Curing kinetics of lignin and cardanol based novolac epoxy resin with methyl tetrahydrophthalic anhydride

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ABSTRACT

Lignin and cardanol based novolac epoxy resin (LCNE) was prepared by reacting epichlorohydrin with the mixture of lignin and cardanol (2/3 in weight ratio). Kinetics of the curing reaction between LCNE and methyl tetrahydrophthalic anhydride (MeTHPA) was studied by differential scanning calorimetry (DSC) and model-free kinetic (MFK) analysis. The apparent activation energy (E_a) of the curing reaction was obtained from Friedman's model-free method. The kinetic model and other kinetic parameters were determined by Málek's method and the reaction process could be simulated favorably by Sestak–Berggren (SB (m, n)) model. Furthermore, the kinetic equation obtained from nonisothermal data was applied to predict the isothermal conversion processes of the crosslinking reaction. The results demonstrated the calculated data from the obtained kinetic equation matched perfectly with the isothermal experimental data.

1. Introduction

Epoxy resin, one of the most important industrial thermosetting resins used in various industrial areas, exhibits excellent properties such as high chemical resistance, low shrinkage, superior thermostability mechanical and electrical properties [1–6]. In chemical industry, especially in the field of epoxy resin production, fossil resources have long been used as raw materials. Whereas with the growth of global environmental crisis and the shortage of fossil resources, the utilization of renewable biomass as substitute resources for preparation of epoxy resins attracts considerable attention in recent years due to their biodegradability, availability, and renewable nature.

Lignin is one of the most important renewable resources and the second most abundant biopolymer [7]. Large amounts of lignin are produced from second generation bio-ethanol production, pulp and paper industry every year. However, due to the lack of efficient utilization methods, there are few lignin-based commodity materials. Most produced-lignin is treated as wastes or burnt directly, which damages surrounding environment [8]. Recently, diverse methods have been developed to produce lignin and lignin derivatives reasonably in large scale. Numerous researches indicate that the preparation of lignin or lignin based epoxy resin is one of the most potential applications. The methods for synthesis of lignin based epoxy resin are summarized into three categories as follows: (a) blending the epoxy resin with lignin obtained directly from the pulp and paper process [9–11]; (b) modifying of lignin by epoxide directly [8,9]; and (c) modifying lignin with reactive molecules to improve their reactivity, followed by epoxidation [10,11]. Generally, epoxy resins synthesized from high reactive modified lignin are of better properties than those synthesized from other methods.

Cardanol is extracted extensively from cashew nut shell liquid considerably. It is a naturally substituted phenol compound with a side chain of C_{15} unsaturated alkane at the meta position and can take part in a large number of distinct chemical reactions. With the unique molecular structure and performance, cardanol and its derivatives can be considered nowadays very attractive precursors in order to develop new materials from renewable bio-sources to be used in eco-friendly processes [12–15]. In our experiment, lignin

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was found to be easily liquefied and modified by cardanol, which provides a potential way to use lignin reasonably in large scale for preparation of lignin-based epoxy resins.

In this work, bio-refinery lignin is liquefied and modified by cardanol in order to improve the contents of phenolic hydroxyl group and then reacts with epichlorohydrin to synthesize LCNE. The kinetics of crosslinking reaction between LCNE and MeTHPA is investigated by DSC.

2. Experimental

2.1. Materials

The lignin was extracted of the butanol bio-refinery residue (from Songyuanbairui Bio-polyols Ltd. Co., Jilin, China). Its composition is 78.2% acid-insoluble lignin, 2.8% acid-soluble lignin, 1.5% sugar, 5.3% water, 11.9% cellulose and 3.9% ash. Cardanol (average molecular weight is 300 g/mol) was supplied by Zaozhuang Nate Biological Materials Ltd. Co. (Shandong, China). MeTHPA, benzyl-triethylammonium chloride (BTEAC), N,N-dimethylbenzylamine (DMBA) and other chemicals were of analytical grade and obtained commercially from Sinopharm Chemical Reagent Ltd. Co. (Shanghai, China).

2.2. Synthesis of LCNE

200.0 g cardanol and 3.0 g sulfuric acid were added into a 250 mL four-necked glass flask equipped with a reflux condenser, a stirrer and a thermometer. After the temperature inside the flask increased to 150 °C, 60.0 g BR was added into the flask under constant stirring. The reaction was continuously refluxed for 3 h and then the product was cooled to room temperature.

A 500 mL four-necked glass flask equipped with a mechanical stirrer, a spherical condenser, a constant pressure dropping funnel and a thermometer was charged with 60.0 g liquefaction solution and 0.6 g concentrated hydrochloric acid. After the temperature inside the flask increased to 90 °C, 8.1 g water solution of formaldehyde (37%) was added dropwise in 1 h. Then the reaction was continued for 3 h. The product was washed to neutral with 5% NaOH solution and distilled under reduced pressure to remove water and then cooled to ambient temperature. 185.0 g epichlorohydrin and 1.8 g BTEAC were added into the above product under constant stirring. The system was heated to reflux and reacted for 4 h, and then cooled to 70 °C. 8.0 g NaOH was added in 8 times within 1 h and reacted for another 4 h under the steady temperature. The reaction solution was cooled to 50 °C and washed with hot water. Excess amounts of epichlorohydrin were evaporated under the reduced pressure and then LCNE was obtained as reddish brown viscous liquid. The possible chemical structure of LCNE was shown in Fig. 1.

All thermograms were recorded using a Perkin-Elmer Diamond DSC calorimeter by Mettler Toledo (Greifensee, Switzerland). An empty alumina crucible was used as standard reference. MeTHPA was used as a comonomer (coreactive curing agent) and DMBA was employed as an initiator. The components of DSC samples were mixed in the ratio LCNE:MeTHPA:DMBA = 100:14:1 by weight. Approximate 5 mg sample was placed in an alumina crucible and then covered by an aluminum lid prior to undergo a specific cure program depending on the mode of measurement. Non-isothermal experiments were carried out at heating rates of 5, 10, 15 and 20 °C/min from 0 to 250 °C in nitrogen atmosphere. Isothermal DSC scans of the sample were made at the temperature of 100 °C until the exothermic reaction was completed. The S-shaped baseline was used for integration of the nonisothermal DSC peaks. The heat flow
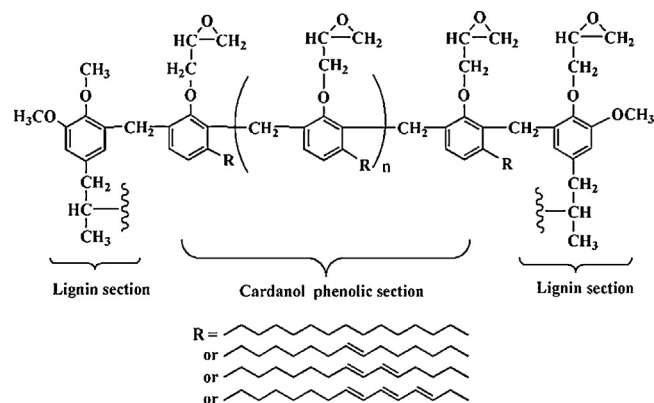

Fig. 1. Possible chemical structure of LCNE.

data, as a function of temperature and time, were obtained by integrating the area under the peak of the exothermal.

3. Experimental principle

DSC measurements were also used to monitor the advancement of cross-linking reactions, by considering that the heat evolved at any time is proportional to the overall extent of reaction of reactive groups consumed. The extent of reaction of reactive groups (α) at any time can be, therefore, defined as [16–18]:

$$\alpha = \frac{\Delta H_t}{\Delta H} \tag{1}$$

where ΔH_t is the curing heat released from the beginning of the curing process until a certain time t, and ΔH is the total curing heat released.

The curing rate of a thermosetting polymer is commonly described by a single step kinetic equation [19,20]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where t is the time; $k(T)$ is the rate constant, which depends on temperature and $f(\alpha)$ is a function of the fractional extent of conversion rate and is associated with the reaction mechanism. k is usually assumed to follow the Arrhenius equation (Eq. (3)):

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is the pre-exponential factor, E_a is the curing activation energy, R is the universal gas constant and T is the absolute temperature.

As to the curing processes of thermosetting polymers, E_a can be calculated by model-fitting kinetics methods and model-free kinetics methods (MFK) [21]. The main drawback of the model-fitting kinetics methods is that when these methods are applied to data obtained under non-isothermal conditions where T and α vary simultaneously, the method fitting procedure leads to the so-called "kinetic compensation effect". This effect is avoided by model-free kinetics methods, also known as isoconversional method. The MFK methods are based on the isoconversional principle according to which the curing rate at a given curing degree depends only on temperature. The conventional MFK methods, such as the Flynn–Wall–Ozawa method [22,23], the Kissinger–Akahira–Sunose method [24,25], and the Friedman (FR) method [26], have been recently developed to better interpret the curing reaction by probing the change of the overall activation energy with cure degree. Of the model-free kinetic methods, the Friedman method is the more appropriate for gaining insight into the curing mechanism of polymers. The Friedman method is