



Curing kinetics and mechanical properties of bio-based epoxy composites comprising lignin-based epoxy resins



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ABSTRACT

Lignin-based epoxy resins derived from de-polymerized Kraft/organosolv lignins were blended with a conventional bisphenol A (BPA)-based epoxy resin at various percentages to prepare bio-based epoxy systems as polymer matrices for manufacturing of fiber-reinforced plastics (FRPs) and coatings. The curing process of epoxy composites was studied using DSC and the activation energy was calculated by isoconversional methods. Epoxy composites comprising a low percentage (25 wt%) of lignin-based epoxy resin can be cured faster than the pure BPA-based epoxy resin used in particular at the early stage of curing. However, blending a large amount (>50 wt%) of lignin-based epoxy resin with the BPA-based epoxy resin retarded the curing process particularly at the late stage of curing. Tensile and flexural strengths of the prepared FRPs using bio-based epoxy composites were found to be superior or comparable to those of the FRP with the pure BPA-based epoxy resin when the lignin-based epoxy resin blending ratio is less than 50–75 wt%. Furthermore, the bio-based epoxy films comprising up to 50 wt% of DOL-based epoxy resin were exhibited high adhesion strength on a metal substrate.

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1. Introduction

In recent decades, synthesis of bio-based chemicals and materials using bio-renewable resources has drawn increasing attention in academia and industry due to the concerns over the environment impacts and the depleting reserves of fossil fuels (currently the dominant sources for chemicals and materials) [1,2].

Epoxy resin is one of the most widely used thermosetting polymers because of its superior properties, e.g., great chemical resistance, good thermal stability and high adhesion strength to various substrates. These properties provide diverse applications of epoxy resins in coatings, adhesives to other engineering applications [3,4]. The ultimate properties of epoxy resins are determined mainly by their chemical composition and their curing conditions [5,6]. Therefore, it is of great significance to investigate on the curing process of epoxy resins for better control of their final properties.

Synthesis of bio-based epoxy resins were reported in several literature studies. Also, several review papers have been published on the potential of production of bio-based epoxy resins [7,8]. However, limited attention has been paid on

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simultaneous characterization of the curing kinetics of the resins and mechanical properties of fiber reinforced plastics (FRPs) and coatings using lignin-based epoxy matrices. Bio-resources including vegetable oil [9,10], tannins [11], vanillin [12,13], rosin [14], bark [15], liquefied biomass [16,17] and lignin [18,19] have been used for the synthesis of bio-based epoxy resins. Kim and Sharma [10] reported a novel process for epoxidation of several plants oils without using solvent, and demonstrating that the epoxidized linseed oil have excellent modulus and impact resistance. Liu et al. [14] developed a 100% rosin-based epoxy resin possessing a high glass transition temperature of around 164 °C. Kuo et al. [15] synthesized a bark-based epoxy resin exhibiting higher tensile strength and stiffness in comparison with other bio-based epoxy resins. Lignin was also demonstrated to be a promising bio-substitute for bisphenol A (BPA) in synthesis of bio-based epoxy resins with mechanical and thermal properties comparable to the conventional BPA-based epoxy resins [17,20]. However, only a small portion of the research focused on curing process and kinetics of lignin-based epoxy resins in order to provide products with excellent performance. Sun et al. [5,6] studied the curing kinetics of lignin-based epoxy resins with three various curing agents including methylhexa-hydrophthalic anhydride, maleic anhydride and 2-methyl-4-methylimidazole using a DSC. The kinetics parameters were evaluated based on Kissinger method and autocatalytic model. Hirose et al. [3] determined the activation energy by Ozawa method for curing of bio-based epoxy resins synthesized with polyester chains derived from biomass components including saccharides, lignin and glycerol. In some studies, lignin was blended with epoxy resin and the curing kinetics of the mixture were studied. For example, Kong et al. [4] blended a conventional epoxy resin with a hydrolyzed lignin at 5% blending ratio, and investigated the curing kinetics and the bonding properties of the resins as adhesives. The results revealed that the introduction of a small amount of lignin promoted the curing process of the epoxy resin and improved the shear strength. Yin et al. [21] studied the mechanical properties and curing of an epoxy resin mixed with enzymatic hydrolysis corn straw lignin. It was suggested that the hydroxyl and carboxyl groups of lignin could react with the epoxy groups, and the polyphenol structure of lignin could catalyze the curing reactions.

As described in our previous published works [22,23], a novel method has been developed for the synthesis of bio-based epoxy resins with reduced side reactions, employing de-polymerized Kraft lignin (DKL) and de-polymerized organosolv lignin (DOL) under alkaline condition in the presence of a phase transfer catalyst, tetrabutylammonium bromide (TBAB). Lignin-based epoxy resins derived from de-polymerized Kraft/organosolv lignins were blended with a conventional bisphenol A (BPA)-based epoxy resin at various percentages (25–100 wt%) to prepare bio-based epoxy systems. The thermal stability of the prepared bio-based epoxy systems were investigated by a TGA-FTIR [24]. The limiting oxygen index (LOI) of all lignin-based epoxy composites are higher than that of the conventional epoxy resin indicating that the lignin-based epoxy systems are more effective fire retardants than the conventional epoxy resin. The percentage of lignin-based epoxy resin in the bio-based epoxy systems had a significant effect on the activation energy of the thermal decomposition process. With increasing the amount of the lignin-based epoxy resins, the activation energy reduces at the early stage of the process but drastically increases at the final stage of the decomposition. In the present work, the curing mechanism and kinetics for the epoxy systems were studied based on differential scanning calorimetry (DSC) measurements. In addition, the epoxy systems were applied as polymer matrices for manufacturing of fiber-reinforced plastics (FRPs) and coatings. The mechanical properties of these FRPs were examined with a universal testing machine (UTM) and by dynamic mechanical analysis (DMA). The adhesion strength of coatings was tested by using a pull-off tester.

2. Experimental

2.1. Materials

As detailed in our previous published works [22,23], two kinds of lignin-based epoxy resins were synthesized from de-polymerized Kraft lignin (DKL, softwood) and de-polymerized organosolv lignin (DOL, hardwood), denoted as DKL-epoxy resin and DOL-epoxy resin, respectively. In a typical run for the synthesis of depolymerized lignin (DL)-based epoxy resin, 4 g of DL dissolved in 12 g epichlorohydrin (ECH) (at an epichlorohydrin/DL molar ratio of 6) and mixed with tetrabutylammonium bromide (TBAB, 0.2 wt% of DL) and 12 mL of distilled water. Then the mixture was loaded into a 200 mL three-neck reactor and heated up to 80 °C and kept at this temperature for 1 h under stirring. Then, the system was cooled to 60 °C and sodium hydroxide solution was added into the reactor and maintained at the reaction temperature. Finally, the system was cooled down to the room temperature and the organic phase was separated. The non-reacted epichlorohydrin was removed using a rotary evaporator at 100 °C under a reduced pressure. The yields of epoxidation for DOL and DKL were 99% and 97%, respectively.

Araldite® GZ 540 X 90, supplied from Huntsman, as a conventional bisphenol A (BPA)-based epoxy resin (DGEBA) was used in this study to prepare epoxy composites comprising the BPA-based epoxy resin and 25–100 wt% of the above lignin-based epoxy resin. The epoxy equivalent weight (EEW), EC and the solid content of this liquid BPA-based epoxy resin are approx. 295 g/eq, 14.6 wt% and 90 wt% (containing 10 wt% of xylene solvent), respectively. Prior to the kinetic study, the BPA-based epoxy resin was completely dried in a vacuum oven to remove the xylene solvent. 4,4'-Diaminodiphenylmethane (DDM) obtained from Sigma Aldrich was used as a curing agent for the epoxy resins. BGF fiberglass cloth (E-Glass, Plain weave fiber glass with 0.015 in. thickness) was purchased from Freeman, Ohio.

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