Construction of Hydrophobic Wood Surface and Mechanical Property of Wood Cell Wall on Nanoscale Modified by Dimethyldichlorosilane

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Abstract. Dimethyldichlorosilane was used to improve the hydrophobicity of wood surface. The water contact angle of the treated wood surface increased from 85° to 143°, which indicated increased hydrophobicity. The nanomechanical properties of the wood cell wall were evaluated using a nanoindentation test to analyse the hydrophobic mechanism on the nano scale. The elastic modulus of the cell wall was significantly affected by the concentration but the influence of treatment time is insignificant. The hardness of the cell wall for treated samples was significantly affected by both treatment time and concentration. The interaction between treatment time and concentration was extremely significant for the elastic modulus of the wood cell wall.

1. Introduction
Chinese Fir (Cunninghamia lanceolata (Lamb.) Hook.) was widely used in large quantities as an important fast-growing resource. The humidity of the environment and the water sorption behavior significantly affect the properties of wood products [1]. Therefore, it is important to improve the hydrophobic properties of Chinese Fir to extend its life span and increase its application in wood products. In recent decades, mainstream hydrophobic modification methods have included but are not limited to impregnation [2, 3], etching [4], sol-gel [5], vapor deposition [6], and plasma treatment [7-8]. Impregnation works by replacing the hydrophilic hydroxyls in lignocelluloses with hydrophobic organics, thereby rendering wood materials water-repellent [3], which effectively improves the wood’s hydrophobic performance and durability [9-10]. Hydrophobic modification not only decreases the wettability of the wood surface but also significantly affects their structures. To gain further understanding of the relationships between hydrophobic modification and mechanical behavior at the cell wall level, in situ experiments are usually required [11]. Nanoindentation is widely used to measure the nanoscale mechanical properties of materials that are relatively isotropic in their elastic properties and to address whether the modulus measured in an indentation test represents a specific crystallographic direction [11, 12]. Many researchers have used this method in wood research, including characterizing the adhesive bond effect on cell wall properties in a defined area [13, 14] and for wood modification [15]. In this study, Chinese Fir samples were impregnated by Dimethyldichlorosilane (DMDCS) at different concentrations and for different durations to modify the wood’s hydrophobicity. We focused on the variation in the water contact angle (WCA) in treated wood samples to evaluate the effect of hydrophobic modification. Simultaneously, the elastic modulus and hardness of the wood cell wall before and after treatment were evaluated using nanoindentation tests to investigate the influence of modification.
2. Materials
Chinese Fir was purchased from the lumber market of Shaoxing, Zhejiang Province, China; samples were obtained from mills and collected around the same ring of late wood. The samples were cut into blocks of 20 mm (longitudinal) × 20 mm (radial) × 20 mm (tangential) and oven dried. The mass was recorded following drying. Wood samples were vacuumized at 0.09 MPa for 20 min and infused with hydrophobic reagents. DMDCS were dissolved in n-hexane solvent at 2%, 5% and 8% (w/w) concentrations. Wood samples were treated with high-pressure impregnation at 5 min, 30 min and 120 min. First, samples were put in a ventilating cabinet, where the hexane was allowed to evaporate overnight [3]. After treatment, all samples were removed and washed with a 0.125% NaOH solution and water. The samples were air dried in air for 3-5 h before vacuum drying for 12 h at 50-60°C. For nanoindentation test, samples measuring approximately 1 mm (tangential) × 1 mm (radial) × 5 mm (longitudinal) were cut from latewood of impregnated and untreated samples and embedded in a Spurr resin composed of 5.0 g of cycloaliphatic epoxide resin, 3.0 g of polycyclodiepoxide, 13 g of nonenyl succinic anhydride, and 0.15 g of dimethylaminoethanol [18]. The embedded specimens were treated with a vacuum-pressure system for several minutes to remove the air bubbles inside the cell wall lumen, which resulted in resin diffusion into the specimen. The specimens were cured at 70°C in an oven for 8 hours. The cured specimens were mounted on holders for the microtome. After the resin was cured, the cross-section of the samples was cut using a ultramicrotome (Ultracut UCT, LEICA, Germany) with a diamond knife to obtain a very smooth surface for indenting.

3. Methods

3.1. Water Contact Angle Measurements
A Contact Angle Meter (Attension Theta, Biolin, Sweden) was used in the WCA measurements. The WCA was the average of the values collected from five spots, including four from four corner areas and one from the center of the cross section on the resultant smooth surface. The WCA was recorded every 20 s, and a total of 100 s were evaluated. The measurements were conducted at 20°C and a humidity of RH=50%.

3.2. Surface Characterization
The surfaces were imaged with an SEM (JSM-7600F, JEOL Ltd., Japan). Prior to the SEM imaging, the samples were gold sputter-coated because of the resistive nature of wood. The specimens were scanned in a high vacuum at an accelerating voltage of 20 kV.

3.3. Nanoindentation Test
Chemically modified samples were randomly selected for a nanoindentation (Triboidenter, Hysitron Inc., USA) test. Quasi-static indentation tests were performed under environmental conditions [18] of 20°C and 45±2% relative humidity (RH) on the cell wall of latewood. All samples were kept in the TriboIndenter chamber for at least 24 h before indentations were made to minimize the effects of thermal expansion or contraction during the indentation process [11]. In a force-controlled mode, the indenter tip was loaded to a peak force of 200 μN at a loading rate of 10 nm∙s⁻¹, and a 9,000 nm approaching distance were used for the first segment. At the end of the experiment, the sample was examined using the video system of the Nano Indenter II to evaluate the position and quality of the indentations [19].

4. Results and Discussion

4.1. Surface Hydrophobicity
The WCA of untreated CF wood was 85°, which indicates fast water absorption (CF usually takes a few seconds to absorb water) [3]. However, the WCA of DMDCS-treated wood samples increased significantly. The plot of WCA from samples treated with DMDCS is shown in figure 1. The concentration of DMDCS and treatment time had an obvious effect on the WCA of the treated wood surface. The higher concentration showed a larger WCA, and a longer treatment time contributed a
larger WCA. When wood was modified using 2% DMDCS with different treatment times, the largest WCA was 105° (treated 120 min), and the WCA decreased obviously after 20 s, indicating unstable hydrophobicity. The effect of treatment time on WCA appeared clearly when the concentration of DMDCS was 5%. When wood samples were treated with 5% DMDCS for 120 min, the WCA exceeded 120° and persistently maintained a high WCA; one water drop stayed on the sample surface for more than 100 s. Compared to 2% and 5% DMDCS, 8% DMDCS-treated sample surface showed the best hydrophobicity: the WCA reached 135° and then decreased after the water droplet stayed on the sample surface for 100 s.

![Figure 1. Water contact angle variation with respect to time for DMDCS treatment](image)

4.2. Surface Morphology
Wood has a rather geometrically inhomogeneous multiscale structure [20]. To correlate the hydrophobicity values with the actual amount of DMDCS on the wood surface, SEM analysis was performed on untreated and DMDCS-treated wood samples to observe the change in the wood surface (figure 2). As shown in figure 2 (a, b, c), the morphology of the untreated wood contained tracheids aligned in parallel along the axial direction, as well as wood rays [21]. There was an obvious boundary between the late wood and early wood tracheids (figure 2 a). The early wood had thin cell walls and large cell cavities (figure 2 b), whereas the late wood had thick cell walls and small cell cavities (figure 2 c). The numerous large cavities, which serve as the structural foundation for the flow of water or other liquids into the wood, clearly demonstrate the porous nature of Chinese Fir wood [21]. Compared with the smooth surface of the untreated wood samples, the DMDCS-treated wood surface was covered by numerous units of DMDCS (figure 2 d). Undoubtedly, the distinct covering of the surface with DMDCS would play a key role in improving the water repellency of the modified wood surface. Additionally, DMDCS partially adheres to the early wood cavities and formed heliciform film (figure 2 d, e); however, a greater amount of DMDCS was deposited on the late wood cavities than on the early wood cavities, as shown in figure 2 (d, f), especially on the boundary of the early wood and late wood tracheids (figure 2 d). This observation could be attributed to late wood cavities close to the annual ring boundary being smaller and having thicker cell walls, which makes the volatilization of the DMDCS filling in the cavities during the drying process more difficult. This DMDCS will affect the mechanical properties of the treated wood cell wall. Therefore, the results of the hydrophobic property test and SEM imaging verified our previous deduction that after the infusion process, DMDCS was assuredly coated onto both the early and late wood surfaces, especially onto the boundary between the early wood and late wood tracheids.
Figure 2. SEM images of the surfaces: (a) untreated wood; (b) Close-up image of untreated early wood; (c) close-up image of untreated late wood; (d) DMDCS-treated wood (e) close-up image of DMDCS-treated early wood; and (f) close-up image of DMDCS-treated late wood.

4.3. Nanomechanical Properties
A two-factor analysis of variance (ANOVA) with replications for modulus and hardness is shown in Table 1. For DMDCS-treated wood samples, the elastic modulus of the cell wall is significantly affected by the concentration \( p=6.7E-20 \). The influence of treatment time is insignificant at a significance level of \( \alpha = 0.05 \). The interaction between treatment time and concentration is also insignificant \( (\alpha = 0.05) \), but the hardness of the cell wall for a DMDCS-treated sample is significantly affected by both treatment time and concentration \( (\alpha = 0.01) \). In such a case, the interaction between treatment time and concentration is extremely significant for the elastic modulus of the wood cell wall.

| Treatment Property | Source of Variation | SS  | df | MS   | F   | P-value   | F_{ crit} |
|--------------------|---------------------|-----|----|------|-----|-----------|-----------|
| DMDCS (sample number: 27) | Modulus | Treatment time | 1174 | 2 | 587.2 | 53.6 | 6.7E-20 | 3.034 |
|                     | Concentration | 69 | 4 | 17.4 | 1.59 | 0.18 | 2.410 |
|                     | Interaction | 2562 | 234 | 10.9 | 3862 | 242 |
|                     | Within | 0.42 | 2 | 0.210 | 31.8 | 5.85E-13 | 3.034 |
|                     | Total | 0.37 | 2 | 0.186 | 28.2 | 1.05E-11 | 3.034 |
|                     | Treatment time | 0.28 | 4 | 0.070 | 10.6 | 6.87E-08 | 2.410 |
|                     | Concentration | 1.54 | 234 | 0.007 | 2.61 | 242 |
The elastic modulus and hardness of the wood cell wall with different treatment conditions for DMDCS is shown in Table 2. This result indicated that when CF samples were treated by DMDCS, the elastic modulus of the wood cell wall showed a continuous decreasing tendency with an increasing reagent content. This decreasing tendency was generally statistically significant at a significance level of $\alpha = 0.05$. It also showed that when the concentration of DMDCS reagent was 2%, the modulus of the wood cell wall decreased slightly to 7.9% when the treatment time increased from 5 min to 120 min; the analysis of variance revealed this decrease as insignificant ($\alpha = 0.05$). For the 8% DMDCS-treated samples treated for 120 min, the modulus of the cell wall was significantly reduced by 45.6%, which agrees well with the two-factor analysis of variance in Table 2. Meanwhile, the hardness of the CF cell wall decreased with an increasing DMDCS treatment time and a higher concentration. When DMDCS treatment time was 120 min and the concentration of DMDCS was 8%, the hardness of the wood samples decreased to 21.7% compared to the untreated wood samples. Therefore, the DMDCS treatment time and the concentration of the reagent may interact in a complex way and generally reduce the mechanical properties of CF cell wall after hydrophobic treatment.

Table 2. Elastic modulus and hardness of wood cell wall with different treatment conditions by method (Single factor analysis of variance, ANOVA)

| Properties | Content | 2% | 5% | 8% |
|------------|---------|----|----|----|
| Modulus (GPa) | 5 min | 17.74(2.13)Aa | 16.03(3.46)Ab | 14.53(5.37)Ab |
| | 30 min | 17.43(2.41)Aa | 15.69(3.15)Ab | 13.11(2.88)Ac |
| | 120 min | 16.33(3.99)Aa | 15.12(3.19)Aa | 11.22(2.58)Bb |
| Hardness (MPa) | 5 min | 685(61)Aa | 589(68)Ab | 501(116)Abc |
| | 30 min | 588(82)Ba | 619(68)Aa | 543(97)Ab |
| | 120 min | 496(92)Ca | 512(65)Ba | 475(84)Ba |

Chinese Fir: Elastic Modulus: 20.63(1.75) Hardness: 607(34)

5. Conclusion
The WCA of wood surface increased significantly after DMDCS modification, indicating that the proposed treatment effectively improved the hydrophobicity of Chinese Fir. The WCA peak value reached 143° after being treated with DMDCS. A higher concentration and longer duration are generally beneficial for improving the hydrophobicity of Chinese Fir. Nanoindentation tests revealed that the hydrophobic modification had a significant effect on the nanomechanical properties of the Chinese Fir cell wall. The elastic modulus and hardness of the Chinese Fir cell wall decreased with DMDCS treatment.

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7. References
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