Electronic Supplementary Material (ESI) for Green Chemistry.

A facile strategy to fabricate lignin-based thermoset alternative to formaldehyde-based wood adhesives

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Tensile properties.

The tensile properties of the lignin based thermoset samples were determined by CMT4304 Universal Testing Machine. Before testing, the samples had the approximate dimensions of 25 mm × 4mm × 0.2 mm. The toughness was obtained from the stress–strain curve and the total area under the stress–strain curve.

Physical and mechanical properties of the samples

The physical properties including density, moisture content, water absorption (WA) and thickness swelling (TS) were carried out according to the Chinese national standard GB/T 17657–2013. A size of 5 cm × 5 cm from each panel was cut for density, thickness swelling and water absorption test. The density was measured by taking the measurements of the length, width, thickness, and weight for each sample. Then, the volume was calculated. The moisture content value was taken from the average result of samples from each type of particleboard. Water absorption and thickness swelling were carried out simultaneously. Initially, the thickness and weight of each sample were recorded before immersing in water. After immersing for 24 h, the increase in thickness and weight of each sample were recorded.

The mechanical properties included modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond (IB) strength were carried out according to the Chinese Industrial Standard. Samples with a size of 200 mm × 50 mm x 7.5 mm were cut from each panel for MOR and MOE tests. The Instron Tensile Machine CMT4304 was used with a crosshead speed of 10 mm/min. Span of supporting beam was 120 mm and a load was applied at the center of the sample. Besides, samples with a size of 50 mm ×

50 mm x 7.5 mm were cut from each panel for IB test. The Instron Tensile Machine CMT4304 was used with a crosshead speed of 10 mm/min for IB test.

Formaldehyde emission by desiccator method

Formaldehyde emission from the produced particleboards was tested using desiccator method based on JIS A 1460: 2001. 300 ml of distilled water was filled into a glass crystalizing dish, which is centrally located at the bottom of the desiccator. Nine pieces of samples (50 mm width x 150 mm length x 12 mm thickness) having surface area approximately 1800 cm^2 were placed into a desiccator, right above the water-filled glass crystalizing dish. After 24 h, the water in the crystalizing dish was collected and the concentration of formaldehyde in the solution was measured by acetylacetone molecular absorption spectrometry.

^{31}P NMR

Quantitative ^{31}P NMR spectra of the lignin was acquired by a Bruker AVANCE 600 MHz spectrometer. A solvent mixture composed of anhydrous pyridine and deuterated chloroform in a 1.6:1 (v/v ratio) was prepared. Chromium (III) acetylacetonate (5.6 mg/mL) solution and HONB (9.23 mg/mL) solution were prepared by utilizing the above solvent mixture, respectively. An accurately weighed amount (40 mg) of a dried sample was then dissolved in 500 μL of above solvent mixture. Thereafter, HONB solution (200 μL) and chromium (III) acetylacetonate solution (50 μL) were added. Finally, 100 μL of phosphitylating reagent (TMDP) was added and then quickly transferred into NMR tube for subsequent analysis.

Gel permeation chromatography

Gel permeation chromatography (GPC) is equipped with Malvern Viscotek 3580 System, including Viscotek GPC2502 refractive detector, a GPC1007 pump, the columnswere T6000M and GeneralMixed Org 300 mm × 7.8 mm (CLM3009). Calibration curve was generated using monodispersed polystyrene (PS) as a standard THF was used as the eluent at a flow rate of 1 mL/min. All samples were filtered over a microfilter with a pore size of 0.22 μm (Nylon, Millex-HN13mm Syringes Filters, Millipore) with the sample concentration of 3 mg/mL.

Table S1. the solid content and viscosity of lignin-based thermoset

sample	[a]solid content (wt%)	viscosity (mPa·s)
LD (1:0.75)	25.3	72.4
LD (1:1)	27.9	52.2
LD (1:1.5)	32.6	43.8
LD (1:2)	36.7	31.9

[a] The solids content is calculated by dividing the mass of the reactant (lignin and D2000) by the total mass of the sample multiplied by 100%.

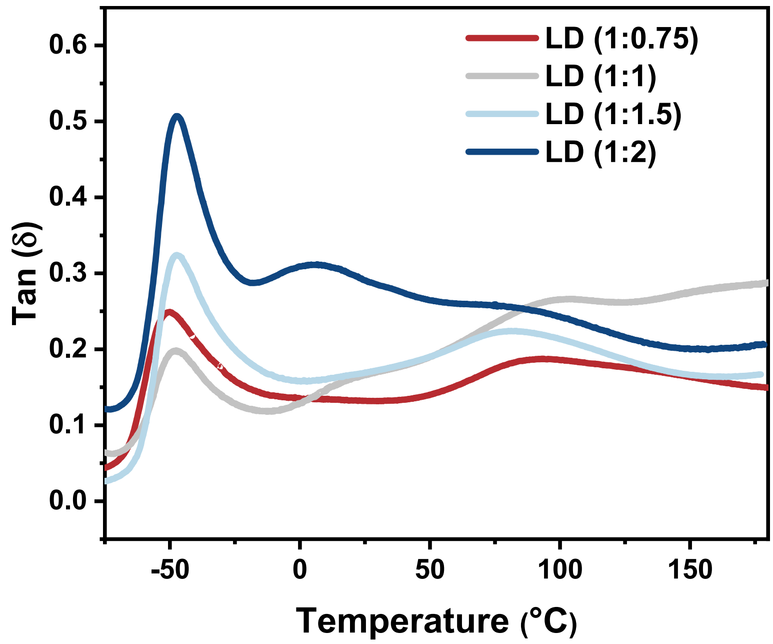

Figure S1. tan delta versus temperature for the thermosets with different lignin contents.

Table S2. Experimental D2000, Lignin and wood flours content

Sample	D2000 (g)	Lignin (g)	Wood flours (g)
LDW-1	12.0	9.0	18.0
LDW-2	9.0	9.0	18.0
LDW-3	6.0	9.0	18.0
LDW-4	3.0	9.0	18.0
LDW-5	1.5	9.0	18.0
LDW-6	0.0	9.0	18.0
LDW-7	3.0	9.0	18.0
LDW-8	3.0	5.4	21.6
LDW-9	3.0	1.7	25.3
LDW-10	3.0	0.0	27.0

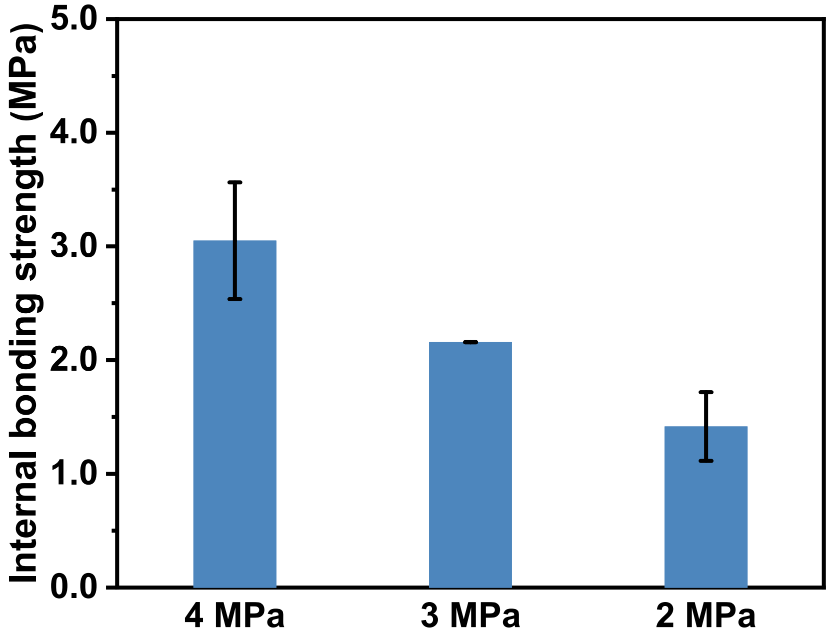

Figure S2. The internal bonding strength of particleboards with different pressures.

Table S3. Characterization of the Lignin Fractions.

Sample	Acid-insoluble lignin (%)	Acid-soluble lignin (%)	Glucan (%)	Xylan (%)
populus	87.80±0.22	3.11±0.02	4.86±0.38	0.03±0.05
corn stover	94.37±0.13	3.90±0.00	0.00±0.00	0.77±0.00
masson pine	70.50±1.30	1.51±0.03	2.40±0.25	0.32±0.00

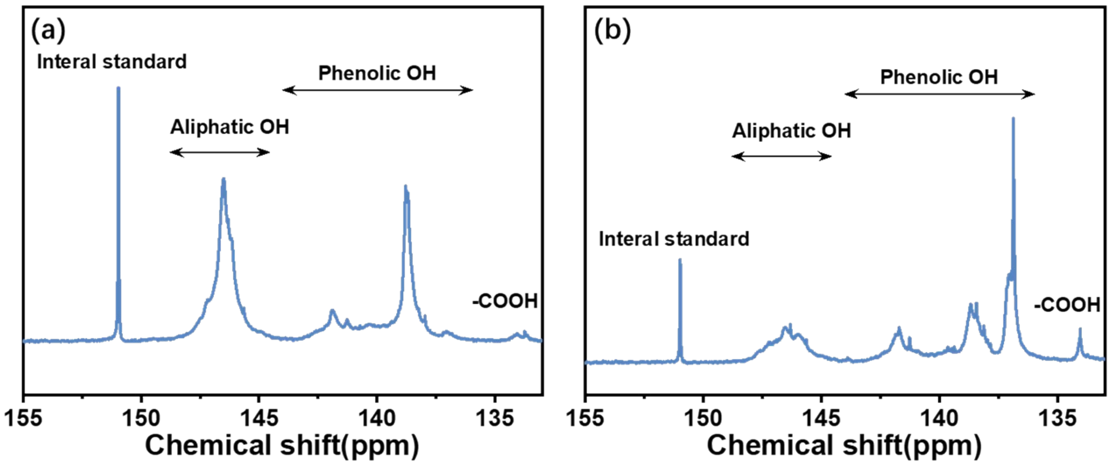

Figure S3. Quantitative 31P NMR spectra of SKL.

Table S4. Concentration of Aliphatic, Phenolic and Carboxylic OH of different lignin according to quantitative ^{31}P NMR

Sample	Aliphatic OH (mmol/g)	Phenolic OH	Carboxylic acid OH	Total OH (mmol/g)
populus	2.69	2.51	0.09	5.29
corn stover	2.68	6.89	0.43	10.00

Table S5. Molecular weight and polydispersity index (PDI) of lignin

Sample	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)
populus	11870	8669	1.369
corn stover	5295	3429	1.544

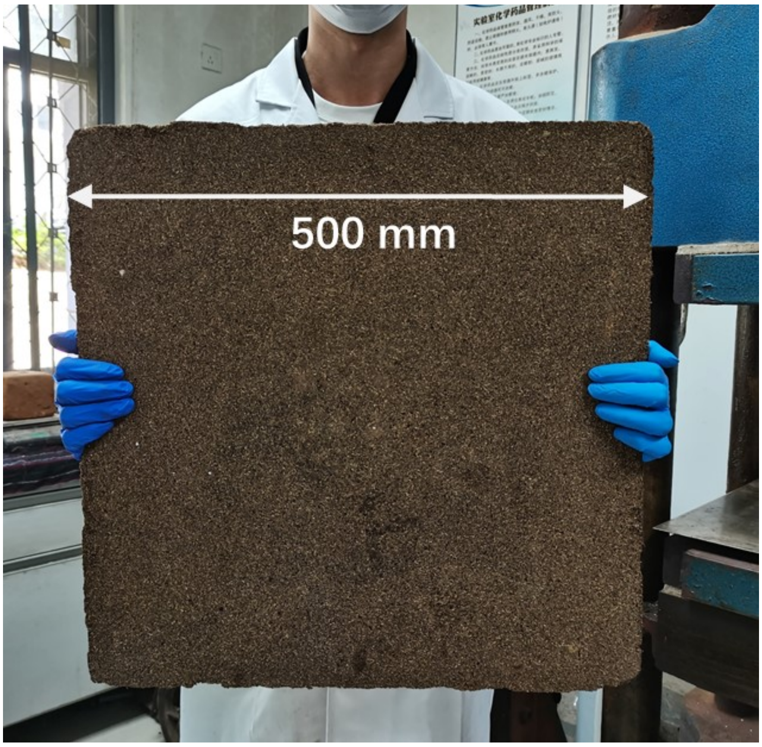

Figure S4. the size of the particleboards to 500 mm ×500 mm ×7.5 mm

Table S6. Physical properties of particleboards.

Density (kg/m^3)	^{a}TS (%)	^{b}WA (%)	^{c}IB (MPa)	^{d}MOR (MPa)	^{e}MOE (MPa)
830.73±2.62	13.46±2.89	68.42±4.34	1.42±0.24	16.74±1.22	1831.80±205.62

[a] the thickness swelling (TS); [b] the water absorption (WA) values; [c] the internal bonding (IB) strength; [d] the modulus of rupture (MOR), and [e] the modulus of elasticity (MOE)

Table S7. Water resistance and aging resistance of the particleboards.

	Initial sample	The samples soaked in water for 24 hours	The samples stored in the laboratory for 300 days
IB (MPa)	1.42±0.24	1.38±0.28	1.27±0.24

Table S8. Comparing the physical properties of particleboards with those of commercially available and under development wood adhesives

Sample	TS (%)	IB (MPa)	MOR (MPa)	MOE (MPa)
This work	13.46	1.42	16.74	1831.80
[a]UF	16.76	0.65	16.38	3504.53
[b]PF	14.75	0.74	19.81	3553.18
[c]LPF+PVA	11.41	0.46	17.41	2405.11
[d]PVAc+MDI	13.4	0.70	19.22	2581.95
[e]LPF+MDI	10.97	0.45	16.09	2482.46

[a] urea-formaldehyde; [b] phenol-formaldehyde; [c] lignin and polyvinyl alcohol; [d] polyvinyl acetate and 4, 4’-diphenylmethane diisocyanate, and [e] lignin and 4, 4’-diphenylmethane diisocyanate.