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# Thermal Polymerization of Softwood Kraft Lignin: Enhanced Adhesion of Lignin-Phenol-Formaldehyde Blends

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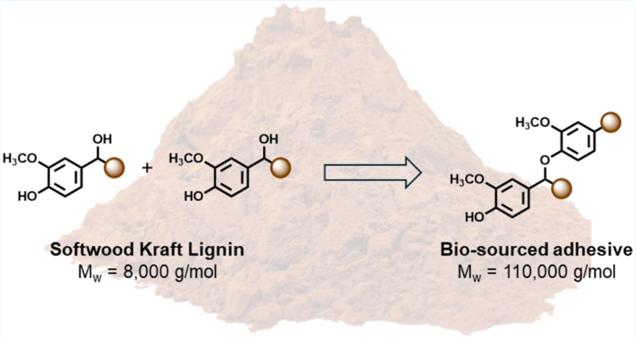
**ABSTRACT:** Thermal polymerization improved the adhesion properties of softwood kraft lignin, making polymerized softwood kraft lignin a viable and sustainable partial substitute for phenol-formaldehyde resins used in engineered wood panels. This was confirmed by the increased shear strengths observed after pressing hardwood veneers with either alkaline aqueous lignin solutions or their blends with commercial phenol-formaldehyde resins. Plywood panels bonded with blends of polymerized kraft lignin and phenol-formaldehyde resins exhibited higher wood failure values compared with those bonded with phenol-formaldehyde resins alone. Extensive polymerization was achieved solely via nonoxidative thermal treatments. The impact of temperature and time on average molar mass, dispersity, and intrinsic viscosity was investigated by size-exclusion chromatography, revealing that the average molar mass of kraft lignin can be increased by more than 40 times its original value. Other critical parameters affecting the polymerization process such as pH and water content were identified, and their influence quantified. Hydroxyl content measured by $^{31}$P NMR before and after polymerization suggests that the formation of ethers between phenols and benzylic hydroxyl groups is mainly responsible for the observed increase in molar mass.



## ■ INTRODUCTION

Interest in creating materials from renewable sources is on the rise, driven by environmental and economic factors. Lignin, the second most abundant biopolymer on Earth after cellulose, is a key structural material found in most plants and is a byproduct of the manufacture of cellulose pulp by the pulp and paper industry, yielding millions of tons annually.[1] The primary method of wood delignification used worldwide is the kraft pulping process, which results in a fragmented and alkali-soluble technical lignin known as kraft lignin. At the present time, virtually all kraft lignin is incinerated in recovery boilers as an energy source. This low-value utilization has prompted research into repurposing this biopolymer for higher-utility functions, and such endeavors have gained momentum in recent years, given the growing emphasis placed on decarbonization and sustainability.

Among the few commercially viable applications of softwood kraft lignin (SKL) is its use as a partial substitute of phenol in the manufacture of phenol-formaldehyde (PF) resins used by the plywood industry.[2,3] The lower reactivity of SKL compared to phenol poses a significant challenge, as it adversely impacts the cure rate of lignin-PF adhesives and severely limits the portion of phenol that can be substituted. Moreover, the copolymerization of SKL with phenol and formaldehyde is a complex process that requires specialized industrial capabilities. A far more desirable approach would be to substitute PF resin itself with SKL, but performances of PF-lignin blends have so far proven insufficient for industrial use.[4] Indeed, SKL is characterized by a relatively low average molar mass and does not cross-link at typical press schedules used in industry. As a result, it exhibits poor mechanical properties in contrast to those of typical wood adhesives.

While some characteristics of SKL must be improved to meet the requirements of commercial wood adhesives, SKL offers multiple sustainability advantages over PF resins. Indeed, the carbon footprint of SKL is significantly lower than that of PF. The cradle-to-gate global warming potential of SKL is estimated to be only 0.1−0.6 kg $CO_2$ eq/kg, which represents an 8-fold reduction compared to PF resins (2.7 kg $CO_2$ eq/kg).[5−7] The complete or partial substitution of PF resins with SKL can, therefore, help decarbonize the wood panel industry. Furthermore, replacing PF resins with SKL reduces the use of

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formaldehyde, a known carcinogen recognized by the World Health Organization.[8]

Extensive research has shown that kraft lignin can be fractionated to produce fractions of relatively high and low average molar mass.[9,10] High molar mass fractions of kraft lignin lead to improved properties in adhesives,[11] carbon fibers,[12] thermoplastics,[13] and polymer-based composites[14] compared to their lower molar mass counterparts. However, fractionation has several limitations: it cannot provide high yields of lignin fractions having particularly elevated average molar mass, it generates other fractions that must also be valorized to reach commercial viability at industrial scale, and it necessitates the use of either solvents, reagents, or membrane filtration systems, all of which has so far proven prohibitively costly.[15,16] Effective approaches to kraft lignin polymerization would help overcome these challenges, but known methods also have their drawbacks. For example, treating lignin with concentrated mineral acids yields highly condensed, insoluble lignins that have found little value as materials.[17,18] Laccase-catalyzed oxidative polymerization can substantially increase the mass average molar mass ($M_w$) of hardwood kraft lignin, but is far less effective at polymerizing SKL.[19−21]

In 2013, Argyropoulos and co-workers reported a 70-fold increase in the mass average molar mass of SKL upon heating the solid under nitrogen at 173 °C for 20 min within a thermogravimetric analyzer.[22] This effect was not studied further, despite its remarkable simplicity. Two years later, Aldaeus and co-workers reported that heating SKL to 160−240 °C for up to 24 h led to only minor increases in average molar mass.[23] These seemingly conflicting results warrant further investigations.

In this work, the behavior of SKL upon nonoxidative thermal treatment was studied with the aim of developing a simple, cost-effective, and easily scalable methodology for the preparation of SKL having $M_w$ values far higher than those typical of commercial products. By analyzing the molar mass distribution of thermally treated SKL, key factors causing inconsistent thermal polymerization in kraft lignin were identified, enabling the method to be scaled to kilogram production. Furthermore, polymerization kinetics, viscometry, and functional group analysis gave insights into the mechanism of polymerization. Finally, the expected improved adhesion properties of polymerized lignins were confirmed by both automated bonding evaluations and lab-scale plywood manufacturing.

## ■ EXPERIMENTAL SECTION

**Materials and methods.** All chemicals used in this study were obtained from commercial sources and used without further purification. SKL was isolated from black liquors sourced from Canadian mills originating from the pulping of mixed northern softwoods using the LignoForce process.[24,25] Relevant properties are listed in Table 1.

**Solid-State Polymerization of Softwood Kraft Lignin.** 200 g of softwood kraft lignin powder having a water content of 5.3% (w/w) and a pH of 3.5 (measured as a 2% w/w aqueous suspension) was charged into a 2-L stainless-steel rotating autoclave. The atmosphere within the autoclave was replaced with nitrogen, and then it was sealed. The autoclave was immersed in an oil bath kept at 150°C and slowly rotated for 20−60 min. Afterward, the autoclave was quickly cooled by immersing it in cold water, and its content was emptied to afford 200 g of polymerized softwood kraft lignin.

**Table 1. Relevant Physicochemical Properties of the Softwood Kraft Lignin Used in This Study**

| properties | units | values |
|---|---|---|
| water content | % (w/w) | 4.9−5.4 |
| pH[a] | | 3.5−3.9 |
| $M_w$ (SEC-RI) | g/mol | 7090−8300 |
| $M_n$ (SEC-RI) | g/mol | 1090−1160 |
| $M_w$ (SEC-MALS) | g/mol | 13,100−24,200 |
| $M_n$ (SEC-MALS) | g/mol | 1960−5250 |
| $[\eta]$ (SEC-IV) | mL/g | 6.96−7.11 |
| $T_g$[b] | °C | 162−168 |
| aliphatic hydroxyls | mmol/g | 1.75−1.92 |
| phenolic hydroxyls | mmol/g | 3.76−4.06 |
| carboxylic hydroxyls | mmol/g | 0.43−0.54 |

[a] Measured at 2% w/w aqueous suspension. [b] Measured by DSC.[22]

**Thermal Polymerization of Aqueous Softwood Kraft Lignin Suspensions.** 2.0 g of softwood kraft lignin powder having a water content of 5.3% (w/w) and a pH of 3.5 (measured as a 2% w/w aqueous suspension) and 20 mL of deionized water were charged into a 45 mL pressure vessel. The resulting mixture was magnetically stirred until a homogeneous suspension was obtained. The atmosphere within the vessel was replaced with nitrogen; then, it was sealed. The reactor was immersed in an oil bath kept at 140 °C and its content was magnetically stirred for 20−120 min. Afterward, the reactor was quickly cooled by immersing it in cold water, and its content was filtered on a fine fritted funnel. The collected solid was finally freeze-dried to afford 2.0 g of polymerized softwood kraft lignin.

**Determination of Molar Mass Distributions and Intrinsic Viscosities.** The molar mass distribution of kraft lignins was determined by size-exclusion chromatography (SEC). The method described by Zinovyev et al. was used.[26] All samples were freeze-dried and then kept in a desiccator ($P_2O_5$) prior to analysis. Samples were dissolved in LiBr/DMSO (0.5% w/v) at 70 °C for 2 h at a concentration of 2−6 mg/mL (poorly soluble samples were dissolved at lower concentrations). Once cooled to ambient temperature, the resulting solutions were filtered through 0.2 $\mu$m PTFE filters prior to analysis. SEC analysis was performed using an Agilent Model 1200 high performance liquid chromatography system (solvent tray, degasser, quaternary pump, autosampler, column heating module, UV diode-array detector) equipped with a Wyatt Dawn multiangle light scattering detector with a laser operating at 785 nm, a Wyatt Optilab differential refractive index detector ($\lambda$ = 785 nm), and a Wyatt Viscostar online differential viscometer. The MALS detector comprises 18 photodiodes at different measuring angles with narrow band-pass filters (±10 nm installed on every second photodiode). The separation was performed with two columns in series: one Agilent PolarGel M column (7.8 mm × 300 mm, 8 $\mu$m) followed by one Agilent PolarGel L column (7.8 mm × 300 mm, 8 $\mu$m). The columns were kept at 50 °C. The SEC system was operated under the following conditions: LiBr/DMSO (0.5% w/v) eluent, 0.5 mL/min flow rate; 50 $\mu$L injection volume; 65 min run time. A set of 10 pullulan polymers standards ($M_p$ = 710, 343, 202, 116, 50.6, 23.0, 9.90, 6.00, 1.26, and 0.342 kg/mol) was used to construct a conventional narrow standard calibration curve for relative molar mass determination. Data evaluation was done using ASTRA software, version 8.0. The determination of the specific refractive index increment at a constant chemical potential $(dn/dc)_\mu$ of each lignin sample in LiBr/DMSO (0.5% w/v) was performed using the online approach by integration of the RI peak area after sample elution from the columns assuming 100% sample mass recovery.

**Determination of Hydroxyl Contents.** The hydroxyl contents in lignin samples were determined by $^{31}$P NMR spectroscopy.[27,28] All samples were freeze-dried and then kept in a desiccator ($P_2O_5$) prior to analysis. Approximately 40 mg of the lignin sample was completely dissolved in 500 $\mu$L of a 1.0:1.6 mixture of $CDCl_3$ and pyridine. Afterward, 100 $\mu$L of a $CDCl_3$:pyridine stock solution containing 22.0 mg of cyclohexanol and 100 $\mu$L of a $CDCl_3$:pyridine stock solution containing 0.5 mg of $Cr(acac)_3$ was added. Finally, 100 $\mu$L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was added, and the resulting solution was shaken for 10 min before being loaded in an NMR tube. $^{31}$P NMR spectra were recorded on a 60 MHz Nanalysis 60PRO benchtop NMR spectrometer. 1024−2048 scans were acquired with a 10 s interscan delay. Integration was done after baseline correction. All spectra were calibrated to anhydride formed by the reaction of the derivatization reagent with water at 132.2 ppm. The quantification limits applied were 150.0−145.4 ppm for aliphatic hydroxyl groups, 144.5−137.0 ppm for phenolic hydroxyl groups, and 136.0−133.6 ppm for carboxylic hydroxyl groups.

## ■ RESULTS AND DISCUSSION

**Solid-State Polymerization of Softwood Kraft Lignin.** To determine whether SKL would polymerize upon thermal treatment in the solid state, a sample of SKL containing approximately 5% water was first heated at 150 °C under nitrogen. The resulting solid was then dissolved in DMSO and analyzed by size-exclusion chromatography (SEC) coupled with multiangle light scattering (MALS) and refractive index (RI) detectors. This revealed a gradual shift toward higher molar mass over time, consistent with the findings of Argyropoulos and co-workers (Figure 1).[22] The essentially monomodal distribution of the initial SKL evolved into a bimodal distribution after only 20 min of treatment and ultimately into a trimodal distribution after 40−60 min of treatment. The polymerized SKL (PSKL) isolated beyond 60 min at 150 °C was only partially soluble in DMSO and could not be properly analyzed by SEC using our system. Thermal polymerization resulted in PSKL with broader molar mass distributions compared with SKL. This behavior is expected when molar mass variations occur in branched polymeric systems. Indeed, cross-coupling between branched and highly functional macromolecules typically results in pronounced dispersity, as evidenced by the broadening of curves measured by SEC. This phenomenon has been experimentally observed in synthetic polymer systems and is predicted by theoretical frameworks.[29−31]

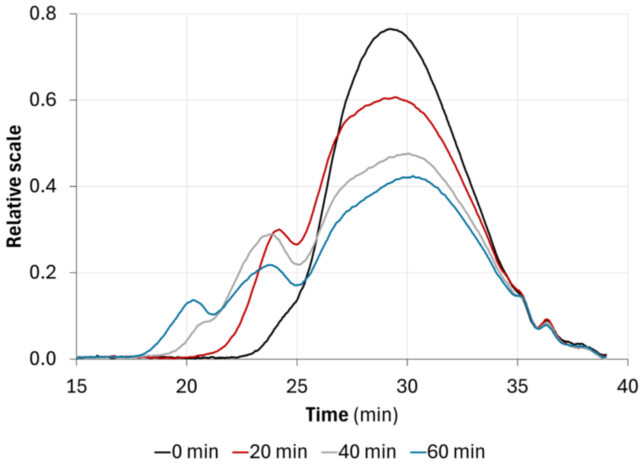

Figure 1. SEC-RI chromatograms of SKL powder (5% water content) heated in a rotating autoclave at 150 °C for 0 min (black), 20 min (red), 40 min (gray), and 60 min (blue).

Remarkably, both MALS and RI detectors showed that the increase in $M_w$ followed an exponential growth, which is typical of step-growth polymerization (Figure 2). After 60 min at 150 °C, $M_w$ had increased by over 40-fold according to SEC-MALS and by over 30-fold according to SEC-RI. Analogous experiments conducted at 130 and 140 °C showed that, while the kinetics of polymerization were much slower at these temperatures, the increase in $M_w$ followed the same trend.

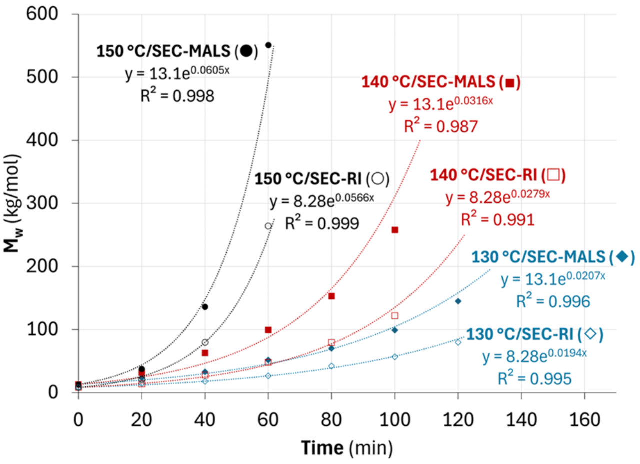

Figure 2. Plot of the mass average molar mass ($M_w$) of SKL thermally polymerized in the solid state as determined by SEC-MALS (full markers) and SEC-RI (empty markers) against heating time in a rotating autoclave at 150 °C (black), 140 °C (red), and 130 °C (blue).

**Effect of Polymerization on Branching Density.** SEC, combined with an online differential viscometer (IV), provided insights into the conformation of PSKL dissolved in 0.5% LiBr/DMSO, via the Mark−Houwink−Sakurada (MHS) plot (Figure 3). A linear relationship between intrinsic viscosity and $M_w$ was determined, which enabled us to determine the MHS parameters. The values of the MHS exponent $\alpha$ were 0.17−0.18, lying in similar range as previously reported values.[32,33] Such low values infer that the scaling behavior of these lignins in 0.5% LiBr/DMSO at 50 °C resembles that of spheres more than that of linear polymer coils, as expected from the branched and condensed structures of SKL.[34,35] Furthermore, the consistent linear relationship between intrinsic viscosity and $M_w$ across all polymerization extents implies that the branching density remained largely unchanged during polymerization.

**Impact of the pH.** To further investigate the mechanism by which polymerization occurs, SKL was heated in aqueous solutions buffered at different pH values (Figure 4). These experiments established that the thermal polymerization of SKL described above is an acid-catalyzed process. Indeed, as

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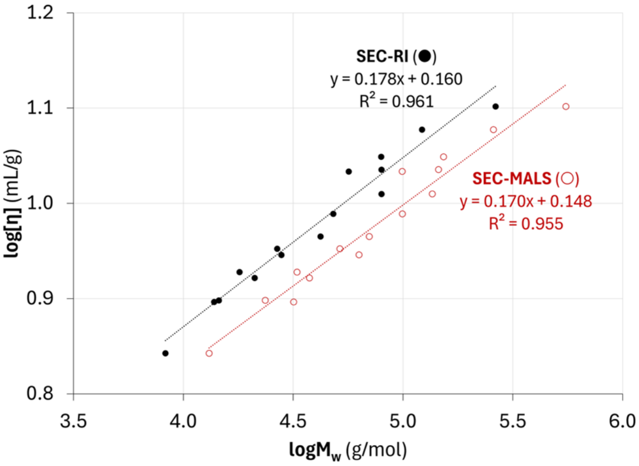


**Figure 3.** Log−log plot of intrinsic viscosity ([$\eta$]) determined by SEC-IV in 0.5% LiBr/DMSO at 50 °C against the mass average molar mass ($M_w$) of thermally polymerized air-dried softwood kraft lignin powder as determined by SEC-RI (black) and SEC-MALS (red).

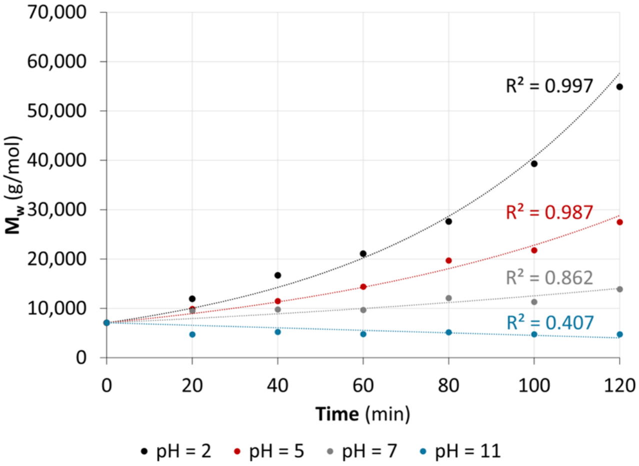


**Figure 4.** Plot of the mass average molar mass ($M_w$) of thermally polymerized softwood kraft lignin in aqueous buffers at pH = 2 (black), pH = 5 (red), pH = 7 (gray), and pH = 11 (blue) as determined by SEC-RI against heating time in sealed vials at 130 °C.

the pH decreased, the kinetics of polymerization became markedly more pronounced. While polymerization still occurs at a very slow rate at neutral pH, no polymerization took place under basic pH conditions. In fact, in alkaline conditions, both $M_n$ and $M_w$ values were found to be slightly inferior to those of the starting lignin, which is indicative of alkaline depolymerization.[36] These findings exclude phenoxy radicals as a significant contributor to the thermal polymerization of SKL within the studied temperature range. The solid-state polymerization of SKL exhibits the same behavior as its buffered suspensions: acidity is essential for polymerization to occur. Indeed, no significant polymerization was observed when air-dried alkaline softwood kraft lignin powder was heated in a rotating autoclave at 140−180 °C for several hours. The SKL utilized in this study contains carboxylic acids within its structure, as well as residual fatty and resin acid impurities,[37] resulting in sufficient acidity to catalyze the polymerization.

**Impact of the Water Content.** Although the oven-dried SKL used in this study had a glass transition temperature ranging between 162 and 168 °C, the glass transition temperature of the air-dried SKL used in the polymerization experiments was below 100 °C due to the presence of about 5% water.[38] Hence, temperatures used in experiments described so far were all much higher than the glass transition temperature of the SKL. Increasing the water content to 90% did not slow the polymerization by a large extent (Figure 5).

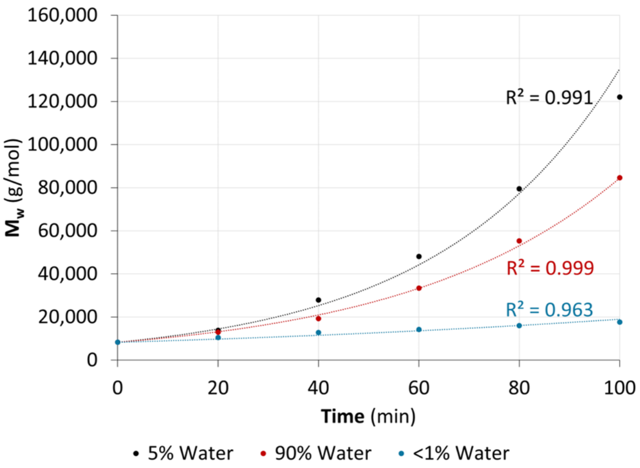


**Figure 5.** Plot of the mass average molar mass ($M_w$) of thermally polymerized softwood kraft lignin at 5% water content (black), 90% water content (red), and <1% water content (blue) as determined by SEC-RI against heating time in a rotating autoclave at 140 °C.

The slightly slower kinetics observed in this case might result from the dilution of acidic compounds acting as catalysts. By contrast, when SKL dried to <1% moisture content was heated at 140 °C, a drastically slower polymerization was observed (Figure 4). This indicates that for polymerization to occur at an appreciable rate, SKL must be heated above its glass transition temperature. This result could explain why Aldaeus and co-workers did not observe significant thermal polymerization as they oven-dried their lignin prior to thermal treatment.[23]

**Effect of Polymerization on Hydroxyl Content.** To gain more insight into the polymerization mechanism, the hydroxyl content of the PSKL was determined by the well-established $^{31}$P NMR technique (Figure 6).[27,28]

In the early stage of polymerization, a simultaneous decrease of both aliphatic and phenolic hydroxyls was observed, which points toward a condensation reaction yielding ether bonds. The same effect was observed in both solid-state and aqueous buffer polymerizations. A similar phenomenon was reported by Cathala and co-workers in 2005 upon treating SKL with a biphasic mixtures of organic solvents and mineral acids for extended periods of time at room temperature.[39] In essence, it is likely that a similar process was described by these authors, but the absence of thermal treatment within their study drastically limited the extent of polymerization. Based on the results presented therein and the conclusions presented by Cathala and co-workers, a mechanism involving reactions between phenols and benzylic carbons seems most probable (Scheme 1). Nevertheless, somewhat perplexing is the fact that the hydroxyl content remains essentially stable after some point while $M_w$ keeps increasing, which suggests that other mechanisms might also be involved.

**Enhanced Adhesion Properties of Polymerized SKL.** SKL dissolves readily in aqueous sodium hydroxide solutions at a pH above 11, allowing for the easy preparation of

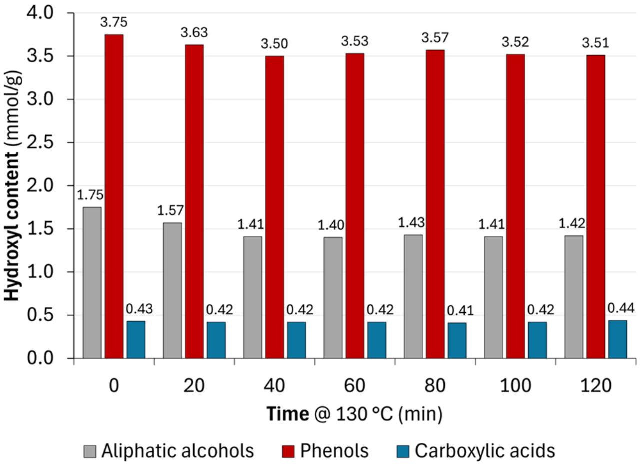


**Figure 6.** Histogram of the hydroxyl content of PSKL in an aqueous buffer at pH = 2 as determined by $^{31}$P NMR against the heating time at 130 °C.

concentrated solutions with 40% solids content.[40] When hard maple veneers were bonded at 130−150 °C with such alkaline solutions of SKL or PSKL and evaluated by using an automated bond evaluation system (ABES), it was found that solutions of PSKL with higher $M_w$ provide better adhesive properties than solutions of untreated SKL (Figure 7). Although the shear strength resulting from hot pressing hard maple veneers with PSKL solutions was significantly better than with untreated SKL solutions, it still fell short of the strength provided by industrial-strength wood adhesives. As such, they cannot be expected to serve as a standalone replacement. However, blends of PSKL solutions and PF also demonstrated better adhesive properties than blends of PF with untreated SKL solutions ($M_w$ = 8160 g/mol). At a $M_w$ of 1,11,000 g/mol and a substitution ratio of 30% (w/w, solids basis), the shear strength of these blends was nearly as high as that of PF alone at all press temperatures tested (Figure 8).

To establish the viability of blends of PSKL solutions and PF as wood adhesives, 24″ × 24″ plywood panels (1/8″ Douglas fir veneers, 3-ply) were produced using conditions mimicking those used by the manufacturing industry (2 panels per press opening, pressed at 146 °C for 255 s). Two commercially available PF resins (PF1 and PF2) were used in separate trials. The rates of wood failure of the panels were then measured under vacuum-pressure water soak treatment, following CSA O151:17 and ASTM D5266-13 standards (Figure 9).

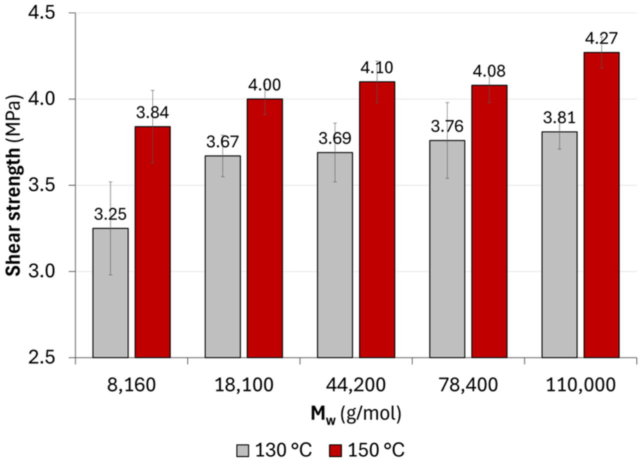


**Figure 7.** Shear strength of hard maple veneers bonded with alkaline solutions of SKL (40% solids content) pressed at 130−150 °C for 90 s using an automated bond evaluation system (ABES). Error bars represent the standard deviation of the mean.

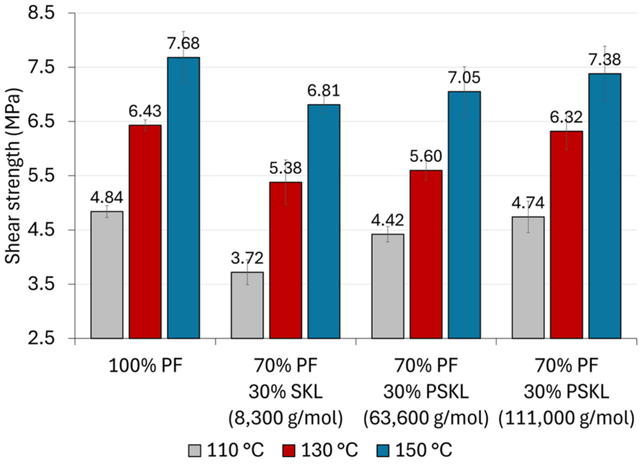
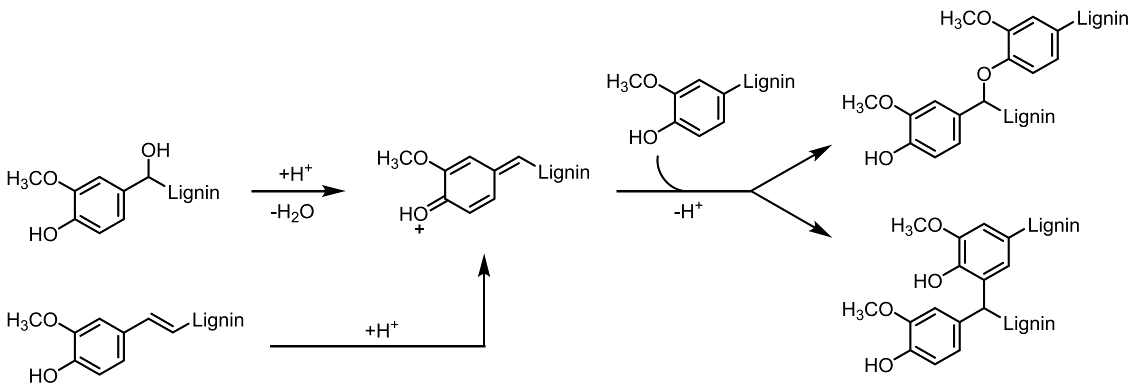


**Figure 8.** Shear strength of hard maple veneers bonded by 70:30 blends of PF and alkaline solutions of softwood kraft lignins pressed at 110−150 °C for 90 s using an automated bond evaluation system (ABES). Error bars represent the standard deviation of the mean.

In the first trial, replacing 20% of PF1 with a solution of untreated SKL resulted in wood failure values that were inferior to the control, while substitution with solutions of PSKL ($M_w$ = 51,000 and 71,000 g/mol) produced superior

**Scheme 1. Plausible Acid-Catalyzed Reactions Underlying the Thermal Polymerization of Softwood Kraft Lignin**



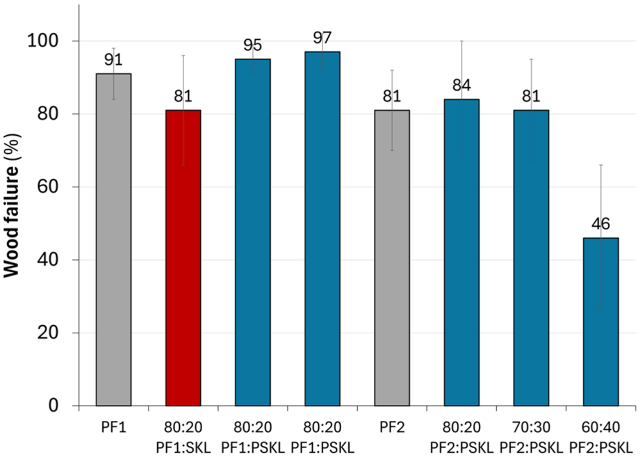


**Figure 9.** Wood failure values of the 3-ply softwood plywood panels bonded with PF and blends of PF with either SKL or PSKL. Error bars represent the standard deviation of the mean.

wood failure values compared to the control. These results confirm the enhanced adhesion properties of PSKL in lignin-PF blends compared to untreated SKL. In the second trial, replacing 20−30% of PF2 with solutions of PSKL ($M_w$ = 48,000 g/mol) led to virtually unchanged wood failure values (81−84%), but at a 40% substitution ratio the wood failure values fell drastically to an unacceptable rate (46%). This confirmed that up to 30% of the PF resin used in the manufacture of plywood can be substituted with alkaline solutions of PSKL.

## CONCLUSIONS

Softwood kraft lignin was shown to undergo thermal step-growth polymerization both in the solid state and in aqueous suspensions. This simple method rapidly generates products with a $M_w$ at least 40 times greater than the untreated kraft lignin. Heating above the glass transition temperature of the lignin was found critical to reach fast polymerization rates, which can be achieved at relatively low temperatures by leveraging the plasticizing effect of water. The adhesion properties of the polymerized kraft lignins were shown to be significantly enhanced using an automated bond evaluation system, which was confirmed in plywood panels. This simple and fast polymerization method, directly applicable to the slightly acidic wet kraft lignin cakes produced industrially by established processes, should pave the way for the utilization of kraft lignin in sustainable applications, where lignins of high molar mass are desired. The method should be especially suitable for the preparation of performant biosourced materials such as composites, thermosetting resin, and fibers.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.5c00746.

> Additional information regarding size exclusion chromatograms, $^{31}$P NMR spectra, preparation of lignin-based adhesives, and conditions for plywood manufacture (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

SKL, softwood kraft lignin; PSKL, polymerized softwood kraft lignin; PF, phenol-formaldehyde; SEC, size-exclusion chromatography; RI, refractive index; MALS, multiangle light scattering; IV, intrinsic viscosity; NMR, nuclear magnetic resonance; DSC, differential scanning calorimetry

## REFERENCES

(1) Dessbesell, L.; Paleologou, M.; Leitch, M.; Pulkki, R.; Xu, C. C. Global Lignin Supply Overview and Kraft Lignin Potential as an Alternative for Petroleum-Based Polymers. *Renewable Sustainable Energy Rev.* **2020**, *123*, No. 109768.

(2) Ang, A. F.; Ashaari, Z.; Lee, S. H.; Tahir, P. M.; Halis, R. Lignin-Based Copolymer Adhesives for Composite Wood Panels−A Review. *Int. J. Adhes. Adhes.* **2019**, *95*, No. 102408.

(3) Kumar, C.; Leggate, W. An Overview of Bio-Adhesives for Engineered Wood Products. *Int. J. Adhes. Adhes.* **2022**, *118*, No. 103187.

(4) Balakshin, M. Y.; Capanema, E. A.; Sulaeva, I.; Schlee, P.; Huang, Z.; Feng, M.; Borghei, M.; Rojas, O. J.; Potthast, A.; Rosenau, T. New Opportunities in the Valorization of Technical Lignins. *ChemSusChem* **2021**, *14* (4), 1016−1036.

(5) Bushi, L.; Meil, J.; Finlayson, G.; O'Connor, J. *A Cradle-to-Gate Life Cycle Assessment of North American Wood Product Resin Systems*; Athena Sustainable Materials Institute, 2022.

(6) Wilson, J. B. Life-Cycle Inventory of Formaldehyde-Based Resins Used in Wood Composites in Terms of Resources, Emissions, Energy and Carbon. *Wood Fiber Sci.* **2010**, *1*, 125−143.

(7) Moretti, C.; Corona, B.; Hoefnagels, R.; Vural-Gürsel, I.; Gosselink, R.; Junginger, M. Review of Life Cycle Assessments of Lignin and Derived Products: Lessons Learned. *Sci. Total Environ.* **2021**, *770*, No. 144656.

(8) *IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxypropan-2-ol*; International Agency for Research on Cancer, 2006; pp 86−99.

(9) Gigli, M.; Crestini, C. Fractionation of Industrial Lignins: Opportunities and Challenges. *Green Chem.* **2020**, *22* (15), 4722−4746.

(10) Xu, J.; Li, C.; Dai, L.; Xu, C.; Zhong, Y.; Yu, F.; Si, C. Biomass Fractionation and Lignin Fractionation towards Lignin Valorization. *ChemSusChem* **2020**, *13* (17), 4284−4295.

(11) Solt, P.; Jääskeläinen, A.-S.; Lingenfelter, P.; Konnerth, J.; van Herwijnen, H. W. G. Impact of Molecular Weight of Kraft Lignin on Adhesive Performance of Lignin-Based Phenol-Formaldehyde Resins. *For. Prod. J.* **2018**, *68* (4), 365−371.

(12) Jin, J.; Ding, J.; Klett, A.; Thies, M. C.; Ogale, A. A. Carbon Fibers Derived from Fractionated−Solvated Lignin Precursors for Enhanced Mechanical Performance. *ACS Sustainable Chem. Eng.* **2018**, *6* (11), 14135−14142.

(13) Saito, T.; Brown, R. H.; Hunt, M. A.; Pickel, D. L.; Pickel, J. M.; Messman, J. M.; Baker, F. S.; Keller, M.; Naskar, A. K. Turning Renewable Resources into Value-Added Polymer: Development of Lignin-Based Thermoplastic. *Green Chem.* **2012**, *14* (12), 3295−3303.

(14) Wang, Y.-Y.; Wyman, C. E.; Cai, C. M.; Ragauskas, A. J. Lignin-Based Polyurethanes from Unmodified Kraft Lignin Fractionated by Sequential Precipitation. *ACS Appl. Polym. Mater.* **2019**, *1* (7), 1672−1679.

(15) Sadeghifar, H.; Ragauskas, A. Perspective on Technical Lignin Fractionation. *ACS Sustainable Chem. Eng.* **2020**, *8* (22), 8086−8101.

(16) Rodrigues, J. S.; Lima, V.; Araújo, L. C. P.; Botaro, V. R. Lignin Fractionation Methods: Can Lignin Fractions Be Separated in a True Industrial Process? *Ind. Eng. Chem. Res.* **2021**, *60* (30), 10863−10881.

(17) Funaoka, M.; Shibata, M.; Abe, I. Structure and Depolymerization of Acid-Condensed Lignin. *Holzforschung* **1990**, *44* (5), 357−366.

(18) Yasuda, S.; Terashima, N.; Hamanaka, A. Chemical Structures of Sulfuric Acid Lignin, 6: Physical and Chemical Properties of Sulfuric Acid Lignin. *Mokuzai Gakkaishi* **1983**, *29*, 11.

(19) Agustin, M. B.; de Carvalho, D. M.; Lahtinen, M. H.; Hilden, K.; Lundell, T.; Mikkonen, K. S. Laccase as a Tool in Building Advanced Lignin-Based Materials. *ChemSusChem* **2021**, *14* (21), 4615−4635.

(20) Gouveia, S.; Fernández-Costas, C.; Sanromán, M. A.; Moldes, D. Polymerisation of Kraft Lignin from Black Liquors by Laccase from Myceliophthora Thermophila: Effect of Operational Conditions and Black Liquor Origin. *Bioresour. Technol.* **2013**, *131*, 288−294.

(21) Moya, R.; Saastamoinen, P.; Hernández, M.; Suurnäkki, A.; Arias, E.; Mattinen, M.-L. Reactivity of Bacterial and Fungal Laccases with Lignin under Alkaline Conditions. *Bioresour. Technol.* **2011**, *102* (21), 10006−10012.

(22) Cui, C.; Sadeghifar, H.; Sen, S.; Argyropoulos, D. S. Toward Thermoplastic Lignin Polymers; Part II: Thermal & Polymer Characteristics of Kraft Lignin & Derivatives. *BioResources* **2012**, *8* (1), 864−886.

(23) Rönnols, J.; Schweinebarth, H.; Jacobs, A.; Stevanic, J. S.; Olsson, A.-M.; Reimann, A.; Aldaeus, F. Structural Changes in Softwood Kraft Lignin during Nonoxidative Thermal Treatment. *Nord. Pulp Pap. Res. J.* **2015**, *30* (4), 550−561.

(24) Kouisni, L.; Holt-Hindle, P.; Maki, K.; Paleologou, M. The Lignoforce System: A New Process for the Production of High-Quality Lignin from Black Liquor. *J. Sci. Technol. For. Prod. Processes* **2012**, *2* (4), 6−10.

(25) Kouisni, L.; Gagné, A.; Maki, K.; Holt-Hindle, P.; Paleologou, M. LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization. *ACS Sustainable Chem. Eng.* **2016**, *4* (10), 5152−5159.

(26) Zinovyev, G.; Sulaeva, I.; Podzimek, S.; Rössner, D.; Kilpeläinen, I.; Sumerskii, I.; Rosenau, T.; Potthast, A. Getting Closer to Absolute Molar Masses of Technical Lignins. *ChemSusChem* **2018**, *11* (18), 3259−3268.

(27) Araneda, J. F.; Burton, I. W.; Paleologou, M.; Riegel, S. D.; Leclerc, M. C. Analysis of Lignins Using 31P Benchtop NMR Spectroscopy: Quantitative Assessment of Substructures and Comparison to High-Field NMR. *Can. J. Chem.* **2022**, *100* (11), 799−808.

(28) Korntner, P.; Sumerskii, I.; Bacher, M.; Rosenau, T.; Potthast, A. Characterization of Technical Lignins by NMR Spectroscopy: Optimization of Functional Group Analysis by 31P NMR Spectroscopy. *Holzforschung* **2015**, *69* (6), 807−814.

(29) Argyropoulos, D. S.; Berry, R. M.; Bolker, H. I. Polymerization beyond the Gel Point. I. The Molecular Weight of Sol as a Function of the Extent of Reaction. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25* (6), 1191−1202.

(30) Argyropoulos, D. S.; Berry, R. M.; Bolker, H. I. Polymerization beyond the Gel Point, 2. A Study of the Soluble Fraction as a Function of the Extent of Reaction. *Macromol. Chem.* **1987**, *188* (8), 1985−1992.

(31) Argyropoulos, D. S.; Berry, R. M.; Bolker, H. I. Species Distribution within the Soluble Phase beyond the Gel Point. *Macromolecules* **1987**, *20* (2), 357−361.

(32) Gaugler, E. C.; Radke, W.; Vogt, A. P.; Smith, D. A. Molar Mass Determination of Lignins and Characterization of Their Polymeric Structures by Multi-Detector Gel Permeation Chromatography. *J. Anal. Sci. Technol.* **2021**, *12* (1), 30.

(33) Dong, D.; Fricke, A. L. Intrinsic Viscosity and the Molecular Weight of Kraft Lignin. *Polymer* **1995**, *36* (10), 2075−2078.

(34) Wang, L.; Shigetomi, K.; Koda, K.; Gele, A.; Uraki, Y. A Branched Structure Provides Kraft Lignins a Denser Morphology and a High Molar Mass for a given Hydrodynamic Radius. *Holzforschung* **2020**, *74* (6), 551−558.

(35) Constant, S.; Wienk, H. L. J.; Frissen, A. E.; Peinder, P. de.; Boelens, R.; van Es, D. S.; Grisel, R. J. H.; Weckhuysen, B. M.; Huijgen, W. J. J.; Gosselink, R. J. A.; Bruijnincx, P. C. A. New Insights into the Structure and Composition of Technical Lignins: A Comparative Characterisation Study. *Green Chem.* **2016**, *18* (9), 2651−2665.

(36) Abdelaziz, O. Y.; Li, K.; Tunå, P.; Hulteberg, C. P. Continuous Catalytic Depolymerisation and Conversion of Industrial Kraft Lignin into Low-Molecular-Weight Aromatics. *Biomass Convers. Biorefin.* **2018**, *8* (2), 455−470.

(37) Beaudoin, D.; Langis-Barsetti, S.; Gagné, A.; Palus, E.; Inwood, J.; Konduri, M. K. R. Aqueous Ethanol Fractionation of Softwood and Hardwood Kraft Lignins: Impact on Purity and Properties. *J. Wood Chem. Technol.* **2024**, *44* (2), 133−144.

(38) Bouajila, J.; Dole, P.; Joly, C.; Limare, A. Some Laws of a Lignin Plasticization. *J. Appl. Polym. Sci.* **2006**, *102* (2), 1445−1451.

(39) Pouteau, C.; Cathala, B.; Dole, P.; Kurek, B.; Monties, B. Structural Modification of Kraft Lignin after Acid Treatment: Characterisation of the Apolar Extracts and Influence on the Antioxidant Properties in Polypropylene. *Ind. Crops Prod.* **2005**, *21* (1), 101−108.

(40) Melro, E.; Filipe, A.; Sousa, D.; Valente, A. J.; Romano, A.; Antunes, F. E.; Medronho, B. Dissolution of Kraft Lignin in Alkaline Solutions. *Int. J. Biol. Macromol.* **2020**, *148*, 688−695.