Bamboo and Wood Structures

journal homepage: https://www.innoviair.cn/journal/BWS

Sustainable High-Performance Biocomposites Based on Wood Fibers and Self-Reinforced Micro-Fibrillated Cellulose Matrices

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ARTICLE INFO

Keywords:
Biocomposites
Ultrasonic treatment
Lignin
Theroforming
Glueless

ABSTRACT

Given the decreasing availability of forest resources as a natural commodity, the efficient utilization of small-diameter shrubs is crucial for global sustainable development. This approach holds significant potential for conserving forest resources and reducing carbon emissions. However, small-diameter timber possesses inherent drawbacks such as its loose structure, susceptibility to cracking and deformation, and low strength, which considerably limit its range of applications. In this study, an efficient and eco-friendly method was developed to prepare adhesive-free biocomposites from discarded small-diameter shrubs through ultrasonic pretreatment followed by thermoforming.After ultrasonic pretreatment, the flexural and tensile strengths of the biocomposites increased by 145 % and 132 %, respectively. The pretreatment disrupted the chemical bonds within the lignocellulosic biomass macromolecules via high-speed shear and micro-jet effects. This process significantly increased the number of binding sites on the cellulose fibers and further densified the cell walls during subsequent hot pressing. Moreover, the ultrasonic treatment removed certain components of the wood flour that act as fillers or density enhancers, leading to a slight reduction in the density of the resulting biocomposite. Simultaneously, lignin acted as an intrinsic binder, improving fiber bonding through both physical entanglement and chemical cross-linking. As a result, a compact cellulose structure with a three-dimensional lattice was formed, yielding a less hydrophilic surface as evidenced by a water contact angle of 81.72 °. Additionally, these high-quality, binder-free biocomposites emitted no harmful gases such as formaldehyde. Consequently, they are promising sustainable materials for future applications in building decoration and furniture manufacturing.

1.Introduction

Wood is a widely distributed and readily available natural renewable resource, making it a material of choice for sustainable production[1-3]. It has been extensively used in construction and furniture manufacturing for a long time. However, due to technological advancement and rapid economic development, global forest resources have been increasingly depleted[4]. To meet the growing demand for wood-based materials while enhancing the utilization of natural resources, small-diameter timber has been identified as a potential raw material for producing biocomposites[5]. Small-diameter wood is sourced from a wide range of origins, including numerous small-diameter trees discarded in plantations, small logs, understory trees in natural forests, and the tops and branches of large-diameter hardwood and softwood trees. The rational and efficient development and use of small-diameter timber can effectively alleviate the supply-demand gap for raw timber, improve timber yield and utilization rates, increase product value-added, and expand its applications in solid wood furniture and interior decoration. Ultimately, this strategy facilitates a transition towards

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Received 12 September 2025; Received in revised form 22 September 2025; Accepted 30 October 2025; Available online 29 November 2025

efficient forest resource utilization and sustainable management.

However, small-diameter wood has disadvantages such as low density, low strength, and a tendency to crack and deform[6]. Therefore, a significant amount of adhesives (e.g., urea-formaldehyde or phenolic resins) is commonly used to synthesize biocomposites with acceptable physical properties from this lower-quality wood. The use of petroleum-based adhesives, however, accelerates the consumption of non-renewable resources and hinders sustainable development. Furthermore, artificial panels continuously emit harmful gases such as formaldehyde during production and use, endangering human health and polluting the environment[7]. Recently, the preparation of energy-saving and environmentally friendly biocomposites using formaldehyde-free or adhesive-free bonding technology has gained popularity as a more promising and greener approach to utilizing these bioresources[8,9]. However, rising adhesive costs in the international market have increased the expense of producing plywood. Coupled with disadvantages like poor adhesive performance and complex production processes, the attractiveness of plywood as a material choice has diminished[10]. In contrast, green biocomposites do not use adhesives, significantly reducing production costs. Consequently, adhesive-free bonding technologies are currently being intensively researched for preparing biocomposites.

Currently, two main methods are used for bonding green composites: formaldehyde-free resin bonding and adhesive-free bonding[11]. However, the significantly higher cost of formaldehyde-free resin adhesives compared to commonly used urea-formaldehyde resins poses a challenge for their adoption in the wood-based panel industry. In contrast, adhesive-free bonding is more feasible[12].

Numerous studies have investigated the adhesive-free bonding of wood products. To date, six non-adhesive bonding strategies have been developed: oxidative bonding[13], free radical initiation[14], acid-catalyzed polycondensation[15], alkali solution activation[16], natural substance transformation[17], and enzyme activation[18]. These provide a theoretical basis for studying adhesive-free bonding technology for wood fibers[19]. Lignin in lignocellulose acts as a binder in the fabrication of adhesive-free wood-based composites. It combines with the polysaccharide matrix via hydrogen bonding to form lignin-carbohydrate complexes and binds hemicellulose to cellulose microfibrils within the biomass[20]. The plasticity of lignin and its cross-linking reaction with furfural are responsible for this self-bonding[21]. Yang et al.[22] directly applied lignin extracted from lignocellulosic biomass, mixed with water, as a binder to wood veneer. After hot pressing, this binder improved the properties of the synthesized boards. In such composites, lignin plays a crucial role in enhancing strength. Adding lignin is considered an effective method for improving the properties of self-bonded fiberboards. However, these self-bonded materials cannot be directly used as structural materials in furniture production due to disadvantages such as poor mechanical properties, weak hydrophobicity, and thermal instability.

Recent studies have attempted various methods to enhance the physical properties of self-bonded materials, such as chemical or physical pretreatments[23]. Grinding small-diameter timber into powder followed by hot pressing is considered an effective method to increase the strength of self-bonded materials[24]. Ye et al[25] ground poplar wood into powders of different particle sizes and hot-pressed them to obtain biocomposites. They found that biocomposites prepared from wood powder with larger particle sizes (80 – 100 mesh) had better tensile strength, while those from smaller particle sizes (0-20 mesh) exhibited different properties. Yang et al[26] prepared adhesive-free biocomposites with excellent mechanical properties from discarded yellow poplar wood powder obtained through an HCl-assisted ball-milling pretreatment. Ren et al[27] prepared self-bonded biocomposites from yellow poplar using an innovative approach combining extraction, alkali treatment, and thermoforming methods. This resulted in biocomposites with enhanced mechanical properties, including both flexural and tensile moduli, and increased hydrophobicity.

Despite their potential, these previous methods were relatively complex and did not efficiently produce clean biocomposites. To overcome these obstacles, the application of ultrasonic technology in biomass pretreatment has emerged as an optimal choice among similar methods because it shortens reaction times and improves the effectiveness of the biomass conversion process. Ultrasonic treatment creates alternating compression and rarefaction zones via ultrasonic waves, leading to acoustic cavitation in the liquid medium. This cavitation separates particles as the wave propagates, with bubbles growing until they reach unstable dimensions and violently collapsing in a continuous cycle[28]~[31]. Thus, the fundamental principle of applying ultrasound to lignocellulosic biomass is to disrupt its integrity by breaking the ether bonds between hemicellulose and lignin. Specifically, the high-speed shear and micro-jets generated by ultrasound break the chemical bonds between the macromolecules of lignocellulosic biomass, thereby separating these components[32,33]. Simultaneously, cavitation generates oxidative free radicals that trigger numerous chemical reactions, promoting the decomposition of the macromolecules constituting the biomass. During the ultrasonication of biomass, frequencies ranging from 20 kHz to 1 MHz are primarily used to generate the oxidative free radicals that break down the complex network of the lignocellulosic structure[34]~[36]. Furthermore, ultrasonic pretreatment breaks the a-O-4 and β-O-4 linkages in lignin and promotes the enzymatic hydrolysis of biomass materials [32]. The ultrasonic pretreatment process is not only energy-efficient and environmentally friendly, as it eliminates the need for environmentally polluting reagents, but it also effectively disrupts the linkages between lignin and other polymers. This increases the solubility of hemicellulose and exposes more active binding sites on cellulose. Therefore, ultrasonic pretreatment can effectively modify fibers and facilitate the fabrication of self-bonded biocomposites with good thermoforming properties.

Several studies have demonstrated these advantages. For example, Kininge et al[37] compared conventional and ultrasonic-bath-assisted alkaline treatments, which achieved 48.09 % and 61.55 % delignification of the biomass, respectively. Their analytical characterization results confirmed that the ultrasonic reactor increased delignification efficiency. Agustin et al[38] revealed that using ultrasound during the preparation of lignin nanoparticles (LNPs) could minimize acid consumption, shorten dialysis time, and directly treat alkaline liquids containing up to 20 wt% lignin.

In this study, biocomposites with excellent mechanical properties were prepared from small-diameter timber or urban green waste as raw materials using an efficient, green, and clean method involving ultrasonic pretreatment and a one-step thermoforming process. The biocomposites were systematically analyzed. Their mechanical properties, hydrophobicity, fire resistance, thermal stability, and morphological characteristics were experimentally assessed using standard mechanical tests, contact angle measurements, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM), respectively. Subsequently, the chemical properties of the biocomposites were characterized, and their internal microstructures and chemical attributes were analyzed in depth to reveal the mechanisms of chemical cross-linking during the ultrasonic pretreatment and thermoforming processes. Finally, the feasibility of using these eco-friendly biocomposites to replace conventional resin-bonded artificial boards was assessed by comparing their respective physical properties and chemical stabilities. The findings demonstrate that the proposed method represents a novel approach for preparing adhesive-free, self-bonded fiberboards.

2.Materials and methods

2.1.Materials

All experiments utilized Vitex negundo wood harvested from Neijiang County, Sichuan, China. The wood was first crushed into powder. The powder was then sieved through a 60 – 80 mesh sieve using a Model 8411 vibrating sieve machine (Zhejiang Chenri Instrument Co. Ltd.). Subsequently, it was heated to 65 ° C for 8 minutes in a digital thermostatic oil bath (Model HH-6S, Hangzhou Peijia Instrument and Equipment Co.) without adding any additives and under consistent conditions. This heating step served to remove impurities that could affect the quality and performance of the wood flour, as well as to partially soften the cellulose, thereby improving its formability and compressibility during the subsequent hot-pressing process.

2.2.Preparation of the wood powder substrates

The Vitex negundo powder was weighed, placed in a beaker, and mixed with water at a liquid-to-solid ratio of 20:1. The beaker containing the mixture was then placed in an ultrasonic generator (Model JG-28K15, Zhejiang Jiugong Automation Co., Ltd.) equipped with a stirrer (Model JJ-1, Jintan Jincheng Xinjingda Experimental Analysis Instrument Factory). The treatment was carried out under the following parameters: an ultrasonic frequency of 20 kHz, an ultrasonic power density of 3 W/cm and total power of 900 W, a heating power of 2000 W (AC 220 V, 50 Hz), a reaction temperature of either 25 °C (room temperature) or 95 °C, a stirring speed of 500 rpm (stirrer power 120 W), and a duration of 2 h.

Subsequently, the treated wood flour was dried in a blast-drying oven (Shanghai Blue Gang Instrument Technology Co.) at 103 °C for 6 h to remove excess moisture. This drying step is essential to prevent delamination and cracking within the final biocomposite that could result from water vaporization during hot pressing. The moisture content of the dried material was measured with a moisture tester (Model ST-50A, Kunshan Lugong Precision Instrument Co., Ltd.) and adjusted to 8 % ± 0.5 % prior to further use.

2.3.Preparation of biocomposites from the ultrasonically pretreated and untreated Vitex negundo wood flour

For each type of pre-treated Vitex negundo powder with a moisture content of 8 % ± 0.5 %, 8 g of the powder was placed into a 5 × 5 cm^2 mold. The mold was then pressed between hot plates of a ZG-100TSD hot press (Dongguan Zhenggong Mechatronic Equipment Technology Co., Ltd.) at 170 °C and 40 MPa for 60 minutes. After hot pressing, the material was rapidly cooled to room temperature and held for an additional 60 minutes to produce a biocomposite sheet approximately 2.5 mm thick, with a target density ranging from 1.3 g/cm^3 to 1.5 g/cm^3.

The biocomposite prepared from untreated Vitex negundo powder is designated as VWP. Those made from powder that underwent ultrasonic pre-treatment at room temperature before hot pressing are labeled VWP(UT), and those from powder ultrasonically pre-treated at 95 °C are referred to as VWP(UT-H).

2.4.Characterisation

2.4.1.Mechanical and physical testing

In accordance with the Chinese national standard GB/T 17657-2013 ("Test Methods for Evaluating the Properties of Wood-based Panels and Surface-Decorated Wood-based Panels"), the density, static flexural strength, and tensile strength of the biocomposites were determined. The density was calculated from the volume and weight of the final samples (weighed to an accuracy of 0.01 g). Tensile and flexural tests were conducted using a universal material testing machine (Shimadzu AGS-X, Japan). The three-point bending test was performed with a span of 25.13 mm and a crosshead speed of 5 mm/min. For the tensile test, the gauge length was set to 17 mm, with the same crosshead speed of 5 mm/min. Specimen dimensions were 50 × 8 × 2.5 mm (length × width × thickness). Five parallel measurements were taken for each sample, and the average value was reported.

Water absorption tests were also carried out to characterize the water-absorption expansion rate and evaluate the water stability of the biocomposites. Additionally, the contact angles of the samples were measured using a contact angle analyzer (DSA100S, Krüss, Germany). During the test, the shape and contact angle of water droplets deposited on the sample surface were recorded at different time intervals (0, 2, 5, and 10 s). These data were analyzed to quantify the surface hydrophobicity of the biocomposites, where higher contact angles indicate lower hydrophilicity[39].

2.4.2.Microscopic morphological characterisation

The cross-sections and surfaces of the biocomposites were examined by scanning electron microscopy (SEM). Observations were performed using a Hitachi SU6600 SEM, and higher-magnification images were acquired with a TESCAN MIRA4 LMH instrument to characterize morphological features. All imaging was conducted at an accelerating voltage of 10 kV. Prior to examination, both cross-sectional and surface samples were coated with a thin gold film using a vacuum evaporator to enhance conductivity.

2.4.3.Chemical structure characterisation

The chemical functional groups of the biocomposites were analyzed using an attenuated total reflection Fourier-transform infrared (FT-IR) spectrometer (Nicolet Instrument Corporation, Madison, WI, USA) with a resolution of 4 cm⁻¹ and 64 scans. Surface elemental composition and carbon-oxygen bonding states were investigated by X-ray photoelectron spectroscopy (XPS) on a K-α instrument (Thermo Scientific), with data processed using PeakFit software.

The compositional content (cellulose, hemicellulose, and lignin) of the biocomposites was determined according to a standard washing protocol: cellulose and hemicellulose were quantified using an ANKOM220 fiber analyzer, while lignin content was measured via combustion in a muffle furnace.

Crystallinity was examined by X-ray diffraction (XRD) using a Rigaku Ultima III diffractometer with Cu Kα radiation in a parallel-beam configuration. Patterns were recorded over a 2θ range of 10–50°. The crystallinity index was estimated using the Segal method[40]:

$$C_s=\frac{I_{002}-I_{Am}}{I_{002}}\times 100\%$$

where C_s is the degree of crystallinity (%), I_{002} is the maximum intensity of the (002) diffraction peak of cellulose, and I_{Am} is the diffraction intensity of the amorphous background. The Segal method shows a linear correlation with other crystallinity determination methods when applied to a consistent sample set.Finally, the UV-absorption properties of the biocomposites were evaluated using a UV–Vis spectrophotometer (PE Lambda 950).

2.4.4.Characterisation of the thermal properties

The thermal stability of the biocomposites was evaluated by thermogravimetric analysis (TGA) using a Mettler Toledo TGA/DSC 3 instrument. Measurements were performed from 20 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere to assess the thermal degradation behavior.

In addition, flame-retardant properties were examined by exposing the biocomposites to an external blowtorch flame for 10 seconds. The burning behavior and residual char were observed and compared at 0, 2, 5, and 10 seconds to evaluate their resistance to direct flame.

3.Results and discussion

3.1.Chemical properties of biocomposites

The chemical compositions of the different biocomposites are presented in Fig 1a. Both VWP(UT) and VWP(UT-H) exhibited an increase in relative lignin content compared with VWP. This rise is attributed to the removal of extractables, resins, and free sugars during ultrasonic pretreatment. The treatment also disrupted lignin-carbohydrate aggregates and partially leached out hemicellulose, leading to a decrease in hemicellulose content. A very small portion of cellulose was likewise decomposed during thermoforming. Due to its amorphous nature and fragile chemical structure, hemicellulose is more readily degraded and removed from biomass than cellulose, which is more resistant owing to its crystalline structure and specific supramolecular organization. Thus, ultrasonic pretreatment effectively removed hemicellulose, resulting in a relative increase in lignin content.

The chemical structures of the samples were further analyzed by FT-IR. As shown in Fig. 1b, the spectra of VWP, VWP(UT), and VWP(UT-H) display characteristic absorption peaks at 3358 cm⁻¹ (–OH stretching vibration), 2918 cm⁻¹ (C–H stretching vibration in methyl and methylene groups), 1682 cm⁻¹ (C=O stretching vibration in non-conjugated ketones and esters), 1590 cm⁻¹ (C=C stretching vibration conjugated with the benzene ring), 1495 cm⁻¹ (C–H deformation vibration), and 1058 cm⁻¹ (C–O–C stretching vibration). The broad absorption band around 3335 cm⁻¹ corresponds to the stretching vibration of various hydroxyl groups. VWP(UT) showed the strongest –OH absorption, indicating the highest hydroxyl content. The peaks at 2918 and 2870 cm⁻¹ were more intense for VWP(UT) and VWP(UT-H) than for VWP, consistent with their higher lignin contents. The peak at 1682 cm⁻¹ was smaller in VWP(UT), as hemicellulose is more susceptible to thermal degradation. Moreover, the more pronounced peaks at 1590 cm⁻¹ in VWP(UT) and VWP(UT-H) suggest that cross-linking between lignin and cellulose reduced the hydrophilicity of the biocomposites, which aligns with the water-resistance and thermal-stability results.

The increase in lignin content can be explained by two main mechanisms: (1) hydrolysis of Vitex negundo wood in aqueous medium, which partially converted cellulose and hemicellulose into water-soluble sugars and oligomers, and (2) ultrasonic pretreatment promoting decomposition of lignocellulosic macromolecules, with hemicellulose being removed at a higher rate than lignin, thereby increasing the relative lignin content.

Additionally, the absorption band at 1058 cm⁻¹ in the VWP spectrum shifted to 1039 cm⁻¹ for VWP(UT) and 1027 cm⁻¹ for VWP(UT-H). This redshift indicates stronger binding between cellulose and lignin in the pretreated samples, which also accounts for their lower lignin removal. In summary, compared with VWP, both VWP(UT) and VWP(UT-H) contained more lignin, which was uniformly dispersed and melted under pressure. This enhanced inter-wall adhesion, promoted tight binding within the biocomposites, and improved their mechanical properties and hydrophobicity.

Fig 1c presents the XRD patterns of the biocomposites under different pretreatment conditions, reflecting changes in crystallinity and related physical and mechanical properties. All samples showed three main diffraction peaks at 16.49°, 22.46°, and 34.58°, corresponding to the (101), (002), and (040) crystalline planes of cellulose, respectively. This indicates that ultrasonic pretreatment and hot pressing did not disrupt the inherent crystalline cellulose structure of Vitex negundo wood.

Lignocellulose contains both crystalline and amorphous regions, and the mass fraction of the crystalline region significantly influences the final properties of the biocomposites. The crystallinity indices were calculated as 43.82% for VWP, 59.43% for VWP(UT), and 63.45% for VWP(UT-H). The increase in crystallinity after ultrasonic pretreatment is due to the removal of amorphous hemicellulose and other non-fibrous materials from the non-crystalline regions, which allowed cellulose molecules to reorganize and form new crystalline domains. Moreover, crystallinity increased with pretreatment temperature, indicating that temperature influences crystalline-zone formation and composite strength. Ultrasonic pretreatment also promotes cross-linking between lignin and cellulose under high temperature and pressure, forming chemical bonds that enhance stability—a finding consistent with XPS and FT-IR results. These chemical bonds further improve the alignment of fibers in amorphous regions, enlarge the crystalline zones, and enhance the physical and mechanical properties of the biocomposites.

XPS analysis was used to examine changes in carbon bonding for biocomposites with and without ultrasonic pretreatment. The spectra were deconvoluted into four carbon peaks (Fig 4d–g): C1 (C–C/C–H), C2 (C–O, e.g., hydroxyl or ether groups), C3 (C=O, carbonyl), and C4 (O–C=O, carboxyl/ester). The content of C2 increased significantly to 67.05% in VWP(UT) and 70.38% in VWP(UT-H), while C3 and C4 contents also rose to 4.83% and 4.45%, respectively. The O/C ratio was higher in the ultrasonically pretreated samples. These changes indicate that ultrasonic pretreatment promoted the formation of additional C–O and C=O bonds between fibers, which can be attributed to the chemical effects of ultrasonic cavitation generating free hydroxyl and hydrogen groups on the fiber surface. These modifications collectively contribute to the enhanced performance of the biocomposites.

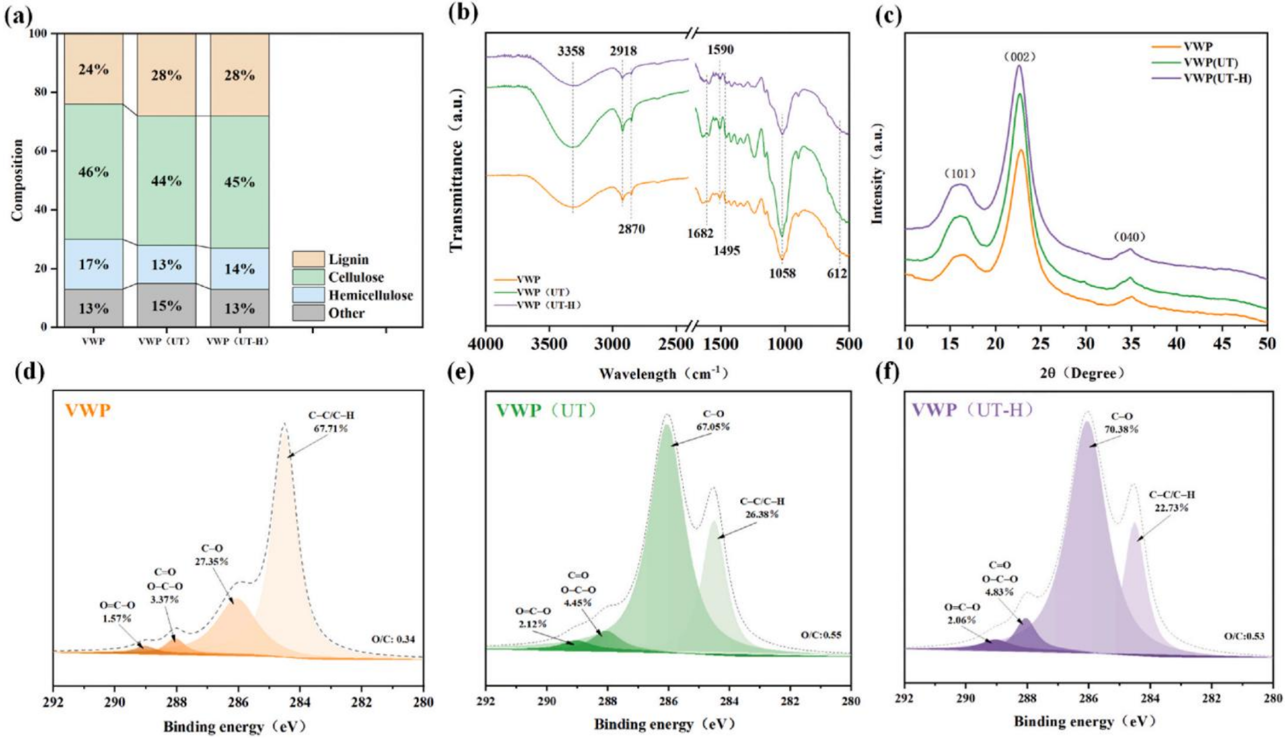

Fig 1. (a) Chemical composition of biocomposites; (b) FTIR curves of biocomposites prepared by different pretreatment processes; (c) XRD curves; (d-f) XPS curves.

3.2. Water resistance of biocomposites

Figure 2a–c presents the contact angles of the biocomposites under different pretreatment conditions. The initial contact angle (0 s) of VWP(UT) (θ = 63.1°) and VWP(UT-H) (θ = 81.72°) were significantly higher than that of VWP (54.72°), indicating that the ultrasonically treated biocomposites, especially VWP(UT-H), are less hydrophilic. VWP(UT-H) also retained the highest water contact angle after 10 s (θ = 75.25°). This improved hydrophobicity is attributed to the formation of a smooth, lignin-rich surface layer during hot pressing.

Figure 2d illustrates the thickness swelling of the biocomposites due to water absorption. VWP exhibited the highest swelling (27 %), which was substantially greater than that of VWP(UT) (21 %) and VWP(UT-H) (20 %). Ultrasonic pretreatment thus reduced water-induced swelling to varying degrees. This reduction can be explained by the development of a more hydrophobic lignin-enriched surface and the formation of a tightly interlocked fibrous network inside the composites, both of which hinder water penetration.

Surface micrographs of VWP (Fig 2e) and VWP(UT-H) (Fig 2f) reveal notable differences. Numerous cracks and pores are visible on the surface of VWP, whereas VWP(UT-H) shows a much denser and smoother morphology. The cracks in VWP are likely caused by the presence of organic extractives in the untreated wood, which can interfere with lignin binding due to their non-polar nature, and by the remaining hemicellulose that leaves voids between collapsed cell walls. These defects provide pathways for water ingress, resulting in lower hydrophobicity.

In contrast, the removal of a portion of hemicellulose and extractives via ultrasonic pretreatment allowed VWP(UT) and VWP(UT-H) to be compressed more effectively during hot pressing. The surfaces of the ultrasonically treated biocomposites exhibited a finer microstructure. Furthermore, the fiber cross-linking reactions that occur under high temperature and pressure promote the formation of a three-dimensional network between fibers, which reduces surface cracks and tubular pores, thereby enhancing hydrophobicity.

Additionally, lignin released during ultrasonic pretreatment undergoes a glass transition to a highly elastic state under the confined high-temperature, high-pressure conditions of hot pressing. This enables the lignin to flow, forming an internal three-dimensional lattice and, upon cooling, a thin continuous film on the sample surface. This mechanism explains both the larger contact angles and the smoother surface morphology observed in the ultrasonically treated samples.).

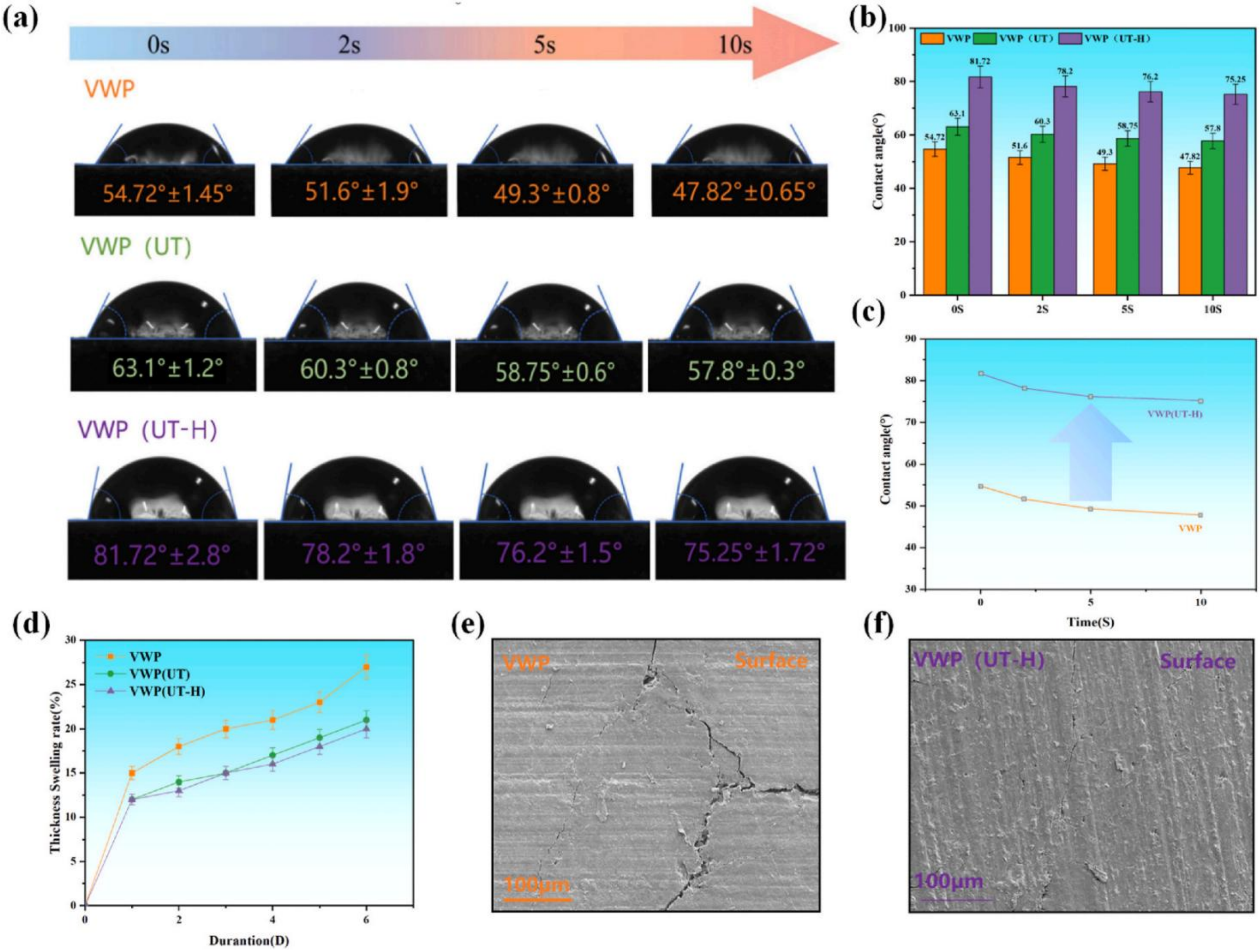

Fig 2. (a–c) Contact angle analysis of the biocomposite; (d) Water absorption and swelling of biocomposites; (f-g) SEM images of the biocomposite surface

3.3.Thermal performance of biocomposites

To examine the combustion-resistant properties and underlying mechanisms of the biocomposites, their thermal stability was evaluated. UV-absorption tests indicated that VWP(UT-H) absorbed the most UV radiation (Fig 3a). Figures 3b and c present the derivative thermogravimetric (DTG) and thermogravimetric (TGA) curves of the biocomposites prepared with different ultrasonic pretreatments. All samples exhibited high mass-loss rates between 210 and 400 °C, with maximum pyrolysis rates occurring at 354 °C for VWP(UT) and 342 °C for VWP(UT-H). The mass loss can be divided into three stages: 30–120 °C, 210–360 °C, and 360–600 °C. The first stage (30–120 °C) corresponds primarily to the evaporation of bound water. The second stage (210–360 °C) involves the thermal decomposition of cellulose and the breakdown of glycosidic bonds in hemicellulose. The third stage (above 360 °C) is mainly associated with the degradation of cellulose and lignin.

The onset of degradation in the second stage occurred at 226 °C for VWP(UT-H), 238 °C for VWP, and 252 °C for VWP(UT), reflecting differences in the thermal stability of cellulose and hemicellulose among the samples. Notably, the DTG curves revealed that the maximum degradation rate was lower for the ultrasonically pretreated biocomposites than for the untreated VWP. Specifically, the maximum degradation rates were 68.2 % for VWP, 63.8 % for VWP(UT), and 62.5 % for VWP(UT-H), indicating that the pretreated composites possess better thermal stability and greater resistance to thermal degradation during pyrolysis.

The TG curves show that VWP experienced the highest total mass loss (58.3 %). At 360 °C, both VWP(UT) and VWP(UT-H) yielded significantly more residual char (22.0 %) than VWP. Furthermore, the degradation rates of these two pretreated biocomposites at high temperature (600 °C) were lower than that of VWP. These results demonstrate that the ultrasonic pretreatment improved the thermal stability of the biocomposites, which can be attributed to the increased lignin content enhancing their resistance to heat and degradation under high-temperature conditions—a finding consistent with the compositional analysis.

The improved thermal performance is likely due to lignin forming a protective coating on the fibers. Owing to its complex structure containing aromatic rings and Cα–Cβ–Cγ side chains, lignin exhibits good heat resistance. This coating substantially raised the pyrolysis temperature of the encapsulated cellulose and hemicellulose, thereby improving the overall thermal stability of the material.

Flame-retardant properties were assessed using a blow-torch test, in which specimens were exposed to a direct flame for over 10 s (Fig 3d). VWP began to burn after 2 s, with the most intense combustion observed at 10 s. In contrast, VWP(UT) and VWP(UT-H) started to burn only after 5 s. This delay in ignition is attributed to the ultrasonic pretreatment, which increased the thermal stability of cellulose and hemicellulose by facilitating their coating with lignin, as evidenced by the higher pyrolysis temperatures of the pretreated biocomposites. Moreover, a dense char layer formed on the surface of the ultrasonically treated samples, indicating that the pretreatment promoted char retention. This charred coating effectively impeded the transfer of heat and oxygen, thereby enhancing the flame retardancy of the biocomposites.

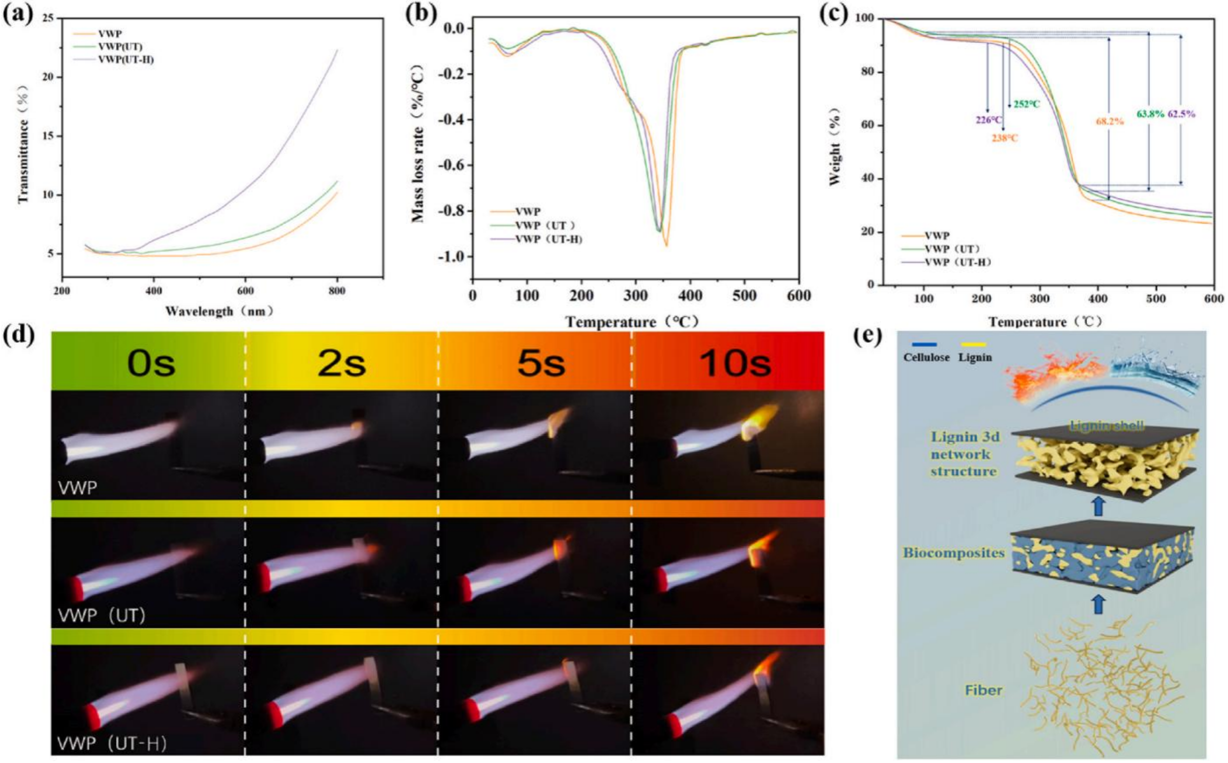

Fig 3. (a) UV absorbance; (b) heat loss mass heat loss rate; (c) heat loss mass; (d) flame retardancy of biocomposites prepared by different pretreatment processes; (e) schematic diagram of flame retardancy and hydrophobicity of biocomposites.

3.4.Physical properties of the biocomposites

Figure 4 presents the density and mechanical properties of the biocomposites prepared by ultrasonic pretreatment and hot-pressing, evaluating their potential for applications requiring high strength. The density of the untreated sample VWP (1.44 g/cm³) was significantly higher than those of VWP(UT) (1.41 g/cm³) and VWP(UT-H) (1.39 g/cm³) (Fig. 4a), indicating that ultrasonic pretreatment reduces the density of the final biocomposites. Cross-sectional images of the untreated *Vitex negundo* wood powder and the corresponding biocomposites (Fig 4b and c) show that the powder exhibits a more porous structure, whereas the biocomposites are denser. This change occurs because the porous wood structure collapses during thermo-compressive molding, leading to tighter fiber connections and reduced porosity in the composite.

Figures 4d–f and 4g–i illustrate the flexural and tensile properties of the biocomposites, respectively, while Fig. 4j and k show their specific flexural and tensile strengths. The mechanical properties of the ultrasonically treated biocomposites were improved to varying degrees compared with those of VWP. Specifically, VWP exhibited flexural and tensile strengths of 55.81 MPa and 27.11 MPa, respectively, which were lower than those of VWP(UT-H) (80.73 MPa and 35.67 MPa) and VWP(UT) (74.27 MPa and 31.15 MPa). In summary, the enhanced mechanical properties can be attributed to the ultrasonic pretreatment, which promotes the formation of stronger chemical bonds and a more tightly bound internal structure. At elevated temperatures, the physical effects of ultrasound, such as cavitation and eddy currents, become more pronounced, thereby accelerating the material treatment process (Table 1).

A comparison of the biocomposites prepared in this study with traditional materials and other biocomposites reveals that their mechanical properties are superior to those of widely

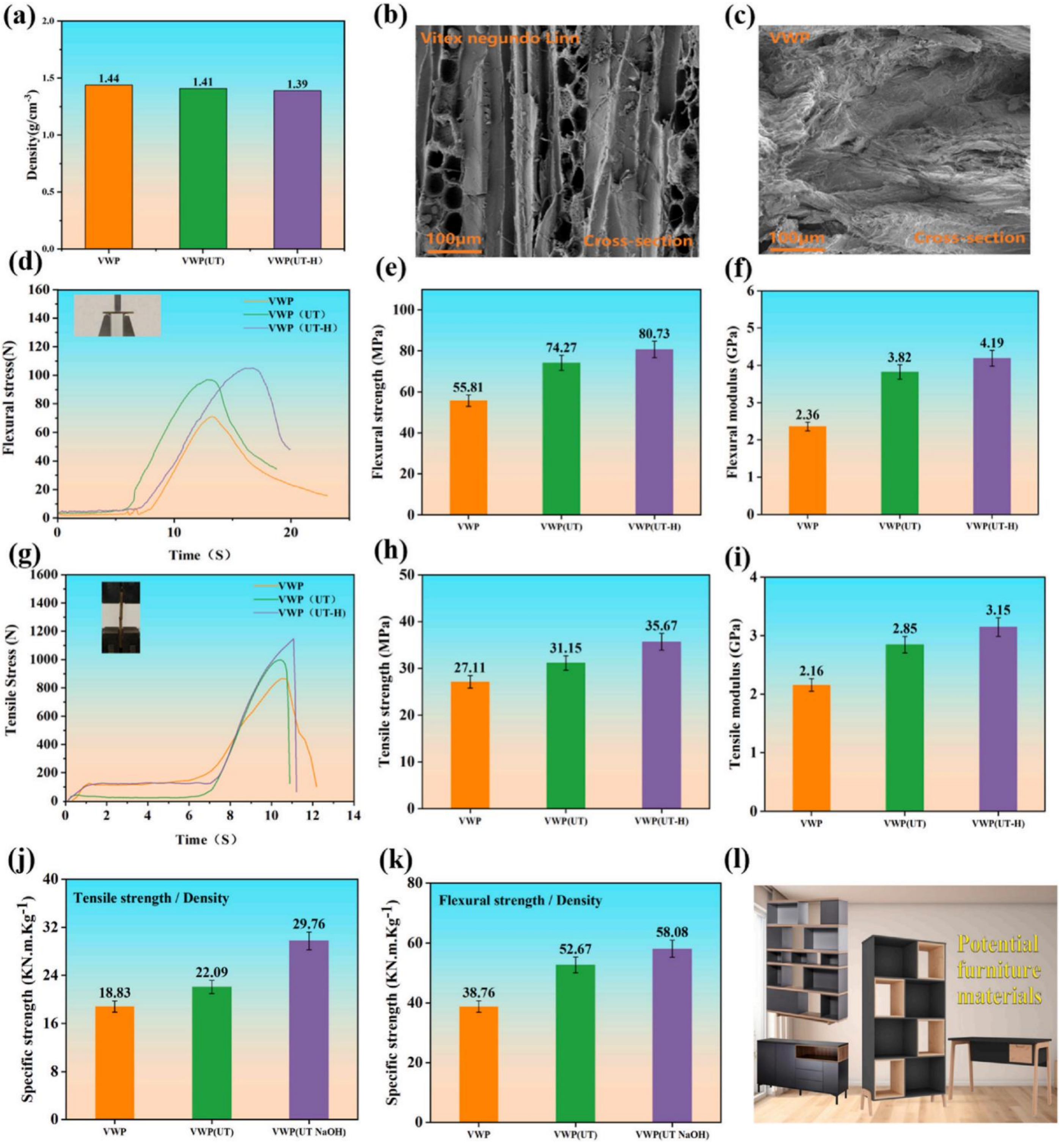

Fig 4. (a) Density of biocomposites; (b) micrographs of the cross-section of Vitex negundo wood; (c) micro images of the cross-section of biocomposites; (d–f) flexural stress-strain curves, flexural strengths, and moduli of Vitex negundo wood and biocomposites; and (g–i) tensile stress-strain curves, strengths, and moduli of Vitex negundo wood and biocomposites. (j–k) Flexural and tensile specific strength of Vitex negundo wood and biocomposites. (l) Examples of biocomposites in upholstery and furniture applications.

used medium-density fiberboard (MDF) and high-density fiberboard (HDF), indicating their potential as substitutes. Furthermore, compared with biocomposites prepared by other methods, those obtained via ultrasonic pretreatment achieve notable mechanical performance without the addition of chemical reagents, making the process greener and more environmentally friendly. This finding underscores the significant potential of these biocomposites for use in furniture and interior upholstery applications (Fig 4l).

3.5.Mechanistic studies

The VWP(UT) and VWP(UT-H) biocomposites exhibited favorable physical and chemical properties, whereas VWP showed inferior performance due to the high hemicellulose content retained in the untreated Vitex negundo wood. This reduction in strength resulted from hemicellulose entangling with cellulose, which hindered hydrogen-bond formation between cellulose and lignin and consequently weakened the biocomposite. Thus, ultrasound played a crucial role in the pretreatment process.

Table 1 Comparison of VWP, VWP(UT), VWP(UT-H) with conventional materials and other study samples.

	Density (g/cm^3)	Tensile strength (MPa)	Flexure strength (MPa)	Ref
MDF	0.60	15.03	31.48	[53]
HDF	0.95	18.92	35.82	
VWP	1.44	27.11	55.81	this work
VWP(UT)	1.41	31.15	74.27	
VWP(UT-H)	1.39	35.67	80.73	
biocomposite (0-20 mesh)	1.39	27.7	50.5	[25]
biocomposite (20-40 mesh)	1.37	28.4	45.2	
biocomposite (40-60 mesh)	1.37	36.7	35.3	
biocomposite (60-80 mesh)	1.38	33.9	34.8	
biocomposite (80-100 mesh)	1.43	40.3	33.3	
BWP	1.46	52.55	49.36	[26]
BWP (HCL)	1.55	98.97	92.21	
BWP (Fe_3O_4)	1.64	118.59	110.56	
RWP (6 %)	1.32	49.54	57.82	[30]
RWP (8 %)	1.36	55.71	63.0	
Fiberboards	1.237-1.350	-	20.0-55.0	[34]
ETF-2 h	1.10	-	95.0	[35]
Binderless fiberboard	1.376-1.386	-	24.0	[36]

First, during ultrasonic pretreatment, the generated high-speed shear and micro-jets imparted high energy to the lignocellulosic macromolecules, disrupting the chemical bonds between them and separating these components. Simultaneously, cavitation produced oxidizing free radicals that initiated numerous chemical reactions, promoting the decomposition of lignocellulosic macromolecules (Fig 5). Acoustic cavitation primarily enhances chemical reaction rates by improving mass and energy transfer through general physicochemical effects. This is because cavitation not only increases shear intensity but also locally raises temperature and pressure within the lignocellulose over an extremely short duration, altering its physical form and accelerating the chemical reactions associated with pretreatment.

During ultrasonic pretreatment, partial degradation of hemicellulose and lignin occurred, leading to an increase in the relative lignin content. More hydroxyl groups were exposed on the cellulose molecules, and lignin became more prone to form hydrogen bonds with the fiber surface, thereby enhancing the strength of the biocomposite. These effects were more pronounced at higher pretreatment temperatures.

Second, ultrasonic pretreatment extracted other substances that affect adhesive properties, such as resins and free sugars, thereby promoting self-bonding within the biocomposites and forming stronger inter-fiber bonds. The pretreatment also broke the α-O-4 and β-O-4 linkages in lignin, modifying the lignocellulose structure, and cleaved the ether bonds between hemicellulose and lignin. In this study, lignin—functioning similarly to phenolic resins in conventional composites—acted as a binder. Part of the lignin formed a charred layer on the surface of the biocomposites, improving thermal stability and water resistance. Additionally, hot-pressing collapsed the porous structure and cell walls of the wood, densifying the biocomposite, while the crystalline regions were disrupted and reorganized, resulting in increased crystallinity and mechanical strength.

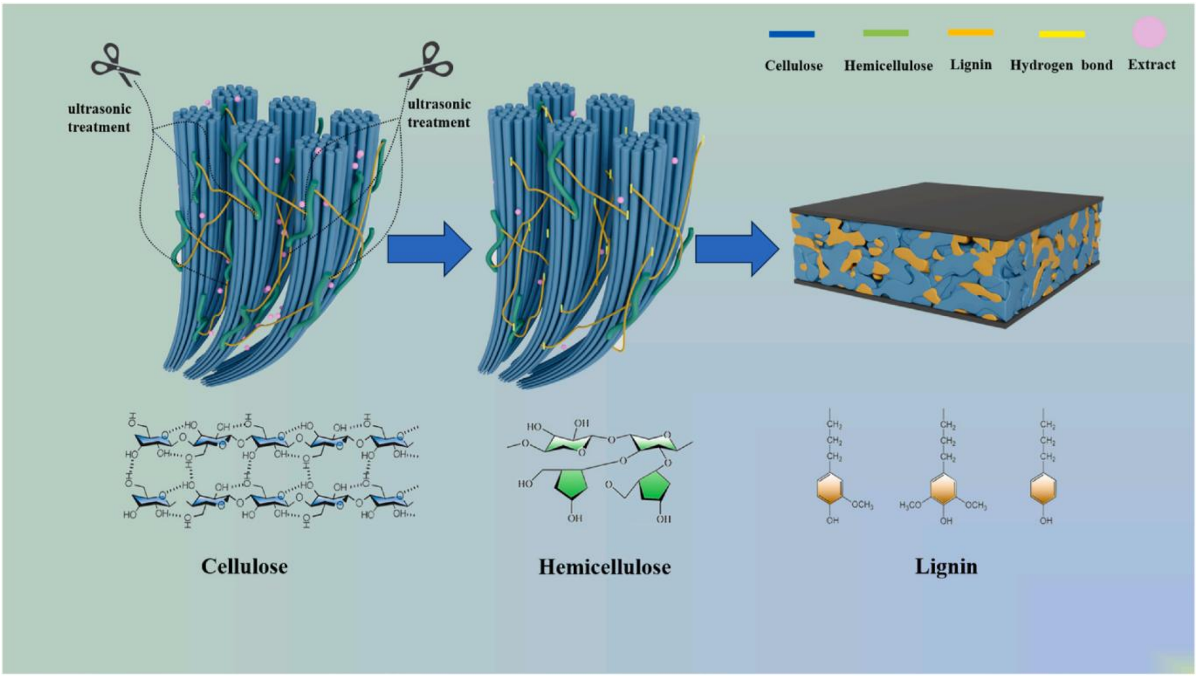

Fig 5. Ultrasonic pre-treatment self-compounding mechanism diagram

4.Conclusions

In this study, a green, efficient, and formaldehyde-free biocomposite with enhanced physical properties was fabricated using ultrasonic pretreatment, and its characteristics were evaluated. This approach offers a novel pathway for biomass conversion by shortening the reaction time, lowering energy consumption, and eliminating the need for toxic or hazardous solvents—thereby aligning with the core principles of green chemistry and sustainability.

Ultrasonic pretreatment disrupts the chemical bonds between lignocellulosic macromolecules via high-speed shear and micro-jet effects, separating the biomass components while preserving the backbone and porous structure of cellulose. This process significantly increases the accessible surface area of cellulose fibers and further densifies the cell walls during subsequent hot pressing. Additionally, the removal of certain wood-flour components that act as fillers or density enhancers leads to a reduction in the overall density of the resulting biocomposite. Concurrently, lignin functions as an intrinsic binder, promoting fiber bonding through both physical entanglement and chemical cross-linking, which contributes to the formation of a dense cellulose network.

The flexural and tensile strengths of the VWP(UT-H) biocomposites reached 80.73 MPa and 35.67 MPa, respectively, representing increases of 144.65 % and 131.57 % compared with the untreated VWP control samples. The pretreatment also yielded biocomposites with low hydrophilicity, evidenced by a water contact angle of 81.72°. Crucially, the process required no external chemical binders and released no formaldehyde, avoiding adverse impacts on human health and making the material a promising candidate for architectural decoration and furniture applications.

These findings demonstrate that ultrasonic pretreatment holds significant potential for converting green waste-such as small-diameter timbe-into high-performance wood-fiber composites. The method may also be adapted to other types of lignocellulosic materials, supporting the production of biocomposites with superior properties in a sustainable and eco-friendly manner.

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