



# Synthesis and mechanical properties of thermoplastic films from lignin, sebacic acid and poly(ethylene glycol)



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## ABSTRACT

Lignin-based thermoplastic copolyester was synthesized via copolymerization of sebacyl dichloride with alkali lignin and poly(ethylene glycol). The copolymers obtained were thermo pressed into films. Lignin from paper making industry is abundantly available, renewable, and inexpensive but its applications are limited owing to its complicated structure. We aim to prepare a thermo-stable and thermoplastic lignin-based material. The effects of reaction conditions on weight gains and the effect of COCl/OH ratio on tensile properties of the copolymer films were studied. The reaction of the hydroxyl groups with sebacyl dichloride was verified by FTIR and <sup>1</sup>H NMR. Films obtained demonstrated good thermal properties and toughness.

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## 1. Introduction

As the second most abundant natural polymer in the world, lignin has drawn the attention of researchers for centuries. Currently, it is most readily available as a co-product of the paper industry. In addition, the rising bio-refinery industry is expected to generate vast amount of lignin enroute to cellulosic ethanol and other biomass-based products (Wang et al., 2011). It is estimated that ~20 billion tons of lignin is generated annually in the world (Buranov and Mazza, 2008), of which only a limited amount (ca. 1–2 wt% isolated from pulping liquors) is employed for value-added specialty products (Lora and Glasser, 2002). Most of the rest is burnt for power generation or simply disposed in landfills as waste, which may cause to potential environmental problems (Stewart, 2008).

Lignin is a highly branched three dimensional polymer with a large variety of functional groups including hydroxyls, phenoxyls, and alkenyls (El Mansouri and Salvadó, 2007). These reactive groups has enable lignin to be used in producing adhesives (Ibrahim et al., 2013; Zhang et al., 2013) and thermosets (Da Silva et al.,

2013; Guo and Gandini, 1991; Stanzione et al., 2013). A great deal of efforts has been dedicated to chemical modifications of lignin (Notley and Norgren, 2009). Representative uses of modified lignin include the productions of epoxy (Sun et al., 2007) and polyurethane (Hatakeyama et al., 2002) resins.

Unlike native lignin, lignin recovered from black liquor has no distinctive glass-to-rubber transition when heated. Therefore, it may not be used directly as a thermoplastic polymer material (Hirose et al., 2002; Nguyen et al., 2009). Lignin and its derivatives have also been blended with other common polymers, such as polyethylene (Alexy et al., 2000), and poly(ethylene oxide) (Kadla and Kubo, 2003), to make lignin-based thermoplastics.

An alternative strategy to obtain thermally stable lignin-based thermoplastic materials is to copolymerize lignin with co-monomers. In this respect, Kim and Kadla (2010) prepared a thermo-responsive lignin-based biomaterial through atom transfer radical polymerization. Nguyen et al. (2009) reported the preparation of lignin-based thermoplastic copolyester using renewable sebacyl chloride as linking agents between lignin macromolecules. However, the resulted lignin-based copolymer was brittle, and no mechanical properties were reported.

In this study, we adapted the sebacyl dichloride strategy and incorporated PEG as a bio-based soft segment to improve flexibility of the copolymer. Then the copolymers obtained were fabricated into films by hot press molding as well as the thermal and tensile properties were investigated.

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## 2. Materials and methods

### 2.1. Materials

Alkali lignin was supplied by the Wuhan East China Chemical Co., Ltd. (Wuhan, China). The black liquor of alkaline pulping process of reed straw was spray dried to produce crude lignin, lignin content is about 20%. The lignin was further purified prior to use as follows: to a suspension of lignin (200 g) in water (4 L), 1 M aqueous NaOH was added with stirring until the pH of the solution reached 12. The heterogeneous mixture was centrifuged at 8000 rpm for 15 min and the supernatant was decanted followed by filtration. One molar aqueous HCl was slowly added to the supernatant until the pH reached two. The beaker containing the mixture was allowed to stand at ambient temperature to allow complete precipitation of the lignin. The precipitated lignin was then filtered and washed with distilled water till the wash liquor became neutral and finally dried under vacuum at 60 °C for 24 h. Elemental analysis, found for lignin: C 49.77%, H 5.79%, N 1.14%.

Poly(ethylene glycol), sebacic acid, sodium hydroxide, hydrochloric acid, thionyl chloride, acetic anhydride, pyridine, ethanol, N,N-dimethyl formamide (DMF) and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received except where noted. Tetramethylsilane (TMS),  $d_3$ -chloroform and  $d_6$ -dimethyl sulfoxide were purchased from Admas Reagent Co., Ltd. and used as received. Poly(ethylene glycol) was dried under vacuum at 60 °C for 24 h. DMF and TEA were distilled over calcium hydride before use.

### 2.2. Determination of lignin hydroxyl content

The lignin hydroxyl content was determined by quantitative  $^1\text{H}$  NMR. Purified alkali lignin sample was treated with pyridine/acetic anhydride using the method described by Lin and Dence (1992). In brief, lignin was acetylated using a mixture of acetic anhydride/pyridine (1:1, v/v) at room temperature for 48 h under nitrogen. Thereafter, ethanol was added and allowed to stand for 30 min. The solvents were removed by evaporation. Repeated addition and removal (evaporation) of ethanol (five to ten times) results in the removal of acetic acid and pyridine from the sample. Quantitative  $^1\text{H}$  NMR spectrum of acetylated lignin sample (5 mg in 0.5 mL  $d_3$ -chloroform) was recorded on a Bruker AM-400 (400 MHz). Tetramethylsilane (1 mg) was used as internal standard. It was determined that the batch of alkali lignin used in these studies had a total hydroxyl content of 3.83 mmol/g.

### 2.3. Synthesis of lignin-based thermoplastic copolyesters

Sebacoyl dichloride was synthesized by reacting sebacic acid (8.92 g, 44.2 mmol) with thionyl chloride (20 mL). Evaporation of the excess thionyl chloride yielded the sebacoyl dichloride (Erdmann and Urich, 2000). 22.1 mL of 2 mol/L sebacoyl dichloride solution in dry DMF was added dropwise into a three-necked flask containing a solution of triethylamine (13.82 g), PEG (5.00 g) and lignin (5.00 g) in anhydrous DMF (60 mL) over 0.5 h at room temperature under a nitrogen atmosphere. The mixture was allowed to react for various time at specified temperatures before quenching with deionized water. The solid precipitation was collected by vacuum filtration and washed with boiling deionized water (400 mL  $\times$  5). The products were collected and dried under vacuum at 60 °C for 24 h. In order to reduce the cost of disposing major wastes generated by the system, we propose following approaches. Excess thionyl chloride could be recycled by reduced pressure distillation. Since sebacic acid reacted with thionyl chloride under

reflux, thionyl chloride could be recycled without cooling after the reaction was completed. Because thionyl chloride is still at the boiling state, energy requirement in subsequent reduced pressure distillation process might not be high. As the reaction was quenched by water, excess sebacoyl dichloride would be converted to sebacic acid, which is a harmless product. Therefore, sebacic acid can be disposed directly to environment or recycled. The other waste generated by the system is triethylamine hydrochloride, which can be used as a basic raw material for organic synthesis. Over all, the cost of these treatments may not be high (Scheme 1).

### 2.4. Developing of lignin-based films

The lignin-based copolymers were spread evenly on aluminum foils and placed in a compression mold (carver, Wabash, IN) at a pressure of approximately 117 MPa and 110 °C for 3 min. After heating, the press was cooled by running cold water and the sample was removed.

### 2.5. Percent weight gain

The percent weight gain was used to describe the reaction efficiency of alkali lignin, sebacoyl dichloride, and PEG. Before determining the percent weight gain, the lignin and copolymer were dried in an oven at 60 °C until constant weight was obtained. The percent weight gain was calculated as follows:

$$\text{Percent weight gain} = \frac{W_p - W_s}{W_s} \times 100\%$$

where  $W_p$  is the weight of copolymer,  $W_s$  is the weight of lignin before polymerization.

### 2.6. Fourier-transform infrareds

FTIR spectra of soda lignin and lignin-based copolymer were collected using a Varian 600-IR FTIR spectrometer. 32 scans were collected for each sample with a resolution of 4  $\text{cm}^{-1}$ .

### 2.7. Nuclear magnetic resonance studies

$^1\text{H}$  NMR spectra were recorded at 25 °C using a Bruker AM-400 (400 MHz) spectrometer. The copolymer was found to be partially dissolved in  $d_6$ -DMSO, which was used as the solvent. Chemical shift were reported using  $d_6$ -DMSO ( $\delta_{\text{H}}$  2.50) as an internal reference.

### 2.8. Morphology

The surface features of the films were observed by environment scanning electron microscopy (ESEM) (Quanta-250, FEI, Czech). Films placed on conductive tapes were sputter coated with gold and observed in the microscope at a voltage of 15 kV. The lignin molecular distribution in the film was estimated by transmission electron microscopy (TEM) (Japan, JEOL JEM-2100F). Film was cooled to -80 °C and cut into 70 nm slice with ultra-thin section method. The slice was transferred to copper mesh and observed at a voltage of 100 kV.

### 2.9. Tensile testing

The thermoplastic films were tested for tensile strength, breaking elongation and Young's modulus according to ASTM D882. All samples for tensile testing were conditioned at 21 °C and 65% relative humidity for 48 h before testing. Tensile tests were performed using a universal material tester (H5K-S, Hounsfield, UK) equipped

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