

## Thermal Stability and Impact and Flexural Properties of Epoxy Resins/Epoxidized Castor Oil/Nano-CaCO<sub>3</sub> Ternary Systems

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**Abstract:** Epoxy ternary systems were prepared from the diglycidylether of bisphenol-A (DGEBA), epoxidized castor oil (ECO), and nano-CaCO<sub>3</sub> using a thermally latent initiator. The effects of ECO and the nano-CaCO<sub>3</sub> contents on the thermal stability and mechanical interfacial properties of the prepared DGEBA/ECO/nano-CaCO<sub>3</sub> ternary systems were examined by thermogravimetric analysis (TGA), Izod impact tests, and mechanical tests. The morphology of the ternary systems was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The statistic heat-resistant index temperature ( $T_i$ ) of the ternary systems was approximately constant up to 30 wt% ECO, and thereafter decreased with increasing ECO content. The impact strength of the ternary systems was improved by the addition of ECO and nano-CaCO<sub>3</sub>. The flexural strength of the ternary systems exhibited a maximum value at 20 wt% ECO. SEM showed that shear deformation occurred, which prevented the propagation of cracks in the DGEBA/ECO/nano-CaCO<sub>3</sub> ternary systems.

**Keywords:** epoxy resins, nano-CaCO<sub>3</sub>, epoxidized castor oil, thermal stabilities, impact strength.

### Introduction

Epoxy resins have been widely used for coatings, electronic materials, adhesives, and matrices for fiber-reinforced composites due to their outstanding mechanical properties ranging from extreme flexibility to high strength and hardness, high adhesion strength, good heat resistance, and high electrical resistance.<sup>1,2</sup> However, cured epoxy resins are inherently brittle due to high crosslinking density, thus posing a constraint on many engineering applications. Epoxy resins are commonly modified by liquid elastomers, thermoplastics, and inorganic particles.<sup>3-6</sup> Recently, several researchers have investigated the preparation and mechanical characterization of epoxy resins using various epoxidized vegetable oils. Chandrashekhara *et al.* reported the preparation and mechanical properties of fiber/epoxy composites using chemically modified soy-based epoxy resins.<sup>7</sup> Erhan *et al.* demonstrated the preparation of soybean oil/epoxy-based composites by solid freeform fabrication methods.<sup>8</sup> Miya-

gawa *et al.* presented the thermo-physical and impact properties of an epoxy resin/epoxidized linseed oil (ELO) system using poly(oxypropylene) triamine as a curing agent. The results indicated that the impact strength radically increased with an increase of ELO beyond 20 wt%.<sup>9</sup> Miyagawa *et al.* also reported on biobased nanocomposites processed from anhydride-cured epoxidized linseed oil/diglycidyl ether of a bisphenol F epoxy matrix and an organically-modified layered silicate clay.<sup>10</sup>

In previous work, we reported the thermal and mechanical properties of both epoxidized soybean oil (ESO) and epoxidized castor oil (ECO)-modified epoxy systems.<sup>11-15</sup> Studies on the properties of these systems have shown that the addition of ESO or ECO can effectively improve the fracture toughness of epoxy resins. However, the thermal stabilities of these systems at high ESO (or ECO) content were degraded with increasing ESO (or ECO) content. In the present study, ECO is used as a toughening phase to increase the toughness of diglycidylether of bisphenol-A (DGEBA) epoxy resins, and nano-CaCO<sub>3</sub> particles are added to recover the thermal property lost due to the addition of ECO. Characterization

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of DGEBA/ECO/nano-CaCO<sub>3</sub> ternary systems was carried out by a thermogravimetric analysis (TGA), an Izod impact tester, a mechanical tester, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

## Experimental

**Materials.** The petroleum-based epoxy resin used in this study was diglycidylether of bisphenol-A (DGEBA), supplied by Feichengdeyuan Chem. of China (E-51) and having an epoxide equivalent weight (EEW) of 185–208 g/eq. A biodegradable epoxy resin, epoxidized castor oil (ECO), was synthesized via a procedure reported in a recent work.<sup>11</sup> ECO has a viscosity of 716 CPS at 25 °C and a specific gravity of 0.975. Nano-CaCO<sub>3</sub> was supplied by WINNOFIL'S, Solvay, and had a mean particle size of 40–70 nm and a specific surface of 20–30 m<sup>2</sup>/g. *N*-Benzylpyrazinium hexafluoroantimonate (BPH), employed as a thermally latent initiator, was synthesized according to a previous report.<sup>12</sup> The chemical structures of DGEBA, ECO, and BPH are shown in Figure 1.

**Synthesis of Epoxidized Castor Oil.** Castor oil (45.9 g, 0.07 mol), glacial acetic acid (8.4 g, 0.14 mol), Amberlite (12.5 g), and toluene (20 g) were placed in a 500 mL four-neck round-bottom flask equipped with a mechanical stirrer, a thermometer sensor, and a reflux condenser. The mixtures were heated to a constant temperature of 55 °C. Then, 30% H<sub>2</sub>O<sub>2</sub> (28.4 g, 0.25 mol) was added slowly via a separating funnel and allowed to react at 55 °C for 7 h. The solution was subsequently filtered and washed with a saturated solution of NaCO<sub>3</sub> and distilled water. The toluene was removed by distillation under vacuum, and the product was further dried under vacuum at 80 °C for 2 h (yield: 84%). FTIR (KBr): 3009 cm<sup>-1</sup> (C=C), 822, 833 cm<sup>-1</sup> (epoxide group). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 5.3 ppm (2H, C=C), 2.9–3.1 (2H, epoxide group). <sup>13</sup>C NMR (CDCl<sub>3</sub>) 129.7–130.2 ppm (C=C), 54.0, 54.3 (epoxide group).

**Sample Preparation.** The weight content of ECO was varied from 5 to 20 wt%, and the weight content of nano-CaCO<sub>3</sub> was 1 wt%. The desired amounts of DGEBA, ECO,

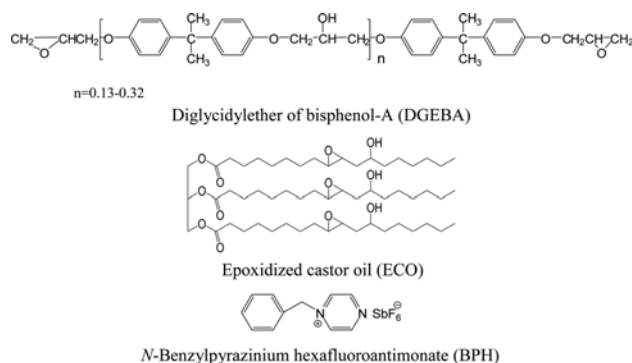


Figure 1. Chemical structures of the materials used.

and nano-CaCO<sub>3</sub> were mixed at 80 °C for 30 min and 1 wt% BPH was then added into the mixture. The mixture was thoroughly stirred by a magnetic stirring bar and sonicated for 1 h. The bubble-free mixture was poured into a pre-heated mold, which was sprayed with a mold release agent. Curing was performed at 120 °C for 1 h, at 160 °C for 2 h, and at 200 °C for 1 h in a convection oven.

**Characterization and Measurements.** IR spectra were obtained by a Jasco International Co., Ltd.'s Model FT/IR-4200 spectrometer by using KBr pellets. <sup>1</sup>H NMR and <sup>13</sup>C NMR characterizations were carried out with an UNITY-INOVA 400/Varian spectrometer using tetramethylsilane (TMS) as an internal standard. The thermal stabilities of the cured samples were studied with a DuPont TGA-2950 analyzer at a heating rate of 10 °C min<sup>-1</sup> from 30 to 850 °C under a nitrogen atmosphere. Impact-strength tests were performed using an Izod impact tester according to ASTM D 256. The sample size was 5×12.7×63.5 mm<sup>3</sup>. The flexural properties of the samples were measured via three-point flexural tests with an Instron Model 1125 mechanical tester according to ASTM D-790. The sample size was 2×25×50 mm<sup>3</sup>. All of the mechanical property values were obtained by averaging the five experimental values. The fracture surfaces after the impact tests were investigated using a scanning electron microscope (FE-SEM S-4300/HITACHI). Transmission electron microscopy photographs were obtained using a field emission-transmission electron microscope (FE-TEM, JEM2100/JEOL) with an accelerating voltage of 200 kV.

## Results and Discussion

**Thermal Stabilities.** The effects of ECO content on the thermal stabilities of the DGEBA/ECO systems were studied by TGA at a heating rate of 10 °C/min under a nitrogen atmosphere, and the results are presented in Figure 2. Thermal stability factors, including initial decomposing temper-

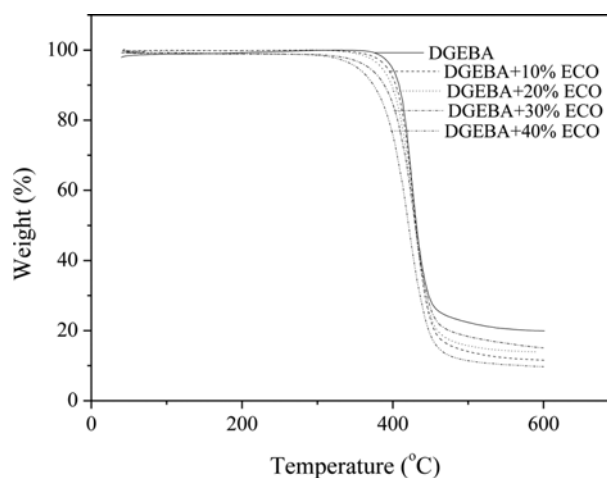


Figure 2. TGA thermograms of DGEBA/ECO systems.