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Fractionation and characterization of industrial lignins

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ABSTRACT

Three industrial lignins (Indulin AT Kraft softwood, Protobind 1000, and corn stover) were fractionated in methanol to obtain soluble and insoluble fractions. The original lignin and obtained lignin fractions were characterized chemically by a combination of FTIR spectroscopy, pyrolysis-gas chromatography–mass spectrum (py-GC–MS), and derivatization followed by reductive cleavage (DFRC). The methanol soluble lignin fractions contained fewer condensed structures than the original lignin and methanol insoluble fractions. The thermal (e.g. glass transition temperature (T_g) and thermal stability) and rheological properties of the lignins were characterized by a combination of DSC, TMA, TGA and parallel plate rheology. TMA and modulated temperature DSC (MTDSC) proved to be sensitive techniques in determining T_g. The methanol soluble lignin fractions had the lowest T_g values relative to the original lignin and methanol insoluble fractions. The original lignin and methanol insoluble fractions had a higher thermal degradation temperature relative to the methanol soluble lignin. Solvent partitioning offers a practical approach to fractionate lignin into low M_w and T_g fractions which show promise as starting materials for making lignin-copolymers.

1. Introduction

Lignin is widely distributed throughout the plant kingdom where lignification is not confined to xylem (wood) and annual plants but also found in fruit, seeds, bark, roots, bast, pith and cork cells (Pearl, 1967). Recently, lignin has also been found in seaweed (Martone et al., 2009). Due to this extensive distribution, lignin is ranked second in content behind cellulose in terrestrial natural resources (Lewis and Lantzy, 1989) and being nature's most abundant aromatic polymer (Lora and Glasser, 2002). Lignin content varies depending on species and typically 20–30% for hardwoods and 25–35% for softwoods (Dimmel, 2010). Although the vast quantities of lignin in nature, historically, lignin has had a negative role in pulp and paper industry as well as an emerging biorefining industry, where efforts are made to remove the polymer. Subsequently, large amounts of lignin are produced annually, for instance, the pulp and paper industry alone produced 45 million metric tons of extracted lignin in 2004 (Zakzeski et al., 2010). The application of value-added lignin, however, is limited to a low level with only approximately 2% of the total availability of lignin from pulp and paper industry (Gosselink et al., 2004). The limited application of industrial lignin is largely due to its complex three-dimensional aromatic structure and heterogeneity based on feedstock type and extraction process. Industrial or extracted lignin is brittle, has a high glass transition temperature (T_g), a complex chemical structure and low solubility in common solvent are contributing factors which limits its use as a polymer (Li et al., 1997). Lignin's brittleness is due to its 3-dimensional structure and inter- and intra-chain hydrogen-bondings (Aracri et al., 2014). Thermoplasticity can be introduced to lignin by substituting hydroxyl groups which will inhibit hydrogen-bonding (McDonald and Ma, 2012; Sivasankarapillai et al., 2012).

There have been considerable efforts to improve lignins properties by substitution, namely methylation (Li et al., 1997), esterification (Fox and McDonald, 2010) and benzylation (McDonald and Ma, 2012), to impart thermoplasticity. Substitution also resulted in lowering the glass T_g of lignin. Other strategies for lignin modification have involved its incorporation into polyurethane, polyester, polyolefin, polyethylene oxide, and vinyl polymers (Chung and Washburn, 2013; Gandini and Belgacem, 2008; Li and Sarkanen, 2000; Miller, 2013; Pohjanlehto et al., 2014; Wang et al., 1992).

To improve lignin's miscibility with other polymers, solvent partitioning, using methanol, have been employed to separate out a low and high molar mass fractions (Sivasankarapillai and McDonald, 2011; Sivasankarapillai et al., 2012). Early work by Yoshida et al. (1987) had fractioned kraft lignin and black liquor by successive extraction with solvents and had characterized the fraction's properties (Morck et al., 1986; Yoshida et al., 1987). A

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similar study was also conducted by Yuan et al. (2009) using successive organic solvents to partition an industrial lignin, and obtained fractions which were subsequently chemically and thermally characterized and showed differing properties. Kraft hardwood lignin was also fractionated in methanol for use in lignin based thermoplastics and lignin-polymer systems (Saito et al., 2012, 2013, 2014). Work by Argyropoulos' group had used an acetone soluble lignin fraction in poly(arylene-ether-sulfone) based copolymer systems (Argyropoulos et al., 2014). Arshanitsa et al. (2013) and Ponomarenko et al. (2014) sequentially applied organic solvents to fractionate industrial lignin to improve their role as antioxidants. Membrane based separation on industrial lignin has been applied for use in adhesives and carbon fibers (Brodin et al., 2009, 2010).

The aim of this study was to fractionate industrial lignin to obtain low molar mass lignin that could be used in lignin-copolymer systems. The original lignin and methanol soluble/insoluble fractions were characterized for chemical characteristics and thermal properties and their relationships.

2. Materials and methods

Protobind 1000 (PB) lignin (agricultural fiber soda pulp) was supplied by ALM India Pvt. Ltd. and used as received. Indulin AT (IN) lignin (softwood kraft) was provided by MeadWestvaco and used as received. Corn stover (CS) lignin (from cellulosic ethanol production) was obtained from the National Renewable Energy Laboratory and washed with hot water (60 °C) and vacuum dried.

2.1. Lignin fractionation

Lignin (250 g) was stirred in methanol (1.5 L) for 5 h at 60 °C. The methanol soluble (MS) and methanol insoluble (MI) fractions were recovered by filtration, vacuum dried and yields recorded. For example, the lignin sample PB was fractionated into PB-MS and PB-MI.

2.2. Chemical analysis

Klason lignin and acid soluble lignin contents were performed on lignin samples (200 mg, in duplicate) according to ASTM D1106-96 (2013) and Tappi UM250 (1991), respectively.

The weight average molar mass (M_w) of IN-MS, PB-MS and CS-MS were determined by electrospray ionization-MS (ESI-MS) on a LCQ-Deca (Thermofinnigan) according to Osman et al. (2012).

Lignin (1.00 g) was acetylated in a 1:1 (v/v) mixture of acetic anhydride/pyridine (6 mL) for 24 h at 20 °C. The acetylated lignin product was precipitated in ice-water. The precipitate was further washed with water, freeze-dried and yield recorded.

FTIR spectra were collected by a ThermoNicolet Avatar 370 spectrometer, in duplicate, operating in the attenuated total reflection (ATR) mode (SmartPerformer, ZnSe crystal). The spectra were ATR and baseline corrected. For the quantitative analysis, the spectra were normalized and curve-fitted using Igor Prof 6.03 software (WaveMetrics, Inc.) (Wei et al., 2013) and the area of each fitted band was integrated. The aromatic/aliphatic OH ratio was calculated as the ratio of areas under the carbonyl (C=O) bands at 1760–1742 cm^{-1} (Glasser and Jain, 1993). The syringyl/guaiacyl (S/G) ratio was calculated as the ratio of the areas for the S unit at 1327 cm^{-1} to G unit at 1267 cm^{-1} (Poursorkhabi et al., 2013). The condensation indices of lignin was determined from the FTIR spectra using Eq. (1) (Faix, 1991a,b):

$$\text{Condensation Indices (CI)} = \frac{\sum \text{minima between 1500 and 1050 cm}^{-1}}{\sum \text{minima between 1600 and 1030 cm}^{-1}} \quad (1)$$

Lignin DFRC analysis was performed as following (Lu and Ralph, 1997): (i) lignin (20 mg) was dissolved in acetic acid/acetyl bromide (4:1 v/v, 5 mL) and stirred for 1 h at 50 °C and reagents removed under vacuum at 40 °C; (ii) the residue was dissolved in dioxane/acetic acid/water (5:4:1 v/v, 5 mL) to which zinc powder (50 mg) was added and the mixture stirred for 30 min at 20 °C. Zinc was removed by filtration and an internal standard (10 mg tetracosane in CH_2Cl_2, 10 mL) was added to the filtrate, mixed, washed with saturated NH_4Cl (10 mL), CH_2Cl_2 layer recovered, dried and concentrated to dryness; (iii) The reduced material was acetylated with acetic anhydride/pyridine (1:1 v/v, 2 mL) for 80 min at 20 °C, then ethanol added to quench the reaction and excess reagents were removed under vacuum. The residue was dissolved in CH_2Cl_2 (1.5 mL) and analyzed by GC–MS (Polaris Q, Thermofinnigan). Separation was performed on a ZB-1 capillary column (30 m × 0.25 mm i.d., Phenomenex) with a temperature program of 100 °C (1 min) to 300 °C at 5 °C/min. *p*-Hydroxy phenyl (P), G, and S units were determined using response factors 1.76, 1.85, and 2.06, respectively.

Pyrolysis GC–MS analysis (Focus-ISQ, ThermoScientific) was performed on lignin (<0.1 mg) in a quartz capillary tube and pyrolyzed (Pyrojector II, SGE) at 500 °C. Separation was achieved on a RTx-5ms capillary column (30 m × 0.25 mm i.d., Restek) with a temperature program of 50–250 °C (10 min) at 5 °C/min. Compounds were identified with known standards, NIST 2008 mass spectral library and literature (Meier and Faix, 1992). The S/G ratios were determined according to Nonier et al. (2006) and Nunes et al. (2010).

2.3. Thermal analysis

DSC was performed on a TA instruments model Q 200 DSC equipped with refrigerated cooling on 5–7 mg of sample. Conventional DSC with annealing the sample was heated to 90 °C and annealed for 10 min, then cooled to 0 °C (3 min), then heated to 200 °C at 10 °C/min (second cycle). DSC without annealing was carried out from 40 to 200 °C at 10 °C/min. MTDSC was equilibrated at 0 °C for 5 min, then heat modulated ±0.66 °C every 50 s, and then ramped from 0 to 250 °C. The inflection point of heat flow change from heating cycle was assigned as T_g. Kinetic studies were carried out using conventional DSC with annealing at 5 °C/min, 10 °C/min, and 15 °C/min to determine activation energy of the T_g transition (Moynihan et al., 1974).

TMA was carried out with Perkin Elmer TMA 7 instrument using the penetration probe (static force 10 mN) from 30 to 300 °C at 5 °C/min. Lignin samples were pressed to a small disk (2 mm × 1 mm). The onset point of softening was assigned as T_g.

Parallel plate rheometry (25 mm dia serrated) was performed using a Bohlin CVO100 instrument with an extended temperature unit. Lignin samples were compression molded into 25 mm × 2 mm discs. Experiments were performed at 1 Hz from 180 to 40 °C at −2 °C/min with a normal force applied at 1 N, and strain of 0.05% (within the linear viscoelastic range). Data was analyzed using the Bolhin software v 06.32 (Fox and McDonald, 2010).

TGA was carried out using a Perkin Elmer TGA 7 instrument from 30 to 900 °C at 20 °C/min under N_2 (30 mL/min). Kinetic study of thermal decomposition was carried out by TGA under 5 °C/min, 10 °C/min, and 15 °C/min.

3. Results and discussion

3.1. Chemical analysis

Partitioning lignin into low and high molar mass fractions based on partial methanol solubility (Hildebrand solubility parameter of 14.3 $(cal/mL)^{1/2}$) was selected because of practical ease of separation (Argyropoulos et al., 2014; Saito et al., 2014; Sivasankarapillai and McDonald, 2011; Schuerch, 1952). Three industrial lignin