



Tough flame-retardant wood fabrication via lignin reassembly

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Abstract

Wood, a renewable and eco-friendly resource, holds significant potential for developing sustainable structural materials. Nevertheless, in advanced engineering applications, natural wood often fails to meet requirements for mechanical performance and flame retardancy. Herein, we present a novel, simple yet highly effective strategy to fabricate tough flame-retardant wood (TF-wood). This approach involves partial delignification using alcohol-amine-based deep eutectic solvents (DESs), followed by N/P-functionalization of the dissolved lignin that is reincorporated into the wood matrix with subsequent hot-pressing. With the incorporation of 20% functionalized lignin, the resulting TF-wood demonstrates a remarkable increase in tensile strength (425.2 MPa), strain (2.9%), and the corresponding toughness reaching 8.1 MJ/m³, 27 times higher than that of natural wood. Additionally, the peak heat release rate (pHRR) of the TF-wood is reduced by 58.3%, and the total heat release (THR) is decreased by 47.8%. Crucially, TF-wood exhibits an ultralow water migration rate, further enhancing its structural stability in humid environments. These combined properties render TF-wood highly attractive for structural applications requiring enhanced fire safety and durability. This study paves the way for designing sustainable, high-performance building materials that integrate multiple functionalities.

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Introduction

Carbon neutrality, which aims to have no negative impact on climate, is a crucial concept in the global fight against climate change. It requires achieving a balance between greenhouse gas emissions and their removal or offsetting. Wood, with its carbon-storage capacity and potential to replace more carbon-intensive materials such as steel, concrete, bricks, and petroleum-based composites, offers a sustainable and renewable solution (Ding et al. 2023). Nevertheless, the widespread application of wood is hindered by its high flammability and low mechanical strength, especially in fire-safety-critical and high-load-bearing scenarios (Chen et al. 2020). The porous physical structure of wood not only facilitates heat transfer and oxygen penetration during combustion but also weakens the intermolecular forces between fibers. Besides, the chemical components of wood, including cellulose, hemicelluloses, and lignin, are rich in combustible elements and functional groups, which also impair its flame-retardant properties.

Inorganic and organic flame retardants have been actively explored to improve wood's flame retardancy via impregnation, chemical reaction or surface coating. For instance, the impregnation of ammonium dihydrogen phosphate can enhance the thermal stability and flame retardancy of delignified wood by creating a dense and cross-linked (P-O-C) structure (Fan et al. 2023). Covalent modification of delignified poplar with boric acid and sodium tetraborate remarkably enhances its flame retardancy, smoke suppression, and mechanical properties (Li et al. 2025). The bio-based flame retardant, phytic acid, also delays ignition, reduces the heat release rate, and lowers the total heat release by promoting the formation of a phosphorus-containing, cross-linked, and aromatic char during wood combustion (Gao et al. 2024; Wang et al. 2023; Yue et al. 2023). However, flame retardants with low water resistance tend to dissolve and leach out from the wood matrix upon water erosion. The loss of key flame-retardant ingredients not only reduces the overall flame retardancy of the wood but also weakens the chemical and physical bonds established during treatment, thereby compromising the wood's mechanical integrity.

The mechanical densification process is regarded as an effective way to enhance the flame retardancy and mechanical properties of wood by reducing porosity, blocking oxygen transmission, and creating intermolecular bonding (Cabral et al. 2022). Still, the rigid lignin in plant cell walls, with a phenylpropane structure, poses challenges to the densification of wood. Therefore, delignification is often employed to facilitate the densification process (Yu et al. 2024; Shi et al. 2024; Song et al. 2018). Notably, lignin plays a crucial role in enhancing wood strength: it binds cellulose and hemicellulose to provide structural support (Jiang et al. 2020), and improves flame retardancy through dual mechanisms: forming a continuous char layer to block heat and oxygen transfer, and releasing active substances to interrupt the combustion chain reaction (Gan et al. 2019). Consequently, the removal of lignin may compromise both the mechanical strength and flame retardancy of wood. Our previous research has shown that alkali lignin can be incorporated as filler and binder into wood followed by densification, reducing molecular transportation and enhancing internal bonding, thereby significantly improving the toughness of reconstructed wood (Gu et al. 2024). Additionally, reactive groups (e.g., phenolic hydroxyl groups)

in wood lignin endow it with high reactivity, enabling facile functionalization with nitrogen- and phosphorus-containing flame retardants (Naseem et al. 2016; Jedrzejczak et al. 2021).

Herein, we designed an alkaline deep eutectic solvent (DES) system by selecting a series of alcohol amines as hydrogen-bond donors (HBDs)—capable of inhibiting the peeling reaction of hemicelluloses—and benzyltrimethylammonium chloride as a hydrogen-bond acceptor (HBA) with phase-catalytic conversion ability for selective delignification. The dissolved lignin was then functionalized with nitrogen and phosphorus and incorporated into wood via hot-pressing to prepare tough and flame-retardant wood. This reconstituted wood, with improved mechanical properties through the formation of hydrogen bonds and chemical bonds, and enhanced flame retardancy via the production of carbonaceous residues, inert gases, and acidic species, holds great promise as a candidate material to meet the growing demands for safety and durability in various applications.

Materials and methods

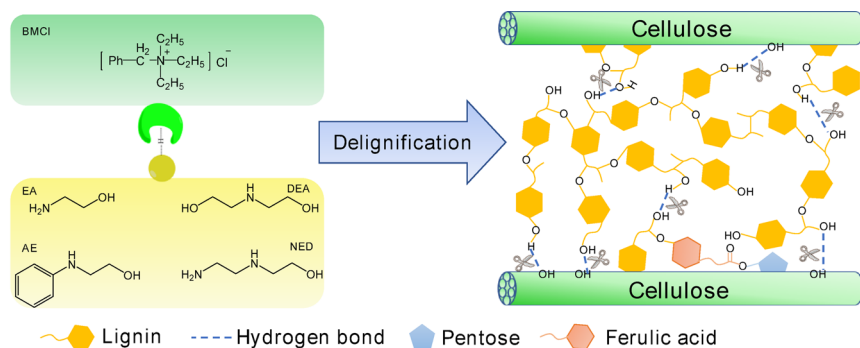
Materials and chemicals

Wood veneer of Amur Linden (*Tilia amurensis* Rupr.) with dimensions of 150 mm × 900 mm × 3 mm was obtained by cutting a tree trunk along the direction of tree growth. Benzyltrimethylammonium chloride (BMCl, AR, 98%), ethanolamine (EA, AR, 99%), diethanolamine (DEA, AR, 98%), N-(2-hydroxyethyl) ethylenediamine (NED, AR, 98%), 2-anilinoethanol (AE, AR, 98%), 37% formaldehyde (HCHO), 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), polyethyleneimine (PEI, Mn = 600), ammonium polyphosphate (APP), N, N-Dimethylformamide (DMF), and other chemicals were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. (China) and were used without further purification.

Wood delignification and lignin separation

Wood veneer was cut into pieces with dimensions of 100 mm (axial) × 100 mm (radial) × 3 mm (tangential) and stored in plastic bags at room temperature prior to treatment. Alcohol amine-based DESs (BMCl/EA, BMCl/DEA, BMCl/NED, BMCl/AE) were first heated in an oil bath to the desired temperature (100 °C) with a molar ratio of 1: 6. Then the prepared wood veneers were put into the solvent with a liquid/wood mass ratio of 10 (mL/g) and treated for 1 to 4 h. At the end of the treatment, the wood veneer was removed from the solvent and washed several times with deionized water to remove residual chemicals and dissolved compounds. The delignification routes are shown in Fig. 1.

The solvent can be recovered and reused with similar wood yields and lignin removals for three cycles, as illustrated in Fig. S1 and Table S1. Briefly, once the wood veneer was removed from the solvent, the spent solvent was poured into an anti-solvent (ethanol and waste solvent at a volume ratio of 5:1). The mixture was thoroughly stirred and then filtered. Subsequently, the brown filtrate was concen-



Note: Benzyltrimethylammonium chloride/monoethanolamine (BMCI/EA), benzyltrimethylammonium chloride/diethanolamine (BMCI/DEA), benzyltrimethylammonium chloride/2-Anilinoethanol (BMCI/AE), benzyltrimethylammonium chloride/N-(2-hydroxyethyl) ethylenediamine (BMCI/NED).

Fig. 1 Alcohol amine-based DESs delignification routes

trated via rotary evaporation. This concentrated filtrate was then added to 500 mL of deionized water to facilitate lignin regeneration. After allowing sufficient time for solid-liquid separation, the precipitate was separated from the supernatant by centrifugation at 6000 rpm. Following centrifugation, the precipitated lignin was further washed with water and then freeze-dried to obtain DES lignin (DL). The supernatant was concentrated by rotary evaporation to remove water and recover DES which was then re-utilized in the subsequent cycle. The lignin extracted under these recycling conditions has a purity of around 90%, indicating the effectiveness of the overall process in recycling the solvent and obtaining high-purity lignin.

Lignin functionalization

The preparation of nitrogen-phosphorus functionalized lignin can be found in our previous work (Gu et al. 2025). Briefly, 1 gram of DES lignin (DL) was dissolved in 20 mL of NaOH (2%, w/v) solution and stirred thoroughly until the lignin was completely dissolved. Then, 0.4 g of PEI, 0.01 g of FeCl_2 , and 0.4 g of HCHO were added to the solution, and the temperature was adjusted to 80 °C for a reaction duration of 5 h. After the reaction, 2 mol/L HCl was used to adjust the pH to 2–3 to precipitate the products. The sediment was washed using distilled water until the pH was neutral and then freeze-dried to obtain N-grafted lignin (NL).

Next, 1 gram of NL was dissolved in 6 mL DMF with the addition of 0.004 mol HCHO and 0.004 mol DOPO. A certain amount of 2 mol/L HCl solution was added to make the reaction mixture slightly acidic (pH=3–4). After reacting for 6 h at 90 °C, DMF was recycled by rotary evaporation, and the reaction products were repeatedly washed with distilled water and then freeze-dried to obtain functionalized lignin (FL), as illustrated in Scheme S1.

Fabrication of tough flame-retardant wood

FL was dissolved in N, N-dimethylformamide (DMF) to prepare flame-retardant lignin solutions with varying concentrations. Delignified wood samples were vacuum-immersed in the lignin solution for at least 24 h to ensure thorough lignin infiltration. The wet-state wood samples were then hot-pressed at 5 MPa and 100 °C for 6 h, yielding tough flame-retardant wood (denoted as TF-wood). For comparison of flame retardant migration, F-wood was prepared by immersing delignified wood in a PEI/APP solution (mass ratio 1:1.5), while densified wood obtained via delignification and densification without FL infiltration was labeled as DW-wood. The weight% gain (WPG) after FL infiltration was calculated using the following formula:

$$WPG(\%) = \frac{M_1 - M_0}{M_0} \times 100 \quad (1)$$

Where M_1 is the oven-dry weight of the wood after flame-retardant lignin infiltration and densification, and M_0 is the oven-dry weight of the wood after delignification. The WPG of TF-wood samples with 10%, 20%, 30%, and 40% FL loadings corresponds to the samples designated as 10% TF-wood, 20% TF-wood, 30% TF-wood, and 40% TF-wood, respectively.

Characterizations

The viscosity and pH value of dissolved DESs at a molar ratio of 1: 6 (BMCI/EA, BMCI/DEA, BMCI/NED, BMCI/AE) were determined using a viscometer (DVS+, BROOKFIELD, USA) and a pH meter (PHS-3 C, Shanghai INESA Scientific Instrument Co., Ltd, China). The lignin contents of raw wood, delignified wood and fractionated lignin were analyzed using the NREL protocol (Sluiter et al. 2008). Morphologies of surface, cross-sectional, and axial sections of the samples were characterized using a Scanning Electron Microscope (SEM, Nova Nano SEM 450, Frequency Electronics Inc., USA) with an accelerating voltage of 10 kV. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet is10, Thermo Scientific, USA) spectra were collected between 4000 and 650 cm^{-1} wavenumbers with 4 cm^{-1} resolution and an average of 32 scans. The chemical states of the elements were investigated by X-ray photoelectron spectroscopy (XPS, ESCA-LAB 250 X_i, Thermo Fisher Scientific, USA) using Al K _{α} radiation. The thermal stability of lignin and wood was analyzed using a thermogravimetric analyzer (TGA, STA 449C3/G, NETZSCH Scientific Instruments Trading Ltd., Germany) at a heating rate of 10 °C/min under a N₂ atmosphere, with the temperature ranging from 30 to 700 °C.

Mechanical properties of wood samples were tested by SANS Model E40 electronic universal testing machine (Metus Industrial Systems Co., LTD, USA) equipped with a 30 kN load cell at a cross-head speed of 5 mm/min according to the standard ASTM D638-10. The wood specimens were cut into dumbbell-shaped pieces with a special die (R32022015, Wuhan Qien Science and Technology Development Co. LTD, China). Flame retardancy of specimens (100 mm × 100 mm × 3 mm) was

evaluated using a cone calorimeter (VOUCH-6810, Suzhou Yangyi Volki Testing Technology Co., LTD, China) according to ISO 5660-1: 2002 under 50 kW/m² external heat fluxes in air. Heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total smoke production (TSP) were measured. The limiting oxygen index (LOI) of wood was measured according to the oxygen index method (ASTM D2863) by a limiting oxygen index instrument (ZR-01, Qingdao Shanfang Instrument Co., ltd., China). Duplicate runs of each test were carried out and the averages were reported.

Results and discussion

Effect of DES treatment on lignin removal

The physicochemical properties of DES, such as viscosity and pH value, are key factors affecting delignification efficiency (Soares et al. 2017). Different solvents exhibit significant differences in viscosity (Fig. 2a). Among these solvents, BMCI/EA shows the lowest viscosity, which is 3.0 CP at 50 °C, while solvent BMCI/AE shows the

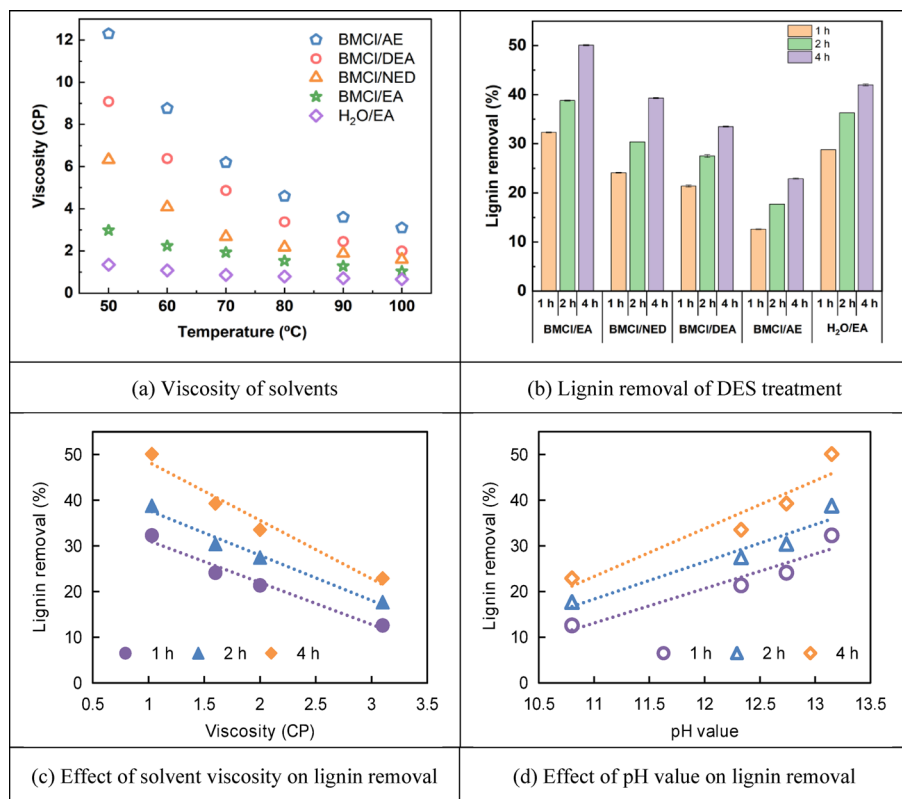


Fig. 2 Effect of DES treatment on lignin removal

highest viscosity, being 12.3 CP at 50 °C. The viscosities of all the solvents decreased with the increase in temperature. When the temperature reaches 100 °C, the viscosity of BMCl/EA drops to 1.0 CP. Solvent H₂O/EA is listed here for comparison with viscosity of 0.7 CP at 100 °C. Solvents with low viscosity tend to penetrate into the interior of wood more readily, facilitating the formation of hydrogen bonds and aiding lignin dissolution. Table 1 shows the pH values of different solvents before treatment. Solvent BMCl/EA has the highest pH value of 13.2, while solvent BMCl/AE has the lowest pH value of 10.8. A strong alkali condition is beneficial for lignin dissolution, but it also increases carbohydrate degradation. Therefore, we selected a series of alcohol-amine solutions because amino groups can effectively inhibit the peeling reaction of hemicelluloses (Zhao et al. 2018), thereby balancing the removal of lignin and the degradation of carbohydrates.

Solvent BMCl/EA shows outstanding delignification selectivity with lignin removal of 50.1% along with a glucan loss of 8.9% and a xylan loss of 27.9% (Fig. 2b). Besides, the lignin removed during the bulk delignification stage mainly derives from the secondary cell wall. This can lower the rigidity of the plant cell wall and aid in the subsequent densification. The viscosity and pH value of a DES solvent are key factors affecting delignification. A low viscosity is beneficial for solvent penetration and hydrogen-bond formation, which facilitates delignification under alkaline conditions (Mišan et al. 2019). As a result, lignin removal was negatively correlated with the viscosity and positively correlated with the pH value of the solvent, as shown in Fig. 2c & d. Solvent H₂O/EA exhibited a notably low viscosity (0.7 CP at 100 °C) and a pH value (13.0) similar to that of BMCl/EA, but resulted in a lignin removal of 42.0%, lower than that of BMCl/EA. Perhaps, BMCl with a strong hydrogen-bonding-forming ability enable it to closely interact with lignin molecules and penetrate the lignin structure, catalytically decreasing the surface energy of the solid-phase solute at the meantime, thus facilitating lignin dissolution (Shen et al. 2019).

Characterization of DES lignin (DL) and functionalized lignin (FL)

FTIR and XPS are employed to explore the surface chemical structure of DL and FL. FL shows C–N stretching vibration at 1660 cm^{−1}. The band at 1205 cm^{−1} is the combination of the stretching and bending vibrations of the P=O bond, the band at 1055 cm^{−1} is the stretching vibration of the P–O bond (Yu et al. 2012), and the absorption band at 755 cm^{−1} is attributed to the stretching vibrations of P–C–N (Fig. 3a). XPS spectra reveal the chemical state and composition of FL (Fig. 3b). The peaks observed at 534, 400, 287, and 133 eV are attributed to O1s, N1s, C1s, and P2p, respectively. For the O1s spectrum (Fig. 3b1), three peaks at 534.9 eV (C=O), 533.1 eV (C–O) and 531.8 eV (P–O or P=O) are observed. Peaks at 400.9, 399.8, and 398.8 eV make up the N1s spectra (Fig. 3b2). These peaks belong to the groups of N–H, C–N, and N–P. Three peaks at 289.0 eV (C–O), 287.2 eV (C–N) and 285.0 eV (C=C or C–C) make up the C1s spectra (Fig. 3b3). In the P2p spectrum (Fig. 3b4),

Table 1 pH values of different solvents

Solvent	BMCl/EA	BMCl/ NED	BMCl/ DEA	BMCl/ AE	H ₂ O/EA
pH	13.2±0.1	12.7±0.1	12.3±0.1	10.8±0.1	13.0±0.1

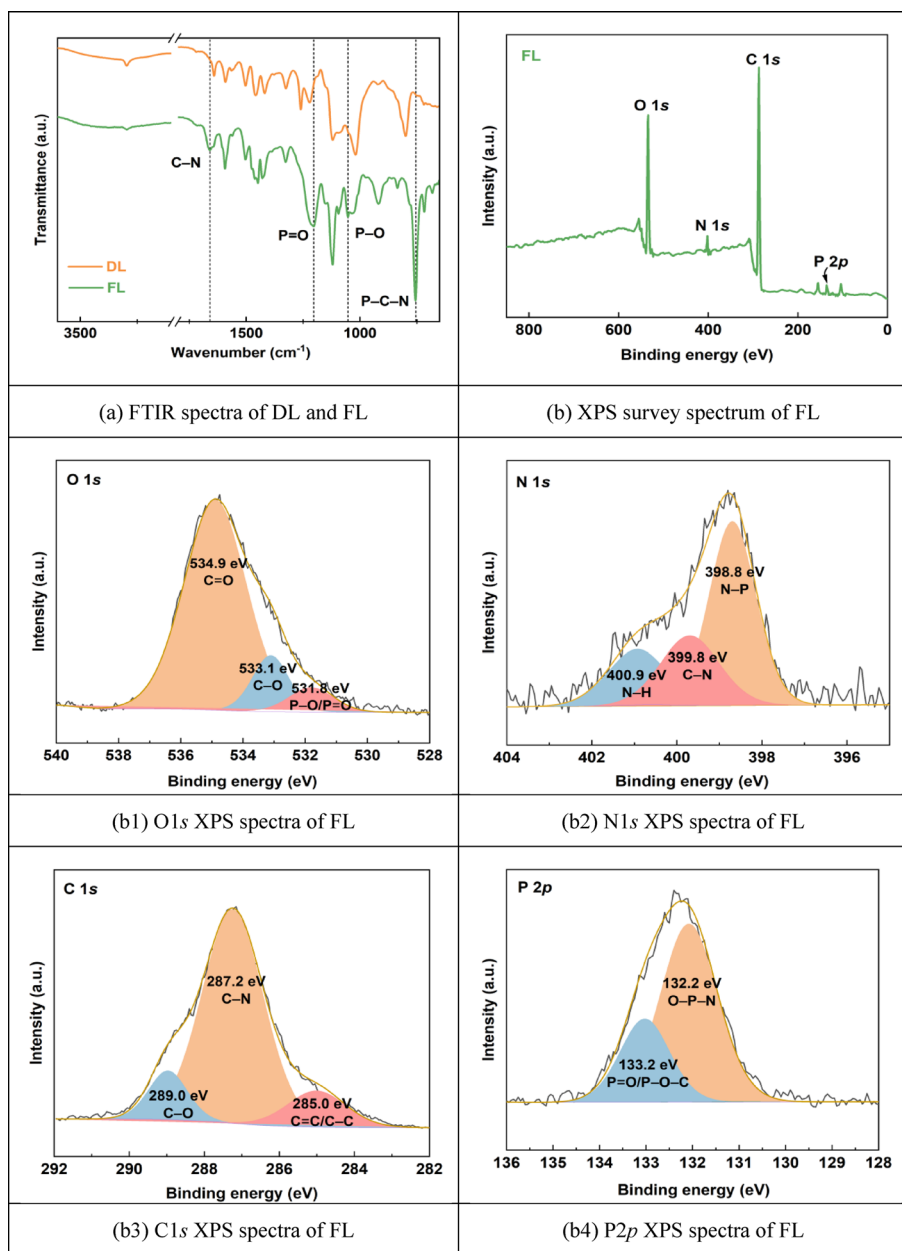


Fig. 3 FTIR spectra (a), XPS spectra (b), TG curves (c) and DTG curves (d) of DL and FL

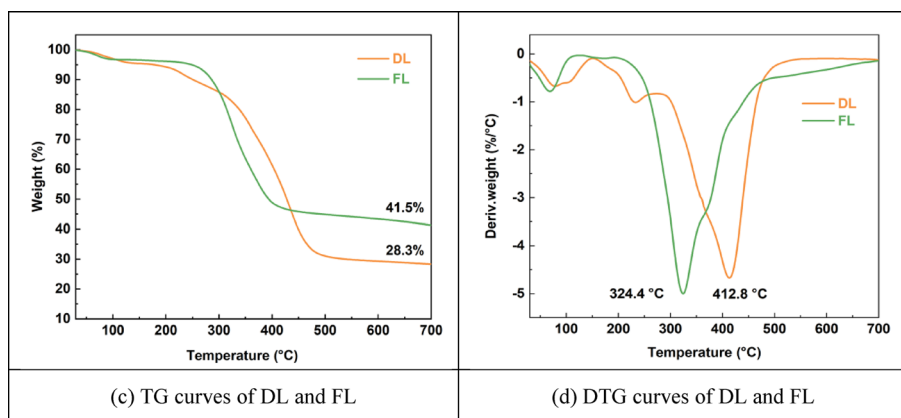


Fig. 3 (continued)

two peaks at 133.2 eV and 132.2 eV are also noted, which are assigned to P=O and O–P–N, respectively (Zhao et al. 2021). The above analyses confirmed that FL has been successfully functionalized with nitrogen and phosphorus.

Thermal stability is a crucial indicator of the fire-performance of FL. As shown in Fig. 3c&d, the maximum weight loss temperature ($T_{\max}$) of FL was increased. This is because after nitrogen- and phosphorus-functionalization, P-containing groups degraded preferentially and released acidic substances, leading to small molecular fragment aggregation and carbonaceous structure formation (Chen et al. 2021). The increased carbon residue of FL functions as an efficient barrier by impeding the transfer of heat and restricting the access of oxygen, which greatly inhibited the combustion reaction and improved the flame retardancy of wood.

Mechanical strength and flame retardancy of tough flame-retardant wood

Wood is a naturally porous material with low density, lacking significant advantages in mechanical properties (Beims et al. 2022). Figure 4a presents the tensile strength

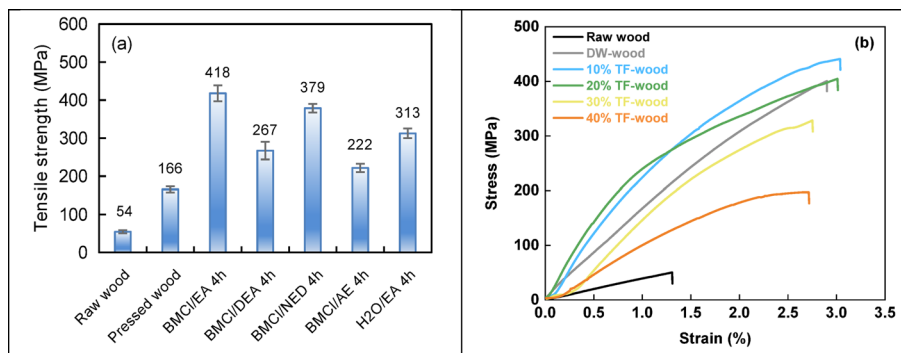


Fig. 4 Mechanical strength of raw wood, different DES treated wood (a) and TF-wood (b)

values of raw wood and densified wood after DES treatments. The raw wood, with a density of 0.5 g/cm^3 , exhibited a tensile stress of 54.5 MPa. This value increased to 165.6 MPa with enhanced density (0.8 g/cm^3) after hot-pressing. Moderate lignin removal can further lower the rigidity of plant cell wall, making the cell lumen easier to compress (Gu et al. 2024; Song et al. 2018). During hot-pressing, the cell walls of wood tend to be closely interlaced in the cross-sectional direction and packed along the length direction (Fig. 5d & e). This facilitates the formation of robust bonds among cell wall components (Burgert et al. 2016; Kim et al. 2019), which highly restricts the separation of fibers from one another after fracture under tensile load, as can be seen in Fig. 5f. As a result, the tensile strength can be improved to 418.0 MPa after BMCl-EA delignification and densification with a strain of 2.8%. The enhancement of tensile strength and strain is accompanied by a significant increase in the toughness to 6.6 MJ/m^3 of BMCl-EA delignified and densified wood, which is 22 times higher than that of natural wood.

When N/P-functionalized lignin was reincorporated into delignified wood through hot-pressing, remarkable alterations in the wood morphology took place (Fig. 5). Initially, the functionalized lignin infiltrates into the pores and lumens present in the fibers and vessels of delignified wood structure. Following this infiltration and subsequent hot-pressing, the material forms a highly dense and homogeneous structure. As shown in Fig. 5, the fracture cross-section of TF-wood (i) exhibits a cohesive, less porous morphology compared to that of Raw wood (c) and DW-wood (f)—a phenomenon attributed to DES-induced structural modifications and lignin reintegration, which collectively enhance interfacial bonding and densification. This lignin

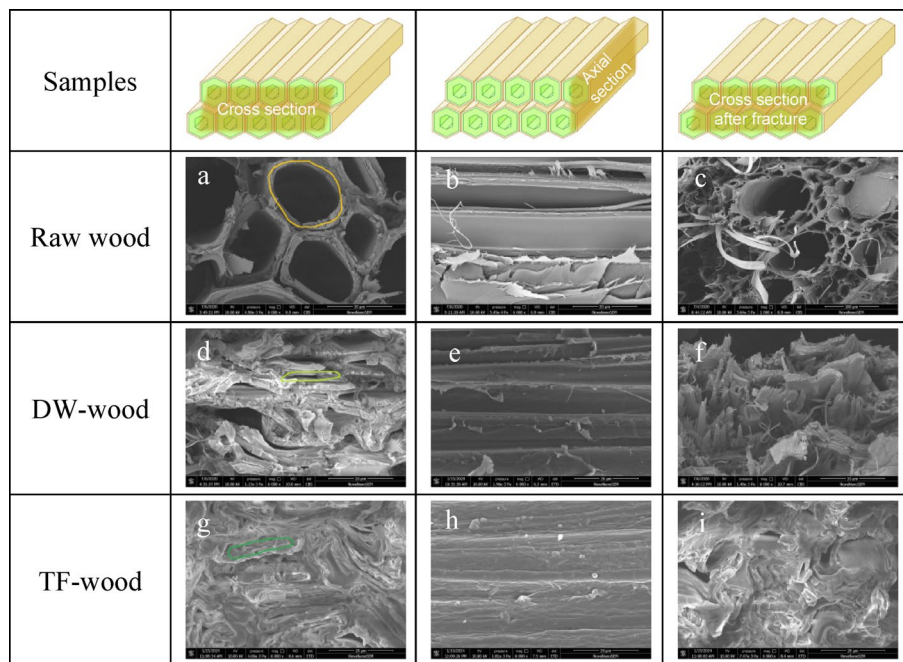


Fig. 5 SEM images of Raw wood (a, b, c), DW-Wood (d, e, f) and TF-Wood (g, h, i)

infiltration not only facilitates tighter adhesion with diminished gaps (Fig. 5g&h) but also enables strengthened interfacial interactions via the additional nitrogen- and phosphorus-containing functional groups in N/P-functionalized lignin. Specifically, these groups form robust hydrogen bonds and chemical cross-links with components in the wood matrix, as evidenced by the ATR-FTIR spectra (Fig. S2a). The enhanced interaction between functionalized lignin and wood fibers augments the overall integrity and stability of the reconstituted wood, as reflected by the increase in toughness from 6.6 to 8.5 MJ/m³ at a 10% FL loading (10% TF-wood). At 20% FL loading (20% TF-wood), the toughness measures 8.1 MJ/m³, a value that remains essentially on par with 10% FL loading. As FL loading continues to increase beyond 20%, the tensile strength exhibits a progressive decline (Fig. 4b): toughness values drop to 5.2 MJ/m³ at 30% FL loading (30% TF-wood) and further to 3.3 MJ/m³ at 40% FL loading (40% TF-wood). Given that, all subsequent mentions of “TF-wood” in this context will specifically refer to 20% FL loading (20% TF-wood) for brevity. This marked decline in performance at FL loadings exceeding 20% can be primarily attributed to the poor compatibility and weak bonding of aggregated lignin particles within the DW-wood matrix, which impede the effective transfer of mechanical stress and compromise the material’s overall strength.

Figure 6a and b illustrate the thermal degradation behavior of wood samples under a N₂ atmosphere. TF-wood exhibits a shift of both the initial and maximum degradation temperatures to lower values compared to the raw wood. This is because at relatively low temperatures, P-containing groups start to decompose and release acidic substances. These acidic substances can catalyze the breaking of chemical bonds within lignin molecules and trigger the thermal decomposition process prematurely (Torun et al. 2020). As the temperature increases, the main chain of lignin further decomposes under the combined influence of acidic substances and heat. During this process, N reacts with free radicals to reduce their number and suppress the combustion chain reaction. P promotes lignin cross-linking, leading to small molecular fragment aggregation and carbonaceous structure formation. The FTIR and XPS spectra of TF-wood (Fig. S2) clearly demonstrate the successful introduction of N and P elements, which is consistent with the observed changes in the thermal degradation behavior. At high temperatures, thermal decomposition stabilizes, forming a stable carbon layer, which is a key product of TF-wood decomposition. The char residue exhibits a significant increase with FL addition, rising from 14.8 to 30.1% (Fig. 6a). It effectively shields the wood substrate and reduces the emission of flammable gases, ultimately improving the overall flame retardancy of the wood composite.

The incorporation of N/P-functionalized lignin into wood exerts a profound and positive influence on enhancing its fireproof performance, as evidenced by the data obtained from the cone calorimeter test (Fig. 6c-f). With the addition of 10% FL, the peak heat release rate (pHRR) drops from 435.4 to 213.0 kW/m², and the total heat release (THR) decreases from 48.1 to 32.5 MJ/m². Increasing the FL addition to 20% (TF-wood) further reduces the pHRR to 181.7 kW/m², and the THR to 25.1 MJ/m². Adding 30% and 40% FL leads to THR values of 22.0 MJ/m² and 19.5 MJ/m², respectively, which clearly attests to the efficacy of the N/P-functionalized lignin in suppressing the combustion process.

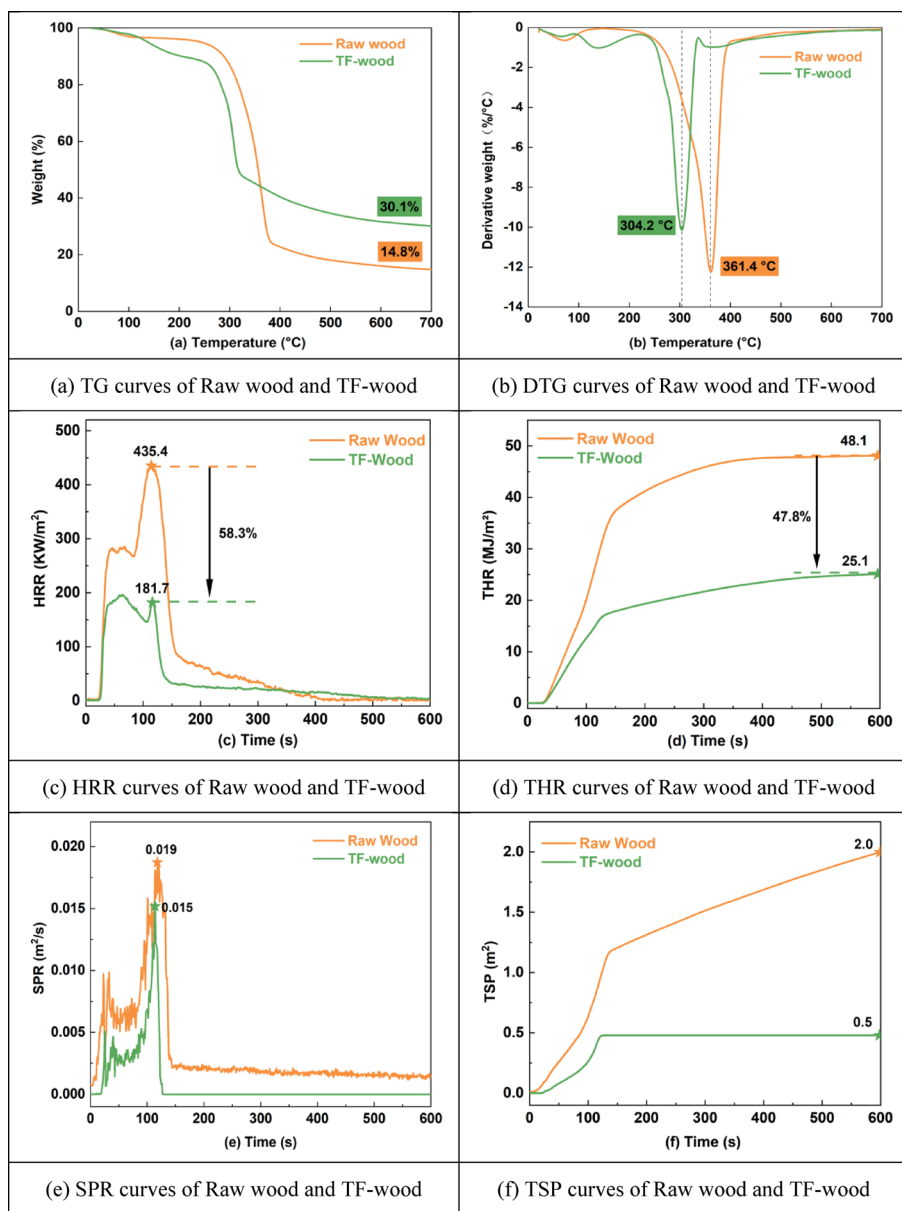


Fig. 6 TG (a), DTG (b), HRR (c), THR (d), SPR (e), and TSP (f) curves of Raw wood and TF-wood

Several key mechanisms drive this reduction (Fig. 7). Firstly, during thermal decomposition, N/P-functionalized lignin promotes cross-linking reactions, facilitating the formation of a compact char layer (Xu et al. 2024). This char acts as an efficient thermal insulator, impeding heat transfer from the combustion zone to unburned wood. By reducing heat transfer, combustion rate is slowed, thereby decreasing the pHRR. The char layer also restricts oxygen access to the underlying wood, further

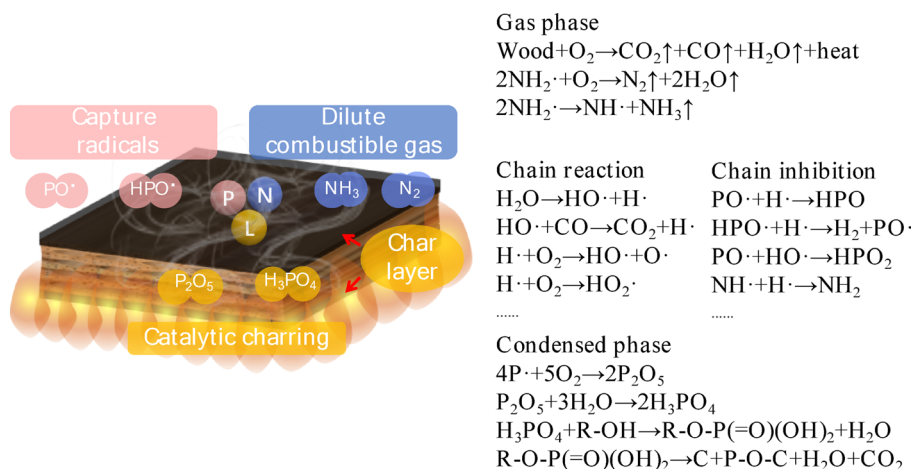


Fig. 7 Schematic illustrations of flame-retardant mechanism

inhibiting combustion and lowering THR. Secondly, N/P moieties decompose during combustion to release radicals (e.g., $\text{PO} \cdot$ and $\text{NH}_2 \cdot$), which scavenge $\text{H} \cdot$ and $\text{OH} \cdot$ radicals to interrupt the combustion chain reaction (Peng et al. 2021). Additionally, non-flammable gases (e.g., CO_2 , NH_3 , N_2 , water vapor) released from TF-wood dilute combustible gases, driving local fuel/oxygen concentrations below flammability limits and reducing combustion intensity (Chu et al. 2022). Finally, the functionalized lignin modifies wood decomposition pathways to generate fewer smoke precursors or alter their reactivity, decreasing peak smoke production rate (pSPR) from 0.019 to 0.015 m^2/s and total smoke production (TSP) from 2.0 to 0.5 m^2 .

To conduct a more in-depth assessment of the flame retardancy of TF-wood, limiting oxygen index (LOI) and vertical burning tests (Fig. 8) were performed. Raw wood is highly flammable, with an LOI value of only 21.6% (Fig. 8a). DW-wood, on the other hand, has an LOI value of 25.1% and undergoes a prolonged combustion process (Fig. 8b). This is due to the fact that during the densification process, the voids in the wood structure were eliminated, forming a highly dense laminated structure that effectively blocks the infiltration of oxygen into the material. TF-wood can be ignited multiple times, but it rapidly self-extinguishes each time the heating source is removed (Fig. 8c, d). The LOI value of TF-wood reaches 33.9%, which clearly demonstrates the significantly enhanced flame-retardant performance resulting from N/P-functionalized lignin reassembly. To assess the impact of lignin functionalization on flame retardancy, we measured the LOI of DL-wood which incorporated unfunctionalized lignin. The lower LOI of 26.2% compared with 33.9% for the TF-wood with functionalized lignin indicated that N/P functionalization plays a crucial role in increasing the LOI. Additionally, incorporating functionalized lignin from delignification using recycled DES after three cycles resulted in a TF-wood with a LOI of 33.5%, suggesting that the utilization of recycled DES can achieve similar performance as that using fresh DES for improving TF-wood flame retardancy. To investigate the migration of N/P-functionalized lignin from wood, we compared the weight variations and LOI values of TF-wood and F-wood (incorporating PEI/APP)

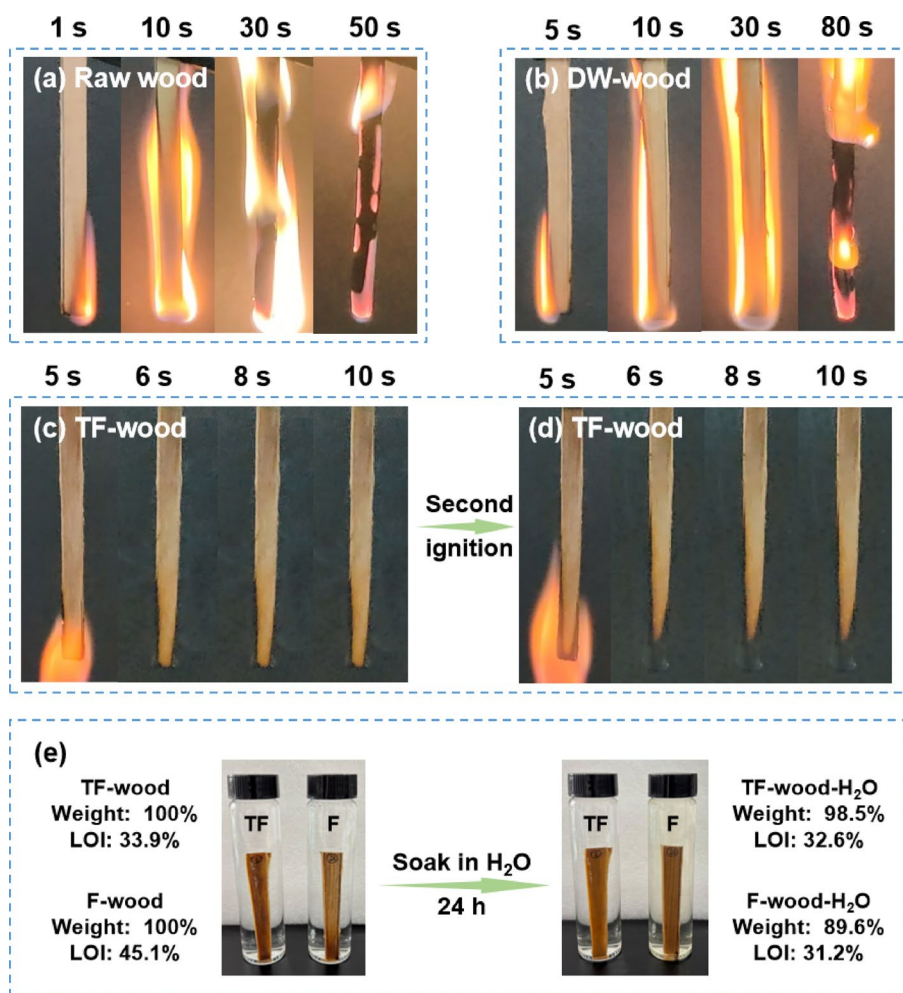


Fig. 8 Burning test of raw wood (a), DW-wood (b), TF-wood (c, d), Weight percentages and LOI values of TF-wood and F-wood before and after 24-hour water soaking (e)

after 24-h water immersion, as shown in Fig. 8e. Upon immersion, F-wood exhibited a significant decrease in LOI from 45.1 to 31.2%, accompanied by over 10% weight loss due to leaching of water-soluble PEI and APP. In contrast, TF-wood retained an LOI of 32.6% after 24 h of water soaking, with weight loss below 2%. This ultra-low water migration rate—attributed to the insolubility of N/P-functionalized lignin in water and the robust cross-links (hydrogen bonds and chemical bonds) formed between the functionalized lignin and wood matrix—not only underscores the structural integrity of TF-wood but also reinforces its stability in humid environments, highlighting a critical advantage for applications under high-humidity conditions.

In light of these experimental findings, the N/P-functionalized lignin enhances the fireproof performance of TF-wood by synergistically promoting char formation, interfering with combustion chemistry, and reducing smoke production (Schartel and

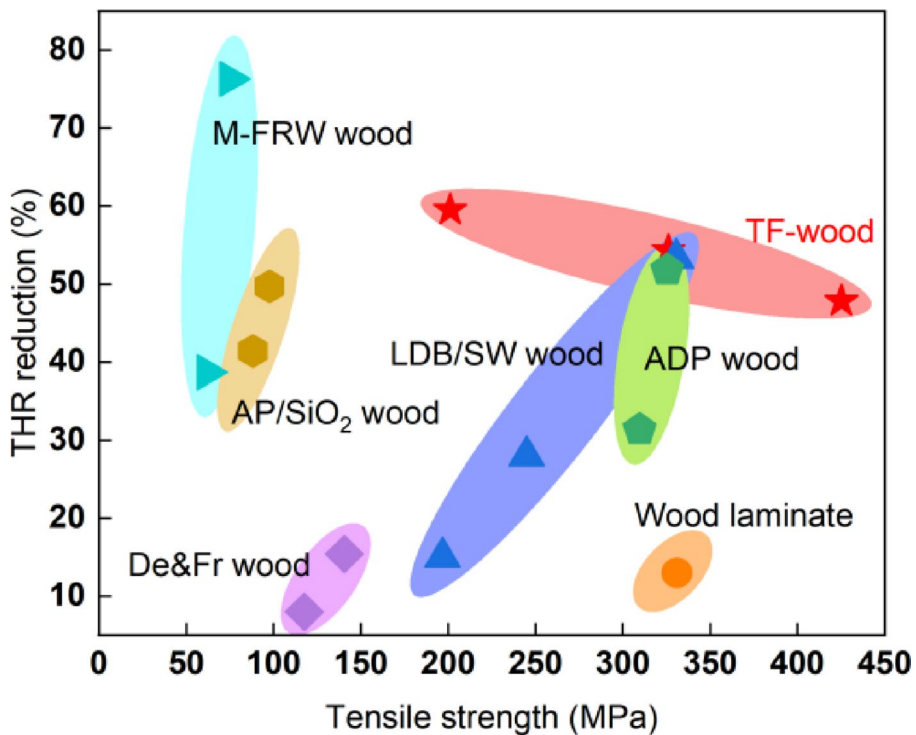


Fig. 9 Comparison of the THR reduction and tensile strength with established techniques

Hull 2007). These mechanisms work in tandem to make the wood more resistant to fire, with lower heat release and smoke production, thereby enhancing the safety and durability of wood products in fire-prone environments. Simultaneously, lignin, as a natural adhesive, tightly binds the wood fibers, which considerably enhances the mechanical strength of the wood. When comparing the tensile strength and THR reduction with established techniques (Li et al. 2025; Fan et al. 2023; Tan et al. 2024; Chen et al. 2020; Che et al. 2024; Lai et al. 2025), the TF-wood demonstrates outstanding performance (Fig. 9). This greatly increases TF-wood market in various fields such as construction, furniture manufacturing, and interior decoration. Moreover, the DES used in this study can be recycled for at least three cycles, and the excess lignin not infiltrated into wood can be further functionalized for other applications (e.g., flame retardants for polymers) aligning with the circular economy principles of lignin valorization (Tardy et al. 2023).

Conclusion

Tough flame-retardant wood (TF-wood) has been successfully fabricated by using alcohol-amine-based deep eutectic solvents (DES) for delignification, followed by N/P-functionalization of the extracted lignin and hot-pressing reassembly into the wood matrix. The incorporation of 20% functionalized lignin results in a substan-

tial improvement in the mechanical properties of the tough flame-retardant (TF) wood. Its tensile strength reaches 425.2 MPa, the strain is 2.9%, and the toughness is 8.1 MJ/m³, which is 27 times higher than that of raw wood. Moreover, the flame retardancy is significantly enhanced, featuring a 58.3% reduction in the pHRR and a 47.8% decrease in the THR. These outstanding mechanical properties, flame-retardant performance, and ultra-low water migration rate collectively ensure TF-wood's suitability for a variety of advanced engineering applications, such as outdoor structural components or high-moisture-resistant constructions. This breakthrough not only expands the application scenarios of sustainable wood-based materials but also opens up new possibilities for the design and production of sustainable structural materials with integrated mechanical strength, fire resistance, and moisture stability.

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Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by WW, WH, NX & WY. The first draft of the manuscript was written by WW & GF, CZ, JB & ZJ commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Declarations

Competing interests The authors declare no competing interests.

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

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