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Mechanical And Morphological Study Of The Modification Of Phenol-Cardanol-Based Epoxidized Novolac Resin

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Abstract: Phenol-cardanol-based epoxidized novolac resin and different weight percentages of carboxyl-terminated butadiene acrylonitrile (CTBN) as a modifier were developed and cured with stoichiometric amounts of aliphatic amine. Upon evaluation, it was found that 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 phenol and cardanol. Chemical and morphological properties of the formulated resins were also determined. The blend morphology, studied by scanning electron microscope, showed the presence of precipitated discrete rubber particles, which dispersed throughout the epoxy matrix—i.e., they revealed the presence of two-phase morphological features.

Keywords: Phenol, Cardanol, Novolac resin, Carboxyl-terminated butadiene acrylonitrile (CTBN), Scanning Electron Miocrocopy (SEM).

Introduction

Natural vegetable oils, as a source of raw materials have been utilized in polymer synthesis via the attachment of functional groups such as hydroxyl; epoxy or carboxyl groups introduced on to the fatty acid chains of the vegetable oil [1]. Moreover polymers produced from vegetable oil and their derivatives have excellent hydrolytic stability and thermomechanical properties due to the presence of hydrophobic nature of the side chain [2]. Cashew Nut Shell Liquid (CNSL) obtained as a byproduct of cashew nut industry is invaluable raw material in many important industries such as polymers, plastics, lubricants, resins and antioxidants [3-5]. Among different renewable resources, cardanol, a major component of Cashew nut shell liquid (CNSL) and agricultural by-product abundantly available in tropical countries such as India, is one of the major and economical resources of naturally occurring phenols [6,7].

The phenol-cardanol based novolac type phenolic resins may be modified by epoxidation reaction with epichlorohydrin to enhance the performance of such resins in various fields [8]. Like other thermosetting resins, however, epoxy resins brittleness is a major deficiency in many applications. To overcome this deficiency, many attempts have been made to blend them with reactive liquid rubbers such as carboxyl- and amine-terminated butadiene acrylonitrile rubber. With an appropriate weight of rubber, the rubber modified resins have strongly improved toughness. In this way, a CTBN copolymer has been used by various workers with diglycidyl ether bisphenol A epoxy resins. CTBN copolymers, however, are rarely used for this purpose with cardanol-based epoxy resins. We have therefore tried to produce such modified epoxy matrices by physical blending of phenol-cardanol-based epoxy novolac resin with CTBN and studied the mechanical and morphological characteristics.

Experimental

1.1 Materials

Cardanol was obtained from M/s Dheer Gramodyog Ltd., Kanpur, India; formaldehyde (37% solution) from M/s Qualikem Industries, New Delhi was used for formylation. Phenol and p-toluene sulphonic acid (PTSA) were procured from M/s S.D. fine chemicals Mumbai. Methonal (BDH), epichlorohydrin, sodium hydroxide and polyamine (M/s Ciba Specialty Chemicals Ltd., Mumbai) with amine value 1240–1400 mg KOH/g, and CTBN copolymer were used during the investigation.

1.2 Preparation of phenol-cardanol-based epoxidized novolac resins and CTBN copolymer blend samples

The phenol-cardanol based novolac resins, thus formed were treated with molar excess of epichlorohydrin and 40% solution of sodium hydroxide at 120^{0}C for about 10 h. The formed product was vacuum distilled for the removal of excess of epichlorohydrin. The epoxide equivalent weights (EEW) of phenol-cardanol based epoxidized novolac resin (EPCN) were found to be 352, 450 and 543 eq g^{-1} for the samples PCN_{107}, PCN_{017} and PCN_{557}, respectively (refer Table 1) as determined by pyridinium chloride method. Blend samples containing 0–15 wt% CTBN were prepared according to the procedure similar to that adopted by Ting [9]. The calculated quantity of epoxy resin (as per the formulation given in Table 1) was first stirred at 120^{0}C for 1 h to entrap all air bubbles from the resin. To this homogenous resin, the calculated quantity of polyamine was added and stirred to get a clear homogeneous mixture.

Table 1: Sample designation and cure time

S.No.	Epoxy (wt%)	CTBN (wt%)	Sample Code
1	100	0	$EPCN_{710}$
2	95	5	$EPCN_{795}$
3	90	10	$EPCN_{790}$
4	85	15	$EPCN_{785}$

1.3 Characterization of the prepared samples

1.3.1 Mechanical analysis

1.3.1.1 Universal testing machine (UTM)

The tensile strength, percentage elongation at break and impact strength of the cured samples were measured on Universal Testing Machine (UTM) of "Patiwana group, Star Testing System", Mumbai, India.

1.3.1.2 Film Applicator

The films of different samples were applied on glass/M.S. panels by using a “Bird Film Applicator” from M/s Sheen Instruments Ltd, U.K.

1.3.1.3 Impact Hardness Tester

The impact hardness of the films of the epoxidized novolac vinyl ester resins and their blends with CTBN was tested using a ‘Tubular Impact Hardness Tester’ (M/s Khushboo Scientific, Mumbai).

1.3.1.4 Scratch Hardness Tester

The scratch hardness of the films of epoxidized novolac vinyl ester resins and their blends were checked by ‘Automatic Scratch Hardness Tester’ (M/s Sheen Instruments Ltd, UK)

1.3.1.5 Cylindrical Mandrel

The flexibility of the cured films of vinyl esters and their blends with CTBN were tested using a ‘Cylinderical Mandrel’ (M/s Sheen Instruments Ltd, UK; Model: 809), the mandrel of the diameters 1/12 to 1.3 of an inch.

1.3.1.6 Triglossometer

Gloss was measured using Triglossometer (M/s Sheen Instruments Ltd, UK). After watching the films from 60° angle. It had been observed that all the coating films had good gloss.

1.3.2 Chemical resistance

For chemical resistance, panels were prepared by applying the blend samples on 150*100* 1.25 mm sand-blasted steel sheet panels with a Bird Film Applicator (M/s Sheen Instruments Ltd.). 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^{0}C.

1.3.3 Morphological studies by Scanning Electron Microscopic (SEM) analysis

The fractured samples under mechanical analysis were sputter coated with gold prior to Scanning Electron Microscopy (SEM) examination. JEOL JSM 5800 Model was used to view of specimen; several micrographs were taken for each sample.

2. Result And Discussion

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

The variation of tensile strength and elongation-atbreak with CTBN contents in the castings of epoxy and CTBN blend samples cured with polyamine is shown in Table 2. A gradual fall in tensile strength was noted as the concentration of the elastomer phase increased. This may have been due to the increase in the relative amount of dissolved rubber as the rubber content increased. The elongation-at-break percentage of the blend samples increased continuously with the amount of 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 by the two-phase nature of the system. Similar behavior has also been reported in other rubber-modified epoxy systems and attributed to the agglomeration of the rubber particles with the increase of the rubber concentration, [10] which might act as nuclei for void formation. This void formation in rubber particles increases the energy dissipation on impact and thus the toughness of the product. The difference in mechanical behavior can be associated with morphological characteristics.

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

Table 2 showed the surface and mechanical properties of the cured films of blend samples. The table clearly indicates that the cured films of all blend samples containing 5–25 wt% CTBN are smooth and uniform with semi-gloss surfaces. The blend samples show improved impact resistance over that of pure epoxy resin. The adhesion and flexibility improvement may be due to the presence of some dissolved rubber particles inside the epoxy matrix. The decrease of crosslink density might also be indicative of improved flexibility, whereas cavitations of rubber particles inside the epoxy matrix improved the impact resistance of the films of blend samples. This table also indicated that the film of pure epoxy (*$EPCN_{710}$*) was harder than the film of pure epoxy and CTBN blend (*ECF_{785}*) samples. The addition of CTBN decreased the hardness due to an increase in the flexibility of resin films. This is further clear from SEM micrographs in the proceeding paragraphs.

2.3 Chemical Resistance

It is clear from the films of coating based on epoxy with 15 wt% CTBN offer the maximum resistance to different concentrations of acid and alkali compared to the cured films of other epoxy and blend samples. This behavior might be attributed to greater reactivity of epoxy and liquid rubber. The film surfaces of the epoxy and 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, and methanol, etc., resulted in first change during 4–6 months, which was more than that for pure epoxy resin. This indicates that the blend samples are more resistant to solvents than pure epoxy resin.

Table 2: Mechanical properties of pure epoxy and its blend with CTBN

Sample Code	**Properties of casting**			**Properties of Fillms**			
	Tensile strength (MPa)	**Impact strength (kJ/m2)**	**Elongationat-break (%)**	**Gloss (60^0angle)**	**Scratch hardness (kg)**	**Adhesion & flexibility**	**Impact resistance (kg cm)**
$EPCN_{710}$	138.5	18.9	40.1	80.2	3.5	Fail	55.0
$EPCN_{795}$	128.5	25.9	49.1	85.3	2.0	Pass	58.9
$EPCN_{790}$	120.8	40.3	52.5	90.5	1.8	Pass	67.9
$EPCN_{785}$	115.2	60.5	70.2	95.7	2.8	Pass	73.5

2.4 Morphological properties

Figures 1 showed the SEM of the fractured surface of the unmodified and CTBN-modified epoxy matrix containing 15 wt% CTBN. The pattern of morphology observed for the unmodified formulation was the characteristics of brittle systems with smooth, glassy fractured surfaces with cracks in different planes. SEM of CTBN-modified systems (i.e., samples ($EPCN_{790}$ *and* ECF_{785}) showed the presence of precipitated, discrete rubber particles that 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 stages of curing. The size of the precipitated rubber particles increased with increasing rubber content in the formulation. The size of the rubber particles in the epoxy matrix was larger in samples of ECF_{785} than that observed in blend samples of ECF_{790}. This increase in size of the dispersed rubber phase might be associated with the reagglomeration or coalescence of the dispersed rubber particles [11].The fractured surfaces of the most of the rubber toughened epoxy systems have a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated particles.

3. Conclusions

The followings conclusions have been drawn from the results of the work:

1. 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 phenol and cardanol.
2. The films of coating based on epoxy with 15 wt% CTBN offered the maximum resistance to different concentrations of acids, alkalies, and solvents compared to the cured films of other blend samples.
3. The pure epoxy resin based on phenol and cardanol fractured in a ductile manner. Whereas the blend samples containing 15 wt% rubbers showed some cavitations of the rubber particles in SEM photographs.

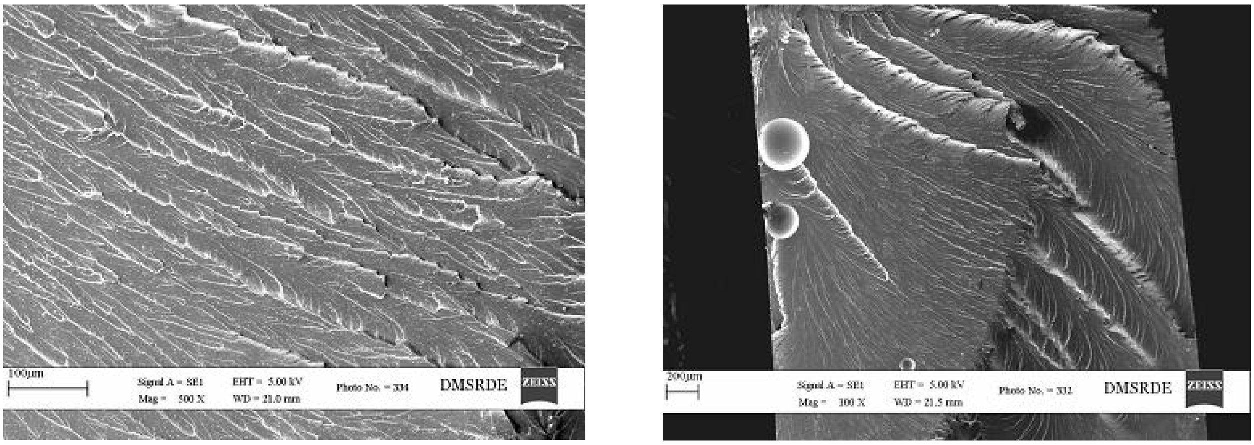

Fig. 1: SEM photographs of pure epoxy matrix system and its blend with CTBN

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