



Structure-property relationships for technical lignins for the production of lignin-phenol-formaldehyde resins



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ABSTRACT

The synthesis and performance of a lignin-phenol-formaldehyde resin are significantly related to the properties of the lignin used. In an effort to provide a fundamental understanding of lignin structure-property relations for lignin-phenol-formaldehyde resin synthesis and application, two distinct technical lignins were examined as-obtained from an acidic (L_1) and an alkaline (L_2) organosolv pulping of bamboo. These samples were thoroughly characterized and the structural and compositional features of them were charted. The content of β -O-4' linkages in L_1 were 23.83 per 100Ar, followed by some β - β' linkages (1.27 per 100Ar). However, almost all the side-chain linkages in L_2 were cleaved. The purities of the two lignins both exceeded 81.0%, but significantly more extractives were found to be present in L_2 . Subsequently, two lignin-phenol-formaldehyde resins were successfully synthesized using L_1 and purified L_2 at a substitution rate of 50% to phenol. The high content of extractives contaminating L_2 , especially long-chain hydrocarbon derivatives, severely affected the synthesis of lignin-phenol-formaldehyde resin. The successful removal of this fraction was necessary before the material could be put to use.

1. Introduction

Technical lignins obtained through the refinery of lignocellulosic biomass (wood and annual plants) represent an attractive potential substitute for fossil-based raw materials. The rational use of this nature compound is the key point to realize the integral valorization of lignocellulosic biomass. The phenolic structure of lignin makes it theoretically applicable to the production of value-added chemicals and materials such as lignin-phenol-formaldehyde (LPF) resins (Duval and Lawoko, 2014). Numerous laboratory and pilot plant studies have been conducted in effort to synthesize LPF resins with alkaline lignins and lignosulfonates (Ghaffar and Fan, 2014; Ten and Vermerris, 2015; Constant et al., 2016; Upton and Kasko, 2016; Kai et al., 2016). In a previous study conducted in our laboratory, alkaline, Kraft, and steam explosion lignins as-obtained from corn cob, poplar wood, and wheat straw, respectively, were used to synthesis LPF resins at a substitution rate of 50% to phenol. The synthesized LPF resins performed well in the preparation of high-quality plywoods (Yang et al., 2015a, 2015b). A lignin-based phenolic resin has already been successfully produced at

large scale with the corn cob alkaline lignin and is currently used in plywood and particleboard industrial production protocols in China.

All technical lignins can serve as potential replacements for phenol to prepare LPF resins per the chemical reaction capabilities of them, but the influence of the structure and impurities of technical lignins on the resin synthesis and final performance of the materials prepared with the synthesized resins generally remain unclear. This information is an important reference in resolving engineering issues that may arise during the industrialized production of LPF resins, however. The composition and properties of technical lignins obtained via the refinery process are determined by factors such as the material species, solvent properties, and cooking conditions. To this effect, any technical lignin produced via a certain process should be regarded as a distinct material even if it shares some characteristics with other technical lignins.

The desired structural properties of technical lignins for LPF resin synthesis include, 1) adequate phenolic hydroxyl groups; 2) abundant unsubstituted aromatic C3- and/or C5-positions; and 3) relatively low and narrow apparent molecular weight molar mass and distribution (El

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Mansouri and Salvadó, 2006). Comprehensive understanding of the structure of the technical lignins can also help in securing materials that are best suited for LPF resin synthesis. Researchers have also found that low carbohydrate and ash contents tend to result in better-performing LPF resin products (Wang and Chen, 2014).

Organosolv pulping is an effective approach to producing technical lignins with almost no residual carbohydrates and ash (Li et al., 2012; Constant et al., 2016). Various organosolv processes (based on different solvents) have been established by previous researchers (Koskela et al., 2005; Constant et al., 2016). The phenolic and somewhat polymeric nature of such lignins make them favorable potential replacements for phenol in a multitude of industrial operations with considerable economic and environmental benefits (Ten and Vermerris, 2015; Upton and Kasko, 2016). The application of organic solvents creates an excess of extractives in the lignocellulosic biomass moves to technical lignin, however. The effects of extractives present in the technical lignins on the preparation details of LPF resins and subsequent application of them have yet to be fully understood.

The presence of specific components such as extractives as well as other structural characteristics can markedly affect the properties of the final products. To this effect, the properties of a given technical lignin are crucial in regards to its practical utilization. The valorization of a technical lignin requires detailed insight into its structural, polymeric, and compositional characteristics. All of these factors are known to impact the kinetics and other mechanistic considerations of LPF resin preparation with concomitant performance characteristics in the final product.

In an effort to create a sound scientific basis for these structure-property relations, this paper examines the composition, structural characteristics, and chemical reactivity of lignin samples collected from two distinct organosolv pulping processes (acidic and alkaline). These two technical lignins were then used to synthesize LPF resins and carefully compared in regards to their respective synthesis and final performance. The properties of the synthesized resins and the bonding strength of plywoods prepared with them were measured in accordance with the standard methods defined for such materials.

2. Materials and methods

2.1. Materials

Two technical lignins (L_1 and L_2) were kindly supplied by Konglong Paint Limited Company and Menghu Bamboo Fiber Limited Company in China, respectively. L_1 was obtained from an organosolv pulping process with acetic acid, and L_2 was acquired from an alkaline (pH = 8–9) organic solvent pulping process. Both processes used bamboo (*Phyllostachys heterocycla* (Carr.) Mitford cv. Pubescens) as raw materials. Prior to use and analysis, the lignin samples were dehydrated at 60 °C in a convection oven and then stored in a desiccator containing competent color changing silica gel. The chemical reagents (phenol, formaldehyde solution (37%), and NaOH) used in this research were all of analytical grade and were not further purified prior to use.

2.2. Purification of L_2

To obtain purified L_2 (L_{p2}), the extractive rich lignin (L_2) was dispersed in an 0.5 mol L⁻¹ NaOH solution followed by vigorous agitation at 75 °C for 1 h. The solid-to-liquid ratio was set as 1:25 (w/w). After dissolution, the mixture was filtered with a Buchner funnel to remove the insoluble substances and the pH of the obtained filtrate was adjusted to 3 with dilute HCl to precipitate the dissolved lignin. After standing for 12 h, the upper phase formed a transparent liquid. The precipitated lignin in the lower phase was separated through centrifugation and rinsed with hot acid water (pH = 2) followed by a freeze-drying to obtain L_{p2} .

2.3. Analyses of the lignin samples

The compositions of the lignin samples in this study were determined based on a general standard method (NREL/TP-510-42618) (Sluiter et al., 2008). Each sample was analyzed in two replications and the results were averaged as the final values reported here. The lignins were acetylated through the method proposed by Pan et al. (2006). The weight-average (M_w) and number-average (M_n) molecular weights of the acetylated lignin samples were determined on a gel permeation chromatography (GPC) instrument equipped with a PL-gel 10 mm Mixed-B 7.5 mm ID column via the method described by Wen et al. (2013a); monodisperse polystyrene served as the standard. Nuclear magnetic resonance (NMR) spectra of the lignin samples were collected on a Bruker AVIII 400 MHz spectrometer (Germany). The instrument parameters were set based on the descriptions of Wen et al. (2013b). For ¹³C NMR analysis, a 100 mg sample was dispersed in 0.5 mL DMSO-*d*₆. Only 90 mg of lignin was used for two-dimensional hetero-nuclear single-quantum coherence spectroscopy (2D HSQC) NMR analysis. A quantitative analysis of the lignin structure based on the 2D HSQC spectra was performed according to a procedure also described by Wen et al. (2013b). The ³¹P NMR spectra were acquired after of the lignin samples were subjected to phosphate modification by 2-chloro-4,4,5,5-tetramethyl-1,3, 2-dioxaphospholane (TMDP) per the method described by Argyropoulos (Crestini and Argyropoulos, 1997). A common internal standard (cholesterol) was used to calculate the content of hydroxyl groups in the lignin samples. Fourier transform infrared (FT-IR) spectra of the lignins were acquired on a Thermo Scientific Nicolet iN10 FT-IR Microscope instrument (USA). The lignins were directly placed on a silver-plated sample table. Data acquisition was conducted in the range of 4000–675 cm⁻¹ with a 3 cm⁻¹ resolution; each sample was scanned 128 times. Thermal gravimetric (TG) analyses of L_1 and L_2 were conducted on a Shimadzu TA-60 (Japan) in the temperature range 40–700 °C at a 10 °C min⁻¹ heating rate. The flow rate of nitrogen for all the measurements was 50 mL min⁻¹. Alumina crucible with a dimension of 4.0 mm in depth and 6.0 mm in diameter was used to hold the lignin samples (3 ~ 5 mg).

2.4. Synthesis and characterization of lignin-phenol-formaldehyde resins

The LPF resins in this study were synthesized in a three-neck flask equipped with a magnetic stirrer, cooling condenser, thermometer, and water bath. The mass ratio of lignin to phenol was 1:1. The total formaldehyde consisted of two parts: one part was calculated according to the molar ratio of phenol to formaldehyde, and the other part was calculated based on the number of active sites of each technical lignin as described by a previous study (Yang et al., 2015b). NaOH was used to catalyze the reaction at a content of 6% of total reactant weight. In the first step, phenol and lignin were adequately mixed. Then, the appropriate amount of NaOH solution (30% wt) was added to adjust the pH value of the mixture to 10. This system was heated to 90 °C and held for 1 h. After this step, the temperature of the resulted mixture was dropped to 80 °C, and 70% of the total formaldehyde and NaOH solution (30% wt) was added. The obtained mixture was kept at 80 °C for 1 h. Next, the remaining formaldehyde was added, and the mixture was kept at 80 °C for 1 h. Finally, the temperature of the mixture was decreased to 65 °C, and the remaining NaOH solution (30% wt) and urea (5% of the total weight of phenol and lignin) was added. This resulted mixture was held at 65 °C for 0.5 h to yield the LPF resin.

The solid content, viscosity, pH value, free formaldehyde content, free phenol content, and gel time of the synthesized resins were measured according to the methods specified by the Chinese National Standard (GB/T 14074-2006). A commercial phenol-formaldehyde (CPF) resin, which was purchased from Beijing Taier Chemical Co., Ltd., was also used as a comparison.

Poplar plywoods (3 layers, 400*400*4.5 mm) were prepared with the synthesized resins to evaluate the performance of them. Wheat flour

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