Effect of Hydrophobic Modification on Mechanical Properties of Chinese Fir Wood

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The water repellency, elastic modulus, and hardness of hydrophobic-treated and untreated wood cell walls were investigated. Chinese fir (CF; *Cunninghamia lanceolata* (Lamb.) Hook) wood was modified using polydimethylsiloxane (PDMS) and dimethyldichlorosilane (DMDCS) dissolved in n-hexane at 2%, 5%, and 8% (w/w) for 5 min, 30 min, and 2 h, respectively. A hydrophobic property was observed in the modified wood. The water contact angle value of the untreated wood surface was 85°, but after treatment this value increased to 147° and 143° for the PDMS- and DMDCS-treated wood, respectively. Increases in the elastic modulus and hardness of the wood cell wall were observed after PDMS treatment. These treatments also improved the water repellency of the wood surface, as verified by the reduction of the hydroxyl group O-H stretching vibrations at 3328 cm^{-1}. Compared to DMDCS, the PDMS treatment improved the hydrophobicity of wood surfaces and increased the nanomechanical properties of the wood cell wall. When an 8% concentration of PDMS and a 2 h treatment time were used, the treated wood showed the best mechanical properties.

Keywords: Cell wall; Nanoindentation; Wettability; Hydrophobicity; Wood

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INTRODUCTION

Wood has been widely used in the construction of homes and structures because of its good machinability and beautiful appearance (Yang *et al*. 2012). The lifespan of wood products is jointly determined by the surrounding conditions, especially the environmental humidity and the water absorption properties of the wood itself. The humidity of the environment and the water sorption behavior also significantly affect the properties of wood products (Shupe *et al*. 2011). Chinese fir (CF) wood, a fast-growing resource, is widely used in large quantities, and its application in the wood industry is universal and significant (Yang *et al.* 2014). The CF wood is extremely hydrophilic, and thus it is important to improve the hydrophobic properties of this resource to extend its lifespan and increase its application in wood products.

In recent decades, mainstream hydrophobic modification methods have included impregnation (Liu *et al.* 2011; Shi *et al.* 2013), etching (Öner and McCarthy 2000), sol-gel treatment (Berendjchi e*t al.* 2011), vapor deposition (Lau *et al.* 2003; Huang *et al.* 2016, 2017), and plasma treatment (Balu *et al.* 2008). Impregnation effectively improves the wood's hydrophobic performance and durability (Liu *et al.* 2011). Impregnation works by replacing the hydrophilic hydroxyls in lignocelluloses with hydrophobic organics, thereby rendering wood materials water-repellant (Shi *et al.* 2013). Numerous hydrophobic reagents have been tested and found effective in hydrophobic treatments, such as anhydride, epoxy, chlorosilane, and olefin (Rowell 2005, 2006).

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 (Wang *et al.* 2016a). 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 (Yang *et al.* 2015; Wang *et al.* 2016a). Many researchers have used this method in wood research to characterize the adhesive bond effect on cell wall properties in a defined area (Konnerth and Gindl 2006; Konnerth *et al.* 2010) and for wood modification (Stanzl-Tschegg *et al.* 2009).

In this study, CF wood samples were impregnated by polydimethylsiloxane (PDMS) and dimethyldichlorosilane (DMDCS) at different concentrations and for different durations to modify the wood's hydrophobicity. This study 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. Lastly, Fourier-transform infrared (FTIR) spectroscopy was used to observe the changes in the micro-mechanical properties of modified wood.

EXPERIMENTAL

Materials

Wood sample preparation

The CF wood was purchased from the lumber market of Shaoxing, Zhejiang Province, China. The samples were obtained from mills and collected around the same ring of latewood. The samples were cut into blocks of 20 mm (longitudinal) × 20 mm (radial) × 20 mm (tangential) and oven-dried. The mass was recorded after drying. The CF samples were vacuumed at 0.09 MPa for 20 min and infused with hydrophobic reagents.

Wood modification

The hydrophobic reagents PDMS (Dow Corning Co., Midland, USA) and DMDCS (Sigma-Aldrich, Berlin, Germany) were dissolved in n-hexane solvent at 2%, 5%, and 8% (w/w) concentrations.

Table 1. Treatment Conditions for Hydrophobic Modification

Reagent	Concentration (%)	Treatment Time (min)
PDMS	2	5
	5	30
	8	120
DMDCS	2	5
	5	30
	8	120

Wood samples were treated with high-pressure impregnation at 5 min, 30 min, and 120 min. Figure 1 shows the detailed sample preparation procedure. Three different concentrations and durations were tested and are mentioned in Table 1.

First, the samples were placed in a ventilating cabinet, where the hexane was allowed to evaporate overnight (Shi *et al*. 2013). After treatment, all of the samples were removed and washed with a 0.125% NaOH solution and water. The samples were air-dried for 3 h to 5 h before vacuum drying for 12 h at 50 °C to 60 °C.

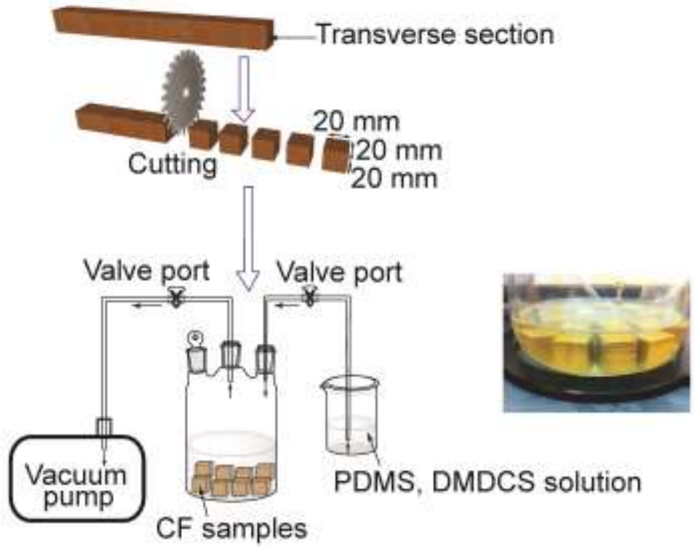

Fig. 1. Impregnation of wood samples

Sample preparation for WCA test

The WCA is an evaluation index for the hydrophobic performance of a surface (Olin *et al.* 2013; Sulym *et al.* 2017). A membrane surface with a WCA value greater than 90° is hydrophobic, and a surface with a value greater than 150° is generally considered to be superhydrophobic (Huang *et al.* 2016). Wood samples were cut from the middle part, and every surface test used five points from the center to edge. The sample preparation procedure is shown in Fig. 2.

Sample preparation 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 nonenyl succinic anhydride, and 0.15 g of dimethylaminoethanol (Zhang *et al.* 2016). 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 h. The cured specimens were mounted on holders for the microtome. Figure 2 shows the sample preparation procedure in detail. After the resin was cured, the cross-section of the samples was cut using a ultramicrotome (Ultracut UCT, LEICA, Wetzlar, Germany) with a diamond knife to obtain a very smooth surface for indenting.

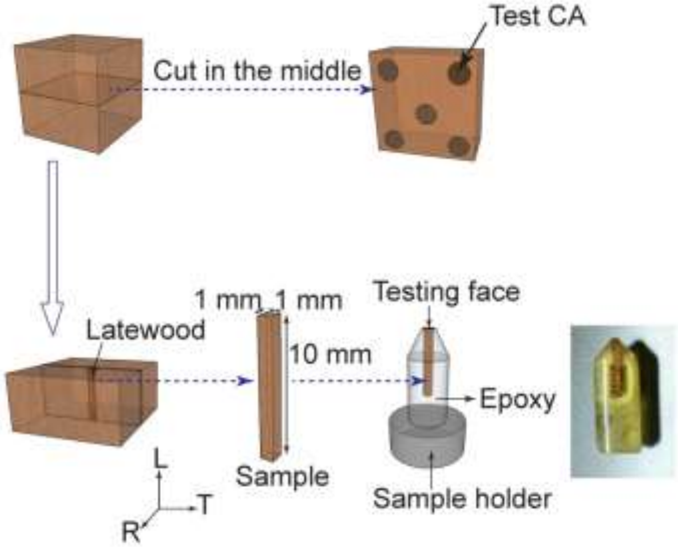

Fig. 2. Sample preparation for CA test and nanoindentation test

Methods

Water contact angle measurements

A contact angle meter (Attension Theta, Biolin, Helsinki, Finland) was used in the WCA measurements. Sessile drops of distilled water (5 μL) were deposited on sample surface. A camera was connected to a computer to capture the images of the depoiting process for every 50 miliseconds (Chen *et al.* 2017). The WCA was the average of the values (Zulfiqar *et al.* 2016, 2017) 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 relative humidity (RH) of 50%.

FTIR analysis

The FTIR measurements were performed on both the untreated and treated wood samples to evaluate the chemical modification of the wood surface after PDMS and DMDCS treatment. A thin slice of wood was cut from the surface of wood samples, and all spectra were collected from 650 cm^{-1} to 4000 cm^{-1} using an infrared spectrometer (VERTEX 80, Bruker Co., Berlin, Germany) with a diffuse reflectance mode. The scanning frequency was 10 KHz, and the scanning time was 16 s.

Nanoindentation test

Chemically modified samples were randomly selected for a nanoindentation (Triboidenter, Hysitron Inc., Minneapolis, MN, USA) test. Quasi-static indentation tests were performed under environmental conditions (Zhang *et al.* 2016) of 20 °C and 45% ± 2% RH on the cell wall of latewood. All of the 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 (Wang *et al.* 2016a). 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 9000 nm approaching distance was used for the first segment. Once the tip contacted the sample surface, a constant strain rate of 0.05 s was applied until the designated indentation depth of 200 nm was reached (second segment). At this depth, the maximum loading force was held for 10 s before ultimate unloading. This holding segment was not essential, but it offered an opportunity to monitor the potential creep or mechanical stabilization of the test materials (Wang 2016b). In the unloading segment, a constant displacement rate of 10 nm·s^{-1} was applied until 90% of the maximum loading force was removed. 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 (Xing *et al.* 2009). Scanning probe microscopy images showing the residual indentation marks on the secondary cell walls are shown in Fig. 3.

The statistical method of a two-factor analysis of variance (ANOVA) was performed with Excel 2010 (Microsoft, Redmond, WA, USA) to investigate the significance of the influence of treatment time, concentration, and their interaction on the modulus and hardness of the tested samples.

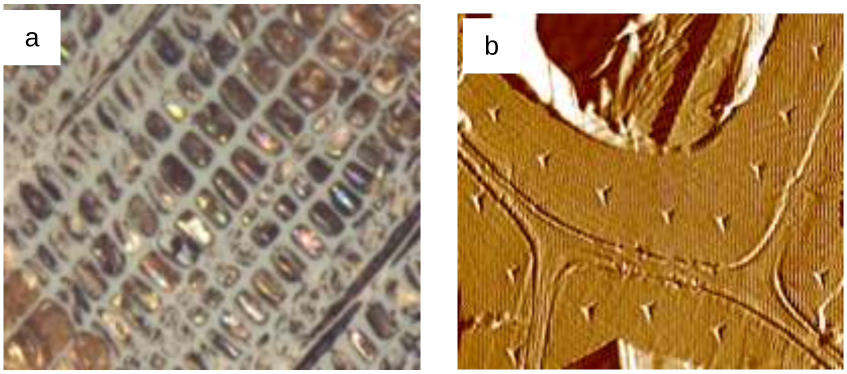

Fig. 3. (a) Light-microscope image of CF and (b) scanning image after indentation

RESULTS AND DISCUSSION

Surface hydrophobicity

The WCA of untreated CF wood was 85°, which indicated fast water absorption because CF usually takes a few seconds to absorb water (Shi *et al*. 2013). However, the WCA of PDMS- and DMDCS-treated wood samples increased considerably.

The plot of the WCA from the samples treated with DMDCS is shown in Fig. 4(a). 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 to 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 greatly decreased after 20 s, which indicated unstable hydrophobicity. The effect of treatment time on WCA appeared clearly when the concentration of DMDCS was 5%. When the CF was 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, the 8% DMDCS-treated CF 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.

In Fig. 4(b), the PDMS-treated wood samples presented better hydrophobic performance than the DMDCS-treated samples. The WCA reached the highest value of 147° when the CF samples were treated with 8% PDMS for 120 min, which indicated that a higher concentration of PDMS and a longer treatment time had conspicuous effects. When the CF samples were treated by 2% PDMS, the WCA exceeded 130° and even reached 140° after 120 min of treatment, but there was a sharp decline in the WCA after the water drop stayed on the sample surface. The WCA continued to increase when the samples were treated with 5% PDMS. The highest value of WCA was 143°, and a slight decrease appeared when the water drop stayed on surface for 100 s, which illustrated a stabilized hydrophobic performance. The 8% PDMS treatment contributed optimum hydrophobicity: the WCA values were all improved above 145°, and with a longer water drop staying time the WCA showed a slight decrease, which suggested extreme hydrophobicity.

Generally, CF treated with PDMS showed extremely higher WCA compared to DMDCS, which indicated that PDMS greatly hydrophobically modified the wood samples. The mechanisms of hydrophobic modification of DMDCS and PDMS are different. The DMDCS-modified silica films are adherent, thermally stable, and durable against humidity (Rao *et al.* 2010). The DMDCS reacted with hydroxyl groups and replaced the Si−OH with a new Si−O−Si structure with alkyl side groups. The DMDCS treatment was effective in removing the hydroxyl groups. When infusing PDMS into wood, these macromolecular compounds filled the interspaces of wood cells and a thin film of PDMS covered on the wood surface (Shah *et al.* 2017) to improve the wood’s hydrophobic performance. The helical shape of PDMS, with six Si-O bonds in a ring, restricts the number of segments that can directly interact with a solid surface to form hydrogen bonds $SiO\text{-}H\ldots O(Si(CH_3)_2\text{-})_2$ (Sulym *et al.* 2017). It has been inferred that the hydrocarbon chain in PDMS efficiently displaced the hydrophilic-OH hydroxide radical with hydrophobic groups. Additionally, the WCA measurement demonstrated that a change in concentration contributed minimally to the hydrophobic properties, but the time span had a clear effect on modification.

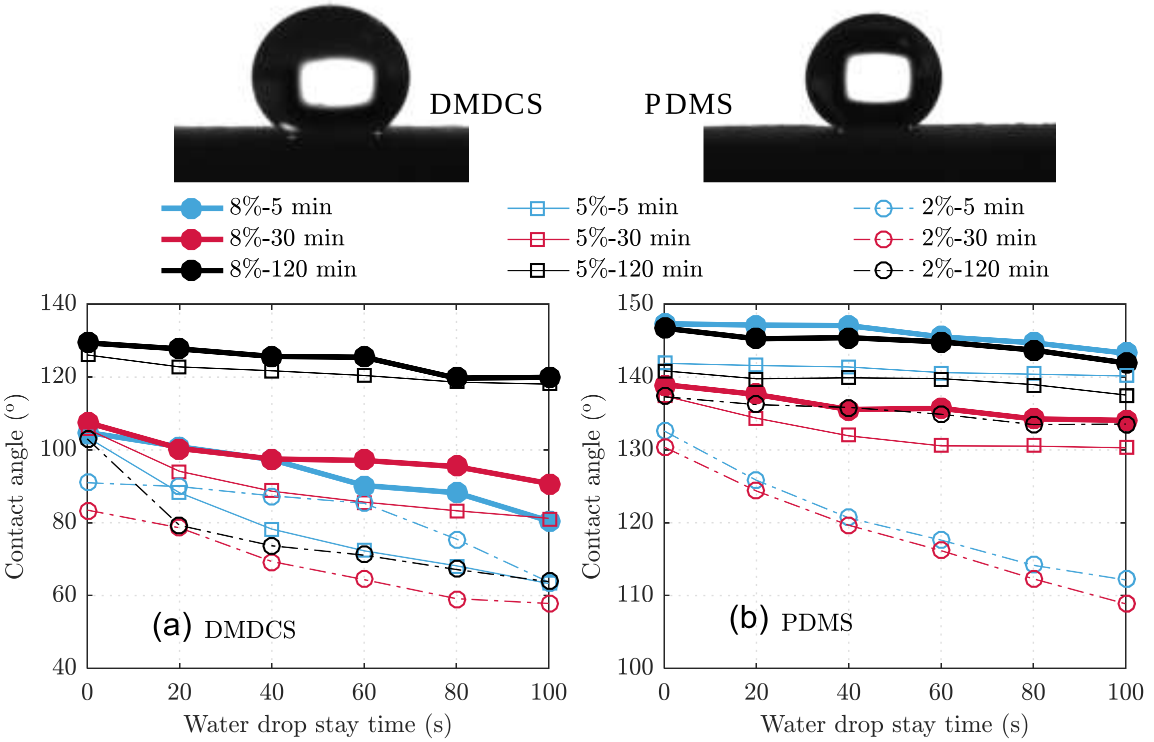

Fig. 4. Water contact angle variation with respect to time for both treatments under different conditions: (a) DMDCS and (b) PDMS

Chemical structure of wood and modified wood

Figure 5 shows the FTIR spectra in the region from 650 cm^{-1} to 4000 cm^{-1} for the CF wood sample and hydrophobic treated samples. For the CF spectrum, the broad peaks at 3050 cm^{-1} to 3700 cm^{-1}, centered at approximately 3364 cm^{-1}, corresponded to the O-H stretching vibrations, due to the surface hydroxyls and adsorbed water (Kapridaki and Maravelaki-Kalaitzaki 2013). The main bands of C=O stretching at 1639 cm^{-1} originate primarily from the unconjugated carbonyl and acetyl groups of hemicellulose (Owen and Thomas 1989). The intensity of the band at 1506 cm^{-1}, related to aromatic skeletal vibration, originates from lignin (Hosseinaei *et al.* 2011). The band at 1268 cm^{-1} is mainly related to the guaiacyl type of lignin and soft wood lignin (guaiacyl lignin) based on coniferyl alcohol (95% of the units) (Pandey 1999). The peak at 1030 cm^{-1} arises from the C-O and C-C stretching vibration in cellulose and the guaiacyl type and C-O deformation of the primary alcohol in wood lignin (Roy *et al.* 1991).

Dimethyldichlorosilane can give rise to effective surface hydrophobization by reacting organosilanes with two or more reactive groups. As these agents can couple to two adjacent OH groups, they may more effectively reduce the number of vicinal OH groups responsible for the strongest hydrophilic interaction (Castricum *et al.* 2006). For the DMDCS-treated sample, the FTIR spectra intensity of the O-H vibrations at 3364 cm^{-1} decreased gradually with increasing polymer absorption. This suggests that a notable amount of surface hydroxyls was disturbed by the DMDCS chains and that the amount of adsorbed water decreases (Sulym *et al.* 2017). The band at 2960 cm^{-1}, *i.e.*, the symmetric and asymmetric C-H stretching vibrations of the methyl groups, was also slightly enhanced. The intensity of the band at 1260 cm^{-1} (Si-CH_3 non-plane angle change vibration) also increased with DMDCS treatment due to the reaction with wood. The peak at 1024 cm^{-1} is associated with the transverse optical vibration mode, corresponding to the asymmetric stretching of the intertetrahedral oxygen atoms in the Si-O-Si linkage (Rao *et al.* 2010). The intensity of the Si–C stretch vibration at approximately 801 cm^{-1} appeared *via* the chlorosilane/wood hydroxy reaction. This indicates that the reaction contributed to the silicon oxygen bond, improving the dimensional stability (Rao *et al.* 2010).

Polydimethylsiloxane is inherently hydrophobic (Zulfiqar *et al.* 2018), and its surface is often modified for increased surface roughness or surface activation (Martin and Bhushan 2017). For the PDMS-modified wood sample, the band located at approximately 3364 cm^{-1} decreased after treatment and verified that PDMS improved the wood repellency. The symmetric and asymmetric C-H stretching vibrations of the methyl groups of PDMS were observed at 2960 cm^{-1}, along with deformation vibrations of the same groups at 1260 cm^{-1} (Maji *et al.* 2012), as observed in the treated samples. The strong band at 1012 cm^{-1} was Si-O-Si illuminated PDMS molecules, which form a helical structure due to the corresponding rotations around the Si-O bonds. The intense bands at 1090 cm^{-1} and 1020 cm^{-1} were Si-O-Si long chain linear siloxane splitting, which indicated a PDMS covered wood surface and improved water repellence property of wood samples. A substitution reaction pairs the Cl atom from the chlorosilane with the H atom from hydroxyl groups to generate HCl and a new Si-O bond. However, C-O-C asymmetric stretching in cellulose and hemicelluloses in the band of 1158 cm^{-1} (Roy *et al.* 1991) was observed in the control samples but not the PDMS-modified samples, and might not be visible due to the Si-O-Si peak. The strong band at 860 cm^{-1} was the -CH$_3$ rocking vibration absorption; at 798 cm^{-1} were the Si-C stretching vibrations, which were not seen in the control samples after PDMS treatment.

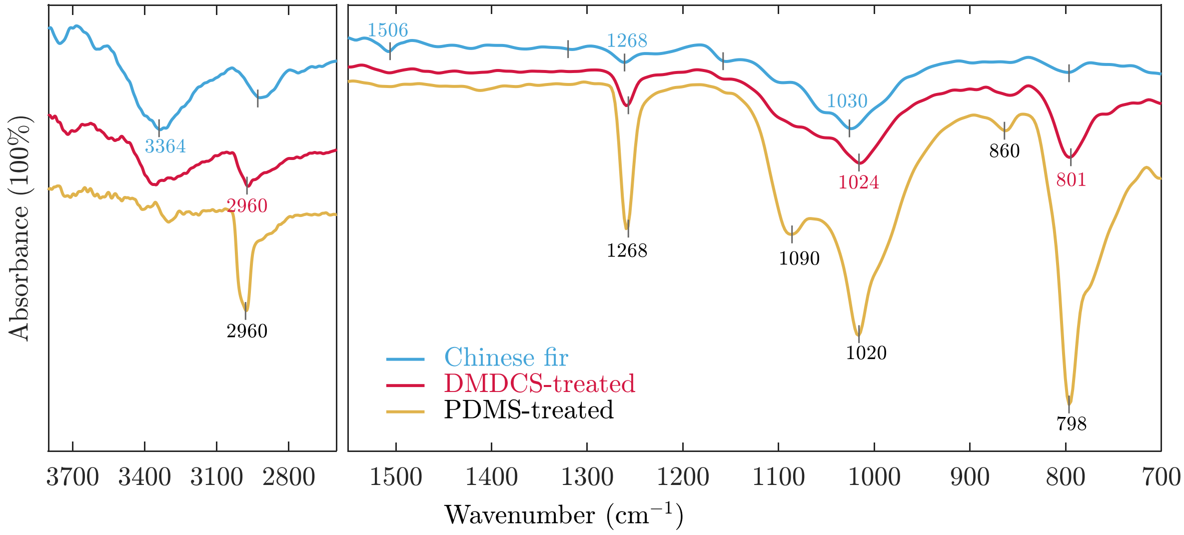

Fig. 5. FTIR spectra of CF, DMDCS-, and PDMS-treated samples

Elastic modulus and hardness

A two-factor analysis of variance (ANOVA) with replications for the modulus and hardness is shown in Table 2. For the DMDCS-treated CF wood samples, the elastic modulus of the cell wall was significantly affected by the concentration ($p = 6.7E-20$). The influence of treatment time was insignificant at a significance level of $\alpha = 0.05$. The interaction between treatment time and concentration was also insignificant ($\alpha = 0.05$), but the hardness of the cell wall for a DMDCS-treated sample was significantly affected by both the treatment time and concentration ($\alpha = 0.01$). In such a case, the interaction between treatment time and concentration was extremely significant for the elastic modulus of the wood cell wall.

For the PDMS-treated CF samples, the elastic modulus of the cell wall was affected by the concentration of the reagent (p = 1.6E-17). The influence of treatment time was significant at a level of $\alpha = 0.05$. The interaction between treatment time and concentration was also insignificant ($\alpha = 0.05$), as observed for the DMDCS treatment, but the hardness of the cell wall for the DMDCS-treated sample was significantly affected by both the treatment time and concentration, at $\alpha = 0.01$. In such a case, the interaction between treatment time and concentration was extremely significant.

These results showed that the influence of the interaction between the treatment time and concentration for both PDMS and DMDCS was insignificant for the modulus but significant for hardness. For both treatments (PDMS and DMDCS), the concentration and treatment time had a significant influence on the hardness but not on the elastic modulus. This might have been because the modulus was measured at the initial loading stage, whereas the hardness was measured in the high stress condition. The hydrophobic treatment affected the strength more significantly than it affected the stiffness.

Table 2 summarizes the results of the ANOVA with replications for the influence of treatment time and concentration on the elastic modulus and hardness of the samples treated with DMDCS and PDMS. The elastic modulus and hardness of the wood cell wall with different treatment conditions for PDMS and DMDCS are shown in Table 3. This result indicated that when the CF samples were treated by DMDCS the elastic modulus of the wood cell wall showed a continuous decreasing tendency with increasing reagent content. This decreasing tendency was generally statistically significant at a level of $\alpha = 0.05$. These findings also showed that when the concentration of the DMDCS reagent was 2%, the modulus of the wood cell wall slightly decreased to 7.9% when the treatment time increased from 5 min to 120 min; the ANOVA revealed this decrease as insignificant ($\alpha = 0.05$). For the 8% DMDCS-treated CF samples treated for 120 min, the modulus of the cell wall was significantly reduced 45.6%, which agreed well with the two-factor ANOVA in Table 2. Meanwhile, the hardness of the CF wood cell wall decreased with an increasing DMDCS treatment time and a higher concentration. When the 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 wood cell after hydrophobic treatment.

Table 2. Two-factor ANOVA with Replication on Modulus and Hardness

Treatment	Property	Source of Variation	SS	df	MS	F	P-value	F_{crit}
DMDCS (sample number: 27)	Modulus	Treatment time	57	2	28.7	2.62	0.075	3.034
		Concentration	1174	2	587.2	53.6	6.7E-20	3.034
		Interaction	69	4	17.4	1.59	0.18	2.410
		Within	2562	234	10.9			
		Total	3862	242				
	Hardness	Treatment time	0.42	2	0.210	31.8	5.85E-13	3.034
		Concentration	0.37	2	0.186	28.2	1.05E-11	3.034
		Interaction	0.28	4	0.070	10.6	6.87E-08	2.410
		Within	1.54	234	0.007			
		Total	2.61	242				
PDMS (sample number: 29)	Modulus	Treatment time	39	2	19.7	3.61	0.028	3.032
		Concentration	494	2	247.0	45.3	1.6E-17	3.032
		Interaction	16	4	4.06	0.743	0.56	2.407
		Within	1374	252	5.45			
		Total	1923	260				
	Hardness	Treatment time	0.30	2	0.151	87.1	1.8E-29	3.032
		Concentration	0.77	2	0.387	224	1.3E-56	3.032
		Interaction	1.45	4	0.374	216	3.3E-80	2.407
		Within	0.44	252	0.002			
		Total	2.96	260				

For the PDMS-treated CF wood samples, the modulus and hardness of the wood cell wall improved with changes in both the reagent content and treatment time. The PDMS treatment did not compromise the mechanical properties of CF wood when increasing the hydrophobicity of the material. The treatment time had a more distinct effect on the modulus of the wood cell wall than the reagent concentration. Generally, a longer treatment time resulted in a greater increase in the mechanical properties. The interaction between treatment time and concentration was additive and further improved the mechanical property of CF. For instance, when the impregnating time was extended, the modulus of the wood cell wall increased greatly in the PDMS-treated sample. For instance, when treated with 5% PDMS, the modulus of the cell for the sample treated for 120 min showed a rate of increase of 6.5 % compared to the sample treated for 5 min. However, modification by PDMS showed an indistinct effect on the hardness of the cell wall.

Table 3. Elastic Modulus and Hardness of Wood Cell Wall with Different Treatment Conditions (Single Factor ANOVA)

Properties			Concentration		
			2%	5%	8%
DMDCS-treated	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
PDMS-treated	Modulus (GPa)	5 min	19.11 (1.87)Ab	19.72 (2.52)Bb	21.94 (2.01)Aa
		30 min	19.15 (1.21)Ab	19.92 (1.76)Bb	22.61 (3.54)Aa
		120 min	19.30 (2.04)Ac	21.10 (1.74)Ab	22.70 (3.01)Aa
	Hardness (MPA)	5 min	614 (36)Ab	690 (48)Aa	534 (29)Bc
		30 min	530 (31)Bc	590 (32)Cb	811 (61)Aa
		120 min	607 (40)Ac	667 (32)Bb	806 (58)Aa
CF	Elastic modulus: 20.63 (1.75)		Hardness: 607 (34)		

Note: For a particular property, within a row, any same lowercase letter between two means indicates an insignificant difference of the property at different incorporation contents; within a column, any same upper-case letter between two means indicates an insignificant difference of the property when treated for different times; Significance level α = 0.05 and the numbers in parenthesis equal values

Distinct nanomechanical properties were observed when CF wood was treated with PDMS and DMDCS. A PDMS modification improved the nanomechanical properties, whereas DMDCS treatment showed the opposite behavior on the mechanical properties of the wood cell wall. This was due to the different reaction mechanisms of DMDCS and PDMS on the wood surface. The mechanism of DMDCS modification was a chemical reaction with the hydroxyl groups in the wood cellulose where hydrophobic groups replaced the hydroxyl groups. This decreased the moisture content of the wood but might have also decreased the mechanical properties of the wood cell wall. In contrast, the hydrocarbon chain in PDMS efficiently displaced the hydrophobic group with a hydrophilic-OH hydroxide radical, and covered and filled in wood tracheids due to the wood's porous structure. This could have been why the nanomechanical properties of the wood cell wall increased after PDMS treatment. The DMDCS reacted with the hydroxyl groups in the cellulose of wood, which produced HCl. Thus, NaOH must be used to neutralize the HCl, but this may decrease the nanomechanical properties of the wood cell wall. In contrast, the mechanism of PDMS modification was that the hydrophobic chain paraffin of PDMS attached and improved the modulus and hardness of the wood cell wall.

CONCLUSIONS

1. The WCA of the wood surface increased remarkably after PDMS and DMDCS modification, which indicated that the proposed treatment effectively improved the hydrophobicity of CF wood. The WCA peak value reached 147° and 143° after being treated with PDMS and DMDCS, respectively. A higher concentration and longer duration were generally beneficial for improving the hydrophobicity of CF wood.

2. For FTIR analysis, the band at approximately 3328 cm^{-1} decreased obviously after hydrophobic modification, which verified that PDMS and DMDCS can improve the water repellency of CF wood. The intensity of the Si–C stretch vibration, Si-CH_3 non-plane angle change vibration, and Si-O-Si linkage appeared in the modified wood sample, which indicated that these two reagents reacted with the wood surface group, which accounted for the improved hydrophobicity.
3. Nanoindentation tests revealed that the hydrophobic modification had a significant effect on the nanomechanical properties of the CF wood cell wall. The elastic modulus and hardness of the CF wood cell wall decreased with DMDCS treatment, but PDMS modification significantly increased the elastic modulus and hardness of the wood cell wall.

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