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Research Paper

Preparation of Lignin-Based Adhesives via Pre-Hydrolysis and Study of Their Bonding Mechanism

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Abstract. To meet the green development demands of the current wood-based panel industry, Mason pine (Pinus massonianaLamb.), poplar (Populus tomentosaCarr.), and wheat straw (Triticum aestivumL.) were used as raw materials. A series of milled wood lignins (MWL) were prepared using an environmentally friendly pre-hydrolysis technology, and the MWL was used as an adhesive for the preparation of three-layer plywood. The results found that the phenolic hydroxyl content and reactivity of pre-hydrolyzed Mason pine MWL were significantly improved, and the bonding strength of the prepared plywood increased. Further optimization of hot-pressing process parameters, under the optimal conditions of a hot-pressing temperature of 150°C, hot-pressing time of 4.17 min/mm, and single-side adhesive spread of 100 g/m², resulted in a plywood dry strength of up to 4.34 MPa. Compared with unhydrolyzed lignin under the same hot-pressing process conditions, the dry strength of the adhesive increased by 214%. Mechanistic studies showed that during the hot-pressing process, lignin formed a uniform and dense adhesive layer on the plywood surface through depolymerization and re-condensation reactions, and constructed a three-dimensional cross-linked structure inside the plywood, thereby imparting excellent mechanical properties to the plywood. Activating MWL through pre-hydrolysis technology provides new ideas for the preparation of high-performance lignin-based adhesives.

Keywords: L*ignin; KOH activation; Porous carbon; Supercapacitorn*

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1 Introduction

The wood-based panel industry stands as a pivotal sector within the global forest products economy, with China's annual production exceeding 300 million cubic meters, consuming over 25 million tons of adhesives annually [1, 2]. For decades, the industry has heavily relied on aldehyde-based thermosetting resins, particularly urea-formaldehyde (UF), phenol-formaldehyde (PF), and melamine-formaldehyde (MF) resins, derived from fossil resources. These adhesives have been favored for their excellent bonding performance, rapid curing, and low cost. However, their widespread application comes with a significant and persistent environmental and health burden: the emission of free formaldehyde during both the curing process and the long-term service life of the final products [3, 4]. Formaldehyde is a known volatile organic compound (VOC) and a human carcinogen. Its continuous release severely deteriorates indoor air quality, posing serious health risks such as respiratory irritation, allergic reactions, and potential long-term carcinogenic effects [3]. This issue starkly contradicts the urgent global shift towards green, low-carbon, and sustainable development principles that the modern forestry sector fervently champions. As environmental regulations become increasingly stringent and consumer awareness of healthy living environments rises, the demand for formaldehyde-free, eco-friendly adhesive alternatives has become more pressing than ever [5].

In this context, lignin, the second most abundant natural polymer after cellulose, has emerged as a highly promising renewable raw material for developing bio-based adhesives [6, 7]. Lignin, a core structural element in plant cell wall architectures, constitutes a spatially networked, non-crystalline aromatic macromolecule that imparts mechanical stiffness and biological decay resistance. Generated in massive volumes as residual output from cellulose extraction processes in papermaking and agro-industrial biomass conversion facilities, the predominant current fate involves thermal combustion for rudimentary energy recuperation. Repurposing lignin as a renewable binding agent precursor simultaneously unlocks value-creation opportunities for this presently squandered bioresource and substantiates foundational tenets of regenerative biological resource management [8]. The native molecular configuration—distinguished by profuse phenylpropanoid subunits coupled with nucleophilic functionalities encompassing phenolic hydroxyl groups, methoxy substituents, and aliphatic alcohol moieties—endows inherent capability for interchain covalent networking, establishing the essential physicochemical substrate for cohesive adhesion performance [9, 10]. Conceptually, lignin itself acts as a natural binder within the lignocellulosic matrix, forming strong connections with cellulose and hemicellulose, suggesting its intrinsic adhesive potential [11].

Recent research on lignin-based adhesives has primarily focused on two strategies: chemical modification to enhance reactivity and component blending to improve performance [12, 13, 14]. Chemical modification routes, such as demethylation, phenolation, hydroxymethylation, and copolymerization with synthetic resins, aim to introduce more reactive sites or improve compatibility [15, 16]. For instance, grafting copolymerization has been explored to develop starch-based adhesives with high adhesion [2]. Blending lignin with other biopolymers or synthetic resins is another common approach to compensate for the shortcomings of pure lignin adhesives, such as brittleness or low water resistance [9, 17]. However, these strategies often face considerable challenges. Chemical modifications can involve complex processes, hazardous reagents, and high costs, undermining the economic and environmental benefits [18]. On the other hand, blending systems frequently suffer from issues of poor compatibility between lignin and other components, leading to unstable bonding performance and difficulties in industrial-scale application [16]. Therefore, there is a compelling need to develop simpler, more economical, and more efficient methods to unlock the adhesive potential of lignin.

A promising alternative lies in directly utilizing lignin's native structure. The three-dimensional network of lignin can provide cohesive strength, while its abundant active groups, particularly phenolic hydroxyl groups, can participate in cross-linking reactions under appropriate conditions to exert bonding action [13]. Milled wood lignin (MWL), extracted using the Bjorkman method, is considered a representative native lignin that closely resembles the protolignin in the cell wall with minimal structural alteration. It typically possesses a relatively high proportion of non-condensed structures (e.g., β-O-4 linkages), which are more amenable to depolymerization and recombination during hot-pressing, facilitating molecular interlocking [19]. Recent groundbreaking work by Yang et al. (2023) demonstrated the potential of using uncondensed lignins as wood adhesives, achieving significant bonding strength [20]. However, the straightforward employment of pristine ball-milled lignin (MWL) commonly faces impediments stemming from its intrinsically restricted availability of accessible phenolic -OH groups—pivotal nucleophilic sites indispensable for generating durable three-dimensional networks during thermally induced curing processes [17].The low reactivity hinders effective cross-linking, resulting in insufficient bonding strength for structural applications.

Pre-hydrolysis, an environmentally friendly autohydrolysis process using only water or steam at elevated temperatures (typically 160-180°C), presents a potential solution for activating lignin without complex chemistry [28, 29]. This protocol is standardly implemented throughout biorefining complexes for lignocellulosic feedstock separation, with principal objective of hemicellulose solubilization. Throughout hydrothermal conditioning, acetyl appendages tethered to hemicellulosic skeletal structures experience cleavage, releasing acetic acid entities that subsequently self-catalyze polysaccharide depolymerization whilst concurrently promoting fractional disintegration of lignin-carbohydrate associations (LCAs) and rupture of lignin's inherently fragile intra-molecular connectors [30, 31]. Of mechanistic significance, the hydrolysis of phenyl-ether junctions—specifically the dominant β-O-4 bonding arrangements intrinsic to protolignin supramolecular organization—generates novel phenolic hydroxyl substituents at the para-loci of benzenoid rings, thereby elevating overall phenolic functionality concentration and intensifying the polymeric reactivity characteristics [22, 23]. Feng et al. (2023) studied the formation of LCCs in pre-hydrolysis liquor, providing insights into the structural changes occurring during this process [23]. Therefore, pre-hydrolysis offers a green and efficient route to "activate" lignin, making it a more reactive precursor for adhesive applications. The modified lignin obtained could possess a more favorable structure for subsequent thermal cross-linking during the hot-pressing of wood composites.

Despite its potential, the systematic application of pre-hydrolysis as a pretreatment specifically for enhancing the adhesive properties of lignin from different biomass feedstocks remains underexplored. Key questions persist: How does pre-hydrolysis intensity (temperature and time) affect the chemical structure and adhesive performance of MWL from different botanical origins (softwood, hardwood, grass)? What are the optimal hot-pressing parameters (temperature, time, resin load) for such pre-hydrolyzed lignin-based adhesives? Most importantly, what is the underlying bonding mechanism? Comprehensive elucidation of lignin's molecular structural transformations throughout thermocompression processing, alongside systematic correlation with resultant interfacial bonding efficacy, constitutes an indispensable prerequisite for the informed engineering of superior lignin-based adhesive formulations.To bridge these investigative voids, the present study sought to engineer a spectrum of lignin-derived adhesive formulations through a facile, environmentally benign aqueous pretreatment activation protocol, whilst concurrently unraveling the mechanistic underpinnings governing interfacial bonding. Mason pine (Pinus massoniana Lamb., a softwood), poplar (Populus tomentosa Carr., a hardwood), and wheat straw (Triticum aestivum L., a grass) were selected as representative raw materials to prepare MWL under various pre-hydrolysis conditions. The chemical structural changes of the MWLs, particularly phenolic hydroxyl content and inter-unit linkage distributions, were comprehensively characterized. The bonding performance of these MWLs as adhesives for three-layer plywood was evaluated. The hot-pressing parameters were optimized for the best-performing lignin adhesive. Furthermore, the interfacial adhesion mechanism was unraveled through integrated characterization of lignin's macromolecular reorganization throughout thermocompression processing—spanning molecular mass distribution patterns, thermo-oxidative stability profiles, and covalent bond architecture modifications—complemented by microscopic interrogation of plywood substrate-adhesive interface morphologies. These outcomes yield groundbreaking perspectives on lignin biorefinement strategies for developing environmentally benign, mechanically robust, non-hazardous wood binding systems, thereby catalyzing the green transition within composite timber product manufacturing sectors.

2 Materials and Methods

2.1 Preparation of Milled Wood Lignin (MWL)

Mason pine (Pinus massonianaLamb.) was obtained from Jiangxi Academy of Forestry Sciences, poplar (Populus tomentosaCarr.) from Hubei Huashengxin Wood-based Panel Co., Ltd., and wheat straw (Triticum aestivumL.) from a Hebei Handan ecological farm. The specified raw materials were mechanically comminuted, and lignocellulosic granules with particle dimensions ranging 0.2–0.9 mm were harvested. These granules underwent continuous Soxhlet extraction for an 8-hour duration utilizing a benzene-ethanol mixed solvent (volumetric ratio 1:2), succeeded by aqueous washing and air-drying. A decuple mass proportion of deionized water was incorporated, with hydrothermal pretreatment performed in a high-pressure oxygen-bleaching reactor (PARR-4530), maintaining temperatures at 160°C or 180°C for processing durations of 30 or 120 minutes. Upon reaction cessation, the pretreated solid residue was filtered and separated, sequentially washed with 1% (mass fraction) sodium hydroxide solution and distilled water to eliminate surface-adsorbed impurities, and then air-dried. Milled wood lignin (MWL) was extracted according to Björkman's method and named based on pretreatment raw material and conditions, as shown in Table 1.**Table 1** The names of MWL according to the raw materials and conditions of pre-hydrolysis

Condition	Raw Material		
	Mason Pine	Poplar	Wheat Straw
Untreated	MWL-M	MWL-P	MWL-W
160°C 30 min	MWL-M1	MWL-P1	MWL-W1
160°C 120 min	MWL-M2	MWL-P2	MWL-W2
180°C 30 min	MWL-M3	MWL-P3	MWL-W3
180°C 120 min	MWL-M4	MWL-P4	MWL-W4

2.2 Preparation of Plywood

The MWL samples were completely dried, mixed with a 10% acetic acid solution at a certain solid-to-liquid ratio (1:3) to form an adhesive solution, and then evenly coated onto the surface of poplar veneers (25 mm × 100 mm

× 2 mm) to prepare three-layer plywood. The vulcanization testing apparatus (BD8820-C) was configured to deliver a thermocompression force of 2.5 MPa.The influences of thermocompression temperature (130–170°C), thermocompression duration (2.5–5.0 min/mm), and unilateral adhesive application rate (70–190 g/m²) on laminated wood panel performance were systematically examined in a stepwise manner.The plywood after hot-pressing was cooled to room temperature and stored.

The MWL was evenly placed in a 5 cm × 5 cm metal mold and hot-pressed under the same conditions. After hot-pressing, it was cooled to room temperature, demolded, and a lignin adhesive sheet was obtained. The sheet was ground into powder and vacuum-dried for later use.

2.3 Testing Methods

2.3.1 Bonding Strength Test

According to the technical requirements for Type I plywood in Clause 6.3.3 of GB/T 9846-2015 "Plywood" and the provisions of Clause 4.17 in GB/T 17657-2022 "Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels", the tensile shear test of plywood was conducted using an electronic universal testing machine (CMT5305). Specimen geometries measured 25 mm × 100 mm × 2 mm. Regarding dry shear strength assessment, samples underwent conditioning within controlled climatic parameters (20 ± 2°C, 65 ± 5% RH) for a 24-hour stabilization period preceding mechanical characterization.Regarding wet bond strength evaluation, specimens were submerged in aqueous medium at 20 ± 3°C for 24 hours prior to mechanical assessment.

2.3.2 Phenolic Hydroxyl Content Analysis

Phenolic hydroxyl group concentrations in the samples were determined through aqueous potentiometric titration, utilizing 0.1 mol/L HCl standard solution as the titrant and 0.05 g p-hydroxybenzoic acid as the internal standard, with analyses performed on a Metrohm 905 automated potentiometric titrator. A sample without the test material served as a blank control.

2.3.3 Alkaline Nitrobenzene Oxidation Analysis

10 mg samples were dispersed into 3.2 mL of 2 M aqueous sodium hydroxide containing 0.2 mL nitrobenzene, then thermally treated at 170°C for 3 hours. The resulting alkaline nitrobenzene oxidation products were quantitatively analyzed by gas chromatography-flame ionization detector (GC-FID, GC128), using 2,6-dimethoxyphenol as the internal standard.

2.3.4 Relative Molecular Weight Analysis

Aliquots of 10 mg were solubilized in 1 mL dimethylformamide. Polydispersity profiles were assessed via gel permeation chromatography (Agilent 1260 Infinity II GPC/SEC) utilizing refractive index monitoring, PL MIXED-C stationary phase, spectroscopic-grade DMF with 0.1% LiBr additive as carrier solvent, 1 mL/min pumping speed, and 45°C thermal regulation.

2.3.5 Thermogravimetric Analysis

Lignin specimens weighing 3–5 mg were transferred into ceramic crucibles.Employing nitrogen as the inert shielding atmosphere and programming a thermal ramp of 10°C/min, specimens were subjected to thermogravimetric analysis (SDT Q600).

2.3.6 Nuclear Magnetic Resonance Analysis

40 mg samples were dissolved in 0.5 mL deuterated dimethyl sulfoxide (DMSO-d_6). 2D-HSQC NMR spectra were measured using a Bruker Avance III 500 MHz NMR spectrometer under the following parameters: one-bond C-H coupling constant of 148 Hz, 256 increments in the F1 (^{13}C) dimension, 1024 data points in the F2 (^{1}H) dimension, relaxation delay of 1.5 s, and 64 accumulated scans.

2.3.7 Differential Scanning Calorimetry Analysis

The vitrification temperatures of lignin samples were assessed utilizing a differential scanning calorimeter (TA DISCOVERY DSC 2500). Specimens of 10 mg were sealed in aluminum pans of consistent mass. With nitrogen shielding at 50 mL/min flow rate, two thermal cycles were performed. First cycle: ramped to 105°C at 10°C/min, maintained for 10 min, then cooled to 40°C at 10°C/min. Second cycle: heated to 180°C at 10°C/min, held for 5 min, then cooled to 40°C at 10°C/min. Data from the second cycle was analyzed.**2.3.8 Scanning Electron Microscopy (SEM) Observation**

The hot-pressed three-layer plywood was cut, and the cross-section was observed for surface morphology. An ultra-high-resolution cold field emission scanning electron microscope (Hitachi Regulus 8100) was used to observe the sample's microstructure at an accelerating voltage of 5 kV. The sample was sputter-coated with gold before scanning to improve its conductivity.

3 Results and Analysis

3.1 Bonding Strength of Lignin-Based Adhesives

The schematic illustration of lignin-based adhesive bonding is presented in Figure 1a. Using milled wood lignin (MWL) from Mason pine, poplar, and wheat straw as adhesives, plywood was prepared under identical hot-pressing conditions (160°C temperature, 2.5 min/mm pressing time, 2.5 MPa pressure, 100 g/m² adhesive spread). Bonding strength was compared under different MWL pre-hydrolysis treatments. The bonding performance of Mason pine MWL is shown in Figure 1b. As pre-hydrolysis intensity increases, the dry strength of plywood first increases and then decreases. The dry strength of plywood made from untreated Mason pine MWL is 1.72 MPa, while the dry strengths of the pre-hydrolyzed MWL groups are 2.21, 1.63, 0.99, and 0.62 MPa, respectively. Wet strength results show that the wet strength of untreated Mason pine MWL is 1.55 MPa, while the wet strengths of pre-hydrolyzed MWL are 1.09, 1.08, 1.11, and 1.10 MPa, respectively. All samples meet the minimum standard for Type III plywood in GB/T 9846-2015 (0.7 MPa). For Mason pine MWL, moderately pre-hydrolyzed MWL-M1 can improve the dry strength of the plywood.

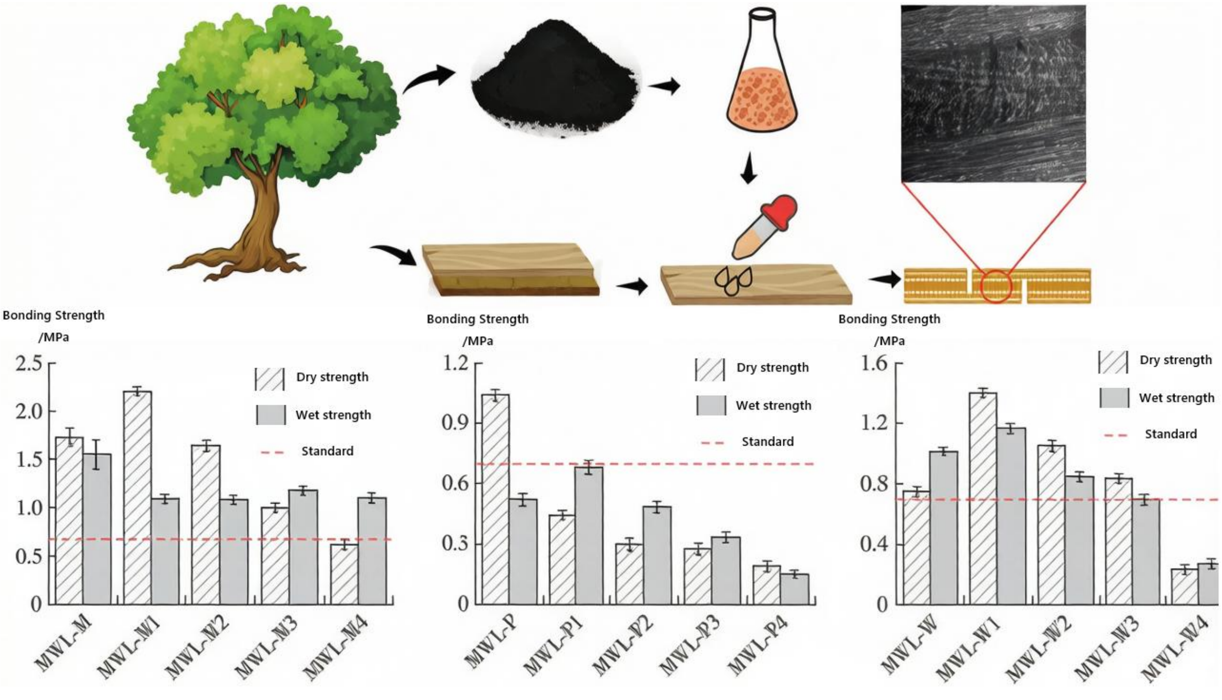

Figure 1 Schematic diagram of lignin-based adhesives (a); the bonding strength of MWL in mason pine (b), poplar (c), and wheat straw (d) under different pre-hydrolysis conditions

The adhesive performance of poplar MWL is depicted in Figure 1c. Results indicate that dry shear strength exhibits a continuous downward trajectory with escalating pre-hydrolysis intensity.The dry strength of plywood made from untreated poplar MWL is 1.04 MPa, while the dry strengths of the pre-hydrolyzed MWL groups are 0.44, 0.30, 0.27, and 0.19 MPa, respectively. Wet strength test results show that the wet strength of untreated poplar MWL is 0.52 MPa, while the wet strengths of pre-hydrolyzed samples are 0.68, 0.48, 0.33, and 0.15 MPa, respectively, none of which meet the strength requirements specified by the national standard.

The bonding strength of wheat straw MWL adhesive is shown in Figure 1d. From Figure 1d, it can be seen that as the pre-hydrolysis intensity increases, the dry strength of the plywood first increases and then decreases. The dry strength of plywood made from untreated wheat straw MWL is 0.75 MPa, while the dry strengths of the pre-hydrolyzed wheat straw MWL groups are 1.41, 1.05, 0.83, and 0.23 MPa, respectively. Wet strength test results show that the wet strength of untreated wheat straw MWL is 1.01 MPa, while the wet strengths of pre-hydrolyzed samples are 1.17, 0.84, 0.69, and 0.27 MPa, respectively, some of which can meet the national standard requirements. For wheat straw MWL, moderately pre-hydrolyzed MWL-W1 can significantly improve the dry strength and wet strength of the plywood.

MWL, especially MWL-M1 (160°C, 30 min) as an adhesive, has good bonding strength. After pre-hydrolysis treatment, the dry strength can be improved to a certain extent, and the wet strength still meets the national standard.

3.2 MWL Chemical Structure Analysis

Aqueous pretreatment strategically alters lignin macromolecular architecture, notably through augmentation of free phenolic hydroxyl functionality.Research shows that due to their high reactivity, phenolic hydroxyl groups can not only promote cross-linking between lignin molecules but also enhance the chemical bonding between lignin and components such as cellulose and hemicellulose in the board, thereby significantly improving the bonding performance of lignin-based adhesives. Experimental results show that for both Mason pine, poplar, and wheat straw, increasing the pre-hydrolysis temperature or extending the holding time can significantly increase the phenolic hydroxyl content of MWL (Figure 2a). This phenomenon is mainly attributed to the cleavage of aryl ether bonds (such as β-O-4) in lignin molecules during the pre-hydrolysis process...changes in chemical bonds and structural units, analyzing the impact of these chemical structural changes on the adhesive effect of MWL. From the side-chain region (δ_C/δ_H 95–50/6.0–2.5) (Figure 3), it can be seen that poplar MWL has a high β-O-4 structure content, reaching 75.5% (Table 2). A higher β-O-4 structure content can not only provide more phenolic hydroxyl active sites, offering effective molecular fragments for lignin re-condensation during hot-pressing, but also imparts a certain flexibility to the lignin molecular chains, which is conducive to the formation of a cross-linked network. However, compared with Mason pine and wheat straw, the adhesive effect of poplar MWL is weaker.

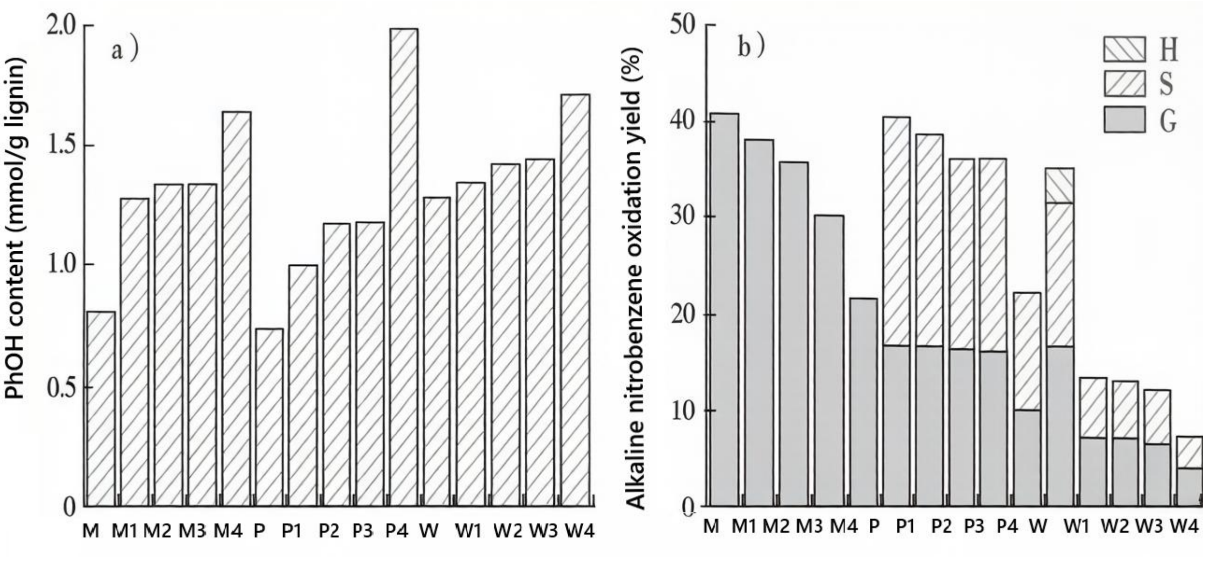

Figure 2 The phenolic hydroxyl content (a) and alkaline nitrobenzene oxidation products (b) of MWLs under different pre-hydrolysis conditions

With increasing pre-hydrolysis intensity, the phenolic hydroxyl content of MWL shows an upward trend, significantly enhancing its reactivity; however, the condensation degree of MWL also increases concurrently. This densification of the molecular structure is detrimental to effective cross-linking between lignin molecules. This indicates that the bonding performance of MWL adhesives will initially increase and then decrease with increasing pre-hydrolysis intensity, exhibiting a maximum. However, MWLs from different raw material sources exhibit differentiated bonding behaviors, which are related to their inherent chemical structures.

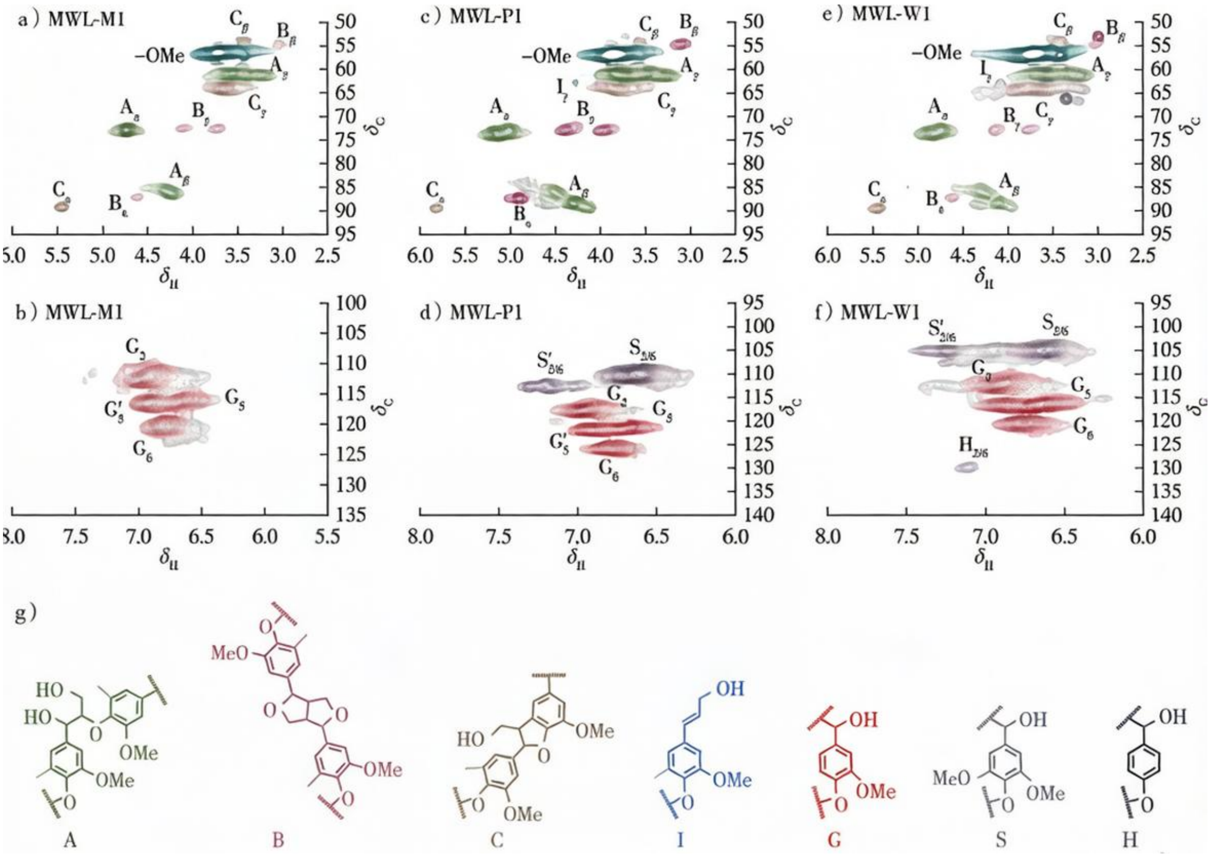

Figure 3 2D-HSQC NMR spectra of MWL-M1 (a, b), MWL-P1 (c, d) and MWL-W1 (e, f), and their structural formula (g)

To investigate this, further analysis using HSQC was conducted to examine changes in chemical bonds and structural units of lignin during pre-hydrolysis, analyzing how these chemical structural changes affect the bonding performance of MWL. From the side-chain region (δC/δH 95–50 / 6.0–2.5) (Figure 3), it is known that poplar MWL has a relatively high content of β-O-4 structures, reaching up to 75.5% (Table 2). A higher content of β-O-4 structures can not only provide more active sites (phenolic hydroxyl groups) and supply effective molecular fragments for lignin re-condensation during hot-pressing but also impart a certain degree of flexibility to the lignin molecular chains, facilitating the formation of cross-linked networks [17]. However, compared to Masson pine and wheat straw, poplar MWL exhibits weaker bonding performance. Further analysis of the aromatic region (δC/δH 140–95 / 8.0–5.5) reveals that MWL-M1 is composed of guaiacyl (G) units; MWL-P1 is composed of G and syringyl (S) units, with an S unit proportion of 52.4%; MWL-W1 is composed of G, S, and p-hydroxyphenyl (H) units, with an S unit proportion of 35.4%. The high proportion of S units in poplar MWL is the key factor for its relatively weaker bonding performance. Unlike guaiacyl (G) and p-hydroxyphenyl (H) units, syringyl (S) units have no reactive condensation position at the C5 site of the aromatic ring [25]. This structural characteristic means that for poplar MWL during thermocompression, although numerous active sites are created, the steric hindrance caused by the C5 methoxy group prevents effective re-condensation. The molecular fragments generated from pre-hydrolysis cannot cross-link to form an effective three-dimensional network structure, ultimately resulting in the relatively lagging bonding performance of poplar MWL.

Table 2 Semi-quantitative analysis of lignin chemical structure based on 2D-HSQC NMR Unit: %

Sample	MWL-M1	MWL-P1	MWL-W1
β-O-4	67.9	75.5	68.6
β-β	12.4	14.0	11.2
β-5	19.7	10.5	20.2
S	0	52.4	35.4

3.3 Optimization of Hot-Pressing Parameters

Drawing from prior experimental results, Mason pine MWL-M1 served as the feedstock for hot-pressing optimization. With pressing time, pressure, and adhesive application held constant at 2.5 min/mm, 2.5 MPa, and 100 g/m² respectively, the influence of temperature on adhesion performance is depicted in Figure 4a. Hot-pressing temperature is a key parameter determining the performance of lignin-based adhesive boards, directly affecting whether lignin reaches its glass transition temperature, thereby achieving softening and cross-linking. If the hot-pressing temperature is too low, lignin softening is incomplete, resulting in poor fluidity and insufficient wettability and penetration on the wood surface; if the temperature is too high, it can lead to overheating decomposition of lignin, making the adhesive layer brittle. Under the optimized hot-pressing temperature condition of 150°C, DSC analysis shows that lignin can reach a suitable flow state (Figure 4b), allowing it to distribute evenly on the veneer surface. At this stage, active groups in lignin molecules can form a stable three-dimensional network structure through the synergy of covalent bonds and non-covalent interactions, and the dry strength of the board reaches its maximum value.

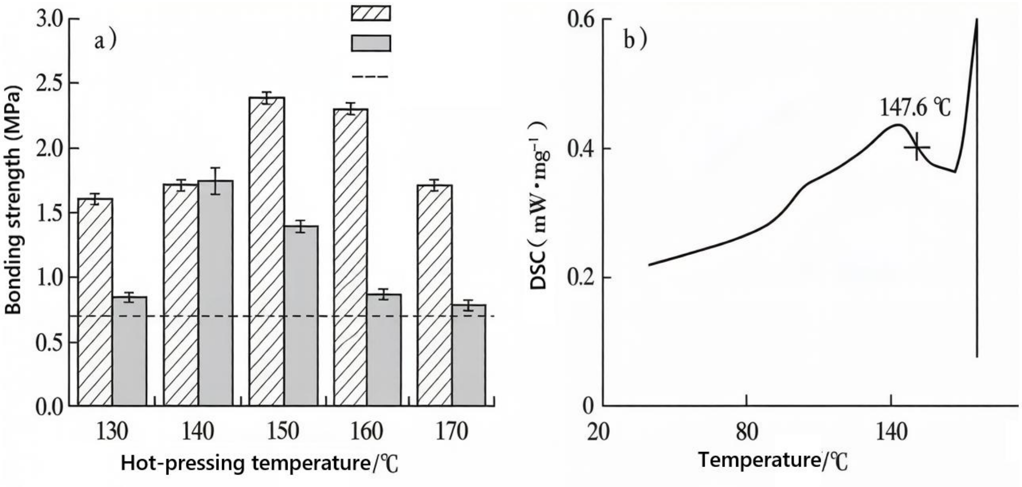

Figure 4 Effect of hot-pressing temperature on bonding strength (a) and DSC curve of lignin MWL-M1 (b)

With optimized hot-pressing temperature at 150°C, pressure at 2.5 MPa, and adhesive spread at 100 g/m², the effect of pressing time on bonding strength is shown in Figure 5a. Dry strength increases with extended pressing time and peaks at 4.17 min/mm. During plywood hot-pressing, after lignin is fully softened, the cross-linker achieves target bonding strength through cross-linking and curing. Excessively extending pressing time provides limited bonding improvement while wasting energy and reducing production efficiency. With optimized parameters of 150°C temperature, 4.17 min/mm time, and 2.5 MPa pressure, the effect of lignin-based adhesive spread on bonding strength is shown in Figure 5b.At a lignin-based adhesive spread of 100 g/m², bonding strength reaches maximum values, with dry strength of 4.34 MPa and wet strength of 1.78 MPa.An appropriate amount of lignin-based adhesive can ensure a continuous adhesive layer without glue starvation, while avoiding local charring or adhesive layer fracture caused by an overly thick adhesive layer and uneven stress. Under the same optimized process conditions, compared with untreated Mason pine MWL (MWL-M (150)), pre-hydrolysis treatment can significantly improve the bonding performance of the lignin-based adhesive (MWL-M1 (150)), with dry strength increasing by 214% and wet strength increasing by 34.8%, once again proving the importance of the pre-hydrolysis process in improving lignin reactivity (Figure 5c).

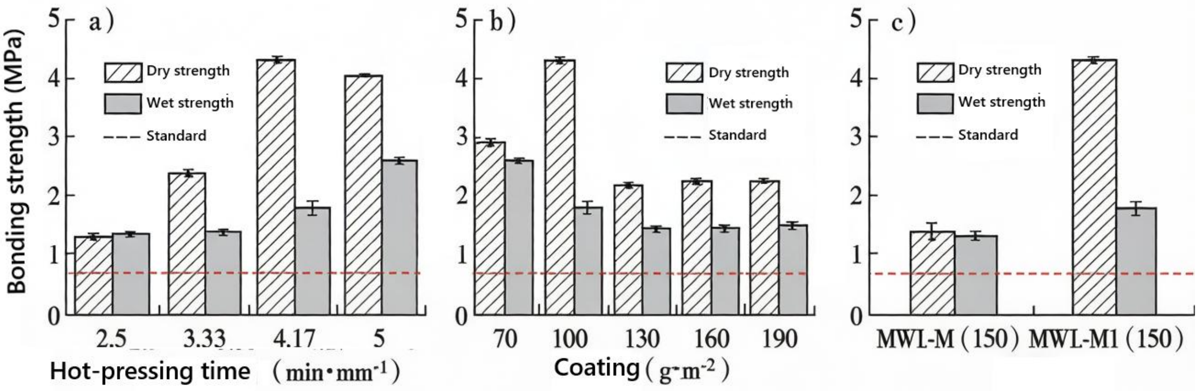

Figure 5 The effect of hot-pressing time (a), and single side application MWL amount (b) on bonding strength; comparison of bonding strength between MWL-M (150) and MWL-M1 (150) under optimal hot-pressing conditions (c)

3.4 Bonding Mechanism of Lignin-Based Adhesives

3.4.1 Effect of Lignin Chemical Structure on Bonding Performance

Figure 6a and Table 3 illustrate the alterations in lignin's relative molecular mass during the hot-pressing procedure. Subsequent to this thermal treatment, MWL-M1P demonstrated significant transformations in its molecular parameters: the number-average molecular mass (M_n) escalated from 4080 g/mol to 5492 g/mol, whereas the weight-average molecular mass (M_w) ascended from 12130 g/mol to 15800 g/mol. Simultaneously, the polydispersity index (PDI) underwent a slight reduction from 2.97 to 2.87. These findings indicate pronounced condensation reactions occurring within lignin macromolecules subjected to high-temperature compression. Such intermolecular networking fulfills two functions: reinforcing the intrinsic binding capacity of the lignin framework and, secondarily, facilitating superior interfacial attachment in plywood structures. These nanoscale structural evolutions culminate in tangible enhancements to the engineered wood product's load-bearing characteristics.

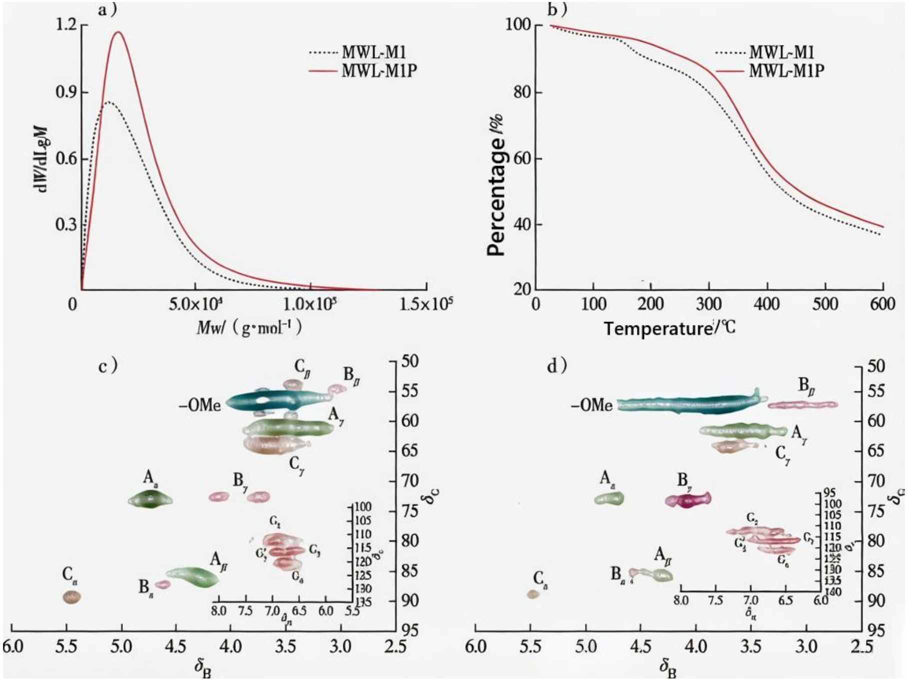

Figure 6 Relative molecular weight distribution (a), TG and DTG curves (b) and HSQC NMR spectra (c, d) of MWL-M1 and MWL-M1P

Thermogravimetric analysis results further confirmed that hot-pressing treatment improved the thermal stability of lignin to a certain extent (Figure 6b). The lignin specimen exhibited elevated residual char formation, rising from 35.4% to 39.9%, alongside an upward shift in the peak thermal decomposition temperature from 351.0°C to 358.9°C.This improvement in thermal stability stems from condensation reactions triggered by hot-pressing, which foster cross-linking among lignin molecules and yield a more robust molecular architecture.The 2D NMR characterization outcomes are presented in Figure 6c and Table 3. Following the hot-pressing treatment, lignin's β-O-4 linkage proportion declined from 67.9% to 60.0%, while its β-5 linkage proportion dropped from 19.7% to 11.9%.This suggests that aryl-alkyl ether linkages (β-O-4 and α-O-4) within lignin underwent cleavage throughout the hot-pressing operation; meanwhile, the proportion of β-β connections expanded from 12.4% to 28.1% post-treatment, signifying the emergence of condensation phenomena in lignin during this thermal process.The scission of β-O-4 and α-O-4 linkages in lignin generates molecular fragments bearing reactive functionalities, thereby imparting enhanced chemical activity to the biopolymer.During hot-pressing, lignin molecules undergo condensation through these active groups and form cross-linked structures, increasing the intermolecular cohesive force within lignin, thereby imparting stronger adhesive effects to the lignin-based adhesive.

Table 3 Changes in relative molecular weight and chemical structure of lignin during hot-pressing process

Sample	MWL-M1	MWL-M1P
Mn / (g·mol^{-1})	4080	5492
Mw / (g·mol^{-1})	12130	15800
PDI	2.97	2.87
β-O-4/ %	67.9	60.0
β-β/ %	12.4	28.1
β-5/ %	19.7	11.9

3.4.2 Effect of Interface Microstructure on Bonding Performance

The microstructure characteristics of the three-layer plywood interface at the same position under different magnifications are shown in Figure 7. After hot-pressing, the cells are arranged tightly with no obvious cracks or pores (Figure 7a). Higher magnification images (Figure 7b) further confirm that the lignin-based adhesive formed a uniform and continuous adhesive layer at the bonding interface, tightly bonded to the veneer surface. This excellent interfacial bonding originates from the thermorheological properties of lignin. When the temperature reaches its softening point, the mobility of lignin molecular chain segments increases, giving it a certain fluidity. Simultaneously, under pressure, the flowing lignin-based adhesive can achieve effective penetration into cell lumens through the micron-sized pits in the wood (Figure 7c), tightly bonding with components such as cellulose and hemicellulose through various interactions like hydrogen bonds or van der Waals forces, and achieving strong mechanical interlocking after curing, further strengthening the adhesive effect. This multi-scale bonding mechanism indicates that lignin-based adhesives can not only construct a three-dimensional cohesive network structure through self-condensation but also form strong interfacial bonds with wood components through physicochemical interactions, achieving an overall improvement in bonding strength.

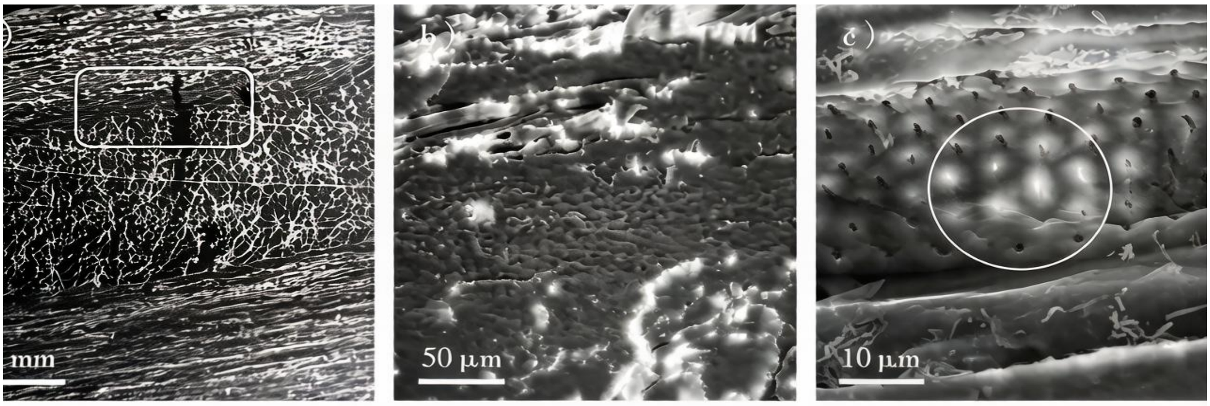

Figure 7 SEM images of interface of three-layer plywood

The significant improvement in the bonding performance of lignin-based adhesives prepared via pre-hydrolysis, as detailed in the document, is attributed to a synergistic mechanism centered on the chemical activation of lignin and its subsequent thermosetting transformation during hot-pressing. The process begins with the pre-hydrolysis treatment itself, an environmentally friendly autohydrolysis using only water at elevated temperatures (160-180°C). This procedure preferentially ruptures the susceptible inter-unit connections present in the native lignin architecture, primarily targeting β-O-4 aryl-ether bonds, under the acidic conditions (pH 3-4) generated in situ.This scission proves critical, as it generates novel phenolic hydroxyl functionalities at the C4 position of the aromatic rings. Phenolic hydroxyl groups are highly reactive sites essential for subsequent cross-linking. Experimental data (Figure 2a in the document) confirms that pre-hydrolysis significantly increases the phenolic hydroxyl content of Mill Wood Lignin (MWL) from all tested feedstocks (Mason pine, poplar, wheat straw), thereby enhancing its intrinsic chemical reactivity as an adhesive precursor.

However, the relationship between pre-hydrolysis intensity and final bond strength is optimized, not linear, often showing an initial increase followed by a decrease, as observed for Mason pine and wheat straw MWL. This is because the same acidic conditions that generate phenolic hydroxyls also promote condensation reactions between lignin fragments. Excessive condensation, evidenced by a decrease in non-condensed structures via alkaline nitrobenzene oxidation (Figure 2b), makes the lignin macromolecules more rigid and dense, hindering the segmental mobility necessary for effective flow and interaction during hot-pressing. Therefore, optimal pre-hydrolysis (e.g., 160°C for 30 min for Mason pine) achieves a critical balance: sufficiently activating lignin by increasing reactive phenolic sites while avoiding excessive condensation that compromises processability. The inherent lignin structure of the source biomass is a decisive factor. For instance, poplar MWL showed poorer performance despite high β-O-4 content because its high syringyl (S) unit proportion (52.4%) presents steric hindrance at the C5 position, impeding effective re-condensation and 3D network formation during curing, unlike the guaiacyl (G)-dominated Mason pine lignin.

The actual bonding network is formed during the optimized hot-pressing stage (150°C, 4.17 min/mm). Here, the pre-activated lignin undergoes a dynamic sequence of depolymerization and re-condensation. The heat first softens the lignin, granting it flowability to wet the wood surface and penetrate cell lumens, ensuring intimate interfacial contact. Subsequently, it further catalyzes the cleavage of remaining β-O-4 and α-O-4 linkages, generating smaller, mobile molecular fragments with active ends. These fragments then undergo intensive re-condensation reactions, primarily through the newly formed and existing phenolic hydroxyl groups. This constructs a robust, three-dimensional cross-linked network within the adhesive layer, as proven by the increase in molecular weight (Mw from 12,130 to 15,800 g/mol for MWL-M1), the rise in resistant β-β linkage content (from 12.4% to 28.1%), and enhanced thermal stability. This cross-linking drastically improves the cohesive strength of the adhesive itself. Simultaneously, the flowing lignin forms strong interfacial bonds with the wood substrate through covalent bonds, hydrogen bonding, and mechanical interlocking upon solidification and penetration, as shown in SEM images (Figure 7). The synergy between this internally strengthened cohesive network and the robust adhesive interface results in the dramatic dry bonding strength improvement to 4.34 MPa for Mason pine MWL-M1, a 214% increase over the untreated control.

This research demonstrates a viable green pathway for valorizing industrial lignin streams into high-performance, formaldehyde-free wood adhesives, presenting a compelling opportunity for the sustainable transformation of the wood-based panel industry. The immediate and most promising application lies in integrating this pre-hydrolysis activation technology into existing biorefinery or pulp mill operations, where lignin is available as a major by-product. This could enable the production of eco-friendly plywood, particleboard, and other engineered wood products, directly addressing regulatory and consumer demand for safer, low-emission materials. Future work must focus on bridging the gap between laboratory proof-of-concept and commercial-scale implementation. This involves technical-economic assessments of the pre-hydrolysis process at scale, optimization of the adhesive formulation for different wood composite manufacturing lines (e.g., adjusting viscosity, curing speed), and comprehensive long-term testing of the panels for durability under various service conditions. Furthermore, future research should explore strategies to broaden the applicability of this method to a wider range of lignin feedstocks. As the study revealed, the performance is highly dependent on the native lignin structure (e.g., the suboptimal results for high-S poplar lignin). Therefore, developing tailored pre-hydrolysis protocols or complementary mild modification techniques for hardwoods and agricultural residues is crucial to create a universally adaptable technology. Another important avenue is the exploration of co-

components or cross-linkers that could be blended with pre-hydrolyzed lignin to further enhance specific properties, such as water resistance or bonding strength under high humidity, potentially expanding its use to meet structural adhesive standards. Ultimately, the success of this application will depend on a collaborative effort between researchers and industry to refine the process economics, ensure consistent quality, and establish performance standards for this new class of bio-based adhesives, thereby accelerating the transition towards a circular bioeconomy in the forest products sector.

4 Conclusion

To fully utilize the role of MWL-based adhesives, this study used Mason pine, poplar, and wheat straw as raw materials, activated MWL through pre-hydrolysis technology, and systematically evaluated its bonding performance in three-layer plywood. The conclusions are as follows:

Pre-hydrolysis treatment increased the phenolic hydroxyl content of MWL. Under pre-treatment conditions of 160°C and 30 min, the reactivity of the lignin-based adhesive was improved, and the bonding strength increased.

Utilizing pre-hydrolyzed Mason pine MWL as the adhesive matrix, the optimized thermal compression protocol was defined as: curing temperature of 150°C, pressing interval of 4.17 min/mm, and unilateral resin loading of 100 g/m². With these parameters, the laminated timber product attained dry shear resistance of 4.34 MPa and wet shear resistance of 1.78 MPa, fulfilling the statutory criteria for Type III plywood under national regulatory frameworks.Mechanistic investigation revealed that throughout the thermal compression process, lignin experienced both depolymerization and re-condensation phenomena, culminating in the formation of a homogeneous and compact adhesive film on the plywood substrate surface.Simultaneously, lignin penetrated into the cell lumens, forming stable cross-links, synergistically enhancing the overall bonding strength.

Pre-hydrolysis significantly improved the reactivity of MWL, effectively enhancing its bonding performance as an adhesive. This provides new ideas for the preparation of lignin-based adhesives.

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