

# Synthesis and Properties of Cardanol-Based Epoxidized Novolac Resins Modified with Carboxyl-Terminated Butadiene–Acrylonitrile Copolymer

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**ABSTRACT:** Cardanol-based, novolac-type phenolic resins were synthesized with a cardanol-to-formaldehyde molar ratio of 1 : 0.7 with different dicarboxylic acid catalysts, including oxalic and succinic acids. These novolac resins were epoxidized with a molar excess of epichlorohydrin at 120°C in a basic medium. The epoxidized novolac resins were separately blended with different weight ratios of carboxyl-terminated butadiene–acrylonitrile copolymer (CTBN) ranging between 0 and 20 wt % with an interval of 5 wt %. All of the blends were cured at 120°C with a stoichiometric amount of polyamine. The formation of various products during the synthesis of the cardanol-based novolac resin and epoxidized novolac resin and the blending of the epoxidized novolac resin with CTBN was studied by Fourier transform infrared spectroscopy analysis. Furthermore, the products were

also confirmed by proton nuclear magnetic resonance and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy analysis. The molecular weights of the prepared novolacs and their epoxidized novolac resins were determined by gel permeation chromatography analysis. The blend samples, in both cases, with 15 wt % CTBN concentrations showed the minimum cure times. These blend samples were also the most thermally stable systems. The blend morphology, studied by scanning electron microscopy analysis, was, finally, correlated with the structural and property changes in the blends. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1670–1681, 2009

**Key words:** blends; differential scanning calorimetry (DSC); FT-IR; gel permeation chromatography (GPC)

## INTRODUCTION

Cashew nut shell liquid (CNSL), an agricultural byproduct abundantly available in the country, is one of the few major and economic sources of naturally occurring phenols and can be regarded as a versatile and valuable raw material for polymer production. Cardanol, a natural alkyl phenol from CNSL and a potential natural source for biomonomers, cannot even today be said to have found its niche in terms of an appropriate industrial applications. By far, the greatest amount of work on polymeric materials derived from CNSL or cardanol have been done on their use in the manufacture or modification of phenolic resins.<sup>1–4</sup> The phenolic nature of the material makes it possible to react it under a variety of conditions to form both base-catalyzed resoles and acid-catalyzed novolacs. Cardanol-based, novolac-type phenolic resins may further be modified by epoxidation with epichlorohydrin

(ECH) to duplicate the performance of such phenolic-type novolacs.<sup>5</sup> Having several outstanding characteristics, epoxy resins show low impact resistance in their cured state<sup>6–11</sup> which limits the applications of epoxy resins. To alleviate this deficiency, epoxy resins are modified by the incorporation of reactive liquid rubber without significant losses in other properties, particularly, the mechanical properties.<sup>12,13</sup> In this way, the carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN) has been used by various workers<sup>6,7,13</sup> with diglycidyl ether of bisphenol A (DGEBA) epoxy resin and epoxidized phenolic novolac resins. However, CTBN has hardly been used with cardanol-based epoxy resins. Therefore, we tried to produce modified epoxy matrices based on cardanol by physical blending with CTBN and studied the effect of CTBN addition on the thermal and morphological changes in the blends.

## EXPERIMENTAL

### Materials

Cardanol (M/s Satya Cashew Pvt., Ltd., Chennai, India), formaldehyde (40% solution), oxalic and succinic acids, sodium hydroxide, ECH (all from M/s

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**TABLE I**  
Physical Characteristic of Cardanol

Property	Calculated		
	Distilled cardanol	From the open market	From the literature
Viscosity (P)	41.5	40.2	32
Specific gravity (g/m <sup>3</sup> )	0.900	0.854	0.873
Iodine value	285.6	280.4	279.8
Moisture content at 100°C (wt %)	3.2	2.8	2.6

Thomas Baker Chemicals, Ltd., Mumbai, India), polyamine (M/s Ciba Specialty Chemicals, Ltd., Mumbai, India) with amine values of 1240–1400 mg of KOH/g, and CTBN (Hycar 1300 × 13) were used during the investigation. CTBN was kindly supplied by M/s Emerald Performance Materials, LLC (Hong Kong) with a number-average molecular weight ( $M_n$ ) of 3500 and acrylonitrile and carboxyl contents of 27 and 32 wt %, respectively.

#### Analysis of cardanol

Cardanol, obtained from the distillation of commercial CNSL under reduced pressure (1 mmHg) and collected at 206–208°C, was subjected to extensive analysis, namely, for iodine value, viscosity, and specific gravity (see Table I), as per the procedure mentioned in IS standard 840-1964.

#### Synthesis of the cardanol-based, novolac-type phenolic resins

Novolac resins with a cardanol-to-formaldehyde molar ratio of 1 : 0.7 were prepared with dicarboxylic acids, namely, oxalic and succinic acids, as catalysts by a method similar to that adopted by Knop and Schieb<sup>14</sup> for phenol-based novolac. The catalyst (1% based on cardanol) was first dissolved in methanol at 60°C. Half of the catalyst solution was added to cardanol (about 30 g), which was charged in a three-necked, round-bottom flask fitted with a Leibig's condenser and mechanical stirrer. The remaining half of the methanolic solution of the catalyst was added to formaldehyde (40%), and this was added to the cardanol dropwise within 1 h once the temperature of the reaction kettle was maintained at 120°C. The initial pH of the reaction mixture was 6.0, which decreased to a value of 2.0 after 5 h of reaction at 120°C. Free-formaldehyde and free-phenol contents were checked after every 45 min to determine the completion of the methylation reaction.<sup>15</sup> The reaction product was cooled and dried *in vacuo* at 60°C overnight before purification by column chromatography. A resin solution prepared

with *n*-hexane and charged to silica gel column chromatographic purification was adopted mainly to remove unreacted components, impurities, and so on from the methylolated cardanol. Purification was effected with the eluent mixture of ethyl acetate and benzene (60 : 40). The purified resin was analyzed by infrared (IR) spectroscopic, nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopic, mass spectroscopic, and gel permeation chromatography (GPC) analysis. Two novolac-type phenolic resins, CF<sub>71</sub> and CF<sub>72</sub>, with catalyst oxalic and succinic acids, respectively, were prepared.

#### Epoxidation of the cardanol-based, novolac-type phenolic resins and preparation of the blends of the epoxidized novolac resin and CTBN

The previously prepared cardanol-based, novolac-type phenolic resins were epoxidized by a method similar to a method given in literature.<sup>16</sup> Approximately, 1.0 mol of the novolac resin was placed in a 500-mL, three-necked, round-bottom flask, and 6.0 mol of ECH was added to it with stirring. Then, a 40% sodium hydroxide solution was added dropwise to this mixture for a period of 5 h at 120°C. The reaction mixture was then subjected to distillation *in vacuo* to remove unreacted ECH. The resulting viscous product was stored for further analysis. Two epoxidized novolac resins, ECF<sub>71</sub> and ECF<sub>72</sub>, with novolac resins CF<sub>71</sub> and CF<sub>72</sub>, respectively, were prepared.

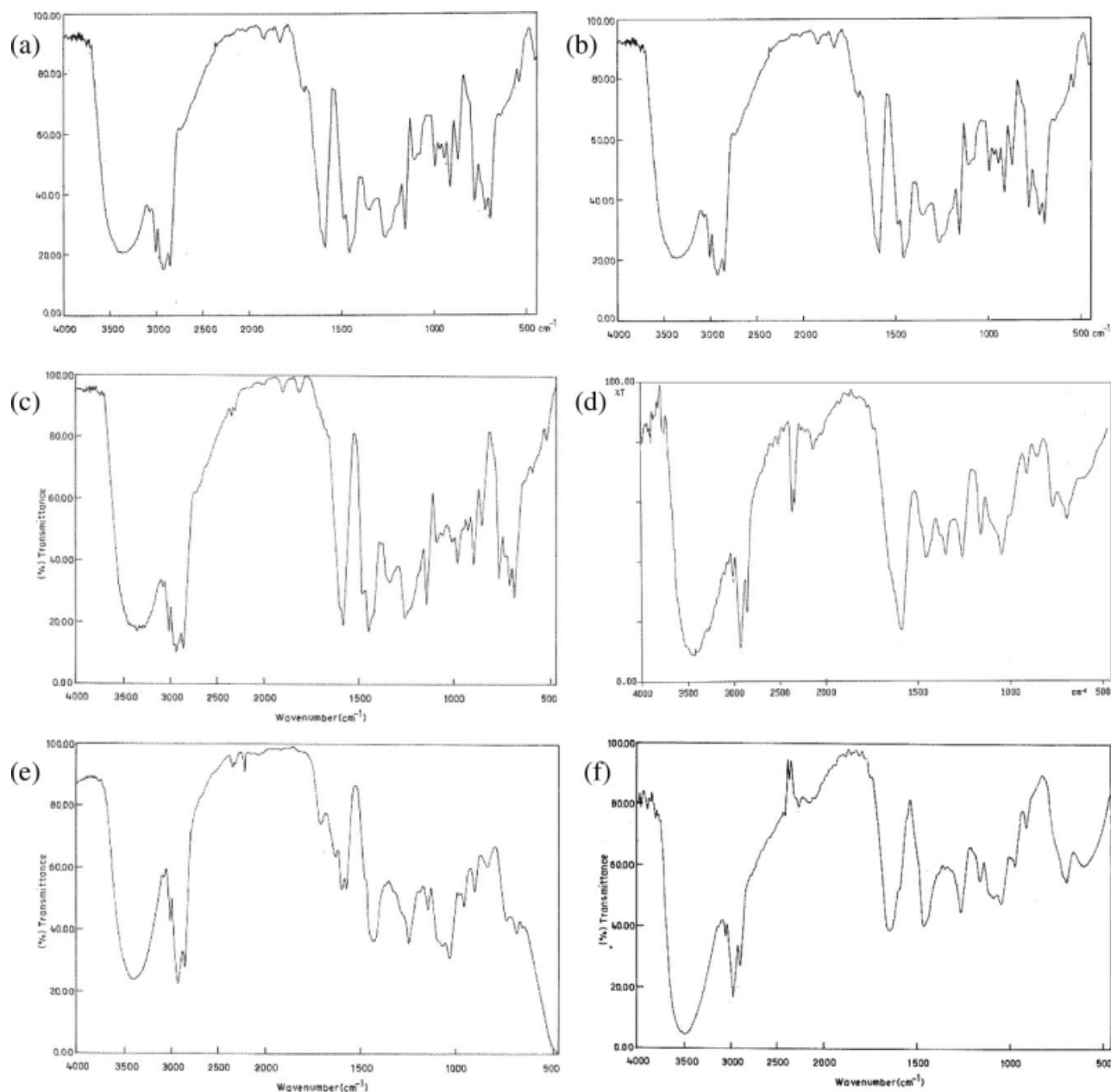
The epoxy resin was mixed physically with various concentration of CTBN ranging between 0 and 20 wt % with an interval of 5 wt %. All of the samples were designated according to Table II.

#### Characterization techniques of the prepared samples

Fourier transform infrared (FTIR) spectra of the prepared samples were recorded on a PerkinElmer

**TABLE II**  
Sample Designations

Sample number	Epoxy (wt %)	CTBN (wt %)	Sample code
Cardanol-based epoxidized novolac resin (prepared from novolac resin CF <sub>71</sub> )			
1	95	5	BECF <sub>711</sub>
2	90	10	BECF <sub>712</sub>
3	85	15	BECF <sub>713</sub>
4	80	20	BECF <sub>714</sub>
Cardanol-based epoxidized novolac resin (prepared from novolac resin CF <sub>72</sub> )			
5	95	5	BECF <sub>721</sub>
6	90	10	BECF <sub>722</sub>
7	85	15	BECF <sub>723</sub>
8	80	20	BECF <sub>724</sub>



**Figure 1** FTIR spectra of (a) cardanol, (b) novolac resin CF<sub>71</sub>, (c) novolac resin CF<sub>72</sub>, (d) epoxidized novolac resin ECF<sub>72</sub>, (e) uncured blend sample BECF<sub>723</sub>, and (f) cured blend sample BECF<sub>723</sub>.

(USA) (model 843) IR spectrophotometer with KBr pellets in the wavelength range 500–4000  $\text{cm}^{-1}$ .

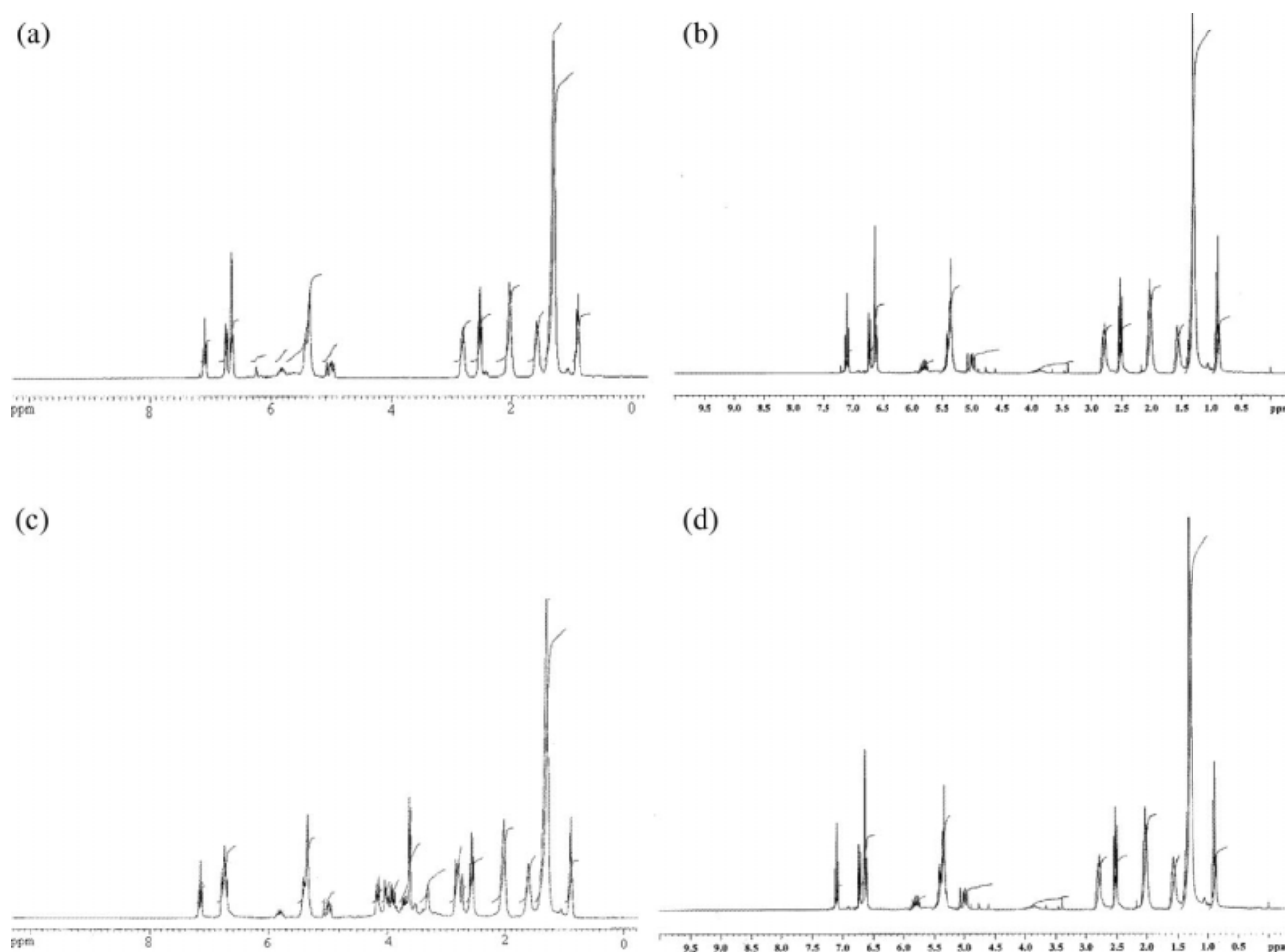
<sup>1</sup>H-NMR spectra of the cardanol-based novolac and epoxidized novolac resins were recorded on a Bruker (Germany) DRX-300 NMR spectrophotometer in the temperature range  $-90$  to  $80^\circ\text{C}$ .

GPC was used (the instrument procured from E. Merck (Germany) consisted of a pump, an L-7350 column oven, and an L-7490 refractive-index detector) to determine the number-average molecular weight of the synthesized cardanol-based novolac resins. A small quantity of the resin was dissolved in tetrahydrofuran; which acted both as a mobile

and stationary phase, and injected into the instrument.

The mass spectra of the prepared samples were recorded on Micromass ToFSpec2e matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) (Waters Micromass UK Ltd., England) and fast atom bombardment (FAB) mass spectrophotometer. The elemental composition of the prepared novolac and epoxy resins were determined with a Heraeus Vario EL III Carlo Erba 1108 elementals analyzer (Heraeus GmbH, Germany).

The cure temperature of the prepared samples were observed by the placement of a very small



**Figure 2**  $^1\text{H-NMR}$  spectra of (a) cardanol, (b) novolac resin  $\text{CF}_{71}$ , (c) novolac resin  $\text{CF}_{72}$ , and (d) epoxidized novolac resin  $\text{ECF}_{72}$ .

quantity of the blend samples into a shallow aluminum pan sealed by an aluminum cover of a differential scanning calorimeter (TA Instruments, USA, model DSC Q20). This was placed in the sample cell of the instrument. The starting temperature, programmed rate, and final temperature were taken at a heating rate of  $10^\circ\text{C}/\text{min}$ . Dynamic scans were obtained, which were used to determine the cure temperature.

The curing of the blend samples with a stoichiometric amount of polyamine was performed in an air oven (M/s Indian Equipment Corp., Mumbai, India) at  $120^\circ\text{C}$ .

The thermal stability of the blend samples was determined by a comparison of the onset degradation temperature (up to 5% weight loss) of the cured samples with a thermogravimetric analyzer (TA Instruments, model Q50 TGA) at a heating rate of  $10^\circ\text{C}/\text{min}$  in a nitrogen atmosphere from 50 to  $650^\circ\text{C}$ .

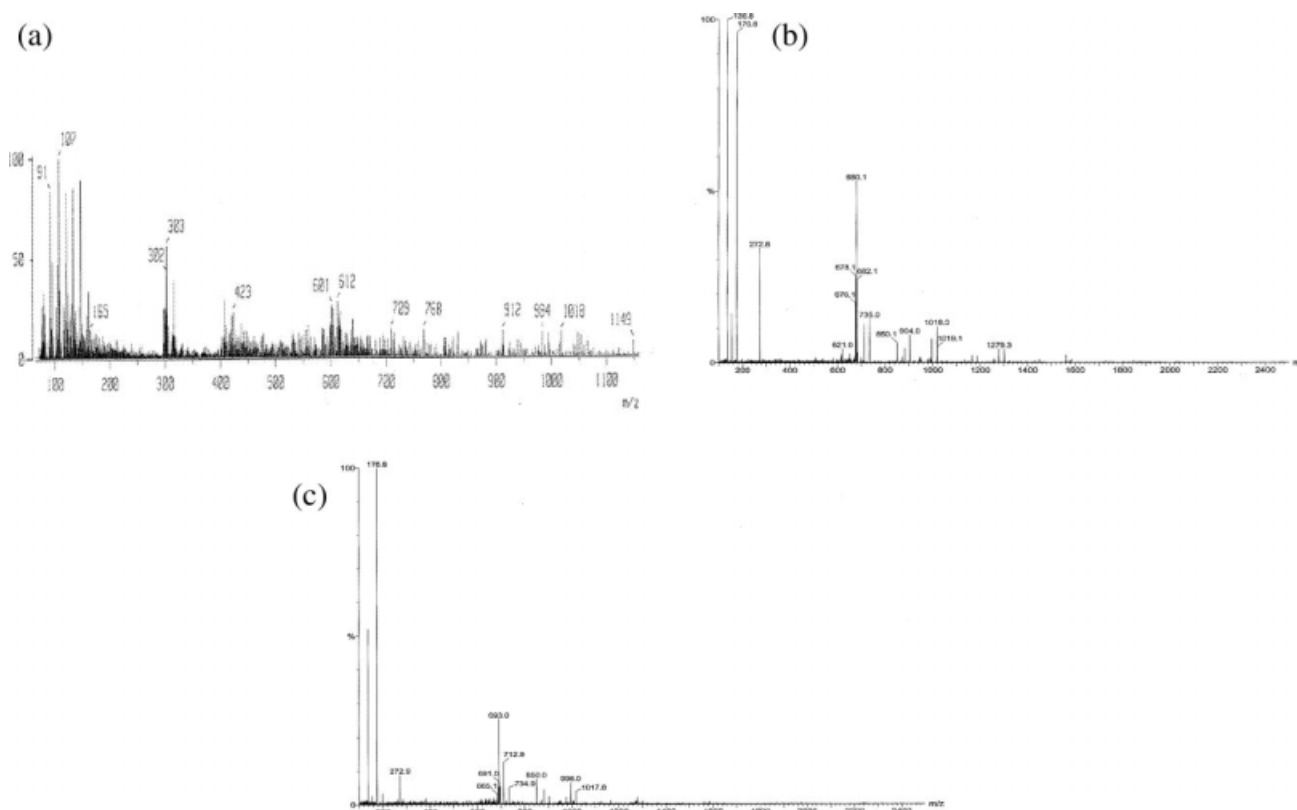
The morphological changes due to the addition of CTBN into the epoxy matrix were studied with a Jeol scanning electron microscope (England) (model JSM 5800). The rubber domains distributed in the

matrix and the interaction of these domains with the epoxy matrix specimen surface were observed by scanning electron microscopy (SEM). For this, the fractured samples were coated with a thin layer of gold-palladium alloy by sputtering to provide conductive surfaces.

## RESULTS AND DISCUSSION

### Synthesis of the cardanol-formaldehyde novolac-type phenolic resins

The methylation of cardanol was carried out with formaldehyde in the presence of dicarboxylic acids, namely, oxalic and succinic acids. The initial pH of the reaction mixture in both cases was found to be 6.0. This indicated that these acid catalysts imparted alkaline pH under these formulations of reaction mixtures as per the norms of pH of phenolic resins.<sup>17</sup> The formylation reactions were carried out with a cardanol-to-formaldehyde molar ratio of 0.7. Therefore, under these experimental conditions, the complete formylation might have been expected to



**Figure 3** (a) FAB mass spectrum of cardanol, (b) MALDI-TOF mass spectrum of novolac resin CF<sub>71</sub>, and (c) MALDI-TOF mass spectrum of novolac resin CF<sub>72</sub>.

yield resins with high ortho–ortho linkages for phenolic novolac resins. The completion of the methylation reaction was checked by periodic withdrawal of the reaction mixture to analyze formaldehyde with the hydroxylamine hydrochloride method.<sup>18</sup> The final pH of the reaction mixture was found to be 2.0. The decrease in pH in the methylolated cardanol might have been due to the formation of monohydroxyl-substituted cardanol. Sperling<sup>19</sup> found that formylated phenol favored hydrogen bonding with *ortho*-methylol and hydroxyl groups, which released hydrogen ions and led to an increase in the acidity of the reaction mixture.

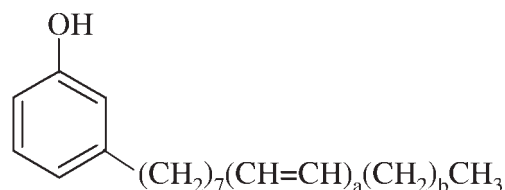
#### Spectral analysis of the cardanol–formaldehyde novolac resins CF<sub>71</sub> and CF<sub>72</sub>

The FTIR [Fig. 1(a)], <sup>1</sup>H-NMR [Fig. 2(a)], and mass [Fig. 3(a)] spectra of cardanol clearly indicated that it was a monoene meta-substituted phenol. Therefore, the empirical formula was taken as C<sub>21</sub>H<sub>34</sub>O,<sup>20,21</sup> and the structure of cardanol is proposed as shown in Scheme 1.

FTIR spectroscopic analysis of CF<sub>71</sub> and CF<sub>72</sub>

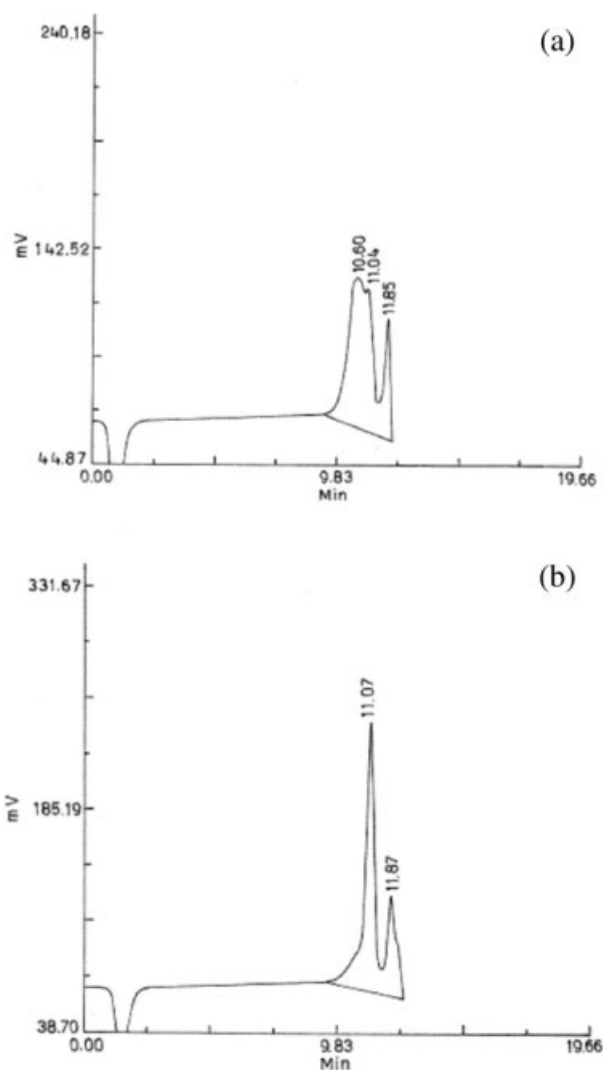
The IR spectral analysis of the cardanol–formaldehyde resins (CF<sub>71</sub> and CF<sub>72</sub>) revealed not only the

condensation of methylolated cardanol but also the degree of ortho and para substitution.<sup>22</sup> A shift of a peak from 1075 to 1090 (CF<sub>71</sub>) and 1104 cm<sup>-1</sup> (CF<sub>72</sub>) and the appearance of a peak near 1708 cm<sup>-1</sup> [Fig. 1(b,c)] were observed in methylolated cardanol because of the C=O stretching from CH<sub>2</sub>OH. Also, the intensity of the peaks at 1594 cm<sup>-1</sup> (C=C stretching), 3010 cm<sup>-1</sup> (C–H stretching of alkene), and 778 cm<sup>-1</sup> (C–H out-of-plane deformation) remained almost unaffected, which indicated that the polymerization took place through the substitution of CH<sub>2</sub>OH and not through the double bonds in the side chain. The bands at 3361 and 3342 cm<sup>-1</sup> for samples CF<sub>71</sub> and CF<sub>72</sub>, respectively, might have been due to the presence of hydroxyl groups in the methylolated cardanol. The most notable differences were the changes in the intensities of the absorption



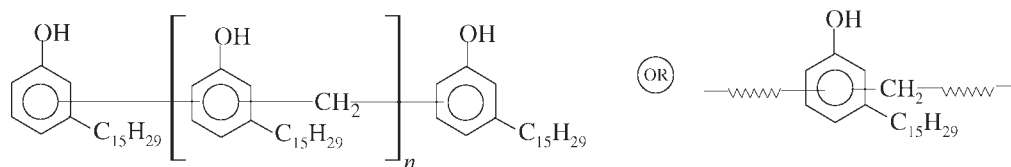
where a = 1; b = 5

**Scheme 1** Structure of cardanol.



**Figure 4** GPC trace of (a) novolac resin CF<sub>71</sub> and (b) novolac resin CF<sub>72</sub>.

bands near 1458 and 994 cm<sup>-1</sup>, which might have been related to the ortho- and para-substituted aromatic rings. The appearance of peaks near 725 and 869 cm<sup>-1</sup> [Fig. 1(b,c)] also indicated ortho and para substitution, respectively, at the benzene nuclei. The preceding spectral data was found to be identical to that given in the literature.<sup>19,23,24</sup>



where  $n = 0.20$  and  $0.25$  for resins CF<sub>71</sub> and CF<sub>72</sub>, respectively.

**Scheme 2** Proposed structure of the cardanol-based novolac resin.

#### <sup>1</sup>H-NMR spectroscopic analysis of CF<sub>71</sub> and CF<sub>72</sub>

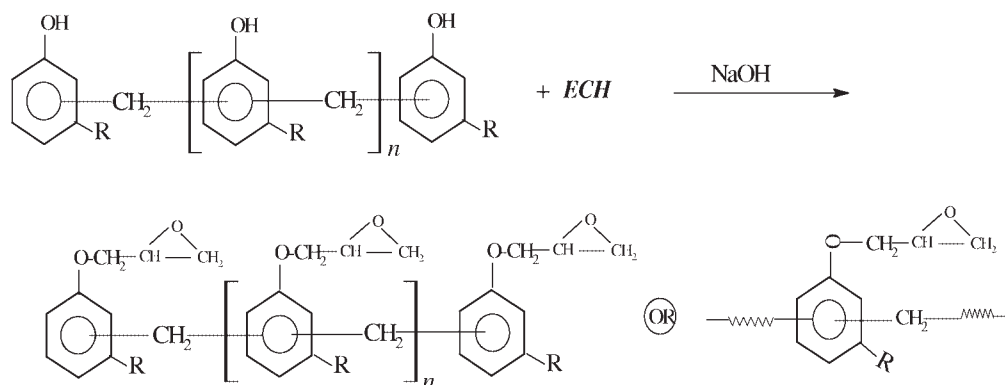
In the <sup>1</sup>H-NMR spectra of the CF<sub>71</sub> [Fig. 2(b)] and CF<sub>72</sub> [Fig. 2(c)] novolac resins, the peak near 6.6–6.8 δ might have been due to the aryl protons of benzene nuclei. The peaks around the region 7.1–7.3 δ appeared to be due to the phenolic hydroxyl in the novolac resins. The peak at 5.3 δ might have been due to the methylene protons, whereas the peaks between 0.8 and 2.8 δ appeared to be due to the presence of a long alkyl aliphatic side chain, originally observed in cardanol [Fig. 2(a)], which was further confirmed by the appearance of a strong peak at 1.3 δ. The terminal methyl group of the alkyl side chain was also seen, as there appeared a small peak at 0.8 δ. The peak at 3.7 δ indicated the presence of methylene protons of C<sub>6</sub>H<sub>5</sub>—CH<sub>2</sub>—C<sub>6</sub>H<sub>5</sub> for the bridge between the phenyl rings.<sup>25–27</sup> All these spectral data indicated that the condensation of methylated cardanol was completed under the experimental conditions [see Fig. 2(b,c)] and was fully consistent with the proposed structure (Scheme 1) resulting from the reaction mechanism shown in our recent article<sup>16</sup> for the cardanol-based novolac resin prepared with a citric acid catalyst.

#### Determination of molecular weights of CF<sub>71</sub> and CF<sub>72</sub> resins by GPC and mass spectroscopic analysis

The number of phenolic units ( $p$ ) per molecule of novolac resins, CF<sub>71</sub> and CF<sub>72</sub>, were determined from the ratio of aromatic methylene ([CH<sub>2</sub>]) to aromatic protons [[AR]; the areas are indicated in the <sup>1</sup>H-NMR spectra for the novolac resins CF<sub>71</sub> and CF<sub>72</sub> in Fig. 2(b,c), respectively], as shown by the following equation:<sup>28</sup>

$$[\text{CH}_2]/[\text{AR}] = (2p - 2)/(3p + 2) \quad (1)$$

The values of  $p$  were calculated to be 2.20 and 2.25, whereas the GPC traces [Fig. 4(a,b)] resulted in  $M_n$  values of 679 and 693 g/mol for samples CF<sub>71</sub> and CF<sub>72</sub>, respectively. The values of  $M_n$  were further confirmed by mass spectroscopic analysis [Fig. 3(b,c)], which yielded values of 680 and 693 g/mol for samples CF<sub>71</sub> and CF<sub>72</sub>, respectively.



Where R:  $C_{15}H_{29}$

**Scheme 3** Proposed structure of the epoxidized novolac resin.

In the mass spectrum of  $CF_{71}$  [Fig. 3(b)], peaks were observed at  $m/z$  values of 680 and 850, which corresponded to  $n = 1$  and  $n = 2$ , respectively, whereas for resin  $CF_{72}$  [Fig. 3(c)], the peaks were at  $m/z$  values of 693 and 850, which corresponded to  $n = 1$  and  $n = 2$ , respectively, as shown in Figure 3(c). The GPC curves clearly indicated the existence of dimers and trimers in the final reaction mixture. So, molecular weights, as obtained from mass spectra [Fig. 3(b,c)], of 680 and 693 g/mol for resins  $CF_{71}$  and  $CF_{72}$ , respectively, were considered for this discussion. These values were very close to the values obtained from the previously discussed  $^1H$ -NMR spectra. Therefore, the values of  $n$  in the structure of the novolac resins, shown in Scheme 2, were calculated to be 0.20 and 0.25 for resins  $CF_{71}$  and  $CF_{72}$ , respectively. These values resembled the values of peak-to-peak mass increments ( $\Delta m$ ) in the mass spectra [Fig. 3(b,c)].

Finally, the structure of the cardanol-based novolac resins is proposed as shown in Scheme 2.

### Epoxidation of the novolac prepolymer

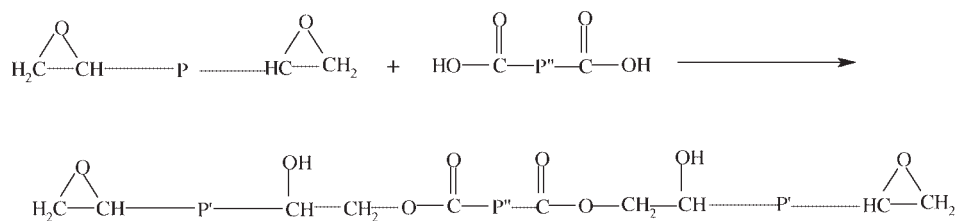
The novolac-based epoxy resins were synthesized by reaction with ECH. The number of glycidyl groups per molecule in the resin was dependent on the number of phenolic hydroxyls in the starting novolac, the extent to which they reacted, and the extent to which the lowest molecular species were polymerized during synthesis. Theoretically, all of the phenolic hydroxyls may react, but, in practice, all of them do not react because of steric hindrance.<sup>29</sup> The reaction between ECH and novolac resin may be thought to proceed in a similar fashion, as in the study by Lee and Neville.<sup>29</sup> The epoxide group of ECH reacted with phenolic hydroxyls in the alkaline medium and formed the chlorohydrin ether, which underwent a dehydrochlorination reaction and

resulted in glycidyl ether. The structure of the epoxy resin is proposed as shown in Scheme 3.

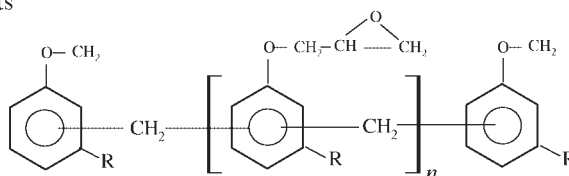
As shown in Figure 1(d), the FTIR spectrum of the uncured cardanol-based epoxidized novolac resins, that is, sample  $ECF_{72}$ , the characteristic band of the oxirane ring was observed near 911 and 856  $cm^{-1}$ . The  $^1H$ -NMR spectrum [Fig. 2(d)] further confirmed the formation of the cardanol-based epoxidized novolac resins.

### FTIR analysis of the uncured and cured blend samples

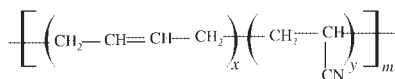
The FTIR spectral analysis of the uncured blend sample containing 15 wt % CTBN in the epoxy resin  $ECF_{72}$  is shown in Figure 1(e). The peaks related to oxirane functionality appeared near 911 and 856  $cm^{-1}$  [Fig. 1(d)]. When CTBN was added to the pure epoxy resin, these peaks disappeared, and new peaks appeared near 914 and 850  $cm^{-1}$  [Fig. 1(e)]. The peaks appearing near 911 and 856  $cm^{-1}$  [Fig. 1(d)] might have overlapped these peaks. The peaks near 1719  $cm^{-1}$  due to carbonyl stretching, at 1440 and 972  $cm^{-1}$  due to C—H bending,<sup>30–32</sup> and a sharp peak near 2239  $cm^{-1}$  due to the  $-C\equiv N$  group of the CTBN molecule were also seen in the spectrum of the uncured blend system [Fig. 1(e)]. These observations clearly indicated that there was no chemical interaction between the oxirane group of the epoxy and the carboxyl group of CTBN. The epoxy resin and CTBN remained as a discrete phase in the uncured stage. However, the addition of CTBN and polyamine to the epoxy caused chemical interaction between the oxirane ring and the carbonyl function of the CTBN, which resulted in the complete diminution of the peaks at 911 and 856  $cm^{-1}$  in the cured blend sample  $BECF_{723}$  [Fig. 1(f)]. The  $-C\equiv N$  group was also not observed in the cured blend. This was perhaps due to the lower volume fraction of CTBN in the blend system. Another possibility is that it



Where P' represents



and P'' represents



**Scheme 4** Proposed carboxyl-epoxide esterification reaction.

could have also been used in network modification. The blend also showed the appearance of new stretched peaks between 1258 and 1635 and 1046  $\text{cm}^{-1}$  and peak broadening at 1608  $\text{cm}^{-1}$  due to C=C multiple stretching. The appearance of these peaks at different positions resembled a discussion on the FTIR analysis of DGEBA/CTBN blend systems given in the literature.<sup>33</sup> The carboxyl-epoxide esterification reactions are illustrated in Scheme 4.

The epoxide group present in P' may have also combined with the carboxyl group of the CTBN, which is shown in Scheme 5.

The products formed by the reactions shown in Schemes 4 and 5 reacted with the polyamine curing agent in the same way as those that reacted with the epoxy resin<sup>34</sup> to form an epoxy network. The FTIR spectrum of the cured blend sample shown in Figure 1(f) confirmed this.

#### Differential scanning calorimetry (DSC) analysis of the blend samples

Figures 5 and 6 show the dynamic DSC scans of the cardanol-based epoxidized novolac resins without and with CTBN (i.e., samples ECF<sub>72</sub> and BECF<sub>723</sub>) at a heating rate of 10°C/min. Also, the effect of CTBN concentration on the cure parameters of different epoxy matrices is compared to that of nonmodified ep-

oxy matrices in Table III. It was clear from the results that the peak exotherms were shifted to lower temperatures because of an enhanced reaction rate, which, finally, reduced the cure time of the CTBN-modified blend systems (see Table III). These peaks appeared during the first heating run but were completely absent during the second heating cycle; this indicated the completion of the curing reaction. The initial addition of CTBN in the epoxy resin decreased the cure time sharply, and this trend remained up to 15 wt % CTBN addition and increased thereafter. The enhanced rate behavior could be interpreted in terms of an intermolecular transition state for the epoxy-amine reaction. According to this mechanism,<sup>35-37</sup> strong hydrogen bonding species, such as acids and alcohols, stabilized the transition state and strongly accelerated the curing reaction. Also, the reaction products containing the carboxylic acid component favored the gelation conditions, which might have created fluctuations in the concentration and induced phase separation.<sup>38</sup> The curing reactions led to an increase in viscosity and, eventually, to the gelation of the entire resin mixture, as evidenced from the decrease in onset temperatures with increased addition of CTBN in the epoxy matrices (Table III). Furthermore, the reduction in molecular mobility lowered the rate of the reaction<sup>39</sup> and demised the epoxy-amine-



**Scheme 5** Proposed reaction between epoxy groups and CTBN.



**TABLE III**  
DSC Results for the Unmodified and CTBN-Modified Cardanol-Based Epoxidized Novolac Resins Cured with Polyamine

Sample	$T_i$ (°C)	$T_{\text{onset}}$ (°C)	$T_p$ (°C)	$T_{\text{stop}}$ (°C)	$\Delta H$ (J/mol)	$t_{\text{cure}}$ (min) <sup>a</sup>
ECF <sub>71</sub>	58.7	115.1	126.2	165.5	64.7	240
BECF <sub>711</sub>	58.1	113.5	123.0	164.8	68.7	223
BECF <sub>712</sub>	57.9	102.5	124.8	163.8	65.3	211
BECF <sub>713</sub>	57.6	76.3	120.1	163.0	76.9	180
BECF <sub>714</sub>	58.6	79.6	125.2	164.3	72.8	191
ECF <sub>72</sub>	65.7	67.7	134.5	195.4	34.1	360
BECF <sub>721</sub>	65.3	66.7	134.0	194.1	39.7	331
BECF <sub>722</sub>	61.0	64.3	135.4	186.5	45.6	317
BECF <sub>723</sub>	46.9	58.2	133.4	184.8	58.6	300
BECF <sub>724</sub>	53.8	62.3	134.6	188.8	53.8	330

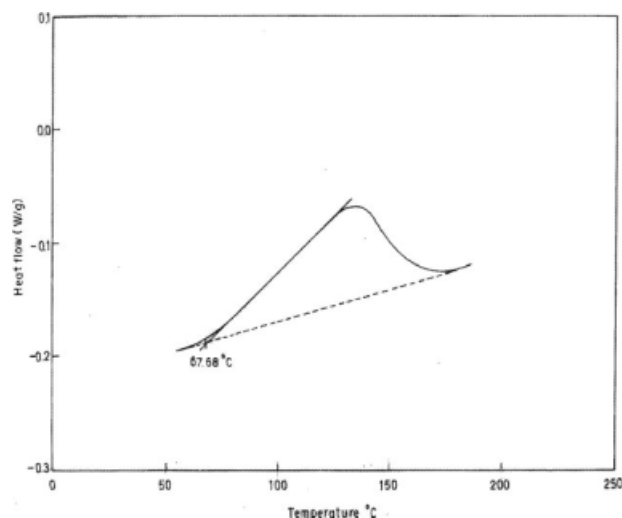
$\Delta H$  = heat of curing;  $t_{\text{cure}}$  = cure time;  $T_i$  = kick-off temperature at which the curing started;  $T_{\text{onset}}$  = temperature at which the first detectable heat was released;  $T_p$  = temperature of the peak position of the exotherm;  $T_{\text{stop}}$  = temperature of the end of the curing exotherm.

<sup>a</sup> Obtained by the curing of the sample in an air oven at 120°C.

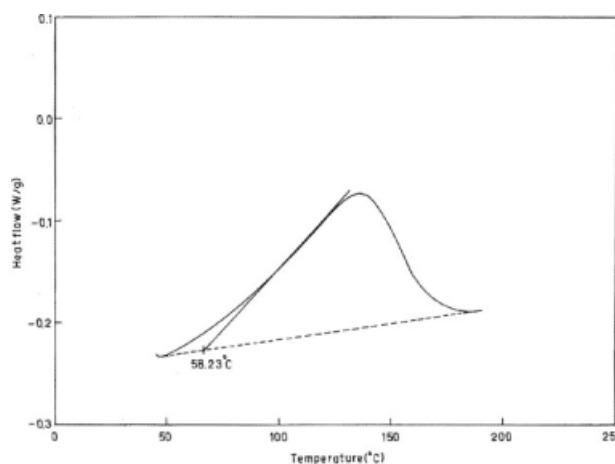
CTBN systems<sup>40</sup> up to 15 wt % CTBN addition. The decrease of cure time could also be explained by the fact that, during the reaction of CTBN with the epoxy resin, some of the exothermic energy released during epoxy crosslinking might have been consumed by CTBN, which resulted in a decrease in the cure time.<sup>41</sup> The high cure rate might have resulted in the formation of spherical domains with fairly uniform particle size. The particle size became smaller with increasing curing rate. These domains might have become bigger and more closely packed and reached phase-inversion conditions<sup>42</sup> beyond 15 wt % CTBN, and so, the curing rate dropped, which increased the cure time.

The heat of polymerization ( $\Delta H$ ) values (Table III) related to the cure process were determined from the area of the exotherm peak obtained from DSC analysis (Figs. 5 and 6) taken in dynamic mode. In contrast, the presence of CTBN did not significantly

affect  $\Delta H$ , which indicated that there was not much influence on the crosslink density of the epoxy matrix. The  $\Delta H$  values ranged from 64.7 J/mol for the unfilled ECF<sub>71</sub>/polyamine to 76.9 J/mol (expressed in terms of the mass of the epoxy/amine mixture) for 15 wt % CTBN and 34.1 J/mol for the unfilled ECF<sub>72</sub>/polyamine to 58.6 J/mol for 15 wt % CTBN (i.e., blend sample BECF<sub>723</sub>). This confirmed that the final reaction state was not significantly affected by the presence of CTBN.  $\Delta H$  was previously found to be 99.9 J/mol for aniline/DGEBA, 98.9 J/mol for DDM/DGEBA, 99.1 J/mol for aniline/DGEBA, and 100–118 J/mol for phenyl glycidyl ether type epoxy-amine reactions, as tabulated in a review by Rozenberg.<sup>37</sup> The  $\Delta H$  values did not compare with those found in our systems, that is, for the blend systems of the cardanol-based epoxidized novolac resins, CTBN, and polyamine and, hence, the cured product was not the same as that for the aforementioned systems.



**Figure 5** DSC scan of sample ECF<sub>72</sub>.



**Figure 6** DSC scan of blend sample BECF<sub>723</sub>.

**TABLE IV**  
**Results of the TG/DTG Traces of the Unmodified and CTBN-Modified Cardanol-Based Epoxidized Novolac Resins Cured with Polyamine**

Blend sample	First step				Second step				Total CY (%)
	$T_o$	$T_{max}$	$T_f$	ML (%)	$T_o$	$T_{max}$	$T_f$	ML (%)	
ECF <sub>71</sub>	223	326	381	42.6	381	442	500	53.2	4.2
BECF <sub>711</sub>	198	318	353	62.6	353	439	514	34.4	3.2
BECF <sub>712</sub>	168	325	357	90.7	357	439	499	7.0	2.3
BECF <sub>713</sub>	155	318	359	61.4	359	439	508	38.5	.1
BECF <sub>714</sub>	149	322	355	55.6	355	441	505	40.5	3.9
ECF <sub>72</sub>	228	317	374	39.8	374	386	508	51.9	8.3
BECF <sub>721</sub>	204	314	369	60.3	369	382	508	32.2	7.5
BECF <sub>722</sub>	176	316	356	54	356	376	504	41.9	4.1
BECF <sub>723</sub>	160	301	349	80.2	349	360	475	13.3	6.5
ECF <sub>724</sub>	155	312	360	51	360	367	498	41.1	7.9

CY = char yield; ML = mass loss.

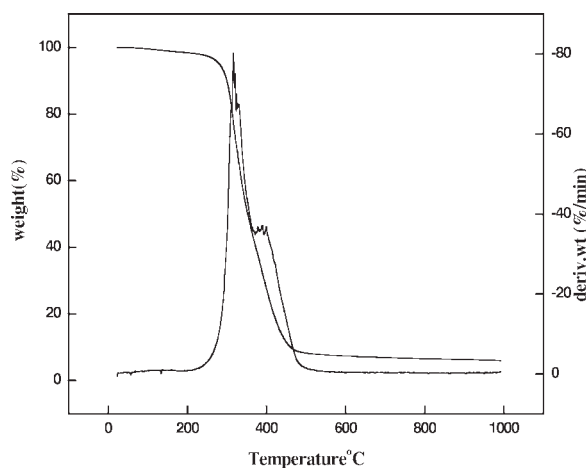
### Thermal stability

The cured polymer samples (ECF<sub>72</sub> and BECF<sub>723</sub>) were analyzed for their thermal stability by thermogravimetry (TG)/differential thermogravimetry (DTG) traces resulting from thermogravimetric analysis (TGA) at a heating rate of 10°C in a nitrogen atmosphere. The onset temperature of degradation ( $T_o$ ), the temperature of the maximum rate of mass loss ( $T_{max}$ ), and the extrapolated final decomposition temperature ( $T_f$ ) were noted from the TG traces and are presented in Table IV. We compared the relative thermal stability of the cured blend resins by determining the percentage char yield at 500°C. A two-step decomposition behavior was observed for all of the unmodified and CTBN-modified samples (Figs. 7 and 8). A major mass loss was observed in the second stage of the decomposition (Table IV), whereas the mass lost only 37–39% in the second step of the decomposition in the temperature range 320–500°C. These two stages of mass loss were attributed to the decomposition of (1) the epoxy and (2) the epoxy–CTBN–amine network. The values of  $T_o$  and  $T_{max}$

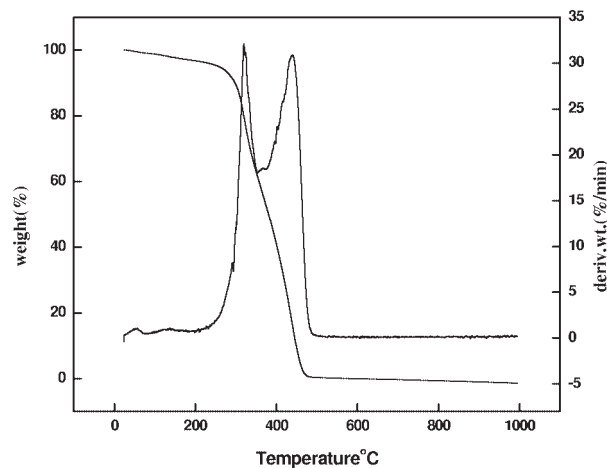
were lower than those of the blend systems cured with 5–15 wt % CTBN. Mass loss in the whole decomposition process was found to be almost independent of CTBN addition in the blends. The mass loss for the blend systems prepared from the epoxy resin ECF<sub>72</sub> was found to be more than that for the blend systems prepared from the epoxy ECF<sub>71</sub>. Also, the char yield was found to be higher in the blend sample prepared from the epoxy resin ECF<sub>72</sub> than that in the blend systems prepared from ECF<sub>71</sub>. This was attributed to the presence of more crosslinks in the ECF<sub>72</sub>–CTBN–amine system than in the ECF<sub>71</sub>–CTBN–amine system. The decreased thermal stability, as observed by  $T_o$ , confirmed this.<sup>43–46</sup>

### SEM analysis

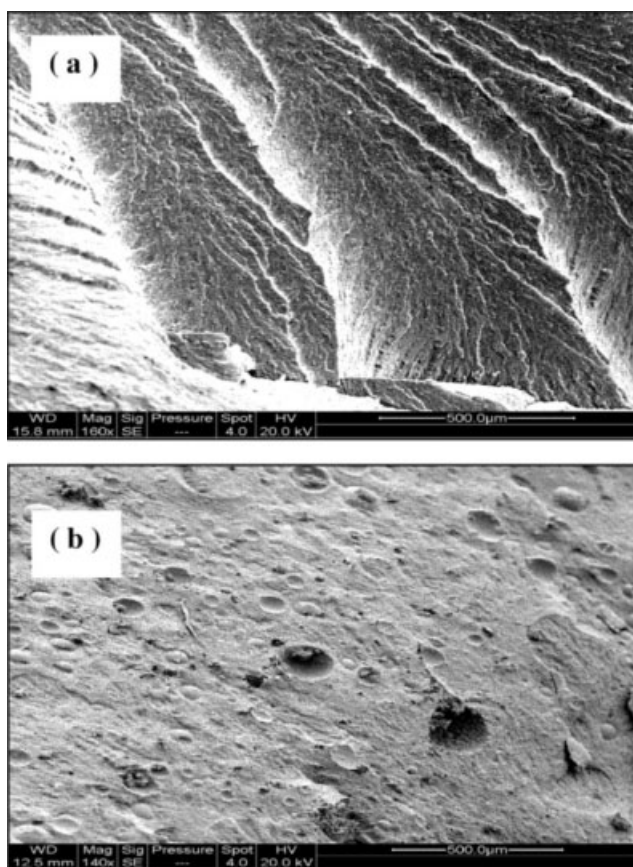
Figure 9(a,b) shows, respectively, the SEM micrographs of fractured surface of the pure epoxy and CTBN-modified epoxy matrix. SEM of the CTBN-modified system showed the presence of precipitated, discrete rubber particles, which were



**Figure 7** TGA trace of blend sample ECF<sub>72</sub>.



**Figure 8** TGA trace of blend sample BECF<sub>723</sub>.



**Figure 9** SEM micrographs of prepared samples: (a) ECF<sub>72</sub> and (b) BECF<sub>723</sub>.

dispersed throughout the epoxy matrix; that is, they revealed the presence of two-phase morphological features. The soft elastomeric phase was separated from the hard epoxy matrix during the early stage of the cure. The fractured surface of most rubber-toughened epoxy systems has a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated particles.<sup>47–49</sup> Some cavitations of the rubber particles accompanied by stress-whitening zones were also observed in the scan [Fig. 9(b)]. This stress-whitening effect may have been related to location deformation at the crack tip. Furthermore, the cavitations were followed by the onset of a shear localization process,<sup>50</sup> which resulted in the observed increase in thermal properties. The SEM analysis also proved that there occurred a chemical reaction between the molecules of the epoxy and rubber, as already shown by the FTIR analysis, which led to strong interactions between the two phases at lower CTBN concentrations.

## CONCLUSIONS

The following conclusions were drawn from the previously discussed results:

1. The proposed mechanism for the curing reaction of the blend of cardanol-based epoxidized novolac resins and CTBN in the presence of polyamine was found to be well suitable for such systems, as confirmed by IR analysis.
2. DSC studies showed the exothermal heat of reaction of the epoxy crosslinking due to the addition of rubber into the epoxy matrix.
3. The thermal stability of the cardanol-based epoxy systems improved with the addition of CTBN, where CTBN might have acted as a thermal stabilizer.
4. The morphological study of the cured system revealed a two-phase region where the liquid rubber particles were distributed in the epoxy matrix. A further increase in the concentration of the elastomer led to a phase-inversion morphology.

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