a–c of eq. (1), shown below] used were based on the cyanoethylated derivatives of triethylenetetramine containing an increased level of polar cyanoethyl ( $-\text{CH}_2\text{CH}_2\text{C}=\text{N}$ ) groups. Triethylenetetramine (TETA) was from G. S. Chemical & Testing Laboratory, New Delhi. Acrylonitrile (AN), a product of BDH, was used to react with TETA to carry out the cyanoethylation reaction as shown in eq. (1).

### Synthesis of hardeners

In this family of hardeners under investigation, three derivatives such as mono-, di-, and tricyanoethylated

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TETA were synthesized in the laboratory by reacting TETA with 1, 2, and 3 moles of AN respectively using the Michael condensation reaction<sup>5,6</sup> following the typical reaction scheme shown in eq. (1).

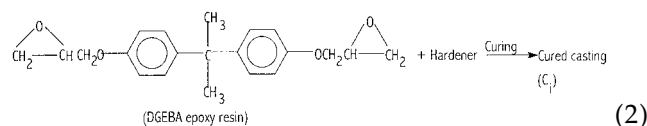


The products [a– c of eq. (1)] were characterized by usual the physicochemical analytical data. Illustratively, Fourier transform infrared (FTIR) spectra of the cyanoethylated amines exhibited sharp absorption near  $2261 \text{ cm}^{-1}$  associated with the nitrile group (CN).<sup>7</sup> The <sup>1</sup>H-NMR spectra of TETA and the cyanoethylated amines showed the presence of the required number of methylene hydrogen atoms attached to the nitrogen atoms of the amines. More specifically, the NMR data are shown as follows: Triethylenetetramine: <sup>1</sup>H-NMR  $\delta$  ( $\text{CDCl}_3$ ) 2.71–2.85 (m, 12H,  $6 \times \text{CH}_2$ ), 1.34 (s, 4H, NH and  $\text{NH}_2$ , exchangeable with  $\text{D}_2\text{O}$ ); monocyanoethylated TETA: <sup>1</sup>H-NMR  $\delta$  ( $\text{CDCl}_3$ ) 2.3–2.8 (m, 16H,  $8 \times \text{CH}_2$ ), 1.7 (s, 5H, NH and  $\text{NH}_2$ , exchangeable with  $\text{D}_2\text{O}$ ); dicyanoethylated TETA: <sup>1</sup>H-NMR  $\delta$  ( $\text{CDCl}_3$ ) 2.53–2.94 (m, 20H,  $10 \times \text{CH}_2$ ), 1.7 (s, 4H, NH and  $\text{NH}_2$ , exchangeable with  $\text{D}_2\text{O}$ ); tricyanoethylated TETA: <sup>1</sup>H-NMR  $\delta$  ( $\text{CDCl}_3$ ) 2.2–2.86 (m, 24H,  $12 \times \text{CH}_2$ ), 1.76 (s, 3H, NH and  $\text{NH}_2$ , exchangeable with  $\text{D}_2\text{O}$ ).

#### Preparation of samples

For conductivity measurements, castings (C) were prepared by pouring stoichiometric proportions of DGEBA and hardener (or crosslinker) as reacting mix according to eq. (2) into a small circular chrome-plated stainless steel mold of diameter 5 mm and thickness 1 mm. The cast resin was then cured at room tempera-

ture for 24 h followed by postcuring in an oven at  $120^\circ\text{C}$  for 2 h in each case.



#### Swelling measurement

The increase in percent swelling as an indirect way of assessing the degree of crosslinking in the matrix network was determined by measuring the densities of the neat casting and the swollen casting after immersing the sample in acetone for 24 h at  $40^\circ\text{C}$ .

#### Hardness measurements

The Rockwell hardness in M scale of all the castings were measured by employing a steel ball of 1/8 in. diameter and a load of 100 kg with the help of a Digital Hardness Tester (Buelar Ltd., Illinois, USA) in accordance with ASTM D785-65.

#### Estimation of glass transition temperature ( $T_g$ )

A thermomechanical analyzer (TMA) was utilized to determine  $T_g$  using a DuPont 943 instrument, employing a load of 5 g through a probe of size 4.3 mm, while the rate of heating was maintained at  $5^\circ\text{C}/\text{min}$ . The  $T_g$ s obtained from such a TMA measurement are shown in Figure 3.

#### Conductivity measurements

A Hewlett Packard 4192A impedance analyzer was used for electrical measurements. For conductivity measurements, the circular sample disks were mounted on a specifically designed sample holder whose spring loading keeps the disk in contact with the steel electrodes. The sample holder was then inserted in a jacketed chamber with a temperature controller and connected to a vacuum pump. The samples were heated to a high temperature (495 K) and allowed to remain at that temperature for sufficiently long time to ensure good contact with the steel electrodes. The measurements were made in the cooling cycle. For each reading enough time was given for the sample to attain steady temperature. All the measurements were done under vacuum to avoid absorption of moisture by the samples and/or deposition of film of water vapor on the surface of the sample.

The electrical measurements were performed in the temperature range of 299–495 K. The data were obtained by a two-probe a.c. technique in the frequency

TABLE I  
Properties of Different Castings ( $C_i$ ) Prepared from DGEBA Epoxy Resin and Cyanoethylated TETA Hardeners

Sample code	100× Volume swelling in acetone	Hardness (Rockwell, M scale)	Glass transition temperature, $T_g$ (from TMA (°C))	Activation energy, $E_c$ (eV) (in the region above $T_e$ )
$C_{11}$	0.95	70.7	118.9	1.11
$C_{12}$	3.97	48.6	80.1	0.94
$C_{13}$	13.62	30.8	67.5	0.83

range from 100 Hz to 13 MHz. The d.c. conductivity was calculated using the impedance analyzer data.

## RESULTS AND DISCUSSION

The cast samples corresponding to mono-, di-, and tricyanoethyl derivatives were designated as  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  respectively in which the digits in the suffices of C represent the respective molar ratios TETA/AN present in the hardeners used for curing. Brief results of properties of the castings evaluated in the laboratory are shown in Table I.

The percent volume swelling data of Table I show that the swelling is maximum for  $C_{13}$ , thereby indicating that  $C_{13}$  has the lowest crosslink density in the matrix network. Table I also indicates that both hardness and glass transition temperature ( $T_g$ ) decrease from  $C_{11}$  through  $C_{13}$  as a consequence of the gradual decrease in the crosslink density.

Figure 1 shows a typical complex impedance plot of sample  $C_{13}$  at 485 K. The real part of the impedance  $Z'$  is plotted against the imaginary part  $Z''$ . The resulting plot is a depressed semicircle, indicating that its equivalent circuit is a parallel combination of a resistance (R) and a constant phase element (CPE). The accompanying short tail in the low frequency side may be due to a small effect of electrode resistance and/or surface polarization. The diameter of the depressed circle along the  $Z'$  axis indicates the contribution of the d.c. resistivity of the cured epoxy resin.

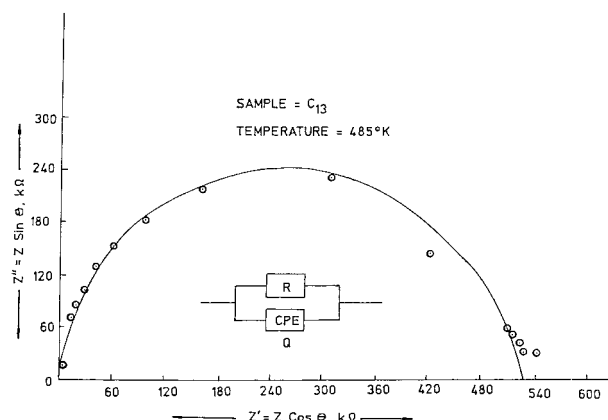


Figure 1 A plot of  $Z'$  against  $Z''$ , where complex impedance  $Z = Z' + iZ''$ , measured at 485 K typically for sample  $C_{13}$ .

Figure 2 shows an Arrhenius-type plot of the conductivity of the  $C_{12}$  and  $C_{13}$  epoxy matrices against the reciprocal temperature,  $1/T$ . The d.c. conductivity was obtained from the diameters of the depressed semicircles in a plot between 299 and 495 K. The relation between  $\sigma$  and  $T$  was found to follow equation (3):

$$\sigma = A \exp(-E_c/kT) \quad (3)$$

where  $A$  is the preexponential factor,  $k$  the Boltzmann constant, and  $E_c$  the activation energy. Figure 2 shows that  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  behaved almost similarly in respect to the characteristic that a more rapid increase of conductivity in both cases occurred above the temperature  $T_e$ , where the temperature  $T_e$  is defined<sup>8-13</sup> by  $T_e = (T_g + \Delta T)$ . Figure 2 indicates the  $T_e$  for  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  as 166.9, 127, and 107.1°C, respectively. The  $T_g$ s of the castings  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  were obtained from the tracings of thermomechanical analyzer (Fig. 3) as 118.9, 80.1, and 67.5°C, respectively. Generally,  $\Delta T$  is reported to remain between  $35 \leq \Delta T \leq 50^\circ\text{C}$ ,

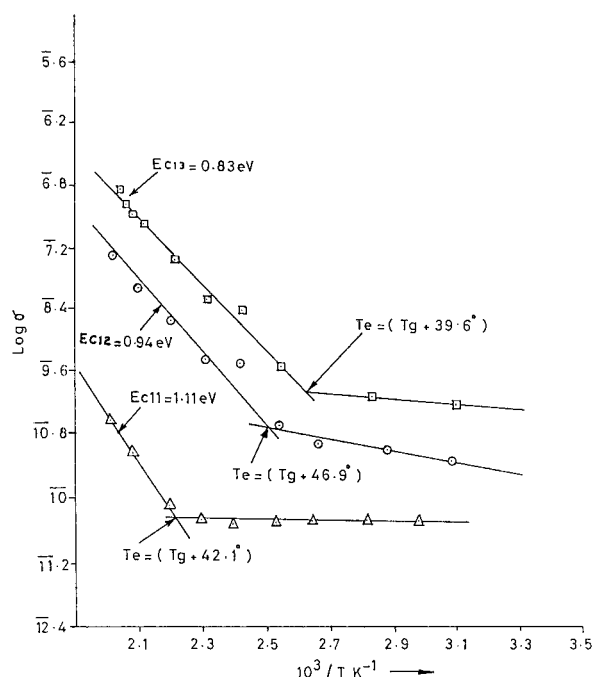
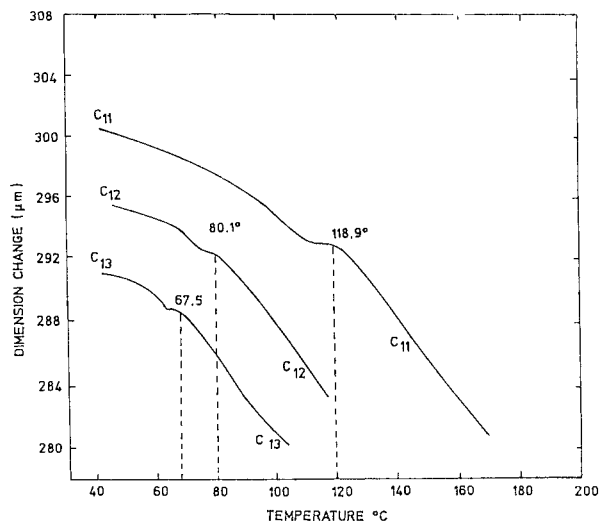


Figure 2 Arrhenius plot of the conductivity ( $\sigma$  in  $\text{mho cm}^{-1}$ ) of castings against reciprocal temperature,  $1/T$  ( $\text{K}^{-1}$ );  $\Delta$  for  $C_{11}$ ,  $\odot$  for  $C_{12}$ ,  $\square$  for  $C_{13}$ .



**Figure 3** TMA curves for the determination of  $T_g$  of different castings based on DGEBA epoxy resin cured with different cyanoethylated TETA hardeners.

depending upon the kind of the matrix system if it has to remain in elastomeric form.<sup>9–13</sup> In the present study  $\Delta T$  for  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  was found to be 48, 46.9, and 39.6°C, respectively (resulting in an average  $\Delta T$ , i.e.,  $\langle T \rangle = 44.87^\circ\text{C}$ , which was the threshold excess temperature above  $T_g$  required to generate elastomeric character in the  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  matrix systems.<sup>8–13</sup> In the literature on thermal analysis for host of epoxy systems, it has been reported that generally crosslinked epoxies behave like elastomers above  $T_e$  because of their discernible viscous “flow,”<sup>8–13</sup> which starts at around  $T_e$  rather than at  $T_g$ . Interestingly, the conductivity of  $C_{11}$ ,  $C_{12}$ , or  $C_{13}$  was rather prominent only when it existed in the elastomeric or rubbery stage. Above  $T_e$ , the conductivity increased rapidly with temperature. And this trend is in good agreement with that reported by Miyatani.<sup>14</sup>

From the plot of Figure 2, it is clear that the conductivity is enhanced at higher temperature and the current arises from an activation process. The charge carrier responsible for the current might have been formed by thermal methods. The electrical conductivity in the resin matrix presumably results from the migration of charge carrier through the polymer matrix.<sup>3</sup> The mobility of such a charge carrier is generally inversely proportional to the internal viscosity of the cured polymer.<sup>3</sup> It may be mentioned here that several researchers have reported that the viscosity of the epoxy resin curing system has a good relationship with the conductivity.<sup>15–19</sup>

The data of swelling and hardness as shown in Table I implies that the crosslink density of the castings follows the order as  $C_{11} > C_{12} > C_{13}$ ; interestingly, the inverse of internal viscosity and corresponding improved mobility of the carriers led to the increased conductivity following the pattern in the

order  $\sigma_{C13} \geq \sigma_{C12} \gg \sigma_{C11}$ . For  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$ , the conductivity increases with temperature presumably because of the decrease in the internal viscosity with temperature.<sup>3</sup> The activation energy of conduction,  $E_{C12}$ ,  $E_{C12}$ , and  $E_{C13}$  associated with the respective rubbery region<sup>8–13</sup> of  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  above  $T_e$  were calculated from eq. (3) as 1.11, 0.94, and 0.83 eV, respectively. Between them, the highest activation energy for  $C_{11}$  seems to be due to the enhanced restriction in the mobility of the charge carrier through the matrix structure having greater internal viscosity due to its highest crosslink density compared to that of  $C_{13}$  (Table I). The activation energy for polyethyleneterephthalate (PET) reported by different authors<sup>20–23</sup> may be compared with the present values of activation energies of the epoxy systems. For example, Smith and Scott reported a value of 0.9 eV for highly crystalline PET,<sup>20</sup> while Lengyel reported a value of 0.88 eV for PET film.<sup>21</sup>

In the present case, it is plausible that the conductivity for  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  at higher temperatures may be due to the breakage of hydrogen bonds between the nitrogen atoms of hardener moieties and the hydrogen atom of hydroxyl groups of DGEBA segments. In other words, the plausible breakage of hydrogen bonds (perhaps involving the moieties like  $-\text{C}\equiv\text{N} \cdots \text{H}-\text{O}-$  or  $-\text{N} \cdots \text{H}-\text{O}-$ , etc.) at elevated temperatures results in loosening of bonded structures to ultimately cause enhanced mobility of the charge carrier to ensure higher conductivity at higher temperatures. It may be noted that  $-\text{C}\equiv\text{N}$  is an ambident and forms hydrogen bonds.<sup>24,25</sup> A similar situation was observed by Sacher et al.<sup>23,25,26</sup> They also suggested that the conductivity for PET above 100°C is due to the breaking of the hydrogen bond between the end groups.<sup>23,25,26</sup>

Therefore, it seems matrix structure plays an important role in the electrical properties of such a family of cyanoethylated amine based epoxy resin matrix systems.

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