Properties of Thermally Modified Southern Pine Wood Pretreated with Alkylalkoxysilanes

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The alkyl-alkoxysilane (AAS) pre-impregnation method and thermal modification were combined to improve the water-related properties of southern yellow pine (*Pinus* spp.) sapwood. Four types of AAS with varied alkyl chain lengths, including butyltrimethoxysilane (BTMOS), octyltrimethoxysilane (OTMOS), dodecyltrimethoxysilane (DTMOS), and cetyltrimethoxysilane (CTMOS), were used to pre-impregnate wood samples at a concentration of 5% or 15% mass fraction, and the subsequent thermal modification was processed at either 180 °C or 200 °C. The water absorption, dimensional stability, equilibrium moisture content (EMC), mechanical properties (modulus of rupture (MOR), and modulus of elasticity (MOE)), and mold resistance of the treated wood were evaluated. Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to reveal the mechanism of the combined treatments in improving the properties of wood. Compared with thermal modification alone, the AAS combined treatment improved the water repellency, mechanical properties, and mold resistance of the modified wood. The study also identified the penetration of AAS into the wood cell wall and its reaction with the chemical components of the cell wall.

Keywords: Thermally-modified wood; Alkylalkoxysilanes (AAS); Water absorption; Dimensional stability; Mechanical property; Mold resistance

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INTRODUCTION

Southern pine is a commercial wood species that is widely used in outdoor applications in China due to its high accessibility (Wang *et al*. 2015). However, its absorption/desorption cycles make it more susceptible to deformation (Rowell 2006), which dramatically limits its use. Thus, studies on modified southern pine with a lower hygroscopicity and a higher dimensional stability are of great interest.

Thermal modification is a technique that resolves the issue of poor dimensional stability of wood. Generally, the treatment temperature is between 160 °C and 260 °C (Esteves and Pereira 2009) and includes a shielding gas, including nitrogen or steam; the treatment may be humid or dry, include oils, *etc*. (Militz 2002). When elevating the treatment temperature, hemicellulose is the first compound to undergo degradation by depolymerization and hydrolysis reactions, thereby decreasing the number of hydroxyl groups (Cademartori *et al*. 2013; Mahnert *et al*. 2013). At the initial stage of the treatment, lignin degradation occurs *via* polycondensation and cross-linking reactions (Tjeerdsma and Militz 2005; Windeisen *et al*. 2007). Through these chemical transformations, the equilibrium moisture content (EMC) of the thermally modified wood decreases, and its dimensional stability increases (Srinivas and Pandey 2012; Wang *et al*. 2015).

The degradation of the cell wall components increases the wood porosity (Andersson *et al*. 2005), and the newly formed voids may increase the long-term water absorption. Moreover, thermal modification decreases the bending mechanical properties of wood significantly (Esteves and Pereira 2009). A high temperature may be necessary to ensure efficient modifications with heat treatment (Hill 2006; Metsä-Kortelainen *et al.* 2006). However, raising the temperature requires more energy consumption, which limits industrial applications. Thus, other modification methods have been combined with thermal treatment to overcome its shortcomings, including melamine-urea-formaldehyde (MUF) resin (Sun *et al.* 2013). Other hydrophobic materials, such as oleic acid and paraffin wax emulsion, have been pre-impregnated before the thermal treatment; all of these treatments increase the hydrophobicity and dimensional stability of thermally modified wood (Esteves *et al.* 2014; Zhu *et al.* 2014; Wang *et al.* 2015).

Trialkoxysilanes have been applied as chemical modifying agents to improve properties in the lignocellulosic materials. Silanes treatment can improve the mechanical and outdoor performance of fiber/polymer composites (Xie *et al.* 2010). Water absorption and thickness swelling of medium density fiberboard was significantly reduced treated by organo-silane (Taghiyari *et al.* 2015). The hydrophobic organic groups in alkoxysilanes and the reactive hydroxyl groups released during their hydrolysis make alkoxysilanes potential candidates to improve the water repellence and dimensional stability of wood (Mai and Militz 2004; Weigenand *et al.* 2007; Vetter *et al.* 2010). An impregnated mixture of alkyltriethoxysilanes and dialkyldiethoxysilanes improves the water repellency of wood (Panov and Terziev 2009), and an organosilicon treatment could improve the durability of wood by inhibiting fungi growth (Hill *et al.* 2004; Ghosh *et al.* 2009).

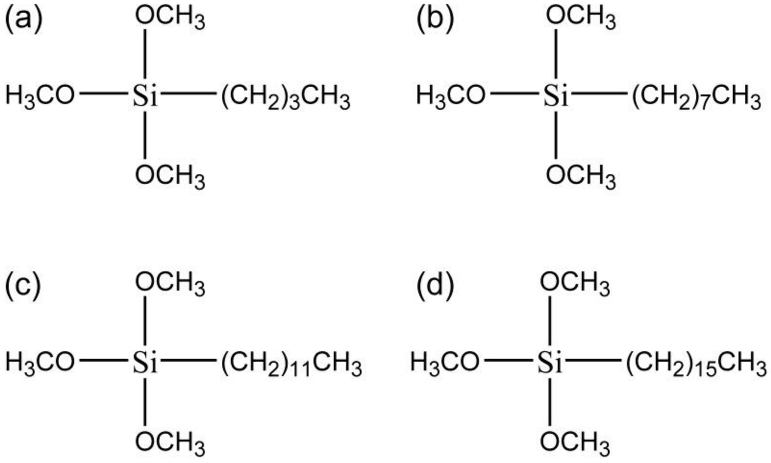
Although thermal treatment and silane treatment are both widely studied modification methods for wood, the combination of them has seldom been investigated. In this study, alkylalkoxysilane (AAS) was first used to impregnate wood prior to the thermal modification process. Due to its small molecules and good dispersibility, AAS easily penetrates the wood cell wall and increases its bulk. Before impregnation, AAS hydrolysis in an ethanol-water solution produces silicon hydroxyls (Arkles 2004), which may react with hydroxyl groups in wood to form unstable hydrogen bonds. It was also suggested that heating could facilitate the converting process of these hydrogen bonds into covalent bonds (Xie *et al*. 2010).

To investigate the effects of AAS pre-impregnation on the properties of thermally modified wood, the water absorption rates, dimensional stability, EMC, mechanical properties, and mold resistance of AAS-thermally modified wood were measured. Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) also revealed the combined effect of AAS pre-impregnation and thermal treatment.

EXPERIMENTAL

Materials

Southern pine (*Pinus* spp.) sapwood was imported from Super Lumber, Inc. (Savannah, GA, USA). It had an air-dry density of 0.4 g cm^{-3} and an average growth ring width of 0.6 cm. The wood was cut to samples of 20 mm (radial) × 20 mm (tangential) × 20 mm (longitudinal) for water-related properties tests, 20 mm (radial) × 20 mm (tangential) × 300 mm (longitudinal) for mechanical test, and 5 mm (radial) × 20 mm (tangential) × 50 mm (longitudinal) for mold resistance test, respectively. Six replicates were used for each test in this study. The samples were oven-dried at 103 °C to a constant mass, m_1 (g), and their dimensions were measured in order to calculate the initial volume, v_1 (cm^3). Four types of AAS (98%) (Fig. 1), including butyltrimethoxysilane (BTMOS), octyltrimethoxysilane (OTMOS), dodecyltrimethoxysilane (DTMOS), and the longest alkyl chain compound cetyltrimethoxysilane (CTMOS) (Qufu Chenguang Chemical Co., Ltd., Jining, Shandong, China) were diluted with deionized water and anhydrous ethanol (BeiJing Chemical Works Co., Ltd., Beijing, China) to obtain 5% or 15% AAS impregnation solutions (AAS:water:ethanol = 5:15:80 or 15:15:70, respectively). The density of BTMOS, OTMOS, DTMOS, and CTMOS are 0.931, 0.907, 0.89, and 0.89 g ml^{-1}, respectively. The impregnating solutions were maintained in a 60 °C water bath for 5 h before the impregnation to achieve the maximum hydrolysis of AAS with the minimum amount of re-polymerization.



$$H_3CO-Si(OCH_3)_2-(CH_2)_3CH_3$$
$$H_3CO-Si(OCH_3)_2-(CH_2)_7CH_3$$
$$H_3CO-Si(OCH_3)_2-(CH_2)_{11}CH_3$$
$$H_3CO-Si(OCH_3)_2-(CH_2)_{15}CH_3$$

Fig. 1. The chemical structures of BTMOS (a), OTMOS (b), DTMOS (c), and CTMOS (d)

Impregnation with AAS

Wood samples were impregnated with the prepared AAS solutions by a full-cell process; they were exposed to a vacuum at -0.1 MPa for 30 min and then pressured at 0.5 MPa by nitrogen for 60 min. The samples were then stored under ambient conditions for 3 days, after which they were dried at 103 °C to a constant mass, m_2 (g) and volume, v_2 (cm^3). The weight percentage gain (WPG) of each AAS-impregnated samples was calculated from the mass before (m_1) and after (m_2) impregnation (Eq. 1).

$$\text{WPG}\ (\%) = \frac{m_2 - m_1}{m_1} \times 100 \tag{1}$$

Thermal Modification

After the AAS impregnation, treated and untreated samples were thermally modified at 180 °C and 200 °C for 6 h in a modified drying oven connected to a water vapor supplying system. The samples were cooled at room temperature and dried at 103 °C to the constant mass, m_3 (g), and the volume, v_3 (cm^3) was calculated. The mass loss

(ML) of thermally treated samples was calculated using Eq. 2 for samples without AAS pre-impregnation or Eq. 3 for AAS pre-impregnated samples.

$$\mathrm{ML}(\%) = \frac{m_1 - m_3}{m_1} \times 100 \qquad (2)$$

$$\mathrm{ML}(\%) = \frac{m_2 - m_3}{m_1} \times 100 \qquad (3)$$

Water Absorption and Dimensional Stability

Six replicates of each sample were completely submerged in deionized water at room temperature (23 °C). The water was replaced every three days, and more was added daily. The weights and dimensions of the samples were measured after 6, 24, 48, 96, 192, 384, and 768 h of immersion. Before measuring the samples, the surface water was removed. The water absorption (WA) and volumetric swelling (VS) were calculated according to Eq. 4 and 6, respectively, for samples without thermal modification, or according to Eq. 5 and 7, respectively, for combined treated samples,

$$\mathrm{WA}\ (\%) = \frac{m_n - m_1}{m_1} \times 100 \qquad (4)$$

$$\mathrm{WAR}\ (\%) = \frac{m_n - m_3}{m_3} \times 100 \qquad (5)$$

$$\mathrm{VSR}\ (\%) = \frac{v_n - v_1(v_2)}{v_1(v_2)} \times 100 \qquad (6)$$

$$\mathrm{VSR}\ (\%) = \frac{v_n - v_3}{v_3} \times 100 \qquad (7)$$

where m_n (g) and v_n (cm^3) are the mass and volume, respectively, of the sample after n hours of immersion, v_1 (cm^3) is the volume of untreated sample, and v_2 (cm^3) is the volume of AAS individually impregnated sample.

Equilibrium Moisture Content

The samples were stored in a climate chamber at 20 °C with a relative humidity of 65% for 2 weeks to reach the equilibrium moisture content, and the equilibrium weights of these samples were measured. The equilibrium moisture content was calculated according to Eq. 8 for samples without thermal modification, and using Eq. 9 for combined treated samples,

$$\mathrm{EMC}(\%) = \frac{m_\mathrm{e} - m_1(m_2)}{m_1(m_2)} \times 100 \qquad (8)$$

$$\mathrm{EMC}(\%) = \frac{m_\mathrm{e} - m_3}{m_3} \times 100 \qquad (9)$$

where m_e (g) is the equilibrium mass of the sample.

Mechanical Test

The modulus of rupture (MOR) and the modulus of elasticity (MOE) in bending of the treated wood were evaluated according to the standards GB 1936.1-91 (1992) and GB 1936.2-91 (1992).

The samples were conditioned at 20 °C with 65% relative humidity of before mechanical tests. The static bending tests were performed on a universal mechanical test machine (model WDW-350A, Jinan Shijin Group Co., Jinan, Shandong, China) by a three-point bending test method with a span of 240 mm. The upper roller at a speed of 5 mm min^{-1} loaded on the radial middle of samples placed on two supporting rollers (curvature radius 30 mm). The same samples were used in the MOR and MOE tests.

Mold Resistance Test

The mold resistance of the AAS-thermally modified wood was evaluated according to the standard GB/T 18261-2000 (2001). The mold fungi *Aspergillus niger* was inoculated on Petri dishes containing potato, glucose, and agar culture medium and incubated at 25 °C for 7 days. Two wood samples were loaded on a sterile U-shaped glass rod (3 mm in diameter), which was then placed on the developed spores in each Petri dish.

The dishes were incubated at 25 °C with 85% relative humidity for 4 weeks, and then the infected area of each sample was visually inspected. The infected area was categorized in one of 5 levels according to the size of the mold growth, as follows: level 0, 0% coverage of the sample; 1, 0% to 25%; 2, 25% to 50%; 3, 50% to 75%; and 4, 75% to 100%.

Scanning Electron Microscopy (SEM) – Energy Dispersive X-ray spectroscopy (EDX)

The samples were taken from treated wood with a size of 3 mm (radial) × 5 mm (tangential) × 5 mm (longitudinal). The AAS distribution in the tangential surface of the control or experimental wood samples was observed under a scanning electron microscope/energy dispersive X-ray spectroscopy (Hitachi S-3400N, Tokyo, Japan) with an acceleration voltage of 15 kV. The samples were coated with a gold alloy prior to examination.

Fourier-Transform Infrared Spectroscopy (FTIR)

The treated and untreated samples were ground to particles that passed through a 100-mesh sieve. FTIR spectra were recorded using a KBr pellet on a Bruker Vertex 70v spectrophotometer (Bremen, Germany). A total of 32 scans were collected at a 4 cm^{-1} resolution within the wavenumber range of 4000 cm^{-1} to 400 cm^{-1}.

Duncan's multiple range test

The data significant difference level was evaluated with Duncan's multiple range test performed in IBM SPSS Statistics 20, with $P < 0.05$ considered statistically significant.

RESULTS AND DISCUSSION

Weight Percent Gain (WPG) and Mass Loss (ML)

The average WPG of 5% BTMOS-, OTMOS-, DTMOS-, and CTMOS-treated wood was 3.39%, 4.22%, 4.60%, and 4.35%, respectively (Fig. 2). When the concentration was increased to 15%, the average WPG was 10.71%, 13.03%, 13.47%, and 13.80%, respectively. Within the same concentration, the WPG of OTMOS-, DTMOS-, and CTMOS-treated wood was higher than that of the BTMOS-impregnated wood, as consistent with the previous experiment (Shateri-Khalilabad and Yazdanshenas 2013). This result was attributed to the shorter alkyl group of BTMOS; BTMOS is more reactive because BTMOS-hydrolyzed monomers condense more easily before the impregnation. Polymeric molecules with larger molecular weights have difficulty penetrating the wood cell wall, which lowered the overall WPG of the BTMOS-treated samples.

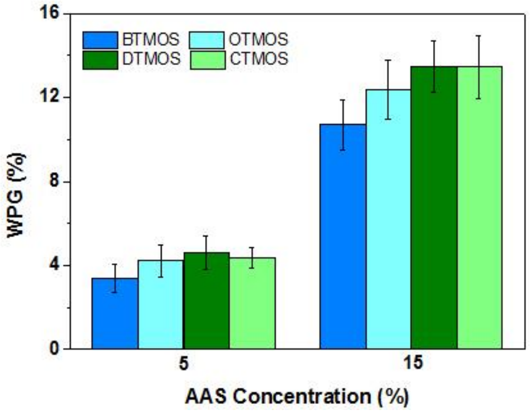


Fig. 2. WPG of AAS-treated wood

The MLs of samples after thermal modification are shown in Fig. 3. The ML of the thermal-only modified wood were 3.51% and 12.04% for 180 °C and 200 °C, respectively. The AAS pretreatment decreased the ML of the wood caused by thermal degradation, which was attributed to cross-linking between AAS and the cell wall components.

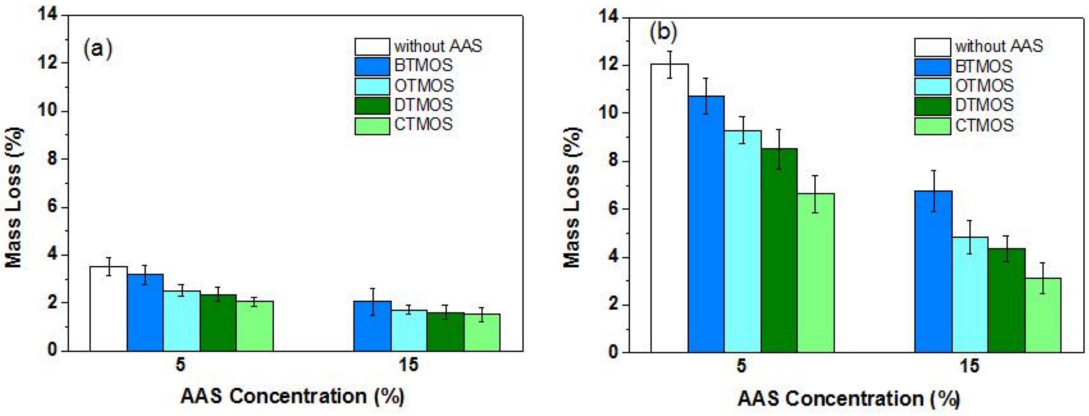


Fig. 3. MLs of wood samples thermally modified at 180°C (a), and 200°C (b)

The decrease in ML was more pronounced after treatment with 15% AAS than with 5% AAS. Moreover, with increasing alkyl chain length in the AAS, the decrease in ML increased. These results confirmed that AAS inhibited the thermal degradation of wood during heat treatments.

Water Absorption (WA) and Dimensional Stability

During the soaking test, the WA rates of the control increased from 58.82% (at 6 h) to 113.79% (after 768 h); these values dropped to a range of 56.01% (at 6 h) to 112.47% (at 768 h) and 48.84% to 112.73% after thermal treatment at 180 °C and 200 °C, respectively (Fig. 4). Hemicellulose degradation lowers the hydroscopicity of wood (Korkut *et al.* 2012). However, the hemicelluloses and lignin degradation increased the porosity of the wood cell wall, leading to a higher water absorption rate (Andersson *et al.* 2005). This effect explains the insignificant WA reduction of the thermally modified wood compared with the control.

The 5% AAS pre-impregnation clearly improved the water repellency of treated wood, and this improvement was linked to the increasing length of the alkyl chain. Because AAS fills wood pores—either original or produced during treatment—it decreases porosity and reduces the space available to water. Furthermore, AAS reacts with hydroxyl groups in wood, reducing the amount of adsorption sites. A longer alkyl chain resulted in better hydrophobicity of the treated wood, as previously noted (Donath *et al*. 2004). For the 15% AAS pre-impregnation, the WA of the CTMOS-treated wood exceeded that of the DTMOS-treated group. This result might be related to the negative effect of a long alkyl chain on wood penetration, which causes uneven distribution.

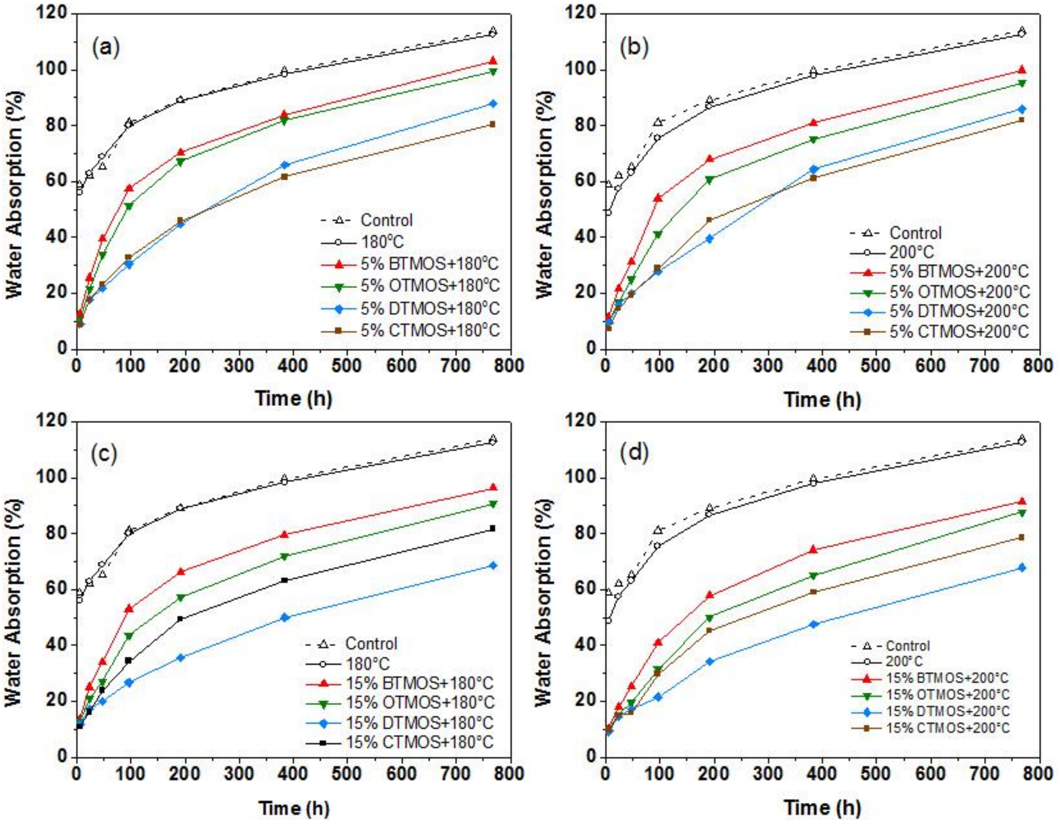


Fig. 4. Water absorption of wood not treated, thermally-treated, or treated with (a) 5% AAS + 180 °C, (b) 5% AAS + 200 °C, (c) 15% AAS + 180 °C, and (d) 15% AAS + 200 °C

The dimensional stability of the samples was also evaluated by the water-soaking test. The volumetric swelling rates decreased to 19.92% and 41.95% for the 180 °C and 200 °C thermally modified samples. The degradation of hydrophilic groups like hydroxyl groups decreased the wood hygroscopicity (Weiland and Guyonnet 2003), which is the main reason for improving the dimensional stability of wood by thermal modification.

Figure 5 shows the effects of thermal modification combined with the AAS pre-impregnation on the volumetric swelling rates of the modified wood. Apart from the 15% AAS/180 °C treatment, the decrease in wood swelling was inconspicuous. AAS pre-impregnation and the volumetric swelling rate was not associated with alkyl chain length. These results suggest that AAS pre-impregnation did not further improve the dimensional stability of thermally modified wood.

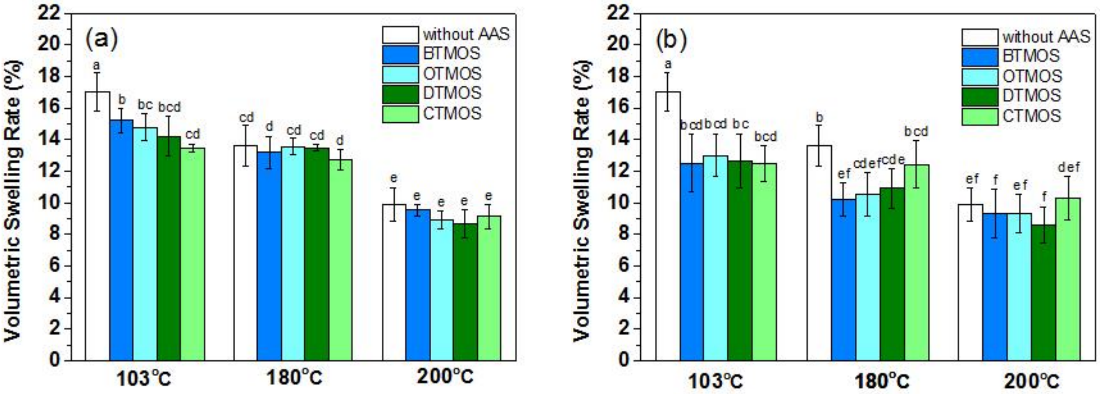


Fig. 5. Volumetric swelling rates of the wood treated with 5% (a) and 15% (b) AAS. Bars accompanied by different letters (a, b, c, d, e, and f) are significantly different at $p < 0.05$ (Duncan test).

Equilibrium Moisture Content (EMC)

The EMC values obtained at 20 °C and 65% relative humidity are presented in Fig. 6. The EMC of 9.86% for untreated wood decreased to 6.72% and 5.54% for wood modified at 180 °C and 200 °C, respectively. Thus, thermal modification decreased the EMC of wood, which was consistent with previous studies. However, AAS pre-impregnation did not affect the EMC of thermally modified wood. AAS inhibited hemicellulose degradation, leading to a more retained hydroxyl groups compared with thermally modified wood.

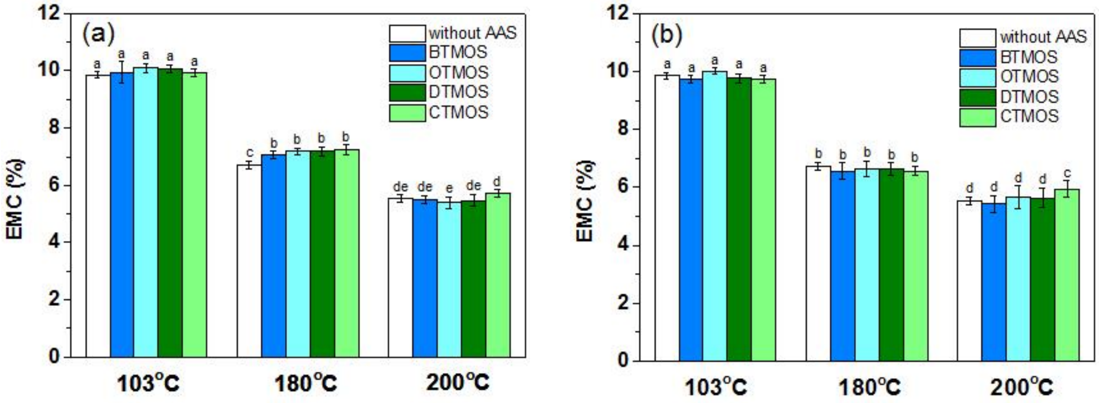


Fig. 6. The EMC of 5% (a) and 15% (b) AAS-modified and unmodified wood. Bars accompanied by different letters (a, b, c, d, and e) are significantly different at $p < 0.05$ (Duncan test).

Mechanical Properties

The modulus of rupture (MOR) and the modulus of elasticity (MOE) of the control and treated samples are illustrated in Fig. 7. Thermal modification significantly reduced the mechanical properties of wood due to the thermal degradation of cell wall structural components (Esteves *et al*. 2007).

AAS impregnation increased the MOR and MOE of samples thermally modified at 200 °C. At 5% concentration, the MOR increased 2.47%, 19.69%, 45.31%, and 23.53% for BTMOS, OTMOS, DTMOS, and CTMOS, respectively. At 15% BTMOS, OTMOS, DTMOS, and CTMOS, the results were 10.35%, 82.98%, 104.10%, and 60.67%, respectively.

Thus, with increasing alkyl chain length, the mechanical properties of the AAS-thermally modified wood first increased and then experienced a decrease. Thermally modified wood that was pre-treated by AAS with the C12 alkyl chain showed the highest mechanical properties. This result is consistent with the hydrophobicity results and reflects the uneven distribution of CTMOS in treated samples.

The enhanced mechanical properties of AAS-treated thermally modified wood were mainly attributed to the lower ML associated with AAS. AAS was deposited within the cell wall (Mai and Militz 2004), which either filled voids that were formed during the thermal modification or formed cross-linked polymers (Bouza *et al*. 2008) within the cell wall, thereby enhancing the wood strength.

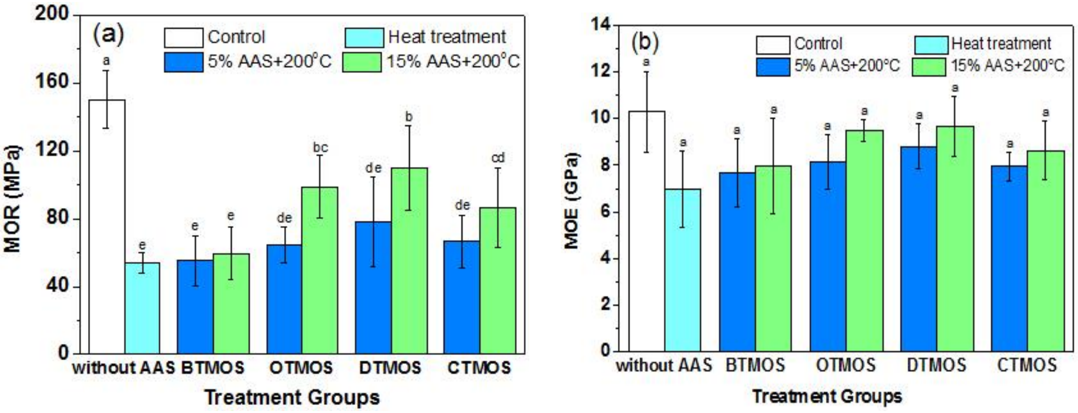


Fig. 7. The MOR (a) and MOE (b) of treated wood samples. Bars accompanied by different letters (a, b, c, d, and e) are significantly different at *p* < 0.05 (Duncan test).

Mold Resistance

All treated and untreated wood samples showed *Aspergillus niger* growth after 4 weeks (Fig. 8). The control wood showed the least mold resistance, with a fungal growth ranking of 4. Both high temperature and AAS improved the mold resistance of wood; a 5% AAS impregnation with a 200 °C thermal treatment had the optimum effect on mold resistance.

This phenomenon could be associated with the following factors: (1) AAS improved the hydrophobicity of the treated wood (Ghosh *et al.* 2009), or (2) AAS in the cell wall blocked micropores that were produced by the thermal treatment, leading to improved mold resistance (Hill *et al.* 2004).

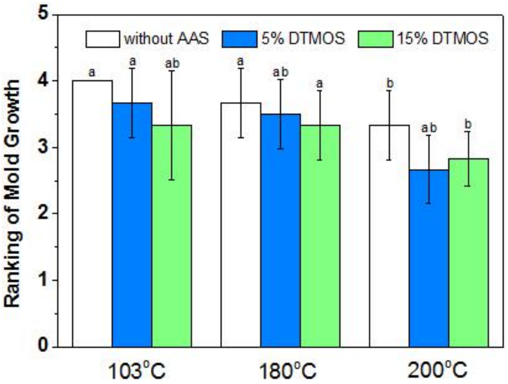


Fig. 8. Ranking of mold growth on modified and unmodified wood

Table 1. FTIR Absorption Peaks

Wavenumber (cm^{-1})	Assignment
2920	-C-H, asymmetric deformation in AAS
2840	-C-H, symmetric deformation in AAS
1740	C=O, stretching (unconjugated) in hemicellulose
1640	C=O, stretching (conjugated) in lignin
1510	C=C, Aromatic skeletal vibration in lignin
1257	Si-C, Stretching vibration
1105	Aromatic skeletal vibration and C-O stretching in lignin
1080	Si-O-Si, skeletal vibration
798	Si-C and/or Si–O
450	O–Si–O, skeletal vibration

Chemical Analysis

The FTIR spectra of selected samples are presented in Fig. 9, and the assignment for FTIR peaks are listed in Table 1. A reduction of the peak intensity at 1740 cm^{-1} (C=O stretching) of the thermally modified wood was attributed to the deacetylation of the hemicellulose (Tjeerdsma *et al*. 1998). Together with the diminution of the band at 1640 cm^{-1}, the increasing intensity of the peaks at 1510 cm^{-1} and 1105 cm^{-1} indicate the condensation and cross-linking of lignin during the thermal treatment (Ercin and Yurum 2003; Hakkou *et al*. 2005; Boonstra and Tjeerdsma 2006).

The new bands at 2920 cm^{-1} and 2840 cm^{-1} (Cappelletto *et al.* 2012) in the AAS-impregnated samples were ascribed to the asymmetrical and symmetrical stretching of C-H bonds (CH_3 and CH_2) in AAS. These peaks were more evident in the sample treated with the longer alkyl chain (DTMOS). The intensities of the absorption bands at 1740 cm^{-1}, 1640 cm^{-1}, 1510 cm^{-1}, and 1105 cm^{-1} changed in the AAS-treated samples compared with the thermal-only modified wood. Thus, AAS pre-impregnation limited the degradation of cell wall components during the thermal treatment. In addition, the AAS-treated samples showed new absorption bands at 1257 cm^{-1}, 1080 cm^{-1}, 798 cm^{-1}, and 450 cm^{-1}, which corresponded to ν (Si-C) stretch vibration, skeletal vibration δ (Si-O-Si), ν (Si-C) and/or ν (Si–O), and weak vibration δ (O–Si–O), respectively (Sèbe *et al.* 2004; Tinguat *et al.* 2005; Ghosh *et al.* 2009; Ouyang *et al.* 2014). These peak changes demonstrated that AAS reacted with the hydroxyl groups in the wood cell wall.

SEM images of the tangential section of thermally modified and AAS-thermally modified wood are shown in Fig. 10. The 200 °C thermal modification caused partial destruction of the ray cell wall, and some cracks appeared on the tracheids (Fig. 10(a)).

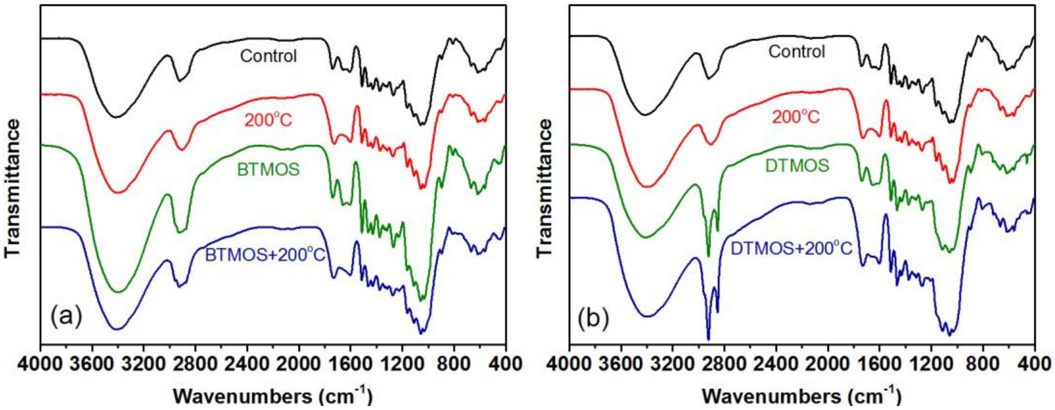


Fig. 9. FTIR spectra of BTMOS-thermally modified wood (a); DTMOS-thermally modified wood (b)

With DTMOS pre-impregnation, the cell wall showed a smooth surface with less cracks (Fig. 10(b)). DTMOS adhered uniformly to the interior wood surfaces. The ray tissue and pits acted as the main horizontal water transport paths, and some of the newly formed cracks and destructed rays were filled by DTMOS molecules. DTMOS was also clearly observed in longitudinal tracheids. The SEM micrograph and EDX results of the cross section of DTMOS treated sample (Fig. 11) show further information about silicate distribution in wood cell wall. The Si concentration represented by bright color in EDX confirms that AAS penetrated into cell wall. These SEM-EDX results explain the better properties of the AAS-thermally modified wood.

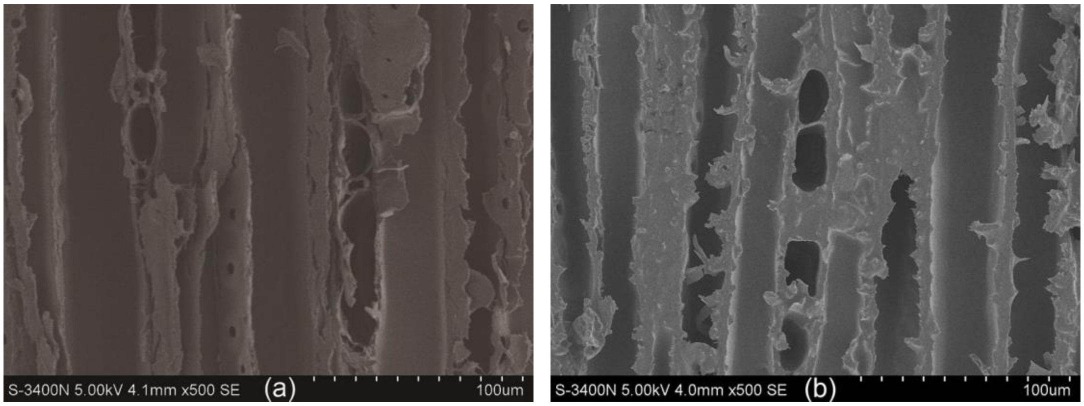


Fig. 10. SEM images of tangential sections from 200 °C thermally modified (a) and DTMOS-200 °C thermally modified wood (b)

CONCLUSIONS

1. Alkyl-alkoxysilane (AAS) pre-impregnation inhibited the degradation of wood during thermal modification and improved the water repellency, mechanical properties, and mold resistance of the thermally modified wood.
2. Combining thermal modification with 5% AAS pre-impregnation could not further decrease the EMC and volumetric swelling of thermally modified wood.

3. FTIR and SEM results indicated that AAS reacted with chemical components of the wood cell wall. This phenomenon explained the mechanism of the water repellency, dimensional stability, and the mechanical properties improvement.

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