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Preparation of blends of epoxidised novolac resin and carboxylic terminated polybutadiene (CTPB) liquid rubber and evaluation of their physico-chemical characteristics

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ABSTRACT

The blend samples were prepared by mechanical mixing of phenol based epoxidised novolac resin with carboxylic terminated polybutadiene (CTPB) liquid rubber ranging 0-25% with an interval of 5 wt% phenol based epoxy resin was prepared by conventional procedure for the preparation of diglycidal ether bisphenol-A (DGEBA) epoxy resin in acidic medium. The novolac resin was prepared by the phenol and formaldehyde with the mole ratio 1:1.6 by using tricarboxylic acid as catalyst. Methylation of phenol was confirmed by Fourier transform infrared (FTIR) spectroscopic analysis and a reaction mechanism was proposed. The number average molecular weight was found to be 838 by the gel permeation chromatographic (GPC) technique on the basis of calculated value of kinetic chain length. The structure of the novolac type phenolic resin were cured with hexamethylene tetraamine (HMTA) confirmation of epoxidised novolac confirmed by FTIR analysis by seeing the appearance of various functional groups during the cured films of blends samples.

Key words: Epoxidised novolac, CTPB, liquid rubber, blend resin FTIR etc.

INTRODUCTION

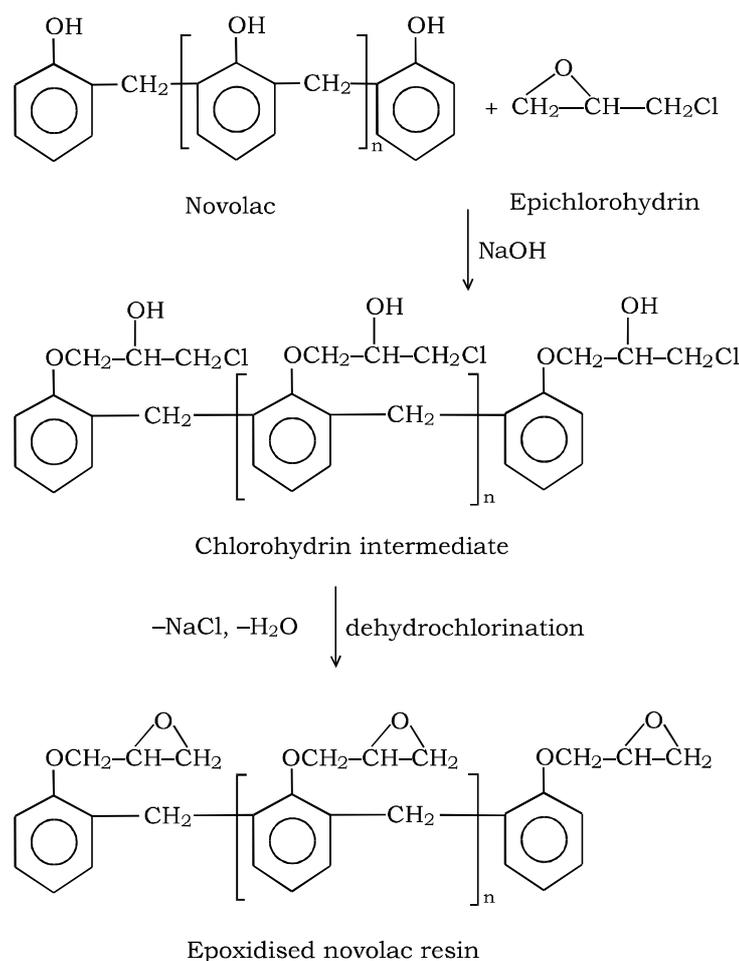
Epoxy resins are of the great importance as synthetic materials that have developed continuously in the term of volume and application for several decades. These are mainly derived from condensation products of formaldehyde and phenols or alkyl substituted phenols, furfural alcohols etc.[1-4].

Epoxy resin has been widely used as adhesive, coating materials and so many other uses because of their excellent properties viz. moisture resistance chemical resistance and corrosion resistance. High tensile strength modulus as good dimensional stability and as binding material in the particle board industry as fire retardant material in the industry [5-6]. The phenol base novolac type phenolic resin may further be modified by epoxidation with epichlorohydrin to duplicate the performance of such phenolic type novolacs [7]. The epoxy resin show low impact resistance in their cured state [8]. The several methods have been proposed to increase the toughness of epoxy resins and one of the most successful involves in the addition of a suitable rubber to uncured epoxy resins and controlled by the polymerization reaction in order to induce phase separation [9-13]. The great majority of studies involves its chemical modification with a reactive elastomer, particularly carboxylic terminated polybutadiene (CTPB) [14]. Blending of phenol based epoxy novolac resin with CTPB and studied the effect of CTPB addition in the blends.

EXPERIMENTAL SECTION

2.1 Raw material:

Phenol [LR] grade 40% obtained from M/s Glaxo Laboratories India Ltd. Mumbai, formaldehyde 40% solution, citric acid epichlorohydrin obtained from Thomas Baker Chemicals Ltd. Mumbai, polyamide [M/s Resinova Chemical Ltd. Kanpur] with amine value 240-400 mg KOH/gm and carboxyl terminated polybutadiene (CTPB) [Hycar 2000 x 162] obtained from M/s Emerald Performance Material CCC Hong Cong were used during the investigation.



2.2 Epoxidation of novolac resin and their blends with CTPB liquid rubber:

The novolac based epoxy resins were synthesized by reaction with epichlorohydrin [ECH]. The reaction between epichlorohydrin and novolac resin may be thought to proceed in a similar fashion as in the work given by Lee and Neville [15]. The epoxide group of epichlorohydrin reacted with phenolic hydroxyls under the alkaline medium and formed the chlorohydrin as per the mechanism proposed in scheme.

The resulting viscous product was stored for further analysis. The synthesized epoxy resins were mixed physically with varying concentration of CTPB ranging between 0-25 wt% with an interval of 5 wt% all the samples were designated according to Table -1.

Table-1: Variation of cure time for the blend samples cured with polyamide at 150°C

S. No.	Sample code ^a	EN ^a resin (wt%)	CTPB (wt%)	Tp ^b (°C)	^c t _{cure} (min)	^d t _{cure} (min)
1.	ENC ₀	100	0	160	390	370
2.	ENC ₅	95	5	155	350	340
3.	ENC ₁₀	90	10	145	339	325
4.	ENC ₁₅	85	15	147	320	300
5.	ENC ₂₀	80	20	155	328	310
6.	ENC ₂₅	75	25	160	335	318

^a Phenol base epoxidized novolac resin'. The first numeric digit is the first digit from the weight percent of epoxy resin and the second numeric digit is the first digit of weight percentage of CTPB.

^b Results from the dynamic DSC scans. Tp : maximum temperature of exothermic peak, ^c Cure time without curing agent; ^d cure time with polyamide.

2.3. Analytical method:

Characterization of blend samples of uncured and cured samples were recorded on a Perkin-Elmer (Model 843) infrared spectrophotometer, using KBr pellet. Dynamic scans were recorded with a Perkin-Elmer differential scanning calorimeter (DSC) (Model Dymaond DSC, Switzerland) at a heating rate of 10°C/min in inert atmosphere upto temperature of 170°C to get cure temperature.

2.4. Preparation coating films:

The curing of blend samples with 40 wt% polyamide were performed in an air oven (M/s Indian Equipment Corporation, Mumbai, India) at 140°C. The panels were prepared by applying the blend samples on sand blasted steel sheet panels of sized 150 x 100 x 1.25 mm with a Bird film Applicator (Sheen, UK). These panels were sealed on three sides with molten paraffin wax. A dry film thickness of about 100 μm was maintained on all the panels.

2.5. Characterization of coating films:

The cure films were tested for their optical, mechanical and chemical resistance properties as per test methods viz. glass at 60° (ASTM: D523-99) scratch hardness (ASTM : D5178), pencil hardness (ASTM : D3363-00), chemical resistance (ASTM : D1308) and solvent resistance (ASTM : D5402).

The adhesion and flexibility of the cured films of the resin was tested by putting the prepared panels into 1/4 inch mandrel keeping the coated side downward. Then the two plates, connected to the mandrel, were readily bent. The bend portion of the panels was examined for any damage in the film. The impact resistance of the cured film samples was conducted by dropping a semi spherical shaped four-pound weight from 40 inch height over the panels. The test were carried out with the uncoated side of the panels facing the falling weights. The panels were also

examined for a visible change in the conditions of the film samples at regular intervals when immersed in different chemicals like solvents, acids and alkalis at ambient temperature for the period of twelve months.

RESULTS AND DISCUSSION

3.1 Studies on the FTIR spectroscopic analysis:

Fig.1 showed the FTIR spectra of phenol based deoxidized novolac resin. A broad absorbance centered about 3382 cm^{-1} might be assigned to H-bonded hydroxyls. As 15 wt% CTPB (sample EN₁₅) was added to the epoxy resin. The intensity of this band decreased and shifted to 3403 cm^{-1} (Fig.2). The region $3100\text{--}2800\text{ cm}^{-1}$ showed the C-H stretching nodes. The epoxide methylene (3008 cm^{-1}) decreased, but that for the ether methylene increased (2925 cm^{-1}). A new, but small peak at 3025 cm^{-1} appeared as CTPB was added to the epoxy resin which could be attributed to the presence of epoxy (CH–OH)–CH. The symmetrical methyl CH was assigned at 2880 cm^{-1} . The peaks at 1600 cm^{-1} (C = C Str) and 778 cm^{-1} (C–H–out of plane deformation) remained almost unaffected which indicate that the polymerization has taken place through substitution of CH₂OH rather through the double bonds in the side chain. The ether linkage resulting from the strained epoxy ring had absorbance assigned at 1259 cm^{-1} , 1045 cm^{-1} , 912 cm^{-1} and 856 cm^{-1} . These band shifted as CTPB was added to the neat epoxy resin (refer Hg-Z). A new stretching peak near 1363 cm^{-1} appeared in the spectrum of blend sample, EN15, which indicate that there occurred a chemical reaction between epoxy group and CTPB and formed a carboxylate amine in the blend.

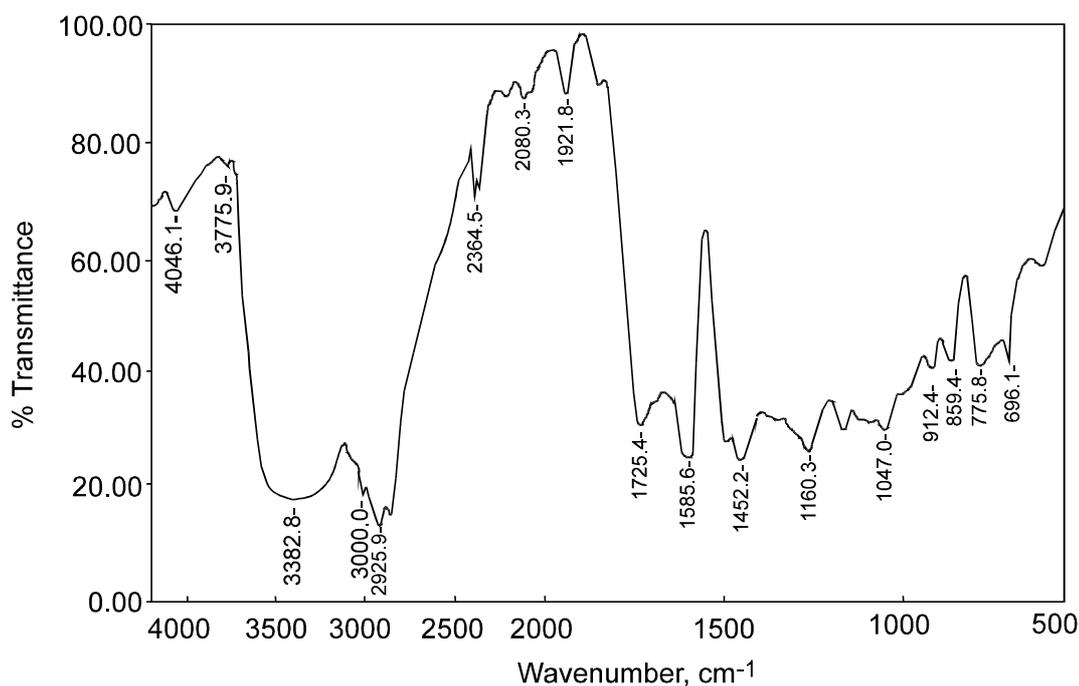
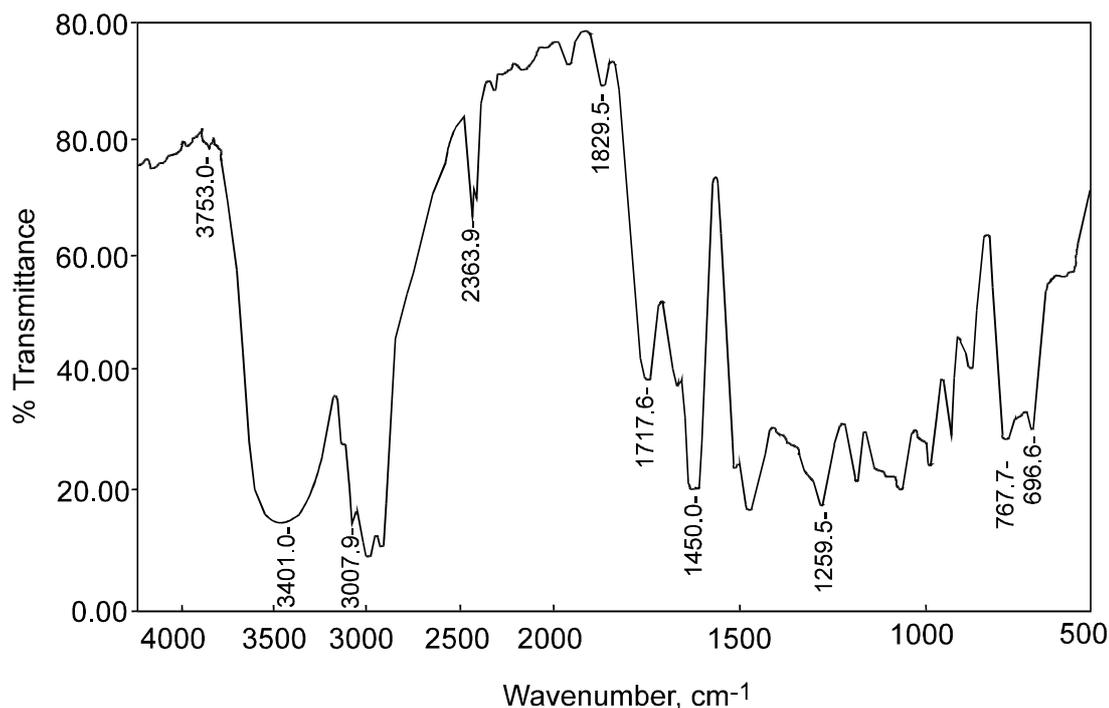
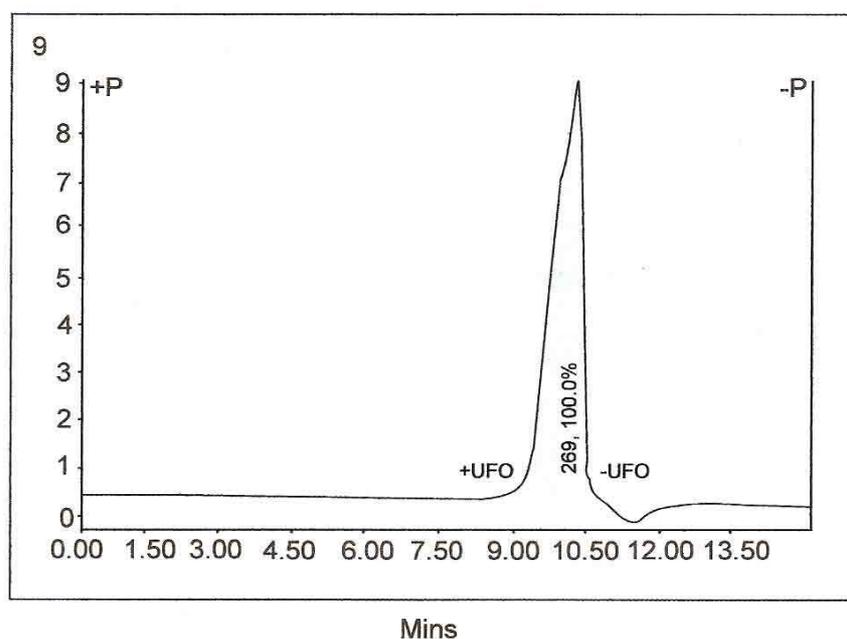


Fig.1: IR spectrum of epoxy-novolac resin

**Fig.2:** IR spectrum of epoxy-novolac and CTPB blend.**Fig. 3** GPC graph of epoxy novolac resin

3.2 Effect of CTPB on cure time of blend samples:

The initial addition of nearly 5 wt% CTPB in the blend decreased the cure time sharply and this trend remained up to 15 wt% CTPB (refer table 1). Beyond 15 wt% CTPB, the increase of cure time was very slow up to 25 wt% addition of CTPB in the blend system. Infrared studies have shown previously that the oligomeric dicarboxylic acid first formed a salt with polyamide [14], which might be responsible for phase separation leading to particle precipitation up to 15 wt% CTPB addition in the blend, the carboxylate salt in fact, would subsequently react very rapidly with the epoxy groups of the epoxidised novolac resin.

3.3 Mechanical properties of coating films:

Mechanical properties of the blend samples, showed in table 2. The cured films of all blend samples containing 5-25 wt% CTPB showed smooth and uniform with semi glassy surfaces.

Table 2: Mechanical properties of modified epoxy and CTPB blend films

S. No.	Properties	Results					
		EN ₀	EN ₅	EN ₁₀	EN ₁₅	EN ₂₀	EN ₂₅
1.	Scratch hardness (g)	2300	2500	2600	2750	2900	3100
2.	Pencil hardness	2H	3H	4H	4H	4H	5H
3.	Cross hatch hardness (%)	100%	100%	100%	100%	100%	100%
4.	Flexibility test in 1/4 mandrel	Pass	Pass	Pass	Pass	Pass	Pass
5.	Impact resistance (cm)	85	110	115	125	140	155
6.	Gloss at 60° (%)	65	70	78	79.5	81.5	85

All the films of blend samples passed through adhesion and flexibility test expect for pure epoxy samples, viz. The blend samples showed improved impact resistance then that of pure epoxy resin. The flexibility improvement may be though due to the presence of some dissolved rubber particle inside the epoxy matrix. These properties illustrated that the coating prepared from the blend samples had a quality appearance, indicate homogeneity throughout the coating and relatively good film properties.

3.4 Chemical resistance properties of blend samples:

Table-3 showed the comparative acids and alkalis of the cured films of phenol based epoxidized novolac resin and its blends with different weight ratio of CTPB. The mixture of different epoxidized novolac resins and HMTA have offered maximum resistance towards different concentrations of acid and alkalis as compared to the films of other epoxies. The cured film of these blend sample was completely unaffected by 10% sulphuric acid solution for the entire period of exposure of 10 months. The films when exposed to 20% sulphuric acid and hydrochloric acid solutions were found to be resistant for 11 months where as in other solutions, they were resistant for less than 81 months. The film of blend samples containing 15 wt% CTPB showed better resistance towards all acid solutions as compared to the film of blend samples containing 5, 10, 20 and 25 wt% CTPB (Table 3). The lower concentration of alkali solution less affect the film surface then higher alkali solution (Table 3). This behaviour might be attributed to the fact formation of more crosslink structure by the addition of epoxy resin.

Table 3: Comparative study of acid, alkali and solvent resistance of modified epoxy and CTPB blend film^a cured at 150°C showing the period after first effect observed

S. No.	Reagents	Period of months					
		EN ₀	EN ₅	EN ₁₀	EN ₁₅	EN ₂₀	EN ₂₅
1.	Sulphuric acid 10%	7	9	11	12	11	11
2.	Hydrochloric acid 10%	8	10	11	11	10	10
3.	Acetic acid 10%	11	11	11	>12	>12	>12
4.	Sodium hydroxide 10%	10	11	11	>12	>12	11
5.	Ammonium hydroxide 10%	10	11	12	>12	>12	12
6.	Xylene	12	12	12	>12	>12	>12
7.	Ethanol	7	9	10	11	11	11
8.	MEK	5	8	10	12	10	9

^a Film thickness of about 100 µm on glass panels with wax sealing from all sides.

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