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Fast Preparation of High-Performance Wood Materials Assisted by Ultrasonic and Vacuum Impregnation

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Abstract: In the absence of high-quality hardwood timber resources, we have gradually turned our attention from natural forests to planted fast-growing forests. However, fast-growing tree timber in general has defects such as low wood density, loose texture, and poor mechanical properties. Therefore, improving the performance of wood through efficient and rapid technological processes and increasing the utilization of inferior wood is a good way to extend the use of wood. Densification of wood increases the strength of low-density wood and extends the range of applications for wood and wood-derived products. In this paper, the effects of ultrasonic and vacuum pretreatment on the properties of high-performance wood were explored by combining sonication, vacuum impregnation, chemical softening, and thermomechanical treatments to densify the wood; then, the changes in the chemical composition, microstructure, and mechanical properties of poplar wood before and after treatment were analyzed comparatively by FT-IR, XRD, SEM, and mechanical tests. The results showed that with ultrasonic pretreatment and vacuum impregnation, the compression ratio of high-performance wood reached its highest level and the MOR and MOE reached their maximums. With the help of this method, fast-growing softwoods can be easily prepared into dense wood materials, and it is hoped that this new material can be applied in the fields of construction, aviation, and automobile manufacturing.

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1. Introduction

As a sustainable resource, wood has been used by human beings since ancient times in a wide variety of applications in daily life and production. Wood, as a pollution-free, carbon-fixing, and sustainable resource, is the biomass material with the largest accumulation and carbon storage in terrestrial plants, providing a continuous source of material and energy for human production and life [1]. Throughout history, mankind has exploited wood extensively, and in addition to its traditional usage for materials such as tools, fuel, and construction, it can be combined with modern materials science and nanotechnology to produce advanced functional materials [2,3]. With the shortage of high-quality wood resources, we have gradually shifted our focus from natural forests to fast-growing plantations [4]. It takes several decades for hardwood to be turned into timber, which cannot meet the needs of human beings in the short term. The sharp increase in demand for wood has led to the destruction of forest resources, and the contradiction between supply and demand limits the process of sustainable development [3]. In recent years, poplars and other fast-growing tree species have attracted more and more interest. Planted forests have a short growth cycle, after the fast-growing trees act as a pioneer species allowing slow-growing trees to establish growth and a reproduction base, they are replaced by degrees and felled for use in the timber market. However, the current fast-growing tree plantations are mainly used to meet the supply requirements of wood-based panels, pulping, and wood-plastic composite materials, and their application scenarios are limited

by their inherent defects, which prevent their widespread use in other fields. The multi-layered and micro-porous structure of natural wood provide the basic conditions for the functional improvement of wood [5]. In this regard, physical and chemical methods, as well as a combination of both, are usually applied in wood modification. Among them, the commonly used methods include densification, carbonization, immersion, heat treatment, etc. Densification treatment, as one of the physical modification methods, forms a material with hard texture, high density, and high strength by applying a certain pressure and temperature to the wood [5]. Chemical modification generally refers to the use of chemical reagents to react with wood components to create new covalent bonds between the wood and the reagents [6–9]. Through a series of treatments, the original shortcomings of wood can be ameliorated and overcome, and the mechanical, hydrophobic, flame-retardant, anti-corrosion, dimensional stability, and weather resistance nature of wood can be effectively improved [3,8,9]. Wood thermomechanical densification is a process that produces a hard, high density, and high strength material through the application of heat and pressure to wood, which not only increases its mechanical properties such as elastic modulus and hardness, but also enhances the original physical properties of wood, so that it can effectively extend the range of applications for wood and wood-based materials [10–13]. The alkaline environment of a solution, to a certain extent, swells the wood's cell walls and activates the lignin group, which makes the cell walls easier to compress and be compacted [14–16]. As an effective method of delignification, alkali treatment is also exerted in the preparation of wood-based advanced functional materials such as flexible wood [17] and transparent wood [18–20]. However, high-temperature densified wood suffers from poor dimensional stability and high recovery of deformation [11]. Therefore, it is necessary to develop rapid and facile treatments to ameliorate the process of chemical solutions entering the wood and to shorten the preparation time. Furthermore, the application of sonication and vacuum impregnation technology in the wood field has slowly attracted people's attention. The thermal, mechanical, and cavitation effect of ultrasound can damage the thin-walled tissues of wood cells, open the internal pores, release the extract from the wood, dredge and broaden the internal structure, and further promote the migration of solution substances in the wood [21]. Scholars have studied the effect of ultrasonic irradiation on hydrogen peroxide bleached pulp [22], ultrasonic-assisted treatment of wood pulp fibers [23], and the application of ultrasonic technology in the area of wood drying [24], additionally, ultrasound often participates in the pretreatment of wood by causing surface modifications [25]. The vacuum impregnation technique allows for the formation of a system equilibrium between the impregnating medium and the substance, which strengthens the concentration gradient effect of the substance on the surface of the medium, reduces the resistance to migration of the substance, improves the diffusion of the substance in the medium, consumes less raw material, and improves the quality of the product compared to that obtained through atmospheric impregnation [26]. Vacuum impregnation is an efficient, high quality, and low cost processing technique that is commonly used to assist in the infusion of chemicals or particles, such as in the fabrication of transparent wood [27–29], resin impregnated high-performance wood [30,31], and superhydrophobic wood [21,32,33]. By investigating the effects of ultrasonic pretreatment and vacuum impregnation on the physicochemical properties of high-performance wood materials and the underlying mechanism of action, we can not only enhance the utilization rate and scope of wood, thereby alleviating the contradiction between wood supply and demand, but also provide a reference for the application of sonochemistry and vacuum technology in wood modification. In this paper, ultrasound, vacuum impregnation, chemical softening, and thermomechanical densification were applied in the fabrication of high-performance wood materials. Through Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and mechanical tests, the effects of ultrasound and vacuum treatment on the chemical functional groups, crystallization characteristics, microstructure, and mechanical properties of wood samples were analyzed, and the internal mechanisms of ultrasonics and vacuum treatment in the process of preparation were further explored. It is hoped that the research results

can ameliorate the preparation efficiency, simplify the process, and provide a theoretical basis for the further development of novel wood-derived functional materials in the fields of construction, aerospace, automotive, and electronics [3,13,34].

2. Materials and Methods

2.1. Materials

The heart wood of 21-year-old poplar wood (*Populus ussuriensis* Kom), provided by a plantation in Shijiazhuang City, Hebei Province, China, was used as the experimental material. The wood samples were cut into a size of 60 mm (longitudinal) $\times$ 20 mm (tangential) $\times$ 20 mm (radial). All the selected samples had no knots, discoloration, or other obvious defects. To avoid the impact of environmental factors, the cut blocks were kept at 20 °C and 65% RH to reach a hygroscopic equilibrium. Other materials: sodium hydroxide (>96%), sodium sulfite (>97%), deionized water, and ethanol were purchased from Harbin. All the chemical materials used in the experiments were analytical grade.

2.2. Delignification Procedure

There were five treatment groups and one control group. The first group was treated with an appropriate amount of ethanol and deionized water at 95 °C for 1 h (labeled as OW); the second group was treated with lye and ethanol at 95 °C for 1 h (labeled as TW); the third group was treated with lye and ethanol under ultrasound for 0.5 h and vacuum impregnation for 0.5 h (labeled as MW); the fourth group was treated with an appropriate amount of the above alkaline mixture and ethanol under sonication for 1 h (labeled as SW); the fifth group was impregnated with an alkaline solution and ethanol under vacuum for 1 h (labeled as VW). The sixth group was set as natural wood (NW) without any treatment. The alkaline solution was prepared through mixing 2.5 M NaOH and 0.4 M Na₂SO₃. First, 1.6 L of deionized water were added to the ultrasonic cleaner. Then, the wood blocks were immersed in the aqueous solution in beakers, and then the beakers containing reasonable amounts of ethanol were put into an ultrasonic cleaner (G-020S, China). The vacuum impregnation process involved placing lye and the sample in a beaker and applying the vacuum pump for one hour at an air pressure of -0.1 MPa. After the sonication and impregnation procedure, the remaining process of delignification was performed in a water bath oscillator at 95 °C with an oscillation frequency of 35 rpm; the entire softening step lasted 4 h. Finally, the delignified wood pieces were washed in deionized water three times and immersed in boiling deionized water to remove the residual chemicals. A detailed schematic of the wood-softening process is shown in Figure 1.

Figure 1. Schematic of the preparation of softened wood through ultrasonic or vacuum technology and chemical treatment.

2.3. Fourier Transform Infrared Spectroscopy

The air-dried natural wood blocks and softened wood samples were milled to 200–300 mesh wood particle size and mixed with potassium bromide at a weight ratio of 1:100 to make tablets. To obtain a better comprehension of the impacts of different pretreatments on the properties of poplar wood, the functional groups of the tablets were then examined with a FTIR (Nicolet is50, Thermo fisher, Waltham, MA, USA) over the range of 800–4000 cm^{-1} by 32 scans at a resolution of 4 cm^{-1} .

2.4. X-ray Diffraction

The original and softened wood samples were milled into flour with a 200–300 mesh, and the flour was analyzed with X-ray diffraction (XRD-6100, Shimadzu corporation, Kyoto, Japan) at 40 kV of radiant tube voltage, 30 mA of radiant tube current, and 3–87 degrees of scanning range. The scanning speed rate for all wood samples was set to 8° per minute.

2.5. Densification Treatment

After chemical treatment, the wood was wrapped with aluminum foil and the delignified wood pieces were densified by using a hot press molding machine (ZS-406, China). Initially, the working temperature of the machine was set at 110 °C, under the pressure of 2 MPa for 1 h and 5 MPa for 23 h, while keeping the pressure for 12 h and turning off the temperature controller. After the hot-pressing procedure, the densified poplar wood samples were removed and stored in an oven at 50–60 °C for 12 h. The details are shown in Figure 2.

Figure 2. Schematic of the hot-pressing densification process. (a) Set the heating temperature to 110 °C and load a pressure of 2 MPa for 1 h, and then maintain the pressure of 5 MPa. (b) Turn off the temperature controller and continue to maintain the pressure for 12 h.

2.6. Physical and Mechanical Properties Measurement

2.6.1. Physical Test

For the compression recovery ratio measurement, three small specimens from each group were sawn into small pieces. To evaluate the enhancement of the dimensional stability of the samples, the compression recovery ratio was estimated by immersing the samples in deionized water for 24 h and measuring the oven-dried sample (40 °C, 24 h) thickness before and after immersing. Thickness was measured twice from each specimen by slide caliper and compression recovery ratio was calculated following Equation (1):

$$\text{Compression recovery ratio} = \frac{T_r - T_d}{T_o - T_d} \times 100\% \quad (1)$$

where T_r is the recovered thickness of immersing and drying, T_d is the thickness of the densified wood, and T_o is the thickness of the original wood.

2.6.2. Mechanical Test

Bending experiments were performed on the wood using a universal mechanical testing machine with reference to the method of GB/T 1936-2009 to test the modulus of rupture and the modulus of elasticity. Considering the realistic testing environment and sample size, the mechanical tests were carried out directly on the densified wood samples. The three-point bending experiment was performed in the middle of the tangential surface of the rectangular wood specimens, using an electronic universal mechanical testing machine (WSM-30KN, China) to characterize the modulus of rupture (MOR) and modulus of elasticity (MOE), adjusting the span between the devices to 46 mm, and loading the samples at a rate of 5 mm/min.

2.7. Scanning Electron Microscope

Cross-sectional samples of wood pieces that were perpendicular to the growth direction and tangential samples that were parallel to the growth direction were prepared and sprayed with gold atoms under vacuum conditions for observation. The scanning electron microscope (SEM, SU8100, Japan) at an accelerating voltage of 2.0 kV was applied to analyze the micro-morphological changes in the cross-section and tangential-section samples of the densified wood and natural wood.

3. Results and Discussion

3.1. Delignification and Densification

The delignification process began from the reaction between the OH^- ions in the aqueous solution and the lignin in the cell wall of the wood samples, that is, the dissolution occurred between the OH^- ions and the major chemical components in the cell wall, leading to the removal of lignin from wood cell wall. With the prolongation of the reaction time and the auxiliary roles of the ultrasound and vacuum, the solution continued to penetrate into the cell wall, resulting in the rapid removal of lignin in the cell wall when the solution reached a certain concentration [15]. Moreover, OH^- ions can dissolve lignin and retain cellulose structure to the greatest extent. Meanwhile, SO_3^{2-} ions can react with lignin and dissolve it, and OH^- helped to increase the sulfonation rate of lignin in this process.

Figure 3 shows detailed optical images. The final treated solution was yellowish brown; according to previous studies, the main factors affecting wood color are the changes in lignin and the pigments [18]. Lignin has an extremely complex structure with dark color, and lignin macromolecules contain many auxiliary color groups, such as hydroxyl, carboxyl, and ether-bonded groups. Under certain conditions, these co-chromatic groups reacted with external inorganic compounds, such as sodium sulfite, to produce a special color that turns the solution a yellowish-brown color. Furthermore, during the delignification process, the ultrasonic cavitation effect and vacuum impregnation open up the internal pores of the wood, allowing more of the wood extractables in the pores and vessels to be released. As the softened wood was compressed, the color of the wood became darker, which can be attributed to the reorganization of wood cells and the aggregation of color components caused by hot pressing, as evidenced by the scanning electron microscopy images.

Figure 3. Optical images of natural wood, softened wood, and densified wood. (a) Longitudinal direction, (b) tangential direction.

3.2. FT-IR Analysis

Wood is a polymeric biomass material composed of cellulose, hemicellulose, and lignin [35]. The hydroxyl group of cellulose vibrates and absorbs very strongly in the infrared spectrum, the hemicellulose has functional groups such as acetyl and hydroxyl groups in the infrared sensitive group, while the carbonyl and benzene rings in lignin can also produce obvious infrared absorption [36]. Ultrasonic and vacuum synergistic chemical treatment had a great impact on the composition and content of wood cell walls. Figure 4 shows the infrared absorption spectra of poplar wood specimens in the range of $800\text{--}4000\text{ cm}^{-1}$ under different pretreatments. The main reason for the poor dimensional stability of wood is that the cellulose, hemicellulose, and lignin within the wood contain a large number of free, highly absorbent hydroxyl groups [37].

Figure 4. Infrared spectrum of natural wood (NW), full water bath treatment wood (TW), control group (OW), ultrasonic and vacuum mixed treatment group (MW), sonication group (SW), and vacuum treatment group (VW).

As can be seen from the Figure 4, the intensity of the characteristic absorption peaks of the three main components in the wood varies with the pretreatment methods. Ultrasonic waves perform a series of alternating expansion and cavitation effects, dredging the microscopic pores in the wood, reducing the intrusion and filling in the pores, and lowering the content of wood extracts to form more pores and channels, which provides a smooth path for chemicals to enter the wood and react with hemicellulose and lignin completely. At the same time, vacuum impregnation exacerbates the difference in concentration, allowing more chemicals to enter the wood cells and participate in more reactions.

Figure 4 shows the changes in the infrared absorption peak intensity of NW and the different pretreatments. Firstly, the intensity of the absorption peak near 3673 cm^{-1} is reduced to varying degrees in both the NW and OW groups compared to those of the remaining four groups. The SW and VW groups, on the other hand, had the weakest relative free hygroscopic hydroxyl vibration, which may be due to the degradation of wood cell wall components caused by the penetration of alkali into the wood under the synergistic effect of sonication and vacuum impregnation. In addition, previous studies [38,39] showed that the reduction of free hydroxyl groups between molecular chains is the main reason for the significant increase in dimensional stability and the significant decrease in moisture absorption of wood. The C–H stretching vibration is around 2992 cm^{-1} and the absorption peak is significantly weaker after the chemical softening treatment, and this result is most evident in the SW and VW groups. This was attributed to the intensive removal of hemicellulose and lignin from the wood cell walls, assisted by ultrasound and vacuum. Furthermore, the characteristic peak of hemicellulose appears to decrease around 1403 cm^{-1} and 1060 cm^{-1} , which is consistent with previous findings [40] and indicates the removal of hemicellulose. In addition, the SW and VW groups exhibit the lowest peak at 1239 cm^{-1} , where the absorption peaks of lignin acetyl and ethers are located, which also implies the dissolution of lignin with the alkaline solution under these two treatment groups.

By summarizing the infrared absorption spectra of the wood samples, it can be found that the chemical changes of cellulose, hemicellulose, and lignin within the wood during the ultrasonic, vacuum-impregnation and chemical synergistic softening treatment of poplar wood resulted in the removal of some hemicellulose and lignin, weakening the connection between the tissues of the wood. Moreover, the changes in each of the above are more pronounced in SW and VW, demonstrating that ultrasonic and vacuum pretreatment have raised the reaction efficiency, and the effect of delignification is better over the same time period. Wood thickness also affects the chemical properties of wood to some extent.

3.3. XRD Analysis

The crystallinity of cellulose refers to the percentage of the crystalline region of cellulose in the whole cellulose, and as the crystallinity increases, the tensile strength and elastic modulus of the fiber also increase. In this work, X-ray diffraction was used to study the position of the diffraction peak, cellulose crystallinity, and the width of the crystalline zone of the poplar specimen 002 crystal plane under various conditions. Figure 5 shows that compared with the control material, the position of the crystalline diffraction peaks of the wood cellulose 002 crystal plane was almost unchanged after treatment, which indicates that the ultrasonic and vacuum treatment had no obvious effect on the crystalline zone of wood [41]. The structure of cellulose in wood is particularly complex, and the X-ray diffraction pattern of natural wood is the result of the joint action of crystallization and non-crystallization regions.

In the X-ray diffraction pattern of natural wood, the highest peak is located at $2\theta = 22^\circ$, and this peak is the 002 crystal plane, which represents the width of the crystalline region, and the small inconspicuous peak that exists near $2\theta = 34^\circ$ is the diffraction peak in the 040 crystal plane, which encompasses the length of the crystalline region. The intensity of the 002 crystal plane is higher, while the intensity of the 040 crystal plane is lower, mainly because the molecules within the cellulose are located in a plane roughly parallel to the 002 crystal plane. There is a trough at $2\theta = 16^\circ$, which is the diffraction intensity of the

amorphous region. As shown in Figure 5, the diffraction peaks of 002 and 040 in the crystalline region and the diffraction troughs in the non-crystalline region are still clearly present on the X-ray diffraction pattern of the poplar wood specimen after processing. This series of results shows that ultrasonic, vacuum, and chemical co-treatment does not change the co-existence of crystalline and non-crystalline regions of the wood. The crystalline zone is not affected before or after the treatment; the diffraction peaks in the 002 plane of the wood samples before and after the treatment are at $2\theta = 22^\circ$. However, when analyzing the level of diffraction peak intensity, the difference in diffraction peak intensity between the groups of samples on the 002 and 040 planes is not significant, which means that the synergistic treatment does not have much of an effect on the width and length of the crystalline zone of the cellulose inside the wood. In the diffraction valleys, there were changes before and after the treatment, which indicated that the softening treatment influenced the non-crystalline zone of the wood, and the crystallinity of the wood changed to a certain extent in the SW and VW groups. This consequence can be jointly interpreted by Li et al. [42]: The removal of lignin and the penetration of chemical reagents into the crystalline region of cellulose during the delignification process resulted in the disintegration of part of the crystalline zone and caused a slight decrease in crystallinity.

Figure 5. XRD map of natural wood (NW), full water bath treatment wood (TW), control group (OW), ultrasonic and vacuum mixed treatment group (MW), sonication group (SW), and vacuum treatment group (VW).

3.4. Physical and Mechanical Analysis

Figure 6a shows the compression level, compression recovery ratio, the modulus of rupture (MOR), and the modulus of elasticity (MOE) of the densified wood under different pretreatments. MOR is one of the most important mechanical properties of wood, which refers to the ability of wood to resist bending without breaking. MOE is also a crucial mechanical property parameter of wood. From a macroscopic point of view, MOE measures the ability of the wood to resist deformation, and from a microscopic point of view, it reflects the strength of the forces acting between the molecules of the wood components. As wood materials are likely subject to excessive bending and sagging deformation in practical applications, the study of enhancing the MOR and MOE of wood is of great significance for the application of wood materials in other fields. A trend of increasing compression levels can be seen from the full water bath treatment to the media co-treatment, and the

compressibility is close in the SW and VW groups, indicating that higher compressibility is obtained under the ultrasonic and vacuum impregnation pretreatment. Compared with previous studies [9,33], one of the reasons why the compressibility of wood has been increased is that the porous and multi-layered structure of wood are more fully exposed under the lye treatment assisted by ultrasound and vacuum, so that a higher compaction rate can be obtained.

At the same time, according to previous research, the arrangement, interactions, and properties of chemical components in wood materials govern their mechanical properties [43,44]. Figure 6b shows the MOR and MOE of natural wood samples (NW) as well as densified wood, and what is known is that the modulus of elasticity and the modulus of rupture are increased for the remaining groups compared with those from the full water bath treatment and the natural wood. However, for the same treatment time, the MOR of the MW group and the MOE of the SW group reached a maximum value of 40.53 MPa and 2765 MPa, respectively. It can be seen that the mechanical properties of the samples were greatly improved after the treatment, with an increase of 60.1% and 77.2% in MOR and MOE, respectively, compared to those of natural wood. Moreover, when analysis is carried out with the full water bath samples, there is an increase of approximately 40.6% and 55.8%, respectively. Previous studies have suggested that the hemicellulose content of densified wood is closely related to the mechanical properties of the wood, which is composed of three main polymers that influence the mechanical properties of the wood: lignin, hemicellulose, and cellulose. Combined with the FTIR results above, it is known that the lower MOR and MOE of the VW group compared to those of other groups in the present work may be due to the significant degradation of the lignin and hemicellulose of the wood cells during the lye pretreatment and hot pressing process, resulting in a relative reduction in mechanical properties.

Figure 6. Physical and mechanical results under different treatment groups. (a) Compression level and compression recovery ratio. (b) Modulus of rupture (MOR) and modulus of elasticity (MOE).

3.5. Microstructure Analysis

It is believed that the removal of lignin does not change the arrangement of fibers, so the multilayer structure of wood and the arrangement of wood fibers remain the same. The fiber arrangement does not change with the increase of delignification degree [15]. Figure 7 shows the SEM results of natural wood and densified wood. The synergistic softening treatment and the hot-press densification treatment changed the cellular morphology of the wood timber, resulting in significant changes in the microstructure of poplar wood. The walls of the ducts of natural wood were very smooth and the pores were well arranged. However, the walls of the ducts of the co-softened wood samples were no longer smooth

and the grain pore membranes were damaged to different degrees to create new pores, which indicated that the co-softening treatment destroyed the weak tissues such as grain pore membranes and formed new pores and channels. Scanning electron micrographs of the hot-press densified samples show that the ducts and wood fiber cells of the wood received compression, resulting in a large deformation, and the cells were squeezed into a flattened shape by heat and pressure. In addition, a bunch of aggregates are shown on the tangential surface of the densified wood, which indicates that the cells underwent sufficient compression and reorganization after the hot-press densification process. Due to the regular radial alignment, cracks are present in the figures, which may be due to the degradation of the middle layer in the direction of pressure loading during hot pressing. By comparing the microstructure diagrams of natural wood and densified wood, it is clear that the space inside the conduit has been squeezed to a very small volume after the wood has been densified by hot pressing.

Figure 7. SEM images of natural wood ((a,b) cross-section, (c,d) tangential section) and densified wood ((e,f) cross-section, (g,h) tangential section) at different magnifications.

4. Conclusions

In this paper, densified wood materials were fabricated by synergistic chemical softening and hot-pressing densification under the pretreatment of sonication and vacuum impregnation. The FTIR analyses showed that the chemical composition of the wood, such as lignin and hemicellulose content, was partially degraded and removed under different conditions, which affected the mechanical and physicochemical properties of the wood to some extent. Nevertheless, according to the XRD studies, the crystalline properties of the cellulose were slightly changed by this series of synergistic treatments. Based on the results of MOR and MOE, it could be confirmed that the mechanical properties of the ultrasonic groups were superior to those of other methods. The SEM images reconfirmed that the removal of wood polymers in cell walls and the rearrangement of cells after the hot-pressing process. Taking all the results into account, the method proposed in this study can easily fabricate high performance densified wood materials from fast-growing softwood, and these wood-derived materials can be used as candidates for new lightweight and high performance materials in the fields of construction, aviation, and automotive. The ultrasonic and vacuum impregnation pretreatments mentioned in this paper, in addition, provide new ideas for wood modification, which can be combined with conventional modification methods in future research to produce novel materials with even better properties.

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References

- Burgert, I.; Cabane, E.; Zollfrank, C.; Berglund, L. Bio-inspired functional wood-based materials—hybrids and replicates. *Int. Mater. Rev.* **2015**, *60*, 431–450. [\[CrossRef\]](#)
- Berglund, L.A.; Burgert, I. Bioinspired wood nanotechnology for functional materials. *Adv. Mater.* **2018**, *30*, 1704285. [\[CrossRef\]](#)
- Jiang, F.; Li, T.; Li, Y.; Zhang, Y.; Gong, A.; Dai, J.; Hitz, E.; Luo, W.; Hu, L. Wood-based nanotechnologies toward sustainability. *Adv. Mater.* **2018**, *30*, 1703453. [\[CrossRef\]](#)
- Li, J.; Zhang, A.; Zhang, S.; Gao, Q.; Chen, H.; Zhang, W.; Li, J. High-performance imitation precious wood from low-cost poplar wood via high-rate permeability of phenolic resins. *Polym. Compos.* **2018**, *39*, 2431–2440. [\[CrossRef\]](#)
- Li, T.; Zhai, Y.; He, S.; Gan, W.; Wei, Z.; Heidarinejad, M.; Dalgo, D.; Mi, R.; Zhao, X.; Song, J.; et al. A radiative cooling structural material. *Science* **2019**, *364*, 760–763. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lang, Q.; Zeng, B.; Pu, J.W. Characterization of chemical wood modification with melamine-urea-formaldehyde prepolymer on fast-growing wood. *Wood. Fiber. Sci.* **2014**, *46*, 1–11.
- Noël, M.; Grigsby, W.J.; Ormondroyd, G.A.; Spear, M.J. Influence of water and humidity on chemically modifying wood with polybutylene succinate bio-polyester. *Inter. Wood. Prod. J.* **2016**, *7*, 80–88. [\[CrossRef\]](#)
- Xiao, Z.; Xie, Y.; Mai, C. The fungal resistance of wood modified with glutaraldehyde. *Holzforschung* **2012**, *66*, 237–243. [\[CrossRef\]](#)
- Tuong, V.M.; Li, J. Changes caused by heat treatment in chemical composition and some physical properties of acacia hybrid sapwood. *Holzforschung* **2011**, *65*, 67–72. [\[CrossRef\]](#)
- Ahmed, S.A.; Morén, T.; Hagman, O.; Cloutier, A.; Fang, C.H.; Elustondo, D. Anatomical properties and process parameters affecting blister/blow formation in densified European aspen and downy birch sapwood boards by thermo-hygro-mechanical compression. *J. Mater. Sci.* **2013**, *48*, 8571–8579. [\[CrossRef\]](#)
- Fang, C.H.; Mariotti, N.; Cloutier, A.; Koubaa, A.; Blanchet, P. Densification of wood veneers by compression combined with heat and steam. *Eur. J. Wood. Wood. Prod.* **2012**, *70*, 155–163. [\[CrossRef\]](#)
- Čabalová, I.; Kačík, F.; Lagaña, R.; Výboňová, E.; Bubeníková, T.; Čaňová, I.; Ďurkovič, J. Effect of Thermal Treatment on the Chemical, Physical, and Mechanical Properties of Pedunculate Oak (*Quercus robur* L.) Wood. *Bioresources* **2017**, *13*, 157–170. [\[CrossRef\]](#)
- Song, J.; Chen, C.; Zhu, S.; Zhu, M.; Hu, L. Processing bulk natural wood into a high-performance structural material. *Nature* **2018**, *554*, 224–228. [\[CrossRef\]](#)
- Xu, E.; Wang, D.; Lin, L. Chemical Structure and Mechanical Properties of Wood Cell Walls Treated with Acid and Alkali Solution. *Forests* **2020**, *11*, 87. [\[CrossRef\]](#)
- Boshi, W.U.; Zhang, X.; Yang, J.; Feng, X.U. Dissolution Mechanism of Lignin in Chinese-fir Cell Walls during Chlorite Pretreatment. *Chem. Ind. For. Prod.* **2017**, *37*, 38–44.
- Mburu, F.; Dumarçay, S.; Bocquet, J.F.; Petrisans, M.; Gérardin, P. Effect of chemical modifications caused by heat treatment on mechanical properties of *Grevillea robusta* wood. *Polym. Degrad. Stabil.* **2008**, *93*, 401–405. [\[CrossRef\]](#)
- Song, J.; Chen, C.; Wang, C.; Kuang, Y.; Li, Y.; Jiang, F.; Li, Y.; Hitz, E.; Zhang, Y.; Liu, B.; et al. Superflexible Wood. *ACS Appl. Mater. Inter.* **2017**, *9*, 23520–23527. [\[CrossRef\]](#)
- Zhu, M.; Song, J.; Li, T.; Gong, A.; Wang, Y.; Dai, J.; Yao, Y.; Luo, W.; Henderson, D.; Hu, L. Highly Anisotropic, Highly Transparent Wood Composites. *Adv. Mater.* **2016**, *28*, 5181–5187. [\[CrossRef\]](#) [\[PubMed\]](#)
- Vasileva, E.; Li, Y.; Sychugov, I.; Mensi, M.; Berglund, L.; Popov, S. Lasing from Organic Dye Molecules Embedded in Transparent Wood. *Adv. Opt. Mater.* **2017**, *5*, 1700057. [\[CrossRef\]](#)
- Chao, J.; Tian, L.; Chen, C.; Dai, J.; Kierzewski, I.M.; Song, J.; Li, Y.; Yang, C.; Wang, C.; Hu, L. Scalable, Anisotropic Transparent Paper Directly from Wood for Light Management in Solar Cells. *Nano Energy* **2017**, *36*, 366–373.
- Lin, L.; Cao, J.; Zhang, J.; Cui, Q.; Liu, Y. Enhanced Anti-Mold Property and Mechanism Description of Ag/TiO₂ Wood-Based Nanocomposites Formation by Ultrasound- and Vacuum-Impregnation. *Nanomaterials* **2020**, *10*, 682. [\[CrossRef\]](#)
- He, Z.; Yang, F.; Yi, S.; Gao, J. Effect of ultrasound pretreatment on vacuum drying of Chinese catalpa wood. *Dry. Technol.* **2012**, *30*, 1750–1755. [\[CrossRef\]](#)
- Chen, J.; Jiang, Q.; Yang, G.; Wang, Q.; Fatehi, P. Ultrasonic-assisted ionic liquid treatment of chemithermomechanical pulp fibers. *Cellulose* **2017**, *24*, 1483–1491. [\[CrossRef\]](#)
- He, Z.; Fei, Y.; Peng, Y.; Yi, S. Ultrasound-Assisted Vacuum Drying of Wood: Effects on Drying Time and Product Quality. *Bioresources* **2013**, *8*, 855–863. [\[CrossRef\]](#)

25. Mu, H.; Wang, Y.; Tian, Y.; Duan, X.; Qi, D. Microstructure and Hydrophobic Properties of Nano-Cu-Coated Wood-Based Composites by Ultrasonic Pretreatment. *Appl. Sci.* **2020**, *10*, 5448. [\[CrossRef\]](#)
26. Dong, Y.; Yan, Y.; Zhang, S.; Li, J. Wood/Polymer Nanocomposites Prepared by Impregnation with Furfuryl Alcohol and Nano-SiO₂. *Bioresources* **2014**, *9*, 6028–6040. [\[CrossRef\]](#)
27. Wu, Y.; Wu, J.; Yang, F.; Tang, C.; Huang, Q. Effect of H₂O₂ Bleaching Treatment on the Properties of Finished Transparent Wood. *Polymers* **2019**, *11*, 776. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Wang, X.; Zhan, T.; Liu, Y.; Shi, J.; Pan, B.; Zhang, Y.; Cai, L.; Shi, S.Q. Large-Size Transparent Wood for Energy-Saving Building Applications. *ChemSusChem* **2018**, *11*, 4086–4093. [\[CrossRef\]](#)
29. Li, Y.; Yu, S.; Veinot, J.; Linnros, J.; Berglund, L.; Sychugov, I. Luminescent Transparent Wood. *Adv. Opt. Mater.* **2017**, *5*, 1600834. [\[CrossRef\]](#)
30. Gindl, W.; Gupta, H.S. Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation. *Compos. Part. A Appl. Sci.* **2002**, *33*, 1141–1145. [\[CrossRef\]](#)
31. Shams, M.I.; Kagemori, N.; Yano, H. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin IV: Species dependency. *J. Wood. Sci.* **2006**, *52*, 179–183. [\[CrossRef\]](#)
32. Wang, K.; Dong, Y.; Yan, Y.; Qi, C.; Zhang, S.; Li, J. Preparation of mechanical abrasion and corrosion resistant bulk highly hydrophobic material based on 3-D wood template. *RSC Adv.* **2016**, *6*, 98248–98256. [\[CrossRef\]](#)
33. Dong, X.; Zhuo, X.; Wei, J.; Zhang, G.; Li, J. Wood-Based Nanocomposite Derived by in Situ Formation of Organic-Inorganic Hybrid Polymer within Wood via a Sol-Gel Method. *ACS Appl. Mater. Inter.* **2017**, *9*, 9070–9078. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Yu, Z.L.; Ning, Y.; Zhou, L.C.; Ma, Z.Y.; Zhu, Y.B.; Lu, Y.Y.; Bing, Q.; Xing, W.Y.; Tao, M.; Li, S.C. Bioinspired polymeric woods. *Sci. Adv.* **2018**, *4*, 7223. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Jia, C.; Chen, C.; Mi, R.; Li, T.; Hu, L. Clear Wood toward High-Performance Building Materials. *ACS Nano* **2019**, *13*, 9993–10001. [\[CrossRef\]](#)
36. Zhou, C.; Wei, J.; Via, B.K.; Fasina, O.; Han, G. Prediction of mixed hardwood lignin and carbohydrate content using ATR-FTIR and FT-NIR. *Carbohydr. Polym.* **2015**, *121*, 336–341. [\[CrossRef\]](#)
37. Shi, J.; Peng, J.; Huang, Q.; Cai, L.; Shi, S.Q. Fabrication of densified wood via synergy of chemical pretreatment, hot-pressing and post mechanical fixation. *J. Wood Sci.* **2020**, *66*, 1–9. [\[CrossRef\]](#)
38. Jiang, B.; Chen, C.; Liang, Z.; He, S.; Kuang, Y.; Song, J.; Mi, R.; Chen, G.; Jiao, M.; Hu, L. Lignin as a Wood-Inspired Binder Enabled Strong, Water Stable, and Biodegradable Paper for Plastic Replacement. *Adv. Funct. Mater.* **2020**, *30*, 1906307. [\[CrossRef\]](#)
39. Zhang, S.Y.; Wang, C.G.; Fei, B.H.; Yu, Y.; Cheng, H.T.; Tian, G.L. Mechanical function of lignin and hemicelluloses in wood cell wall revealed with microtension of single wood fiber. *BioResources* **2013**, *8*, 2376–2385. [\[CrossRef\]](#)
40. Wu, Y.; Han, Y.; Huang, N.; Wu, J.M.; Tang, C.Y.; Zhou, J.C.; Huang, Q.T. Effect of delignification process on properties of transparent wood (in Chinese). *J. For. Eng.* **2019**, *4*, 98–104.
41. French, A.D. Idealized powder diffraction patterns for cellulose polymorphs. *Cellulose* **2014**, *21*, 885–896. [\[CrossRef\]](#)
42. Li, Z.; He, W.; Qiang, H.; Wang, R.; Guo, F.Y.; Cao, J.Z.; Lu, M.T. Preparation and properties of directionally reconstituted bamboo cellulose fiber/phenolic resin composites (in Chinese). *Acta Mater. Compos. Sin.* **2021**, *38*, 1–9.
43. Zhu, R.; Yadama, V. Effects of hot water extraction pretreatment on physicochemical changes of Douglas fir. *Biomass Bioenerg.* **2016**, *90*, 78–89. [\[CrossRef\]](#)
44. Pramreiter, M.; Stadlmann, A.; Huber, C.; Konnerth, J.; Müller, U. The Influence of Thickness on the Tensile Strength of Finnish Birch Veneers under Varying Load Angles. *Forests* **2021**, *12*, 87. [\[CrossRef\]](#)