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Synthesis and characterization of aminated lignin

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ABSTRACT

Amination of lignin can bring reactive amino groups onto the natural polymer and enable it to be employed in engineering materials. The amination reaction was successfully implemented after some of the hydroxyl groups on lignin were epoxidized. The resulted products showed a great quantity of primary amine group and secondary amine group which can be used as curing agents of epoxy resin. The results revealed that several factors including reaction temperature and time, as well as ratios of compounds, could influence the epoxidation and amination reactions. The resulted products were characterized by FT-IR spectra, ^{1}H NMR, ^{13}C NMR, element analysis, XPS and thermogravimetry analysis.

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1. Introduction

Lignin is one of the most abundant natural polymers produced by plants and also the only one containing aromatic structures. It can be separated from wood during wood pulping and papermaking and has been used primarily as a resource of fuels. Only a small amount (ca. 1–2%) of lignin is isolated from spent pulping liquor and has been employed in a wide range of specialty chemical products [1]. Lignin contains numerous hydroxyl groups including both phenolic and aliphatic hydroxyl groups at C-α and C-λ positions on the side chain [2]. The different hydroxyl groups have varied reactivities, and the aromatic ring structures are necessary building blocks for many chemical products. These structural features make lignin a potential source of chemicals and novel materials. Therefore, chemical modifications of lignin for various material applications have attracted increased attentions from researchers in recent years [3–5].

In fact, several chemical modification methods of lignin have been reported, including esterification, etherification, and amination reactions, all utilizing the reactivity of hydroxyl groups on the natural polymer [6–8]. Among these approaches, introduction of the more reactive amino groups onto lignin has been considered as one of the most promising process, since the aminated lignin, as a reactive additive, could be employed in preparation of polyurethane or epoxy resins. So far, most of aminations of lignin were achieved by using the Mannich reaction [9,10], however, the quantity of reactive amine groups on the product cannot be easily controlled in the reaction process, and the product contains more tertiary amine groups than primary amine and secondary amine groups, which have restricted the applications of the aminated lignin. In this study, a new two step modification process was adopted to prepare aminated lignin, and the product contains a great quantity of primary amine and secondary amine groups. The modified lignin still possesses aliphatic hydroxyl groups in addition to the reactive amine groups, which renders the lignin derivative many potential applications. With the existence of amino groups in the modified lignin, it can serve as a curing agent in epoxy resins instead of a filler of the polymer materials. Both hydroxyl and amino groups also make the lignin derivative a reactive species in preparation of polyurethanes.

2. Experimental

2.1. Materials

Alkaline lignin (methoxyl value: 10.0–12.0%, ash content: 20.0–29.0%, water content: <10%) was purchased from TCI (Shanghai) Development Co., Ltd; epichlorohydrin (AR), propane diamine (AR), hydrochloric acid (AR), sodium hydroxide (AR) and other chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd. and were used without further purification.

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2.2. Purification of alkaline lignin

An acid-precipitation method was used to remove any residual cellulose, inorganic salt, sugar and other impurities in alkaline lignin. The alkaline lignin was dissolved in water to prepare a lignin solution in a concentration of 30 wt%, and the solution was kept at 70 °C for 15 min in a water bath while stirring at a moderate speed. Then, 12 wt% HCl was added to adjust the pH value of the thick brown liquid to 2. The mixture was kept at room temperature for overnight and filtered to separate solid from the liquid [11]. Solid residue obtained was washed with distilled water repeatedly until the liquid is clear, the refined alkali lignin was obtained after drying at 80 °C and then was used in the following procedures.

2.3. Epoxidation of lignin

The purified lignin in an amount of 5 g was dissolved in 50 mL sodium hydroxide solution (wt% = 12%). Then, epichlorohydrin (molar ratio of phenolic hydroxyl group:epoxy group was 1:1.1) was dropped into the reaction system. The mixture was heated up to and kept at 50 °C for 8 h under stirring. The reaction mixture was filtered, and the residue solid was washed with distilled water and ethanol, respectively, to remove alkaline agent and residual epichlorohydrin. The black residue solid was dried at 40 °C under vacuum for 2 days. After grinding into powder, the resulted powder was used for the following amination reactions, shown in Scheme 1.

2.4. Amination of epoxy lignin

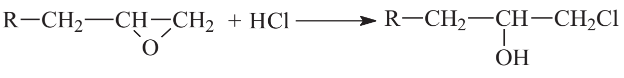
The lignin containing certain amount of epoxy groups was added into a three-neck flask, and then propane diamine (molar ratio of epoxy groups to amine groups was 1:4) was dropped into the reaction system. The reaction was kept under 80 °C for 4–6 h. After the reaction was completed, acetone was used to remove the residual diamine. The brownish product was separated by a filtration process and dried at 80 °C in oven. The reaction process and possible side reactions are shown in Scheme 2.

2.5. Ninhydrin test

About 2 mg of the sample were added into 1 mL of a solution prepared from dissolving 0.2 g of ninhydrin (1,2,3-indanetrione monohydrate) in 50 mL of ethanol, then a droplet of KCN solution and LiOH solution was added into the system. The reactor was heated to boiling for 15–20 s. Finally, the color of sample was observed and recorded as qualitative test results.

2.6. Epoxy index (E) measurement

Determination of content of epoxide groups in the materials (epoxy index) was carried out by hydrolysis of epoxide with HCl (0.1 N) according to the following reaction (Eq. (1)) [2], and titration of the excess acid in the system with NaOH solution (0.1 N). The measurement was performed in triplicate, and the average value was used for analysis.



$$R{-}CH_2{-}\underset{\diagdown\, O\, \diagup}{CH{-}CH_2} + HCl \longrightarrow R{-}CH_2{-}\underset{|\atop OH}{CH}{-}CH_2Cl \qquad (1)$$

2.7. Amine value (A) measurement

Amine values of the aminated lignin were measured by following an alternative indicator method (ASTM 2074-92 standard method), which could determine the total, primary, secondary, and tertiary amine values of amines, respectively.

Table 1
Effect of different conditions on epoxy index and yields of epoxidated lignin.

Temperature (°C)	Molar ratio (L:EPC)	Time (h)	Content of alkaline (%)	Yield (%)	Epoxy index (%)
50	1:1.1	4	12	37.3	0.177
50	1:1.1	6	12	45.2	0.164
50	1:1.1	8	12	57.8	0.196
50	1:1.1	10	12	60.3	0.194
50	1:1.1	14	12	69.9	0.123
50	1:0.9	8	12	42.6	0.063
50	1:1.0	8	12	53.7	0.091
50	1:1.05	8	12	50.1	0.114
50	1:1.15	8	12	59.1	0.194
50	1:1.2	8	12	57.6	0.201
40	1:1.05	8	12	44.9	0.101
60	1:1.05	8	12	91.6	0.138
80	1:1.05	8	12	89.2	0.091
50	1:1.05	8	8	47.9	0.164
50	1:1.05	8	16	55.6	0.220

2.8. Characterization

Structures of all samples were characterized with FT-IR and nuclear magnetic resonance (NMR). FT-IR was measured by a Nicolet AT-380 spectrometer using potassium bromide pellets, with acquisition conditions of spectral range of 4000–400 cm^{-1}, resolution at 4 cm^{-1}, and 32 accumulations. ^1H NMR spectra of lignin and its derivatives in DMSO-d_6 were recorded on a Bruker AV 400 (400 MHz) spectrometer using tetramethylsilane as an internal standard. Solid-state ^{13}C NMR spectra were recorded on the Bruker AV 400 spectrometer. German Elmentar Vario EL III element analyzer was used to measure the contents of C, H, O and N elements in samples. The chemical compositions of lignin and products were examined by X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos, UK). Thermal stability of materials was measured using a Netzsch TG 209 F1 instrument operating from 25 °C to 900 °C at 10 °C/min under a nitrogen atmosphere.

3. Results and discussions

3.1. Epoxidation of purified lignin

Lignin was successfully epoxidized under the reaction conditions, and a black powder-epoxy lignin was obtained. Reaction time, temperature, raw material ratio and the quantity of alkaline solution influenced the yields and epoxy indexes of the epoxidation reaction. Results obtained from the epoxidation reaction of lignin are presented in Table 1.

Generally speaking, increasing reaction temperature resulted in increase in the epoxy index, except in the range of 60–80 °C (Table 1). The similar trend was observed on product yields, which could be due to competing primary and side reactions. At the temperature range of 40–60 °C, epoxidation of lignin with epichlorohydrin was the primary reaction in the whole reaction system. The production rate of epoxy ring would be increased with the increasing temperature. After 60 °C, the rate of a secondary reaction between epoxidated lignin and lignin will be enhanced, leading to decrease in epoxy rings on the products in this temperature range. As a result, the proper synthesis temperature of epoxy lignin was considered at a range of 40–50 °C.

When the ratio of lignin to epichlorohydrin was changed, epoxy index would increase with more epichlorohydrin in the system. However, the increase of the epoxy index tends to be small after the ratio of lignin to epichlorohydrin reached 1:1.1. Prolonged reaction time generally increased the epoxy index until 8 h. Longer than 8 h, potential crosslinking reaction may become significant which could

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