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Cationic polymerization and physicochemical properties of a biobased epoxy resin initiated by thermally latent catalysts

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Abstract

The cationic polymerization and physicochemical properties of a biobased epoxy resin, epoxidized castor oil (ECO), initiated by *N*-benzylpyrazinium hexafluoroantimonate (BPH) and *N*-benzylquinoxalinium hexafluoroantimonate (BQH) as thermally latent catalysts were studied. As a result, BPH and BQH show an activity at different temperatures in the present systems. The cured ECO/BPH system showed a higher glass transition temperature, a lower coefficient of thermal expansion, and higher thermal stability factors than those of the ECO/BQH system. On the other hand, the mechanical properties of the ECO/BQH system were higher than those of the ECO/BPH system. These have been attributed to the differences in crosslinking level of cured resins, which were induced by the different activity of the latent catalysts.

Keywords: Castor oil; Epoxy resin; Cationic polymerization; Thermal properties; Mechanical properties

1. Introduction

Replacement of petroleum-derivated raw materials with vegetable oil-based polymeric materials is important in the social and environmental viewpoints [1–4]. Vegetable oil from plant sources is readily regenerated via photosynthesis. Recently, a variety of vegetable oil has been developed with knowledge of their physical and chemical properties obtained through the application of scientific research and development [5,6]. Among them, castor oil represents a promising raw material based on its low toxicity and its availability as a renewable agricultural resource [7].

Several families of castor oil-based polymers are synthesized and investigated with respect to their physicochemical properties, such as thermal stabilities, flame retardancy, and mechanical properties. The castor oil or brominated castor oil used as reinforcing agent is added to epoxy resins and good toughness and flame retardancy of cured epoxy resins are obtained [8,9]. And the synthesis and properties of castor oil-based polyurethane hybrid materials has been reported [10]. Recently, the synthesis and thermal properties of epoxidized vegetable oil initiated by a thermally latent catalyst are also studied [11].

Latent catalysts are inert under normal conditions, i.e., at an ambient temperature and light, but they show activity by only certain external stimulation, such as

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heating or photoirradiation. Latent catalysts are widely used on the synthesis of various polymeric materials, such as thermosetting resins, adhesives, paintings, inks, and photoresists [12]. In recent years, the cationic polymerization of thermosetting resins has been investigated intensively using various thermally latent cationic catalysts. Several classes of cationic catalysts, such as iodonium, ammonium, pyridinium, and sulfonium salts, have been developed as thermally latent and photolatent initiators for the polymerization of thermosetting resins [13–16]. Development of efficient latent catalysts is desirable for the enhancement of both storage stability and handling of thermosetting resins.

N-benzylpyrazinium and *N*-benzylquinolinium salts have been shown to be excellent latent initiators for epoxy resins. They dissolve readily in epoxy resins and exhibit a longer pot life than the more commonly used BF_3-4-methoxyaniline complex [17,18].

As previously mentioned, although many studies of epoxy/castor oil-based polymer blends have been described, but there little work has been reported on the cationic polymerization, thermal stabilities, and mechanical properties of epoxidized castor oil (ECO) initiated by cationic latent catalysts [8,9].

In this work, we present new data on the cationic polymerization and physicochemical properties of a biobased epoxy resin, ECO, initiated by *N*-benzylpyrazinium hexafluoroantimonate (BPH) and *N*-benzylquinoxalinium hexafluoroantimonate (BQH). The characterization of the properties was performed by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermal mechanical analysis (TMA), thermogravimetric analysis (TGA), and an universal test machine (UTM).

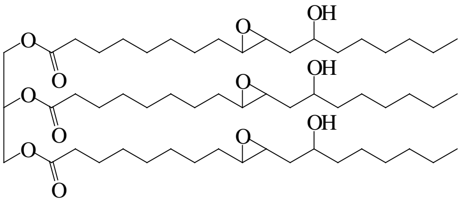
2. Experimental

2.1. Materials

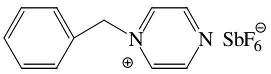
ECO used in this study was synthesized by reaction of castor oil with glacial acetic acid and hydrogen peroxide using Amberite IR-120 as a catalyst in our lab scale [11,19]. BPH and BQH as cationic latent catalysts were prepared from previous work [18,20]. The chemical structures of ECO, BPH, and BQH are shown in Fig. 1.

2.2. Synthesis of epoxidized castor oil

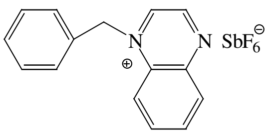
Castor oil (91.8 g, 0.14 mol), glacial acetic acid (21.0 g, 0.35 mol), Amberlite (23 g), and toluene (40 g) were added to a 500 ml four-neck round-bottom flask equipped with a mechanical stirrer, thermometer sensor, and reflux condenser. The temperature was maintained at 55 °C. To this solution, 30% H_2O_2 (56.7 g, 0.5 mol) was added with stirring. The reaction was run at 55 °C for 7 h. The solution was then filtered and washed with a saturated solution of $NaCO_3$, distilled water, and then dried with anhydrous sodium sulfate. Finally, the toluene was removed by distillation under vacuum to give epoxidized castor oil, which was further dried under vacuum at 80 °C for 2 h: yield 84%.



Epoxidized castor oil (ECO)



N-benzylpyrazinium hexafluoroantimonate (BPH)



N-benzylquinoxalinium hexafluoroantimonate (BQH)

Fig. 1. Chemical structure of the materials used.

FT-IR (cm^{-1}): 3009 (C=C), 843 (epoxide group).
^1H NMR ($CDCI_3$), δ (ppm): 5.3 (2H, C=C), 2.9–3.1 (2H, epoxide group).
^{13}C NMR ($CDCI_3$), δ (ppm): 129.7–130.2 (C=C), 54.0, 54.3 (epoxide group).

2.3. Sample preparation

One wt% catalyst (BPH or BQH) was dissolved in acetone and then was mixed with ECO at the ambient temperature. The mixture was fully stirred by a mechanical stirrer and then degassed in a vacuum oven before a DSC test. The preparation of the specimens for thermal and mechanical tests was as follows: The formulated mixtures were poured into the mold and cured first at 110 °C for 1 h, then at 140 °C for 2 h, and finally post cured at 160 °C for 1 h in a convection oven.

2.4. Characterization and measurements

IR spectrum was examined with a Bio-Rad Co. digilab FTS-165 spectrometer using KBr pellets. ^1H NMR