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Studies on the synthesis and curing of epoxidized novolac vinyl ester resin from renewable resource material

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ABSTRACT

Cardanol-based epoxidized novolac vinyl ester resin (CNEVER) was synthesized by reacting cardanol-based epoxidized novolac (CNE) resin and methacrylic acid (MA) (CNE:MA molar ratio 1:0.9) in presence of triphenylphosphine as catalyst at 90 °C. The CNE resin was prepared by the reaction of cardanol-based novolac-type phenolic (CFN) resin and epichlorohydrin, in basic medium, at 120 °C. The CFN resin was synthesized by reacting cardanol (C) and formaldehyde (F) (C/F ratio = 1:0.7) with *p*-toluene sulphonic acid (PTSA) as catalyst (0.5 wt.%) at 120 °C for 7 h. The resin products were analyzed by Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopic analysis. The number-average molecular weight of the prepared CNEVER was found to be 859 gmol^{-1} as determined by gel permeation chromatographic (GPC) analysis. The resin was cured by using the mixture of resin, benzoyl peroxide, and styrene at 120 °C. The CNEVER resin was found to be cured in 60 min at 120 °C. Differential scanning calorimetric (DSC) technique was used to investigate the curing behaviour. Single step mass loss in dynamic thermogravimetric (TG) trace of CNEVER was observed. Thermal stability of the vinyl ester sample containing 40 wt.% styrene was the highest amongst all other prepared systems.

1. Introduction

Vinyl ester resins (VERs) are one of the most important class of thermosetting polymers that combine the chemical, mechanical and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins (UPEs) which make them suitable product for various industrial applications such as surface coatings, adhesives, printed circuit board coatings, radiation curable inks, spherical lens materials and composite [1–10]. From structural point of view, VERs are the addition products between different epoxy resins and unsaturated monocarboxylic acids [1–4]. By means of the two terminal reactive double bonds, VERs can easily form cross-linked network structures by a free-radical polymerization mechanism, with or without other comonomers. Due to the high viscosity of VERs, it is necessary to add some reactive diluents such as vinyl monomers, viz., styrene, α-methyl styrene, acrylates and methacrylates [11–14]. These diluents take part in the curing reactions and create a link between adjacent vinyl ester molecules [12].

Cardanol, a major component of CNSL (*Anacardium Occidentale* L.) and a phenol derivative having a meta substituent of a C_{15} unsaturated hydrocarbon chain with one to three double bonds as the major, has considerably drawn the attention of many researchers for the production of phenolic resins under different sets of conditions to form both base-catalyzed resoles and acid-catalyzed novolacs [15–22]. The cardanol-based novolac-type phenolic resins may be modified by epoxidation reaction with epichlorohydrin to enhance the performance of such resins in various fields [22–25]. The introduction of unsaturation at the end of the epoxy resin backbone by the reaction with acid functional acrylic/methacrylic monomer can produce

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a hybrid resin system in which the optimum properties can be derived. In this sequence, an eco-friendly VER resin system could be derived from the cardanol.

Various epoxy resin, viz., DGEBA (diglycidyl ether of bisphenol-A) epoxy, epoxidized novolac resin etc. have been used for the synthesis of VERs [26–28], in the past, but there is a considerable dearth of available literature on the synthesis of VER from renewable resource material. The present paper reports the synthesis of cardanol-based novolac epoxy vinyl ester resin (CNEVER) and the study of its cure characteristics.

2. Experimental

2.1. Materials

Cardanol (M/s Dheer Gramodyog Ltd., Kanpur), formaldehyde (40% solution from M/s Qualikem Industries, New Delhi), *p*-toluene sulphonic acid (PTSA) obtained from E. Merck, New Delhi, methanol (BDH), epichlorohydrin (M/s Ranbaxy Laboratories Ltd., Punjab), sodium hydroxide, methacrylic acid and triphenylphosphine (from M/s CDH Pvt. Ltd., New Delhi), styrene, benzoyl peroxide and hydroquinone (from E. Merck, New Delhi) were used during the investigation.

2.2. Methods

2.2.1. Synthesis of cardanol-based novolac resin

Novolac resin with mole ratio 1:0.7 of cardanol (C) to formaldehyde (F) was prepared using PTSA as catalyst (0.5% based on cardanol) dissolved in 2 ml methanol under warm conditions by a method given in the past [17]. Samples were drawn at regular intervals of 45 min from the reaction mixture, taken in a three-necked round bottom (R.B.) flask, for determining the free-phenol (as per ASTM standard D 1312-56) and free-formaldehyde content (as per ISO standard 9397). The reaction product was cooled and dried under vacuum at 60 °C overnight before purification by column chromatography. A resin solution prepared in *n*-hexane, charged to the silica gel column chromatographic purification, was adopted mainly to remove the unreacted components, impurities etc. from the methylolated cardanol. Purification was effected using the eluent mixture of ethyl acetate–benzene (60:40).

2.2.2. Synthesis of cardanol-based epoxidized novolac resin

The cardanol-based novolac resin (CFN), thus formed, was treated with molar excess of epichlorohydrin and 40% solution of sodium hydroxide at 120 °C for about 10 h. The formed product was vacuum distilled for the removal of excess of epichlorohydrin. The epoxide equivalent weight (EEW) of cardanol-based epoxidized novolac resin (CNE) resin was found to be 320 eq g^{-1}as determined by pyridinium chloride method.

2.2.3. Synthesis of cardanol-based novolac epoxy vinyl ester resin (CNEVER)

Cardanol-based novolac epoxy vinyl ester resin (CNEVER) was prepared by using 1:0.9 mol ratio of CNE and methacrylic acid (MA). The reaction was carried out in the presence of TPP catalyst (1% by weight of the resin) and hydroquinone (200 ppm as inhibitor) at 90 °C in nitrogen atmosphere for about 5 h to obtain a product with acid value less than 10 [29]. In order to remove the free methacrylic acid, the prepared resin was dissolved in benzene and treated with potassium carbonate, stirring for 2 h at 30 °C. The acid, in the form of an acid salt, was extracted by water and benzene was evaporated using a rotatory vacuum film evaporator under vacuum [30].

2.2.4. Curing of CNEVER

The curing of CNEVER was done according to the method as given by Kant et al. [12] by using a reactive diluent, viz., styrene and free-radical initiator benzoyl peroxide in the ratio 10:4:0.2 (w/w). Half of the styrene was mixed with the resin and to the other half of the resin benzoyl peroxide was added in two separate flasks. Both the flasks were sealed and kept under refrigeration to avoid premature polymerization prior to use. Equal amounts of the solution were then taken and stirred vigorously with a glass rod at room temperature in a glass vial. Finally, the mixture was poured in an iron-mould placed in a preheated hot air oven.

2.3. Characterization of the prepared samples

2.3.1. FTIR spectroscopic analysis

The purified resins were subjected to Fourier-transform infra-red (FTIR) spectroscopic analysis, to monitor the various functional groups in the wavelength range of 400–4000 cm^{-1} by Perkin Elmer FTIR, RX-1 spectrophotometer.

2.3.2. ^1H NMR and ^{13}C NMR spectroscopic analysis

^1H NMR and ^{13}C NMR (Nuclear Magnetic Resonance), analysis of the purified resins were recorded on Bruker 400 MHz FT-NMR spectrophotometer in the temperature range of −90 to 80 °C. About 20 mg of the sample, in 10 mm diameter sample tube, was dissolved in about 5 ml of chloroform-d_1 ($CDCl_3$), which was used as a solvent, along with tetramethylsilane (TMS) as internal standard. Finally, the spectra were recorded on computer.

2.3.3. Gel permeation chromatographic analysis (GPC) and viscosity measurement

Gel permeation chromatograph was recorded with E. Merck A.G., Darmstadt Germany, GPC (E. Merck column oven injection Model L-7350, E Merck Lachrome-7490 R.I. Detector) to determine the number-average molecular weight of the synthesized resins. The column (E. Merck) used for GPC calibration was of crosslinked polystyrene. THF was used both as mobile and stationary phase for the experiment. Polystyrene standards of different molecular weights viz. 580, 950, 2050, 5100, 11,600 and 30,300 g mol^{-1} were used for the calibration, which gave the retention times of 11.01, 10.92, 10.70, 10.43, 10.11 and 9.66 min, respectively. Brookfield R/S-CPS + Rheometer (Ver. 9.00) with spindle C-25-2 DIN was used to measure the viscosity of the resins. These values are given in Table 1.

Table 1
Viscosity of various resins.

S. No.	Resin	Viscosity (Pa s)
1.	CFN	30.28
2.	CNE	13.92
3.	CNEVER	39.18
4.	PVER[a]	327.00

[a] Phenol-based vinyl ester resin.

2.3.4. Differential scanning calorimetric analysis

Cure temperatures of the prepared CNEVER samples containing varying amounts of styrene ranging between 0 and 50 wt.% and PVER with styrene concentration ranging between 30 and 50 wt.%, were observed by taking very little quantity of the sample into shallow aluminum pan sealed by an aluminum cover of differential scanning calorimetric (DSC) (TA, Instrument, USA; Model DSC 2920). 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}. Dynamic scans were obtained which were used for assuming the cure temperature.

2.3.5. Thermogravimetric analysis

The percent weight loss and thermal degradation characteristics of the prepared samples were evaluated by thermogravimetric analyzer (TGA) recorded on TA Instrument (Model Hi. Res. 2950) TGA unit interfaced with TA instruments Inc. Thermal Analyst 2100 (Du Pont) control unit. The TGA cell was purged with nitrogen at 60 mL min^{-1} during degradation runs. The amount of sample taken was approximately 5–10 mg in a platinum sample pan. The heating rate in each run was kept at 10 °C min^{-1} and the temperature range was ambient to 700 °C.

2.3.6. Mechanical properties

Dumbbell-shaped cured samples (size: 7.5 × ¾ × 1/8 inch) of vinyl ester 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. The impact strength of the specimen was determined by using Izod Mandate Tensometer using rectangular specimen of 75 mm × 15 mm × 3 mm according to ASTM D-256 standards.

3. Results and discussion

3.1. Studies of CFN and CNE resins

3.1.1. Synthesis of CFN and CNE resins

The methylolation of the cardanol was carried out with formaldehyde in the presence of *p*-toluene sulphonic acid. The release of hydrogen ion as a result of reaction between cardanol and ortho methylol group led to an increase in the acidity of the reaction mixture [31], and hence the decrease in pH of the reaction mixture. The novolac based epoxy resin (CNE) was synthesized by the reaction with

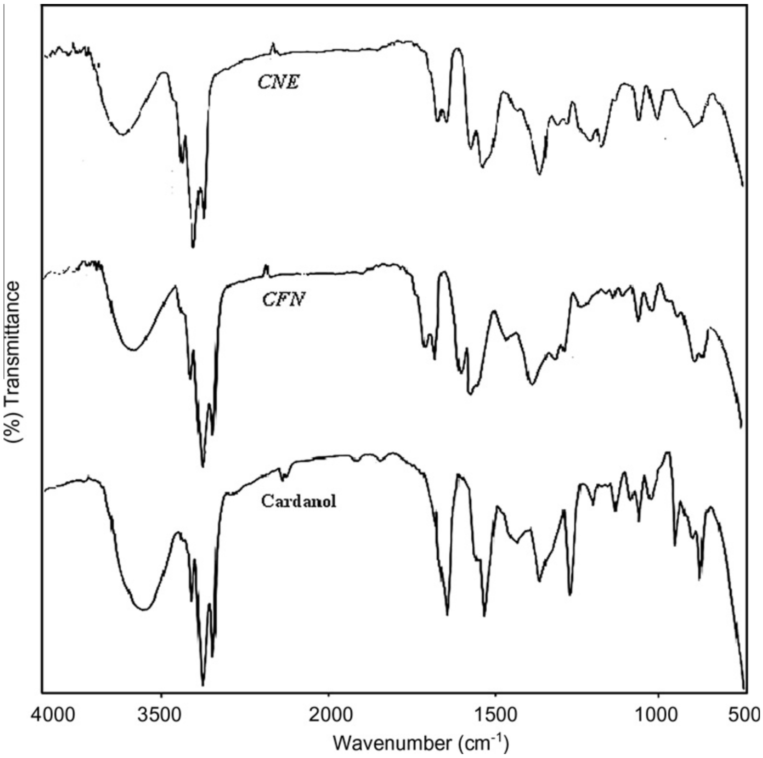


Fig. 1. FTIR spectra of cardanol, CFN and CNE resins.

epichlorohydrin and 40% solution of sodium hydroxide at 120 °C for about 10 h. The number of glycidal groups in the resin is dependent on the number of phenolic hydroxyl in the starting novolac, the extent to which they are reacted and the extent to which the lowest molecular weight species are polymerized during the synthesis. Theoretically, all the hydroxyls may be reacted but practically this does not happen due to steric hindrance.

3.1.2. FTIR spectroscopic and gel permeation chromatographic analysis of CFN and CNE resins

FTIR spectral analysis of CFN resin revealed not only the condensation of methylolated cardanol, but also the degree of ortho- and para-substitution [34]. A shift of a peak from 1073, in cardanol, to 1101.1 (in CFN resin, Fig. 1) and appearance of a very small peak near 1497 cm^{-1} was observed in methylolated cardanol due to the alcoholic –OH deformation from CH_2OH. It has also been found that the intensity of peaks at 1608 cm^{-1}, due to C=C stretching vibration, 3007 cm^{-1} (C–H stretching vibration of alkene) and 720 cm^{-1} (C–H out-of-plane deformation) remained almost unaffected which indicated that the polymerization had taken place through substitution of CH_2OH and not through the double bonds in the side chain. A broad peak centered at 3435 cm^{-1} could be ascribed to the vibration of the O–H linkage of the phenolic group. Small peaks near 963 and 992 cm^{-1} indicated the substitution in benzene nuclei. The small peaks near 911 and 720 cm^{-1} might be due to three adjacent hydrogen atoms in the benzene nuclei. The most notable difference was the change in the intensity of the absorption band near 1455 cm^{-1} that might be related to the ortho aromatic rings. The peaks at 1264 and 1188 cm^{-1} could be ascribed to the asymmetric vibrations of the C–O–C linkage and to the C–OH vibration, respectively, and a peak at 1157 cm^{-1} represents the symmetric vibration of the ether bond. The preceding

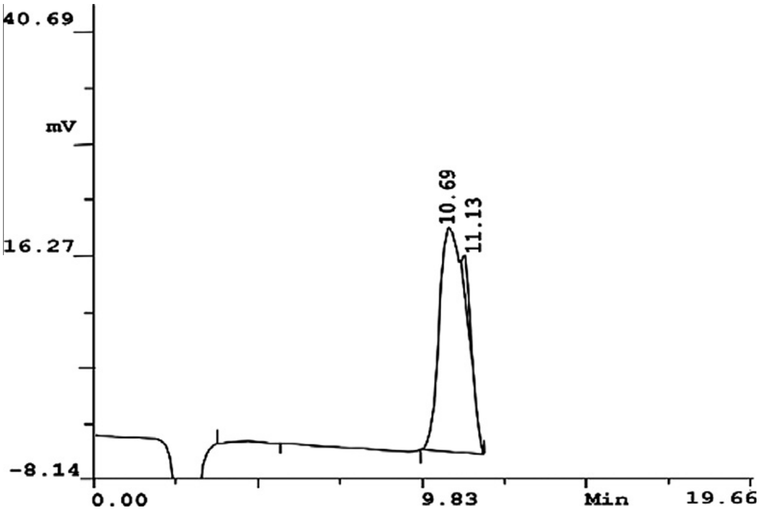


Fig. 2. GPC trace of cardanol-based novolac resin, CFN.

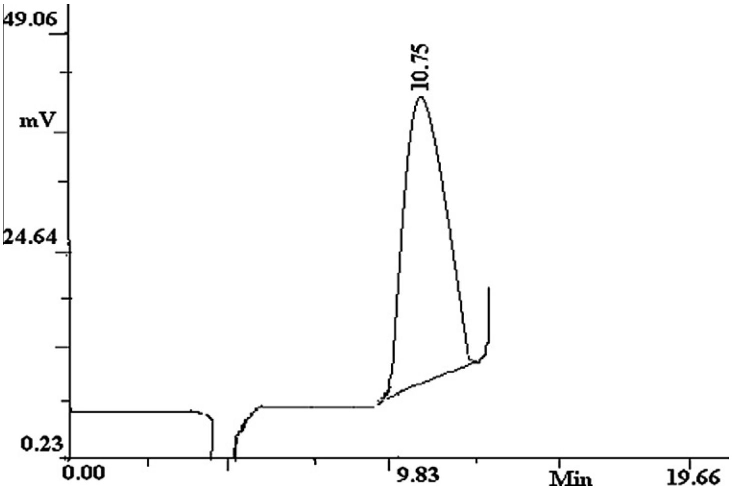


Fig. 3. GPC trace of cardanol-based epoxidized novolac resin, CNE.

spectral data was found to be identical with that given in the literature [32–34]. In the FTIR spectrum of CNE appearance of peaks near 1042 and 912 cm^{-1} confirmed the presence of oxirane group of the epoxide linkage in CNE resin.

Fig. 2 showed the GPC trace of CFN resin. The number-average molecular weight of CFN resin was obtained to be 807 $g\,mol^{-1}$. Thus, the value of average kinetic chain length (n) was calculated as 0.61. The theoretical value of epoxide equivalent weight (EEW) of the cardanol-based epoxy is 357 $eq\,g^{-1}$, but it was found to be 320 $eq\,g^{-1}$ as calculated by titration [35]. The theoretical value of number-average molecular weight was calculated to be 930 $g\,mol^{-1}$, but the GPC trace gave 832 $g\,mol^{-1}$ (Fig. 3) which indicated that about 90% epoxidation had taken place.

3.1.3. ^{1}H NMR and ^{13}C NMR spectroscopic analysis of CFN and CNE resins

Fig. 4 showed the ^{1}H NMR spectrum of CFN resin, in which the appearance of a peak at 3.6 ppm indicated methylene protons for the bridge between the phenyl rings, i.e. $C_6H_5{-}CH_2{-}C_6H_5$ [22–24]. The band around the region

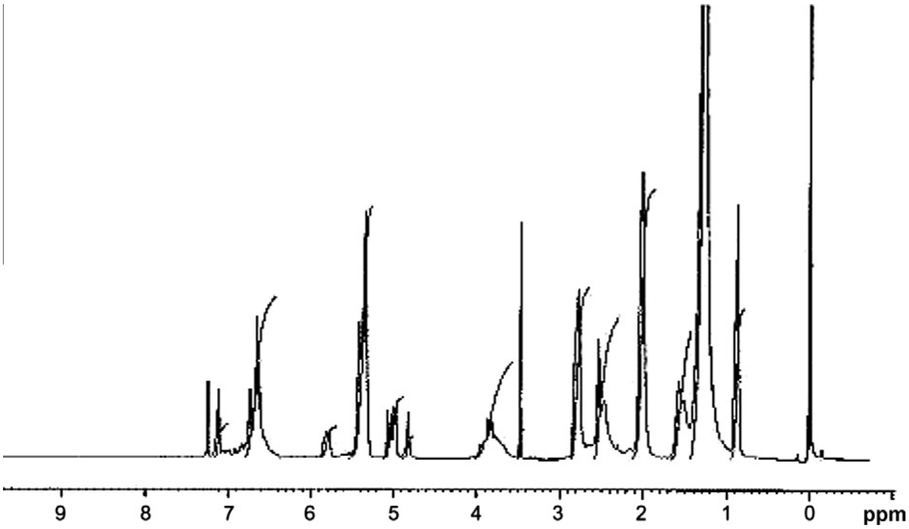


Fig. 4. ^{1}H NMR spectrum of cardanol-based novolac resin.

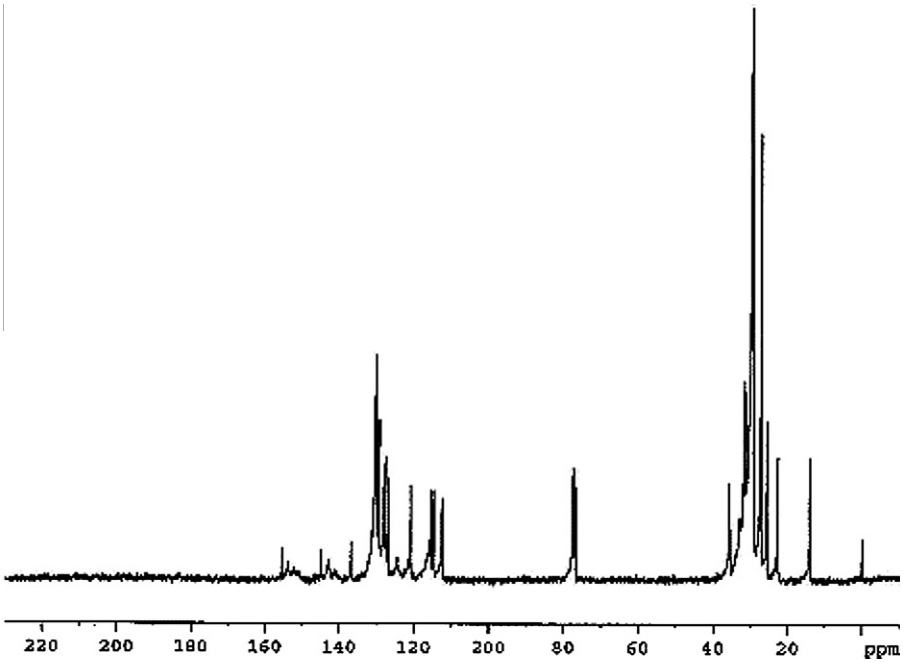


Fig. 5. ^{13}C NMR spectrum of cardanol-based novolac resin.

6.70–7.30 ppm might be due to aryl protons of the benzene nuclei. The peak at 6.5 ppm was due to phenolic hydroxyl of cardanol. The doublets near 5.3 ppm might be due to the presence of methylene protons whereas the appearance of peaks between 0.88 and 2.7 ppm might be due to the presence of long alkyl aliphatic side chain, originally observed in cardanol. This was further confirmed by the appearance of strong singlet at 1.30 ppm. The terminal methyl group of the alkyl side chain could also be seen as there appeared a small peak at 0.8 ppm. The area of the

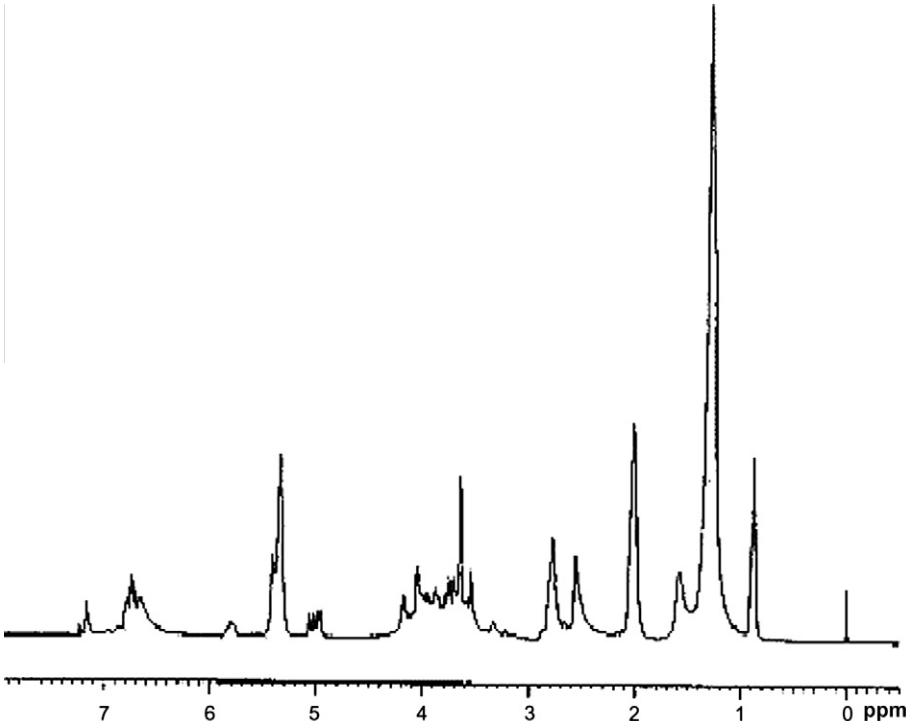


Fig. 6. ^{1}H NMR spectrum of cardanol-based epoxidized novolac resin.

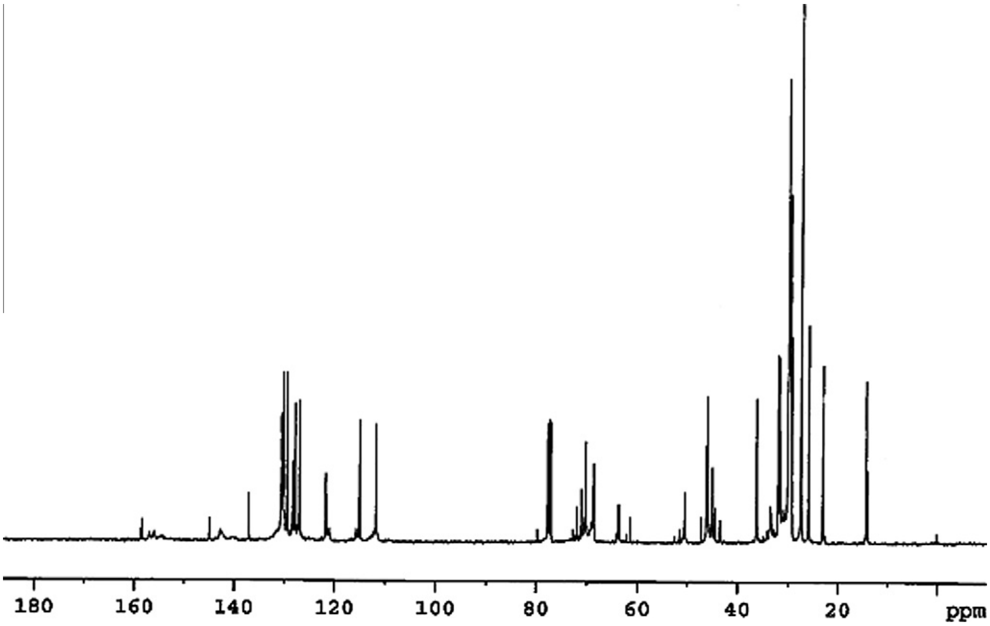


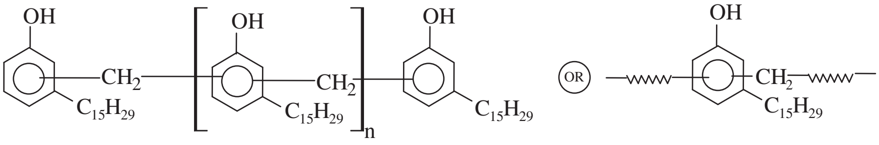
Fig. 7. ^{13}C NMR spectrum of cardanol-based epoxidised novolac resin.

peaks depicted that there might be more than five methylene groups of the side chain. Fig. 5 showed the ^{13}C NMR spectrum of CFN resin, which contains the resonance associated with the bridging methylene carbons that are the characteristic of novolac resins. The appearance of signal at 30.5 ppm clearly evidenced the presence of o–o′ bridge carbon which indicated that one cardanol molecule is attached at ortho position to another cardanol molecule by a methylene group. The peak at 155 ppm might be due to the hydroxyl bearing carbon and the substituted meta carbon of cardanol resonated between 132 and 136 ppm.

In the ^1H NMR spectrum of CNE resin (Fig. 6) the peaks around the region 3.54–4.18 ppm were mainly methyl protons attached to the oxygen of epoxy group. The remaining peaks were similar to the peaks present in the backbone structure of novolac resin. ^{13}C NMR spectrum (Fig. 7) showed peak at 44.5 ppm which might be due to the presence of the methylene carbon ($-CH_2$) of the epoxy ring whereas the peak at 52.60 ppm might correspond to the –CH of the oxirane functional group. The peaks around 68.70–72.73 ppm might be due to the methylene carbon adjacent to the carbon of the epoxy ring.

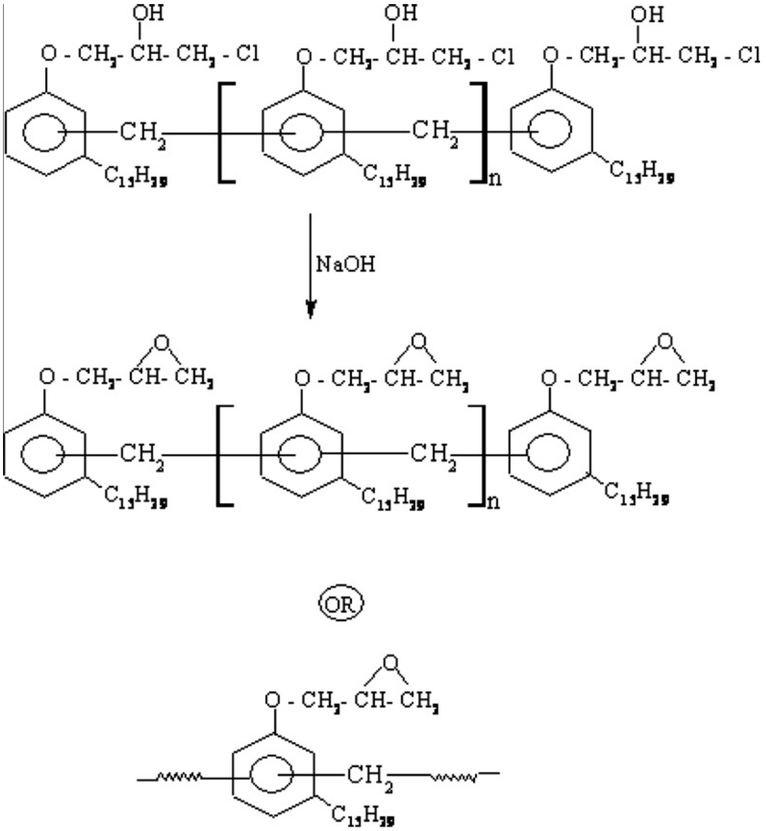
Thus, cardanol could be considered a monoene meta substituted phenol with molecular weight of 302 g mol^{-1} and having the empirical formula $C_{21}H_{34}O$ [32,33]. From the preceding discussion on IR, NMR and GPC, the confirmation of the formation of novolac resin having methylene linkages at o–o′ positions could be considered. Thus, the structure as shown in Scheme 1 can be proposed for CFN.

The epoxide group of epichlorohydrin might react with phenolic hydroxyls under the alkaline medium and forming the chlorohydrin ether. This might undergo



where, n= 0.61

Scheme 1. Structure of cardanol-based novolac resin.



Where n = 0.61

Scheme 2. Structure of cardanol-based epoxidised novolac resin, CNE.

dehydrochlorination reaction by alkali and might result the glycidyl ether together with sodium chloride and water. The structure of the epoxy resin may be proposed as in Scheme 2.

3.2. Studies on CNEVER resin

The esterification reaction of CNE resin was carried out with methacrylic acid in the presence of TPP at 90 °C. Initially, the acid value of the reaction mixture was 120 mg KOH g^{-1} which reduced gradually to 10 mg KOH g^{-1}, indicating the consumption of carboxylic acid present in methacrylic acid and hence gave inference for the formation of vinyl ester resin. The extent of conversion was calculated to be approximately 88% as was determined by Carother's equation [36].

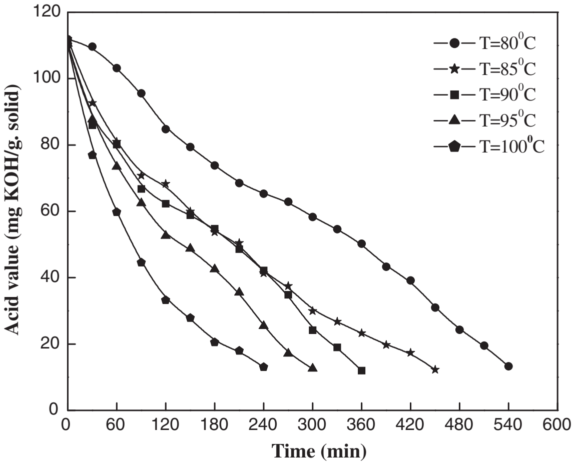


Fig. 8. Acid value versus reaction time for CNEVER.

Fig. 8 showed the esterification of CNE resin and methacrylic acid in the presence of TPP. The results were typical of the behaviour generally observed for polyesterification reactions. It was apparent from the figures that the acid value decreases with increase in reaction time and is not linear in the initial stages of the reaction. This was attributed to the high concentration of the reactive sites and the greater possibility of association of acid and epoxide groups.

3.2.1. FTIR spectroscopic and gel permeation chromatographic analysis of CNEVER resin

The FTIR analysis of uncured CNEVER has been shown in Fig. 9. The disappearance of peak near 911 cm^{-1} due to oxirane group of epoxide linkage and appearance of a new peak near 1714 cm^{-1}, due to ester functional group of vinyl ester resin, confirmed the formation of VER. Further, there appeared a peak near 1633 cm^{-1} which might be attributed to the formation of double bond during the synthesis of VER. The occurrence of the band near 1167 cm^{-1} was probably due to the C–O–C stretching and the peak at 945 cm^{-1} depicted the out-of-plane bending of vinyl ester monomer. These findings were consistent with the previous work by Rodriguez [37].

The theoretical value of number-average molecular weight of CNEVER was calculated to be 969 KOH g^{-1}, but the GPC trace gave 859 KOH g^{-1} (Fig. 3) which indicated that about 88% esterification had taken place (Fig. 10).

3.2.2. ^1H NMR and ^{13}C NMR spectroscopic analysis of CNEVER resin

In the ^1H NMR spectrum of CNEVER (Fig. 11), the methylene and methyl protons of methacrylates end group showed signals around 5.78–6.13 and 2.00 ppm, respectively. The peaks around the region 2.53–2.79 ppm might have appeared due to methylene protons of the ethoxylated group. Other peaks which appeared in the spectrum

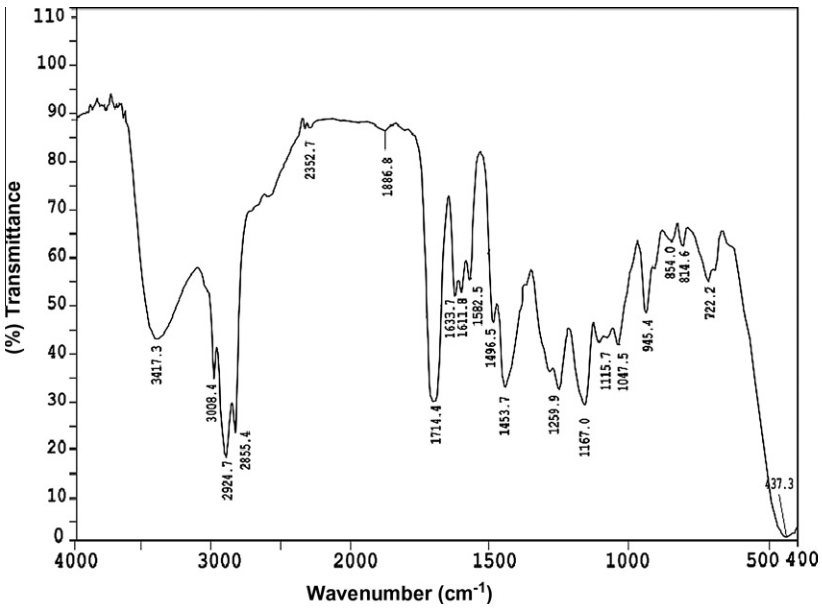


Fig. 9. FTIR spectrum of CNEVER sample.

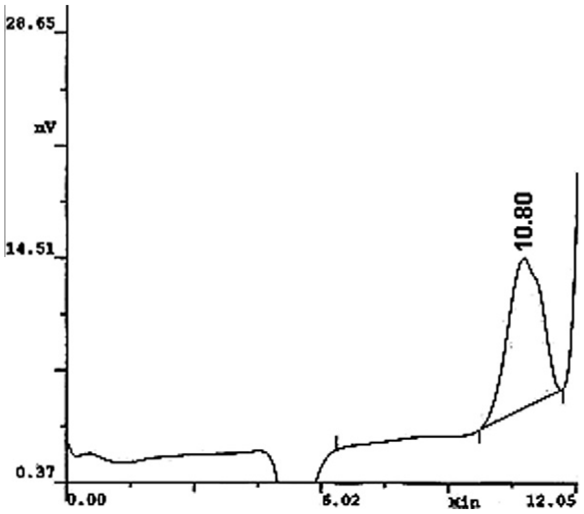


Fig. 10. GPC trace spectrum of CNEVER sample.

were due to the methyl groups present in the backbone structure of novolac resin. In the ^{13}C NMR spectrum (Fig. 12) the peaks observed in the 170–167.3 ppm region were present which might be due to ester functional group of vinyl ester resin. The occurrence of small peak at 52.60 ppm indicated the presence of small amount of epoxy functional group. These results showed good agreement with that found in the literature [28].

Based on the above discussions a mechanism, as shown in Scheme 3, may be proposed for the esterification of epoxy resin with methacrylic acid. The proposed mechanism was consistent with the results of the FTIR, GPC and NMR analysis.

3.2.3. Differential scanning calorimetric analysis for curing of CNEVER

CNEVER was cured using varying concentration of styrene ranging between 0 and 50 wt.% and a comparison is also made from vinyl ester resin based on epoxidized phenolic novolac resin (PVER). From the scans, the temperature of onset (T_o), peak temperature (T_p), and the temperature of completion of the exotherm (T_f) were noted and the data related to this are summarized in Table 2. Fig. 13 showed dynamic DSC scan for curing of CNEVER containing 40% of styrene with the initiator concentration of 2% at a heating rate of 10 °Cmin^{-1}. The onset temperature (T_i) and the final temperature (T_f) were found in the range of 61.7–77.8 °C and 152.4–168.1 °C, respectively. Exothermic peaks appeared which clearly evidenced the maximum cure temperature (T_p) lied in the range of 120.3–128.2 °C. Therefore, cure temperature of 120 °C was considered for curing the samples in air oven which took about 60 min as pre-curing of CNEVER. Finally, the samples were post-cured at 150 °C for two hours. The ΔH values (Table 2) increased up to 40% styrene addition into CNEVER samples and then decreased. All these values are also given in Table 2 for PVER samples with 40% styrene for comparing the data obtained for CNEVER samples. The cure time without styrene is less than the value with 40% styrene, in case of CNEVER, indicating that CNEVER can even be cured without the use of reactive diluents. But, this is not applicable in case of vinyl ester resin based on epoxidized phenolic novolac resin since it is highly viscous (viscosity = 327 Pa s) and is not processible without the reactive diluent and hence cannot be cured without using styrene. When the second scan was done for CNEVER and PVER, the T_g's were found to be 70 and 82, respectively. Similar values of T_g for PVER were obtained in the case of

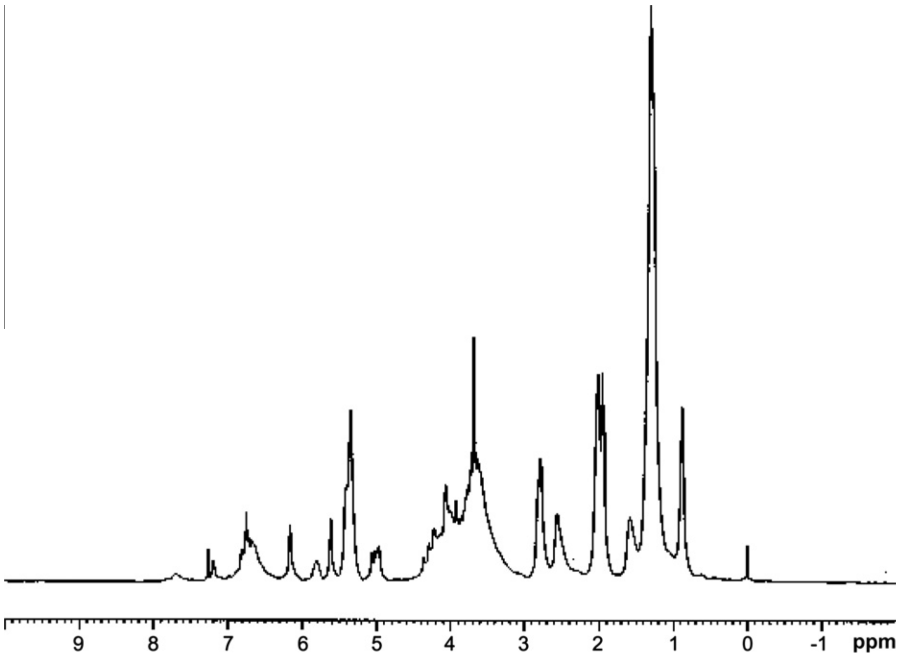


Fig. 11. ^1H NMR spectrum of CNEVER sample.

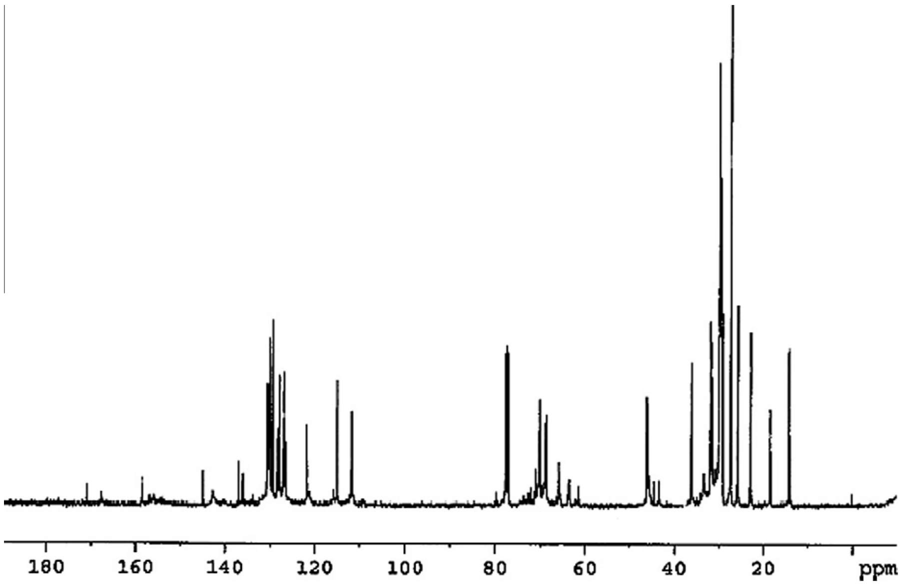
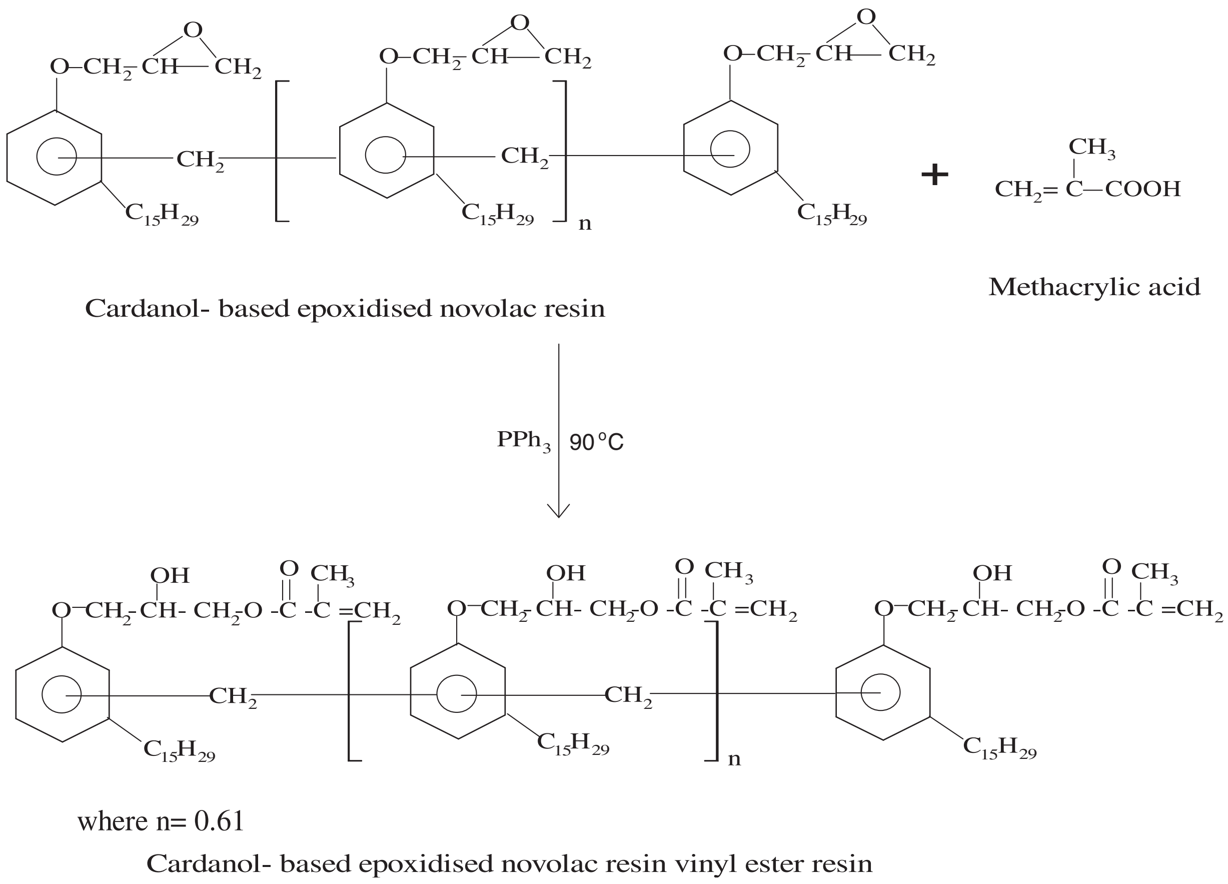


Fig. 12. ^{13}C NMR spectrum of CNEVER sample.



Scheme 3. Mechanism for the synthesis of CNEVER.

Table 2
DSC results of CNEVER and PVER.

S. No.	Samples CNEVER	${}^{a}T_i$ (°C)	${}^{b}T_{onset}$ (°C)	${}^{c}T_p$ (°C)	${}^{d}T_{stop}$ (°C)	ΔH (J g^{-1})	${}^{e}t_c$ (min)	Samples PVER	${}^{a}T_i$ (°C)	${}^{b}T_{onset}$ (°C)	${}^{c}T_p$ (°C)	${}^{d}T_{stop}$ (°C)	ΔH (J g^{-1})	${}^{e}t_c$ (min)
1.	CNEVER$_{00}$	61.7	87.2	120.3	152.4	36.2	53.6	–	–	–	–	–	–	–
2.	CNEVER$_{10}$	65.7	90.4	123.9	165.5	66.1	61.0	–	–	–	–	–	–	–
3.	CNEVER$_{20}$	63.2	92.0	125.7	167.7	62.6	59.0	–	–	–	–	–	–	–
4.	CNEVER$_{30}$	63.9	95.9	126.5	163.9	69.9	58.0	PVER$_{30}$	88.2	97.4	117.1	132.3	80.1	60.5
5.	CNEVER$_{40}$	60.3	95.2	127.7	168.1	72.8	57.3	PVER$_{40}$	60.9	82.9	127.3	147.1	73.1	58.2
6.	CNEVER$_{50}$	77.8	98.8	128.2	160.7	63.7	59.5	PVER$_{50}$	51.8	62.5	128.7	153.6	70.8	57.5

where
[a] Temperature of cure initiation.
[b] Onset temperature by extrapolation.
[c] Temperature of cure maximum.
[d] Temperature of end of cure.
[e] Cure time obtained from samples cured in oven at 120 °C.

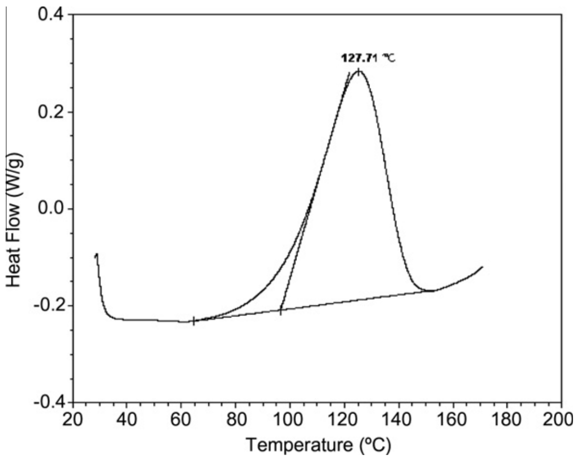


Fig. 13. DSC scans at of CNEVER cured with 40 wt.% styrene and 2 wt.% benzoyl peroxide.

PVER samples with different styrene concentrations in our previous publication [38] from the DMA studies.

The curing reactions led to increase in viscosity as evidenced from the increase of onset temperature (T_i) with increased styrene concentration. These curing reactions can be proposed similar to that given by Cardona et al. [39] for DGEBA based VER. Initially, CNEVER with styrene might proceed with the decomposition of benzoyl peroxide initiator followed by the formation of monomer free-radical. These radicals might have provided the active sites required to overcome inhibition and to sustain the chain reaction [40,41]. FTIR analysis of cured CNEVER (Fig. 14) clearly indicated the decrease in the intensity of the ester functional group peak at 1718 cm^{-1} and the disappearance of peaks due to styrene, i.e., peaks at 1641 and 1612 cm^{-1}.

3.2.4. Thermogravimetric analysis (TGA) of cured CNEVER

The system was evaluated for thermal stability in nitrogen atmosphere by thermogravimetric analysis. The thermogravimetric curve obtained for sample CNEVER has been shown in Fig. 15 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 final decomposition temperature (T_f) were noted from TGA traces (Table 3). TG analysis confirmed the occurrence of degradation of the sample. The degradation of the system was found to occur in a single step. A clear-cut single step mass loss in TG trace of vinyl ester system indicated single step decomposition behaviour (both for CNEVER and PVER samples). The sample was stable up to 260–285 °C and started loosing weight above this temperature. Rapid decomposition was observed in the temperature range of 350–500 °C and almost total volatilization of the sample was occurred around 700 °C. The decrease in the weight loss, assumed to be proportional to the extent of cure, with increasing temperature was attributed to quenching of the reaction upon vitrification, which occurred at successively higher cure levels with increasing temperature [42]. The lower weight loss at higher

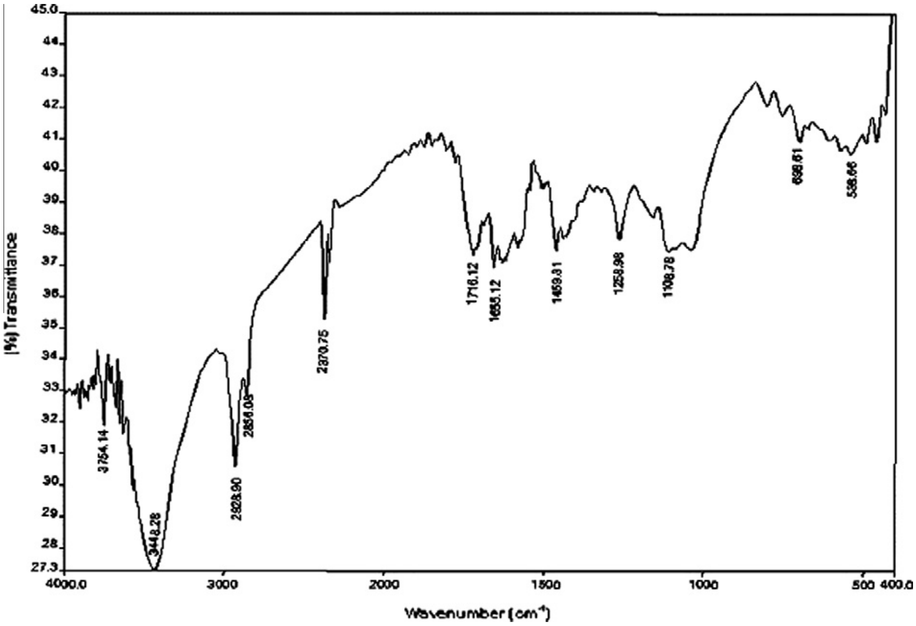


Fig. 14. FTIR spectrum of cured CNEVER.

temperature suggested that other process (e.g. oxidative crosslinking) may be contributed to cure at high temperatures. The oxidative crosslinking at high cure temperature caused vitrification and significant reduction in rate of further condensation reaction prior to complete or ultimate conversion. The higher char yield could be attributed to the presence of more cross-links present as a result of curing which further confirmed the higher thermal stability of the vinyl ester-styrene systems.

3.2.5. Mechanical properties of CNEVER

The variation of tensile strength, elongation-at-break and impact strength in the castings of the vinyl ester samples (CNEVER and PVER samples) containing varying amounts of styrene has been shown in Table 4. A gradual increase in tensile strength was noted as the concentration of the styrene was increased up to 40 wt.% and then-after decreased. The tensile strength increased from 63.2 to 71.3 MPa as the styrene concentration was increased from 0% to 40% indicating only 14% increase in CNEVER samples. The values of tensile strength were found to be higher for PVER samples which were lied in the range of 82–85.1 MPa. The lower values of tensile strength of CNEVER might be attributed to the steric hinderance and reduced intermolecular interactions imparted by the C_{15} side chain present in cardanol. The percent elongation-at-break of the vinyl ester samples increased continuously with styrene content (Table 4). This might be due to the increased

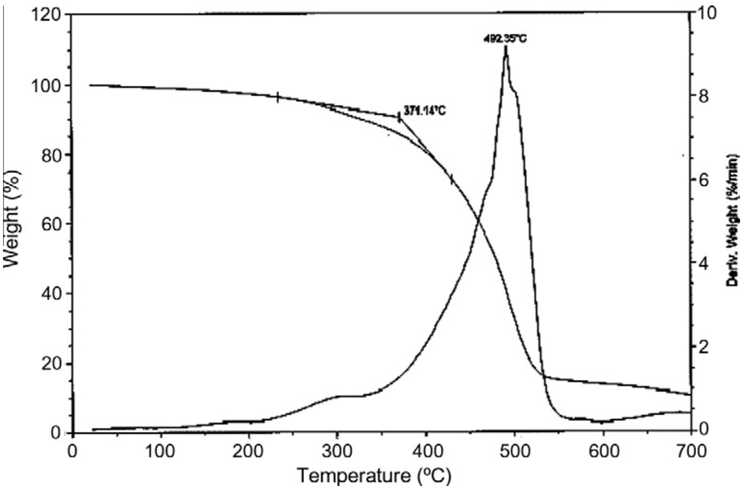


Fig. 15. TGA trace of cured CNEVER sample.

Table 4
Mechanical properties of CNEVER and PVER resins.

S. No.	Styrene (wt.%)	Samples CNEVER	Tensile strength (MPa)	Impact strength (kJ/m^2)	Elongation at break (%)	Samples PVER	Tensile strength (MPa)	Impact strength (kJ/m^2)	Elongation at break (%)
1.	0	CNEVER$_{00}$	53.2	14.8	9.7	–	–	–	–
2.	10	CNEVER$_{10}$	54.8	20.5	11.2	–	–	–	–
3.	20	CNEVER$_{20}$	55.1	18.1	12.4	–	–	–	–
4.	30	CNEVER$_{30}$	60.3	17.2	13.9	PVER$_{30}$	82.0	20.2	11.3
5.	40	CNEVER$_{40}$	62.5	15.0	15.2	PVER$_{40}$	85.1	19.4	13.7
6.	50	CNEVER$_{50}$	61.3	18.4	14.7	PVER$_{50}$	83.5	22.1	15.5

Table 3
Data obtained from TG traces of prepared samples.

S. No.	Styrene (wt.%)	Samples	T_o	T_{max}	T_f	Total %CY	Samples	T_o	T_{max}	T_f	Total %CY
1.	0	CNEVER$_{00}$	260	468	560	17.86	–	–	–	–	–
2.	10	CNEVER$_{10}$	260	471	564	8.53	–	–	–	–	–
3.	20	CNEVER$_{20}$	285	470	570	12.33	–	–	–	–	–
4.	30	CNEVER$_{30}$	275	473	572	6.72	PVER$_{30}$	250	491	600	20
5.	40	CNEVER$_{40}$	265	492	575	11.0	PVER$_{40}$	275	488	620	28
6.	50	CNEVER$_{50}$	270	473	565	5.80	PVER$_{50}$	260	488	625	19

T_q, initial degradation temperature; T_{max}, peak degradation temperature; T_f, stop degradation temperature; CY, char yield.

flexibility caused by the uncrosslinked styrene monomer present in the vinyl ester matrix. The styrene chains might form as cross-linked through the VER molecules and, thus, the inhomogeneous shear deformation might change from much localized to more diffuse region which could give the observed behaviour [43]. Such behaviour can be related to the existence of residual styrene in the cross-linked resin. The change of impact strength of cured vinyl ester samples could be explained on the two phase nature of the system.

4. Conclusion

The synthesis of low viscosity vinyl ester resin (viscosity = 39 Pa s) from renewable resource material such as cardanol might reduce the use of concentration of harmful chemical like styrene during curing of such resin. The temperature of curing was found to be very close to the curing temperature for VERs from epoxidized phenolic novolac resin cured using 40% styrene. The cure time, using 40% styrene, for CNEVER sample was less than that for PVER sample. Also the cure time was found to be least when the CNEVER sample was used without styrene. If one can compromise the mechanical properties and color, the VER from cardanol could be a better substitute. No doubt the cost of the resin will be less than that of already existing VERs. Thus, an environmental friendly hybrid resin can be obtained in which optimum properties can be achieved, which may be used for the development of reinforced plastics, eco-friendly coating systems etc.

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