RENEWABLE RESOURCE MATERIAL - I : A STUDY TO UTILIZE THE POTENTIAL ATTRIBUTES OF CARDANOL

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ABSTRACT

Cardanol-based vinyl ester resin (*CVER*) was blended with varying concentrations of CTBN ranging between 0 to 15 wt% with an interval of 5 wt%, by two different approaches, viz., physical and chemical blending. The formation of various products during the curing of blend samples has been studied by FTIR spectroscopic analysis. The dynamic DSC scans showed that the blend samples of *CVERs* cured in the temperature range of 100-150°C. It was observed that the blend sample containing 5 wt% and 10 wt% liquid rubber, for physical and chemical blending, respectively, showed least cure time, at 120°C, amongst all other blend samples. On evaluation, it was found that blend samples (5 wt% for physical blending and 10wt% for chemical blending) exhibited better thermal and mechanical properties as compared to pure vinyl ester resin. The blend morphology, studied by scanning electron microscopy analysis, showed the presence of precipitated discrete rubber particles which dispersed throughout the vinyl ester matrix i.e. they revealed the presence of two phase morphology.

INTRODUCTION

Renewable organic resources continue to be in the common interest of both academic and industrial laboratories at all the times. Among the renewable resources, cardanol [1-4], a distillate of cashew nut shell liquid (CNSL), obtained as a byproduct of the cashew processing industry, is unique in that it contains a phenolic moiety with an unsaturated 15-carbon side chain.. Cardanol-based epoxy and vinyl ester resins [5-8] have also been developed and find innumerable applications as base materials for adhesives and thermosetting matrix materials for composites. Because of their network structure, vinyl ester resin (*VER*) possess high tensile strength and modulus, excellent chemical and corrosion resistance as well as good dimensional stability and elevated heat distortion temperatures. Unfortunately, these materials are usually brittle and so, modifiers are added. Elastomeric modifiers which can be used to improve the toughness of thermosetting materials, have reactive functional groups, be miscible with the thermosetting components of the material before cure. Toughness can also be improved for VERs by incorporating a carboxyl terminated reactive liquid polymer during the synthesis [9-11]. Similar behaviour was found for novolac-based epoxy acrylate resins to achieve greater toughness [12]. The present paper deals with the toughening of cardanol-based vinyl ester resin (*CVER*) with CTBN by two different approaches, viz. chemical and physical toughening.

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EXPERIMENTAL

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 (TPP) (from M/s CDH Pvt. Ltd, New Delhi), styrene, benzoyl peroxide and hydroquinone (from E. Merck, New Delhi) and Carboxyl-terminated butadiene – acrylonitrile copolymer (CTBN) (Hycar 1300 x 8) was supplied by M/s Emerald Performance Materials, LLC, Hong Kong having molecular weight M_n of 3500 and acrylonitrile and carboxyl contents 27 and 32 percent, respectively were used during the investigation.

Preparation of blends of cardanol-based vinyl ester resin (CVER) and carboxyl-terminated butadiene acrylonitrile copolymer (CTBN)

CVER was synthesized using cardanol by employing a similar procedure as mentioned in our previous publications [5, 6]. Physical blends of *CVER* with CTBN were prepared according to the procedure similar to that adopted by Pham and Burchill [9]. The calculated quantity of vinyl ester resin and CTBN was, firstly, stirred at 50°C for 1 h to entrap all air bubbles from the resin. To this homogenous resin, the calculated quantity of styrene and benzoyl peroxide was added and stirred to get a clear homogeneous mixture.

Chemical blends of *CVER* with CTBN were prepared by taking requisite amount of *CVER* (100g) and CTBN in the desired proportions. 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. The progress of the reaction was checked by determining the acid value by periodic withdrawal of the reaction mixture, till it reaches the lowest value. Then calculated amount of methacrylic acid was added and the reaction was allowed to proceed until the acid value decreased to the minimum value. To this toughened resin, calculated quantity of styrene and benzoyl peroxide was added and stirred to get a clear homogeneous mixture. All the samples were designated according to Table 1.

Table 1: Sample designation

S. No.	CTBN (%)	Sample code	
		Physical Toughening	**Chemical Toughening**
1.	0	$CVER_{00}$	$CVER_{00}$
2.	5	$CVERP_{05}$	$CVERC_{05}$
3.	10	$CVERP_{10}$	$CVERC_{10}$
4.	15	$CVERP_{15}$	$CVERC_{15}$

Characterization of the prepared samples

The blends of *CVER* were subjected to Fourier-transform infra-red (FTIR) spectroscopic analysis, to monitor the appearance and disappearance of various functional groups in the wavelength range of 400 to 4000 cm^{-1} by Perkin Elmer FTIR, RX-1 spectrophotometer. The curing of blend samples of *CVER* was monitored by recording dynamic Differential scanning calorimetry (DSC) (TA, Instrument, USA; Model DSC Q 20) scans at heating rate of 10°$Cmin^{-1}$ in nitrogen atmosphere.

Dumbbell-shaped cured blend samples (size : 7.5 x ¾ x 1/8 inch) of *CVER* 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 75mm x 15mm x 3mm according to ASTM D-256 standards.

The morphological changes due to addition of CTBN into the *CVER* matrix were studied by Carl Zeiss EVO-50Vp Low vaccum scanning electron microscopy (SEM). The rubber domains distributed in the matrix and interaction of these domains with the vinyl ester 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

FTIR spectroscopic analysis of blend samples

The FTIR spectra of uncured physically blended sample *CVERP*$_{05}$ containing 5% CTBN and uncured chemically blended sample (i.e. sample *CVERC*$_{10}$) containing 10% CTBN confirmed the formation of various groups, during blending, have been given in Figs. 1 and 2, respectively. Absorption bands at 1735 and 1713 cm^{-1}, which can be ascribed to the carboxylic group of CTBN [9], were not observed in the FTIR spectra of blend sample *CVERC*$_{10}$ (Fig. 2). On the other hand, the absorption band at 1720 cm^{-1} was observed that might indicate the formation of functional group esters.

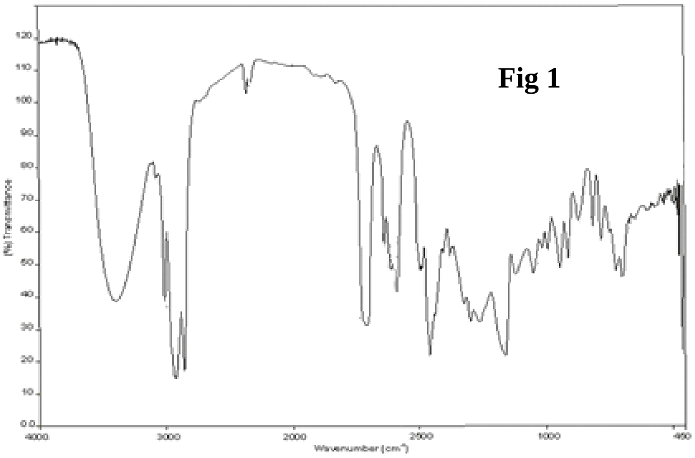

Fig 1

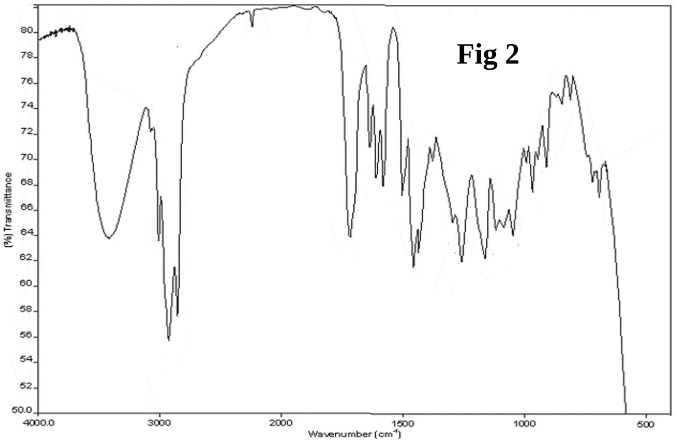

Fig 2

The absence of the absorption band at 3232 cm^{-1}, in the spectra of blend samples could be ascribed to the –OH and –COOH groups of CTBN and the presence of an absorption band near 3400 cm^{-1} in blend samples that might be ascribed to the –OH group of vinyl ester resin. A sharp –C≡N peak at 2238 cm^{-1} was also observed in the spectrum of CTBN [9]. However, the addition of CTBN into epoxy caused chemical interaction between the oxirane ring of epoxy and carboxyl forming epoxy-terminated CTBN, which further produced vinyl-terminated CTBN by reaction with methacrylic acid.

3.2. Curing Mechanism

The FTIR spectra of cured physically blended sample *CVERP$_{05}$* containing 5% CTBN and uncured chemically blended sample (i.e. sample *CVERC$_{10}$*) containing 10% CTBN confirmed the formation of various groups, during blending, have been given in Figs. 3 and 4, respectively. Absorption bands at 1735 and 1713 cm^{-1}, which can be ascribed to the presence of carboxylic group of CTBN [9], were not observed in the FTIR spectrum of cured blend sample *CVERC$_{10}$* (Fig. 4). All other peaks, appeared in uncured samples, also shifted.

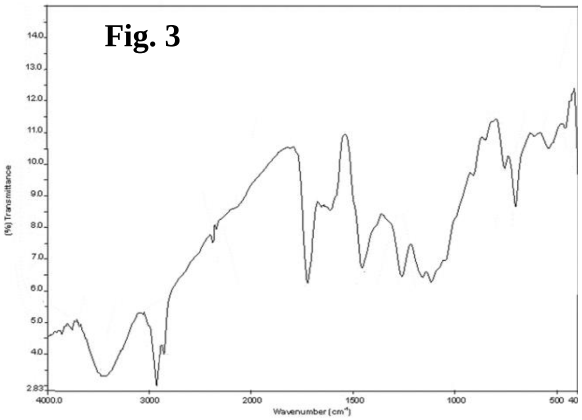
Fig. 3

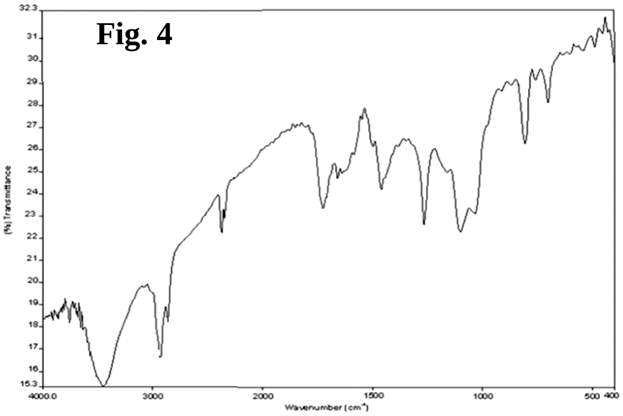
Fig. 4

Differential Scanning Calorimetric Analysis

Figs. 5 and 6 show the DSC scans of *CVERP$_{05}$* and *CVERC$_{10}$* respectively toughened using 5 and 10 wt% CTBN and cured by using 40% styrene and 2% benzoyl peroxide.

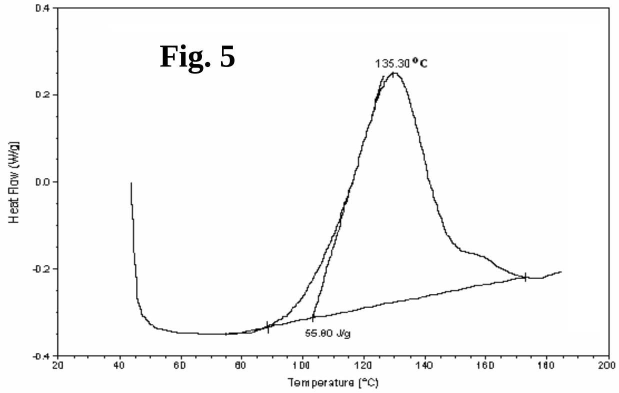
Fig. 5

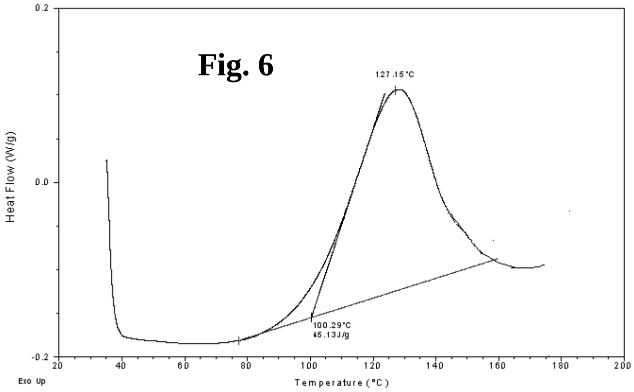
Fig. 6

Toughening of *CVERs* with different concentrations of CTBN was observed to have marginal affect on the curing process as investigated by DSC. It is evidenced from the results that the peak exotherms are shifted to lower temperatures due to enhanced reaction rate which, finally, reduces the cure time of the CTBN- modified blend systems. These peaks appear during the first heating run but is completely absent during the second heating cycle indicates the completion of the curing reaction. The initial addition of CTBN decreased the cure time up to the 5 wt% in physically toughened *CVER* and 10 wt% CTBN addition in chemically toughened *CVER* and increases thereafter. The enhanced rate behavior could be interpreted in terms of intermolecular transition state for the vinyl ester-styrene reaction. According to this mechanism [16], strong hydrogen bonding species, such as acids and alcohols, stabilized the transition state and strongly accelerated the curing reaction. Also, the reaction products containing carboxylic acid component favoured gelation condition which might create fluctuations of concentrations and induced phase separation [6-11, 17].

Mechanical analysis

Table 2 shows the tensile strength, elongation-at-break and impact strength of the blends of *CVER* with CTBN. Just by the incorporation of 5 wt% CTBN, the tensile strength of vinyl ester decreased to 26% for physical toughening of *CVER* and 22% for chemical toughening. In case of physical toughening it increased with the increase of CTBN content but was reduced significantly from 91.1 MPa to 55.6 MPa on addition of 10 wt% CTBN and then after increased to 93.4 MPa in a 15 wt% CTBN containing sample in case of chemical toughening. This could be due to the increase in the relative amount of dissolved rubber as the rubber content increases. The percent elongation-at-break of the blend samples increased continuously with CTBN content in the blend. The difference in mechanical behaviour can be associated to morphological characteristics.

Table 2

S. No.	Sample	Tensile Strength (MPa)	Impact Strength (kJm^{-2})	Elongation at Break (%)	Sample	Tensile Strength (MPa)	Impact Strength (kJm^{-2})	Elongation at Break (%)
		Physical Toughening				Chemical Toughening		
1.	$CVER_{00}$	116.5	16.2	13.7	$CVER_{00}$	116.5	16.2	13.7
2.	$CVERP_{05}$	86.8	24.0	14.2	$CVERC_{05}$	91.1	30.6	14.2
3.	$CVERP_{10}$	90.2	20.7	16.1	$CVERC_{10}$	95.6	50.8	17.1
4.	$CVERP_{15}$	96.1	15.8	18.6	$CVERC_{15}$	93.4	41.3	18.9

Morphological study

SEM micrographs of CTBN modified VER showed that at low concentration of CTBN (i.e., 5%) (Figs. 7 and 8) there were small irregular domains rich in CTBN, which appeared included in the VE matrix i.e., some toughening was achieved even if distinct stress whitening was achieved. As the concentration was increased upto 10 wt% (Fig. 8), the dark areas appeared larger and more localized.

SEM of the samples with high CTBN concentration showed globular nodules interconnected by what seemed to be a coating film. These morphologies were essentially co-continuous and with microvoids formed during the last stages of the curing (resulting from the different volumetric contraction of the two phases) [11].

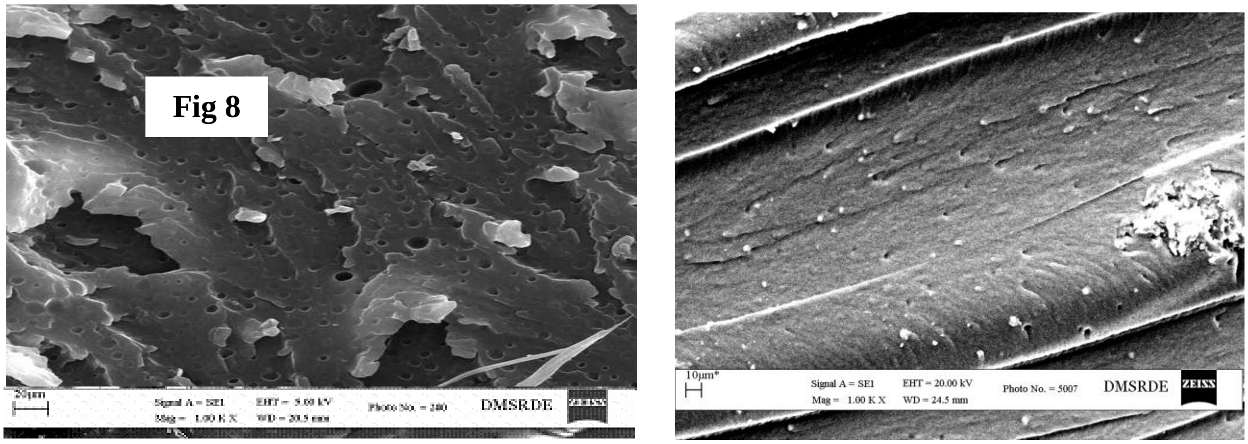

Fig 8

When this microstructure is present in island, it reduces the volume contraction of the overall sample (void formation reduces the high volume contraction of the thermoset). However, since in the present case the microvoid spanned the whole sample, the material became more fragile. Moreover, the fracture surfaces of these high concentration CTBN species were very rough as seen by SEM. Naked eye inspection of these surfaces also indicated macroscopically rough surface with little material coherence.

Conclusion

Toughened cardanol-based vinyl ester resins exhibited superior properties in comparison to their non-toughened counterparts i.e. neat *CVERs* . Following conclusions were drawn from the above work:

(i) The FTIR spectroscopic analysis revealed a chemical reaction between the oxirane and the carboxyl group of CTBN which was further confirmed by SEM analysis.

(ii) DSC studies showed the exothermal heat of reaction of epoxy crosslinking due to addition of rubber into epoxy matrix in case of chemical toughening.

(iii) Cardanol–based vinyl ester network modified with CTBN displayed two phase separated morphology with dispersed rubber globules in the matrix resin.

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