Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin

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Ⓢ Supporting Information
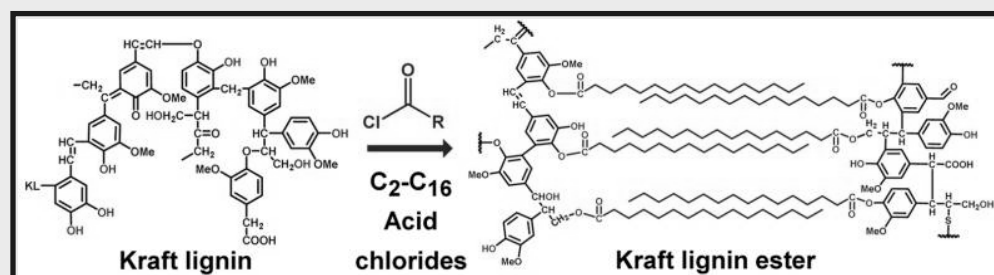
ABSTRACT: Esterification of kraft lignin inherently addresses its potential for thermoplastic applications either on its own or as a component of polymer blends. In this effort, we have investigated the selectivity of softwood kraft lignin toward esterification via acylation. LignoBoost kraft lignin was esterified with acetyl (C_2), octanoyl (C_8), lauroyl (C_{12}), and palmitoyl (C_{16}) chlorides at various molar ratios with respect to the total hydroxyls present. Quantitative ^{31}P NMR spectroscopy, Fourier transform infrared spectroscopy (FTIR), and gel permeation chromatography (GPC) were used to evaluate the selectivity and efficiency of these reactions on the various hydroxyl groups present. The C_8–C_{16} acyl chlorides showed distinct enhanced reactivity toward the aliphatic hydroxyl groups, whereas C_2 acyl chloride was found to react uniformly with any available OH irrespective of their chemical nature. The effects of long chain acylation on the polymer and material properties were also examined using solution viscosity, thermal, and rheological measurements. Polymer blends were also produced and studied by melt extrusion. The long aliphatic chains when installed on the lignin displayed peculiar association effects in solution and enhanced the melt flow characteristics of the lignin–polymer blends.

KEYWORDS: Softwood kraft lignin, Fatty acid esterification, Methylation, Characterization, Quantitative ^{31}P NMR, Thermal and rheological properties, Polymer blends

INTRODUCTION

Lignin is an amorphous polyphenol found in plant cell walls. Native lignin has a random, three-dimensional structure created via an enzyme-mediated dehydrogenative polymerization of phenyl propanoic precursors such as coniferyl, sinapyl and p-coumaryl alcohols.[1] Softwood trees contain about 28 mass % of lignin composed of over 95% 4-hydroxy-3-methoxy (guaiacyl) and traces of p-hydroxyphenyl units.[2]

The main linkages between the phenylpropane units in softwood lignin (about 45% of all C9-structures) are aryl-alkyl ethers, or β-0-4′ bonds.[3] During the industrial kraft pulping process, which is aimed at delignifying wood for cellulose production, most of the β-0-4′ linkages are cleaved to yield large amounts of small phenolic compounds.[4] Under kraft process conditions, this material forms highly condensed structures with enol ether and stilbene linkages as well as various types of carbon–carbon linkages. Furthermore, these so-called "kraft lignins" (spent liquor lignins, or black liquor lignins) possess various aliphatic hydroxyls, methoxyls, catechols, some carboxyl groups and sulfur bridges.[5,6] Marton, in 1971, proposed a tentative structure for softwood kraft lignin (Scheme S1) admittedly in need of serious revision.[7]

In the United States, the kraft pulping processes account for more than 85% of wood pulp production with 56 million tons of pulp produced in 2006.[8] However, most of the available lignin is not isolated, but provides a major source of energy for pulp mills. Only about 1 million tons per year (2%) is actually commercialized.[9]

Recent technology developments have brought about the design of the LignoBoost process, which offers granular kraft lignin of good quality with lower costs and concomitant benefits of higher pulp production. These lignins contain typically 0.3–1.2% ash and 1–3% sulfur.[10]

Unmodified kraft lignin has been viewed as a source of chemicals and carbon fiber from biorefineries,[11] and as a component of polymer composites.[12] However, when unmodified it is poorly soluble in organic solvents and resists thermal flow when heated. Thermal flow is necessary for melt-processing in the production of polymer blends.[13] Furthermore, unmodified pine kraft lignin starts decomposing at temperatures of around 120 °C through evolution of formic acid, formaldehyde, sulfur dioxide, carbon dioxide and water, and breakdown of bonds in the phenyl propane side chains.[14] This has been recently evidenced in experiments where softwood kraft lignin was thermally heated into its T_g.[15]

Derivatization of kraft lignin opens up its potential for thermoplastic applications either on its own or as a component of polymer blends.[16−19] Most widely studied methods are based on hydroxyl propylation and esterification. In esterification, most of the published papers have utilized short chain fatty acids. Lignin acetylation offers an enhanced solubility characteristic useful for NMR spectroscopy and GPC lignin structural analyses.[20] Lewis and Brauns made a range of C_2–C_{18} esters and found them usable as mold lubricants and plasticizers for plastics.[21] Pruett et al. used C_2 to C_4 esters for preparation of colored polyesters for plastic containers that show low light transmittance in the UV range.[22] Tinnemans and Greidanus tested C_2, C_7, and C_{18} acylated lignins as part of maleic anhydride copolymer blends in water swelling materials. The esters functioned also as components in blends of recycled low-density polyethylene and polypropylene.[23] Thielemans and Wool examined how C_4 esters improve resin and fiber compatibility in thermoset composites.[24] Mariotti et al. used C_4 and C_{18} esters to make biocomposites of high-density polyethylene.[25] Tamminen et al. applied tall oil fatty acid (C_{16}, oleates, linoleates) esters as barrier materials in fiber-based packaging.[26] Hult et al. measured the properties of C_{12} and C_{16} ester coated fiberboard for packaging applications.[27] Pawar et al. synthesized C_{18} lignin esters and studied thermal properties of polystyrene blends.[28]

Esterification of lignin can be achieved in various ways. The oldest references reported mixtures of acyl chloride with pyridine or triethylamine.[21] A model compound study has shown pyridine catalysis to favor aliphatic hydroxyl groups, and triethylamine to favor phenolic hydroxyl groups.[29] Glasser and Jain used either equimolar pyridine:acyl anhydride, or acyl anhydride:acyl acid with sodium alkanoate as catalyst.[13] Thielemans and Wool used acyl anhydride:acyl acid (1:1) with 1-methylimidazole (1-MIM) as catalyst.[24] Pyridine-catalyzed reactions have been generally slow (up to 48 h), whereas 1-MIM offered complete esterification in approximately 1 h.[30] Trans-esterification can be used to add lignin to polyesters. Pruett et al. produced poly(ethylene terephthalate) (PET) by reacting dimethylesters of dicarboxylic acids with ethylene glycol and C_2–C_4 esterified lignin.[22] Recently, Hulin et al. used lipase catalyzed transesterification to react kraft lignin with ethyl oleate in ionic liquids.[31]

For the elucidation of the material properties of lignin and its derivatives for different technical applications, a thorough understanding of the effects affecting lignin thermal properties are required.[32] In this study, we have systematically examined

the effect of acid chain length and degree of substitution on the structure and thermal properties of technical softwood kraft lignin esters. For this purpose, 20 ester samples using a set of four acids (C_2–C_{16}) with five various loadings (10−100 mol %) were prepared. For melt flow studies, an additional set of 4-O methylated esterified SWKL lignins were synthesized. The structural determination was performed by FTIR, GPC, and ^{31}P NMR, and the thermal properties were determined by DSC and TGA. In general, esterification with long-tail fatty acids was found to lower significantly the T_g values of SWKL esters even at lower degrees of substitution and to enhance the melt flow properties of lignin-polyethylene blends. Also, new information to understand the reactivity of different types of phenolic hydroxyls in kraft lignins in the esterification process was obtained. To our best knowledge, no previous systematic study with such a big data set on kraft lignin esterification has been previously performed.

■ EXPERIMENTAL SECTION

Materials and Methods. *Chemicals.* Softwood LignoBoost kraft lignin (SWKL) was obtained from Stora Enso Oyj, Finland. The lignin was dried for 2 h under high vacuum at 50 °C before use. Acetyl chloride (C_2) (≥99%), octanoyl chloride (C_8) (99%), lauroyl chloride (C_{12}) (98%), and palmitoyl chloride (C_{16}) (98%) were obtained from Sigma-Aldrich and were used as received. Dimethyl sulfate (≥99%) was obtained from Aldrich. Polyethylene was obtained from Sigma-Aldrich. Pyridine (99.8%), tetrahydrofuran (THF) (≥99.9%), dimethylformamide (DMF) (99.8%), and Celite 535 were obtained from Sigma-Aldrich. All solvents were used from freshly opened bottles.

Methods. *Partial Esterification of Softwood KL.* Typically, 5.0 g of lignin (containing 6.67 mmol/g of total phenolic and aliphatic hydroxyls measured by quantitative ^{31}P NMR analysis) was dissolved for 30 min in 30 mL of tetrahydrofuran, 7.5 mL of dimethylformamide, and 3.9 mL of pyridine (9.4 mmol/1 g lignin) at 60 °C under argon. Different amounts of acyl chlorides (C_2, C_8, C_{12}, C_{16}, 0.66–8.57 mmol/g lignin, 0.1–1.3 equiv vs total aliphatic and phenolic hydroxyls, Table 1) were injected with a syringe (Scheme 1A). The reaction was kept for 48 h at 65 °C under argon with efficient stirring. The isolation of the esterified lignin was performed by adding Celite 535 into the reaction solution in sufficient amounts to make the mixture powdery, precipitating by adding water and washing with water and ethanol (cooled to 0 °C) to yield dry powder. Celite was removed by Soxhlet extraction using THF. The product was dried on a watch glass after most of the solvent was removed. The masses of products were 4–8 g (theoretical masses 5–13 g, yields 60−80%).

Complete and Selective Methylation of the Phenolic OHs of Softwood KL. The lignin (50 g, containing 4.40 mmol/g of total phenolic hydroxyls measured by quantitative ^{31}P NMR analysis) was fully methylated using excess dimethyl sulfate (3.8 times vs total phenolic hydroxyls) following the procedure by Sadeghifar et al. (Scheme 1B).[33] The product was precipitated by adding sufficient amount of 2 M HCl (pH 2−3) and washed with excess water up to 6 times using efficient vacuum filtration to reach neutral pH. The mass of product was 48 g (yield 90%). The product was analyzed by quantitative ^{31}P NMR for free hydroxyls (2.3 mmol/g aliphatic, 0.15 mmol/g condensed phenolic, 0.02 mmol/g noncondensed phenolic) and used in melt extrusion as a matrix.

Partial Methylation of Softwood KL Followed by Complete Esterification. First, the lignin (50 g, containing 2.27 mmol/g of aliphatic hydroxyls and 4.40 mmol/g of total phenolic hydroxyls measured by quantitative ^{31}P NMR analysis) was methylated using an equimolar amount (per total phenolic hydroxyls) of dimethyl sulfate in aqueous 0.8 M NaOH (Scheme 1B). After workup, as detailed in complete methylation synthesis, the product was analyzed by quantitative ^{31}P NMR for free hydroxyls (2.2 mmol/g aliphatic, 2.2 mmol/g total phenolic, 1.2 mmol/g condensed phenolic, 1.1 mmol/g noncondensed phenolic). The mass of product was 47 g (yield 91%).

Table 1. Total Hydroxyl Contents and Degrees of Substitution (DS) for 10–130 mol % Loaded C_2–C_{16} KL Esters[a]

sample	AcylCl loaded (mol %)	AcylCl loaded (mmol/g)	lignin mass %	total OH (^{31}P NMR) (mmol/g)	DS (^{31}P NMR) (mol %)
SWKL			100	6.7	
C_2 KL esters	10	0.66	97	5.2	22
	30	1.98	92	4.6	31
	50	3.33	87	3.5	47
	70	4.66	83	2.5	62
	130	8.57	78	0.01	100
C_8 KL esters	10	0.66	92	5.2	22
	30	1.98	80	4.9	27
	49	3.30	70	3.8	43
	69	4.61	63	2.6	61
	130	8.57	54	0.01	100
C_{12} KL esters	10	0.66	89	5.3	20
	30	1.98	73	4.9	27
	49	3.30	62	3.9	41
	69	4.61	54	2.6	60
	130	8.57	45	0.01	100
C_{16} KL esters	10	0.66	86	5.3	21
	30	1.98	68	5.0	25
	49	3.30	56	3.8	43
	69	4.61	47	2.5	63
	130	8.57	38	1.3	80

[a]Results derived from quantitative ^{31}P NMR using the theoretical lignin mass %. All the 10 mol % KL esters had their lower MW fraction washed away during the workup. The 130 mol % C_{16} KL ester used milder reaction conditions (20 h, rt).

Scheme 1. (A) Esterification of SWKL Aliphatic and Phenolic Hydroxyl Groups with C_2, C_8, C_{12} and C_{16} Fatty Acid Chlorides in Pyridine, THF and DMF; (B) Methylation of SWKL Phenolic Hydroxyl Groups with Dimethyl Sulfate in Aqueous Sodium Hydroxide[a]
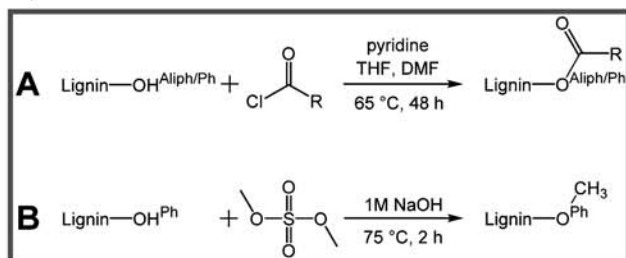
[a]Aliph/Ph = Aliphatic or phenolic group. Ph = Phenolic group. R = –CH_3, –$(CH_2)_6CH_3$, –$(CH_2)_{10}CH_3$, or –$(CH_2)_{14}CH_3$.

Next, the dried powder (20 g) was subjected to full esterification by adding excess fatty acid chlorides (C_2, C_8, C_{12}, C_{16}, 5.72 mmol/g, 1.3 equiv vs total remaining aliphatic and phenolic hydroxyls) as before (Scheme 1A). After workup as detailed in the partial esterification synthesis, the products were analyzed by quantitative ^{31}P NMR for free hydroxyls (<0.01 mmol/g total aliphatic and phenolic) and used in melt extrusion as samples. The masses of products were 18–20 g (yields 50–75%).

Quantitative ^{31}P NMR Spectroscopy. The ^{31}P NMR spectra were recorded by inverse gated proton decoupling sequences on a Bruker 300 spectrometer with 5 mm direct detection broadband probe-head. The spectra were collected at 27 °C with 384 transients using 90° pulse

flip angle, 85 000 Hz spectral width, 1 s acquisition time, and 5 s relaxation delay. The samples (SWKL and the synthesized KL esters) were phosphitylated following the method of Granata and Argyropoulos using DMF as the cosolvent.[34] The phosphitylation reagent was 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Cl-TMDP), which was synthesized in-house following the method of Zwierzak,[35] and the internal standard was N-hydroxy-5-norbornene-2,3-dicarbocylic acid imide (e-NHI) and the relaxation agent was chromium(III) acetylacetonate. Samples were dried in a vacuum oven at 30 °C for 24 h, and spectra were recorded within 5 min of phosphitylation. Manually, carefully phased spectra were referenced to the peak of the reaction product of Cl-TMDP with water at 132.2 ppm. The integration regions were: internal standard 152.4–151.5, aliphatic 149.0–145.0, condensed phenolic 145.0–140.4, and noncondensed phenolic 140.4–137.2. The integrals of KL esters were converted to mmol/g lignin using eq 1, which is the theoretical lignin mass % in the samples (38–97%, listed in Table 1).

FTIR-ATR. FTIR spectra were measured using PerkinElmer Frontier with attenuated total reflection (ATR) accessory. The spectra were collected between 4000 and 650 cm^{-1} with resolution of 4 cm^{-1} using 64 scans.

Gel Permeation Chromatography. GPC measurements were performed on a Waters setup using a set of Styragel HR5-E and HR-2 columns (Waters Corporation, Milford, USA) in a series. THF was used as an eluent with a flow rate of 0.7 mL/min. UV-detector (280 nm) was used for monitoring. Calibration was performed using 10 polystyrene standards (Polymer Standards Service, Warwick, USA) with molecular weights between 820 and 1 860 000 g/mol. All the samples, both SWKL and the KL esters, were acetylated through acetobromination to make them fully soluble in THF prior to the GPC analyses, following the method of Asikkala et al.[20] The sample concentration was 0.33 mg/mL and all samples were filtered through a 0.45 μm syringe filter (Acrodisc Pall GBH, Waters, USA) prior to injection.

Viscosimetry. Intrinsic viscosities were measured using a Cannon No. 25 Ubbelohde capillary viscometer (Cannon Instruments Co.) in a temperature-controlled water bath at 25 °C. The sample solutions of 50 mol % substituted C_2–C_{16} KL esters in THF were prepared separately in different concentrations (% w/v) at ranges of 10–4% (C_2, C_8) and 8–3.2% (C_{12}, C_{16}) and by stirring for 24 h. A volume of 5.0 mL was needed for each measurement. A stopwatch was used to record the efflux time three times (with error of ±0.1 s) and the average value was calculated. The efflux time for THF was 15.4 s and for samples ranged between 18 and 26 s.

Thermogravimetry. These measurements were conducted prior to DSC so as to determine the degradation temperatures (T_D) of SWKL and KL esters. For this purpose, a TA Instruments TGA Q500 with a ramp of 10 °C/min was used. T_D values of samples were evident at temperatures ranging from 190 to 210 °C.

Differential Scanning Calorimetry. Glass transition temperatures (T_g) and melting temperatures (T_m) of samples were determined using a TA Instruments DSC Q100 equipped with nitrogen cooling accessory (flow rate 50 mL/min). Samples (6–15 mg) were used in aluminum hermetic pans with two drilled holes (diameter 0.28 mm). The temperature program used a ramp speed of 10 °C/min: (annealing cycle) ramp to 105 °C, isothermal 20 min, ramp to −50 °C, isothermal 1 min, (first measurement cycle) ramp to 190 °C, ramp to −50 °C, isothermal 1 min, (second measurement cycle) ramp to 190 °C. The T_g for SWKL was defined as one-half the change in heat capacity occurring over the transition, for 130 mol % substituted KL esters as the point where diagonal curve turns more horizontal, and for 10–70 mol % substituted KL esters as a mixture of the above two definitions. T_m values were taken as the minimum point of the endotherm.

Melt Extrusion. Melt extrusion was studied using a DSM Xplore Micro Compounder Extruder, 15 mL. The mixture size was 15 g, consisting of 25% sample in 75% matrix (w/w). Two matrices were tested, methylated lignin and commercial polyethylene (melting point 128 °C, density 0.93 g/cm^3, and melt index 1.2). The mixtures with methylated lignin matrix were mixed at 100 rpm for 10 min at 150 °C,
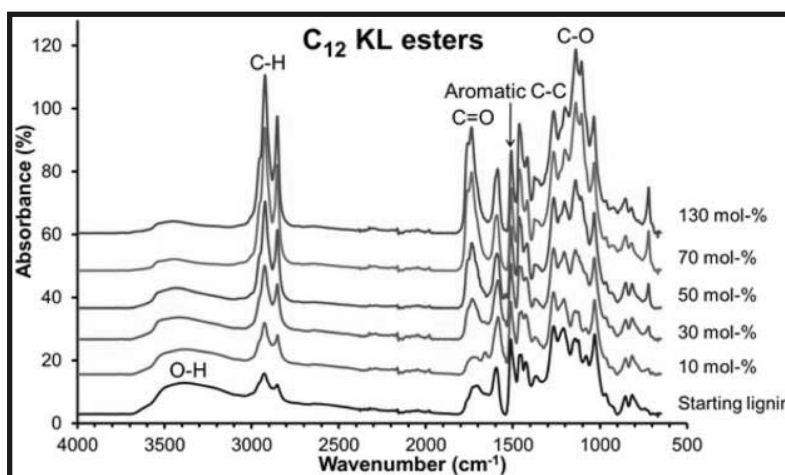
Figure 1. FTIR-ATR spectra of SWKL and 10−130 mol % loaded C_{12} KL esters with signal assignments (normalized to 1510 cm^{-1} aromatic C−C stretch).

and with polyethylene matrix at 140 °C, extruding a melt fiber of approximate diameter 3.5 mm. The torque values were determined from the last 2 min of extrusion. The samples used in the blends were the methylated, esterified (C_2−C_{16}) kraft lignins. Methylated lignin was used as the control.

■ RESULTS AND DISCUSSION

Esterification of KL and Degree of Substitution. The total hydroxyl content of SWKL was determined by quantitative ^{31}P NMR as 6.67 mmol/g, which consists of 2.27 mmol/g aliphatic, 2.14 mmol/g condensed phenolic, and 2.26 mmol/g noncondensed phenolic hydroxyls in ratios of 1:0.94:0.99 (with an error of ±0.05 mmol/g). A more comphrehensive list of hydroxyl contents is shown in Table S1.

Esterifications with C_2 (acetyl), C_8 (octanoyl), C_{12} (lauroyl), and C_{16} (palmitoyl) fatty acid chlorides were carried out as molar percentages of approximately 10, 30, 50, 70, and 130 mol % to the total hydroxyl amounts in SWKL. In total 20 samples were obtained.

To calculate the hydroxyl contents of the lignin esters from quantitative ^{31}P NMR as mmol/g of lignin (and not mmol/g of lignin ester), it was essential to use a theoretical mass percentage of lignin component m % of the synthesized lignin esters. This assumes esterification reactions are 100% complete, which was sufficiently accurate in this case. The mass values can be calculated using eq 1. The total hydroxyl amounts and degrees of substitution (DS) for all KL esters (derived using quantitative ^{31}P NMR) are shown in Table 1.

Calculation of theoretical lignin mass percentage for a lignin ester. AcylCl/KL is the molar ratio of loaded fatty acid chloride to total hydroxyl content of lignin (values range from 0 to 1, i.e., a 130 mol % loading equals 1), m(H %) and m(R %) are mass effects related to hydrogen and acyl group, and M(R) is molar mass of acyl group

$$
\begin{aligned}
m\%(\text{lignin}) &= \frac{1\ \text{g} - m(\text{H\%})}{1\ \text{g} - m(\text{H\%}) + m(\text{R\%})} \cdot 100\% \\
&= \frac{1\ \text{g} - (\text{AcylCl/KL} \cdot 0.00667\ \text{mol} \cdot M(\text{H}))}{1\ \text{g} + (\text{AcylCl/KL} \cdot 0.00667\ \text{mol} \cdot M(\text{R}) - M(\text{H})))} \cdot 100\%
\end{aligned}
$$

(1)

Typically, reaction conditions of 48 h and 65 °C were applied to achieve complete esterification. The syntheses were monitored by FTIR-ATR after 48 h and the spectra showed no free fatty acid peaks as would be evidenced between 1700 and 1710 cm^{-1} (an example of the C_{12} KL esters is shown in Figure 1). However, less than 10% free acids were detected by ^{31}P NMR for C_{12} and C_{16} KL esters mostly (an example of the C_{12} KL esters is shown in Figure 2). Also, the DS values suggest that especially in the case of 10 mol % substituted KL esters the lower MW fraction was washed away during the workup.

As the error in the calculated lignin mass percentage and amount of free fatty acid in samples was small, the 30, 50, and 70 mol % substituted KL esters were considered valid to estimate the degree of substitution and used for further selectivity studies.

Characterization of the SW Kraft Lignin Esters by FTIR and GPC. The degrees of acylation and the structural features of the polymers were also assessed by FTIR-ATR and GPC.

As an example of FTIR-ATR, the spectra for C_{12} KL esters and unmodified lignin (starting lignin) are illustrated in Figure 1. The acylation can be distinctly monitored by the incremental decline of the OH band at 3440 cm^{-1}, and the incremental appearance of ester bands at 1760 and 1737 cm^{-1} (phenolic and aliphatic, respectively) with a degree of added C_{12} fatty acid chloride. There was no sign of free fatty acid as a peak between 1700 and 1710 cm^{-1}, but the ^{31}P NMR measurements revealed its existence (under 10%, Figure 2).

The molecular weight distribution of the SWKL and its esters was analyzed by GPC after acetylation with acetyl bromide. Following this treatment, the SWKL showed a number-average molecular weight (M_n) of 2100 g/mol, weight-average molecular weight (M_w) of 19 000 g/mol, and a polydispersity index (PDI) of 8.9. In comparison, Indulin AT's (a commercially available SWKL from MeadWestvaco) molecular weight data has been reported as M_n = 1700 g/mol, M_w = 6200 g/mol, and PDI = 3.6.[36] Our data showed that acylation increased the molecular weight (M_n) of lignin in accordance with the molar ratio of acyl chloride to total hydroxyl content of KL, accordingly affecting the effective hydrodynamic size depending on the acyl chain length (C_2−C_{16}). Molecular weights (M_n) for KL esters ranged between 2100 and 4100 g/mol. As an example, the GPC chromatograms of the C_8 KL esters are shown in Figure S1. All GPC data for KL esters are shown in Table S2.
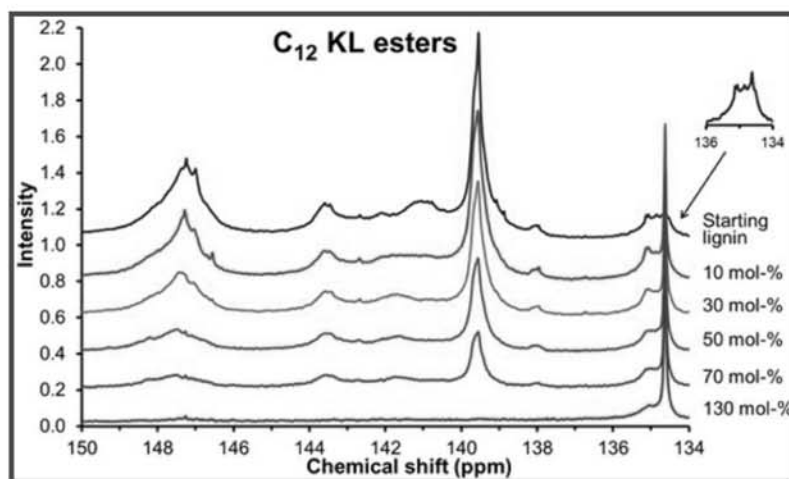
Figure 2. Quantitative ^{31}P NMR spectra of SWKL and C_{12} KL esters at various loadings per total hydroxyl groups of the SW kraft lignin (normalized to internal standard peak at 152 ppm).

Selectivity of Different Hydroxyls of KL on Acylation as Revealed by ^{31}P NMR.

The SW kraft lignin and its C_2–C_{16} esters were examined with quantitative ^{31}P NMR (using theoretical lignin mass percentage) in order to determine the hydroxyl contents of different lignin substructures and thus arrive at an accurate definition of the structures created. This effort offered further estimation of the selectivity of different hydroxyl groups present in kraft lignin toward the various acyl chlorides used. As anticipated, the amounts of free hydroxyl groups decreased with increasing acyl chloride ratio (Figure 2 showing the case of C_{12} KL esters). When a 130 mol % acyl chloride to total OH ratio was used, all the hydroxyl signals were eliminated resulting in quantitative esterification (99.5%) as evidenced by the flat baseline of the ^{31}P NMR spectrum. Some unreacted C_{12} fatty acid was also detected as a sharp peak at 134.6 ppm in all synthesized esters (excess fatty acid chloride hydrolyzed to fatty acid during washing and was found hard to remove completely).

To comprehend further the selectivity of three types of hydroxyl groups present in kraft lignin, the percentages of the remaining free OHs were plotted as a function of acyl chloride added. On the basis of the Table S3 hydroxyl selectivity data, the plots for C_2 and C_{12} KL esters are shown in Figure 3A,B, respectively. The case of C_2 represents straightforward esterification whereas that of C_{12} attempts to shed light on the possibility of hydrophobic and steric effect imposed on the reaction progress. Also, the mildly basic and nucleophilic solvent system (mixture of THF, pyridine, and DMF) may affect the chemoselectivity of esterification and result in a thermodynamic rather than kinetic outcome of the esterification (mechanism shown in Scheme 2.)

The results indicated that the aliphatic hydroxyls were somewhat more esterified compared to their phenolic counterparts. This is most probably due to combination of steric and thermodynamic effects, especially the esters originating from primary aliphatic hydroxyls being more stable and less sterically demanding than the esters of phenolic hydroxyls. Interestingly, among the phenolic OH units the condensed phenols were found to be slightly more reactive than the noncondensed phenolic units. In our SWKL, the 5,5′-biphenolic hydroxyls total 0.88 mmol/g, which is 41% of the total condensed phenolic hydroxyls. These structures possess a much more acidic phenolic hydroxyl than noncondensed guaiacyl phenols (pK_a 6.5 vs 10.5).[37] In our reaction conditions, some of them will most probably be ionized to phenolates, that are much more nucleophilic than the
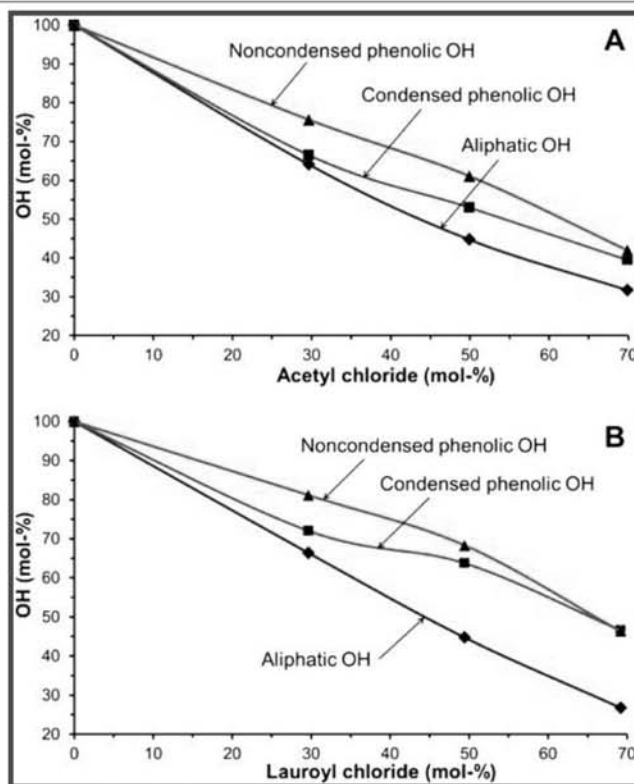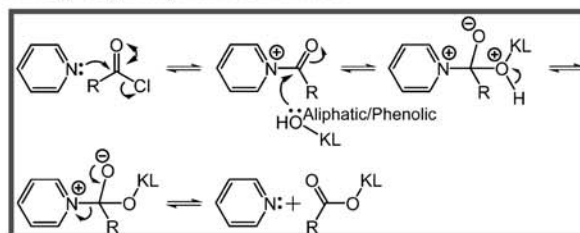

Figure 3. Hydroxyl group selectivity graphs of SWKL esterified with (A) acetyl chloride and (B) lauroyl chloride (determined via quantitative ^{31}P NMR).

Scheme 2. Mechanism of Pyridine Catalyzed KL Esterification with C_2–C_{16} Fatty Acid Chlorides.[39,a]

^{a}R = $-CH_3$, $-(CH_2)_6CH_3$, $-(CH_2)_{10}CH_3$, or $-(CH_2)_{14}CH_3$.

undissociated phenolic hydroxyls and react preferably with the acyl chloride. The results also demonstrate that partial esterification gives possibility to leave free phenolic hydroxyls to maintain lignin's antioxidative property.[38]

Thermal Behavior: DSC of Esterified Lignins. Differential scanning calorimetry (DSC) was used to study the effect of various ratios of different length fatty acid chains (C_2–C_{16}) bonded to SWKL on the glass transition temperature (T_g). Kraft lignin's abundant rigid condensed phenolic structures and strong intermolecular hydrogen bonding interactions restrict the thermal mobility of lignin.[40] Therefore, the introduction of ester moieties into the lignin's free hydroxyls is expected to result in a modified polymer with affected thermal properties and increased thermal mobility.

The T_g of the unmodified SWKL was relatively high, 145 ± 1 °C. Glass transition temperatures for all lignin esters were determined to be lower than that of the starting lignin and decreased with increasing degree of substitution (DS). There was also indication that the T_g decreased with increasing chain length of the fatty acid, but beyond C_8 they were found to be practically similar (C_8–C_{16}). As an example, the C_8 KL ester thermograms are shown in Figure 4A. The complete thermal data for C_2–C_{16} KL esters is shown in Table 2.

More specifically, during the initial thermal scan cycle the lower substituted (10–50 mol %) C_{12} and C_{16} KL esters showed thermograms with clear melting endotherms displaying T_m values between 120 and 130 °C and the highest heat of fusion (ΔH_f 7.5 J/g) was determined for the 30 mol % substituted C_{16} KL ester. Whereas, the 70 mol % and fully substituted C_{12} and C_{16} KL esters showed glass transitions with T_g values between 45 and 60 °C. This is depicted for C_{16} KL esters in Figure 4B. As explained, the second measurement cycles showed only glass transitions and this is depicted for the C_{12} KL esters in Figure 4C.

Overall, this segment of our effort implied that the 10–50 mol % substituted C_{12} and C_{16} KL esters showed evidence for aliphatic chain clustering or aggregation manifested in a melting transition during the first heating cycle. These structures are most probably caused by hydrophobic clustering of the long aliphatic chains of the bonded C_{12} and C_{16} fatty acids via van der Waals forces, which are generally one tenth the strength of covalent bonds. Scheme 3A attempts to pictorially represent the ordered part of the 30 mol % substituted C_{16} KL ester. The actual DSC thermograms shown in Scheme 3B show the sharp endothermic "melting" transition during the initial heating cycle and T_g type of discontinuous transition during the second heating cycle.

One possible way to rationalize for these observations could be as follows: The synthesis of the acylated KL lignin polymers is carried out in solution followed by precipitation with a nonsolvent. Once in solution, the long acyl chains of the KL esters are free to move and agglomerate via hydrophobic interactions. These clusters seem to be "frozen in" upon precipitation. The energy required to break them apart is manifested as an endothermic sharp transition apparent during the initial heating cycle. Once in the melt state and after cooling, the random structure of lignin, coupled with hydrogen bonds, pi stacking interactions and other forces precludes these clusters from reforming. Consequently, the second heating cycle offers only a T_g-like discontinuous transition.

The hypothesis brought forward to rationalize for the observed thermal effects is further supported by solution viscosity measurements shown in Figure 5. The acylated KL esters (50 mol % C_{12} and C_{16} KL esters in THF) containing the longer chain lengths showed greater intrinsic viscosities. This is very
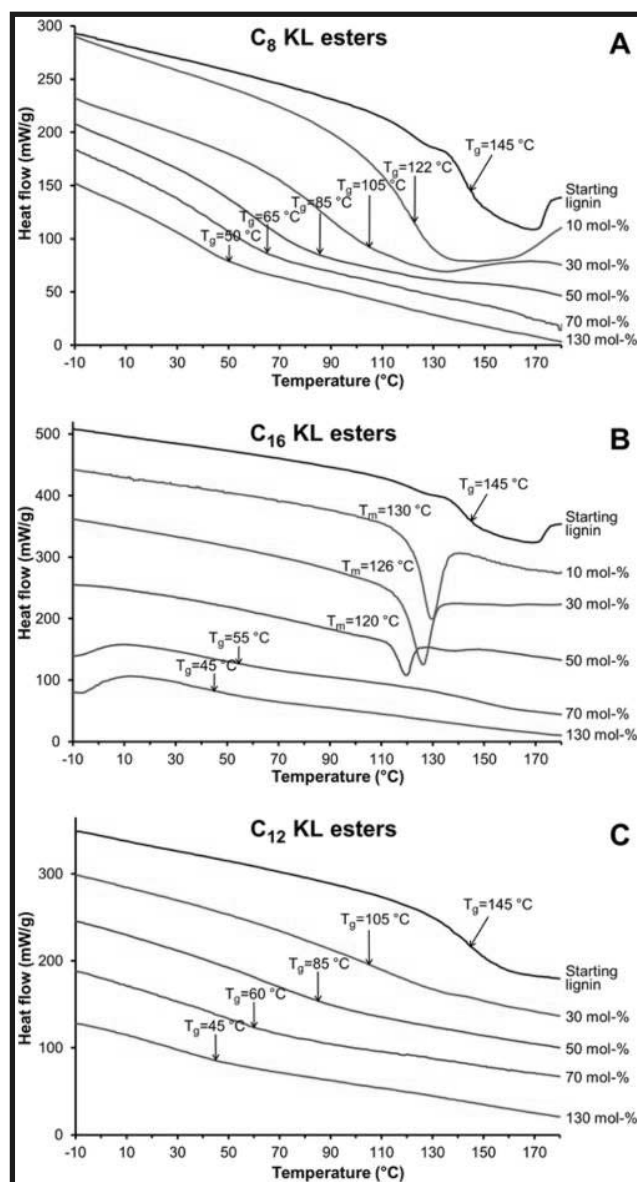

Figure 4. DSC thermograms for SWKL and 10–130 mol % loaded (A) C_8 KL esters on first measurement cycle, (B) C_{16} KL esters on first measurement cycle and (C) C_{12} KL esters on second measurement cycle. The 130 mol % loaded C_{16} KL ester had different reaction conditions (20 h, rt). The 10 mol % loaded C_{12} KL ester had an incomparable curve.

likely due to the enumerated clustering effects of the acyl chains. The hydrophobic interactions, operating in solution, may be the reason for the observed augmented intrinsic viscosities since these clusters would cause a form of physical chain association that will manifest itself in greater flow restrictions and thus higher intrinsic viscosities.

The agglomeration of acyl chains of C_{12} and C_{16} KL esters up to 50 mol % substitution is most probably due to the flexible aliphatic hydroxyl esters and less so with the more rigid phenolic hydroxyl esters. When the phenolic hydroxyls are esterified over 50 mol % (for example, case of 70 mol % loaded C_{12} and C_{16} KL esters), the orderly grouping behavior is effectively disrupted. This hypothesis is supported by DSC of two specially prepared melt extrusion samples, 50 mol % phenolic hydroxyl methylated, fully C_{12} and C_{16} esterified KL. These samples have a 66 mol %

Table 2. Thermal Data on SWKL, 10–130 mol % Loaded C₂–C₁₆ KL Esters, Methylated KL, and Methylated, Fully Esterified KL Esters[a]

sample	AcylCl loaded (mol %)	T_g (°C)	ΔT_g (°C)	T_m (°C)	ΔH_f (J/g)
SWKL		145			
C₂ KL esters	10	127	−18		
	30	124	−21		
	50	123	−22		
	70	122	−23		
	130	121	−24		
C₈ KL esters	10	122	−23		
	30	105	−40		
	50	85	−60		
	70	65	−80		
	130	50	−95		
C₁₂ KL esters	10	n/a	n/a	120	2.1
	30	105	−40	120	2.4
	50	85	−60	130	0.8
	70	60	−85		
	130	45	−100		
C₁₆ KL esters	10	n/a	n/a	130	7.3
	30	100	−45	126	7.5
	50	75	−70	119	2.7
	70	55	−90		
	130	45	−100		
methylated SWKL		120	−25		
meth. C₂ KL ester	130	n/a	n/a		
meth. C₈ KL ester	130	65	−80		
meth. C₁₂ KL ester	130	n/a	n/a	119	1.5
meth. C₁₆ KL ester	130	60	−85	122	0.7

[a]Esterification degree: 66 mol %. Errors for T_g: SWKL ± 1 °C, C₂ KL esters ±2 °C, others ±5 °C. n/a = Uninterpretable curve. The 130 mol % loaded C₁₆ KL ester was prepared in milder reaction conditions (20 h, rt).

esterification degree, and yet they exhibit melting endotherms on the first measurement cycle (T_m approximately 120 °C) and glass transitions on the second measurement cycle (thermal data in Table 2).

Pawar et al. observed also irreversible endotherms (T_m on first heating cycle only) for 90 mol % or lower substituted C₁₈ SWKL esters. They took scanning electron microscopy (SEM) images of 90 mol % KL ester with 10 000× magnification and found that the sample initially is porous and crystalline, but after heating above T_m, it turns nonporous and amorphous. In their schematic drawing, the lignin cores that once were separated by erected acyl chains now appear much more closely together. They also hypothesized that the lignin segments interfere with the reordering back to a crystalline state. Quite contrary to our results, reversible endotherms were observed with 97 mol % substituted C₁₈ KL ester (T_m = 46 °C for first heating cycle, T_m = 31 °C for second heating cycle).[28]

Aburto et al. observed similar endotherms in their DSC thermograms using C₁₆ and C₁₈ esterified starch.[41,42] They also speculated on the probability of T_m values having some correlation with the melting points of the fatty acid counterparts.

Melt Extrusion Behavior. As the esterification of KL was found to lower successfully and predictably the glass transition temperature of kraft lignin, some KL esters were further prepared and tested in melt extrusion.

To create stable, thermoplastic KL esters suitable for melt extrusion, the kraft lignin was first 50% methylated on the phenolic hydroxyls, followed by full esterification with C₂–C₁₆ fatty acid

Scheme 3. (A) Structures, Possibly Forming via Hydrophobic Clustering of the Aliphatic Chains, Depicted for the 30 mol % Substituted C₁₆ KL ester; (B) DSC Thermogram of 30 mol % Substituted C₁₆ KL Ester
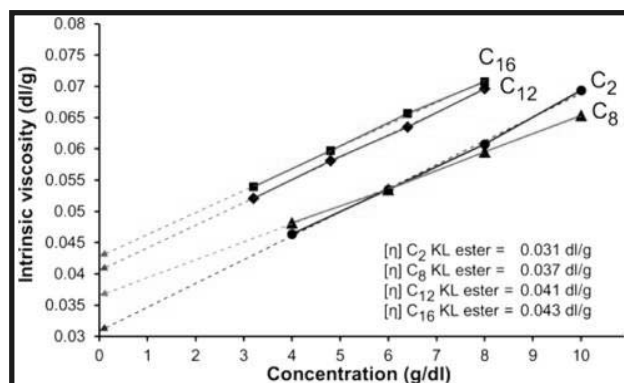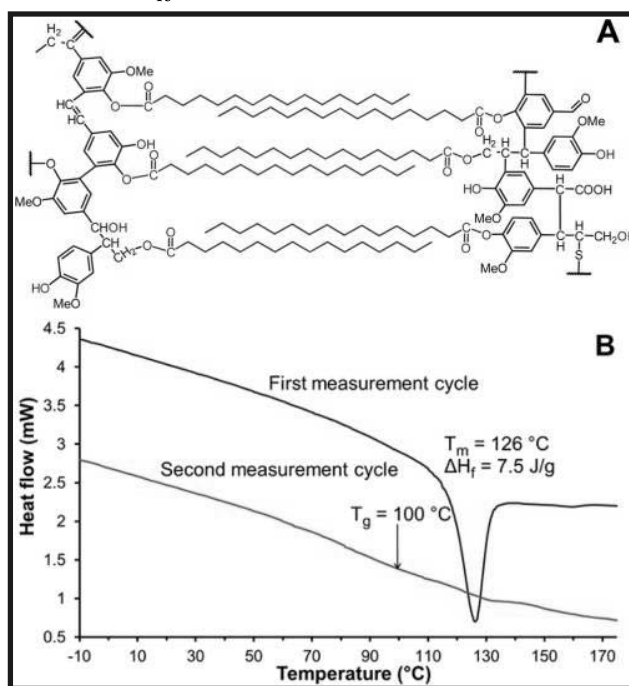
Figure 5. Intrinsic viscosity plots for the 50 mol % substituted C₂–C₁₆ KL esters measured as THF solutions.

chlorides. This provided a fixed 66 mol % degree of esterification, and a fully substituted lignin. The thermal data for these samples is shown in Table 2.

In an effort to explore the application potential of the KL esters as thermoplastic components, we performed melt extrusion and melt torque measurements for the methylated C₂–C₁₆ KL esters in both methylated kraft lignin and polyethylene matrices and the thermal extrusion behavior of different length aliphatic chains of KL esters were compared to a control (methylated KL).

It is important to note here that methylation (using dimethyl sulfate) was used throughout this work aimed to mask all available phenolic OH groups prior to any experiments that would involve a thermal treatment. This was done due to the documented evidence that phenolic OH groups may cause phenoxy radical initiated gelation in lignin that would obscure the fundamental information sought.[15]

Table 3. Melt Extrusion Results[a]

blend	matrix (75 mass %)	sample (25 mass %)	torque (N)	extrusion capability
1	methylated KL	methylated KL (control)	(3600)	N/A
2	methylated KL	methylated C_2 KL ester	(2400)	N/A
3	methylated KL	methylated C_8 KL ester	3200	+
4	methylated KL	methylated C_{12} KL ester	3350	+
5	methylated KL	methylated C_{16} KL ester	2400	++
6	polyethylene	methylated KL (control)	(1700)	N/A
7	polyethylene	methylated C_2 KL ester	2400	+
8	polyethylene	methylated C_{16} KL ester	950	++

[a]Extrusion capability: N/A = nonapplicable for melt extrusion, + = mixed but extrusion was difficult, ++ = extruded easily. The torque values in parentheses were considered unreliable due to machine stress as a result of weak thermal flow.

The blends and their torques are shown in Table 3.

The methylated lignin sample (control) in the methylated lignin matrix resulted in the highest extruder torque of 3 600 N, but was considered lowered due to poor thermal flow in the extruder. The C_2 KL ester encountered similar problems. The C_8 and C_{12} KL samples were easier to mix and had appropriate torques (3 200 and 3350, N respectively), but did not extrude. The C_{16} KL sample mixed smoothly with excellent thermal flow properties (torque 2400 N, 30% lower than the control torque) and extruded after 10 min of extrusion. The extruder was also easiest to clean after this blend. The torque profiles are available in Figure S2A. The DSC thermograms of C_2–C_{16} KL ester blends showed a typical T_g for a 17 mol % esterified KL (120–127 °C on first measurement cycle).

In an effort to blend esterified lignin with plastics, polyethylene was selected as the matrix. The methylated KL (control) and methylated C_2 KL ester blends resulted in high torque values experienced by the extruder. This data was thus considered unreliable and erratic (torque values ranging from 1700 to 2400 N). Under these conditions the mixing was considered to be inadequate. However, the polyethylene blend with the C_{16} KL sample showed a much reduced torque value (950 N) and was seen to extrude adequately well. As anticipated, the compatibility between the C_{16} KL ester and polyethylene was evident. The torque profiles for polyethylene matrix blends are available in Figure S2B.

The described technique of synthesizing methylated KL esters for melt extrusion can provide C_8–C_{16} KL esters with esterification degrees in range of 33 to 100 mol % by varying the amount of methylation (T_g's vary between 110 and 45 °C, respectively). The KL esters can be used to affect the T_g of plastics via blending in desired ratios. Recently, Pawar et al. successfully lowered the T_g of polystyrene (100 °C) by 22 °C by blending it with 25 m % of 97 mol % substituted C_{18} SWKL ester. They performed blending by solvent casting and letting the plasticization occur on the first heating cycle of DSC.[28] However, in our case the effect of blending on the T_g of polyethylene (typically around −120 °C) was not measured. For example, our C_{16} KL ester polyethylene blend showed a T_m of 114 °C on the first measuring cycle (using a ramp from −50 °C to +190 °C), which corresponds to the melting point of the polyethylene used.

Further characterization of the C_{16} KL ester polyethylene blend by stretching and other means was inapplicable, as the composite proved too brittle. In general, a higher sample:matrix ratio would help the thermal flow issues. Mechanical properties testing has recently been described by Dehne et al. for C_2 to C_4 esterified lignins blended with polyethylene (PE-HD) in 1:1 ratios.

Blend properties were found to be enhanced with increasing length of the ester carbon chains compared to unmodified lignins.[19]

Overall, the KL esters possessing longer aliphatic chains displayed lower torque values in the extruder and overall better melt flow characteristics compared to C_2 KL ester, methylated lignin, and polyethylene itself. Similarly, the longer aliphatic chain KL esters showed obvious augmented compatibility and less phase separation with polyethylene.

■ CONCLUSIONS

Technical softwood kraft lignin was modified by esterification with acetyl, octanoyl, lauroyl, and palmitoyl chlorides using various molar ratios with respect to total hydroxyls of lignin. In total, 20 ester samples were successfully synthesized and characterized. The remaining free hydroxyl contents were analyzed using quantitative ^{31}P NMR spectroscopy (using a theoretical lignin mass percentage) to compare the acylation selectivities of aliphatic and condensed and noncondensed phenolic hydroxyl groups of softwood kraft lignin. The selectivities of the acylation reactions with C_8–C_{16} acyl chlorides were found to vary between different types of hydroxyls in order of aliphatics, condensed phenolics and noncondensed phenolics, whereas C_2 acyl chloride was found to attach evenly to all groups.

The modified polymers were subjected to thermogravimetric analyses, because the introduction of ester moieties into the lignin's free hydroxyls was expected to affect the thermal properties of the polymers. The degradations temperatures (T_D) of SWKL and KL esters determined were in the range of 190–210 °C. DSC analyses were also performed to study the effect of various ratios of different length fatty acid chains bonded to SWKL on the glass transition temperature, T_g, of the SWKL. All C_2–C_{16} KL esters showed a decrease of T_g temperature with increasing loading of fatty acid chloride. The longer chained C_8–C_{16} KL esters showed lower T_g temperatures than C_2 KL esters at equal loading of fatty acid chloride. Lower substituted C_{12} and C_{16} KL esters also showed melting endotherms of crystalline structures arising from precipitation that were unable to reform after heating.

Since the T_g's of the modified KL polymers were substantially lower to that of unmodified SWKL, the application potential of the esterified lignins as additives for polymer blends was examined by melt extrusion. On the basis of the accumulated data, the longer acyl chains were seen to lower the melt torque by 10–30% compared to the control data. The C_{16} KL ester was found to blend well with polyethylene.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b01048.

> SWKL molecular structure, total OH content of SWKL, GPC spectrograms for C_8 KL esters and all GPC data for KL esters, OH group selectivity data for KL esters, and extruder torque profiles for KL ester blends (PDF).

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS

^{31}P NMR, phosphorus-31 nuclear magnetic resonance spectroscopy
DSC, differential scanning calorimetry
FTIR-ATR, Fourier transform infrared spectroscopy with attenuated total reflectance
GPC, gel permeation chromatography
KL, kraft lignin
SWKL, softwood kraft lignin
TGA, thermogravimetric analysis

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