Supplementary Data and Supporting Information

Table S 1 Commercially available lignins and their sources.

<table>
<thead>
<tr>
<th>Lignin</th>
<th>Type</th>
<th>Source / Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>KL</td>
<td>Kraft (Indulin AT)</td>
<td>MeadWestvaco</td>
</tr>
<tr>
<td>KL (Sigma)</td>
<td>Kraft</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>KL-LS</td>
<td>Kraft, low sulfonate</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Alk-L</td>
<td>Lignin (Alkaline)</td>
<td>TCI America</td>
</tr>
<tr>
<td>Dealk-L</td>
<td>Lignin (Dealkaline)</td>
<td>TCI America</td>
</tr>
</tbody>
</table>

Table S 2 Hydroxyl group content of commercially available lignins as determined by $^{31}$P-NMR. Abbreviations are as defined in Table S 1.

<table>
<thead>
<tr>
<th>Lignin</th>
<th>OH content (mmole OH / g lignin)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aliphatic (149–146 ppm)</td>
<td>Phenolic (144 – 137.5 ppm)</td>
<td>Carboxylic (136 – 134 ppm)</td>
<td></td>
</tr>
<tr>
<td>KL</td>
<td>1.9</td>
<td>4.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>KL-GRD</td>
<td>1.9</td>
<td>4.0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>KL (Sigma)</td>
<td>2.0</td>
<td>4.0</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>KL-LS</td>
<td>1.7</td>
<td>2.7</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Alk-L</td>
<td>1.8</td>
<td>3.1</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Dealk-L</td>
<td>1.7</td>
<td>2.9</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

Table S 3 Particle size of Kraft lignin affecting form of KL-GDE resin. Values for % GDE indicates the amount of GDE required in formulation for resin to be in the liquid form.

<table>
<thead>
<tr>
<th>Lignin Type</th>
<th>Particle size</th>
<th>% Lignin</th>
<th>% GDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>KL</td>
<td>N.A</td>
<td>32</td>
<td>68</td>
</tr>
<tr>
<td>KL-COA</td>
<td>250 – 500 µm</td>
<td>29</td>
<td>71</td>
</tr>
<tr>
<td>KL-FINE</td>
<td>&lt;37 µm</td>
<td>37</td>
<td>63</td>
</tr>
<tr>
<td>KL-GRD</td>
<td>&lt;37 µm</td>
<td>54</td>
<td>46</td>
</tr>
<tr>
<td>KL-COA-GRD</td>
<td>&lt;37 µm</td>
<td>54</td>
<td>46</td>
</tr>
</tbody>
</table>
$\Delta H(140 \, ^\circ\text{C}, 2 \, \text{min}) = 26 \, \text{J/g}$

$\Delta H(140 \, ^\circ\text{C}, 5 \, \text{min}) = 5 \, \text{J/g}$

$\Delta H(140 \, ^\circ\text{C}, 8 \, \text{min}) < 0.5 \, \text{J/g}$
Fig. S 1 Characterization of KL-GDE resin before and after curing. a) DSC analysis of cured resin subjected to various curing duration and temperatures. 2 min time point was not taken for experiments at 145 °C and 150 °C. DSC traces for resin cured at 140 °C for 2, 5, and 8 min, with their respective residual enthalpy (ΔH) values. b) TGA analysis of uncured KL, GDE, KL-GDE resin, and cured KL-GDE resin. “Cured” samples refer to samples that have been pre-heated at 150 °C for 15 min. c) FTIR analysis of KL, GDE, KL-GDE before (uncured) and after curing (cured).
**Fig. S 2** Increasing amount of GDE to convert KL-GDE resin to liquid form. a) GDE amount indicated is in terms of weight percent of resin, with KL making up the remaining content. b) Effects of increasing GDE content on physical state of resin.

**Fig. S 3** Obtaining KL of varying particle size, and their impact on adhesion. a) KL was fractionated by particle size using sieves. b) Adhesion strength of lignin-crosslinker resin as measured in a three-ply plywood sample. In all cases, resin comprised of 65% lignin and 35% GDE. Data in panel b) are average values (15 test samples cut from 3 identically prepared plywood panels with each panel giving five test samples) ± one SD.
Fig. S 4 Molecular weight profiles of lignins used. Lignins were derivatized by acetyl bromide(1) prior to analysis via gel permeation chromatography (GPC). Abbreviations are as defined in Table S 1.
**Fig. S 5** Addition of diluents in lignin-GDE resin negatively impacts adhesion strength. GVL, gamma-valerolactone; PC, propylene carbonate; TA, triacetin. Data are average values (15 test pieces cut from 3 identically prepared plywood panels with each panel giving five test pieces) ± one SD.

**Fig. S 6** Initial attempts to improve adhesion strength of KL-LS-GDE resin. a) Improving reactivity of OH-containing model lignin with catalytic amount of triazabicyclodecene, TBD. b) Attempts at improving adhesion strength by increasing press temperature, prolonging press duration, or addition of catalyst did not result in improvement. Data in panel b) are average values (15 test pieces cut from 3 identically prepared plywood panels with each panel giving five test pieces) ± one SD.
Fig. S 7 Effects of the addition of water to KLLS-GDE resin. a) Aerial view of plywood panel made with KL-LS-GDE resin, which have weaker adhesion; b) aerial view of plywood panel made with KL-LS-GDE-H₂O resin, which have improved adhesion; c) magnification showing resin penetration in plywood; d) post-test specimen from plywood panel made with KLLS-GDE-H₂O resin, showing failure mode in wood rather than at the resin; e) cross-sectional view of d); f) magnification of e) showing resin penetration; g) cross-sectional view comparing thickness plywood panels made with KL-LS-GDE-H₂O and KL-LS-GDE resins.
Calibration curves for quantification of consumption of model lignin. Quantification of BzOH and BzSH were performed on GCMS while quantification of GOH and GSH were performed on LCMS. BzOH, benzyl alcohol; BzSH, benzyl mercaptan; GOH, guaiacol; and GSH, thiophenol.
Current ($/kg)  |  Projected¹ ($/kg)
--- | ---
Lignin | 4.07 – 4.85²  | 0.45³
GDE⁴ | 1.10  | 0.88⁵
Resin (Lignin-GDE-water) | 1.72 – 1.98  | 0.43
Other cost (100% of raw material) | 1.72 – 1.98  | 0.43
Breakeven cost of production | 3.44 – 3.96  | 0.86
Profit margin (10%) | 0.34 – 0.40  | 0.08
**Sale price** | **3.78 – 4.36**  | **0.94**

Phenol-formaldehyde resin | 1 – 2  | 1 – 2⁸

**Chart S 1 Economics of plywood production**

1, Net present value, not accounting for inflation.

2, Quote from Meadwestvaco, for ton scale orders

3, $0.45/kg is a profit-generating sale price of lignin based on two possible scenarios for source of lignin – (i) from Kraft pulping process; and (ii) from lignocellulose fractionation for biofuel fuel production. In scenario (i) the break-even cost is $0.26. It is calculated as the sum of lignin’s inherent value as a fuel at $0.18/kg,(2) as well as cost of isolation of Kraft lignin from the lignin-rich liquor, at $0.04-0.08/kg.(3) In scenario two, the breakeven sale price of lignin for lignocellulosic-derived biofuel production to be economical is estimated to be $0.09/kg.(4)

4, Quote from Inner Mongolia Set Sail Chem, CN, for 1ton/month orders

5, Assuming 20% decline in price upon scale up

6, Resin formulation is 33% lignin, 33% GDE, and 33% water, assuming cost of water is negligible compared to lignin and GDE

7, Assumption that raw materials comprise 50% of overall cost of producing resin is reasonable as the production of resin involves mechanical ball milling of lignin, repacking of ball milled lignin, and shipment of lignin and crosslinker to wood product plants. This also assumes that GDE may be shipped directly from suppliers, without need for logistical consideration in resin production plant. Mixing of solid and liquid components are typically done onsite right before use

8, Cost of phenol-formaldehyde resin have stayed constant, and there is no reason to predict a major fluctuation in price.
Materials and Methods

Materials

Lignin sources and preparation

Kraft lignin (KL, Indulin AT, Meadwestvaco; and Sigma-Aldrich) low-sulfonate Kraft lignin (LS, Sigma), alkaline (alk, TCI) and dealkaline lignin (dealk, TCI) were subject to ball mill homogenization (2 min, 30 Hz, see below) prior to use. In some instances, lignins were used directly as received. In all instances, no chemical treatment or fractionation were performed on lignins prior to use.

Other Chemicals

Glycerol diglycidyl ether (GDE, technical grade, Sigma-Aldrich), Ethylene glycol diglycidyl ether (EGDE, TCI), sodium carbonate (EMD Chemicals) 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Sigma-Aldrich), cyclohexanol (Alfa Aesar), chromium(III) acetylacetonate (Strem Chemicals), deuterated chloroform (Cambridge Isotope Laboratories), pyridine (EMD Chemicals), acetic anhydride (EMD Chemicals), N-methyimidazole (Acros Organics), p-dioxane (JT Baker), chloroform (Fisher), acetyl bromide (Acros), acetic acid (Fisher), tetrahydrofuran (THF, HPLC grade, Fisher), ethyl acetate (EtOAc, HPLC grade, Fisher), methanol (MeOH, HPLC grade, Fisher), benzyl alcohol (BzOH, Acros), benzyl mercaptan (BzSH, Acros), Guaiacol (GOH, Santa Cruz Biotechnology Inc.), and 2-methoxythiophenol (GSH, Acros) were used as received without further purification or fractionation unless otherwise stated.

Commercially available plywood and household wood glue

Commercial wood adhesives used were Elmer’s wood glue (part number) and titebond II (part number). Commercial plywood samples were obtained from Aura Hardwood, San Jose, CA.

Veneer sheets (plies) for plywood

Veneer: Birch veneer (thickness = 1.6 mm) was purchased from Roarockit Skateboard Company, and douglas fir veneer (thickness = 0.25 mm) was a kindly donated by Plum Creek Timber Company Inc.

Methods

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on a TA instruments Q500 thermogravimetric analyzer using a heating rate of 20 °C/min from 20 to 800 °C, with balance and sample purge rates set to 20 mL/min or 10 mL/min or nitrogen.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 differential scanning calorimeter using a heating and cooling rate of 10 °C/min and nitrogen flow rate of 50 mL/min. The samples were heated from 0 to 190 °C, cooled to 0 °C, and then heated to 190 °C again.

Attenuated total reflectance (ATR) Fourier transform infrared (FT-IR)

Attenuated total reflectance (ATR) Fourier transform Infrared (FT-IR) spectroscopic analysis was carried out on a Thermo scientific Nicolet iS50 FT-IR spectrometer equipped with is50 ATR.

Plywood manufacturing.
Plywood manufacturing: Resin was prepared by mixing lignin and GDE at room temperature right before application to veneer sheets. For preparation of GRD-GDE-\(\text{H}_2\text{O}\), KL-GRD and DI water were combined to form a well-dispersed suspension before the addition of GDE. For the preparation of resin with KL-LS, Alk-L, and Dealk-L, lignin and GDE were combined to form a well-mixed paste before the addition of water (or sodium bicarbonate in the case of Dealk-L). Note: reversing the order of addition would result in the formation of clumps and longer mixing time to achieve smooth consistency for application onto veneer. All lignins used were subject to ball mill homogenization (2 min, 30 Hz) unless otherwise stated.

The resulting resin was spread evenly on each interface between two veneer layers (102x152 mm; 4x6 inch). Resin loading was kept constant at 6.4–7.2 g per interface (equivalent to 0.25–0.30 g / interface•in\(^2\), or 0.41–0.46 kg / interface•m\(^2\)). However, it should be noted that in many instances a portion of the resin is lost outside of the panel interface during the pressing process. Therefore, actual resin content between the panels is not equal between all samples. The three-ply specimens were assembled with the fiber direction of the center veneer perpendicular to the two out-facing veneers. The specimen was kept on the hot-presser (PHI-Tulip Model 225H-X6-13, USA) at 150 °C (302 F) for 1 minute at 0.3 MPa and then further 14 minutes at 1.4 MPa, or 0.1 MPa and further 14 minutes at 0.7 MPa. Once removed from the hot-press, plywood samples were cooled at ambient temperature under a constant weight of 20 kg at room temperature, for 30 mins. The application of commercial wood adhesives to plywood assembly was performed in accordance with the adhesive manufacturer’s instructions.

Testing of plywood

Interfacial shear strength (ultimate shear stress, T) of three-ply plywood is a direct measurement of the adhesion strength of the resin, and is determined in accordance to ASTM D906.(5) Plywood panels were cut into test specimens of dimensions specified in ASTM D906 using a table saw. Simulations of interfacial shear strength in a moist (wet condition) environment were conducted in accordance to ASTM 4690, with samples soaked in deionized water for 48 hours.(6) The testing of samples was conducted with the MTS Criterion model 43 with a 30 kN model LPS.304 load cell.

Unless otherwise stated, error bar on charts represents mean and standard deviation from four identically prepared plywood panels with five test specimens from each panel.

Ball mill homogenization

Ball mill homogenization was carried out using a Retsch (MM 400) mix miller. Lignin (~15 g) was packed into one half of a 50 mL screw top stainless steel grinding jar followed by the addition of a 25 mm stainless steel ball. The jar was secured and further sealed with Teflon tape to prevent pulverized lignin from escaping the jar during homogenization. The equipment was set to homogenize at 30 Hz for 2 min.

Phosphorus-31 Nuclear Magnetic Resonance

\(^{31}\text{P}\) nuclear magnetic resonance (NMR) spectra were obtained on a Varian mercury plus spectrometer, equipped with a four-nucleus switchable and pulse field gradient probe operating at 162 MHz, using methods described in Chung et al.(7) Experiments were recorded at 25 °C in CDCl\(_3\). Chemical shifts were calibrated from the sharp \(^{31}\text{P}\) NMR signal at 132.2 ppm arising from the reaction product between residual water and TMDP. Spectra were quantitative with proton broad bands decoupling only during acquisition time. Cyclohexanol was used as an internal standard for the quantitative evaluation of the lignin hydroxyl group content. \(^{31}\text{P}\) NMR spectra were obtained with a 100 kHz spectral width, 128,000 data points, 8 s relaxation delay,
0.64 s acquisition time, 8 μs for a 55.4° pulse, and 1 Hz line broadening using 128 scans. Content of different hydroxyl groups were obtained by the integration values of the spectral regions arising from aliphatic hydroxyls (149–146 ppm), phenolic hydroxyls (144–137.5 ppm), and carboxyls (136–134 ppm) relative to the internal standard (145.5–144.5 ppm).

**Phosphorus-31 Nuclear Magnetic Resonance**

$^{31}$P NMR spectra and phosphitylation of lignin were performed based on modification of the method described by Chung et al.(7) A solvent mixture composed of deuterated chloroform (CDCl$_3$) and pyridine (1.6/1.0, v/v) was prepared and dried over molecular sieves overnight prior to use. This solution was used for the preparation of relaxation reagent solution (RR, chromium(III) acetylacetonate, 5.0 mg/mL) and the internal standard solution (IS, cyclohexanol, 10.0 mg/mL). A total of 15 mg of oven-dried (80 °C, overnight) sample was dissolved in a CDCl$_3$-pyridine solvent (400 μL) followed by the addition of RR (50 μL) and IS (50 μL). The resulting solution was left to stand for 1 h to ensure total dissolution. TMDP (50 μL) was then added and let stand for at least a day to ensure complete derivatization prior to $^{31}$P NMR analysis.

**Molecular weight profiling of lignin samples**

For Molecular weight profiling, samples were derivatized via acetyl bromination(1) prior analysis. The Gel Permeation chromatography (GPC) system consisted of an Agilent 1260 HPLC system using a series of Jordi DVB size exclusion columns comprising of a guard column (500 Å) and two analytical columns (500 Å and $10^4$ Å, 7.8x300 mm). Eluting solvent was THF (1 mL/min) and column eluent was monitored by an Agilent 1260 diode array detector, at 280±4 nm. (Fig. S2) The system was calibrated using polystyrene standards from agilent (PS calibration kit SM2-10, supplemented with PL2012-1001, PL2012-0001, and PL2013-9001). Derivatized samples were dissolved in THF and filtered through a 0.22 μm PTFE membrane before injection into the GPC system.

**Reactions of lignin monomers with GDE.**

Reactions of lignin monomers with GDE were carried out at 1 mmole scale. 1 mmole of substrate (benzyl alcohol, benzyl mercaptan, guaiacol, or 2-methoxythiophenol) and 1 mmole of GDE (2 eq. epoxide) were combined in a 22 mL glass vial. In some instance, 0.1 mmole (10 mole %) TBD was also added to the mixture. This was followed by the addition of 1 mL THF to obtain a homogeneous mixture. THF was then removed *in vacuo* before the mixture was subject to 150 °C for 15 min in air, after which the reaction was left to cool at room temperature (rt). Once the reaction was cooled to rt, EtOAc (for reactions with BzOH and BzSH) or MeOH (for reactions with GOH and GSH) was added to extract unreacted starting materials. Starting material conversion was then analyzed by GC-MS (BzOH and BzH) or LC-MS analysis of extracts.

**Gas chromatography mass spectrometry (GC-MS) analysis**

Gas chromatography mass spectrometry (GC-MS) analysis was carried out on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 quadrupole mass spectrometer. Injections (2 μL) were made in splitless mode with the injection port temperature at 220 °C. Analytes were separated on an Agilent HP-5 column (30 m × 0.25 mm × 0.25 μm). The column oven was held at 65 °C for 2 minutes, ramped to 128 °C at 4 °C/minute, held at 128 °C for 1 min, ramped to 260 °C at 45 °C/minute, and held at 260 °C for 1 minute. Detector temperature was set at 250 °C. Solvent delay was set to 6.10 min, and analytes were detected by selected ion monitoring (SIM) mode for m/z values of 77, 79, 107, and 109 (BzOH), and 65, 91, and 124 (BzSH).
Liquid chromatography tandem to mass spectrometry (LC-MS)

Liquid chromatography tandem mass spectrometry (LC-MS) was performed on an Agilent 1260 HPLC, using a Gemini NX-C18 column (Phenomenex, 5 μm, 2 x 100 mm). Water and acetonitrile—both supplemented with 0.1% formic acid—were used as the mobile phase components, with a flow rate of 0.5 mL/min. The following 17-min gradient was used (percentages indicate acetonitrile concentration): 3% for 2 min; 3–97% over 4 min; 97% for 3 min; 93–3% over 1 min; 3% for 1 min, 3-97% over 1 min; 97% for 2 min; 97-3% over 1 min; and 3% for 2 min. Column eluent was monitored by an Agilent 1260 diode array detector followed by an Agilent 6520 Accurate-Mass Q-TOF mass spectrometer with an ESI source (parameters: mass range: 50-1200 m/z; drying gas: 350°C, 11 L/min; nebulizer: 35 psig; capillary: 3000 V; fragmentor: 150 V; skimmer: 65 V; octupole 1 RF Vpp: 750 V; 1000 ms per spectrum). Mass spectrometry data were collected in positive ion mode and analyzed using MassHunter Qualitative Analysis software (Agilent). Residual GOH and GSH content were calculated from the integrated peak area of UV (280±4 nm) to a standard curve. (Fig. S 8)

References


