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Lignin-based catalysts for Chinese fir furfurylation to improve dimensional stability and mechanical properties

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ABSTRACT

In order to valorize lignin from spent liquor of pulping mills, a novel catalyzing system for wood furfurylation which composed of lignin-derived acids (LDAs, i.e. lignosulfonic acid and sulfomethylated lignin acid) and buffer sodium borate was developed, and was applied to Chinese fir furfurylation for improved dimensional stability and mechanical properties. LDAs were prepared by protonating of sulfomethylated lignin and lignosulfonate through cation exchange resin. The catalyzing system was optimized by the storage duration of FA formulas with respective catalyzing system at room temperature and the curing time at elevated temperature. Then, three formulas were selected out to treat Chinese fir and their performance was evaluated by weight percentage gain, dimensional stability, and compressive strength. The results showed that LDAs, especially sulfomethylated lignin acid, penetrated into cell walls and catalyzed furfurylation reaction quite well. The best performance achieved in this study by Formula III was with weight percentage gain of 66.4%, equilibrium moisture content 12.9%, anti-swelling efficiency 61.9% and 70.6% for the conditions of high humidity and water-soaking, respectively; its parallel-to-grain compressive strength was improved by 45.4%. It hints lignin-derived acids combined with borate would be a promising catalyst system for wood furfurylation since it valorizes both the waste lignin and low-valued wood.

1. Introduction

Chinese fir (*C. lanceolate*) is the wood species with the largest plantation area in South China, due to its rapid growth, straight texture, less pests and diseases, and easy processing etc. (Chen and Wu, 2000; Peng et al., 2006). However, its mechanical property and dimensional stability are poor, with a deficient resistance to moisture and wear, leading to quite limited practical applications in wood industry (Peng et al., 2006). Therefore, how to increase the added value of Chinese fir and how to utilize this resource more properly and efficiently is an issue faced by China's timber industry (Xu et al., 2014).

Furfurylation is a promising green process to improve the dimensional stability and strength properties of low-valued wood (Li et al., 2014). Furfural, a renewable chemical from bioresources, is obtained xylose resulting from hydrolysis of pentosan-rich biomass, such as wood, and agricultural residues of sugarcane, corn and wheat (Wang et al., 2006). Furfuryl alcohol (FA) is a derivative of furfural through hydrotreating (Venås and Rinnan, 2008; Wang et al., 2006). FA resin, a brown red viscous liquid formed by polymerization of FA under the actions of acidic catalysts, is a kind of thermosetting polymer (Bertarione et al., 2008; Choura et al., 1996; Kim et al., 2014; Lande et al., 2004a). The reaction is an exothermic reaction itself but the process is very slow. The solidified FA resin has a good tolerance for acid, alkali, high temperature, water, fungi, corrosion, etc. (Lande et al., 2004a; Yuan et al., 2007). A number of researches showed that wood furfurylation can effectively improve the quality and the durability of wood but without any harm to the environment (Epmeier et al., 2007a,b; Esteves et al., 2011; Gerardin, 2016; He et al., 2012; Lande et al., 2004a,b; Li et al., 2014, 2015, 2016, 2017; Pilgård et al., 2010a,b; Venås and Rinnan, 2008).

Wood furfurylation is a very complicated process. Currently, a three-stage production process is widely employed: pressure impregnation, resin curing, and product drying (He et al., 2012; Li et al., 2014, 2015; Yao et al., 2017). The curing duration varies from a few hours to twenty hours depending on the size of wood blocks. Catalysts commonly used in furfurylation are maleic acid, malic acid, malonic acid, phthalic acid, benzoic acid, benzenesulfonic acid, *p*-toluenesulfonic acid, sulfonic acid, maleic anhydride, and other cyclic carboxylic acid anhydrides, etc. (Epmeier et al., 2007a,b; Esteves et al., 2011; He et al., 2012; Lande et al., 2004a,b; Li et al., 2014, 2015, 2016, 2017; Pilgård

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et al., 2010a; Sejati et al., 2017; Venås and Rinnan, 2008). Borates were also used as catalyst for wood furfurylaltion and as a wood preservative, since they not only impart flame retardancy of wood, provide sufficient protection against wood destroying organisms, such as termites and wood decay fungi, but have a low volatility (Baysal et al., 2004).

Lignin is an organic substance in plant cell walls cementing microfibrils together and binding the cells (Rowell, 2013). It is the second most abundant renewable carbon source on Earth just after cellulose. There are 40–50 million tons lignin per annum produced worldwide, usually as a non-commercialized waste (Rowell, 2013; Sjöström, 1993). Lignosulfonate (usually as sodium salt) is a by-product of sulfite pulping, while alkali lignin is a by-product from the effluent of soda pulping or kraft pulping (Hon et al., 2001). For lignosulfonate, its acid can be easily obtained by protonation through a cation exchange resin. In term of alkali lignin, its acid needs to be derived at first by sulfonation or sulfomethylation and then subjected to ion exchange (He et al., 2016). Nordstierna et al. (2008) reported that lignin-like model compounds can form covalent bonds between FA. While Guigo et al. (2010) demonstrated a plasticized lignin is compatible with furanic resins and the blend of composites were monophasic.

In order to valorize both waste lignin and low-valued Chinese fir wood, lignin derived acids (LDAs, one from protonation of lignosulfonate, and the other from protonation of sulfomethylated alkali lignin) combined with borate were explored as the catalysts for Chinese fir furfurylation in this investigation. The weight percentage gain, the stability (equilibrium moisture content and anti-swelling efficiency), and the mechanical property (compressive strength) of Chinese fir wood blocks were tested. In addition, the specimens were analyzed by scanning electron microscopy and fluorescent microscopy to see the distribution of FA resin in plant cells.

2. Material and methods

2.1. Materials

Furfuryl alcohol (CAS: 98-00-0, light yellow liquid, ≥98%) was purchased from Aladdin Co. Ltd. (Shanghai, China). Toluidine blue (CAS: 3209-30-1) which used in wood stain was supplied by Sinopharm Chemical Reagent Co.,Ltd. (Shanghai, China). Sulfomethylated lignin (CAS: 68512-34-5) was provided by Jiefa Tech Co., Ltd. (Zhejiang, China), while lignosulfonate (CAS: 8061-51-6) by Shixian Paper Corp. (Jilin, China). Sodium borate etc. common chemicals were all analytical grade and ordered from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). All solutions were prepared with deionized water.

The wood of Chinese fir used in this experiment was cut from Shunchang County, Fujian Province. The test materials used in the experiment were the sapwood part and all from the mature wood above the chest height and. The test specimens were prepared according to Chinese standard GB/T1929-2009: 6 samples with size of 20 mm × 20 mm × 30 mm (Tangential × Radial × Longitudinal) for parallel-to-grain compression strength test, and 12 samples with size of 20 mm × 20 mm × 20 mm for dimensional stability test. The specimens used required no knots, cracks, decay, oblique texture, or other defects.

2.2. Preparation of lignosulfonic acid (LSA) and sulfomethylated lignin acid (SLA)

Ion exchange was employed to convert lignosulfonate and sulfomethylated alkali lignin which provided by pulp mills into respective acid, sulfomethylated lignin acid (SLA) and lignosulfonic acid (LSA). Lignin solutions flowed through a fixed bed ion exchange column (30 mm inner diameter × 300 mm length) packed with strong acid cation exchange resin macroporous 001 × 7 (732, Jinda Zhengtong Corp., Tianjin, China). The column had sand cores at both ends to prevent the entrainment of resin particles. In addition, it was operated in up flow mode to reduce channeling. The solution was fed at 30 mL/h with a pump. The chemical structures of SLA and LSA were illustrated in Fig. 1. The obtained SLA and LSA solution were then concentrated to a certain mass fraction for future use.

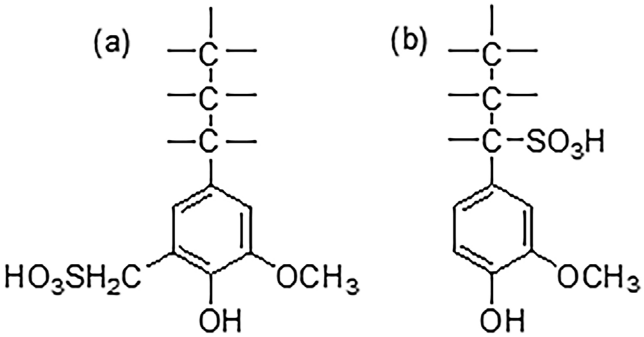

Fig. 1. Chemical structures of (a) sulfomethylated lignin acid (SLA) and (b) lignosulfonic acid (LSA).

2.3. Formula storage stability

The formulas for wood furfurylation were composed of monomer FA, catalyst LSA or SLA, buffer sodium borate, and deionized water. The mixture of the latter three components was put in a water bath at 35 °C to preheat for 30 min till the solution became clear, and then FA was slowly added into the system under magnetic stirring. Formula storage stability was assessed by observation the duration when formula became turbid at ambient temperature. Usually, the storage time required for manufacturing was several days, e.g. seven days, since FA formula needs to be recycled and reused in the process of industrial production.

2.4. Curing time of FA resin

The curing time for FA resin was assessed by heating the formulas in an oven at 105 °C. The FA concentration used for curing time test was 70% and the borate dosage was 0.5%.

2.5. Chinese fir furfurylation

The specimens were subjected two steps for furfurylation: impregnation and curing. In impregnation, the specimens firstly were placed in an autoclave and a negative pressure was applied to expel air and nonvolatile gas in wood for 30 min. Then the FA formulas were loaded in the system under the vacuum and then the pressure of autoclave was raised to 0.8 MPa for 5 h. Finally, the specimens were taken out of the device, using a gauze to absorb the liquid on the surface of wood blocks. In curing, wood blocks were wrapped using aluminum foils and then cured in an oven at 103 °C to avoid evaporation of FA. After 7 h of curing, aluminum foils were removed, and the specimens were dried at 60 °C and 80 °C for 40 min each, and finally dried at 103 °C until absolute dry.

2.6. Dimensional stability and mechanical properties test

2.6.1. Weight percentage gain

The oven-dried weight of Chinese fir specimens before and after furfurylation was recorded as m_0 and m_1, respectively. The Weight percentage gain was assessed by Eq. (1).

$$\mathrm{WPG} = \frac{(m_1 - m_0)}{m_0} \times 100\% \tag{1}$$