

Succinylation of Three Different Lignins by Reactive Extrusion

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ABSTRACT: Succinate esters of three lignin materials were prepared by reactive extrusion. Reactive extrusion was developed as a facile route to chemically modify lignin with the benefits of being a scalable, solvent-free, and economic process. Kraft lignin and crude and purified enzyme saccharification lignins were reactively extruded with varying amounts of succinic anhydride. The resulting products were characterized chemically and thermally. Succinylation occurred preferentially at the aliphatic hydroxyl groups of kraft lignin, with phenolic substitution occurring at higher amounts of succinic anhydride addition. The degree of substitution was dependent on the relative amounts of succinic anhydride and lignin substrate. Thermal stability of the products decreased with increasing levels of substitution, primarily due to the loss of succinate groups on heating. The degree of substitution influenced the glass transition temperature, which reflected the melt flow and solubility of the products. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4355–4360, 2013

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INTRODUCTION

Lignin is a major component of lignocellulosic biomass and is likely to become an important renewable feedstock for chemicals and polymers.¹ The kraft process is the dominant chemical pulping process producing vast quantities of lignin with increased sulfur, hydroxyl, and condensed functionality compared to the native lignin in biomass.² The development of a bio-refinery industry using lignocellulose to produce bio-fuels would lead to further supplies of lignin. The envisaged bio-refinery fractionation processes may produce lignin of high purity with low sulfur or ash content, and minimal condensation.^{3,4} These lignin materials are a valuable bio-based resource that offers potential to replace petrochemical derived feedstocks.

The industrial application of lignin is generally limited by its physio-chemical properties, such as solubility, molecular weight, and melt flow behavior. The properties of lignin are influenced by many factors including its origin, method of fractionation, and subsequent modification.³ Esterification is a typical route to chemically modify lignin, predominately through reaction with acid chlorides or anhydrides of varying chain length.^{5–8} These modifications typically improve solubility in organic solvents, lower the glass transition temperature, and introduce melt flow characteristics.⁶ Cyclic anhydrides are used to modify lignin in aqueous and solvent systems, to change the reactivity through the pendant carboxylic acid group and alter the thermal stability.^{8,9}

Reactive extrusion is a facile route to chemically modify various biomaterials.^{10,11} This method is becoming increasingly viable, offering the benefits of a clean, solvent-free, scalable, and economic process. Starch has been modified by reactive extrusion with cyclic anhydrides to give products with improved physio-chemical properties suitable for various applications.^{12–14} While lignin is commonly blended and processed by extrusion,^{3,15} there are few reports on the reactive extrusion of lignin.

The goal of this research was to examine if reactive extrusion was a feasible approach to chemically modify lignin. More specifically, this study examined how different lignin substrates behave in such a process and the physio-chemical properties of the resulting products. Three lignin materials, with widely different properties and methods of preparation, were reactively extruded with succinic anhydride. The resulting products were chemically and thermally characterized to evaluate their potential for material applications.

EXPERIMENTAL

Materials

A softwood kraft lignin (KL) was purchased from MeadWestvaco (Indulin AT, USA). Enzyme saccharification lignin (ESL) was the undigested material recovered after enzymatic hydrolysis of a pretreated *Pinus radiata* wood pulp (prepared using a proprietary process at Scion). Enzymatic hydrolysis was performed using a cocktail of Celluclast 1.5 L cellulase and Novozym 188

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cellobiase (Novozymes, Denmark). The ESL was extracted by a method adapted from Chang,¹⁶ using 1% sodium hydroxide at 121°C for 90 min to give a purified enzyme saccharification lignin (PESL) in 16% yield. All lignin materials were dried under vacuum (40°C) before use. Succinic anhydride was used as received from Merck (>98%, Germany).

Preparation of Lignin Succinate Esters

Lignin (KL, ESL, and PESL) was blended with succinic anhydride (0, 0.1, 0.2, or 0.3 succinic anhydride to lignin ratio (w/w)) and processed using a co-rotating twin screw extruder (19 mm screws with 30:1 length to diameter ratio (OMC, Italy)). Samples were extruded at 175°C (all temperature zones) with a screw speed of 300 rpm (residence time approximately 90 s) using a profile die with air cooling. Samples were prepared in triplicate where sufficient material was available.

After extrusion, the samples (KL and PESL) were reprecipitated from 9:1 acetone/water with water, centrifuged (30,000 rcf), washed (water, 4 × 50 mL) and freeze dried to yield a brown powder. Due to insolubility, the ESL samples were ground into a fine powder, washed (water, 4 × 50 mL), collected by filtration and dried under vacuum.

Analyses

Total lignin content was determined in duplicate as the sum of Klason lignin and acid-soluble lignin following standard methods (TAPPI standard T222 and TAPPI standard UM 250) scaled down to analyze 0.25 g of sample. Monomeric carbohydrates in the filtrate were determined by ion chromatography.¹⁷

Elemental analyses (C, H, and N) were carried out by the Campbell Microanalytical Laboratory (University of Otago, New Zealand).

Fourier transform infrared (FTIR) spectra were recorded on a Tensor 27 FTIR instrument (Bruker, Germany) with samples prepared as KBr discs.

Solid-state ¹³C CP-MAS NMR spectra were obtained on a 200 DRX spectrometer (Bruker, Germany) by spinning at 5 kHz in a 4 mm Bruker SB magic-angle spinning probe. Hartmann–Hahn matching was conducted using glycine. A standard cross-polarization experiment was used with a 1.5 s pulse delay, proton preparation pulse of 5.6 μs, a 1 ms contact time and a 30 ms acquisition time. The proton transmitter power was increased to a value corresponding to a 90° pulse width of 1.4 μs for proton decoupling during ¹³C data acquisition. Spectra were referenced to the lignin methoxyl peak (56 ppm), with the degree of substitution (DS) calculated using eq. 1,

$$DS = \frac{I_1/n_1}{I_2} \quad (1)$$

where I_1 is the sum of succinate carbonyl and methylene integrals, n_1 is the number of succinate carbons (4) and I_2 is the methoxyl integral (assuming a stoichiometric number of methoxyl groups). The reaction efficiency (RE) was determined using eq. 2 adapted from Wang et al.,¹³

$$RE = \frac{DS}{SA/L} \times 100 \quad (2)$$

where DS is the degree of substitution as calculated from eq. 1 and SA/L is the mole ratio of succinic anhydride (SA) to a lignin C₉ unit (L).

All KL samples and unmodified PESL were phosphitylated by a method adapted from Granata and Argyropoulos,¹⁸ using endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide as the internal standard.¹⁹ ³¹P NMR spectra were acquired on a DPX 400 spectrometer (Bruker, Germany) using a 5 s delay with the ppm shift calibrated to phosphitylated water (132.2 ppm). Samples were analyzed in duplicate.

All KL samples and unmodified PESL were acetylated prior to gel permeation chromatography (GPC) by a method adopted from Gellerstedt.²⁰ The samples were prepared in tetrahydrofuran at 0.5 mg/mL and analyzed using a PL-GPC 50 integrated GPC system (Polymer Laboratories, UK) with two PLgel 5 μm mixed-C columns (300 mm × 7.5 mm) connected in series. Samples were eluted with tetrahydrofuran at 1 mL/min at a column temperature of 30°C with UV detection (280 nm). Calibration was based on monodisperse polystyrene standards with samples analyzed in duplicate and results reported as weight average molecular weight.

Thermogravimetric analysis (TGA) was performed using a Q500 thermogravimetric analyzer (TA Instruments, USA). Samples were placed into platinum pans and heated at 10°C min⁻¹ to 600°C under a nitrogen atmosphere.

Differential scanning calorimetry (DSC) experiments were carried out using a Q1000 DSC (TA Instruments, USA). Samples were transferred to aluminium pans and run using a heat-cool-heat cycle at a rate of 10°C min⁻¹ under a nitrogen atmosphere. Glass transitions were determined from the second heating cycle at the inflection of the step transition.

RESULTS AND DISCUSSION

Comparison of Lignin Starting Materials

The three lignin materials selected for this study varied widely in their chemical properties, as a result of their different methods of preparation (Table I). Total hydroxyl group concentration in KL was 6.92 mmol g⁻¹, which was approximately 50% more than the 4.53 mmol g⁻¹ in PESL. However, the aliphatic hydroxyl concentration in these two lignins was similar. Literature indicates that the level of β-ether linkages is likely to be higher in PESL compared with KL, while KL is likely to be more condensed.^{21,22} Furthermore, the average molecular weight of KL (4420 Da) was considerably less than PESL (16,600 Da). A crude ESL was included in the study to assess whether an impure lignin could be processed by reactive extrusion without the need for purification. This ESL contained 65% lignin with the residual material consisting primarily of carbohydrates (23%). In comparison, the KL and PESL consisted of 97% and 84% lignin, respectively.

Processing Behavior and Chemical Properties

Reactive extrusion proved to be a simple and fast process, allowing the processing of all three lignin materials. KL and PESL showed a small level of melt flow behavior when extruded without succinic anhydride (KL0 and PESL0). The addition of

Table I. Chemical Properties of KL, ESL and PESL

Lignin	Lignin content (%)	Molecular weight (Da)	Hydroxyl concentration (mmol g ⁻¹)		
			Aliphatic	Aromatic	Acidic
KL	97	4420	2.53	3.93	0.46
ESL	65	ND	ND	ND	ND
PESL	84	16600	2.03	2.05	0.45

ND = not determined due to insolubility.

succinic anhydride, which was molten at the 175°C processing temperatures, improved the melt flow behavior. For example, KL and PESL extruded with succinic anhydride produced a molten black solid that was easily malleable while hot, but brittle at room temperature. In contrast, the ESL showed no melt flow behavior even when extruded with succinic anhydride. In this case a brown powder exited the extruder barrel that was visually similar to the feed material. Overall, the melt flow behavior decreased in accordance with the lignin content of the substrates.

During reactive extrusion, succinic anhydride was expected to react with lignin at any of the free hydroxyl groups to produce the half-ester, as illustrated (Figure 1). Side reactions can occur during succinylation, including cross linking to form di-esters or hydrolysis of succinic anhydride to form succinic acid.¹³ Any free acid or unreacted succinic anhydride was removed using simple work-up procedures.

Qualitative analysis confirmed the succinylation of lignin and the absence of free succinic acid. Elemental analysis showed a decrease in the amount of carbon in the products relative to the unmodified lignins. For example, the carbon content after extrusion of KL with and without succinic anhydride was 62.1% (KL0.3) and 65.2% (KL0), respectively. This was consistent with adding succinate groups to the lignin, which contain a lower proportion of carbon. FTIR spectroscopy showed two carbonyl stretches at 1717 and 1732 cm⁻¹ corresponding to acid and ester functional groups, respectively (Supporting Information Figures S1, S2, and S3). The relative intensity of the two carbonyl peaks was similar for all samples, indicating that di-ester formation was minimal. This was consistent with previous reports on the succinylation of lignin in solvent based sys-

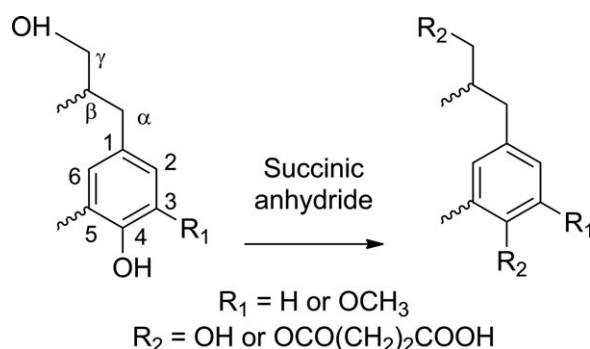


Figure 1. Scheme illustrating the succinylation of a simplified lignin C_γ unit.

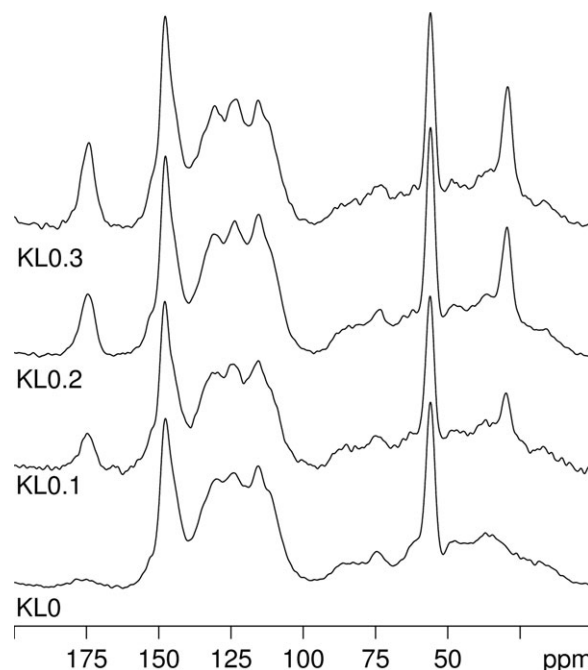


Figure 2. Example ¹³C CP-MAS NMR spectra of KL succinates.

tems.^{8,9} Solid state ¹³C CP-MAS NMR spectroscopy showed signals at 174 and 30 ppm corresponding to carbonyl and CH₂ groups, respectively (Figure 2 and Supporting Information Figures S4 and S5). Signals corresponding to C_γ-OH and C_γ-OR were also identified at 62 and 74 ppm, respectively.²³ A decrease in the C_γ-OH peak relative to the C_γ-OR peak upon succinylation suggested that esterification occurred at the aliphatic hydroxyl groups of KL and PESL.

The DS varied within a 0.00 to 0.25 range depending on the ratio of succinic anhydride addition and type of lignin (Table II). An increase in the DS was seen for all three lignins as the ratio of succinic anhydride increased, but this was accompanied by a decrease in the RE. Reaction efficiencies were within an 18% to

Table II. Ratio of Succinic Anhydride to Lignin (SA:L), Percent Recovery, DS and RE

Entry	Ratio SA:L (w/w)	Recovery (%) ^a	DS ^b	RE (%)
KL0	0	87	0.00 (0.02)	N/A
KL0.1	0.1	75	0.10 (0.02)	55
KL0.2	0.2	76	0.15 (0.02)	41
KL0.3	0.3	62	0.21 (0.02)	38
PESL0	0	64	0.00 (0.04)	N/A
PESL0.2	0.2	83	0.25 (0.04)	69
ESL0	0	90	0.00 (0.02)	N/A
ESL0.1	0.1	87	0.06 (0.02)	33
ESL0.2	0.2	84	0.08 (0.02)	22
ESL0.3	0.3	82	0.10 (0.02)	18

^aMean percent recovery after work-up (w/w).

^bMean ± (95% confidence interval).

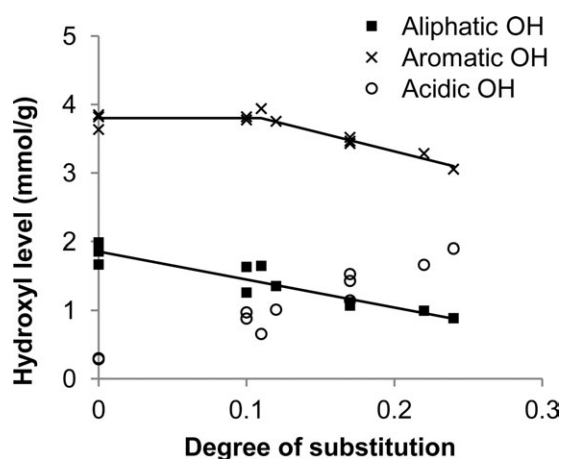


Figure 3. Plot of aliphatic, aromatic, and acidic hydroxyl levels compared with the DS for KL succinates.

69% range for all three lignins. Interestingly, the range of DS was of similar magnitude to the analogous reactions with starch (0.03 to 0.46),¹³ however the RE was considerably better than starch (5 to 29%).¹³ It is likely that improvements to the RE could be realized by increasing the residence time or minimizing moisture. When the products were compared at a succinic anhydride addition ratio of 0.2 (**KL0.2**, **PESL0.2**, and **ESL0.2**), some clear differences between the performance of the three lignins were evident. The DS decreased in the order PESL > KL > ESL, the differences being significant at the 95% confidence level. The higher DS for PESL over KL was unexpected, given the lower concentrations of lignin and hydroxyl groups in the PESL compared with KL. In contrast, the low DS for ESL was probably due to a combination of factors such as lack of melt flow behavior, impurities in the lignin material and fewer free hydroxyl groups.

Hydroxyl groups were quantified in the KL samples using ³¹P NMR spectroscopy. Both the PESL and ESL products were unable to be analyzed due to insolubility in the phosphitylating reagents. An increase in acidic hydroxyl groups (Figure 3) was consistent with FTIR and ¹³C CP-MAS NMR spectroscopy, confirming the formation of succinate esters. Furthermore, the increase in acidic hydroxyl groups compared well with the DS calculated by ¹³C CP-MAS NMR spectroscopy. Changes in the concentration of hydroxyl groups were used to identify the site of succinylation. A decrease in aliphatic hydroxyls at low DS indicated preferential substitution of the aliphatic groups. In contrast, phenolic substitution was only evident at a DS greater than approximately 0.15. This initial preference for substitution at the aliphatic hydroxyl groups was consistent with known reactivity under nucleophilic acyl substitution.

Condensation reactions are thought to occur during extrusion of lignin, as previously described in the literature.^{24,25} In this study, cross-linking was evident with an increase in the average molecular weight of KL from 4420 to 10,230 Da after extrusion (**KL0**) (Supporting Information Table S1). The increase in molecular weight was greater than reported during the fiber spinning of organosolv and hardwood kraft lignins.²⁴ This was

probably due to differences in the chemical structure between softwood and hardwood lignins. A reduction in the level of aliphatic (1.84 mmol g⁻¹) and acidic (0.30 mmol g⁻¹) hydroxyl groups was observed upon extrusion of KL without succinic anhydride (**KL0**). As previously described by Uraki et al.,²⁵ a decrease in hydroxyl levels is likely due to dehydration reactions leading to cross linking. These findings highlight condensation reactions as a consideration when using reactive extrusion as a means to modify lignin. Condensation reactions may be constrained by altering the processing parameters, such as temperature or residence time. However, such changes would likely compromise the RE. Alternatively, condensation may provide a route to co-polymerize lignin if suitable reagents were used during extrusion.

Thermal Analysis

The thermal properties of the lignin succinates were characterized using both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table III). Thermogravimetric analysis showed a weight loss of approximately 5% for all samples at temperatures up to 100°C, attributed to loss of water (Figure 4). Upon further heating the onset of degradation occurred between 120°C and 235°C. Typically the rate of degradation (DTG) reached a maximum between 300°C and 400°C. KL extruded without succinic anhydride (**KL0**) showed an increase in thermal stability with the onset of degradation increasing from approximately 130°C to 205°C. This increase in thermal stability was consistent with an increase in molecular weight, as previously observed by Yoshida et al.²⁶ and Sun et al.²⁷ The thermal stability of PESL also increased upon extrusion without succinic anhydride (**PESL0**), however no discernible increase was observed for ESL (**ESL0**).

The degradation profile of all three lignin materials changed upon succinylation, with the initial onset of degradation occurring at lower temperature. This initial decomposition of

Table III. Thermal Stability and Glass Transition (*T_g*) Data for Succinylated Lignins

Entry	Temperature (°C) at % weight loss		<i>T_g</i> (°C)
	10%	20%	
KL	280	329	140
KL0	305	354	158
KL0.1	271	315	140
KL0.2	262	313	135
KL0.3	251	299	127
PESL	283	329	161
PESL0	299	350	198
PESL0.2	261	319	158
ESL	293	321	201
ESL0	296	322	200
ESL0.1	283	315	195
ESL0.2	274	311	194
ESL0.3	272	309	196

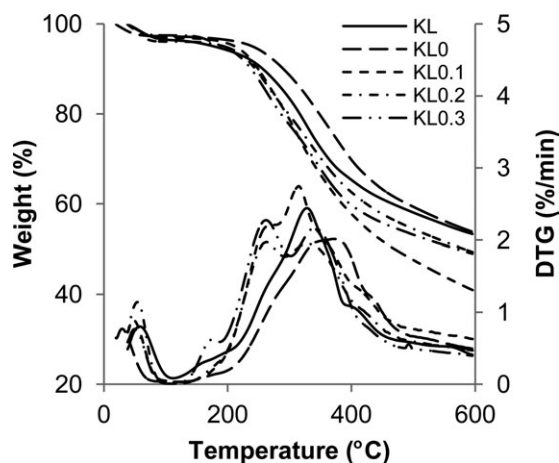


Figure 4. Example TGA thermograms of KL succinates.

succinylated lignins was associated with the rupture of ester groups as previously described by Jakab et al.²⁸ and Rudnik et al.²⁹ For KL, this ester group loss occurred with a maximum rate of decomposition occurring at approximately 264°C. Furthermore, KL succinates of high DS showed a lower temperature (176°C) peak in the DTG (Figure 4). The intensity of this peak correlated with the level of aromatic substitution, suggesting this was due to a loss of aromatic ester groups. As a consequence, the temperature for onset of degradation decreased with increasing levels of substitution. This low temperature (176°C) degradation peak was not evident in PESL and ESL thermograms, possibly indicating no aromatic substitution of these lignins. As such, PESL was of higher thermal stability compared with KL of a similar DS. The observed decrease in thermal stability was in contrast to the increase in thermal stability upon aqueous succinylation of oil palm and rye straw lignins.⁸

Differential scanning calorimetry of all lignin samples showed a broad endotherm in the first heating cycle at approximately 100°C due to water loss, this was consistent with the TGA. The second heating cycle showed an endothermic event above 100°C, assigned to the glass transition (T_g). The T_g of KL and PESL increased upon extrusion without succinic anhydride

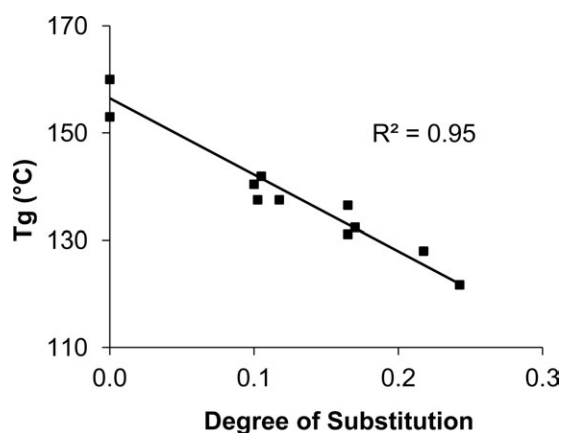


Figure 5. Correlation between the glass transition temperature and DS for KL.

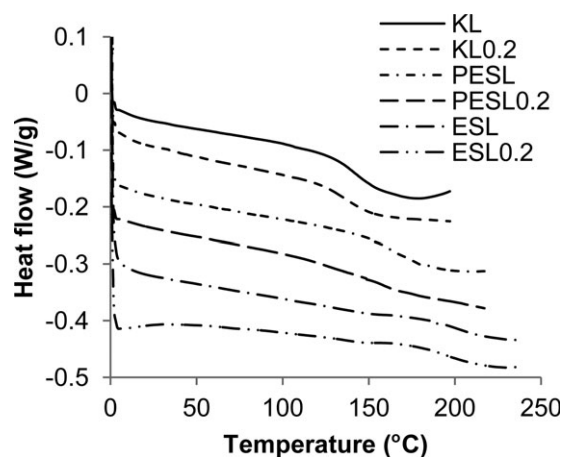


Figure 6. Example DSC thermograms of KL, PESL and ESL and their succinate derivatives (second heating cycle).

(Table III). This increase in T_g was consistent with an increase in molecular weight due to condensation and cross-linking reactions.³ In contrast, ESL showed no increase in the T_g upon extrusion.

The glass transition temperature of both KL and PESL decreased upon succinylation, revealing opposing effects from condensation and succinylation reactions. For KL, the decrease in T_g showed a linear relationship with the DS (Figure 5). Likewise, PESL showed comparable behavior, with a similar decrease in T_g due to succinylation. The observed relationship between the T_g and DS agrees with the thermal properties of esterified lignins as reported by Bouajila et al.³⁰ In the case of acetylation, this was attributed to the disruption of hydrogen bonding and an increase in the free volume.³⁰ However, the disruption of hydrogen bonding may be a minor influence upon succinylation as the introduced acid functionality would enable a greater level of hydrogen bonding. Minimal changes were observed in the glass transition temperature of ESL.

Some trends become evident when comparing the DSC thermograms of the three lignin materials (Figure 6). Firstly, the glass transition temperature decreased in the order $ESL > PESL > KL$. Secondly, a narrowing of the glass transition was observed in the same order. For example, the transition for KL was comparatively sharp and well defined, whereas ESL showed a broad transition between 175°C and 225°C. A broad transition is likely the result of a combination of factors, including higher molecular weight and greater polydispersity. A lower glass transition temperature and narrower transition can be associated with better solubility in organic solvents and improved melt flow behavior.^{6,31} These trends of solubility and melt flow behavior were observed for all three lignin materials during processing, work-up, and analysis. For example, KL was the most soluble in organic solvents such as acetone/water (9:1), while ESL was completely insoluble.

CONCLUSIONS

Three lignin materials were successfully modified with succinic anhydride using reactive extrusion. KL and PESL had the

highest DS, which was controllable by altering the ratio of reagents. Reactive extrusion of lignin was complicated by condensation reactions which increased the molecular weight and adversely affected the thermal properties. Careful control of processing conditions may be required to minimize these reactions in future work. In general, the succinylated KL and PESL products both showed desirable thermal properties, offering promise for application in resin, adhesive or coating formulations. Products prepared from ESL had less desirable physicochemical properties, indicating that purification or pretreatment may be required in utilizing this resource. Reactive extrusion is a simple, industrially-relevant process and these results suggest that it offers good potential to be more widely used for chemical modification of lignin or other biomaterials.

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