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CURE CHARACTERIZATION OF RUBBER MODIFIED EPOXY NOVOLACS

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Abstract

A new type of toughened epoxy polymer based on epoxy cresol novolac resin (ECN) and carboxy terminated polybutadiene (CTPB) liquid functional rubber has been studied. ECN has been synthesized in the laboratory and CTPB used was also of indigenised origin. Rubber modified epoxies were characterized with the help of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) techniques.

Keywords: carboxyterminated polybutadiene, DSC, DMA, SEM, toughened epoxy

Introduction

The toughness of polymeric systems especially thermosets and thermoplastics has been studied extensively in the past and this subject still remains a matter of great debate concerning the paramount factors governing fracture, deformation and ultimate ductility [1, 2]. Amongst various thermosets, epoxies are the only class where rubber toughening has proven to be much more efficacious compared to those of unsaturated polyesters, polyimides or phenolics. Epoxy resins can also be toughened with a variety of substances, including reactive liquid acrylonitrile copolymers, [carboxyterminated butadiene-nitrile (CTBN) or amino terminated butadiene-nitrile (ATBN)], solid rubbers e.g., fluoroelastomers, acrylic rubbers, etc., acrylonitrile-butadiene-styrene copolymers (ABS) and ether-ester type of copolymers [3]. The role of matrix ductility on the toughenability and toughening mechanism of CTBN modified diglycidyl ether – Bisphenol A (DGEBA) based epoxies have been investigated by Pearson and Yee [4–7], Sultan and McGarry [8] and Bascom *et al.* [9].

Evaluation of effective crosslink density of matrix resin, measurement of glass transition temperature (T_g) and cure characterization through differential scanning calorimetry (DSC) and dynamic mechanical properties of DGEBA modified with CTBN have also been reported [4, 10].

In the present work attempt has been made to develop a toughened thermoset i.e. ECN using carboxy terminated polybutadiene (CTPB) as a potential additive. Cure characterization of the matrix resin through differential scanning calorimetry in presence of the liquid rubber, determination of their dynamic mechanical prop-

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erties and as well as evolution of phase morphology using scanning electron microscopy technique have been reported.

Experimental

Synthesis of o-cresol novolac

A mixture of *o*-cresol and formaldehyde (40% solution) in a ratio of 1.00:0.85 was refluxed in a three-necked flask for 3 h at *pH* 4–5 in presence of trichloroacetic acid till a standard molecular weight (Mw 450–500) for the novolac was attained.

Synthesis of epoxy novolac resin

A mixture of the novolac, as synthesized above and epichlorohydrin was heated at 120°C and at a *pH* of 9–10 with continuous addition of aqueous solution of NaOH (40%) for 3 h and a half. Afterwards, the unreacted epichlorohydrin and water has been removed by distillation. The residue was dissolved in toluene and filtered to remove sodium chloride. The filtrate was distilled under vacuum and thus epoxy cresol novolac (ECN) resin of 215 epoxide equivalent weight (EEW) and 0.476 epoxide content (EC) was obtained. EEW of ECN resin was determined by standard ASTM D-1652 method.

Blending of ECN with CTPB

Table 1 shows the characteristic properties of CTPB used in the present study.

Table 1 Typical properties of CTPB

No.	Property	Values
1	Brookfield viscosity mPa's (27°C)	60000
2	Carboxyl content %	1.9
3	Specific gravity (25°C)	0.907
4	Percent volatiles	<2.0
5	Functionality	2.0

Table 2 Composition of ECN and CTPB blends containing DDM

No_{blends}	ECN	CTPB	DDM
		gm	
I.	95	5	21.5
II.	90	10	20.0
III.	85	15	19.0
IV.	80	20	18.0
V.	75	25	17.0

Table 2 shows the formulation of the mixes with varied ECN and CTPB contents along with requisite amount of diaminodiphenyl methane (DDM) used as curing agent for epoxy. The weight of DDM was affixed on EEW of the ECN. To a preheated and mechanically stirred epoxy novolac resin in a reaction kettle at 60°C, DDM pellets were added. After complete dissolution of the DDM, CTPB was added and blended with the epoxy. Castings of the blends were prepared in a pretreated iron moulds at 160–165°C.

Infrared spectroscopy

FTIR experiments for both the *o*-cresol novolac and ECN resin were carried out in NICOLET MAGNA IR 750 SPECTROMETER with standard KBr pellets.

Differential scanning calorimetry (DSC)

DuPont's 9900 model thermal analyser was used to obtain the DSC curves of the blends. The blends were heated from room temperature upto +350°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere and corresponding curve for each blend was recorded.

Dynamic mechanical analysis (DMA)

DuPont's 983 dynamic mechanical analyser was used to analyse the DMA characteristics of the blends. The samples were heated from ambient to +450°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere. Flat samples for each blends of size 5×1×0.3 cm^3 were prepared from cast sheets and used for the DMA studies.

Scanning electron microscopy (SEM)

JEOL JSM-35 CF scanning electron microscope was used to analyse the morphology of the blends. The cast sheet samples were fractured under liquid nitrogen to avoid any deformation of the rubber capsules inside the epoxy matrix. The fractured surfaces were then sputter coated with gold without touching the surface. Subsequently, the gold coated samples were studied under the SEM for morphological informations.

Results and discussion

Both the synthesized monomer (novolac) as well as the polymer (ECN) were characterized through FTIR and the corresponding spectrums are shown in Figs 1 and 2 respectively.

The IR spectra of *o*-cresol novolac shows the absorption band at 3401 cm^{-1} (–OH phenolic); 2912 cm^{-1} (–CH, str.); 1591 and 1490 cm^{-1} (C=C, aromatic) and additional bands at 1378 and 1250 cm^{-1} (C=C, aliphatic). Similarly, IR spectra of ECN shows the absorption bands at 2922 –30 cm^{-1} (–CH, str); 1608 cm^{-1} (–CH, bend.); 1503 and 1453 cm^{-1} (C=C, aromatic); and additional bands at 1379, 1341 and 1291 cm^{-1} (C –C); 1254 and 1131 cm^{-1} (C –O) and 912 and 860 cm^{-1} due to epoxy functionalities.

In *o*-cresol novolac monomer the intensity of hydroxyl peak at 3401 cm^{-1} diminishes due to replacement of hydroxyl group by the epoxy group. In the IR spectra of polymerised resin, the peak intensities at 912 and 860 cm^{-1} increase which again confirms the epoxidation of *o*-cresol novolac.

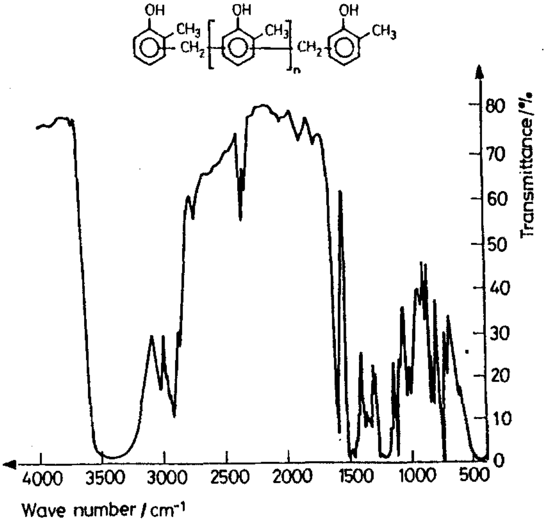

Fig. 1 IR spectra of *o*-cresol novolac

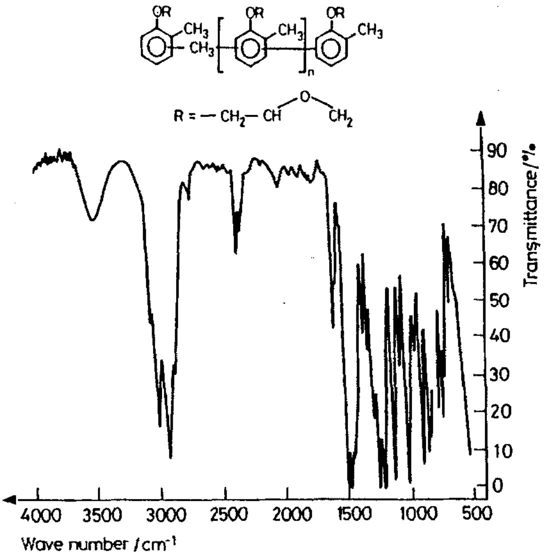

Fig. 2 IR spectra of epoxy cresol novolac resin

Table 3 Thermal properties of ECN and CTPB blends

No$_{\text{blends}}$	T_{onset}/	T_{exo}/	$T_{\text{std. cure}}$/	$t_{\text{total cure}}$/	Heat of reaction/
		°C		min	J g^{-1}
I.	80.0	160.49	160.0	16.0	287.7
II.	70.0	163.74	170.0	17.0	219.3
III.	70.0	156.11	170.0	17.0	172.2
IV.	80.0	150.77	145.0	14.5	152.5
V.	90.0	145.51	130.0	13.0	126.8

Table 3 gives the results of thermal properties during curing of ECN and CTPB blends in presence of DDM. Curing starts around 80±10°C irrespective of the CTPB content in the blends. CTPB does not affect either the cure rate or the final cured state of the resin. This is reflected in the gradual decrease of the peak exotherm temperatures, curing temperatures and curing times with increasing CTPB concentration in the blends. Heat of reaction shows a decreasing trend as the CTPB content is increased. The decrease may be due to the compatibility of ECN and CTPB which results adduct between CTPB and ECN more so at higher CTPB content.

Table 4 Dynamic mechanical properties of ECN and CTPB blends

No$_{\text{blend}}$	Crosslink density (× 10^{-3} mol cm^{-3})	$E'_{\text{(storage modulus)}}$/ GPa	$E''_{\text{(loss modulus)}}$/ MPa	tanδ	T_g/ °C
1	0.446	0.3087	74.72	0.2423	160
2	0.426	0.2960	63.50	0.2144	145
3	0.295	0.1679	40.63	0.2420	180
4	0.267	0.1395	33.93	0.2432	180
5	0.231	0.0986	24.74	0.2507	180

DMA analysis of the ECN-CTPB blends with varied CTPB concentrations have also been carried out and the results are appended in Table 4. Crosslink density data show marginal fall upto 10 wt% concentration of CTPB beyond which a sharp fall is observed. The values for both tanδ and T_g also showed marked changes upto 10 wt% CTPB beyond which no significant changes occurred with increasing CTPB content in the blends. Sharp decrease in crosslink density with increasing CTPB content beyond 10% may be due to copolymerization of oxirane group of epoxy with CTPB. Formation of extra crosslinks between CTPB and epoxy caused a simultaneous increase in the rigidity of the system and thereby increasing both T_g and tanδ values. However, as expected, both storage modulus (E') and loss modulus (E'') at T_g showed monotonic decrease with increasing CTPB content in the blends.

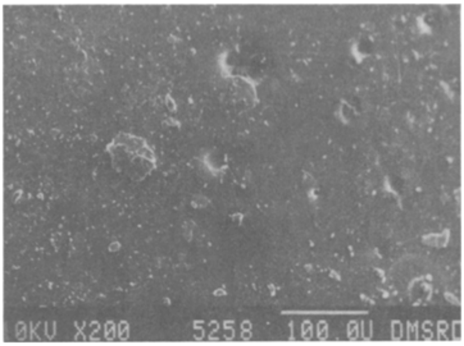

Fig. 3 SEM photomicrograph of the cross section of ECN-CTPB blend containing 5 wt% CTPB

The phase morphology of the cross-sections of the cast film were studied through SEM. Figure 3 is the SEM photograph of the morphology of the blend containing 5 wt% CTPB. Discrete microscopic rubber particles with average size of the order of 3–6 μm and spread uniformly over the entire matrix have been observed. Increasing CTPB content changes the size and distribution of the discrete phase embedded in the continuous rigid resin matrix. At 10 wt% CTPB content (Fig. 4), dispersed globules (average size of 17 μm) were found to contain two groups of particles in the average size distribution. One group of particles with smaller average particle size of the order of 3–6 μm and comparatively larger particles having an average size of 25 μm. Particles with lower scale of dimensions, act as stress absorbers and enhances the toughness characteristics of the matrix by efficient stress softening and crazing processes involved during the growth of fracture. However, when the particle size grows larger, of the order of 10 μm or more, flexibility of the matrix is improved both due to improvement of the ductility as well as shear deformation during fracture propagation. An improvement in the fracture toughness properties of the matrix is, therefore, evident even when the CTPB con-

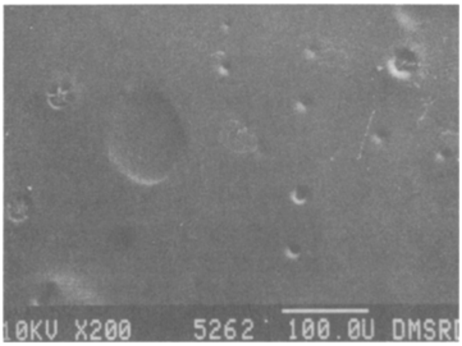

Fig. 4 SEM photomicrograph of the cross section of ECN-CTPB blend containing 10 wt% CTPB

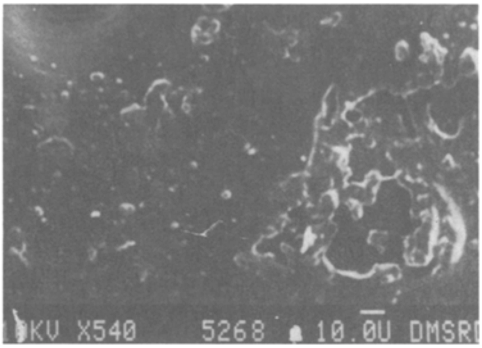

Fig. 5 SEM photomicrograph of the cross section of ECN-CTPB blend containing 25 wt% CTPB

tent is increased beyond 10 wt%. At much higher concentration of CTPB e.g., at 25 wt%, coalescence of the dispersed particles was evident. The system in this case behaves more like a binary blend of ECN and CTPB rather than a rubber-toughened epoxy system.

Conclusion

1. ECN based resins find wide usages in applications where high strength, strong adhesions, excellent dielectric property, improved oxidation and flame resistance are desired in the end product. However, these resins are brittle. In the present study, functionalised liquid elastomer CTPB has successfully been utilized as a potential toughening agent for the ECN system.

2. DSC, DMA and SEM are found to be useful tools for measurement of cure characterization, performance evaluation as well as determination of the phase morphology of these rubber toughened epoxy systems.

3. Further work on mechanical and impact properties, effect of chain extenders and possibility of evolving other such systems based on more reactive additives in ECN's needs to be carried out for better understanding of the mechanism of fracture and scope of applications.

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