Preparation and Performance Optimization of Tannin-modified Cold-Setting MUF Resin and Glued Wood

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The modification of melamine-urea-formaldehyde (MUF) resin was studied using plant tannins, focusing on the effects of tannin addition stage and dosage on resin properties. Second-stage addition failed due to system gelation caused by the acidic polycondensation environment. Although third-stage addition further reduced free formaldehyde content, the resulting viscosity surge led to difficulties in glue spreading, accompanied by significant deterioration in bond strength and water resistance. First-stage addition of bayberry tannin yielded optimal results, with 6% identified as the critical optimal dosage. At this level, the resin exhibited a viscosity of 206 mPa·s, free formaldehyde content of 0.09%, dry and wet shear strengths of 7.2 and 5.8 MPa, and impact toughness of 6.8 kJ/m^2. Beyond 6% addition, viscosity increased exponentially, free formaldehyde rebounded, and water resistance deteriorated sharply. Differential scanning calorimetry (DSC) analysis revealed that tannin modification reduced the curing peak temperature (by 2.7°C for bayberry tannin) and accelerated crosslinking reactions. The first-stage addition of 6% bayberry tannin was determined as the optimal technical solution, achieving a balanced compromise among impact toughness, shear strength, formaldehyde reduction efficacy, and process feasibility.

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INTRODUCTION

Glued wood maximally preserves the solid structure of wood. Through processes including drying, defect removal, and optimized lay-up, its compressive resistance, tensile strength, and material uniformity are significantly enhanced compared to solid wood. This enables the efficient utilization of small-diameter and inferior-grade timber resources, thereby substantially improving the comprehensive utilization rate of wood. Consequently, glued wood has become one of the primary forms of timber construction in technologically advanced countries, with broad application prospects (Yin *et al.* 2022; Du *et al*. 2024; Giv *et al*. 2024; Santos *et al*. 2024; Wight *et al*. 2024).

The adhesive is the critical factor determining the water resistance, durability, and mechanical properties of glued wood. Currently, melamine-urea-formaldehyde (MUF) cocondensation resin has emerged as a hotspot in structural adhesive development due to its excellent water resistance and bonding strength.

However, the cured MUF resin exhibits short molecular network segments, excessively high crosslinking density, and substantial steric hindrance, restricting molecular chain rotation and bending. This results in significant brittleness of the adhesive layer and poor impact resistance. During service, stress concentration readily initiates microcrack propagation, compromising structural safety (Song *et al*. 2022; Zhang *et al*. 2022; Li *et al*. 2023; Xu *et al*. 2024).

To address the issues of high brittleness and insufficient toughness in MUF resins, extensive modification studies have been conducted domestically and internationally. Early research primarily focused on adjusting the melamine-to-urea molar ratio, reducing the formaldehyde-to-urea molar ratio, or introducing flexible chain segments to decrease crosslinking density and enhance molecular chain flexibility, thereby improving resin toughness (Luo *et al*. 2019; Zhou *et al*. 2020; Autengruber *et al*. 2021; Zhang *et al*. 2022; Xu *et al*. 2024; Liang *et al*. 2025a). Nevertheless, reducing crosslinking density typically compromises water resistance and bonding strength, making it difficult to simultaneously satisfy the high-strength and water-resistant requirements for structural adhesives. In recent years, utilizing biomass resources to modify MUF resins has attracted considerable research interest. Among these, soy protein, with its long molecular chains and amino acid side chains rich in active functional groups, can toughen MUF resins through dual mechanisms of physical entanglement and chemical crosslinking (Wu *et al*. 2019; Jiang *et al*. 2021; Kan *et al*. 2021; Kawalerczyk *et al*. 2021; Nazerian *et al*. 2023; Liang *et al*. 2025b). However, the poor compatibility between soy protein and MUF resin, coupled with susceptibility to mildew, limits its storage stability.

The modification using natural polyphenolic substances provides an effective pathway to enhance comprehensive performance. Plant tannins, as abundant renewable forest resources widely present in wood, bark, and fruits, possess molecular structures rich in pyrogallol or catechol-type polyphenolic hydroxyl groups, exhibiting high reactivity and strong hydrogen-bonding capability. The phenolic hydroxyl groups in tannins can undergo hydroxymethylation reactions with free formaldehyde in MUF resins, thereby effectively reducing formaldehyde emission (Arias *et al*. 2021; Wu *et al*. 2021; Gu *et al*. 2023; Li *et al*. 2023). Additionally, the rigid benzene ring structures of tannins serve as physical crosslinking nodes interspersed within the resin network (Xiao *et al*. 2022; Xu *et al*. 2022; Liang *et al*. 2024; Oktay *et al*. 2024). By regulating crosslinking density, a "flexibility-rigidity" balance is established, which enhances stress transfer efficiency between molecular chains while introducing energy dissipation mechanisms. This alleviates the brittleness increase caused by excessive crosslinking in MUF systems, thereby improving the toughness and impact resistance of the adhesive layer.

In this study, *Acacia* tannin and bayberry tannin were employed as modifiers to investigate their effects on rheological characteristics, free formaldehyde content, bonding strength, and water resistance when added at different stages of the "alkali-acid-alkali" MUF synthesis process. Furthermore, the dose-response relationship of bayberry tannin added at the first stage was optimized, elucidating the structure-performance relationships between tannin dosage and resin viscosity, formaldehyde reduction efficiency, mechanical properties, and water resistance. This approach of modifying synthetic resins with natural tannins not only provides an effective strategy for reducing the environmental burden of MUF resins and enhancing their toughness and durability, but also offers theoretical foundation and technical reference for developing high-performance, environmentally friendly wood adhesives.

EXPERIMENTAL

Materials

Melamine and urea (both analytical reagent grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. Formaldehyde (37% concentration) and sodium hydroxide (both analytical reagent grade) were obtained from Chengdu Jinshan Chemical Reagent Co., Ltd. Formic acid (analytical reagent grade) was supplied by Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. Bayberry tannin and *Acacia* tannin (industrial grade, particle size approximately 150 μm) with flavonoids content about 78 to 82 wt%, and the non-tannin impurities (mainly carbohydrates, a small amount of inorganic salts and water) content approximately 15 to 18 wt% were provided by Guangxi Wuming Tannin Extract Factory. Rubberwood panels with a density of 650 kg/m³ were purchased from Jinshan Wood Industry, Baoshan District, Shanghai.

Pretreatment of Tannins

Acid-catalyzed hydrolysis was employed for tannin pretreatment. A three-neck round-bottom flask equipped with a mechanical stirrer and reflux condenser was charged with distilled water and tannin raw material. The mixture was stirred and heated to 70 °C, followed by the addition of p-toluenesulfonic acid. The temperature was subsequently raised to 85 °C and maintained for 1 h. After cooling to room temperature, the pH was adjusted to neutral. The resulting products were dried, pulverized, and designated as pretreated *Acacia* tannin and bayberry tannin powders, respectively.

Preparation of MUF Resins

Control MUF resins were synthesized using a three-stage "alkali-acid-alkali" polycondensation process (Liang *et al*. 2025b). In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, and reflux condenser, a predetermined quantity of formaldehyde was added at 50 °C under water bath conditions. The pH was adjusted to 9.0, followed by the addition of the first batch of urea and melamine. The temperature was raised to 90 °C for the hydroxymethylation reaction (Stage 1). The pH was then adjusted to 5.0, and the mixture was maintained at 90 °C for 60 min for polycondensation (Stage 2). Subsequently, the pH was readjusted to 8.7 to 8.9, the second batch of melamine was added, and the reaction continued at constant temperature for 100 min (Stage 3). Upon completion, the pH was adjusted to 9.0, the temperature was lowered to 45 °C, and the second batch of urea was added and maintained for 10 min. Finally, the pH was ultimately set to 8.0 to balance storage stability against curing activity, and the product was discharged and stored.

Tannin-modified MUF resins were prepared by staged addition, with 6% pretreated tannin introduced (based on total urea) at Stages 1, 2, and 3 of the aforementioned process, respectively. Sample nomenclature was designated as follows: *Acacia* tannin-modified groups were denoted as XMUF1 (Stage 1 addition), XMUF2 (Stage 2 addition), and XMUF3 (Stage 3 addition) according to addition sequence. Bayberry tannin-modified groups were designated as YMUF1 (Stage 1 addition), YMUF2 (Stage 2 addition), and YMUF3 (Stage 3 addition). During the preparation of the adhesive, 3% of the curing agent was added and thoroughly mixed. Then it was used for the production of glued wood.

The tests for viscosity, solid content and free formaldehyde content were in accordance with GB/T 14074 (2017).

Preparation and Performance Testing of Glued Wood

Glued wood specimens were fabricated using cold-pressing in accordance with GB/T 26899 (2022). Rubberwood sapwood with dimensions of 30 mm × 25 mm × 10 mm was selected. Double-sided glue application of 300 g/m^2 was conducted using a manual double-sided roller coating method, followed by 20 min open assembly time at room temperature. The assemblies were then pressed in a flat vulcanizing machine (pressure 3.5 MPa, duration 2 h) with a bonding area of 25 mm × 25 mm. Cured specimens were subjected to shear strength testing.

Rubberwood glued wood specimens with dimensions of 75 mm × 50 mm × 10 mm were prepared using the aforementioned cold-pressing and subjected to 24 h water immersion delamination testing at room temperature according to GB/T 26899 (2022).

Impact Toughness Testing

Impact strength was determined in accordance with GB/T 1043.1 (2008). Resin samples were cast and cured into unnotched Charpy specimens with a width of 10 mm and thickness of 4 mm. Impact strength was measured using a Charpy impact tester.

Differential Scanning Calorimetry (DSC) Analysis

DSC measurements were performed using a DSC 204 F1 instrument (Netzsch, Germany). Test parameters: temperature range 30 to 170 °C, heating rate 10 °C/min, nitrogen atmosphere, sample mass 5 to 8 mg.

Statistical Analysis

The data were processed using Origin 2024 software, and the significance of differences was judged *via* the one-way analysis of variance (ANOVA) ($p < 0.05$). The error bars represent standard deviation.

RESULTS AND DISCUSSION

Effects of Tannin Addition Stage on Performances of MUF

The classical "alkali-acid-alkali" synthesis process of MUF resin provides three potential reaction windows for tannin introduction (Zhang *et al*. 2022; Xu *et al*. 2024). The selection of tannin addition stage directly determines the rheological characteristics, chemical structure, and ultimate bonding performance of the modified resin. The influence patterns of *Acacia* tannin and bayberry tannin addition at different stages including hydroxymethylation stage (Stage 1), acidic condensation stage (Stage 2), and alkaline post-condensation stage (Stage 3) on MUF resin properties are presented in Table 1.

The viscosity of control MUF resin was 38 mPa·s. When 6% *Acacia* tannin was added at Stage 1, the viscosity of XMUF1 increased sharply to 346 mPa·s; addition at Stage 2 resulted in immediate gelation and synthesis failure. This phenomenon occurs because Stage 2 primarily involves MUF polycondensation reactions, where the system pH is adjusted to acidic conditions. Such conditions significantly accelerate the dehydration condensation between hydroxymethylurea and hydroxymethylmelamine molecules with exponential molecular weight growth. The introduction of tannin at this stage, with its abundant phenolic hydroxyl groups undergoing vigorous condensation reactions with highly reactive hydroxymethyl groups under acidic catalysis, disrupts the kinetic equilibrium of the original polycondensation process. This exogenous introduction of

highly reactive sites causes local crosslinking density to increase dramatically, forming an irreversible three-dimensional network structure, macroscopically manifested as instantaneous viscosity increase and rapid gelation. XMUF3 (Stage 3 addition) exhibited a further viscosity increase to 1880 mPa·s, reaching nearly 50 times that of the control, indicating that even under alkaline conditions, *Acacia* tannin can undergo significant crosslinking reactions with hydroxymethyl and amino groups in the resin, resulting in sharp molecular weight increase. In contrast, bayberry tannin-modified systems demonstrated similar yet distinct patterns. YMUF1 (Stage 1 addition) showed a viscosity of 206 mPa·s, which was 40.5% lower than XMUF1. YMUF2 also underwent gelation at Stage 2, confirming that the rapid reaction characteristics between tannin and hydroxymethylated products under acidic conditions are independent of tannin species, exhibiting universal regularity. YMUF3 (Stage 3 addition) exhibited a viscosity of 1540 mPa·s, though lower than XMUF3, still reaching 40.5 times that of the control. These results demonstrate that tannin addition stage is a critical factor governing the rheological performance of MUF resins. Stage 2 addition leads to an increase in viscosity or even gelation due to the high reactivity of tannins, while Stage 3 addition, although yielding stable resins, results in significantly elevated viscosity, posing challenges to glue application processes.

The introduction of both tannins substantially reduced free formaldehyde content in MUF resin, with pronounced stage-dependent effects. The control group exhibited 0.27% free formaldehyde, while XMUF1 and XMUF3 decreased to 0.15% and 0.11%, respectively, representing reductions of 45% and 59%. Bayberry tannin demonstrated superior formaldehyde reduction efficacy, with YMUF1 and YMUF3 achieving free formaldehyde contents of merely 0.09% and 0.06%, corresponding to 67% and 78% reductions compared to the control. This result is expected to primarily originate from the abundant phenolic hydroxyl groups in tannin molecules undergoing hydroxymethylation at the activated aromatic positions of tannin flavonoid units with free formaldehyde in the resin, converting formaldehyde into stable chemically bonded forms, thereby effectively reducing free formaldehyde emission (Li *et al*. 2023; Xu *et al*. 2024). Notably, tannin addition stage significantly influences formaldehyde reduction effectiveness. For both tannins, Stage 3 addition (XMUF3, YMUF3) exhibited superior formaldehyde scavenging compared to Stage 1 addition (XMUF1, YMUF1). This may be attributed to the fact that at Stage 3, the resin system has completed primary condensation reactions with relatively higher free formaldehyde concentrations, allowing more efficient formaldehyde capture by introduced tannins. At Stage 1, however, portions of formaldehyde have not yet participated in urea and melamine hydroxymethylation reactions. Competitive reactions with tannin may affect subsequent resin construction. There may be incomplete hydroxymethylation, leaving residual free formaldehyde physically entrapped rather than chemically bonded. Such formaldehyde has the potential to be released during curing or service, resulting in relatively lower formaldehyde reduction efficiency. Bayberry tannin exhibited superior formaldehyde reduction performance, possibly related to its unique chemical composition and molecular structural characteristics, where these structural units possess stronger formaldehyde capture capabilities (Liang *et al*. 2025c,d).

The tannin addition stage exerted complex influences on dry shear strength of glued wood. The control group demonstrated 6.4 MPa dry shear strength. XMUF1 exhibited reduced dry shear strength of 5.2 MPa, a 19% decrease from control, indicating that *Acacia* tannin introduction at the hydroxymethylation stage negatively impacts resin crosslinking density and bonding performance. However, YMUF1 significantly enhanced dry shear strength to 7.2 MPa, an 12% improvement over control, demonstrating a reinforcing effect.

This discrepancy reveals essential differences in chemical composition and reaction characteristics between the two tannins. Bayberry tannin likely forms a more favorable "flexibility-rigidity" balance within the resin network through its specific molecular structure (moderate reactivity and steric hindrance), participating in crosslinking reactions without excessively interfering with backbone formation, thereby optimizing adhesive layer mechanical properties (Liang *et al*. 2025c,d). XMUF3 and YMUF3 exhibited dry shear strengths of 4.66 and 4.82 MPa, respectively, further decreasing from their Stage 1 counterparts by 27% and 25% relative to control; high viscosity during Stage 3 addition impedes adequate resin wetting of wood surfaces, while late-introduced tannins primarily distribute at resin surfaces or localized regions. The late addition causes difficulty in forming uniform and effective crosslinking networks and results in significantly diminished bonding strength.

Comprehensive analysis indicates that Stage 1 represents the optimal window for tannin introduction. The alkaline environment at this stage effectively regulates reaction rates between tannin and hydroxymethylated products, avoiding gelation risks under acidic conditions. In addition, the viscosity increase remains controllable, ensuring resin fluidity and processability for glue application. From a chemical structural perspective, early introduction enables tannins to fully participate in resin construction, embedding into crosslinking networks through hydroxymethylation reactions rather than surface enrichment observed in late addition, thereby forming more uniform and effective cocondensation structures.

Table 1. The Influence of Adding Tannin at Three Stages on the Performance of MUF Resin

Resin	Viscosity (mPa·s)	Free formaldehyde (%)	Dry bonding strength (MPa)
Control	38	0.27	6.42
XMUF1	346	0.15	5.18
XMUF2	--	--	--
XMUF3	1880	0.11	4.66
YMUF1	206	0.09	7.16
YMUF2	--	--	--
YMUF3	1540	0.06	4.82

Note: "--" indicates that the adhesive has undergone gelation.

Effects of Bayberry Tannin Dosage on Viscosity of MUF

Based on the preceding results, bayberry tannin was employed as a modifier and incorporated at Stage 1 for MUF modification. The test results are presented in Fig. 1. The influence of bayberry tannin dosage on MUF resin rheological properties exhibited characteristic dose-dependent behavior. As the dosage increased from 4% to 10%, resin viscosity progressively rose from 160 to 1144 mPa·s, representing a 6.2-fold increase, demonstrating the substantial regulatory effect of tannin on system fluidity. In the low-dosage range (4 to 6%), viscosities of 160 and 206 mPa·s, respectively, were observed. Although these values represented 3.2 to 5.4-fold increases compared to the control, they remained within acceptable ranges for laboratory cold-pressing application, though industrial roller coating may tolerate higher viscosities. However, upon exceeding the 6% critical threshold, viscosity exhibited nonlinear surge: at 8% dosage, viscosity jumped to 884 mPa·s, more than 3-fold abrupt increase from the 6% level; at 10% dosage, viscosity further increased to 1144 mPa·s, reaching 30.1 times that of the control. At this point, resin

wetting and spreading properties deteriorated significantly, rendering uniform coating application impractical.

This viscosity abrupt transition phenomenon reveals the critical effect in reaction kinetics between parallel hydroxymethylation of urea, melamine, and tannin with formaldehyde, followed by intermolecular cocondensation. At lower dosages (≤6%), phenolic hydroxyl groups in tannin molecules undergo controlled hydroxymethylation reactions with formaldehyde and hydroxymethylated products. The generated hydroxymethyl tannins serve as branching units orderly embedded within the resin network, with molecular chain growth proceeding steadily and viscosity increasing linearly. When the dosage exceeds the critical threshold (6 to 8%), excessive tannin molecules provide an overabundance of reactive sites, resulting in sharply increased intermolecular crosslinking density. Simultaneously, the self-condensation tendency of high-concentration tannins and the formation of multiple hydrogen-bonding networks disrupt the original reaction kinetic equilibrium, triggering nonlinear viscosity surge. These findings indicate that a dosage of approximately 6% represents an optimal compromise between fluidity and reactivity.

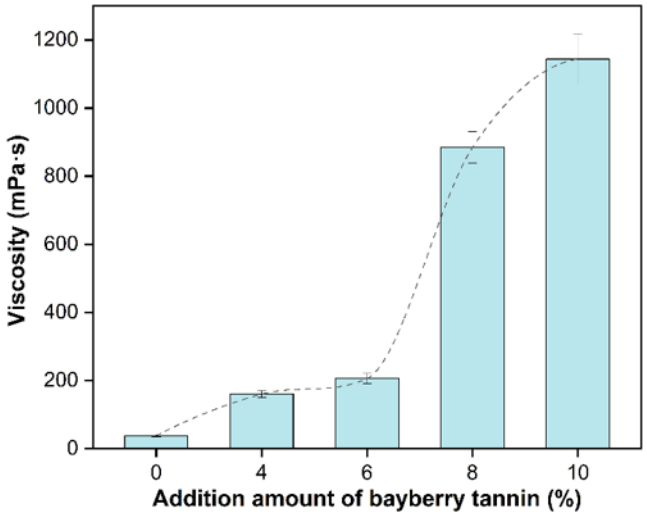

Fig. 1. The effect of addition amount of bayberry tannin on the viscosity of MUF resin

Effects of Bayberry Tannin Dosage on Free Formaldehyde Content of MUF

As illustrated in Fig. 2, the influence of bayberry tannin dosage on free formaldehyde content of MUF resin exhibited a descending-ascending pattern, revealing the complex equilibrium between formaldehyde capture and reaction competition. The control group demonstrated 0.27% free formaldehyde content. Upon addition of 4% bayberry tannin, free formaldehyde decreased to 0.13%, representing a halving, indicating that even small quantities of tannin can effectively capture formaldehyde through hydroxymethylation reactions between phenolic hydroxyl groups and free formaldehyde. When dosage increased to 6%, free formaldehyde further declined to 0.09%, achieving two third reduction from control and representing the highest formaldehyde reduction efficacy within the experimental range. However, as dosage continued to increase to 8% and 10%, free formaldehyde content rebounded to 0.12% and 0.14%, respectively.

At lower dosages (4 to 6%), tannin molecules function as formaldehyde scavengers, with their phenolic hydroxyl groups undergoing electrophilic addition reactions with free formaldehyde in the resin to generate stable hydroxymethyl tannin derivatives. These

parallel reactions are competitive in formaldehyde consumption but synergistic in building up hybrid molecular networks. Tannins fully participate in resin network construction, with formaldehyde effectively immobilized within crosslinked structures. When dosage exceeds the critical value (approximately 6%), excessive tannin molecules compete with urea and melamine for limited formaldehyde resources, with portions of tannin remaining in free or semi-bound states within the resin system due to incomplete hydroxymethylation. Simultaneously, high-concentration tannin causes sharp viscosity increase in the system, restricting molecular diffusion and impeding hydroxymethylation reaction kinetics, thereby preventing adequate capture of unreacted free formaldehyde.

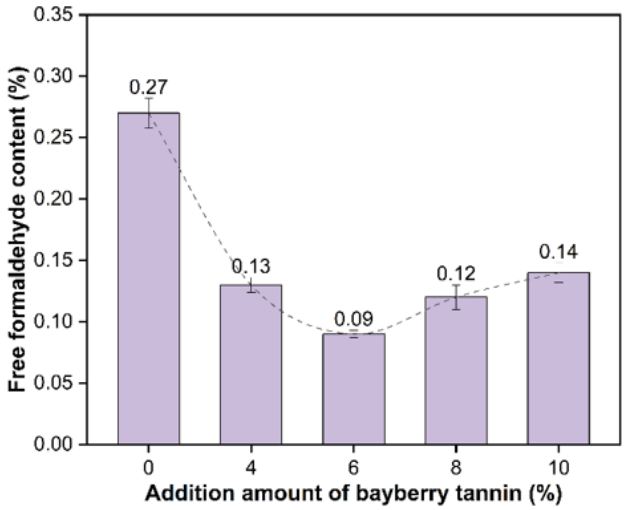

Fig. 2. The effect of addition amount of bayberry tannin on the free formaldehyde of MUF resin

Effects of Bayberry Tannin Dosage on Bonding Strength of Glued Wood

As illustrated in Fig. 3, tannin dosage significantly influenced shear strength. Dry shear strength reached a peak of 7.2 MPa at 6% dosage, representing an 11.5% increase over the control (6.4 MPa), and subsequently declined to 6.1 MPa at 10% dosage. Wet shear strength also achieved optimum performance at 6% dosage (5.8 MPa); however, its deterioration trend was more pronounced, falling to 5.1 MPa at 8% dosage—below that of the unmodified control (5.4 MPa)—and further decreasing to 4.8 MPa at 10% dosage, representing an 19% loss from peak value. At this point, wet-state load-bearing capacity had significantly deteriorated below baseline levels.

This differential response between dry and wet strength reveals the essential distinction in bond interface failure mechanisms. At the optimal 6% dosage, tannins are orderly incorporated into the MUF network through hydroxymethylation reactions. The moderate viscosity (206 mPa·s) ensures adequate resin wetting of wood surfaces and penetration into cell lumens, forming a dense and uniform interfacial transition layer capable of effective stress transfer under both dry and wet conditions. When dosage exceeds the 6% critical threshold, viscosity increases exponentially, causing loss of resin fluidity and preventing the formation of continuous adhesive layers on wood surfaces. Localized interfacial defects including glue starvation, bubble entrapment, and microporosity emerge. In dry shear testing, these defects can be partially compensated by the high cohesive strength of the resin bulk, resulting in moderate macroscopic strength decay. Under wet water-immersion conditions, however, interfacial micropores serve as preferential channels for moisture ingress. Water molecules penetrating the glue line

weaken interfacial adhesion while inducing adhesive layer swelling and internal stress concentration, leading to preferential interfacial debonding failure. Consequently, wet shear strength exhibits higher sensitivity to interfacial integrity defects, enabling earlier and more pronounced indication of process deterioration caused by excessive addition.

In summary, 6% bayberry tannin dosage represents the sole critical point for simultaneous synergistic optimization of dry and wet shear strength. Under this condition, glued wood possesses excellent dry-state load-bearing capacity (7.2 MPa) combined with superior wet-state durability (5.8 MPa).

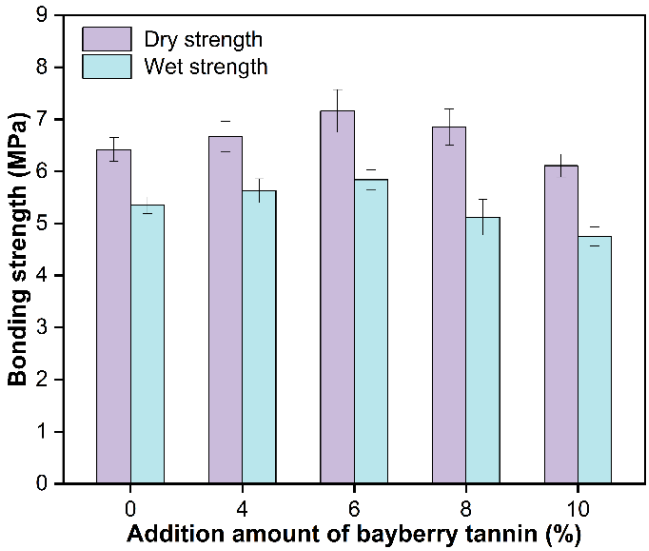

Fig. 3. The effect of addition amount of bayberry tannin on bonding strength of glued wood

Effects of Bayberry Tannin Dosage on Water Resistance of Glued Wood

Water resistance represents a core indicator for evaluating the anti-erosion capability of glued wood against moisture in actual service environments (Liang *et al*. 2025c,d). According to GB/T 26899 (2022), the total delamination percentage after 24 h room-temperature water immersion must be less than 5%, with the maximum delamination rate of any single glue line not exceeding 25%, to qualify as acceptable. The delamination percentage characterizes the degree of cracking and separation of adhesive layers under wet-state stress, reflecting both the intrinsic water resistance of the adhesive and the durability of interfacial adhesion. As illustrated in Fig. 4, bayberry tannin dosage exerted significant modulating effects on wet-state durability of glued wood, with delamination percentages exhibiting non-monotonic variation. Initial optimization was followed by deterioration. The control group demonstrated a total delamination of 4.3% and maximum single-layer delamination of 11.5%, satisfying standard requirements but approaching the critical total delamination threshold (5%). These findings indicated the presence of localized water-resistance weak links in glue lines of unmodified MUF resin. Upon addition of 4% bayberry tannin, total delamination percentage marginally increased to 4.5%, remaining within acceptable limits, while maximum single-layer delamination decreased to 9.6%, demonstrating improved adhesive layer uniformity. When dosage increased to 6%, both total and maximum single-layer delamination dropped to 0%, indicating no cracking or separation in glue lines after water immersion-drying cycles, with adhesive layer integrity reaching ideal conditions and water resistance substantially exceeding standard qualification thresholds.

However, upon exceeding the 6% critical threshold, delamination failure modes underwent reversal deterioration. At 8% dosage, although the total delamination percentage maintained qualified levels at 3.9%, maximum single-layer delamination rebounded to 8.4%, foreshadowing the initiation of localized adhesive layer defects. More critically, at 10% dosage, total delamination surged abruptly to 15.6%, substantially exceeding the 5% qualification limit. Despite the maximum single-layer delamination of 18.8% remaining below the 25% individual indicator, the exceeding total delamination resulted in overall disqualification of this sample group for water resistance performance. This deterioration originated from process failure induced by viscosity surge. Specifically, at 10% dosage, resin viscosity reached 1144 mPa·s with severely restricted fluidity; high-viscosity resin inadequately wetted wood surfaces and failed to penetrate vessels and cell lumens, resulting in substantial microporosity and weak bonding zones at the interface after curing. These interfacial defects constituted preferential channels for moisture ingress and stress concentration. During room-temperature water immersion, water molecules readily infiltrated glue lines along these micropores, weakening interfacial adhesion and causing adhesive layer debonding and delamination under wet conditions.

Therefore, 6% bayberry tannin dosage was found to represent the sole window ensuring excellent wet-state durability and process stability of glued wood. Under this condition, glue line integrity is optimal, with delamination rates far superior to qualified thresholds specified in GB/T 26899 (2022). Exceeding this threshold, particularly at 10% dosage, results in serious quality defects and service safety hazards due to excessive adhesive layer delamination.

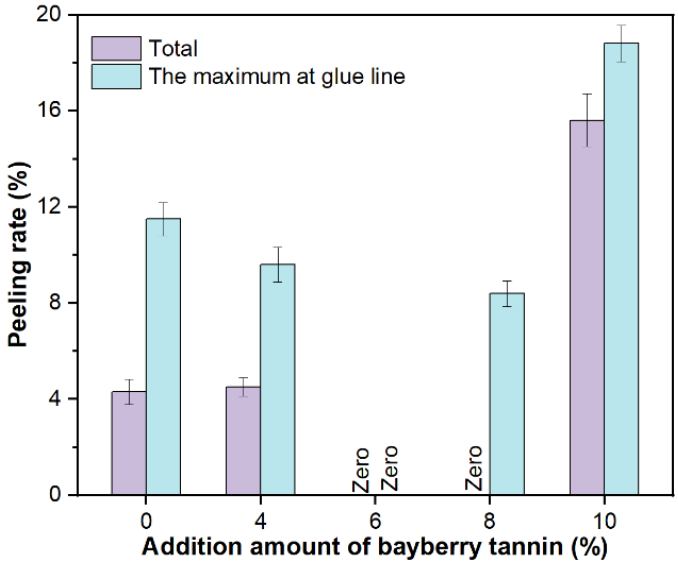

Fig. 4. The effect of addition amount of bayberry tannin on the percent delamination of glued wood

Effects of Bayberry Tannin Dosage on Impact Toughness of MUF

As illustrated in Fig. 5, the influence of bayberry tannin dosage on impact toughness of MUF resin exhibited an ascending-descending pattern, reflecting the delicate regulation of resin rigidity-toughness balance by tannin introduction. The control group demonstrated an impact toughness of 6.3 kJ/m^2. Upon addition of 4% bayberry tannin, impact toughness increased to 6.6 kJ/m^2, representing a 3.8% improvement, indicating that even small

quantities of tannin can enhance resin mechanical properties. When dosage increased to 6%, impact toughness reached a peak of 6.8 kJ/m^2, a 7.4% improvement over the control, with dry shear strength of this group simultaneously achieving optimum performance (7.2 MPa), realizing synergistic enhancement of strength and toughness. However, when dosage increased to 8% and 10%, impact toughness declined to 6.7 and 6.4 kJ/m^2, respectively—although still slightly above or approaching control levels, an evident decay trend had emerged.

This variation pattern corroborates the dosage-dependent behavior of viscosity and free formaldehyde content, collectively revealing the structure-property relationships of bayberry tannin in MUF resins. At low dosages (4 to 6%), tannins are embedded into crosslinked networks through hydroxymethylation reactions. Their rigid benzene ring structures provide skeletal support for stress transfer, while hydrogen bonding between phenolic hydroxyl groups and resin chain segments imparts deformation capability to adhesive layers. This reinforcing and toughening effect originates from tannins serving as multifunctional crosslinking nodes that optimize network topology—increasing crosslinking density to bear static loads while introducing energy dissipation mechanisms to resist dynamic impact (Fig. 6).

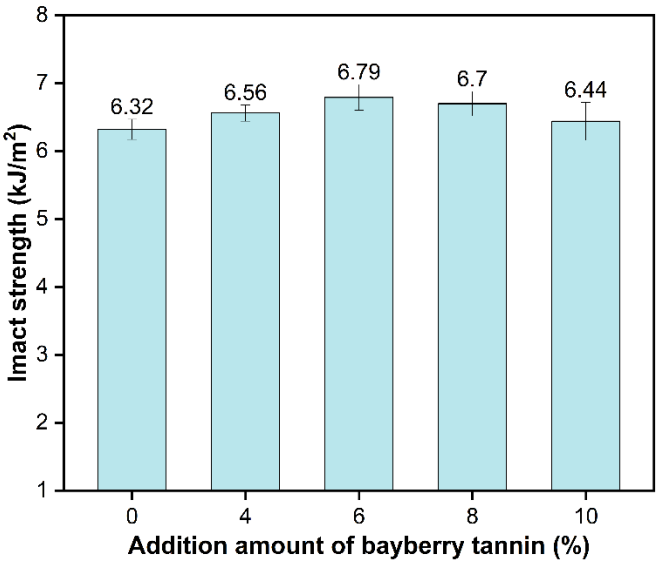

Fig. 5. The effect of addition amount of bayberry tannin on the impact strength of MUF resin

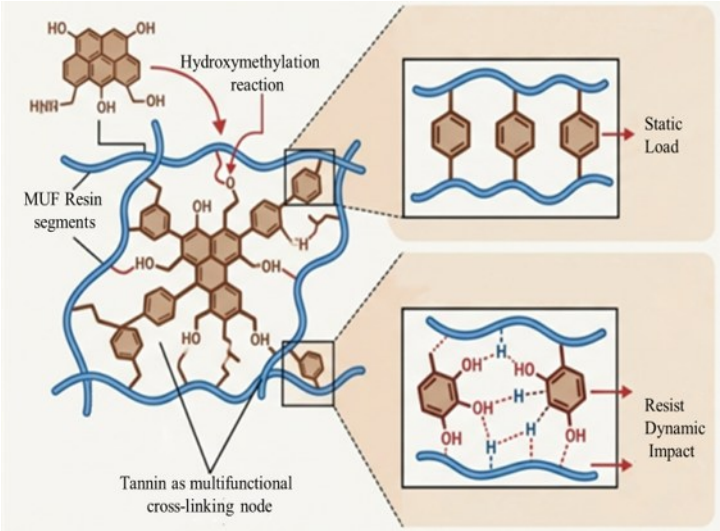

Fig. 6. The mechanism of tannin toughening modification of MUF resin

When dosage exceeds 6%, sharply elevated viscosity leads to uneven glue application, readily forming stress concentration points within the resin; simultaneously, the self-condensation tendency of excessive tannin causes local over-crosslinking and regionalized defects in the network structure, lacking effective energy dissipation pathways during crack propagation, resulting in decreased impact toughness. Notably, at 10% dosage, impact toughness (6.4 kJ/m^2) had declined to approach control levels, while free formaldehyde content rebounded to 0.14%, indicating that excessive addition not only causes process performance deterioration but may also result in dual losses in environmental and mechanical performance. Therefore, 6% bayberry tannin dosage represents the optimal balance point compromising impact toughness, shear strength, formaldehyde reduction efficacy, and process feasibility.

Curing Performance Analysis

The effects of tannin modification on curing behavior of MUF resins were investigated using DSC, with results presented in Fig. 7. The control MUF exhibited a curing peak temperature of 111.5 °C (a), whereas tannin modification significantly reduced curing temperatures with species-dependent magnitude. *Acacia* tannin-modified MUF showed a decreased curing peak temperature of 110.7 °C (b), representing a 0.8 °C reduction from the control; bayberry tannin modification further decreased this to 108.8 °C (c), achieving a reduction magnitude of 2.7 °C. This systematic variation demonstrates that tannin introduction effectively regulated resin curing reaction kinetics, altering the construction process of crosslinked networks.

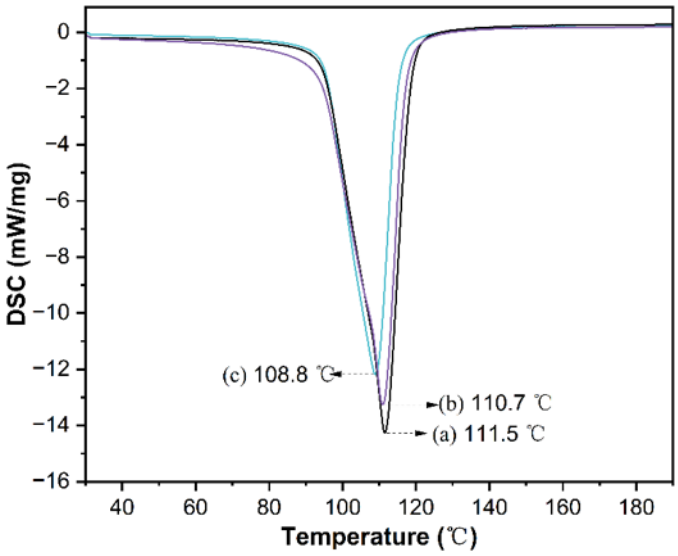

Fig. 7. DSC results of MUF resin

The reduction in curing peak temperature primarily originates from the incorporation of reactive polyphenolic structures into the MUF resin network. During thermal curing, the polyphenolic structure of tannins serves as exogenous reaction sites, with their phenolic hydroxyl groups undergoing electrophilic substitution reactions with residual hydroxymethyl groups and methylene ether linkages in MUF resins. This introduction of exogenous multifunctional crosslinking nodes significantly increases intermolecular collision frequency and reaction probability, effectively reducing the apparent activation energy of crosslinking reactions. Consequently, the resin system achieves peak crosslinking reaction rates under lower thermal input conditions, macroscopically manifested as DSC exothermic peak shift toward lower temperatures. The more pronounced curing temperature reduction induced by bayberry tannin compared to *Acacia* tannin is consistent with its higher reactivity demonstrated in this study, indicating that active structural units such as pyrogallol in bayberry tannin molecules more readily react with electrophilic groups in the resin, accelerating rapid construction of crosslinked networks during initial curing stages.

CONCLUSIONS

1. Tannin addition stage is a critical factor governing melamine urea formaldehyde (MUF) resin performance. Stage 2 addition resulted in gelation due to violent reactions between tannin and hydroxymethyl groups under acidic polycondensation conditions, rendering the process infeasible. Although Stage 3 addition was able to capture more free formaldehyde, excessively high viscosity resulted in poor wetting, with significant deterioration in bonding strength and water resistance. Stage 1 was found to represent the optimal window for tannin introduction, where alkaline conditions enable controlled reaction rates, ensuring resin fluidity and process feasibility.
2. Tannin species significantly influence modification efficacy. Bayberry tannin exhibited superior performance due to its moderate reactivity and lower steric hindrance of proanthocyanidin structures, enabling more uniform cocondensation and effective

formaldehyde capture compared to *Acacia* tannin.

3. Bayberry tannin dosage exhibited critical threshold effects. As dosage was increased from 4% to 10%, resin viscosity demonstrated an initial linear rise followed by exponential growth, with 6% serving as the inflection point. Free formaldehyde content followed a descending-ascending pattern, reaching minimum of 0.09% at 6% dosage. Bonding strength, delamination rate, and impact toughness all achieved optimal values at 6% dosage, with sharp deterioration observed beyond this threshold.
4. Integrating rheological, environmental, mechanical, and durability indicators, 6% bayberry tannin added at Stage 1 was determined as the optimal process parameter for cold-setting MUF resins. This study provides precise formulation design and process control guidelines for industrial application of tannin-modified amino resins.

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REFERENCES CITED

Arias, A., Gonzalez-Garcia, S., Feijoo, G., and Moreira, M. (2021). "Tannin-based bio-adhesives for the wood panel industry as sustainable alternatives to petrochemical resins," *J. Ind. Ecol.* 26(2), 627-642. https://doi.org/10.1111/jiec.13210

Autengruber, M., Lukacevic, M., Gröstlinger, C., and Füssl, J. (2021). "Finite-element-based prediction of moisture-induced crack patterns for cross sections of solid wood and glued laminated timber exposed to a realistic climate condition," *Constr. Build. Mater.* 271, article 121775. https://doi.org/10.1016/j.conbuildmat.2020.121775

Du, H., Chen, G., Fu, W., and Hu, X. (2024). "Study on bending performance of prefabricated glulam-cross laminated timber composite floor," *Rev. Adv. Mater. Sci.* 63(1), article 20240053. https://doi.org/10.1515/rams-2024-0053

GB/T 1043.1 (2008). "Determination of impact performance of simply supported plastic beams," Standardization Administration of China, Beijing.

GB/T 14074 (2017). "Testing methods for wood adhesives and resins," Standardization Administration of China, Beijing.

GB/T 26899 (2022). "Structural glued laminated timber," Standardization Administration of China, Beijing.

Giv, A.N., Fu, Q., Chen, Z., Leusmann, T., Kasal, B., Lowke, D., and Yan, L. (2024). "Experimental study and numerical simulation of adhesively bonded timber-concrete composite panels: Bending behavior, adhesive shear and peel stress distributions," *Eng. Struct.* 307, article 117872. https://doi.org/10.1016/j.engstruct.2024.117872

Gu, W., Ding, X., Tang, M., Gong, F., Yuan, S., and Duan, J. (2023). "Study on the preparation process optimization of plywood based on a full biomass tannin-sucrose wood adhesive," *J. Renew. Mater.* 11(8), 3245-3259. https://doi.org/10.32604/jrm.2023.027461

Jiang, K., Lei, Z., Yi, M., Lv, W., Jing, M., Feng, Q., Tan, H., Chen, Y., and Xiao, H. (2021). "Improved performance of soy protein adhesive with melamine-urea-formaldehyde prepolymer," *RSC Adv.* 11(44), 27126-27134. https://doi.org/10.1039/D1RA00850A

Kan, Y., Sun, B., Kan, H., Bai, Y., and Gao, Z. (2021). "Preparation and characterization of a melamine-urea-glyoxal resin and its modified soybean adhesive," *Int. J. Adhes. Adhes.* 111, article 102986. https://doi.org/10.1016/j.ijadhadh.2021.102986

Kawalerczyk, J., Siuda, J., Dziurka, D., Mirski, R., Wozniak, M., and Stuper-Szablewska, K. (2021). "The soy flour as an extender for UF and MUF adhesives in birch plywood production," *Wood Research* 66(6), 1015-1031. https://doi.org/10.37763/wr.1336-4561/66.6.10151031

Li, D., Yu, L., Li, L., Liang, J., Wu, Z., Xu, X., Zhong, X., and Gong, F. (2023). "Melamine-urea-formaldehyde resin adhesive modified with recycling lignin: Preparation, structures and properties," *Forests* 14(8), article 1625. https://doi.org/10.3390/f14081625

Li, J., Lei, H., Xi, X., Li, C., Hou, D., Song, J., and Du, G. (2023). "A sustainable tannin-citric acid wood adhesive with favorable bonding properties and water resistance," *Ind. Crop. Prod.* 201(1), article 116933. https://doi.org/10.1016/j.indcrop.2023.116933

Liang, J., Li, D., Zhong, X., Wu, Z., Cao, M., Yang, G., Yin, S., and Gong, F. (2024). "Crosslinking mechanism of tannin-based adhesives based on model compounds: Copolycondensation of resorcinol with dimethylol urea," *Forests* 15(1), article 98. https://doi.org/10.3390/f15010098

Liang, J., Zhang, B., Wu, L., Yang, Y., Long, C., Song, Z., Yang, H., and Wu, Z. (2025a). "Effect of poly (vinyl alcohol) on the properties of cold-setting melamine-urea-formaldehyde resin adhesive," *Materials* 18(22), article 5125. https://doi.org/10.3390/ma18225125

Liang, J., Zhang, B., Yang, H., Meng, T., Chen, C., Li, H., Cheng, L., and Wu, Z. (2025b). "Effect of soy protein on the toughness and bonding performances of cold-setting melamine-urea-formaldehyde resin adhesive," *BioResources* 20(3), 5828-5842. https://doi.org/10.15376/biores.20.3.5828-5842

Liang, J., Yang, G., Zhang, M., Lan, L., He, X., Yang, H., Yang, Y., He, Y., Yang, H., and Wu, Z. (2025c). "Morphological remodeling and performance of cured tannin-sucrose adhesive layer: Enhancement by catalyst," *BioResources* 20(4), 10605-10617. https://doi.org/10.15376/biores.20.4.10605-10617

Liang, J., Yin, S., Li, C., Lan, L., He, X., Yang, H., Yang, Y., He, Y., Yang, H., and Wu, Z. (2025d). "Tannin-sucrose adhesive properties: A comparison of bayberry and *Acacia* tannins," *BioResources* 20(4), 10594-10604. https://doi.org/10.15376/biores.20.4.10594-10604

Luo, J., Zhang, J., Gao, Q., Mao, A., and Li, J. (2019). "Toughening and enhancing melamine-urea-formaldehyde resin properties *via in situ* polymerization of dialdehyde starch and microphase separation," *Polymers* 11(7), article 1167. https://doi.org/10.3390/polym11071167

Nazerian, M., Naderi, F., and Papadopoulos, A.N. (2023). "Application of the artificial neural network to predict the bending strength of the engineered laminated wood produced using the hydrolyzed soy protein-melamine urea formaldehyde copolymer adhesive," *J. Compos. Sci.* 7(5), article 191. https://doi.org/10.3390/jcs7050191

Oktay, S., Pizzi, A., Köken, N., and Bengü, B. (2024). "Tannin-based wood panel adhesives," *Int. J. Adhes. Adhes.* 130, article 103621. https://doi.org/10.1016/j.ijadhadh.2024.103621

Santos, P., Cardoso, L., and Dias, A.M.P.G. (2024). "Alternated cross-laminated timber (aCLT) panels: development and mechanical characterization," *Eur. J. Wood Prod.* 82, 2065-2083. https://doi.org/10.1007/s00107-024-01583-3

Song, B., Zhu, X., Wang, W., Wang, L., Pei, X., Qian, X., Liu, L., and Xu, Z. (2022). "Toughening of melamine-formaldehyde foams and advanced applications based on functional design," *J. Ind. Eng. Chem.* 119, 130-152. https://doi.org/10.1016/j.jiec.2022.11.069

Wight, N., Viau, C., and Heffernan, P. (2024). "Behaviour of glued-laminated timber beams under impact loading," *Can. J. Civil Eng.* 51(7), 753-768. https://doi.org/10.1139/cjce-2023-0298

Wu, Z., Chen, S., Liang, J., Li, L., Xi, X., Deng, X., Zhang, B., and Lei, H. (2021). "Plasma treatment induced chemical changes of alkali lignin to enhance the performances of lignin-phenol-formaldehyde resin adhesive," *J. Renew. Mate.* 9(11), 1959-1972. https://doi.org/10.32604/jrm.2021.016786

Wu, Z., Zhang, B., Zhou, X., Li, L., Yu, L., Liao, J., and Du, G. (2019). "Influence of single/collective use of curing agents on the curing behavior and bond strength of soy protein-melamine-urea-formaldehyde (SMUF) resin for plywood assembly," *Polymers* 11(12), article 1995. https://doi.org/10.3390/polym11121995

Xiao, G., Liang, J., Li, D., Tu, Y., Zhang, B., Gong, F., Gu, W., Tang, M., Ding, X., Wu, Z., and Lei, H. (2022). "Fully bio-based adhesive from tannin and sucrose for plywood manufacturing with high performances," *Materials* 15(24), article 8725. https://doi.org/10.3390/ma15248725

Xu, G., Tian, H., Xi, X., Song, J., Lei, H., and Du, G. (2022). "Preparation and characterization of urea-formaldehyde adhesives modified with glyoxalated tannin," *Eur. J. Wood Prod.* 80(5), 1215-1223. https://doi.org/10.1007/s00107-022-01819-1

Xu, X., Zhang, B., Yu, L., Li, D., Wu, Z., Liang, J., and Lei, H. (2024). "Melamine formaldehyde resin adhesive toughened with graphene oxide: Structures and properties," *Polym. Test.* 138, article 108557. https://doi.org/10.1016/j.polymertesting.2024.108557

Yin, T., Zhang, J., Wang, Z., Zheng, W., Huang, Q., and Gong, M. (2022). "Shear performance of tongue-and-groove joints for CLT," *Const. Build. Mater.* 322, article 126449. https://doi.org/10.1016/j.conbuildmat.2022.126449

Zhang, B., Wu, Z., Liang, J., Yu, L., Xi, X., Lei, H., and Du, G. (2022). "Effects of polyethylene glycol on the flexibility of cold-setting melamine-urea-formaldehyde resin," *Eur. J. Wood Prod.* 80, 975-984. https://doi.org/10.1007/s00107-022-01801-x

Zhou, X., Peng, J., Wang, W., Essawy, H., and Du, G. (2020). "A novel route to enhance the ductile performance of MF resins by addition of polyamide amine (PA)," *Eur. J. Wood Prod.* 78, 835-837. https://doi.org/10.1007/s00107-020-01555-4

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