

Preparation and characterization of novolac phenol–formaldehyde resins with enzymatic hydrolysis lignin

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ABSTRACT

Enzymatic hydrolysis lignin (EHL) derived from bio-ethanol production is attracting increased attention for use as a substitute for petroleum-based phenol in phenolic resins. In this work, EHL was successfully liquefied into small phenolic compounds catalyzed by oxalic acid in the presence of phenol. Experiments were designed to determine the effects of different replacement percentages of phenol by EHL on the residue content (RC) and the combined phenol (CP). Up to a 55% weight of phenol was substituted by liquefied EHL to formulate a novolac bio-based phenolic resin (EHL–PF). The differences between EHL and liquefied EHL, PF and EHL–PF were studied by Fourier transform infrared (FT-IR) spectroscopy, gel permeation chromatography (GPC), ^1H NMR spectroscopy, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). RC was found to increase with the increasing replacement percentage, while CP was found to increase at a lower replacement percentage and decrease at a higher replacement percentage. EHL–PF possessed comparable properties to those of commercial products.

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1. Introduction

Lignin is the second most abundant biopolymer after cellulose on earth, and it has been incorporated into PF due to its similar structure to phenol [1,2]. Lignin is considered to have the greatest potential to substitute petroleum-based phenol in the phenolic resin industry, which is important because of the increasing concerns regarding the shortage of fossil resources and the environmental impact from petroleum-based products [3]. EHL was obtained from the residues of the bio-ethanol preparation process; compared with other forms of industrial lignin, the benzene ring, phenol hydroxyl and other functional groups of EHL were limited because the enzymatic hydrolysis process was conducted under relatively mild conditions [4,5]. Fully utilizing EHL is a feasible method of reducing the current high bio-ethanol production cost, thereby promoting the large-scale development of bio-ethanol.

Lignin (including EHL) is well known to have lower reactive activity due to its large molecular space structure. In recent decades, many efforts have been made to improve the reactivity of lignin [6–8]. Generally, the usage of lignin in phenolic resin involves phenolation under acidic condition, such as hydrochloric acid and sulfuric acid. However, strong acids cause serious corrosion to equipment, and the liquefaction effect of weak acids is poor. Currently, EHL usage in phenolic

resin only involves the direct substitution of phenol [9,10]. Several researchers reported that wood is liquefied using oxalic acid as a catalyst in the presence of phenol [11–13]. However, no reports exist on lignin liquefaction catalyzed by oxalic acid and the application of the liquefied fractions in novolac resin. Oxalic acid, as an organic weak acid, is less corrosive to equipment. Oxalic acid could not only catalyze the reaction between phenol and formaldehyde but also played a role in the catalytic degradation of EHL.

In this work, EHL was liquefied using oxalic acid in the presence of phenol. EHL–PF was synthesized by the polymerization of phenol and the partial replacement of liquefied EHL with formaldehyde. According to the effects of different replacement percentages on the residue rate, the appropriate amount of liquefied EHL was prepared and characterized using FT-IR, GPC, ^1H NMR spectroscopy and SEM. The differences between PF and EHL–PF were investigated by comparing the results of measurements via FT-IR spectroscopy, DSC, and other techniques.

2. Material and methods

2.1. Materials

EHL (M_w 3107, M_n 1288), kindly donated by the Guangxi Academy of Science, was dried in an oven at 50 °C for 24 h and then kept in a desiccator at room temperature until it was used. The phenol, oxalic acid and formaldehyde (37% solution) were technical grade.

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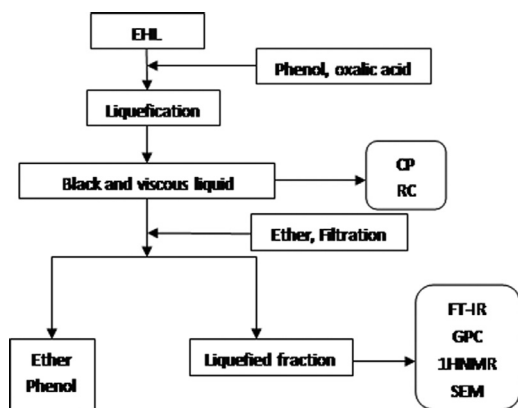


Fig. 1. Flowchart of EHL liquefaction diagram.

2.2. Preparation of liquefied EHL

Liquefaction experiments were conducted at different replacement percentages of phenol by EHL, ranging from 20% to 55%, and the oxalic acid dosages used were based on previous studies [14]. A 100-mL four-neck flask provided with a thermocouple, mechanical stirrer, and condenser was charged with 20 g of melted phenol and the appropriate amount of oxalic acid; the system was heated to 100 °C until the oxalic acid was completely dissolved, and then, a certain amount of EHL powder was loaded into the system slowly while continuously stirring. After adding EHL, the system temperature increased to 115 °C for 2 h, and then, the reactor was cooled to room temperature. The mixture was a type of black and viscous liquid.

2.3. Preparation of EHL–PF

The use of liquefied EHL as the phenolic feedstock for phenolic resin synthesis was the main objective of this study. At fixed molar ratio of phenol and formaldehyde of 1:0.85, calculated formaldehyde was poured into the above system. The mixture was heated slowly to 85–90 °C, and then, the heater was turned off. Subsequently, the system temperature increased due to exothermal reaction and eventually boiled; the temperature was maintained for a certain time, and then, the product was dehydrated in vacuum to remove the residual volatiles. The obtained EHL–PF resin was black and friable.

2.4. Characterization of the liquefied fractions and the EHL–PF products

Fig. 1 shows the flowchart of EHL liquefaction. The liquefied mixture was diluted with ether, filtrated and washed three times. The insoluble residues were oven dried at 105 °C to a constant weight. The residue content of the liquefied EHL was calculated using Eq. (1).

$$RC(\%) = \frac{W_r}{W_0} \times 100\% \quad (1)$$

where W_r and W_0 are the amounts of the oven-dried insoluble residues and the original EHL, respectively.

To determine the combined phenol percentages (CP), a sample of the mixture was diluted with methanol and fixed to a constant 100 mL with methanol. The CP, as defined by Eq. (2), was calculated based on the concentration of free phenol in the methanol solution of liquefied products, which was detected via HPLC using methanol–water (v/v = 1:2) as the eluent.

$$CP(\%) = \frac{W_0 - W_r}{W_0} \times 100\% \quad (2)$$

where W_0 and W_r are the amounts of originally added phenol and remaining phenol after the liquefaction, respectively.

Table 1
Residue rate and CP% for the EHL liquefaction.

Replacement percentage of phenol by EHL	RC (%)	CP (%)
20%	11.9	1.1
30%	15.0	4.9
40%	16.8	6.1
50%	22.6	3.8
55%	28.1	3.7

The structures of pre- and post-liquefaction EHL were analyzed using FT–IR spectroscopy and ^1H NMR spectroscopy, respectively. The FT–IR spectra of lignin samples were obtained using a Nicolet iS10 IR spectrometer (Nicolet Co., USA) within the wave number range of 500–4000 cm^{-1} . For ^1H NMR inspection, the samples were prepared by dissolving approximately 5–6 mg of product in 0.5 mL of deuterated chloroform.

GPC was performed at room temperature. Pre- and post-liquefaction EHL were dissolved in THF (0.5%, W_t/W_r) to determine M_n and M_w using a Waters 1550–2410 system with the following equipment: 1550 HPLC Pump, 2410 Refractive Index Detector, and Column Styragel HR1 and HR2. THF was used as a mobile phase at the flow rate of 1 mL/min, and the injection volume was 1 μL . The calibration curve was made using polystyrene standards at different molecular weights.

The structure of the pre- and post-liquefaction EHL was investigated using a scanning electron microscope, 3400N Hitachi Co., Japan. The specimens were mounted on an aluminum stub and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

DSC measurements of PF and EHL–PF were performed at 20 °C/min under a nitrogen flow rate of 10 mL/min. Before being tested, the samples were extensively dried for 48 h using vacuum freeze-drying to eliminate water. Two sample powders were mixed with urotropine (10% sample powders weight) and then characterized using a differential scanning calorimeter to compare their curing processes.

The characteristics of free phenol, softening point, flowing distance and gelation time of EHL–PF were determined according to the standards HG/T 2621-94, GB/T 12007.6–1989 and JB/T 8834-2001.

3. Results and discussion

3.1. EHL characterization

3.1.1. EHL liquefaction in phenol medium

Lignin can be liquefied into small fractions that are dissolved in phenol under acidic conditions; the effects of different replacement percentages catalyzed by oxalic acid on RC and CP are presented in Table 1.

When the replacement percentage increased from 20% to 55%, RC was gradually increased from 11.9% to 28.1%. It could be seen that more phenol contributed to the liquefying process; at the same time, lignin produced more radicals, although phenol can act as a capping agent, which prohibits lignin re-polymerization [15,16]. CP had an adverse trend compared with RC; its values gradually increased at a lower replacement percentage, with more phenol reacting with lignin radicals, which increased the replacement percentage. During the liquefied process, the first step involves the protonation of the benzyl hydroxyl group, followed by dehydration at the α -carbon to yield a carbonium ion. The phenol molecule undergoes an electrophilic attack by a carbonium ion, giving rise to phenol condensation production. Phenol could react with the liquefied fractions easily when the replacement percentage increased from 20% to 40%, at which point CP obtained its maximum of 6.1%; surprisingly, CP decreased to 3.1% at the replacement percentage of 55%. This behavior occurred because

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