



Synthesis and characterization of hydrolysis lignin-based epoxy resins



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ABSTRACT

A novel bio-based epoxy resin was synthesized using de-polymerized hydrolysis lignin (DHL) as a feed-stock under alkaline condition. The chemical functionality of DHL-based epoxy resin was studied using Fourier Transformation Infrared spectroscopy (FTIR). The curing behavior of DHL-based epoxy resin with a selective curing agent (4,4'-diaminodiphenyl methane; DDM) was also investigated using differential scanning calorimetry (DSC). The curing process was found to proceed via a ring opening reaction involving the epoxy and the amine groups followed by etherification reactions at the end. The thermal and mechanical behavior of the resulting DHL-based epoxy resin were investigated using a thermogravimetric analysis (TGA) and a universal testing machine (UTM), respectively. The cured DHL-based epoxy-DDM system demonstrated good thermal and mechanical performances, suggesting its potential of utilizing hydrolysis lignin—a byproduct/waste stream from cellulosic ethanol processes for the production of value-added bio-based materials.

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1. Introduction

Epoxy resins, currently produced dominantly from petroleum-based chemicals of bisphenol-A (BPA) and epichlorohydrin, have an indispensable role in electronics and composites industries (Abdul Khalil et al., 2011; May, 1988). The depletion of fossil fuel resources and the environmental issues of their products/derivatives have encouraged industry and academia to seek for renewable resources for the production of epoxy resins (Kishi et al., 2006; Knut, 1980; Ma et al., 2013).

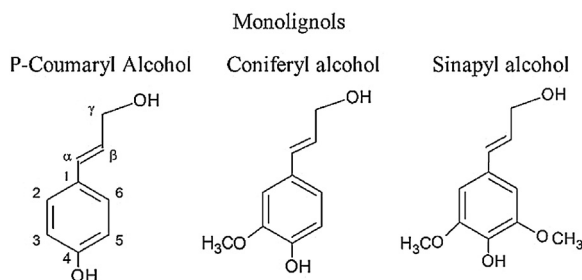
Recently, several researches have been reported on the synthesis of bio-based epoxy resins from various renewable resources such as gallic acid (Aouf et al., 2013), tannins, vegetable oils (Shah and Ahmad, 2012) and lignins (Nonaka et al., 1997; Singh et al., 2012). The synthesis of lignin-based epoxy resins derived from de-polymerized organosolv lignin and de-polymerized Kraft lignin was described in details in our previous papers (Ferdosian et al., 2014, 2012). The current study was focused on the synthesis of a sustainable epoxy resin from hydrolysis lignin (HL). The hydrolytic lignin, extracted from the residues of the cellulosic ethanol production, is commonly known as “enzymatic hydrolysis lignin (EHL)”. As enzymatic hydrolysis processes of biomass normally operates

under relatively mild conditions, the most active functional groups such as phenolic hydroxyl and alcoholic hydroxyl can be preserved (Yin et al., 2012). As a consequence, the resulting EHL is expected to be more reactive in comparison with lignosulfonate lignin or Kraft lignin (Jin et al., 2010; Yin et al., 2012). Enzymatic hydrolysis lignin is usually used as a fuel in combustion or gasification processes to generate steam or electricity (Yin et al., 2012). In order to maximize its economic value, EHL could be used as a precursor for the production of bio-based chemicals such as phenol–formaldehyde resins, polyurethane foams, and epoxy resins. However, the crude hydrolysis lignin from a cellulosic ethanol process is not a pure lignin, but a complex mixture comprising 50–60% of lignin, 20–30% cellulose and hemicelluloses, and the rest is ash, and water.

Lignin is a natural phenolic polymer of three phenyl propanols, i.e., *p*-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, which is illustrated in Scheme 1. The phenoly-propanols are linked together by mainly ether linkages (e.g., β -O-4, α -O-4 and 5-O-4) and condensed linkages (e.g., 5-5, β - β , β -5 and β -1 linkages) (Delmas et al., 2013). Direct utilization of lignin as an alternative to bisphenol A (BPA) for the synthesis of bio-based epoxy resins would be challenging due to large molecular weight, less solubility in some solvents and the lower reactivity towards epichlorohydrin in the synthesis process. To address these challenges, commonly it is necessary to carry out some chemical modifications such as phenolation (Koike, 2012), hydroxyalkylation (Hofmann and Glasser, 1993), methylolation (El Mansouri et al., 2011) and de-polymerization (Cheng et al., 2013) on lignin to

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Scheme 1. Structure of three lignin monomers.

enhance its reactivity in the reaction. Among these processes, de-polymerization of lignin has demonstrated its potential to provide a suitable feedstock for the synthesis of epoxy resins. It enhances the activity of functional groups present on lignin with a substantial reduction in the average molecular weight of lignin.

In recent years, several studies have been reported on the production of lignin-based epoxy resins (Asada et al., 2015; Chikako, 2013; Delmas et al., 2013; Simionescu et al., 1987). To the best of our knowledge, no published work has been conducted on the utilization of de-polymerized hydrolysis lignin as a feedstock in the synthesis of epoxy resins. So, the main objective of this research is the synthesis of a bio-based epoxy resin using a de-polymerized hydrolytic lignin. In the present study, hydrolysis lignin was de-polymerized at relatively low pressure and temperature, then reacted with epichlorohydrin to generate a lignin-based epoxy resin and the performance of the resin was evaluated. The curing kinetics of the bio-based epoxy resin was studied with a differential scanning calorimetry (DSC). In addition, the thermal performance and mechanical properties of the lignin-based epoxy resin were investigated by using a thermogravimetric analyzer (TGA) and a universal testing machine (UTM), respectively.

2. Experimental

2.1. Materials

Hydrolysis lignin (HL, hardwood) was supplied by FPIInnovations and was not soluble in any solvent to measure the molecular weight by GPC. HL was the residual of sugar/ethanol production from Aspen wood. The HL received is a yellowish powder that is composed of 56.7 wt% lignin and 29.8 wt% carbohydrates balanced by the residual ash and others. In this study, the HL was de-polymerized to obtain de-polymerized HL (DHL) before using as a feedstock for the preparation of lignin-based epoxy resin by grafting of epoxy groups. The DHL was obtained by a low-pressure proprietary lignin de-polymerization process whose process conditions are not yet disclosed for patent filing purpose. The de-polymerization process led to a product yield of 52%, and the resulted DHL has a mass-average molecular mass (M_w) of ~2100 g/mol (polydispersity index (PDI)=2.98). A commercial epoxy resin (Araldite® GZ 540 × 90, DGEBA) was supplied by Huntsman with the epoxide equivalent weight (EEW) ≈ 295 g/eq and used as a reference to compare with the curing kinetics and the thermo-mechanical properties of the lignin-based epoxy resin. All other chemicals, including sodium hydroxide, epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB) and 4,4'-diaminodiphenyl methane (DDM) were purchased from Sigma-Aldrich and used without further purification. DDM was used as a curing agent for the lignin-based epoxy resin and the reference DGEBA. BGF fiberglass cloth (E-Glass, Plain weave fiber glass with 0.015 in. thickness) was purchased from Freeman, Ohio.

2.2. Synthesis of de-polymerized-hydrolysis lignin (DHL)-based epoxy resin

In a typical run for the synthesis of DHL-based epoxy resin, 4 g of DHL dissolved in 12 g epichlorohydrin (ECH) (at an epichlorohydrin/lignin molar ratio of 6, assuming the average molecular mass of monomers of lignin is 180 g/mol) and mixed with tetrabutylammonium bromide (TBAB, 0.2 wt.% of DHL) 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 a lower temperature 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 by-products were separated by dissolving the obtained product in acetone followed by filtration. Finally, acetone was removed using the rotary evaporator. The yield of DHL-based epoxy resin from the above epoxidation process was ≈95%. Synthesis path and structural model of DHL-based epoxy resin is shown in Scheme 2.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer) was used to analyze the chemical structure of the de-polymerized hydrolysis lignin (DHL), epoxy resins and the cured epoxy resins with DDM by scanning from 500 to 4000 cm^{-1} . The total hydroxyl number/phenolic hydroxyl number of the DHL as well as the epoxy content (EC, weight percent epoxide) of DHL-based epoxy resin were measured according to ASTM D4247-11 and ASTM D1652-11 standards, respectively. The epoxy content was measured with a potentiometric titrator (Titroline 7000 Titrator). In this method, the resins dissolved in 30 mL of methylene chloride (MECL) and 15 mL of tetraethylammonium bromide (TEAB) solution in acetic acid. The resulting solution is titrated with perchloric acid solution. As the reaction progresses, the potential of the solution gradually increases until the reaction approaches to completion at which point the potential increases very quickly. This equivalence point of titration was used to calculate the epoxy content (EC) of resin as follows:

$$EC = (4.3 \times V \times N) / W \quad (1)$$

where V is the actual mL perchloric acid used to reach equivalence point, N is normality of perchloric acid reagent, W is the weight of the sample used and 4.3 is the theoretical molecular weight of the epoxide ring, 43, and it is adjusted to 4.3 for the calculation to percent epoxide.

The average molecular masses of DHL and DHL-based epoxy resins as well as the reference DGEBA epoxy resin were measured by using a GPC instrument (Waters Breeze 1525 binary lamp, UV detector set at 270 nm, Waters Styragel HR1 column at 40 °C). The samples were dissolved in THF and the molecular masses were obtained using a method based on the molecular mass calibration curve as determined from the linear polystyrene standards.

The curing behavior of the lignin-based epoxy resin with amine was studied on a differential scanning calorimetry (Mettler Toledo DSC 1). A stoichiometric amount of the curing agent was mixed with the DHL-based epoxy resin and kept in a sealed vial at 5 °C to prevent further reaction before the DSC analysis. For the DSC analysis, around 7 mg of the sample was loaded into an aluminum pan and the measurements were conducted from room temperature to 350 °C at four different heating ramps 4, 6, 8 and 10 °C/min under a N_2 flow of 50 mL/min.

Carver (hydraulic unit model 3925) hot press was used for the preparation of the fabricated fiber reinforces plastics (FRP). The pre-

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