Supporting Information for

Mild-depolymerized lignin for reinforced polyvinyl alcohol wood adhesives

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1. Materials and chemicals

Lignin, separated from the Eucalyptus pre-hydrolysis liquor, was kindly provided by Jining Mingsheng New Material Co., Ltd., China. The above industrial lignin was used directly without any pretreatment such as drying and impurity removal to conform to the industrial application requirements of low energy consumption and simple process. PVA (hydrolysis degree: 87% – 89%) was purchased from Aladdin Co., Ltd (Shanghai, China). Sodium hydroxide (NaOH), potassium persulfate ($K_2S_2O_8$), glutaraldehyde (GA, 50 wt% aqueous solution), Methanol (CH_3OH) were purchased from Energy-Chemical Co., Ltd (Anhui, China).

2. Lignin depolymerization

The Depolymerization reaction of lignin was performed in a Parr reactor (100 mL). Typically, lignin (3 – 4.5% of the total solid mass in the reaction system), sodium hydroxide (0.9 g), and a methanol-water mixture with a volume ratio of 1:4 was added to the reactor. Under the stirring of a glass rotor at 800 rpm , the reactor was evacuated and flushed with N_2 three times to expel air. Next, the reactor was heated up to the target temperature (120 – 180 ^{o}C) and held at atmospheric pressure for 1 h without additional gas introduction. After the reaction, the Parr reactor was cooled and depressurized carefully.

3. Characterizations

Fourier transform infrared spectroscopy (FT-IR). FT-IR spectra of lignin were recorded using a Perkin-Elmer spectrophotometer. The spectra of powdered lignin supported by KBr pellets were recorded in the range of 400 to 4000 cm^{-1} with 32 scans averaged at 4.0 cm^{-1} resolution at room temperature.

Nuclear magnetic resonance (NMR). All NMR spectra were recorded on a Bruker Ascend-400 MHz spectrometer instrument (Bruker, Germany). Specifically, the structural characteristics of lignin samples were analyzed using 2D HSQC NMR and the amount and distribution of hydroxyl groups in lignin were determined by quantitative ^{31}P NMR. The spectra obtained from all tests were analyzed by TopSpin 4.0 software.

Gel permeation chromatography (GPC) analysis. To investigate the molecular weight (M_w and M_n) and polydispersity index (Đ) of the lignin samples after acetylation, gel permeation chromatography analysis was performed as previously described.[1]

Thermal Analysis. The thermal degradability of the samples was tested using TA Q500 thermal analyzer (TA, Inc., USA). Under a nitrogen atmosphere, the sample was heated from 30 °C to 800 °C at a rate of 10 °C min^{-1}. Differential Scanning Calorimetry (DSC). DSC on a DSC6000 apparatus (TA Instruments) by subjecting the resin adhesive to a hot-cold-heat cycle at 80 – 150 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere. The samples were heated to 300 °C at a rate of 10 °C min^{-1}.

Rheology. Place a quantified amount of adhesive into a beaker and their rheological behavior was followed using the HR 20 rheometer (TA Instruments Ltd). The storage modulus(G') and loss modulus (G'') of the adhesives were measured at an angular frequency (ω) of 10 rad s^{-1} and a constant strain (γ) of 12.5%.

Bonding Strength. The plywood test specimens were prepared by lapping two natural moso bamboo veneers, with a single veneer size of 9 cm (length) × 2 cm (width) × 0.25 cm (thickness), the final specimen overall size of 16 cm × 2 cm, and a lap joint area of 190 mm² – 200 mm². As shown in Figure S, the plywood was then hot pressed (70 °C, 0.5 MPa, 10 min). The hot-pressing process adopted a constant pressure of 0.5 MPa throughout the whole process; after the hot-pressing time was reached, the pressure was released immediately, and the plywood samples were taken out and naturally cooled to room temperature under ambient conditions (25 °C, 60% relative humidity). Three-layer plywood specimens (20 mm × 20 mm) were made following GB/T 17657-2022, and bonding strength was determined following GB/T 9846-2015.Tensile testing was performed on a 5000 N loadcell Instron 5965 machine at 24 mm initial gauge and 20 mm min^{-1} crosshead speed. For each result a minimum of five rectangular adhesives samples were tested to obtain the average bonding strength.

Scanning electron microscope (SEM). A scanning electron microscope (SEM, JEOL JSM-7800F) was used to analyze the surface and cross-sectional characteristics of adhesive samples. Before the SEM observation, the samples were sputtered with a thin layer of gold coating.

Volatile Organic Compound (VOCs) Content Test. In accordance with GB33372-2020 Limits of VOCs in adhesives for wood-based panels and furniture, the VOCs content of the adhesive was tested using the gravimetric method. A certain mass of adhesive sample (accurate to 0.001 g) was weighed and placed in a clean aluminum alloy container, which was then placed in a constant temperature oven set at (105 ± 2) ^{o}C for 3 hours of heat treatment. After cooling to room temperature in a desiccator, the residual mass of the sample was weighed. The VOCs content was calculated by the mass loss before and after heating, excluding the moisture content (tested separately by Karl Fischer method). The test was conducted with 3 parallel samples, and the average value was taken as the final VOCs content. The result was compared with the limit value specified in GB33372-2020 to evaluate the environmental friendliness of the adhesive.

Free Formaldehyde Emission Test. The free formaldehyde emission of the adhesive and bonded plywood was tested using the desiccator method specified in GB18583-2008 Limits of harmful substances in adhesives for interior decoration and finishing materials.

Solvent Resistance Test. An equal amount of solvent (e.g., methanol, ethyl acetate solution) was added to a beaker. Plywood samples were placed into the beaker, sealed with plastic wrap, and soaked for the same duration (5 parallel samples per group). After soaking, the samples were taken out and dried in a well-ventilated area, and their performance changes were tested by tensile test.

UV Aging Resistance Test. For plywood samples prepared with different depolymerization temperature gradients, long-term weathering tests were conducted in an ultraviolet accelerated weathering test chamber, respectively. A four-stage cyclic program was adopted, and the samples were subjected to 20 repeated cycles from Stage 1 to Stage 3. In Stage 1 (UV irradiation), the samples were exposed to UV radiation for 7.00 h at an irradiance of 0.76 $W \cdot m^{-2}$ with a black panel temperature of 55 ^{o}C, both front and rear UV lamps of the chamber being turned on. In Stage 2 (condensation), the samples were placed under a condensation environment at 50 °C for 4.00 h. In Stage 3 (water spray), the samples were sprayed with water for 1.00 h. In Stage 4 (holding), the chamber system was stabilized for 0.10 h before the next cycle.

Plywood Grade Test. Referring to the national standard GB/T 17657-2022 Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels, the plywood bonded with the prepared adhesive was subjected to comprehensive performance testing to determine its product grade. The standard categorizes plywood into three classes based on water resistance, with specific immersion-drying cycle protocols as follows: Class I (weather-resistant, for outdoor use): Specimens were initially immersed in boiling water for 4 h, followed by drying at (63 ± 3) °C for 20 h; subsequent re-immersion in boiling water for 4 h was conducted, and the cycle was completed by final drying at (63 ± 3) °C for 3 h; Class II (water-resistant, for humid indoor use): Specimens were immersed in (63 ± 3) °C hot water for 3 h, and subsequently dried at (63 ± 3) °C for 3 h to complete the test cycle; Class III (ordinary, for dry indoor use): Specimens were immersed in (35 ± 3) °C warm water for 2 h, followed by drying at (63 ± 3) °C for 3 h to finish the evaluation.

Solid Content Test. The solid content of the adhesive was determined in accordance with GB/T 2793-1995 Determination of non-volatile matter content of adhesives.

4. Oxidation mechanism of polyvinyl alcohol

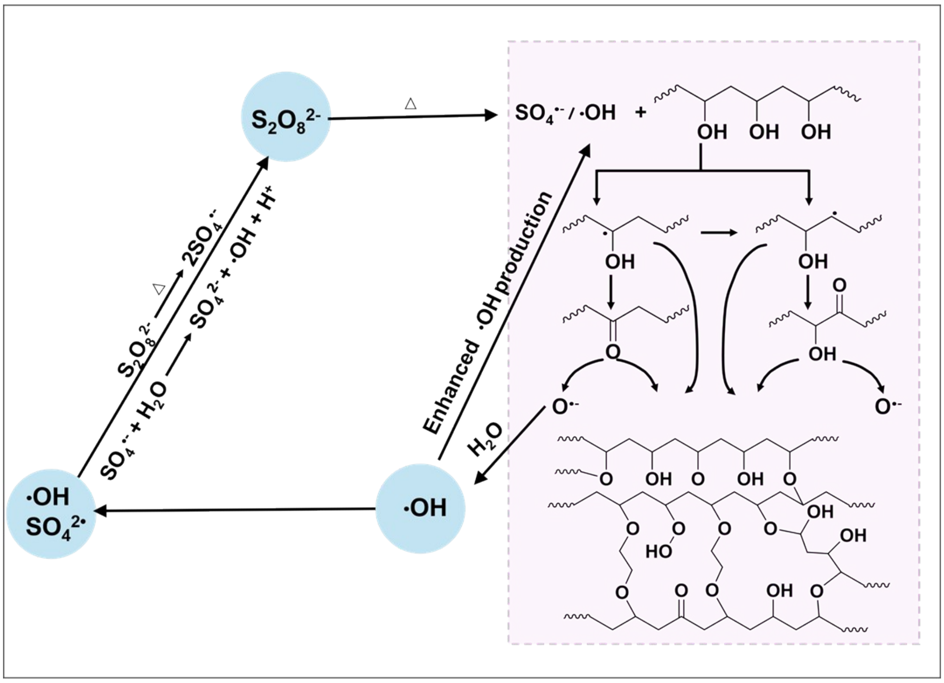

Figure S1. Oxidation mechanism of polyvinyl alcohol.[2]

5. GC-MS details of lignin oil

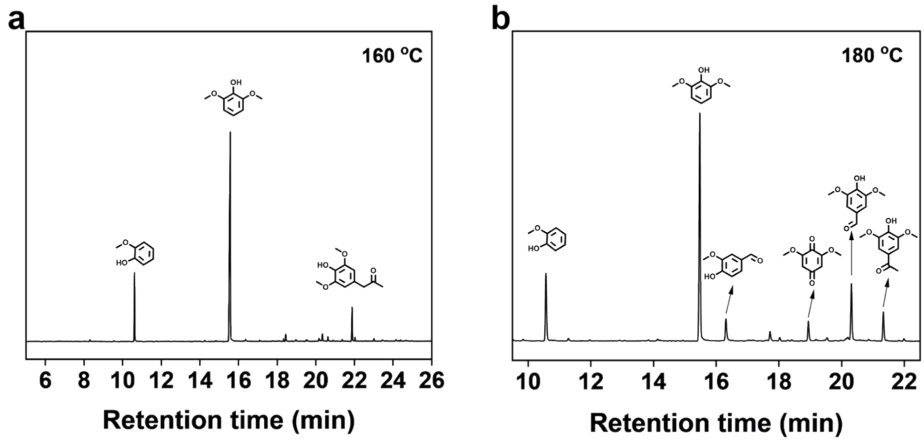

Figure S2. GC-MS spectra of lignin oil obtained at depolymerized temperatures of 160 °C (a) and 180 °C (b).

6. 2D-HSQC NMR details of lignin and lignin oil

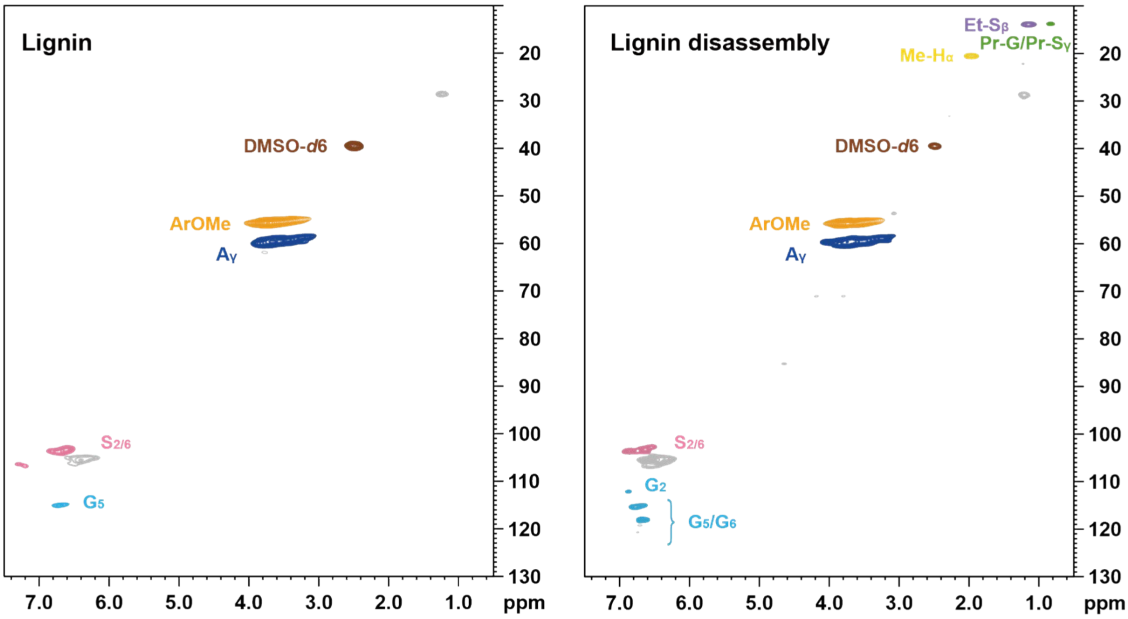

Figure S3. 2D HSQC NMR spectra of native lignin and lignin oil.

7. TG and DTG details of adhesive samples and lignin

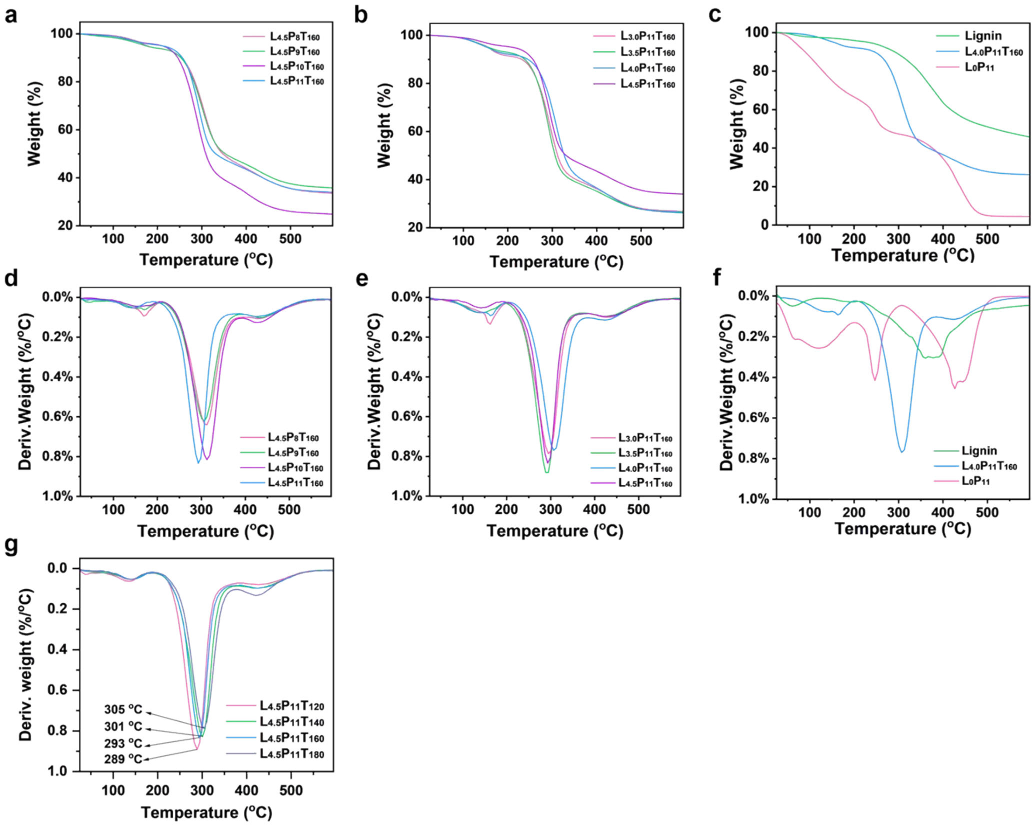

Figure S4. (a) Thermogravimetric curves of adhesives prepared with different PVA contents. (b) Thermogravimetric curves of adhesives prepared with different lignin contents. (c) Thermogravimetric curves of the lignin-containing raw material, the optimal-performance adhesive, and the blank adhesive (without lignin). (d)Differential thermogravimetric curves of adhesives prepared with different PVA contents. (e) Differential thermogravimetric curves of adhesives prepared with different lignin contents. (f) Differential thermogravimetric curves of the lignin-containing raw material, the optimal-performance adhesive, and the blank adhesive (without lignin). (g) Differential thermogravimetric curves of adhesives prepared at different temperatures.

8. DSC details of adhesive samples and lignin

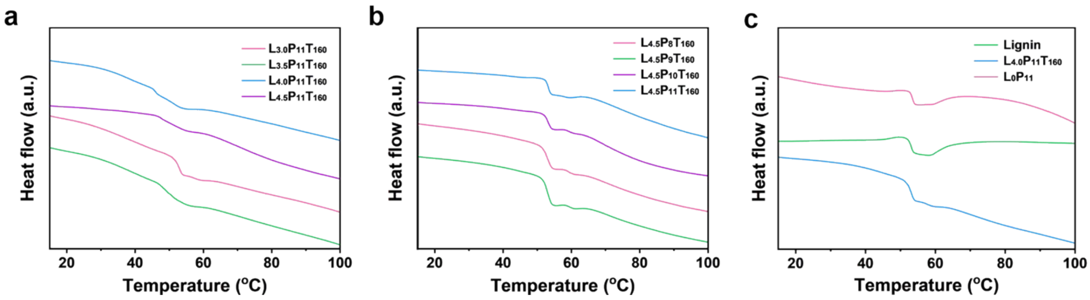

Figure S5. (a) DSC curves of adhesives prepared with different lignin contents. (b) DSC curves of adhesives prepared with different PVA contents. (c) DSC curves of the lignin-containing raw material, the optimal-performance adhesive, and the blank adhesive (without lignin).

9. FTIR details of adhesive samples and lignin

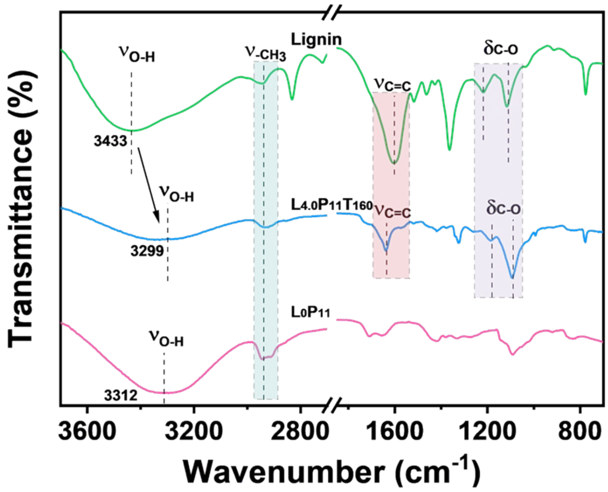

Figure S6. FT-IR curves of the lignin-containing raw material, the optimal-performance adhesive, and the blank adhesive (without lignin).

10. Rheological characterization of adhesive samples

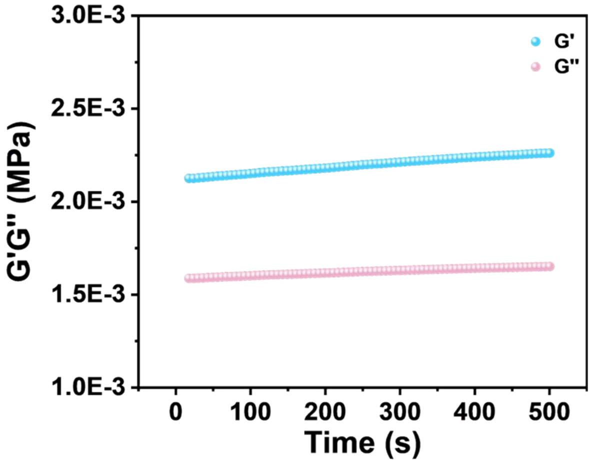

Figure S7. Time-dependent rheological characterization of adhesives.

11. Bonding properties of adhesives

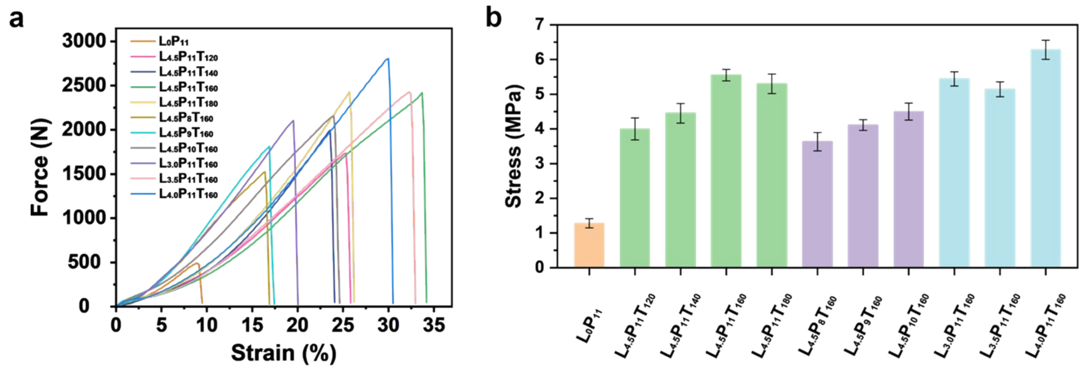

Figure S8. (a) Force-Strain curves of all plywood samples prepared with different adhesives. (b) Dry shear strength of all plywood samples prepared with different adhesives.

12. Direct preparation of adhesives from lignin

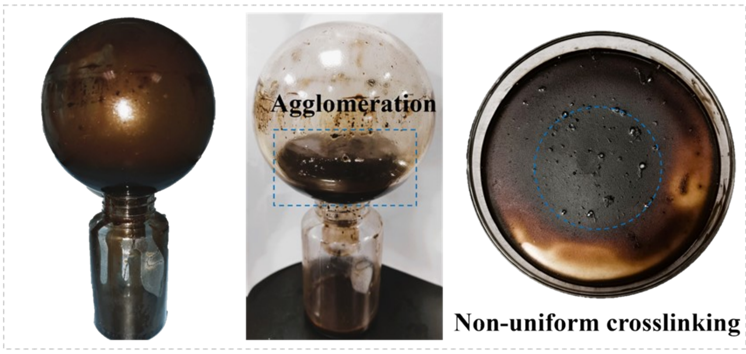

Figure S9. Images of adhesive prepared by incorporating undecomposed lignin into the system.

13. Curing conditions of plywood samples

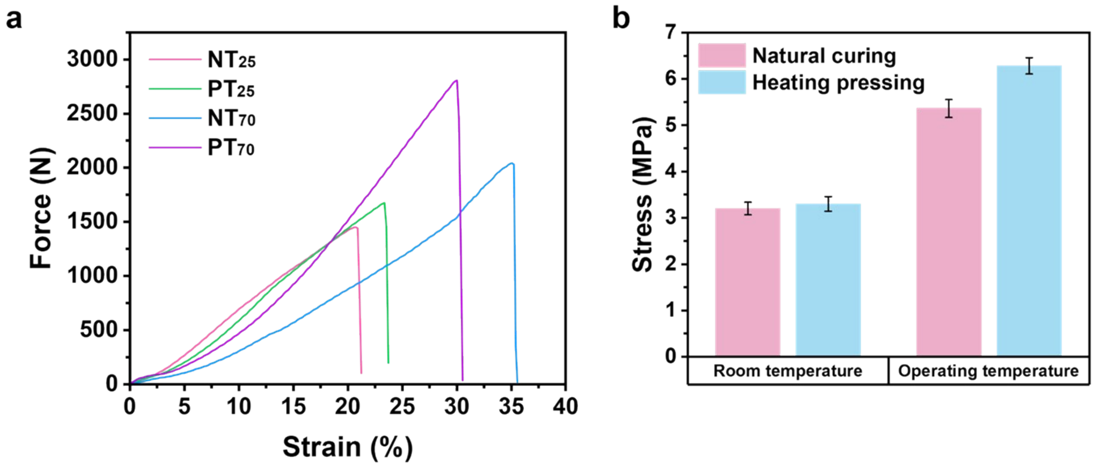

Figure S10. (a) Stress-strain curves of plywood prepared at room temperature without pressure, room temperature with pressure, working temperature (70 °C) without pressure, and working temperature (70 °C) with pressure. (b) Tensile shear strength curves of plywood prepared at room temperature without pressure, room temperature with pressure, working temperature (70 °C) without pressure, and working temperature (70 °C) with pressure.

14. Practical application scenarios for adhesives

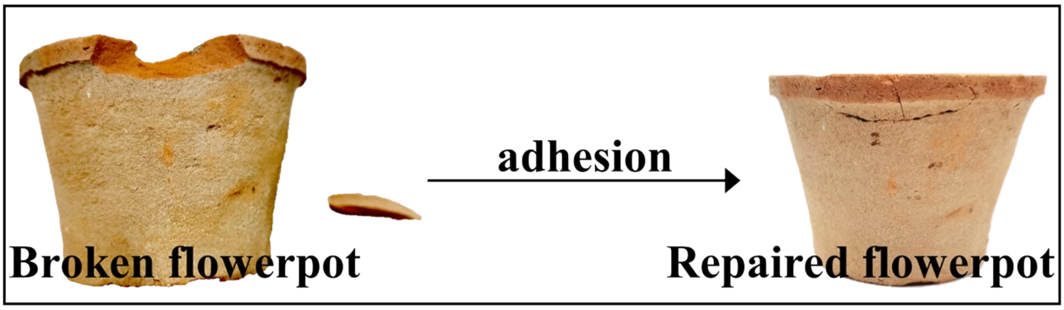

Figure S11. Schematic diagram of repairing flowerpot with adhesive under normal temperature and non-pressure condition.

Figure S12. Image of LPT adhesives-bonded wood sheets to support a dumbbell weighing 12 kg (185 cm of height) with a bonding area of 18.5 x 48.5 mm^2.

15. VOCs details of adhesives

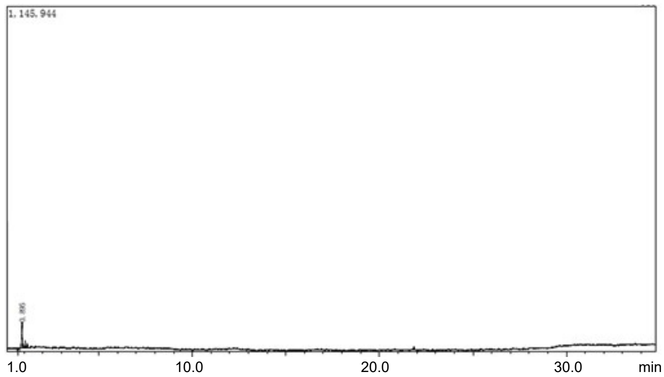

Figure S13. GC-MS total ion chromatogram (TIC) of VOCs emitted from LPT adhesives.

16. Screening of hot-pressing conditions for plywood

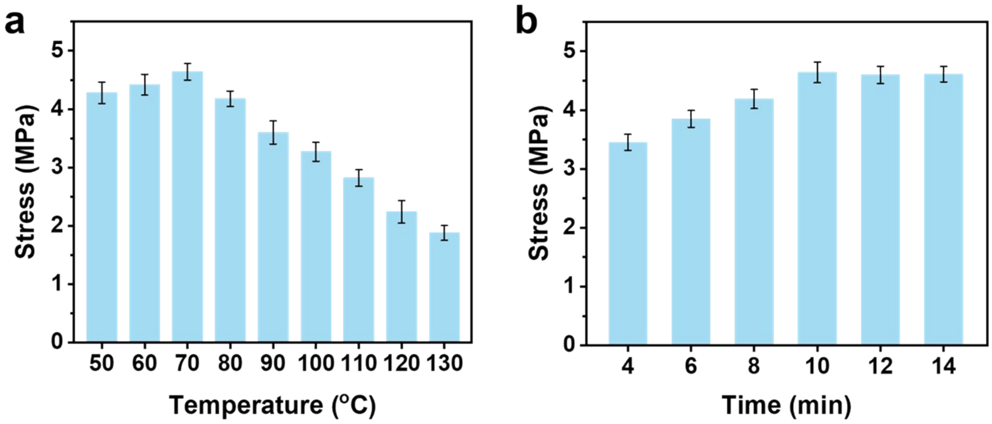

Figure S14. (a) Tensile shear strength of $L_{4.0}P_{11}T_{140}$-bonded plywood at different hot-pressing temperatures (0.5 MPa, 10 min). (b) Tensile shear strength of $L_{4.0}P_{11}T_{140}$-bonded plywood at different hot-pressing times (70 °C, 0.5 MPa).

17. ^{31}P NMR details of adhesive samples and lignin

Table S1. Hydroxyl group content and its distribution in lignin at different depolymerization temperatures

	Aliphatic hydroxyl (mmol g^{-1})	S (mmol g^{-1})	G (mmol g^{-1})	H (mmol g^{-1})	Carboxyl (mmol g^{-1})	Phenolic hydroxyl (mmol g^{-1})	Total hydroxyl content (mmol g^{-1})
Lignin	0.35	1.93	0.26	0	0	2.19	2.54
T_{120}	0.22	2.46	0.44	0	0.02	2.92	3.14
T_{140}	0.19	2.47	0.71	0	0.01	3.19	3.38
T_{160}	0.38	3.28	0.77	0.03	0.01	4.09	4.47
T_{180}	0.58	2.74	0.61	0.02	0.01	3.38	3.96

18. Properties comparison

Table S2. Comparison of mechanical properties and water resistance of LPT with other biomass-based adhesives.

Adhesive sample	Categories	Dry stress (MPa)	Wet stress (MPa)	Reference
T_1	TA	1.82	0.98	[3]
T_2	TA	1.67	0.73	[4]
T_3	TA	1.07	0.95	[5]
S_1	SM	2.24	1.37	[6]
S_2	SM	2.00	0.94	[7]
S_3	SM	2.44	1.35	[8]
CS_1	CS	2.71	1.92	[9]
CS_2	CS	3.09	1.54	[10]
CS_3	CS	2.10	1.10	[11]
C_1	Cellulose	3.09	1.20	[12]
C_2	Cellulose	4.04	2.42	[13]
C_3	Cellulose	4.90	1.70	[14]
L_1	Lignin	5.40	3.50	[15]
L_2	Lignin	3.50	1.50	[16]
This work	Lignin	6.28	3.26	------

Table S3. Comparison of cost estimation (all raw materials), temperature tolerance range, types of solvent resistance, water resistance and material sustainability of LPT with other biomass-based adhesives.

	ETGSO	SMAP	SSFP	SP/LPU	BD/P-NSD	This work
1 costs^{-1} (RMB ton^{-1})	16843	2704	14286	2420	1994	2628.6
Low temperature tolerance	-200	-40	-196	-40	30	-196
Temperature tolerance range	-200 – 85	-40 – 120	-196 – 55	-40 – 63	30 – 150	-196 –100
Types of solvent resistance	9	4	6	4	1	4
Water resistance	Yes	Yes	Yes	Yes	NO	Yes
Sustainability	NO	Yes	Yes	Yes	Yes	Yes
Reference	[17]	[18]	[19]	[20]	[21]	------

19. Cost accounting for adhesives

Table S4. The unit price of $L_{4.0}P_{11}T_{160}$ adhesive in tons.

Materials	Price (RMB ton^{-1})	Sources	Consumption (kg)	Cost (RMB ton^{-1})
Lignin	2000	Alibaba 1688	27500	55
PVA	10800	Alibaba 1688	75000	810
GA	152000	Alibaba 1688	3370	512
$K_2S_2O_8$	250000	Alibaba 1688	3125	781
CH_3OH	13600	Alibaba 1688	15840	252
NaOH	56000	Alibaba 1688	4500	215
Water	4.16	Government pricing	866500	3.6
		Total cost		2628.6

20. Formaldehyde emission

Table S5. Formaldehyde emission released from LPT adhesives

Adhesive sample	(ρ_t-ρ_b) (μg mL^{-1})	V (mL)	f	M (g)	Content (g Kg^{-1})	Average content (g Kg^{-1})
1-1	0.4523	50	5	1.1292	0.100	0.100
1-2	0.4514	50	5	1.1292	0.100	
1-3	0.4800	50	5	1.2201	0.098	
1-4	0.4786	50	5	1.2201	0.098	

ρ_t: Mass concentration of formaldehyde in the sample solution read from the standard curve.

ρ_b: Mass concentration of formaldehyde in the blank solution read from the standard curve.

V: Volume of the distillate after dilution to a fixed volume.

M: Mass of the sample.

f: Dilution factor of the sample solution.

21. Solid content

Table S6. Solid content of the LPT adhesives

Adhesive sample	$(m_1 - m_0)$ (g)	m_s (g)	S	$\overline{S}$
1-1	0.2391	1.4490	16.50%	
1-2	0.4251	2.6206	16.22%	16.04%
1-3	0.3265	2.1211	15.39%	

22. Limits of harmful substances in adhesives

Table S7. Limits of hazardous substances in water-based adhesives

Item	Urea-formaldehyde resin adhesives	Polyvinyl acetate emulsion adhesives	Phenolic resin adhesives	Polyurethane adhesives	Other adhesives
Free formaldehyde (g kg^{-1})	≤1.0	≤1.0	≤1.0	—	≤1.0
Benzene (g kg^{-1})	—	≤0.2	—	—	—
Toluene + Xylene (g kg^{-1})	—	≤10.0	—	—	—
Total volatile organic compounds (g kg^{-1})	≤350.0	≤110.0	≤250.0	≤100.0	≤350.0

Notes:

1. The symbol "—" indicates that no limit is specified for the corresponding item in the applicable standard.

2. The limits for free formaldehyde, benzene, toluene + xylene, and total volatile organic compounds are in accordance with the national standard for water-based wood adhesives (GB 18583-2008).

3. All values are expressed on a mass or volume basis as specified and were determined using standard test methods for adhesive hazardous substance analysis.

23. Key operating parameters of the UV aging chamber

Table S8. Detailed operation parameters for the four-stage cyclic ultraviolet accelerated weathering test.

Stage	Stage type	Irradiation time (h)	Condensation time (h)	Sprinkling time (h)	Holding time (h)	Black panel temperature (°C)	Irradiance (W m^{-2})	Front lamp	Rear lamp
1	Irradiation	7.00	—	—	—	55.0	0.76	On	On
2	Condensation	—	4.00	—	—	—	—	Off	Off
3	Water sprinkling	—	—	1.00	—	—	—	Off	ON
4	Holding	—	—	—	0.10	—	—	Off	Off

On/Off: Lamp status.

—: Not applicable in this stage.

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