



Engineering physical and chemical properties of softwood kraft lignin by fatty acid substitution



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ABSTRACT

A process to attach fatty acids to lignin is reported which alters its thermal behavior. By attaching saturated C_{18} fatty acids to OH groups, stable lignin stearates (LS) of controllable degrees of substitution (DS) were synthesized. Interesting physical properties were observed, wherein LS was observed to melt and flow at temperatures as low as 50°C . Melting was possible due to the crystallization of stearate chains when LS was purified by precipitation. A NMR method was established for quantification of the degree of substitution. At very high %DS values (close to 100%), the melting phenomenon was reversible, but at low %DS, melting occurred only during the 1st heating ramp during thermal cycling. The ability of LS to plasticize polystyrene (PS) is reported wherein integral blend films containing up to 25% by weight of LS were formed. The T_g of the blended films could be lowered by 22°C using LS relative to PS. Lignin stearates have the potential to serve as interesting compounds for their ability to plasticize not only PS but other thermoplastic materials as well.

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1. Introduction

Lignin is an important component of biomass, both in terms of its mass contribution and functionality. Lignin's structure as part of the wood composite is a topic of intense scientific debate. For example, while it is widely reported in the literature as a cross-linked network polymer, a recent report indicated to lignin being a linear oligomer (Crestini et al., 2011; Mariotti et al., 2014; Hulin et al., 2015). The pulp and paper industry is estimated to produce more than 50 million tons of lignin annually, most of which is combusted to meet the energy demands of the pulp mills (Gosselink et al., 2004). Lignin when used as a fuel yields a value equivalent of $\$0.18/\text{kg}$. However, if converted to high-value products, the value equivalent can potentially be raised up to $\$1.08/\text{kg}$ (Vishtal and Kraslawski, 2011). Therefore, there is enormous interest in transforming lignin to attain properties competitive with commercial high volume polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC). Factors influencing the physicochemical properties of lignin are the type and specie of woody or non-woody biomass, the technical process used for pulping, and the method used to separate lignin from black liquor. Depending on these factors, technical lignins may contain

varying amounts of methoxyl, phenolic hydroxyl, primary and secondary aliphatic hydroxyl, carbonyl and carboxyl groups. In this study we shall focus on utilization of the hydroxyl groups for lignin modification.

Several ways of modifying lignin via hydroxyl group reactions were previously reported. Cui et al. (2013) described methylation of lignin using dimethyl sulfate or methyl iodide to create a lignin based thermoplastic material. Laurichesse and Averous (2014) summarized most of the applications based on esterified lignins. The applications were devoted to the development of elastomeric products, epoxy resins and polyesters. Sailaja and Deepthi (2010) developed a new biobased composite of polyethylene and esterified lignin. The esterification of lignin has been used to enhance interfacial adhesion where the tensile strength of the blends improved with values approaching close to that of neat polyethylene.

Wu and Glasser (1984) previously reported the hydroxyalkylation of lignin by reaction with alkylene oxides to create engineering plastics. Hydroxypropyl lignin (HPL) derivatives were subsequently epoxidized and crosslinked networks formed using aromatic diamines as curing agents (Kelley et al., 1988). Saraf and Glasser (1984) also described lignin based polyurethane films using HPL reaction with diisocyanates. To improve stretching, polyethylene glycol (PEG) and poly(butadiene glycol) extended polyurethanes were also reported (Saraf et al., 1985). In addition to polymeric modification of the hydroxyl groups, simple acetylation procedures involving acetic anhydride and pyridine are routinely performed in

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laboratories for lignin analysis (Capanema et al., 2004). These types of chemical modification derivatives improve the solubility of the lignin in organic solvents and some other physical properties as Laurichesse and Averous (2014) reported.

Recently, a solvent less system comprising of softwood kraft lignin and styrene monomer was subjected to γ -irradiation to prepare polystyrene grafted lignin derivatives via radical chemistry (Ayoub et al., 2014). This work has demonstrated that the effect of irradiation to make the material more thermally stable relative to lignin alone, thus improving its processability at high temperatures.

While the lignin modification literature is vast, large scale commercialization of lignin based products have been stifled due to supply chain issues and poor mechanical and thermal properties relative to synthetic polymers (Vishtal and Kraslawski, 2011).

A survey of the patent literature showed a recent invention in which acetylated lignin was reacted with tall oil fatty acids to obtain fatty acid esters of lignin, as acetic acid was distilled off during reaction (Pietarinen et al., 2014). These new derivatives were reported to be more hydrophobic and possessed low melting points. A proceedings article briefly described the reaction of lignin with fatty acid chlorides but did not present resulting thermal properties (Mariotti et al., 2012). Mariotti et al. (2014) reported a new wood plastic composite while exploring for the first time the potential of using esterified kraft lignin as a coupling agent. Two types of lignin esterification with maleic and succinic acids anhydrides were explored and improved mechanical properties were shown. Hulin et al. (2015) described for the first time a new method of lignin esterification with long acyl chains in ionic liquids. The chemical esterification improved the miscibility of lignin in apolar polyolefin matrices. The final product exhibited interesting thermal and textural properties comparing to the kraft lignin.

Historically, the idea of reacting fatty acids with lignin has been explored by Lewis et al. (1943). Additionally, the esterification of lignin with tall oil fatty acids (containing 3.5% saturated and 86.3% unsaturated fatty acids) for water vapor and oxygen barrier coatings has been previously described (Hult et al., 2013). That study reported that the glass transition temperature could not be observed for esterified samples. The % mass addition of fatty acids was around 0.1% for that report. Our study herein, advances this research in that it shows the synthesis of lignin esters with mass addition of up to 100%. Within this larger range of DS, this study shows a much more robust change in the thermal behavior with esterification of lignin, with the lignin esters showing interesting melting phenomena. In a related study, Sagar and Merrill, (1995) examined the properties of fatty-acid esters of starch and found that the fatty acids acted as internal plasticizers, with larger ester groups making the material more melt processable and ductile.

In this study, we explore the reaction, characterization and applicability of lignin esters to use as compatibilizers or plasticizers, not described previously. Further, we show the changes in thermal properties with degree of substitution of fatty acids, not previously reported. It has become of great interest to develop compatible blends of synthetic and natural polymers such that properties like biodegradability or water uptake can be modified. We describe the

synthesis of fatty acid esters of non-acetylated commercial softwood kraft lignin using acid chlorides. Depending on the type of fatty acid chain attached, interesting thermal and physical properties of the lignin esters can be expected. While a commercial fatty acid chloride, stearoyl chloride (St-Cl) was used in the study, other saturated or unsaturated acid chlorides can also be used to react with lignin. Products with varying degrees of substitution (DS) were prepared. A ^1H NMR method for quantifying the addition of fatty acid chains attached to the lignin molecule is described. Thermal analysis was performed using TGA and DSC. Finally, compatibility of the derivatives with polystyrene (PS) and their ability to plasticize PS is reported for the first time.

2. Materials and methods

2.1. Materials

Biochoice™ (BCL) softwood Kraft Lignin was provided by Domtar Corporation. Chemical composition of BCL was as follows: lignin=98.2%, arabinan=0.2%, galactan=0.7%, glucan=0.1%, xylan=0.4%, and ash=0.73%, with pH=3.9. Molecular weight=5500 g/mol. Elemental composition was as follows: Methoxyl content = 13.8%; Carbon = 64.4%; Hydrogen = 6.24%; Oxygen = 27.9%; Nitrogen = 0.36%; Sulfur = 1.36%. Molecular formula of C_9 unit = $\text{C}_9\text{H}_{8.93}\text{O}_{2.37}(\text{OCH}_3)_{0.814}\text{S}_{0.079}$ with an average M_w of 182.6 g/mol; Quantitative ^{13}C NMR analysis yielded the following groups per 100 aromatic rings: 5–5' ether = 31.8, β -1 = 1.2, β -5 = 4.0, primary aliphatic OH = 26.6, secondary aliphatic OH = 17.6, phenolic OH = 49.4, total etherified = 52.0, methoxyl = 63.2, C_γ in β -O-4 without $\text{C}\alpha=\text{O}$ = 11.5, aliphatic COOR = 8.7, conjugated COOR = 4.3, and degree of condensation = 71.4. Stearoyl chloride (St-Cl), pyridine (Pyr), 1,4-dioxane, methanol, reagent alcohol, hexane, acetone, chloroform, KBr, CDCl_3 , DMSO- d_6 and polystyrene (PS) were obtained from Sigma-Aldrich (St., Louis, MO, USA). All chemicals were used as purchased except 1,4-dioxane, which was distilled over NaOH and stored under N_2 .

2.2. Synthesis of lignin stearate (LS)

Lignin (2 g) was weighed into a 3-neck flask. A volume of 50 mL dioxane was added and stirred at room temperature for roughly 2–3 h under N_2 to dissolve the lignin. The required amounts of St-Cl and Pyr (calculated based on total OH groups available) were then added to the flask and stirred at 80 °C for roughly 18 h. Following the reaction, the mixture was added dropwise to a suitable precipitating solvent, either hexane or ethanol, see Table 1. The crude solid was then filtered under vacuum and recovered. To further purify the crude product, it was washed in a Soxhlet extractor overnight using a suitable extraction solvent. Generally, the precipitation solvent was the same as extraction solvent. The choice of precipitation and extractions solvent depended on the amount of St-Cl added for reaction (Table 1). After extraction, the solid was dried in air first and then under vacuum at room temperature.

Table 1
Amounts of reagents in reaction, corresponding DS and product solubilities.

Sample	St-Cl eq. added per OH	Pyr eq. added per OH	DS per 100 aromatic rings	% DS	H	C	E	D	W
LS-7%	0.30	0	6.09	7	I	I	S	S	I
LS-13%	0.59	0	12.29	13	I	I	S	S	I
LS-46%	1.18	0	43.43	46	S	S	I	I	I
LS-90%	2.36	0	84.40	90	S	S	I	I	I
LS-95%	2.36	0.12	89.28	95	S	S	I	I	I
LS-97%	2.36	0.50	90.72	97	S	S	I	I	I

Soluble—S; Insoluble—I.

H—Hexane; C—Chloroform; E—Ethanol; D—DMSO; W—Water.

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