

Modification of bifunctional epoxy resin using CO₂ fixation process and nanoclay



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HIGHLIGHTS

- A new epoxy resin was synthesized using CO₂ fixation reaction.
- The synthesized epoxy resin was modified by an organo nano-clay.
- CO₂ fixation noticeably changed the curing mechanism.
- CO₂ fixation reaction consumes CO₂ which is a harmful greenhouse gas.

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ABSTRACT

A bifunctional epoxy resin was modified by using a CO₂ fixation solution process in the presence of tetra n-butyl ammonium bromide (TBAB) as catalyst and the modified treated resin was treated by cloisite 30B as nano additive. The Unmodified epoxy resin (UME), CO₂ fixated modified epoxy resin (CFME), and CFME/clay nano composite (CFMEN), were cured by diethylenetriamine (DETA). A cycloaliphatic compound as a reactive diluent was used to control the viscosity of high viscose CFME. The exfoliation of organoclay in UME and CFME was investigated by X-ray diffraction and activation energy was computed using the advanced integral isoconversional method. The activation energy dependency demonstrated that the mechanism of UME curing did not change in the presence of nanoclay. In contrast, the CO₂ fixation results showed a significant change in the activation energy dependency. The Thermal stability parameters include the initial degradation temperature (IDT), the temperature at the maximum rate of weight loss (T_{max}), and the decomposition activation energy (E_d) were determined by thermal gravimetry analysis. Dynamic mechanical thermal analysis measurements showed that the presence of organoclay in CFME increases the T_g of nano composite in contrast to UME. The fracture roughness of UME, CFME and CFNE were determined by scanning electron microscope. The exfoliated UME/1%clay nanocomposite was confirmed by TEM image.

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1. Introduction

Epoxy resins are an important class of thermoset resins where synthesized and crosslinked by mixing with suitable catalysis show brittle behavior after curing. The application of epoxy resins is widespread, including adhesives, foams, coatings, laminates and composites. Epoxy resins as adhesives have ability to form a strong bond with various surfaces. Epoxy based- foams, composites and laminates are used in air- and spacecraft industries [1].

Epoxy modification methods are reported by many researchers [2–6]. In some methods, organo- montmorillonite (O-MMT) has

been dispersed in epoxy resins to form nano composite [7,8]. Epoxy/nanoclay composites have superior properties such as flame retardancy, enhanced barrier properties and anti corrosive properties [9]. The properties of epoxy based nanocomposites such as thermal stability depend on the dispersion of organo montmorillonite into the matrix [10,11]. The toughness of epoxy resins has been modified by elastomeric modifiers such as poly siloxanes and fluoroelastomers [12]. The thermal stability, mechanical properties, fracture toughness, morphology of epoxy/Al₂O₃ nanocomposites and the catalytic effect of alumina nano-particles on the curing of epoxy resins has been investigated [13–17].

Due to the increase in the amount of greenhouse gases such as Carbon dioxide, it is increasing to find ways to consume these gases. Carbon dioxide may be used as a profound resource for

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manufacturing commercially viable products through carbonation reaction. The fixation of carbon dioxide is one of the important processes which consumes CO₂ as primary material [18]. Carbon dioxide fixation is carried out in the presence of various catalysts such as, Alkali ammonium halides [19], halide salts [20], ionic liquid salts [21–24], polymeric ion liquid [25], quaternary phosphonium salts [26,27], transition-metal complexes [28,29], and ion-exchange resins [30]. This reaction may be carried out by a class of materials having epoxy group such as, epoxy resin [31], GMA based polymer [24,32,33], natural rubber [34], Vernonia Oil [35], and epoxidized Soybean Oil [36].

Cyclic carbonate, a result of reaction between CO₂ and epoxy group, is an important and attractive reaction in the variety of chemical systems. Because of high solubility, high boiling and flash point, low toxicity, and biodegradability, the cyclic carbonate is a useful aprotic solvent for paint stripping and cleaning [22]. The cyclic carbonates may react with various compounds such as, aromatic amines, alcohols, carboxylic acids and aliphatic alcohols, to synthesis polycarbonates and aliphatic amines to form urethane group [37].

CO₂ fixation reaction has been carried out on a bifunctional epoxy resin and the gel time, deflection temperature, impact resistant, dynamic viscosity, and mechanical properties have been investigated [31,38]. It is shown that, the gel time of the modified epoxy resin depends on the epoxy content and is less than that of unmodified epoxy resin. The reason is that, the activation energy of epoxy resin curing is higher than that of cyclic carbonate curing. The deflection temperature and the impact resistant of modified epoxy resin are higher than those of unmodified epoxy resin. The dynamic viscosity of the modified epoxy resin is also higher than that of unmodified epoxy resin due to the strong interactions between epoxy chains in modified epoxy resins. In the modified epoxy resin, the tensile strength and elongation at break are less than those of unmodified epoxy but the compressive strength and plastic strain are higher than those of unmodified epoxy resin.

In this work, an epoxy resin was modified using the carbon dioxide and bifunctional epoxy resin in the presence of methyl ethyl ketone as solvent and TBAB as catalysis, and characterized using FT-IR technique. Both unmodified epoxy resin (UME) and CO₂ fixation modified epoxy resin (CFME) were treated by organically modified clay (Cloisite[®] 30B). The effect of CFME polarity on the dispersion of organoclay for this new CFME/clay nano composite (CFMEN) was investigated. The curing behavior, dynamic mechanical properties, thermal stability and surface morphology of prepared resins were studied.

2. Experimental

2.1. Material

Chemical structures of technical-grade epoxy, curing agent and catalyst are shown in Table 1. A commercial grade epoxy resin mainly based on diglycidyl ether bisphenol A (DGEBA) with 185–192 EEW was cured with diethylene triamine in the presence of tetra-n-butyl ammonium bromide as catalyst. Organo-montmorillonite (Cloisite 30B) from Southern Clay Products was used as nanoclay. Reactive diluent (3,4 epoxy cyclo hexyl methyl -3,4 epoxy-cyclo hexane carboxylate) (ECC) was used to reduce the viscosity of system. Methyl ethyl ketone (MEK) was used as solvent provided by DAE Jung.

2.2. Preparation of CO₂ fixation modified epoxy resin (CFME)

65 g of epoxy resin, 3gr TBAB and 65 g MEK were poured into a flask and mixed at 78 °C for 1 h, and then CO₂ was purged into the vessel. CO₂ fixation reaction was conducted in two successive steps, after 160 min and 225 min respectively, 25% (25%CFME) and 39% (39%CFME) cyclic carbonate were formed. Then 39 g reactive diluent was added to 25%CFME and 39% CFME.

2.3. Preparation of CO₂ fixation nano composite modified epoxy resin (CFMEN) by solution method

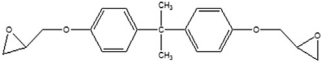
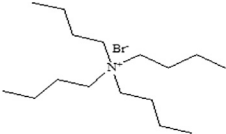
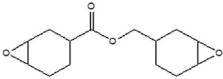
1%wt and 3%wt of cloisite 30B were added to MEK and sonicated for 10 min with a Bandelin HD3200 ultrasonic. The solution was added to CFME and vigorously mixed at 1700 rpm for 4 h. CFME was placed in a vacuum oven to remove the solvent, and then curing agent (DETA) was added by the weight ratio of 100:12 (DGEBA/hardener). The slurry mixtures were poured into aluminum molds and cured at 25 °C for 2 days and followed by post curing at 120 °C for two hours.

2.4. Characterization techniques

The curing behaviors of organoclay modified epoxy resin were studied using a differential scanning calorimeter (200-F3Maia) at heating rates of 8, 10, 12 and 15 °C min⁻¹ and at temperature range of 30–300 °C.

The dynamic mechanical properties and the glass transition temperature were determined using a dynamic mechanical analyzer (TRITEC 2000 DMA) in a bending mode with

Table 1
Technical-grade epoxy, curing agent, catalyst and reactive diluents used in this study.

Material	Chemical structure	Chemical name	Commercial name
Epoxy resin		Diglycidyl ether bisphenol A (DGEBA)	EPON 828
catalyst		Tetra n-butyl ammonium bromide	TBAB
Reactive diluent		3,4 epoxy cyclo hexyl methyl -3,4 epoxy-cyclo hexane carboxylate (ECC)	Cyclo aliphatic reactive diluent
Curing agent	$2\text{HNCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$	Diethylenetriamine	DETA

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