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Novolak PF resins prepared from phenol liquefied *Cryptomeria japonica* and used in manufacturing moldings

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Abstract

The wood of Japanese cedar (*Cryptomeria japonica*) was liquefied in phenol with H_2SO_4 and HCl as catalysts. The liquefied wood was reacted with formalin to prepare the novolak PF resin. The results showed that the reaction of liquefied Japanese cedar with formalin was an exothermic reaction, and formed a solid-like resin without extra heating. Two novolak PF resins were prepared from the liquefied wood which were identified as SF and CF that using the liquefied wood with H_2SO_4 and HCl as catalyst respectively. The novolak PF powder displayed thermo-melting characteristic. The resins of SF and CF had weight average molecular weight of 3638 and 3941 respectively and melting temperature of 149.4 °C and 127.5 °C respectively. Both of the novolak resins could be used to make moldings with good performance by mixing the novolak resin with wood powder, hardener and zinc stearate at the weight ratio of 60:30:10:1 and hot-pressed under 200 °C for 10 min.

Keywords: *Cryptomeria japonica*; Liquefied wood; Moldings; Novolak PF resin

1. Introduction

Solvent liquefaction is one of the effective methods to convert the wood materials from solid to liquid. Liquefaction wood materials in phenol or polyhydric alcohol with inorganic acid as a catalyst were one of the major methods nowadays. The acid catalyst can degrade the wood components to small ingredients. And then, these ingredients react with phenol or polyhydric alcohol to form a derivative and dissolve in the liquefaction solvent. The liquefied products can be used as raw materials for the synthesis of resins.

Zhang et al. (2006) researched the liquefaction mechanism of cellulose in phenol. They indicated the pyranose that decomposed from cellulose could combine with phenol to form a hydroxyl benzyl form derivative. It retained the characteristic of phenolic functional group. Lin et al. (2004) examined the mechanism of cellulose in the presence of phenol under acid catalysis too. Acemioglu and Alma (2002) examined the kinetic of wood phenolation in the presence of HCl as a catalyst. Lee and Ohkata (2003) indicated wood could be rapidly liquefied at the supercritical temperature of phenol. Under this condition, over 90% of wood was liquefied for 0.5 min, and the properties of the products were similar to those obtained by conventional liquefaction methods. Honglu and Tiejun (2006) used the imidazole-based ionic liquid as wood liquefaction agent, they found using this method a rapid and complete liquefaction could be acquired at 120 °C for 25 min without acid catalyst. Lee et al. (2002a,b) used the phenolated wood to prepare the resol type PF resin, and liquefied wastepaper to prepare the novolak type phenolic PF. Kishi et al. (2006) used resorcinol to replace phenol to liquefy wood and indicated the products could react with epichlorohydrin to prepare the epoxy resin. In our previous study (Lee et al., 2004, 2006; Lee and Liu, 2001, 2003), resol type PF resins had prepared from the liquefied wood and bark and those were used in the manufacturing of plywood and particleboard.

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Novolak PF resins are synthesized from phenol with an insufficient amount of formaldehyde under acidic conditions to form a linear prepolymer. They are a thermoplastic resin without hydroxymethyl group in the molecular structure. Cross-linking agent such as hexamine is needed for them to form a three-dimensional networks structure under heating. Alma et al. (1996) investigated the flowability of phenolated wood and using it directly as a novolak resin. But it needed the extra process to remove the un-reacted phenol. Furthermore, the temperature needed to flow the dry liquefied wood was too high to practical use. However, the acid catalyzed phenolated wood has high acidity and possesses the constituents which can react with formaldehyde. For example, the free phenols those are un-reacted and rich in the liquefied wood and the derivatives those formed by the reaction of wood component with phenol, both of them can react with formaldehyde. In addition, lignin, one of the major wood components including the hydroxyl–benzyl structure, has the potential to react with formaldehyde.

For all these characteristics, the formalin was added directly to the acidic phenol liquefied *C. japonica* wood to prepare the novolak type PF resin in this study. The properties of the prepared novolak PF resins and the feasibility of using them as raw materials for moldings were also researched.

2. Methods

2.1. Materials

Japanese cedar (*C. japonica*) was air-dried and ground to powder in a hammer mill with a 2 mm diameter screen. The wood powder with a dimension passing 20 meshes was used for liquefaction, and passing 200 meshes were used as filler for moldings. All the wood powder was dehydrated in an oven at 105 °C for 12 h. Chemicals such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), phenol, formalin (37% aq), methanol, acetic anhydride, pyridine, dichloromethane, hexamine ($C_6H_{12}N_4$), zinc stearate and acetone were the reagent grade and were used without further purification. Tetrahydrofuran (THF) was HPLC grade, used as solvent and eluant for the gel permeation chromatography. Potassium bromide (KBr) was used for FT-IR spectrometry.

2.2. Liquefaction of Japanese cedar

To liquefy the wood of Japanese cedar, phenol and acid catalyst were premixed thoroughly in a 1000 mL separable glass flask equipped with a stirrer, thermometer, and reflux condenser. The wood powder was added gradually to the reaction flask after the temperature reached 110 °C. For the liquefaction using H_2SO_4 as a catalyst, the weight ratio of phenol/wood/H_2SO_4 was 2.5/1/0.125 and heating under 130 °C for 60 min to carry out the liquefaction reaction, the liquefied product was identified as S. For the liquefaction using HCl as a catalyst, the weight ratio of phenol/wood/HCl was 3/1/0.3 heated under 110 °C for 60 min, and the liquefied product was identified as C.

2.3. Characterization of liquefied wood

2.3.1. Residue content

About 5 g of liquefied wood was weighted and diluted with 100 mL of methanol, and then filtered through a G3 glass filter in vacuum. The residue was dried to a constant weight in a heating oven at 103 ± 2 °C. The residue content was calculated by the following equation: $R\ (\%) = W_R/W_O \times 100$. Where W_R is the oven-dry weight of the solid residue, and W_O is the oven-dry weight of the starting wood.

2.3.2. Viscosity

The viscosity of liquefied wood was measured with a Brookfield rotary viscometer at 25 ± 2 °C.

2.3.3. Nonvolatility

About 2 g of liquefied wood was weighted and dried using a rotary vacuum evaporator heating at 180 °C to remove the un-reacted phenol and calculated by the following equation: $S\,(\%) = W_S/W_1 \times 100$. Where W_S is the weight of the nonvolatility, and W_1 is the weight of the sample.

2.3.4. Combined phenol and free phenol

The combined phenol and free phenol were used to show the phenol existing in the liquefied wood that were combined with wood components or free in the system, respectively. Both the combined and free phenol were calculated from the nonvolatile content in the liquefied wood. The combined phenol was calculated by subtracting the content of wood used in the liquefaction system from the nonvolatile content after liquefaction. The free phenol was calculated by subtracting the content of combined phenol from the content of phenol used in the initial liquefaction system.

2.3.5. GPC molecular weight measuring

Liquefied wood was acetylated by acetic anhydride/pyridine (1/1; v/v). The molecular weight and weight distributions of acetylated and unacetylated liquefied woods were determined using a Hitachi L-6200A gel permeation chromatograph (GPC) equipped with the Shodex KF-802 column. The chromatograms were monitored with a UV detector at a wavelength of 280 nm. THF was used as the solvent and eluant. The concentration of testing sample was 0.1%, and filtrated with a 0.45 μm filter film. The flowing rate and injection volume were 1 mL/min and 20 μL, respectively. The monodisperse polystyrenes were used as the standards for calibrating the molecular weight.

2.4. Preparation of novolak PF resin

For preparing novolak PF resin, the molar ratio of free phenol in liquefied wood to formaldehyde was set at 1/0.8.