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Laminating wood fiber mats into a densified material with high performance

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A B S T R A C T

To develop high-performance wood materials, a novel preparation strategy is presented in this study. Wood fiber mats impregnated with phenolic resin, were laminated into a densified material. Wood lumens collapsed layer by layer during densification, leading to a compact multi-layered structure. The densified material had excellent mechanical properties and favorable water resistance. The flexural, compressive, and short-beam shearing strength were approximately 230%, 400%, and 260% higher than that of natural wood, respectively. The water absorption rate and thickness swelling rate in boiled water were 19% and 5.7%, respectively. Surface water repellency was also enhanced due to reduction of hydrophilic groups on the surface. Such high performance makes the material a promising candidate for advanced engineering structures and applications.

1. Introduction

Wood possesses certain advantages such as high specific strength, good processability, and favorable aesthetics, and has been used for millennia as a structural material in the fields of architecture and furniture [1]. However, mechanical performance, dimensional stability, and durability of natural wood, particularly many fast-growing species, cannot yet meet the need of advanced engineering structures and applications due to inherent heterogeneity (*e.g.,* tissue cell types and anatomical variability) and natural defects (*e.g.* knots) [2]. A prominent approach to overcome the drawbacks is densification, by which high homogeneity and directionality of wood structure and thus excellent mechanical properties can be achieved [3].

Softening of the wood is essential to facilitate the densification at low pressure. Heat and steam are the most frequently used methods but they are costly [4]. Another method is delignification, by which complete densification can be achieved under low pressure [5]. However, this option requires waste disposal and has environmental problems [6]. Phenolic resin can prominently soften wood cell walls and decrease the Young's modulus (MOE) of wood fibers [7]. It has been proven that phenolic resin impregnation is an environmentally friendly and effective method to enhance wood densification [8]. Moreover, the method is cost-efficient to improve the dimensional stability and resistance to biological attack of wood [9].

To add more resin into wood lumens and cell walls, high permeability must be achieved. Directional splitting is a process to produce wood fiber mats for new-type scrimbers [10]. The mats exhibit a web-like structure comprising long and narrow fiber bundles, which can substantially improve liquid permeability. Furthermore, the fiber orientation and the natural appearance of the wood are not affected by the process.

In this study, fiber mats were prepared using fast-growing pine wood, impregnated with phenol formaldehyde resin, and laminated into a densified material. The structure, mechanical properties and water resistance of the densified material were investigated. The objective of this study was to develop a novel strategy for the preparation of high-performance wood material.

2. Materials and methods

2.1. Materials

Radiata pine (*Pinus radiata D. Don.*) was purchased from Linyi Jinshan Wood Co., Ltd (China). Low-weight-molecular (~300) phenol formaldehyde (PF) resin was supplied by Dynea (Guangdong) Co., Ltd. All reagents were of chemical grade and purchased from Aldrich Chemical (Shanghai) Co., Ltd.

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2.2. Methods

2.2.1. Preparation of densified wood

Wood fiber mats were processed according to a standard method [10]. In brief, the softened log was peeled into veneers with 6 mm thickness, and then split along the wood grain into fiber mats (Fig. S1). The densified wood ($300 \times 50 \times 20\ \mathrm{mm}^3$) was obtained through laminating the mats impregnated with PF resin at 145 °C under ~10 MPa for 30 min. The resin content was approximately 13% based on the weight of oven-dried mats. Prior to laminating, the mats were dried at 40 °C to a moisture content of ~11%.

2.2.2. Characterization

Micromorphology was observed using a S3400 scanning electron microscope (SEM) (Hitachi, Japan). Wetting behavior was determined by an OCA20 contact angle analyzer (Dataphysics, Germany) and free energy was calculated according to the Lifshitze-van der Waals/acid-base (LW-AB) approach [11]. Surface energy was measured on an AXIS Ultra XPS spectrometer (Kratos Analytical, Japan) equipped with a monochromated Al-Kα source ($h\nu = 1486.6$ eV). Flexural, compressive, and short-beam shearing properties were tested on a CMT5105 universal testing machine (MTS systems, China) according to ASTM D-1037, D3501-2005, and D2344, respectively [12]. Water absorption rate (*WAR*) was determined by the following method: Dried samples were boiled for 4 h, then dried at 63 ± 3 °C for 20 h, and finally boiled for another 4 h. *WAR* was calculated by Eq. (1):

$$WAR = (m_2 - m_1) \times 100\%/m_1, \tag{1}$$

where m_1 and m_2 were the weight of samples before and after treated, respectively. Thickness swelling rate (*TSR*) was calculated using Eq. (2):

$$TSR = (t_2 - t_1) \times 100\%/t_1, \tag{2}$$

where t_1 and t_2 were the thickness of samples before and after treated, respectively.

3. Results and discussion

3.1. Densified wood formation

Fig. 1a shows that the process for densified wood involved processing of fiber mats, impregnating with phenolic resin, and hot pressing. The pine wood comprised many aligned lumens along the wood growth direction (Fig. 1c, d), but the recalcitrant microstructure (*e.g.,* denser cell walls and aspirated pits) protected from external liquid penetration, and thus the water loading rate (*WLR*) was only 11.31% (Fig. S2). As the pine log was peeled into thick veneers, tiny cracks on the surface (Fig. 1b) were formed by the stress induced by peeling. These cracks opened the paths to water, and *WLR* reached 30.28% (Fig. S2). Directionally split by the fluffing machine (Fig. S1), the veneers turned into fiber mats with the chink-rich structure (Fig. 1e), and thus higher *WLR* (*i.e.,* 161.34%) was achieved (Fig. S2). High permeability allowed more resin molecules to penetrate into the lumens and cell walls, which facilitated the densification of fiber mats. More than threefold increase in density was achieved for densified wood (Table S1). Upon hot-pressing perpendicular to the wood grain, cell walls tightly collapsed layer by layer, forming a compact multi-layered structure (Fig. 1f, g) with a porosity of 2.11 v/v%. Because of the softening function of phenolic resin, there were only a few cracked cell walls within the densified wood (Fig. S3).

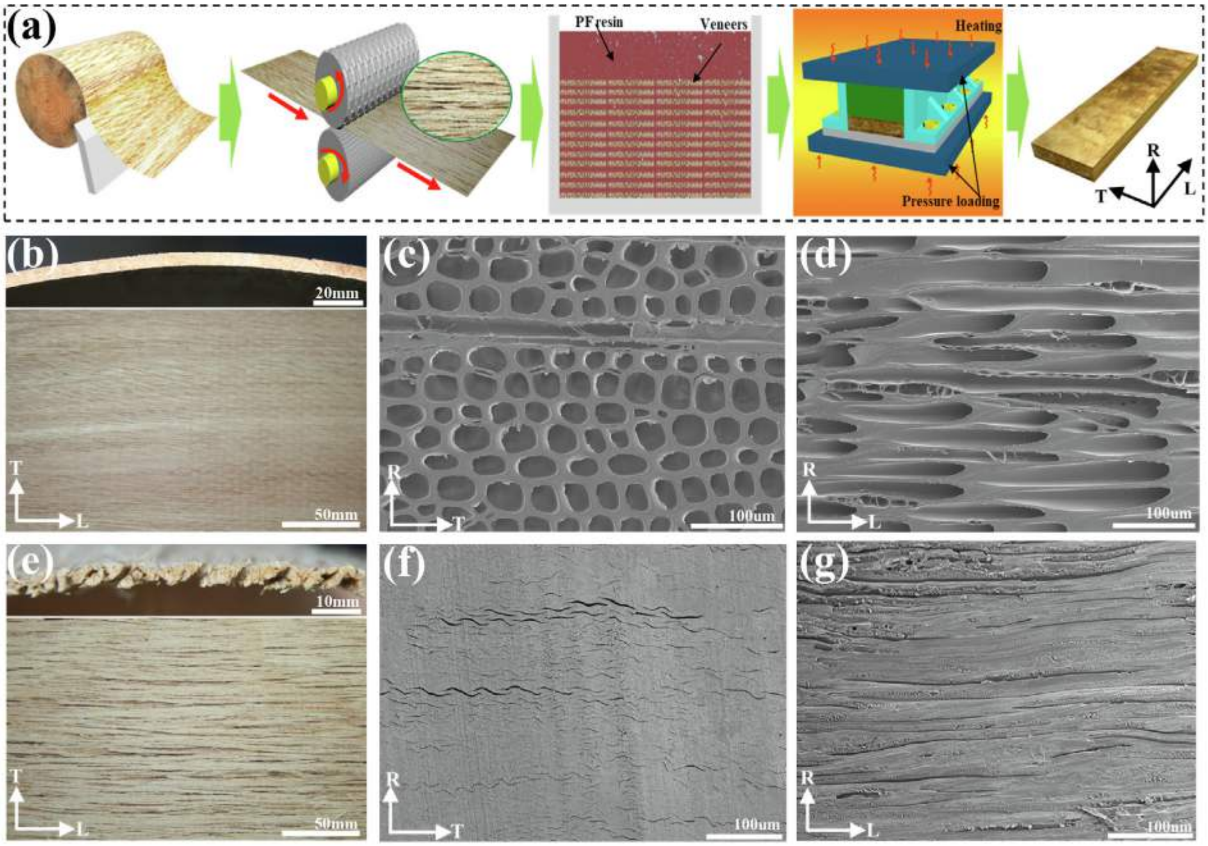


Fig. 1. Processing approach and structure observation of densified wood. a, Processing Schematic of densified wood. b, Photographs of thick veneer. c, d, SEM images of natural wood. e, Photographs of fiber mats. f, g, SEM images of densified wood.

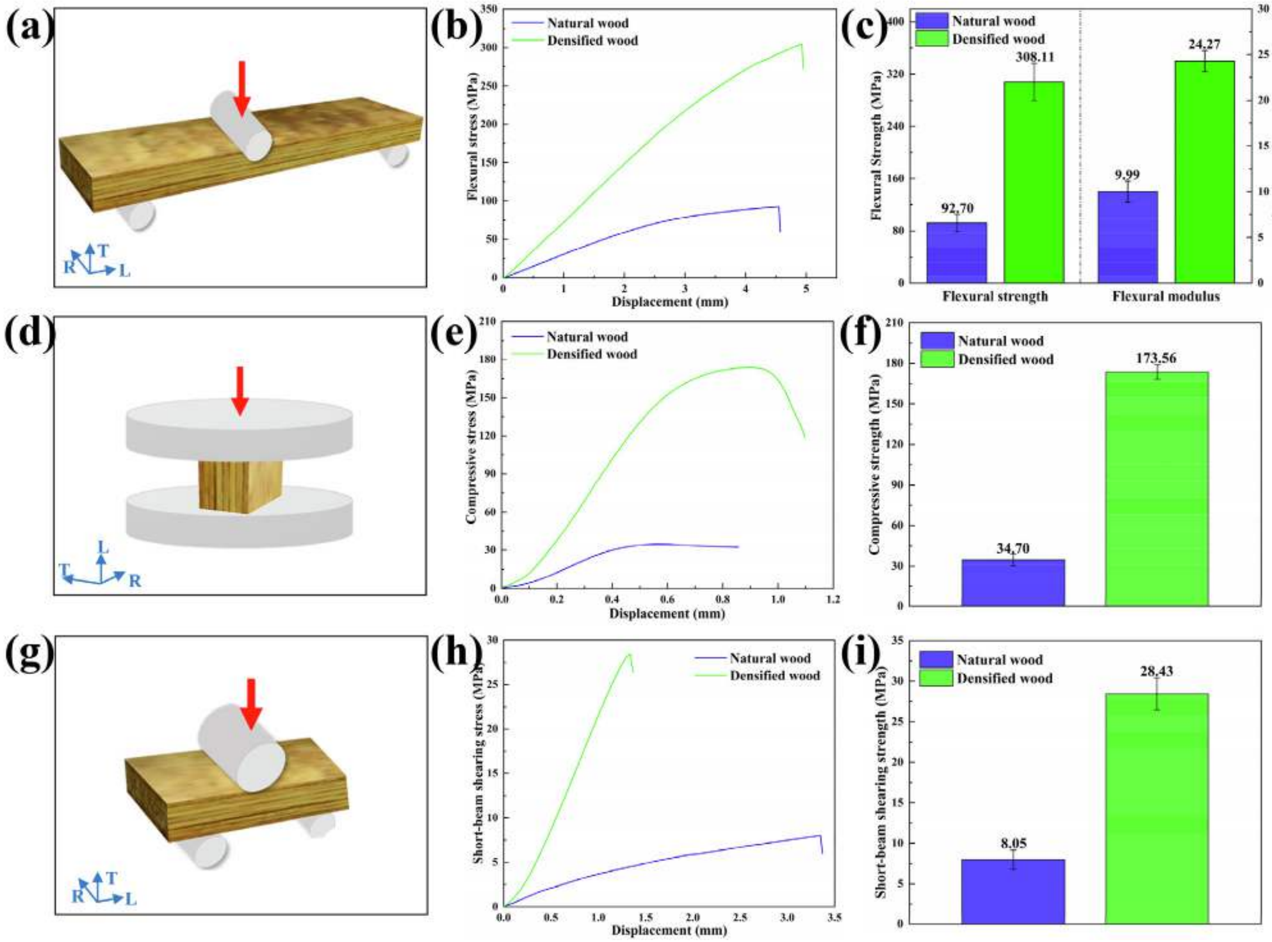
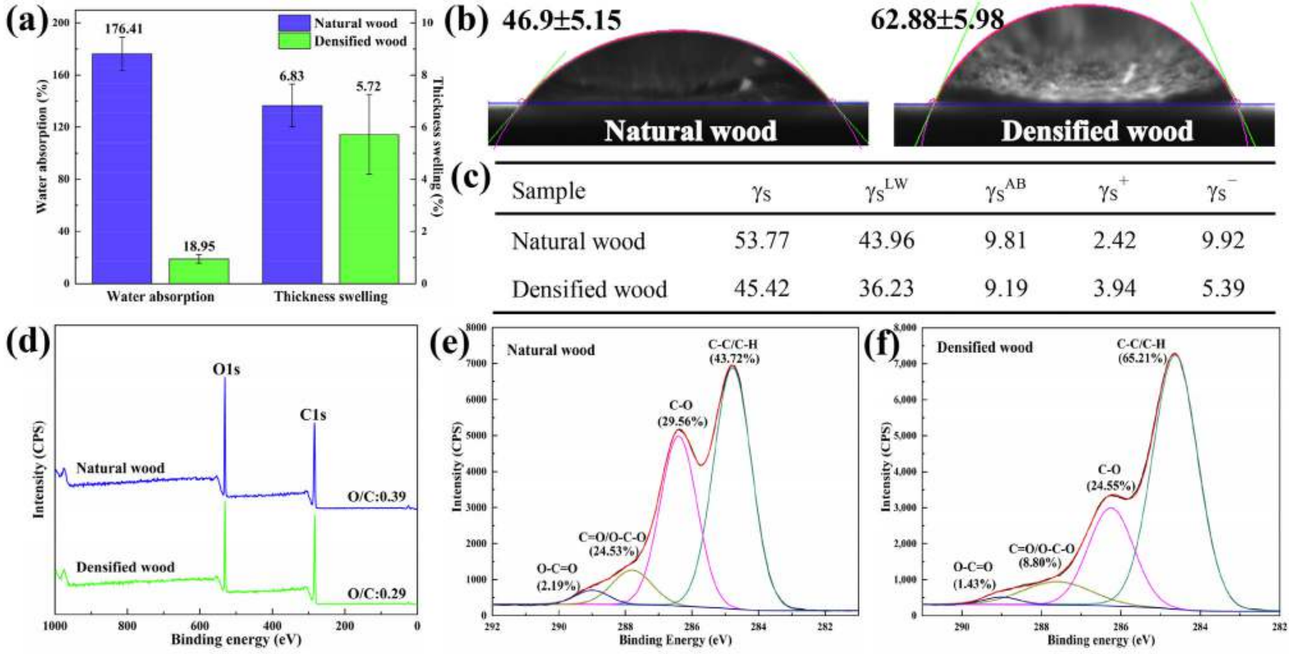


Fig. 2. Comparison on mechanical properties between natural and densified wood. a, b, c, The stress-displacement curves of corresponding tests. c, f, i, Corresponding strength.



Sample	γ_S	γ_S^{LW}	γ_S^{AB}	γ_S^{+}	γ_S^{-}
Natural wood	53.77	43.96	9.81	2.42	9.92
Densified wood	45.42	36.23	9.19	3.94	5.39

Fig. 3. Water resistance and surface wettability. a, Water absorption and thickness swelling. b, Contact angle of water on the surface. c, Surface free energy. d, XPS survey spectra. e, f, High-resolution spectra of C1s.

3.2. Mechanical properties

Fig. 2 shows that remarkable mechanical properties were achieved for densified wood. The steep stress-displacement curves indicated that denitrified wood had great stiffness (Fig. 2b, e, h). The flexural modulus was approximately 1.5 times higher than natural wood, and Over two times higher flexural strength was obtained with densified wood (Fig. 2c). The specific flexural strength was 221.66 MPa $cm^3 g^{-1}$ on average, which was 5.23% lower than the delignified and densified wood (*i.e.* 233.89 MPa $cm^3 g^{-1}$) [5]. But it should be noted that nothing was removed from natural wood in this study, thus without concern for chemical waste disposal. Compressive and shearing properties of densified wood were also significantly increased. The compressive strength was four times greater than that of natural wood (Fig. 2f). The short-beam shearing strength was more than two times that of natural wood (Fig. 2i). Such great improvements should be ascribed to high identification and bonding quality of fiber mats.

3.3. Water resistance

Wood is hygroscopic, leading to dimensional instability, biological attack and lower mechanical strength at elevated moisture contents [13]. To evaluate water resistance of densified wood, a harsh condition was used. As shown in Fig. 3a, the absorbed water of densified wood was only 18.95%, which decreased over 8 fold in comparison with natural wood. The thickness swelling rate, in spite of compression rate of ~68%, was 16.25% lower than that of natural wood. Apart from low water absorption and favorable dimensional stability, densified wood also had a better water-repellent surface. It possessed larger contact angles of water on the surface (62.88 vs. 46.90) and lower total free energy (45.42 vs. 53.77) than natural wood (Fig. 3b, c). As found in the XPS spectra, densified wood had 25.64% lower ratio of oxygen-to-carbon atom (O/C) (Fig. 3d), 49.15% higher content of C—C/C—H groups (related to hydrophobicity), and 16.95% lower content of C—O groups (related to hydrophilicity) than natural wood (Fig. 3e, f). In the Fourier-transform infrared spectra (Fig. S4), a decrease in the peaks of hydrophilic groups (*e.g.* C═O and —OH groups) was found on the surface of densified wood. Those changes in the surface chemical composition contributed to the small contact angles and low free energy on the densified wood [14].

4. Conclusion

In this study, laminating wood fiber mats were used to prepare densified wood using fast-growing pine wood as raw material. The mats with a highly permeable fiber structure had high permeability which facilitated phenolic resin impregnation. The densified wood exhibited a compact multi-layered microstructure. Superior mechanical performance and favorable water resistance were achieved. These results suggest that this novel strategy can successfully fabricate high-performance wood materials using abundant and low-cost fast-growing wood.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.06.097.

References

[1] M.H. Ramage, H. Burridge, M. Busse-Wicher, G. Fereday, T. Reynolds, D.U. Shah, G. Wu, L. Yu, P. Fleming, D. Densley-Tingley, The wood from the trees: the use of timber in construction, Renew. Sustain. Energy Rev. 68 (2017) 333–359.

[2] M. Frey, D. Widner, J.S. Segmehl, K. Casdorff, T. Keplinger, I. Burgert, Delignified and densified cellulose bulk materials with excellent tensile properties for sustainable engineering, ACS Appl. Mater. Interfaces 10 (5) (2018) 5030–5037.

[3] P. Navi, F. Heger, Combined densification and thermo-hydro-mechanical processing of wood, MRS Bull. 29 (5) (2004) 332–336.

[4] A. Kutnar, F.A. Kamke, Compression of wood under saturated steam, superheated steam, and transient conditions at 150 °C, 160 °C, and 170 °C, Wood Sci. Technol. 46 (1–3) (2012) 73–88.

[5] J. Song, C. Chen, S. Zhu, M. Zhu, J. Dai, U. Ray, Y. Li, Y. Kuang, Y. Li, N. Quispe, Processing bulk natural wood into a high-performance structural material, Nature 554 (7691) (2018) 224–228.

[6] M.L. Brusseau, J. Artiola, Chemical Contaminants, Environmental and Pollution Science, Elsevier, 2019, pp. 175–190.

[7] M.I. Shams, H. Yano, Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin II: effects of processing parameters, J. Wood Sci. 50 (4) (2004) 343–350.

[8] H. Yano, A. Hirose, S. Inaba, High-strength wood-based materials, J. Mater. Sci. Lett. 16 (23) (1997) 1906–1909.

[9] H. Kajita, Y. Imamura, Improvement of physical and biological properties of particleboards by impregnation with phenolic resin, Wood Sci. Technol. 26 (1) (1991) 63–70.

[10] Y. Zhang, Y. Zhang, Y. Yu, W. Yu, Scrimber board (SB) manufacturing by a new method and characterization of SB's mechanical properties and dimensional stability, Holzforschung 72 (4) (2018) 283–289.

[11] C. Van Oss, Hydrophobicity of biosurfaces—origin, quantitative determination and interaction energies, Colloids Surf. B: Biointerfaces 5 (3–4) (1995) 91–110.

[12] Y. Yu, X. Huang, W. Yu, A novel process to improve yield and mechanical performance of bamboo fiber reinforced composite via mechanical treatments, Compos. Part B: Eng. 56 (1) (2014) 48–53.

[13] E.E. Thybring, L.G. Thygesen, I. Burgert, Hydroxyl accessibility in wood cell walls as affected by drying and re-wetting procedures, Cellulose 24 (6) (2017) 2375–2384.

[14] F.P. Liu, T.G. Rials, J. Simonsen, Relationship of wood surface energy to surface composition, Langmuir 14 (2) (1998) 536–541.