

Sustainable lignin-based epoxy resins cured with aromatic and aliphatic amine curing agents: Curing kinetics and thermal properties



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ABSTRACT

Lignin-based epoxy resins were synthesized by reacting de-polymerized organosolv lignin (DOL) or de-polymerized Kraft lignin (DKL) with epichlorohydrin under an alkaline condition in the presence of a phase transfer catalyst. The synthesized lignin-based epoxy resins were cured with 4,4'-diaminodiphenyl methane (DDM, an aromatic amine) and diethylenetriamine (DETA, an aliphatic amine) to generate a 3-dimensional cross-linked structure. The effects of curing agents on the curing process were investigated by non-isothermal differential scanning calorimetry (DSC). The dependency of activation energy of the curing reaction on the extent of curing (conversion) was determined in this study by model-free kinetics based on the DSC results. In addition, it was found that the thermal stability of the cured lignin-based epoxy resins was also influenced by the type of curing agents and the types of lignin used in the synthesis of the bio-based epoxy resins.

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1. Introduction

Epoxy resins are known as very versatile thermosetting resins which are used in a wide variety of applications such as adhesive, high performance composite, coatings and electronics [1–4] due to their unique characteristics including excellent chemical resistance, high moisture and solvent resistances, good thermal and dimensional stabilities, high adhesion strength, superior electrical properties, etc. [2,5]. Epoxy resins were first commercialized in 1946 [6] and around 45–50% of the worldwide production of epoxy resins are used in surface coating industries [7]. The production of epoxy resins has long relied upon fossil fuel resources to provide starting raw materials i.e. bisphenol A and epichlorohydrin. Around 67% of molar mass of conventional epoxy resins (i.e. diglycidyl ether of bisphenol A (DGEBA)) is bisphenol A (BPA) derived from fossil fuels [8]. However, increasing health and the environmental concerns over using BPA, due to its toxicity and carcinogenic effects, have been raised in recent decades [8]. On the other hand, the huge usage of fossil fuels is considered as a large contributor to the global warming and the climate change [9,10], and the fossil fuels are depleted, which in collection have encouraged

scientists and researchers to find an alternative resources to produce polymeric materials [11]. Therefore, there is an arousing interest in seeking green alternative to BPA for developing bio-based and eco-friendly epoxy resins.

Various biomass resources such as plant oils [12], rosin [13], gallic acid [14], tannins [15,16], itaconic acid [8], lignin [17–19] have been used in synthesis of epoxy resins. Among these resources, lignin has demonstrated by many studies to be one of the most promising candidates for replacement of bisphenol A in production of bio-based epoxy resins, as it has aromatic structure with hydroxyl, carboxylic acid and phenolic functional groups that can react with epichlorohydrin to form bio-based epoxy resins [20–22]. Quite a few other studies have been reported on utilization of lignin in epoxy resin production [17,23,24]. However, only a small portion of the research focused on curing kinetics of lignin-based epoxy resins. It is well known that for any thermosetting polymer system, the final properties of the thermosetting resin would depend upon both the chemical structure and the curing process [25]. Thus, it is of significance to investigate on the curing process and kinetics for the lignin-based epoxy resin in order to provide products with excellent performance.

Sun et al. [25,26] 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

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model. Hirose et al. [27] 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. [1] 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. [28] studied the mechanical properties and curing of an epoxy resin mixed with enzymatic hydrolysis corn straw lignin. The study of Yin et al. [28] 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 reaction.

The aim of this work was to investigate the curing behavior and kinetics of lignin-based epoxy resins derived from de-polymerized organosolv lignin and de-polymerized Kraft lignin, cured with two different curing agents. Differential scanning calorimetry (DSC) was used to monitor the curing behavior and the obtained data were evaluated by three model free methods i.e. Friedman, Vyazovkin, and Kissinger. In addition, thermal stability of the cured lignin-based epoxy resins was studied by thermogravimetric analysis (TGA).

2. Kinetic analysis

In general, the rate of reaction can be expressed as a function of temperature, $f(T)$, and degree of curing or conversion, $f(\alpha)$, (Eq. (1)) [29]. The functionality of temperature can be described by Arrhenius equation [30], while, the functionality of conversion depends on the mechanism of the curing reaction.

$$d\alpha/dt = f(T) \times f(\alpha) = A \exp(-E/RT) \cdot f(\alpha) \quad (1)$$

where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant and T is the temperature. The kinetic parameters can be calculated without any assumption of $f(\alpha)$ by using model-free methods. The common method to evaluate the overall apparent activation energy is the Kissinger method. Kissinger model can be presented by Eq. (2) [31].

$$\ln(\beta_i/T_{p,i}^2) = \text{Const.} - E/RT_{p,i} \quad (2)$$

where β is the heating rate, T_p is the peak temperature, the subscript i denotes different heating rates. The overall activation energy can be obtained from the slope of plot of $\ln(\beta_i/T_{p,i}^2)$ against $1/T_p$. A limitation of the Kissinger method is that it cannot predict the mechanism of the curing reaction throughout the curing process. However, the curing of an epoxy resin is known as a multi-step reaction [32,33] and a specific activation energy is associated with each step. Therefore, model-free isoconversional methods have been used to determine the variation in the activation energy. In the isoconversional principle, the rate of reaction only depends on temperature at the constant extent of the curing conversion. At each conversion, the activation energy can be determined and the mechanism of crosslinking reaction can be explored [33]. The isoconversional methods are classified into two categories, i.e. differential and integral methods [34]. The well-known differential method is the Friedman method expressed by Eq. (3) [34].

$$\ln[(d\alpha/dt)_{\alpha,i}] = \ln[\beta_i \times d\alpha/dT] = \ln[A_\alpha f(\alpha)] - E_\alpha/RT_{\alpha,i} \quad (3)$$

Hence, the slope of a plot of $\ln[\beta d\alpha/dT]$ versus $1/T$ at a constant degree of conversion (α) for a set of heating rates (β) gives the activation energy at the specific value of α .

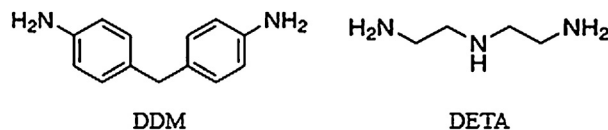


Fig. 1. Chemical structure of the curing agents, DDM and DETA.

One of the accurate integral methods is the advanced isoconversional method proposed by Vyazovkin and described as follows [35];

$$\phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n (J[E_\alpha, T_i(t_\alpha)]/J[E_\alpha, T_j(t_\alpha)]) \quad (4)$$

where

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp[-E_\alpha/RT_i(t)] dt \quad (5)$$

where the subscript i and j denote different heating rates and n is the total number of heating rates.

3. Experimental

3.1. Materials

Kraft lignin (KL, softwood) and organosolv lignin (OL, hardwood) used in this study were kindly provided from Lignol and FPIinnovations, respectively. KL is the yellowish powder and its mass-average molecular mass is $M_w \approx 8300$ g/mol (with a polydispersity index $PDI \approx 8.2$) based on our SEC analysis. While, OL is a dark brown powder with its $M_w \approx 2600$ g/mol (and $PDI \approx 3.6$). In this study, the OL and KL were depolymerized to obtain de-polymerized OL (DOL) and de-polymerized KL (DKL) before using as feedstock for the preparation of lignin-based epoxy resins by grafting of epoxy groups. The de-polymerization process of OL was described in a previous publication by the authors [36], and DKL was obtained by a low-pressure proprietary lignin de-polymerization process whose process conditions are not yet disclosed for patent filing purpose. Both lignin de-polymerization processes were operated at 150–350 °C for 1–3 h, so they are pretty efficient processes. The de-polymerization treatments reduced the molecular mass of the technical lignins and increased their reactivities for epoxidation. Both de-polymerization processes led to a high product yield >80–85%, and the resulted DOL and DKL has a mass-average molecular mass (M_w) of 760 g/mol (polydispersity index (PDI) = 2.0) and 1400 g/mol (PDI = 2.4), respectively.

Other chemicals used in this study, acetone, sodium hydroxide, epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB), and curing agents (4,4'-diaminodiphenyl methane (DDM) and diethylenetriamine (DETA), as depicted in Fig. 1) were purchased from Sigma–Aldrich and used without any further purification.

3.2. Synthesis of lignin-based epoxy resins

4 g DOL or DKL dissolved in 12 g epichlorohydrin (ECH) (the molar ratio of DOL or DKL to ECH was 6, assuming the average molecular mass of lignin monomers is 180 g/mol) were added to a three-neck round flask, followed by adding 12 ml distilled water and 8 mg tetrabutylammonium bromide (0.2 wt.% of lignin). The reactor (equipped with a reflux condenser and a magnetic stirrer) was heated to 80 °C and maintained at this temperature for 1 h under stirring. Then, the system was cooled to the lower temperature and sodium hydroxyl solution was added dropwise into

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