Studies on Synthesis of Modified Epoxidized Novolac Resin from Renewable Resource Material for Application in Surface Coating

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ABSTRACT: Five blend samples of cardanol-based epoxidized novolac resin containing varying concentrations of carboxyl-terminated poly(butadiene-co-acrylonitrile) (CTBN) ranging between 0 and 25 wt % with an interval of 5 wt % were prepared. The epoxidized novolac resin (ECF) was synthesized from the epoxidation of cardanol-based novolac-type phenolic resin (CF) with molar excess of epichlorohydrin (i.e., about 10 mol at 120°C in basic medium). The CF resin was synthesized with a molar ratio of 1 : 0.5 of CF using dicarboxylic acid catalyst such as succinic acid at 120°C for 5 h. The pure epoxy and its blend were cured with stoichiometric amounts of polyamine curing agent. The formation of various products during the synthesis of cardanol-based novolac resin, epoxidized novolac resin, and blending of epoxidized novolac resin with CTBN have been studied by Fourier transform infrared (FTIR) spectroscopic analysis. Further, a reaction mechanism for the step-growth reaction was proposed on the basis of the results of FTIR analysis. Also, the structures of CF and ECF were proposed on the basis of the results of nuclear magnetic resonance and MALDI-TOF mass spectroscopic analysis along with gel permeation chromatographic (GPC) analysis. GPC analysis resulted in M_n of 670 gmol^{-1}. The blend sample having 15 wt % CTBN concentration showed minimum cure time, whereas the presence of CTBN in blend systems showed marginal change in the values of ΔH. A clear-cut two-step mass loss in dynamic thermogravimetric trace of unmodified and CTBN-modified systems was observed. Thermal stability of the blend sample containing 15 wt % CTBN into the pure epoxy resin was the highest among all other prepared systems. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1471–1484, 2009

Key words: cardanol-based epoxidized novolac resin; carboxyl-terminated butadiene acrylonitrile copolymer; mechanical properties; chemical resistance thermal stability

INTRODUCTION

Cashew nut shell liquid (CNSL), a phenolic-based monomer, is commercially available as a natural plant-based resin precursor for coatings and reinforced composite matrix.[1–6] The main constituents of CNSL are anarcadic acid, cardanol, and cardol. Other constituents include 2-methyl cardol and a small amount of polymeric material. CNSL extracted by the cold-solvent method is called natural CNSL, whereas hot-oil and roasting processed CNSL is called technical CNSL.[7] In the extraction processes involving heat, anacardic acid is usually decarboxylated into cardanol[8] and hence cardanol is the main constituent of technical CNSL. It is a phenolic compound with a C_{15} aliphatic chain in the meta position having a mixture of saturated and unsaturated

(mono-, di-, and tri-) compounds. Because cardanol is the major component of technical CNSL, its application in resin production is of great practical interest and can be polymerized in a variety of ways.[1–4] In the condensation polymerization process, cardanol can be condensed with active hydrogen-containing compounds such as formaldehyde at the ortho- and para-positions of the phenolic ring under acidic or alkaline conditions to yield a series of polymers of "novolac" or "resole" type, respectively.[9] The cardanol-based novolac-type phenolic resin may further be modified by epoxidation with epichlorohydrin to improve the performance of such phenolic-type novolac.

Apart from having several outstanding characteristics of cured epoxy resins, they have one main drawback: their considerable brittleness, which shows poor fracture toughness, poor resistance to crack propagation, and low impact strength. This inherent brittleness has limited their applications in the field, requiring high impact and fracture strength such as in composites and coatings. To alleviate this deficiency, epoxy resins are modified by the

TABLE I
Sample Designation

Sample No.	Cardanol-based Epoxidized Novolac Resin (wt %)	CTBN (wt %)	Sample Code
1	100	0	ECF_{520}
2	95	5	ECF_{521}
3	90	10	ECF_{522}
4	85	15	ECF_{523}
5	80	20	ECF_{524}
6	75	25	ECF_{525}

incorporation of reactive liquid rubber without significant loss in other properties.[10–14] In the past, carboxyl-terminated poly(butadiene-co-acrylonitrile) (CTBN) liquid rubber was used by various workers[15–19] with diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and epoxidized phenolic novolac resins. However, CTBN is nowhere used with cardanol-based epoxy resins. Therefore, we have tried to produce the modified epoxy matrices, based on cardanol, by physical blending with CTBN and to study the effect of CTBN addition on thermal and morphological changes in the blends.

MATERIALS AND METHODS

Materials

The following materials were used: cardanol (M/s Satya Cashew, Chennai, India), formaldehyde (40% solution), succinic acid, sodium hydroxide, epichlorohydrin (all from M/s Thomas Baker Chemicals, Mumbai, India), polyamine (M/s Ciba Specialty Chemicals, Mumbai, India) with amine value 1240-1400 mg KOH g^{-1}, and CTBN (Hycar 1300 × 13). CTBN was kindly supplied by M/s Emerald Performance Materials (Hong Kong) having molecular weight M_n of 3500 $gmol^{-1}$ and acrylonitrile and carboxyl contents 27 and 32%, respectively.

Synthesis of cardanol-based novolac-type phenolic resin

Novolac resin with a mol ratio of 1 : 0.5 of cardanol (C) to formaldehyde (F) was prepared by using dicarboxylic acid (viz., succinic acid), as catalyst, by a method similar to that adopted by Knop and Schieb[20] for phenol-based novolac. 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) and charged in a three-necked round-bottom flask fitted with a Liebig's condenser and mechanical stirrer. The remaining half of the methanolic solution of catalyst was added to the formaldehyde (40%) and this was added to the cardanol dropwise within 1 h. once the temperature of

the reaction kettle was maintained to 120°C. The initial pH of the reaction mixture was 6.0, which reduced to a value of 4.8 after 5 h of reaction at 120°C. Free-formaldehyde and free-phenol contents were checked every 45 min to see the completion of the methylolation reaction.[21] The reaction product was cooled and dried under vacuum at 60°C overnight before purification by column chromatography. A resin solution prepared with *n*-hexane, charged to the silica gel column chromatographic purification, using an eluent mixture of ethyl acetate (60 : 40) was adopted mainly to remove unreacted components, impurities, etc., from the methylolated cardanol. The purified resin was analyzed by infrared (IR) spectroscopic, nuclear magnetic resonance (^{1}H-NMR) spectroscopic, mass spectroscopic, and gel permeation chromatographic (GPC) analysis.

Epoxidation of cardanol-based novolac-type phenolic resin

The cardanol-based novolac-type phenolic resin was epoxidized by a method similar to the method given in literature.[22] Approximately 1.0 mol of novolac resin was taken in a 500 mL three-necked round-bottomed flask and 10 mol epichlorohydrin was added to it while stirring. Then, 40% sodium hydroxide solution was added dropwise to the above mixture for a period of 5 h at 120°C. The reaction mixture was then subjected to distillation under vacuum for removal of unreacted epichlorohydrin. The resulting viscous product was stored for further analysis. The epoxide equivalent weight of epoxidized novolac resin was 305 g/equiv.

Preparation of blends of epoxidized novolac resin and carboxyl-terminated butadiene acrylonitrile copolymer (CTBN)

Blend samples containing 0–25 wt % CTBN were prepared according to the procedure similar to that adopted by Ting.[23] The calculated quantity of epoxy resin (as per the formulation given in Table I) was first stirred at 120°C for 1 h to entrap all air bubbles from the resin. To this homogenous resin, the stoichiometric amount of polyamine (11.96 parts by weight polyamine per 100 parts by weight resin) was added and stirred to get a clear homogeneous mixture.

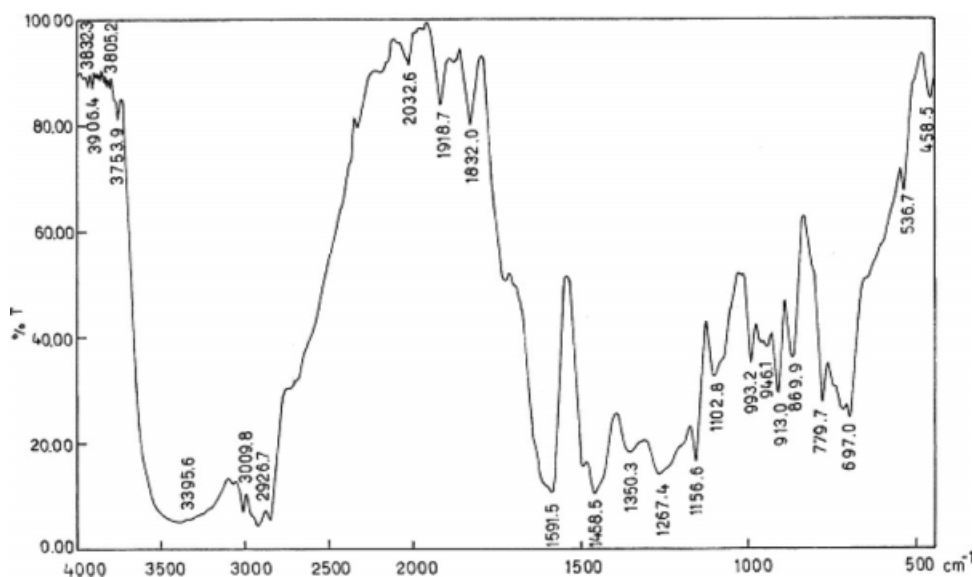where, a = 1; b = 5

Scheme 1 Structure of cardanol.

Figure 1 FTIR spectrum of novolac resin CF_{52}.

Fourier transform infrared spectroscopic analysis and ^{1}H-NMR spectroscopic analysis

Fourier transform infrared (FTIR) spectra of the prepared samples were recorded on a Perkin-Elmer (model 843) IR spectrophotometer in the wave length range of 500–4000 cm^{-1}. Sodium chloride (NaCl) pellets were used to get the spectra of uncured material. For this, a drop of viscous material was kept in between two pellets and the pellet was placed near the window of FTIR spectrophotometer. For the cured material potassium bromide (KBr) pallets were prepared. The cured product and potassium bromide were ground in the ratio of 1 : 4 and then pressed in IR pellet die at 40 psi pressure. Finally, the pellets were placed near the window of FTIR spectrophotometer. By using a computerized recorder, changes in the structure of the polymer at molecular level was studied from the recorded spectra.

^{1}H-NMR spectra of cardanol-based novolac and epoxidized novolac resins were recorded on a Bruker DRX-300 NMR spectrophotometer in the temperature range of −90 to +80°C.

GPC analysis and mass spectroscopic analysis

GPC was recorded (instrument procured from Merck consisting of a pump, L-7350 column oven, and L-7490 R.I. Detector) to determine the number-average molecular weight of the synthesized cardanol-based novolac resin. A small quantity of the resin, dissolved in tetrahydrofluran (acted both as mobile and stationary phase), was injected into the instrument. Mass spectra of the prepared samples were recorded on Micromass TofSpec2e MALDI TOF mass spectrophotometer.

Viscosity

A Brookfield R/S-CPS+ Rheometer (ver. 9.00) was used to measure the viscosity of cardanol-based novolac resin and epoxidized novolac resin systems. The spindle used was C-25-2 DIN.

Differential scanning calorimetric analysis

Cure temperature of the prepared sample was measured by taking a small quantity of blend sample into shallow aluminum pan sealed by an aluminum cover of differential scanning calorimetry (DSC; model DSC Q20; TA Instruments). This was placed in sample cell of the instrument. The starting temperature, programmed rate, and final temperature were taken at heating rate of 10°C min^{-1}.
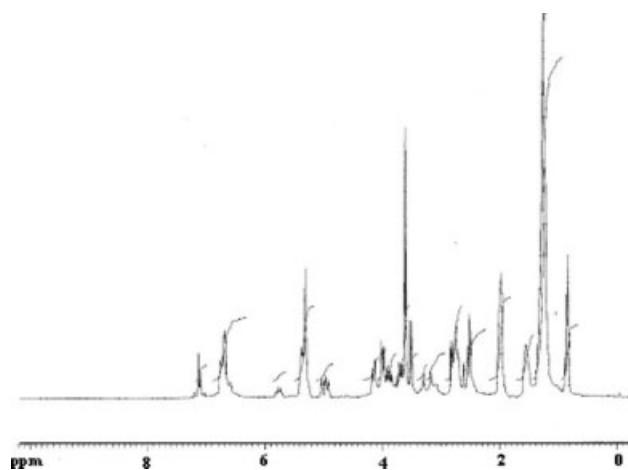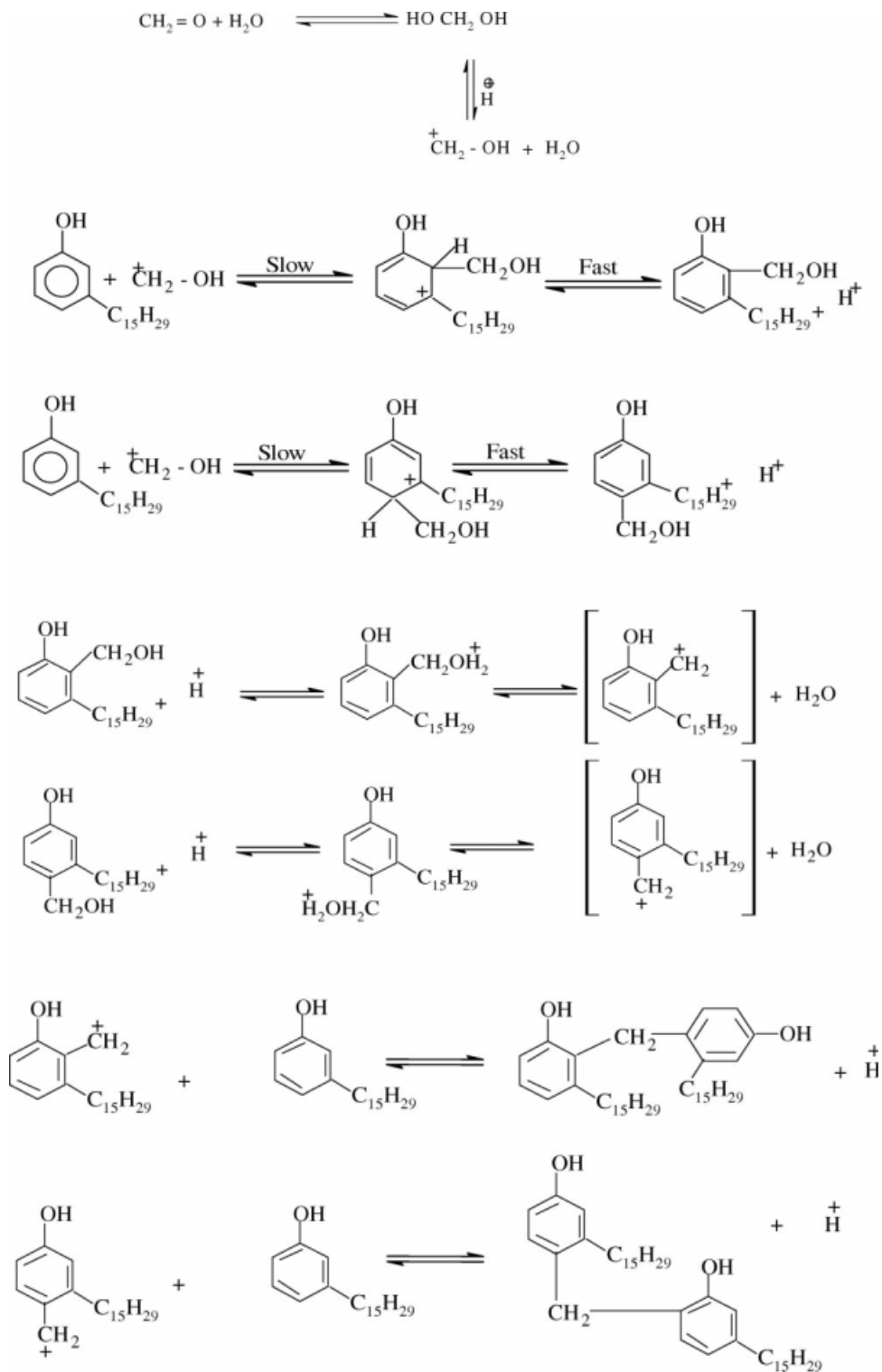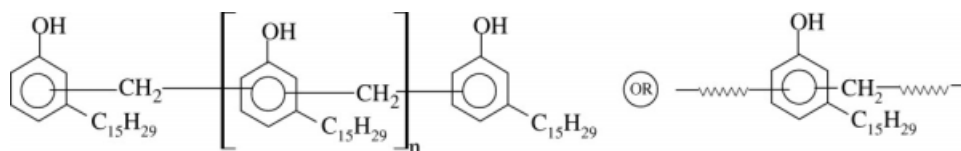

Figure 2 ^{1}H-NMR spectrum of novolac resin CF_{52}.

Scheme 2   Reaction mechanism for the condensation reaction of cardanol and formaldehyde.

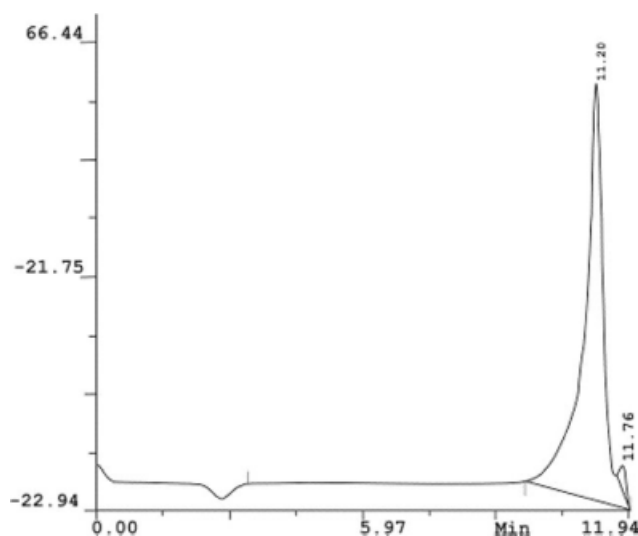**Scheme 3**   Structure of cardanol-based novolac-type phenolic resin with C/F = 1 : 0.5.

Figure 3 GPC trace of novolac resin CF_{52}.

Mechanical and chemical properties

The panels were prepared by applying the blend samples on sand-blasted steel sheet and glass panels of sized $150 \times 100 \times 1.25$ mm with a Bird Film Applicator (M/s Sheen Instruments, UK). These panels were sealed on three sides with molten paraffin wax. A dry film thickness of about 150 μm was maintained on all the panels. These films were then cured at 120°C. The adhesion and flexibility of the cured films of the resin were tested by putting the prepared steel panels into a $1/4$-inch mandrel keeping the coated side downward. Then the two plates, connected to the mandrel, were readily bent. The bent portion of the panel was examined for any damage in the film. The impact resistance of the cured film samples was conducted by dropping a hemi-spherical shaped 2-pound weight from 25-inch height over the panels. The tests were carried out with the uncoated side of the panel facing the falling weights. Gloss was measured by using Triglossometer (Sheen). After watching the films from 60° angle, it had been observed that all the coating films had good gloss.

Dumbbell-shaped cured samples (size: $7.5 \times 3/4 \times 1/8$ inch) of blend samples were used for the determination of tensile strength and elongation-at-break according to the ASTM D 638 standard on a Universal Testing Machine (UTM; M/s Patiwana Group, Star Testing Systems, Mumbai, India). The crosshead speed of the machine was kept at 25 mm/min.

Thermogravimetric analysis

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 thermogravimetric analyzer (TGA) of TA Instru-

ments (model Q50 TGA) at a heating rate of 10°C min^{-1} in nitrogen atmosphere from 25 to 650°C.

Morphology

The morphological changes due to addition of CTBN into the epoxy matrix were studied by JOEL scanning electron microscope (SEM; model JSM 5800). The rubber domains distributed in the matrix and interaction of these domains with the epoxy matrix specimen surface could be observed by 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 cardanol-formaldehyde novolac-type phenolic resin

The formylation reaction was carried out with 1.0 mol of cardanol and 0.5 mol of formaldehyde in the presence of dicarboxylic acid (viz., succinic acid). The initial pH of the reaction mixture was found to be 6.0. Therefore, under this experimental condition, the complete formylation might yield resin with high ortho–ortho linkages for phenolic novolac resin. The completion of the methylolation reaction was checked by periodic withdrawal of reaction mixture to analyze free formaldehyde content by using hydroxylamine hydrochloride method.[24] The final pH of the reaction mixture was found to be 4.8 after 4 h of reaction. The decrease of pH in the methylolated cardanol might be ascribed to the formation of monohydroxyl substituted cardanol.[25] Viscosity of the prepared cardanol-based novolac resin was 15.732 Pa s at 60 s.

FTIR and ^{1}H-NMR spectroscopic analysis of cardanol-based novolac-type phenolic resin

On the basis of FTIR, NMR, mass spectroscopic, and GPC analysis, the structure of cardanol was elucidated and it was found that the cardanol elucidated could be a monoene meta-substituted phenol. Therefore, the empirical formula can be taken as
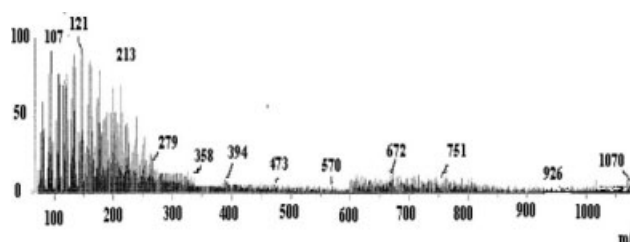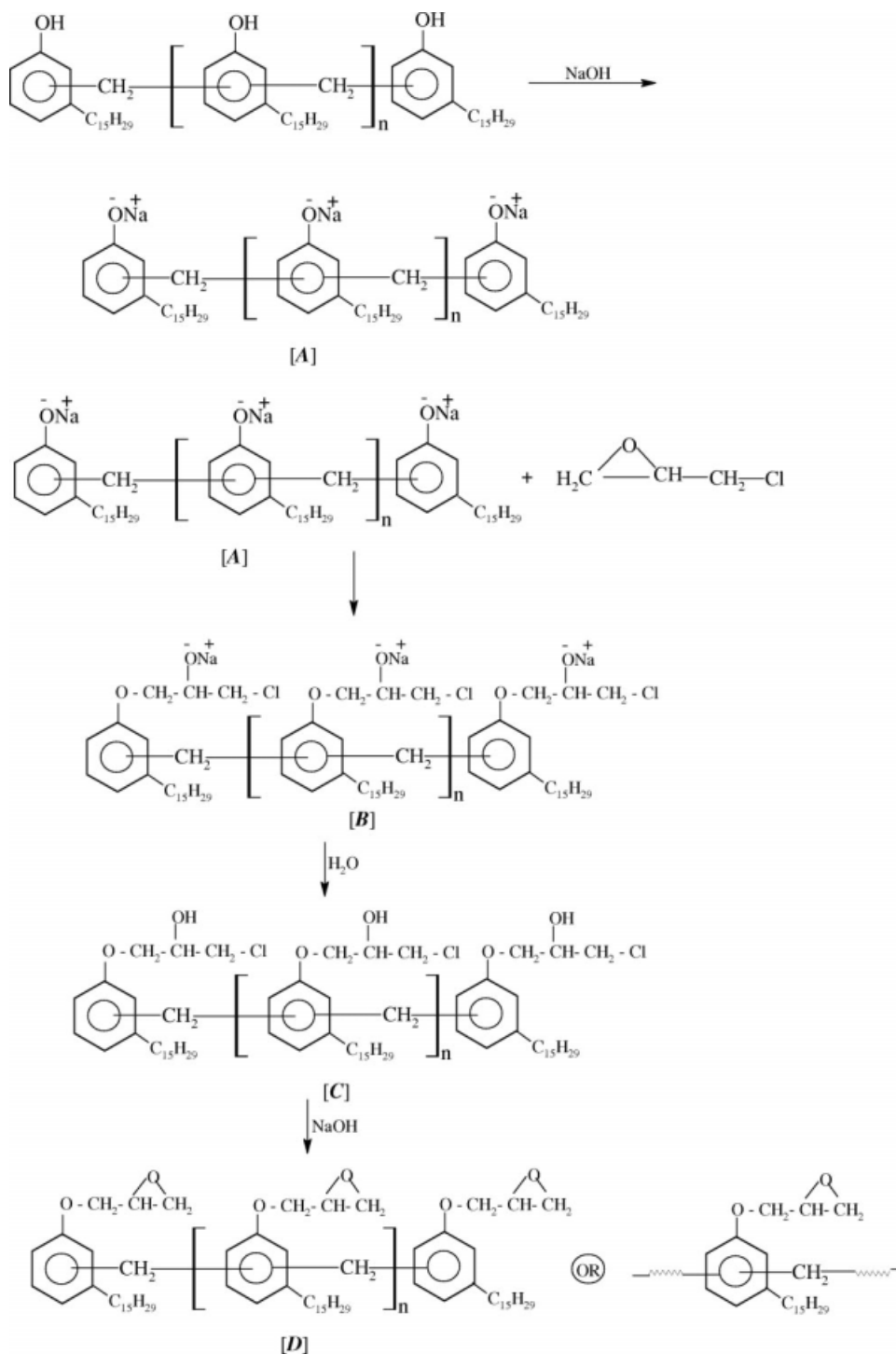

Figure 4 MALDI-TOF mass spectrum of novolac resin CF_{52}.

Scheme 4 Reactions involved during epoxidation of CF_{52} novolac resin.

$C_{21}H_{34}O.$[26,27] The structure of cardanol may be proposed as in Scheme 1.

A shift of a peak from 1075 to 1102 cm^{-1} and appearance of peak near 1708 cm^{-1} (Fig. 1) were observed in methylolated cardanol due to the C=O stretching from CH$_2$OH. It has also been found that the intensity of peaks at 1594 cm^{-1} (C=C, str), 3009 cm^{-1} (C—H str of alkene), and 779 cm^{-1} (C—H out-

of-plane deformation) remained almost unaffected, which indicated that the polymerization took place through substitution of CH$_2$OH and not through the double bonds in the side chain. The band at 3395 cm^{-1} for sample CF_{52} might be due to the presence of hydroxyl groups in the methylolated cardanol. Small peaks near 946 and 973 cm^{-1} indicated the substitution in benzene nuclei. The small peaks near
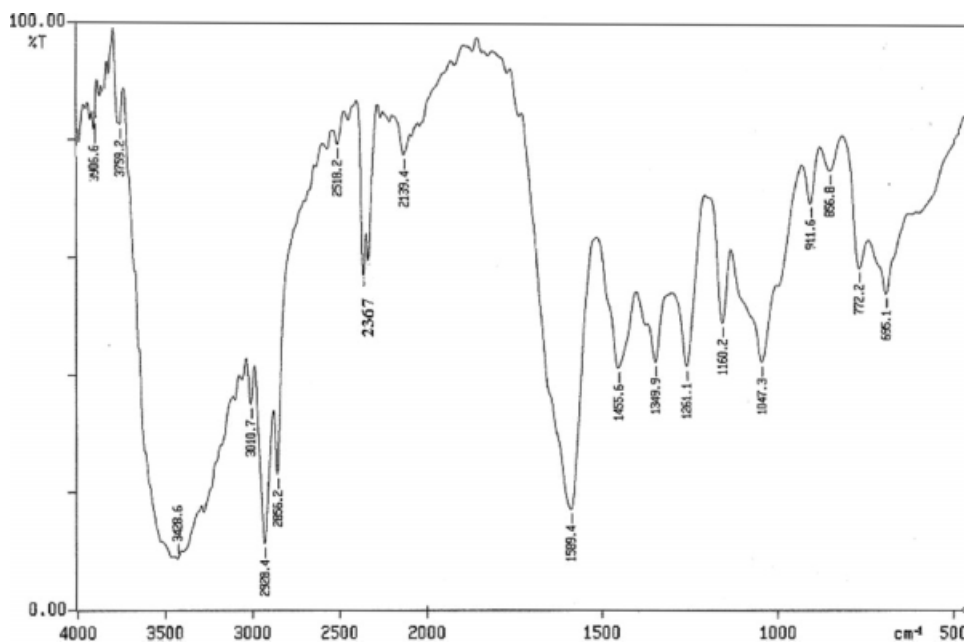
Figure 5 FTIR spectrum of epoxidized novolac resin ECF_{520}.

913 and 697 cm^{-1} might be due to three adjacent hydrogen atoms in the benzene nuclei. The peak appearance near 722 cm^{-1} (Fig. 1) indicated the ortho and para substitution at benzene nuclei. The preceding spectral data were found to be identical with that given in the literature.[28,29]

In the ^{1}H-NMR spectra CF_{52} (Fig. 2) novolac resin, the peak near 6.6–6.8 δ might be due to the aryl protons of benzene nuclei. The peaks around the region 7.1–7.3 δ appeared due to the phenolic hydroxyl in the novolac resin. The peak at 5.3 δ might be attributed to the methylene protons, whereas the peaks between 0.8 and 2.8 δ appeared due to the presence of long alkyl aliphatic side-chain, originally observed in cardanol. The terminal methyl group of the alkyl side chain may also be 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$_6$H$_5$—CH$_2$—C$_6$H$_5$ for the bridge between the phenyl rings.[30] All these spectral data indicated that the condensation of methylolated cardanol has been completed under experimental conditions and was fully consisted with the proposed mechanism.

On the basis of the preceding discussions, the reaction mechanism, similar to that given by Kuriaposa and Manjooran,[31] may be proposed in Scheme 2. The mechanism of formation of novolac oligomers, in acidic media, using excess of cardanol over formaldehyde, might proceed in four steps. First, a methylene glycol was protonated by an acid from the reaction medium, which then released water to form a hydroxyl methylene carbonium ion. This ion acted as a hydroxy alkylating agent by reacting with

a cardanol via electrophilic aromatic substitution. A pair of electrons from the benzene ring attacked the electrophilic, forming a carbocation intermediate followed by deprotonation and regained the aromaticity of the ring (Scheme 2). The methylol group of the hydroxy methylolated cardanol was unstable under acidic conditions and might lose water readily to form a benzylic carbonium ion as shown in Scheme 2. The products formed in Scheme 4 reacted with another cardanol molecule to form a methylene bridge in another electrophilic aromatic substitution. This process was repeated until all the formaldehyde was exhausted (Scheme 2).
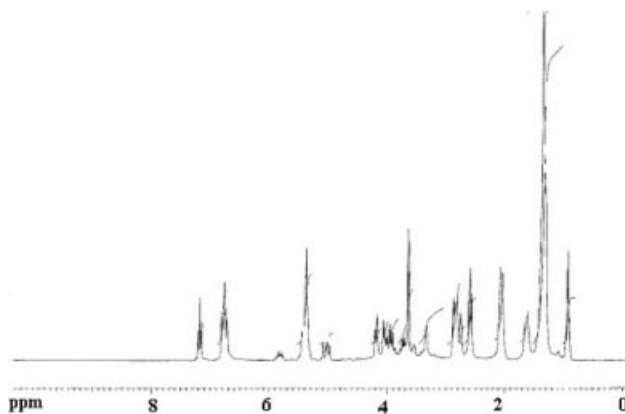

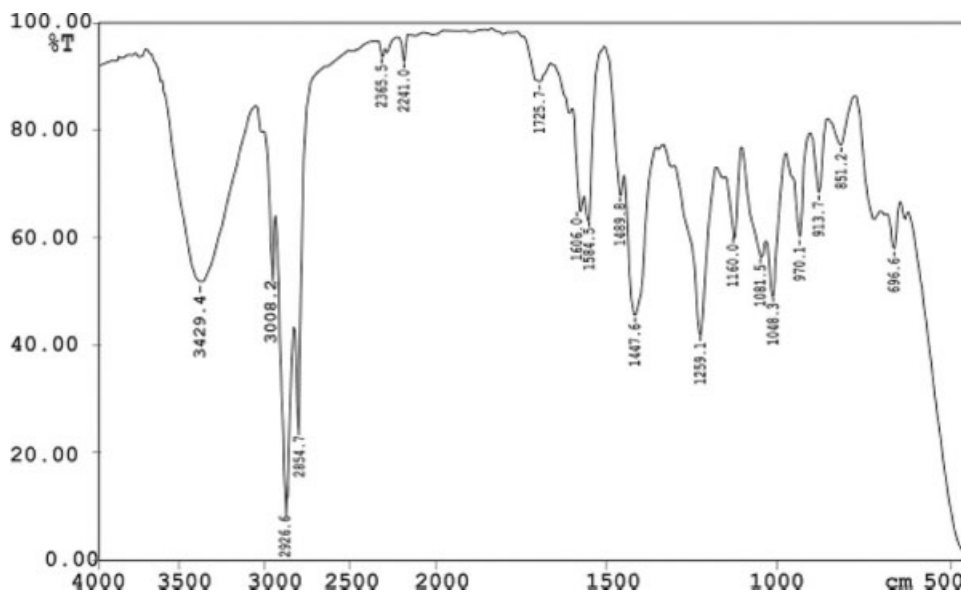**Figure 6** ^{1}H-NMR spectrum of epoxidized novolac resin ECF_{520}.

Figure 7 FTIR spectrum of uncured blend sample ECF_{523}.

Molecular weight of cardanol-based novolac-type phenolic resin by GPC technique and mass spectroscopic analysis

The average number molecular weight, M_n, of CF_{52} calculated from the number of phenolic units (p) in the novolac resin (proposed structure in Scheme 3), was determined from the ratio of aromatic–methylene, [CH$_2$], to aromatic protons, [AR], protons of the ^{1}H-NMR spectra as the following equation.[32,33]

$$[CH_2]/[AR] = (2p - 2)/(3p + 2) \qquad (1)$$

Figure 3 showed the GPC curves of novolac resin, CF_{52}. The value of M_n was calculated as 670 g/mol and $p = 2.17$ for phenolic groups per molecule for novolac resin, CF_{52}. The value of the molecular weight was further confirmed by mass spectroscopic analysis (Fig. 4). The GPC clearly indicated the existence of dimer and trimer in the final reaction. These values were very close to the values obtained from ^{1}H-NMR spectra above. Therefore, the value of n in the structure of novolac resin, shown in Scheme 3, was calculated as 0.17 for resin, CF_{52}. This value resembled the values of Δm in the mass spectra.

Epoxidation of novolac prepolymer

The novolac-based epoxy resin was synthesized by reaction with epichlorohydrin (*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 were reacted, and the extent to which the lowest molecular species were polymerized during synthesis. Theoretically, all the phenolic hydroxyls might be reacted, but in practice all of them did not react

because of steric hindrance.[34] The reaction between *ECH* and novolac resin might be thought to proceed in a similar fashion as in the work given by Lee and Neville.[34] The epoxide group of *ECH* reacted with phenolic hydroxyls under the alkaline medium and formed chlorohydrin ether, which underwent dehydrochlorination reaction and resulted in to glycidyl ether. The structure of the epoxy resin may be proposed as in Scheme 4. Viscosity of the prepared ECF_{520} sample was 13.831 Pa°s at 60 s.

In the FTIR spectra of uncured cardanol-based epoxidized novolac resin [i.e., sample, ECF_{520} (Fig. 5)], the characteristic band of the oxirane ring was observed near 911 and 856 cm^{-1}. The ^{1}H-NMR spectrum (Fig. 6) further confirmed the formation of cardanol-based epoxidized novolac resin.

FTIR analysis of uncured and cured blend samples

The peaks related to oxirane functionality appeared near 911 and 856 cm^{-1} (Fig. 5). When CTBN is added to pure epoxy resin, these peaks disappeared and new peaks appeared near 913 and 851 cm^{-1} (Fig. 7). The peaks appeared near 911 and 856 cm^{-1} (Fig. 5) might overlap these peaks. The peaks near 1725 cm^{-1} due to carbonyl stretching, 1447 and 970 cm^{-1} due to C—H bending, along with a sharp peak near 2241 cm^{-1}, due to CN group of the CTBN molecule, were also seen in the spectrum of uncured blend system (Fig. 7). These observations clearly indicated that there occurred no chemical interaction between the oxirane group of epoxy and carboxyl group of CTBN. The epoxy resin and CTBN remained a discrete phase in the uncured stage. However, the addition of CTBN and polyamine into epoxy caused chemical interaction between the
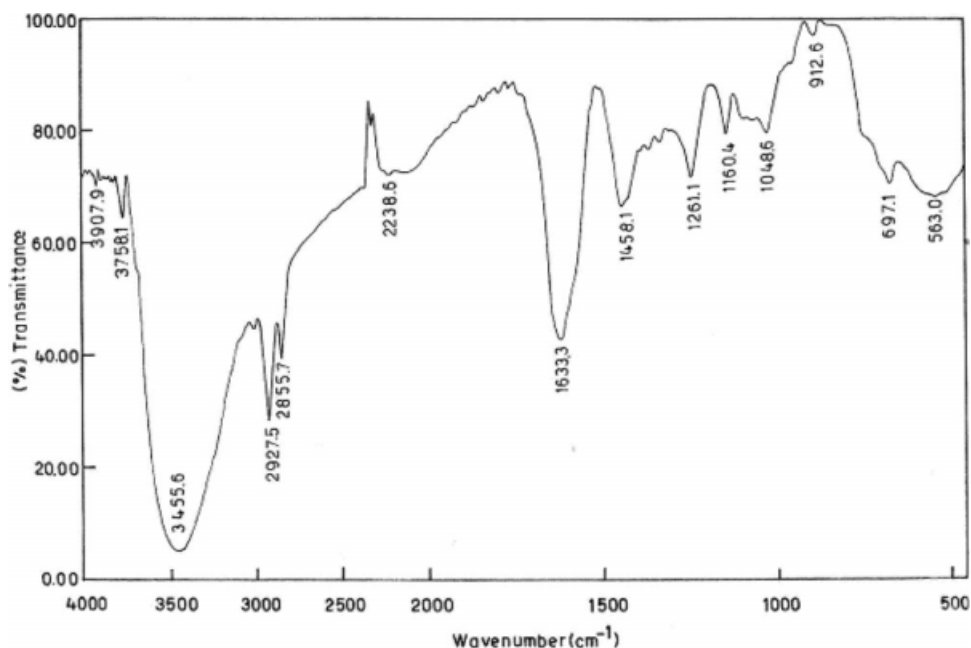
Figure 8 FTIR of cured blend sample ECF_{523}.

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 cured blend samples ECF_{523} (Fig. 8). The $—C{\equiv}N$ group was also not observed in the cured blend. This was perhaps due to lower volume fraction of CTBN in the blend system. Another possibility is that it could also be utilized in network modification. The blend also showed the appearance of new stretched peaks between 1261–1633 cm^{-1} and 1048 cm^{-1} and peak broadening at 1606 cm^{-1} due to C—C multiple stretching.[35,36]

DSC analysis of blend samples

Figures 9 and 10 showed the dynamic DSC scans of cardanol-based epoxidized novolac resins without and with CTBN (i.e., samples ECF_{520} and ECF_{523}) at a heating rate of 10°C min^{-1}. Also, the effect of CTBN concentration on cure parameters of different epoxy matrix has been compared to that of unmodified epoxy matrices in Table II. It is proven from the results that the peak exotherm was shifted to lower temperature due to enhanced reaction rate, which, finally, reduced the cure time of the CTBN-modified blend system (Table II). 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 intermolecular transition state for the epoxy-amine reaction. According to this mechanism[37,38] strong hydrogen bonding species, such as acids and alcohols,
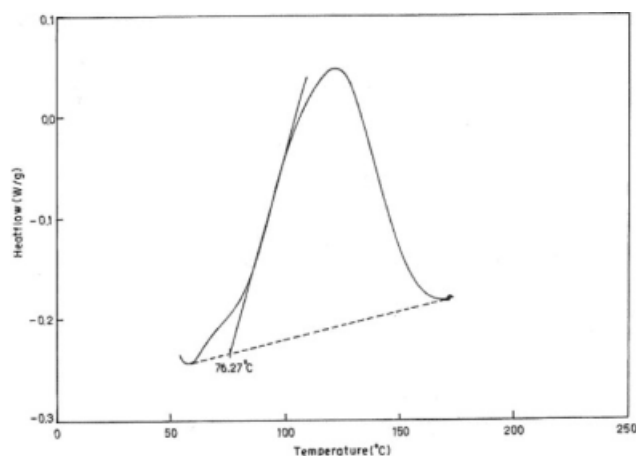

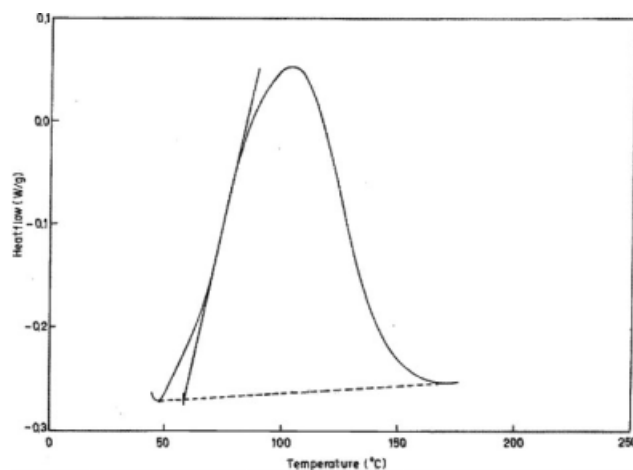**Figure 9** DSC scan of epoxidized novolac resin ECF_{520}.

Figure 10 DSC scan of blend sample ECF_{523}.

TABLE II
DSC Results of Unmodified and CTBN-Modified Cardanol-based Epoxidized
Novolac Resin Cured with Polyamine

Blend Sample	T_i (°C)	T_{onset} (°C)	T_P (°C)	T_{stop} (°C)	ΔH (J mol^{-1})	t_{cure}[a] (min)
ECF_{520}	76.3	115.1	126.2	165.5	49.4	240
ECF_{521}	70.2	109.4	125.8	165.6	53.2	223
ECF_{522}	67.2	91.8	127.2	170.3	59.8	211
ECF_{523}	63.5	76.3	120.1	163.0	62.9	180
ECF_{524}	68.6	98.5	123.6	169.8	58.4	191
ECF_{525}	70.0	105.6	130.6	165.4	53.7	223

T_i: kick-off temperature, where the curing starts; T_{onset}: temperature where the first detectable heat is released; T_P: temperature of peak position of exotherm; T_{stop}: temperature of end of curing exotherm; ΔH: heat of curing; t_{cure}: cure time in minutes.
[a] Cure time obtained by curing the sample in air oven at 120°C

stabilized the transition state and strongly accelerated the curing reaction. The decrease of cure time could also be explained by the fact that during the reaction of CTBN with epoxy resin, some of the exothermic energy released during epoxy crosslinking might have been consumed by CTBN, resulting in a decrease of cure time.[39] The ΔH values (Table II) related to the cure process were determined from the area of the exotherm peak obtained from DSC analysis (Figs. 9 and 10) taken in dynamic mode. In contrast, the presence of CTBN did not affect significantly the heat of polymerization (ΔH), indicating little influence on the crosslink density of the epoxy matrix.[40]

Mechanical properties of blend samples of epoxidized novolac resin

Tensile strength, elongation-at-break, and impact strength of castings of blend samples

The variation of tensile strength and elongation-at-break with CTBN contents in the castings of the blend samples of epoxy and CTBN cured with polyamine is shown in Table III. A gradual fall in tensile strength was noted as the concentration of the elastomer phase increased. This may be due to the increase in the relative amount of dissolved rubber as rubber content increases. The percent elongation-at-break of the blend samples increased continuously

with CTBN content in the blend. The formulation with 15 wt % of CTBN showed greater impact strength, which means that it likely absorbed greater impact energies. The impact behavior of the cured epoxy could be explained on the two-phase nature of the system. Similar behavior has been also reported in other rubber-modified epoxy systems and attributed to the agglomeration of the rubber particles with the increase of the rubber concentration.[41–45] The presence of agglomerates acts as a defect and initiates catastrophic failure. The difference in mechanical behavior can be associated with morphological characteristics.

Scratch hardness, adhesion, flexibility, gloss, and impact resistance of cured films of blend samples

Table III showed the surface and mechanical properties of cured films of blend samples. The table clearly indicated that the cured films of all blend samples containing 5–25 wt % CTBN showed smooth and uniform with semi-glossy surfaces. The blend samples showed improved impact resistance than that of pure epoxy resin. The adhesion and flexibility improvement may be thought to be due to the presence of some dissolved rubber particles inside the epoxy matrix. The decrease of cross-link density might also be an indicative of improved flexibility, whereas cavitations of rubber particles inside

TABLE III
Mechanical Properties of Pure Epoxy and Its Blend with CTBN

| Sample Code	Properties of Castings			Properties of Films			
	Tensile Strength (MPa)	Impact Strength (kJ/m^2)	Elongation-at-Break (%)	Gloss (60° angle)	Scratch Hardness	Adhesion and Flexibility	Impact Resistance (kg/cm)
ECF_{520}	283.3	15.6	30.69	75.6	3.1	Fail	63.0
ECF_{521}	276.7	23.7	38.6	79.8	1.4	Pass	72.0
ECF_{522}	256.8	30.5	47.4	82.3	1.8	Pass	83.0
ECF_{523}	191.7	65.6	65.0	85.6	2.3	Pass	126.0
ECF_{524}	187.0	33.8	69.5	81.4	1.8	Pass	99.0
ECF_{525}	178.4	20.5	73.2	77.2	1.7	Pass	72.0
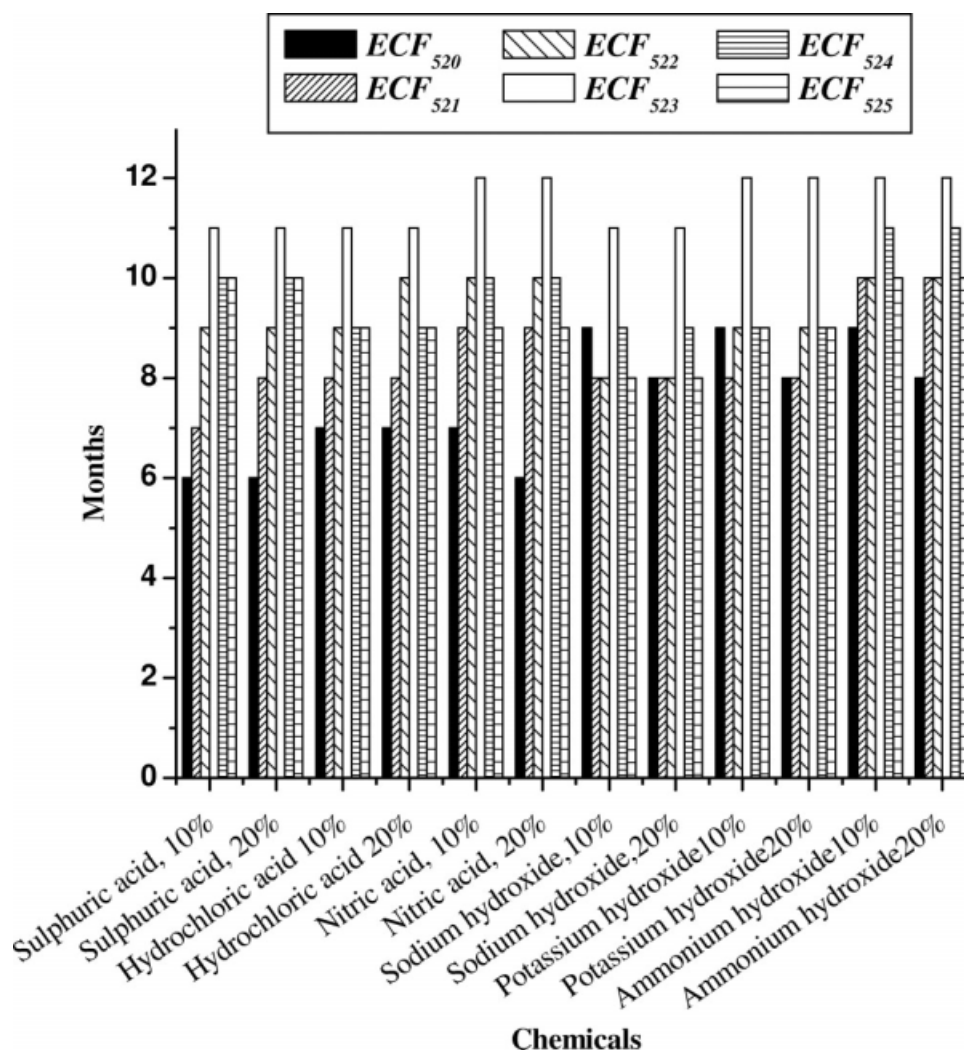
Figure 11 Comparative acid and alkali resistance of epoxy and epoxy/CTBN film showing the period after which the first effect was detected when immersed for 12 months at ambient temperature.

the epoxy matrix improved the impact resistance of the films of blend samples. This table also indicated that the film of pure epoxy, ECF_{530}, was harder than the film of pure epoxy, ECF_{510}, and blend samples. The addition of CTBN decreased the hardness due to an increase in flexibility of resin films. This is further evidence from SEM micrographs in the proceeding paragraphs.

Chemical resistance

The acid and alkali resistance of cardanol-based epoxidized novolac resin and their blends with CTBN are shown in Figure 11. It is clear from the figure that films of coating based on epoxy with 15 wt % CTBN have offered the maximum resistance toward different concentrations of acids and alkalis as compared to the cured films of other epoxy and its blend samples. This behavior might be attributed to greater reactivity of epoxy and liquid rubber.

The effect of different solvents on the surface of the cured films of pure epoxy and various blend samples of epoxy and CTBN is shown in Figure 12. It is evident from the figure that the surfaces of the epoxy and its blends with CTBN were completely unaffected by deionized and synthetic sea water. The exposure of cured films of blend samples in solvents like acetone, toluene, MEK, methanol, etc., resulted first in a change during 10–12 months, which was more than that for pure epoxy resin. This indicated that the blend samples were more resistant toward solvents than pure epoxy resin. The better thermal stability of the blend samples confirmed the same.

Thermal stability

Thermogravimetric (TG) analysis is one of the most widely used techniques to measure the thermal stability of the polymeric samples. In this, the rate of
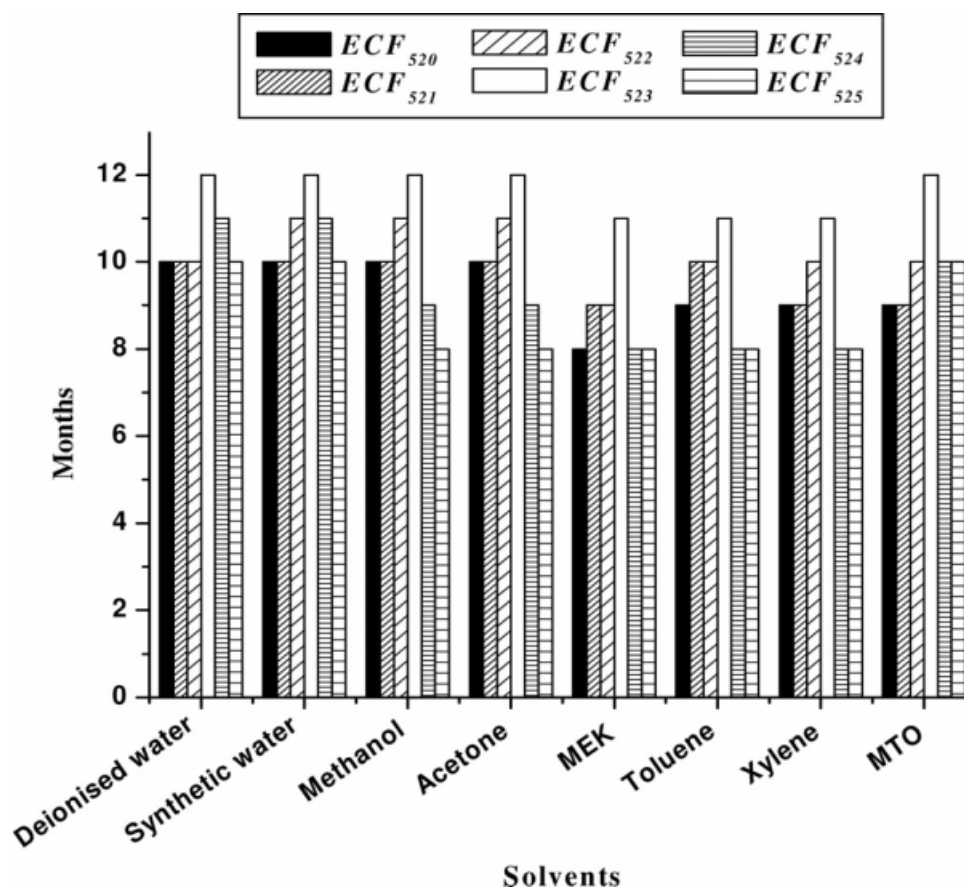
Figure 12 Comparative solvent resistance of epoxy and epoxy/CTBN film showing the period after which the first effect was detected when immersed for 12 months at ambient temperature.

weight loss is measured as a function of programmed rate of increase in temperature (dynamic mode). The TG obtained for samples ECF_{520} and ECF_{523} are shown in Figures 13 and 14 for the evaluation of thermal stability in nitrogen atmosphere. The onset temperature of degradation (T_o), temperature of maximum rate of mass loss (T_{max}), and extrapolated final decomposi-

tion temperature (T_f) were noted from TG traces and are presented in Table IV. TG analysis confirmed the occurrence of degradation of the samples. The degradation of the blend systems was found to occur in two steps. The temperature of 5% weight loss improved slightly from 294°C for pure epoxy (sample ECF_{520}) resin to 300°C for the epoxy/CTBN blend (i.e., blend sample ECF_{523}). The addition of the appropriate
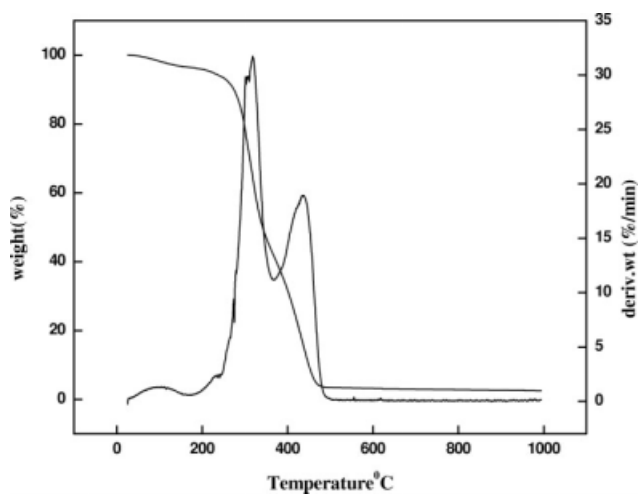

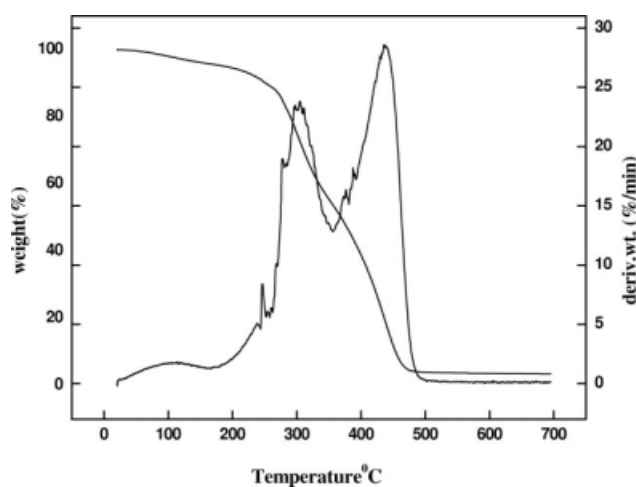**Figure 13** TGA trace of blend sample ECF_{520}.

Figure 14 TGA trace of blend sample ECF_{523}.

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

Blend Sample	First Step				Second Step				Total % CY
	T_0	T_{max}	T_f	%ML	T_0	T_{max}	T_f	%ML	
ECF_{520}	199	316	343	49.3	343	438	498	47.2	3.5
ECF_{521}	200	318	353	62.6	353	429	514	34.4	3.2
ECF_{522}	201	325	357	90.7	357	440	499	7.0	2.3
ECF_{523}	202	305	355	53.8	355	438	491	42.1	4.1
ECF_{524}	200	322	355	55.6	355	441	505	40.5	3.9
ECF_{525}	198	325	360	60.4	360	446	510	36.1	3.5

T_0: onset temperature of degradation; T_{max}: temperature of maximum rate of mass loss; T_f: extrapolated final decomposition temperature; ML: mass loss; CY: char yield.

amount of epoxy could decrease the mobility and increase the stability of CTBN via the reaction between the thermal carboxyl group of CTBN and the hydroxyl group of epoxy.[46–49]

Scanning electron microscopic analysis

Figure 15(a,b) showed, 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 dispersed throughout the epoxy matrix (i.e., 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 of the rubber-toughened epoxy system has a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated particles.[50] Some cavitations of the rubber particles accompanied by stress whitening zones were also observed in the scan [Fig. 15(b)]. This stress whitening effect may be related to the location deformation at the crack tip. Furthermore, the cavitations were followed by the onset of the shear localization process[51–53] resulting in the observed increase in thermal properties.

CONCLUSIONS

The FTIR spectroscopic analysis revealed a chemical reaction between the oxirane and the carboxyl group of CTBN, which was further confirmed by SEM analysis. DSC studies showed the exothermal heat of reaction of epoxy crosslinking due to addition of rubber into epoxy matrix. Blend samples exhibit better properties compared to pure epoxy resin in terms of increase in impact strength and elongation-at-break of the casting and gloss, scratch hardness, adhesion, and flexibility of the film. The improvement in these properties indicates that the rubber-modified resin would be more durable than the epoxy

based on cardanol. The films of coating based on epoxy with 15 wt % CTBN offered the maximum resistance toward different concentrations of acids, alkalis, and solvents compared to the cured films of other blend samples. The thermal stability of the cardanol-based epoxy resin was increased with the addition of 15 wt % CTBN in epoxy matrix.
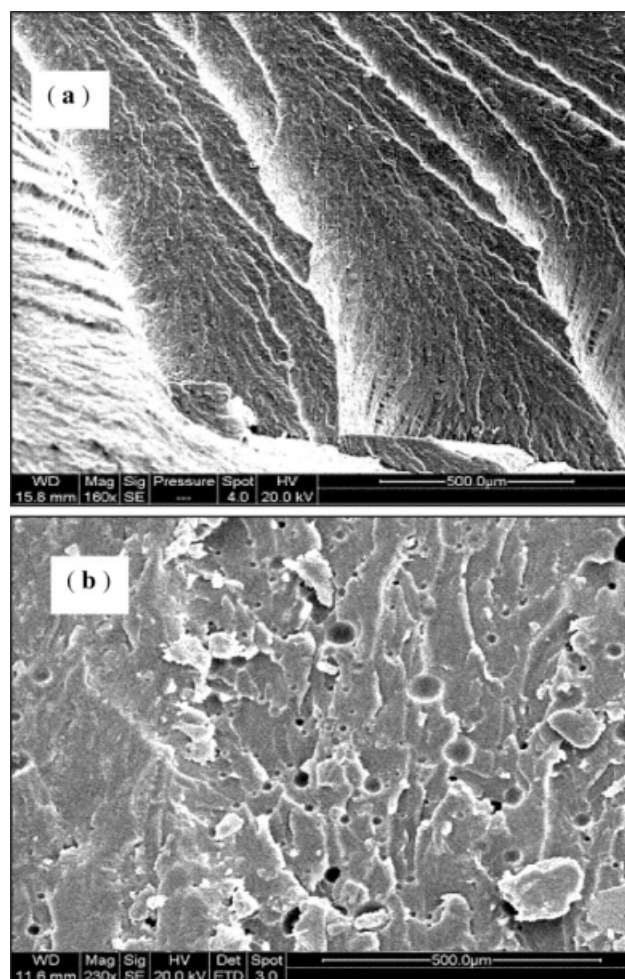

Figure 15 SEM micrographs of prepared samples (a) ECF_{520} and (b) ECF_{523}.

Cardanol-based epoxy network modified with CTBN displayed two-phase separated morphology with dispersed rubber globules in the matrix resin (i.e., they revealed the presence of two-phase morphological features).

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