



Cross-linking of technical lignin via esterification and thermally initiated free radical reaction



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ABSTRACT

A strategy of enhancing the reactivity of lignin molecule towards thermally initiated free radical polymerization was examined. Technical lignin samples were reacted with selected esterification agents (butyric and crotonic anhydrides) leading to extensive conversion of the available hydroxyl groups. The esterified lignins were then subjected to thermal processing in the presence or absence of dicumyl peroxide (DCP). The rheological and viscoelasticity behavior during this process were examined by in-situ rheology and dynamic mechanical analysis (DMA). The functionality and glass transition temperature (T_g) of samples before and after modification were assessed for evaluating the validity of modification. After crotonylation, the lignin derivatives were susceptible to thermally initiated free radical polymerization, especially in the presence of DCP. Upon heating, the lignin crotonate showed a significant increase in storage modulus (E') from around 200 °C to 260 °C. The T_g of lignin crotonate increased by about 20 °C after thermal treatment in the presence of DCP. Fourier transform infrared spectroscopy (FTIR) analysis of samples that were collected from rheological test confirmed the reaction of C=C took place. Vanillyl alcohol as a lignin model compound was subjected to the same modification procedure with lignin to uncover the mechanism by FTIR and nuclear magnetic resonance (NMR) analysis, indicating there are three potential reaction sites: C=C, C=O and $-\text{CH}_2-$, among which C=C is likely to form a cross-linked network. The conclusions from this study may provide the foundations for a rational design of technical lignin-based polymeric materials, by providing the double bonds to anchor the lignin molecules in the resin or copolymers.

1. Introduction

Rising environmental concerns and incessant consumption of petrochemical resources have resulted in an increased interest in biorenewable polymer-based environmental friendly materials. As the second most naturally abundant polymer in the world, lignin has been explored to be used as a replacement for aromatic components of petrochemical origin (Argyropoulos and Crestini, 2016). Technical lignin is abundantly available as the by-product of pulping and paper-making industries together with an emerging biorefinery industry sector that would generate significant quantities of lignin, yet its utilization (other than fuel) makes up only a tiny fraction (less than 2%) of the nearly 70 million tons produced from wood and other lignocellulosic crops every year (Argyropoulos and Crestini, 2016; Kai et al., 2016). Lignin is readily available at low cost and possesses attractive properties such as high thermal stability, biodegradability, antioxidant, antimicrobial

activity and favorable stiffness (Graichen et al., 2017; Kai et al., 2016). These advantages have made lignin an ideal candidate for developing value-added products for various applications. However, the brittle nature and poor compatibility of lignin with other polymer systems have led to little success in creating lignin-based high performance materials (Kai et al., 2016). For example, directly using unmodified lignin as a filler often lowers the mechanical properties (tensile especially) of the blend due to its poor miscibility with many other thermoplastics (Camargo et al., 2011; Gordobil et al., 2015).

Promising strategies to overcome these drawbacks are chemical modification of lignin and synthesis of lignin-derived copolymers (Kai et al., 2016). Chemical modification of lignin includes introduction of new chemical active sites (e.g. alkylation and alkoxylation) and functionalization of the hydroxyl (OH) groups. Esterification is one of the most feasible ways to modify the OH groups of lignin considering the reaction parameters employed (Laurichesse and Averous, 2014). By

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attaching different sized substituents to lignin, physicochemical and thermal properties of lignin (e.g. molar mass, solubility, and softening temperature) can be manipulated, which allows for tailoring the properties of resulting products for various applications. Previous studies on lignin esterification mostly reported modification using saturated carboxylic acid anhydrides (e.g. C₂-C₁₈ anhydrides). An increase of solubility of lignin in non-polar solvent, reduction of polarity and the melting point were observed (Koivu et al., 2016; Monteil-Rivera and Paquet, 2015; Thielemans and Wool, 2005). Besides, esterification of lignin improved its miscibility with other polymers, which turned out to be beneficial for blend properties (Dehne et al., 2016; Luo et al., 2017).

Apart from application as the filler or reinforcement, lignin has also been used as a macromonomer for polymer synthesis via “grafting onto” or “grafting from” approaches (Wang and Venditti, 2015). In the “graft onto” method, polymers are coupled to the hydroxyl or other functional groups of lignin via covalent bond formation (e.g. lignin-xylaric acid-polyurethane (Pohjanlehto et al., 2014) and lignin-polyacrylic acid (PAA) copolymer (Mohamad Ibrahim et al., 2010)). In the “graft from” approach, monomers can be polymerized directly from the lignin cores via ring opening polymerization (e.g. lignin-PLA copolymer) (Chung et al., 2013), atom transfer radical polymerization (Kim and Kadla, 2010), and free radical polymerization (Mai, 2000).

Regarding free radical copolymerization, there has been some research on grafting of synthetic vinyl monomers, like styrene and acrylamide, onto lignin via chemical initiation of radicals, chemo-enzymatic, or high-energy irradiation (Mamiński et al., 2013; Meister and Chen, 2002). For example, Chen et al. (1995) prepared lignin-styrene graft copolymers by conducting free-radical polymerization in dimethylsulfoxide, initiated by calcium chloride and hydrogen peroxide. Ayoub et al. (2014) modified lignin with styrene using γ -irradiation, and found irradiation at low dosage facilitated the grafting of styrene monomer to lignin. Recently, due to its technical and environmental advantages over irradiation and traditional solvent-based treatment, thermally initiated solvent-free radical polymerization is attracting great interest (Mamiński et al., 2013). This technique has been exploited to induce cross-linking of thermoplastics (e.g. low density polyethylene (LDPE) (Ramos et al., 2004), poly(L-lactide) (PLA) (Takamura et al., 2008), and poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] (PHBV) (Fei et al., 2004)) or inter-macromolecular radical coupling in thermoplastic based polymer blends like PHBV/ α -cellulose (Wei et al., 2015), PHBV/lignin (Luo et al., 2016), and PLA/cellulose nanocrystal (Dhar et al., 2016) during reactive extrusion process using DCP as the initiator. When exposed to heat during processing, the DCP will decompose into strong radicals which tend to abstract H atoms from the molecules and initiate the grafting between them (Takamura et al., 2008). This method is both eco-friendly and economically advantageous, since it is carried out in the molten state in conventional plastic processing equipment (e.g. extrusion) with only minor amount of peroxide, and neither special apparatus nor extra purification step are required (Luo et al., 2016).

Although lignin can be used in free-radical copolymerization with unsaturated polymers, this potential is limited by the ability of the phenolic OH groups in lignin to act as radical scavengers, initiating the formation of quinonic structures (Barclay et al., 1997; Lu et al., 1998). Besides, the residual double bonds in lignin are 1,2-distributed and hence not reactive towards free-radical attack (Doherty et al., 2011). Our previous study prepared polymer alloy using as-received softwood Kraft lignin and PHBV via DCP initiated free radical grafting during melt extrusion, and found the highest graft efficiency was around 20% (Luo et al., 2016). If technical lignins are to be copolymerized with other polymers via thermally initiated free radical reaction, improving their reactivity has to be taken into consideration.

In this study, to verify the hypothesis that reactivity of lignin towards free-radical polymerization will be enhanced by introducing vinyl groups into the lignin macromolecule, a two-step treatment was implemented. Two types of readily available technical lignins

(softwood Kraft and agricultural fiber soda) were respectively esterified with crotonic (unsaturated) and butyric (saturated control) anhydrides. This is mainly for introducing double bonds into lignin, which is expected to promote the subsequent cross-linking. Then the obtained lignin esters were coated with DCP and subjected to thermal processing in the absence or presence of DCP. The obtained products were assessed for T_g or softening temperature, and the rheological behavior of lignin esters during the thermal processing was monitored by dynamic rheometry. In order to unravel the reaction mechanism, 4-hydroxy-3-methoxybenzyl alcohol as a lignin model compound underwent the same two-step treatment with lignin and the products were characterized using FTIR and NMR.

2. Experimental section

2.1. Materials

Indulin AT (IN, weight average molar mass (M_w) = 212 000 g/mol) softwood Kraft lignin was provided by MeadWestvaco Co. Protobind 1000 (PB, M_w = 700 000 g/mol) lignin from agricultural fiber soda pulping was supplied by ALM India Pvt. Ltd. They were used as received. The M_w of two lignins was determined by size exclusion chromatography (SEC) with triple detection on tetrahydrofuran as their acetate derivative and corrected for weight gain due to acetylation (Luo et al., 2017). The purity of IN and PB lignin (total content of Klason and acid soluble lignin) was determined in a previous study to be 93.5% and 90.3% (Li and McDonald, 2014). Dicumyl peroxide (DCP: 98%) was a product of Sigma-Aldrich (USA). Crotonic anhydride (98%), butyric anhydride (98%), 1-methylimidazole (1-MIM, 99%), 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, 98%) were obtained from Acros Organics and used as received.

2.2. Lignin esterification

The esterification procedure was revised from a previously reported esterification method (Fox and McDonald, 2010). Briefly, lignin samples of each type (10 g) were placed in a 100 mL round-bottomed flask with a magnetic stirrer. Butyric or crotonic anhydride (25 mL) and 1-MIM (catalyst, 1 mL) were added. The reaction was conducted at 120 °C for 24 h with efficient stirring, using only the anhydride as solvent. To ensure complete esterification, the amount of anhydride used was in excess than an equimolar of OH groups in lignin, based on 5.10 mmol OH/g lignin (Chung et al., 2013). The esterified lignins were recovered by adding the reaction mixture drop wise into ice water with stirring to allow for complete precipitation, followed by centrifugation, and washed exhaustively with distilled water (until no strong odor of acid was smelt) to remove residual catalyst and carboxylic acids. The reaction scheme was shown as in Fig. 1. The resulting products were vacuum-dried and weighed to determine the weight percentage gain (WPG). Vanillyl alcohol as a lignin model compound was used to undergo the same modification procedure to reveal the reaction mechanism.

2.3. DCP coating and thermal treatment for esterified lignins

Pre-dried lignin esters (butyrate and crotonate) were separately coated in a previously prepared acetone solution of DCP (8 mg/mL), using 1 wt% concentration (based on the weight of lignin ester) for 30 min under magnetic stirring. Acetone was removed by evaporating the uniform slurry at room temperature followed by vacuum drying for 24 h.

As lignin alone hardly flowed during melt processing, it was difficult to take out the sample from the extruder after processing. Therefore, esterified lignin samples were hot pressed at 175 °C, 5 MPa for 10 min and then used for testing. The experimental groups and nomenclature of lignin samples are shown in Table 1.

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