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Studies on the physico-mechanical and thermal characteristics of blends of DGEBA epoxy, 3,4 epoxy cyclohexylmethyl, 3′, 4′-epoxycylohexane carboxylate and carboxyl terminated butadiene co-acrylonitrile (CTBN)

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ABSTRACT

Toughening of blend of diglycidyl ether of bisphenol-A (DGEBA) and 3,4 epoxy cyclohexylmethyl, 3′,4′-epoxycylohexane carboxylate, i.e. cycloaliphatic epoxy resin (CAE) with varying weight ratios (0–25 wt%) of carboxyl terminated butadiene acrylonitrile (CTBN) copolymer have been investigated. Fourier transform infrared (FTIR) spectroscopic analysis established that the interaction between oxirane groups of DGEBA, CAE and CTBN were responsible for characteristics peak shifts in the blends compared to their counterparts. Physico-mechanical properties of the prepared samples, e.g. tensile, flexural and impact strengths showed an optimum concentration of CTBN (15 wt%) into epoxy matrix, which offered maximum toughening. Thermal stability of the prepared samples was analyzed by dynamic thermogravimetric runs. Cross-sections of the cured samples which failed during impact testing have been critically studied through scanning electron microscopic (SEM) analysis to gain insight into the phase morphology.

1. Introduction

Cured epoxy resins are widely used in the fields of coatings, adhesives, insulating materials, matrices for fibrous composites, etc. for their appropriate material properties including mechanical properties, thermal and chemical stability. On the other hand, because of their high cross-linking density, epoxy resins are inherently brittle. This brittleness of epoxy resins is one of the major obstacles preventing epoxy's wider application use in industries. Therefore, much research have been carried out to enhance the toughness of the cured epoxy resins and one of the most well known methods is to incorporate various amounts of reactive rubber into the epoxy matrix [1,2]. In this way, carboxyl-terminated butadiene acrylonitrile (CTBN) copolymer was introduced to the epoxy systems particularly with glycidyl-type epoxy resins such as diglycidyl ether of bisphenol-A (DGEBA) epoxy resin along with the curing agent. When such epoxy resin together with liquid rubber is cured, the rubber domain improves the toughness by absorbing the impact energy [2]. It is well known that the cured resins are two phase systems, in which the liquid rubber is dispersed in a matrix of epoxy with a spherical domain structure or a continuous structure, as a result of phase separation, which proceeds via spinodal decomposition induced by the increase in molecular weight of the epoxy during the curing process [3].

The toughening of non-glycidyl-type epoxy resin such as cycloaliphatic epoxy resin (CAE), i.e. 3,4 epoxy cyclohexylmethyl, 3′,4′-epoxycylohexane carboxylate had also been done with different reactive agents [4–7]. The toughness of these resins has been increased by blending them with reactive liquid rubber like CTBN [4], terminally functionalized engineering thermoplastic [5,6] and carboxyl terminated latex [7]. There are also some reports [8–11] on the blend system containing 3,4 epoxy cyclohexylmethyl, 3′,4′-epoxycylohexane carboxylate (CAE) with DGEBA with special emphasis on the studies on thermal and mechanical properties. Therefore, we have tried to prepare the blend system containing 3,4 epoxy cyclohexylmethyl, 3′,4′-epoxycylohexane carboxylate and DGEBA epoxy resins and toughened with CTBN, in the present investigation, and co-related their micro and macro properties.

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Table 1
Sample designation

S. no.	DGEBA:CAE (3:1) (wt%)	CTBN (wt%)	DDS (wt%)	Sample code
1	100	0	36	EP_{3100}
2	95	5	34.2	EP_{3105}
3	90	10	32.4	EP_{3110}
4	85	15	30.6	EP_{3115}
5	80	20	28.7	EP_{3120}
6	75	25	27.0	EP_{3125}

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol-A based epoxy resin (viscosity: 1000–1500 mPas at 27 °C and non-glycidyl type cycloaliphatic epoxy resin, i.e. 3,4 epoxy cyclohexylmethyl, 3′,4′-epoxycylohexane carboxylate (viscosity: 1300–1800 mPas at 27 °C) used in all experiments were LY 556 and CY 230 (epoxide equivalent weight: 192 and 145 eq/g) and cure agent 4,4′-diamino diphenyl sulphone (DDS) (HT 976) were procured M/s Ciba Specialty Chemicals Pvt. Ltd., Mumbai, India. The elastomer employed was carboxyl terminated butadiene acrylonitrile copolymer (viscosity: 625,000 mPas at 27 °C) (Trade name: Hycar 1300X13) and was kindly supplied by M/s Emerland Performance Materials, LLC, Hong Kong, with molecular weight $\overline{Mn}$ of 3500 g/mole, containing 27% acrylonotrile content and 32% carboxyl content.

2.2. Preparation of samples

Six samples containing 0–25 wt% CTBN were prepared according to the procedure as reported in our previous publication for DGEBA epoxy resin [12]. The calculated quantity of DGEBA epoxy and CAE epoxy resin (as per formulation given in Table 1) was, firstly, stirred at 120 °C for 1 h to entrap out all air bubbles from the resin. To this homogeneous resin system, the calculated quantity of DDS was added and stirred at 150–155 °C for 45 min to get clear homogeneous mixture.

2.3. Curing of blend samples

The cure process of all blend samples followed four steps: first, the epoxy resin was degassed followed by addition of 0–25 wt% CTBN in the epoxy resin. To this mixture 36 phr DDS was added and finally, the whole mixture degassed again. The mixture were poured into preheated iron mold and cured into hot air oven at 170 °C for 1 h and then post cured for 2 h at 200 °C. Specimens for the entire test were cut from this block.

2.4. Characterization of samples

2.4.1. Fourier-transform infra-red (FTIR) spectroscopy

FTIR spectroscopy has been used to monitor the chemical reactions between DGEBA epoxy resin/cycloaliphatic epoxy resin/CTBN/DDS blend systems. For the infrared (IR) measurement a small portion of the cured epoxy system was grind to a fine powder, mixed with potassium bromide (KBr) powder and pressed into a pellet by hand press. For the liquid (uncured) samples, sodium chloride (NaCl) pellets were used and very little quantity of the material was kept in between them. FTIR were recorded by Nicollet Magna 750 spectrophotometer in the wavelength range of 4000–400 cm^{-1}.

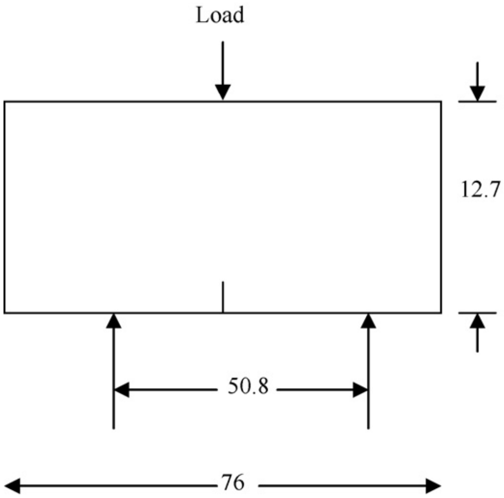

Fig. 1. Schematic illustration of the SEN-3PB specimen used in this study. Dimensions are in millimeters.

2.4.2. Differential scanning calorimetric (DSC) analysis

Cure temperature of the prepared samples was observed by taking very little quantity of blend samples into shallow aluminium pan of DSC (TA Instrument, USA; Model DSC 2920), which was sealed by an aluminium cover. This was placed in sample cell of the instrument. The starting temperature was ambient, programmed rate was 10 °C/min and final temperature was 350 °C. Dynamic scans were obtained which were used for assuming the cure temperature.

2.4.3. Mechanical testing

Flexural tests were performed using Hounsfield Tensometer W-5236 testing machine fitted with a three-point-bending fixture at a cross-head speed of 1 mm/min. according to ASTM D-790. The dimensions of the specimens were 75 mm × 15 mm × 3 mm and the span to thickness ratio was set at L/D = 32–1 in all cases. The values were taken from an average of at least five specimens.

The tensile tests were performed in Tinius Olsen Patent No-2, 784, 048 machine at a cross-head speed of 1 mm/min according to ASTM D-638. The values were taken from an average of four specimens.

The impact strength of the specimen was determined by using Charpy Mandate Tensometer using rectangular specimens of 75 mm × 15 mm × 3 mm according to ASTM D-256. The tests were carried out at room temperature and values were taken from an average of at least four samples. Samples for all the tests were cut from the cured sheet of 6″ × 6″ with the help of cutting machine.

Six-millimeter thick samples were used for specimens to determine fracture toughness (Fig. 1). It employed precracked, single-edge notched (SEN) specimens loaded in three-point bending geometry. The ASTM D-5045 guidelines were followed to measure the plane strain fracture toughness (K_{IC}). Pre-cracks were introduced to the notched bars by hammering a razor blade which was chilled in liquid nitrogen. These tests were performed over UTM at a cross-head speed of 5 mm/min. K_{IC} values reported represent averages of a minimum of five tests. The following equations were used to calculate K_{IC} which was in accordance to reference [13].

$$K_{IC} = \frac{10^{3/2} \times P \times S}{t \times w^{3/2}} f(x) \quad (1)$$