

Hygroscopicity and Characterization of Wood Fibers Modified by Alkoxysilanes with Different Chain Lengths

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As the main raw material for fiberboard, the hygroscopicity of wood fibers is of great concern. In this study, three alkoxysilanes with different chain lengths—methyl trimethoxy silane (MTMS), octyl trimethoxy silane (OTMS), and dodecyl trimethoxysilane (DTMS)—were used respectively to treat wood fibers to reduce their hygroscopicity and surface hydrophilicity. After alkoxysilane properties were evaluated, the chemical structures, surface groups, and morphology and distribution of alkoxysilanes within modified wood fibers were characterized using scanning electron microscopy (SEM) coupled with energy-dispersed X-ray analyzer (EDXA), Fourier Transform Infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The study found that after modification, the moisture adsorption rate of wood fibers had decreased and the surface hydrophobicity of the fibers had been promoted. The fibers modified with MTMS adsorbed the least amount of moisture. The study also found that while hydrolyzed silane penetrated into wood fibers and reacted with their chemical components, long chains of the silane hindered the degree of that penetration.

Keywords: Wood fiber; Alkoxysilane; Hygroscopicity

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INTRODUCTION

As the raw material of medium density fiberboards (MDFs), wood fibers have many advantages, such as widely available sources, low cost, environment-friendliness, and renewability. However, the thickness swelling of fiberboards resulting from the inherent hygroscopicity of fiber cell walls, attenuation of adhesive bonding, and the breakage of hydrogen bonds between fibers in high humidity environments pose critical challenges to the performance and service life of MDFs. Some methods have been proposed to improve the dimensional stability of MDFs, such as heat treatment of fibers (Garcia *et al.* 2008; Ayrilmis *et al.* 2011; Jarusombuti *et al.* 2011), adding water repellents (Roffael *et al.* 2005; Grigsby and Thumm 2012), and applying modified adhesives (Alvarez *et al.* 2011; Yang *et al.* 2011). Unfortunately, however, these methods have documented shortcomings that limit their exploration in applications, such as high-energy consumption during the modification process, short-term effectiveness, and varying degrees of negative influence on the mechanical properties of boards (Jarusombuti *et al.* 2011; Li *et al.* 2011). Hence, new treatment processes of fiber materials with long efficacy and low resource consumption should be developed to improve the dimensional stability of MDF, while simultaneously ensuring their mechanical strength.

Silane coupling agents are low molecular weight organic silicon compounds with a generic chemical structure of RSiX_3 , where R represents groups such as amino groups, mercapto groups, vinyl groups, and epoxy groups, and X represents hydrolyzable groups, such as halogen, alkoxy groups, and acyloxy groups (Abdelmouleh *et al.* 2002; Donath *et al.* 2006). Therefore, silane coupling agents can interact with both hydroxyl groups in inorganic materials and long molecular chains in organic polymers to bond these two materials more tightly, thereby improving the performance of the materials. They can be widely applied in the fields of rubber, plastic, filled composite materials, epoxy encapsulation materials, elastomers, coatings, and adhesion promoters between organic and inorganic materials (Donath *et al.* 2004; Xie *et al.* 2010; Wu *et al.* 2013).

A basic reaction of alkoxysilanes is the so-called sol-gel process. Alkoxy groups of silanes can be hydrolyzed to form silanols, which subsequently condense to 3-dimensional units (Donath *et al.* 2006; Brochier and Belgacem 2010). Based on this theory, silane coupling agents have been applied to modify solid wood by researchers in recent years. Results to date have indicated that after using an appropriate type of silane modification process, silane molecules are capable of filling the large pores of wood cell cavities. Some of the molecules enter the amorphous region of cell walls and react with the hydroxyl groups during the sol-gel process (Tshabalala and Gangstad 2003; Tshabalala *et al.* 2003; De Vetter *et al.* 2010), which improves the dimensional stability and surface hydrophobicity of silane modified wood. Other physical and mechanical properties (*e.g.*, flexural strength or compressive strength) are also improved (Zollfrank 2001; Mohammed and Ziegler *et al.* 2006; Xie *et al.* 2011). While numerous studies have been conducted on silane modification of solid wood, there is scant research on the efficacy and influencing mechanism of silane modification on the hygroscopicity of wood fibers.

To address this important question, this study investigated the effect of hydrolyzed alkoxysilanes with different chain lengths on the hydrophobicity of modified wood fibers. The moisture adsorption and contact angles were measured before and after fiber treatments. The microscopic distribution and bonding state of silanes in wood fibers were also investigated by using scanning electron microscopy (SEM), coupled with energy-dispersed X-ray analyzer (EDXA), Fourier Transform Infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The study was structured so that its results might provide technical support for the production of MDFs with high mechanical properties and good dimensional stability.

EXPERIMENTAL

Materials

Mechanical hot-milled wood fibers made of hybrid wood species containing Mongolian Oak (*Quercus mongolica* Fisch. ex Ledeb.) and some fruitwoods such as *Pyrus* spp. were obtained from Kenuo (Beijing) Co., Ltd., China. The majority of the fibers had lengths ranging from 2 to 10 mm. Three types of silane—methyl trimethoxy silane (MTMS), octyl trimethoxy silane (OTMS), and dodecyl trimethoxysilane (DTMS)—with concentration of 96% were purchased from Qufu Chenguang (Shandong) Chemical Co., Ltd., China. Figure 1 shows the structural formula of the silanes.

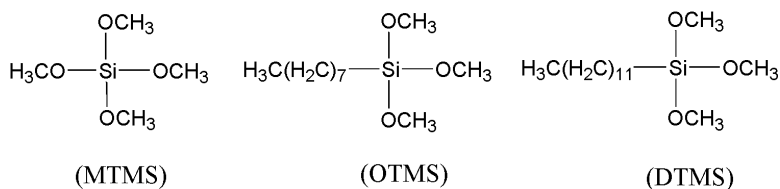


Fig. 1. The structural formula of applied silanes

Modification of Fibers by Silanes

The silanes (MTMS, OTMS, and DTMS) were diluted to 5 wt% and then prehydrolysed in 90 vol% acidulated alcohol (pH=3) at room temperature for 1 h. The hydrolyzed silane was used to immerse the dried fibers (MC ≤ 1%) in a beaker. The control group without modification was simultaneously soaked in the same amount of deionized water and stirred well. All of these mixtures were kept still at room temperature for 2 h. After processing, excess liquid was filtered out with a sieve and the fibers were dried in an oven at 103 °C until reaching the constant weight.

Moisture Adsorption of Wood Fibers

The four samples of modified and unmodified wood fibers (about 2 ± 0.01 g) were placed into tin trays and then kept in a desiccator at 23 ± 2 °C. The bottom of the desiccator was filled with deionized water to create a relative humidity environment approaching 100%. After a certain time interval, the tin trays were taken out to be weighed. The moisture content of wood fibers was calculated according to Eq. 1,

$$\text{MC} = \frac{m_t - m_0}{m_0} \times 100\% \quad (1)$$

where MC is the moisture content in percent, m_0 is the oven-dry weight, and m_t is the weight of the sample after a given adsorption time, respectively.

Contact Angle Measurements

Wood fibers were pressed into disks with a tableting machine, and a contact angle goniometer (Data Physic OAC20, Germany) was used to determine the contact angles of distilled water droplets on sample surfaces after different durations of exposure in a sessile drop method. For each group, eight replicates were used and three measurements were performed on each sample. The average value of the 24 measurements was taken as the final result.

SEM-EDXA Analysis

The surface and cross-section morphologies of unmodified and modified wood fibers were observed by using a SEM (Hitachi S-3400, Japan) coupled with an energy dispersed X-ray analyzer (Horiba 7021-H, Japan) under an acceleration voltage of 10KV. The samples were sputter-coated with gold prior to observation.

FTIR Analysis

The unmodified and silane modified wood fibers were pulverized to pass through a 100 mesh sieve. After drying to the constant weight in an oven, they were mixed with

potassium bromide at a mass ratio of 1:100 in an agate mortar. Then they were pressed into disks after grinding to be tested. The spectrometer was set to collect 32 scans at 4 cm^{-1} resolution, within the range of 400 to 4000 cm^{-1} frequency region.

XPS Analysis

XPS analyses of the unmodified and silane modified samples were performed on an Escalab 250Xi instrument (Thermo Scientific, USA) to determine the number of functional groups present on the surface of the samples, with a pass energy of 10 eV and non-monochromatic Mg Ka and Al Ka X-radiations ($h\nu = 1253.7$ eV and 1486.7 eV, respectively). A current of 10 mA and a voltage of 13 kV were used. The survey scans were collected from the binding energy range of 0 to 1350 eV.

Statistical Analysis

Two-way analysis of variance for all statistics were performed using SPSS 11.0 software, with $P < 0.05$ considered statistically significant.

RESULTS AND DISCUSSION

Moisture Adsorption of Wood Fibers

The changing MCs of the unmodified and silane modified fibers are shown in Fig. 2. It is clear from the figure that all the wood fibers after silane modification showed reduction in moisture adsorption compared with that of the control group.

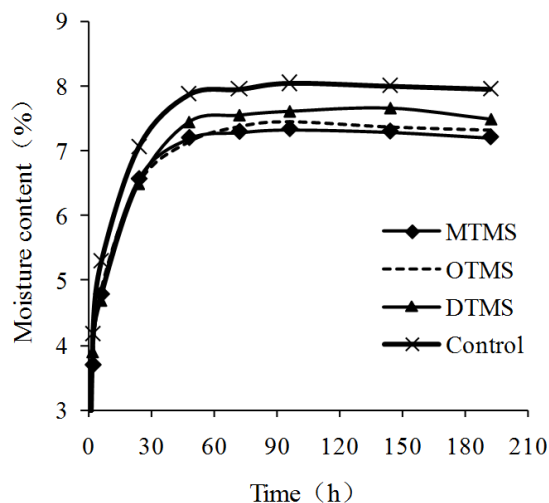


Fig. 2. Moisture adsorbed on control and silane modified wood fibers

After 192 h of moisture adsorption, MCs of the control group had reached 8.0%, while MCs of fibers after modification with 5 wt% MTMS, OTMS, and DTMS were 7.2%, 7.3%, and 7.5%, respectively. This suggested that silane might inhibit the moisture adsorption of wood fibers to some degree, perhaps resulting from the following two mechanisms. First, hydrophobic alkoxy silane could enter into the cell wall of wood fibers or attach on their surfaces, thereby physically occupying the space for water and hindering the adsorption of water molecules to wood fibers. Secondly, silanol, hydrolysate, or silane could form ether bonds via a polycondensation process with the

hydroxyl groups inside wood fibers at high temperatures, therefore reducing the amount of available hydroxyl groups for moisture adsorption. The difference between the three types of silane was not obvious, suggesting that the influence of chain length of silane on moisture adsorption of fibers was insignificant.

Contact Angle of Wood Fibers after Silane Modification

The contact angle of water reflects the surface hydrophobicity of an object. Higher contact angle corresponds to a more hydrophobic surface. Figure 2 shows the contact angles of distilled water on unmodified and silane modified wood fibers. According to Fig. 3, the contact angles of three types of silane modified fibers were 136.0 °C, 127.9 °C, and 139.7 °C, respectively, values much higher than that of the control (103.4 °C). This suggests that silane treatment was able to improve the hydrophobicity of wood fiber surface. Statistical analysis of the wood fiber surfaces indicated no significant difference between the MTMS and DTMS treated groups, while the OTMS-treated group demonstrated slightly weaker hydrophobia, indicating that increased silane chain length had little impact on hydrophobicity. Instead, improvement in hydrophobicity appears to relate to the reduced amount of hydrophilic hydroxyl groups on the surface of wood fibers.

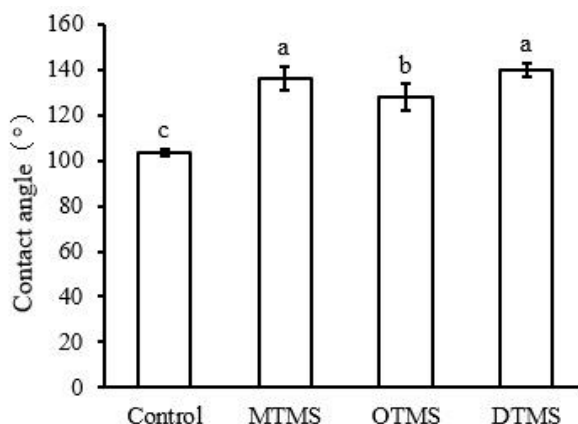


Fig. 3. Contact angles of distilled water on the surfaces of control and silane modified wood fibers. Bars accompanied by a different letter (a,b,c) are significantly different at $p < 0.05$ (Tukey's HSD test).

SEM Analysis

Figure 4 shows the SEM images of unmodified and modified wood fibers. The control samples appeared to have a slightly rough surface with clear grains of microfibrils. As the red arrows point out, a small amount of granular substances appeared on the surface of fibers after MTMS modification, which indicated that most parts of MTMS could penetrate into the wood fibers and react with cell wall substance, leaving only a small part on the surface. As the alkyl chain of silanes became longer, the quantity of silane remained on the fiber surface became greater. The fiber surface modified by DTMS with long chain length was found to be covered by a smooth film, which wrapped a bundle of fibers and made the microfibrils invisible. Presumably the long chains in DTMS blocked the pathways into the cell wall so that they remained on the surface of fibers and formed filmed polysiloxane by polycondensation reaction at high temperatures.

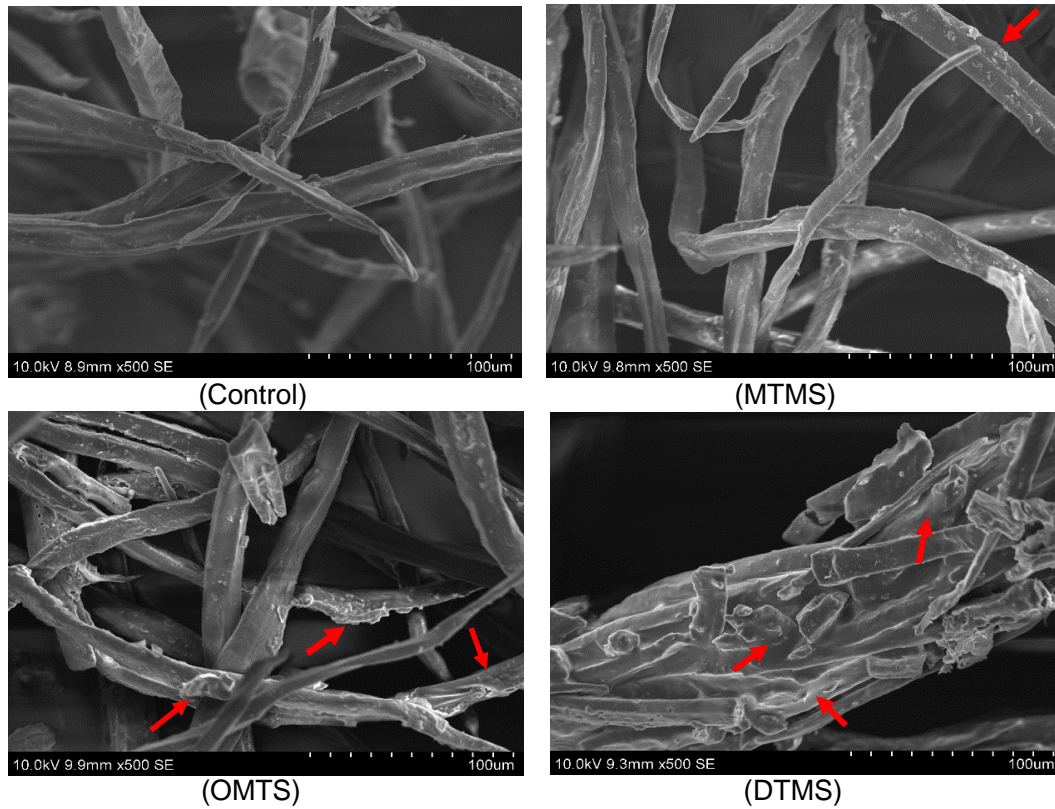


Fig. 4. SEM images of wood fibers unmodified or modified by different silanes

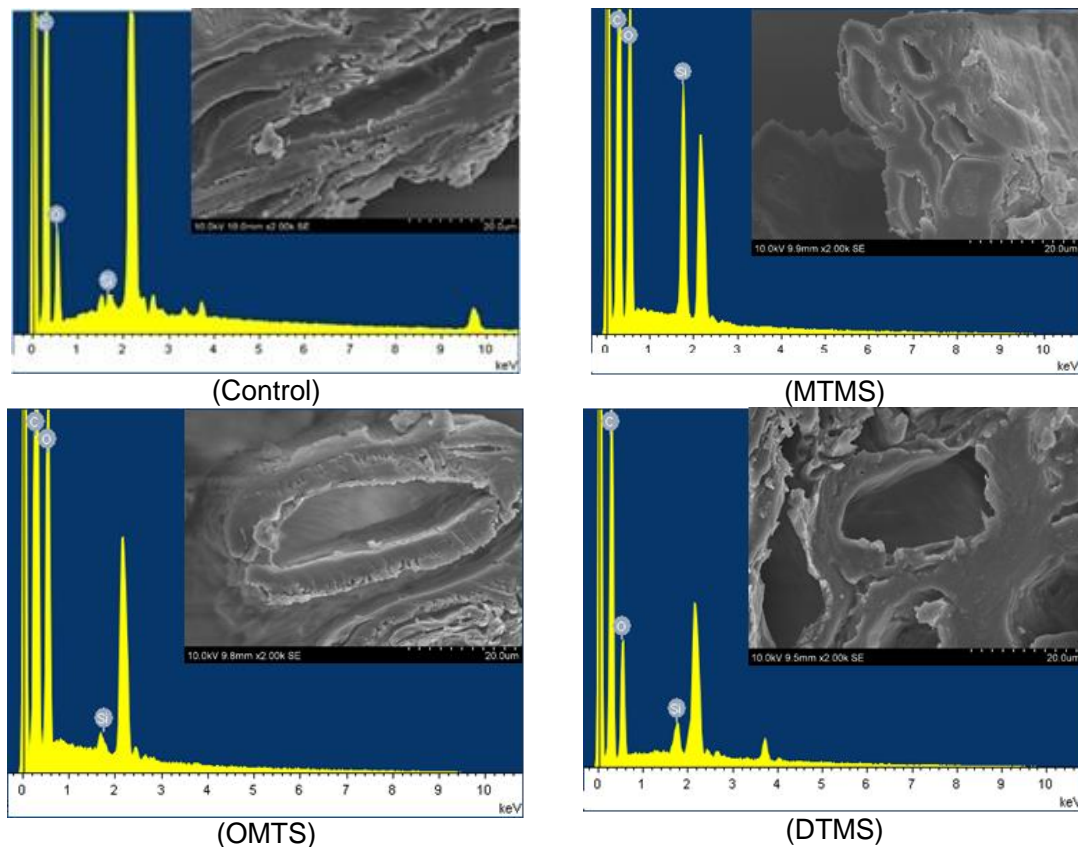


Fig. 5. SEM-EDXA analyses of wood fibers unmodified or modified by different silanes

The SEM-EDXA analyses were carried out on the fiber cross-section to explore the distribution of different silanes in the fibers. The results are shown in Fig. 5 and Table 1. The three groups of silane modified fibers all showed the presence of the element Si in the wood cell wall, which further confirmed that these silanes can penetrate into the cell wall and react with the chemical components of fiber. Among the treated groups, MTMS modified fibers exhibited the highest counts of Si element, while the Si element in the fibers modified by OTMS or DTMS was much less. The above results illustrate that the permeability of MTMS with short chain length is better than that of the other two kinds of silane, which agrees well with the SEM observations.

FTIR Analysis

FTIR spectra were used to characterize the combination of chemical bonds between silane and wood fiber components. The results are shown in Fig. 6. Being different from the control, all the treated fibers presented new adsorption bands at 450 cm^{-1} (Si-O-Si or Si-O-C) and 775 cm^{-1} (Si-O, Si-C, or Si-O-C) (Tshabalala *et al.* 2003; Sener *et al.* 2005; Rachini *et al.* 2012) after being modified by prehydrolyzed silane, demonstrating that silane entered into the wood fibers and polymerized with the hydroxyl groups in wood fibers. The presence of these bands suggested that both the grafting of silane onto wood fibers and the intermolecular condensation between adjacent adsorbed -Si-OH groups took place (Rachini *et al.* 2012).

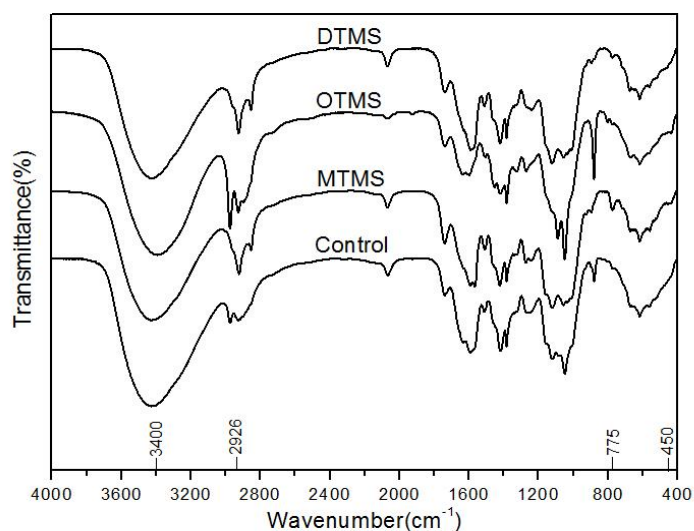


Fig. 6. FTIR analysis of control and silane modified fibers

The signal intensity of the treated fibers corresponding to O-H stretching at 3400 cm^{-1} range decreased compared with that of the control. This provides additional evidence for the reduced amount of hydrophilic hydroxyl groups in wood fibers after silane modification.

MTMS modification obtained the strongest intensity and a wider range of several bands at 450 cm^{-1} (Si-O-Si or Si-O-C) and 775 cm^{-1} (Si-O, Si-C or Si-O-C), illustrating more reaction sites in MTMS than the other two silanes with long alkyl chains. In addition, the weak peaks at 2926 cm^{-1} caused by the C-H stretching of wood fiber components in OTMS- and DTMS-treated groups were replaced by sharper and stronger

peaks. This resulted from the C-H stretching (CH_2 , CH_3) of the long hydrocarbon chains in OTMS and DTMS bound to wood by the sol-gel process (Gwon *et al.* 2010).

The results just described confirmed the occurrence of a chemical reaction between the hydrolyzed silane and wood fibers and also indicated the existence of a polysiloxane network.

XPS Analysis

XPS analysis was carried out to analyze the change of the functional groups on the surface of unmodified and silane modified wood fibers, as shown in Fig. 7. As distinct from the control, the spectra of the modified wood fibers showed $\text{Si}2s^*$ and $\text{Si}2p^*$ peaks in addition to $\text{O}1s^*$ and $\text{C}1s^*$ peaks, which confirmed the deposition of the polysiloxane film on the wood fiber surface.

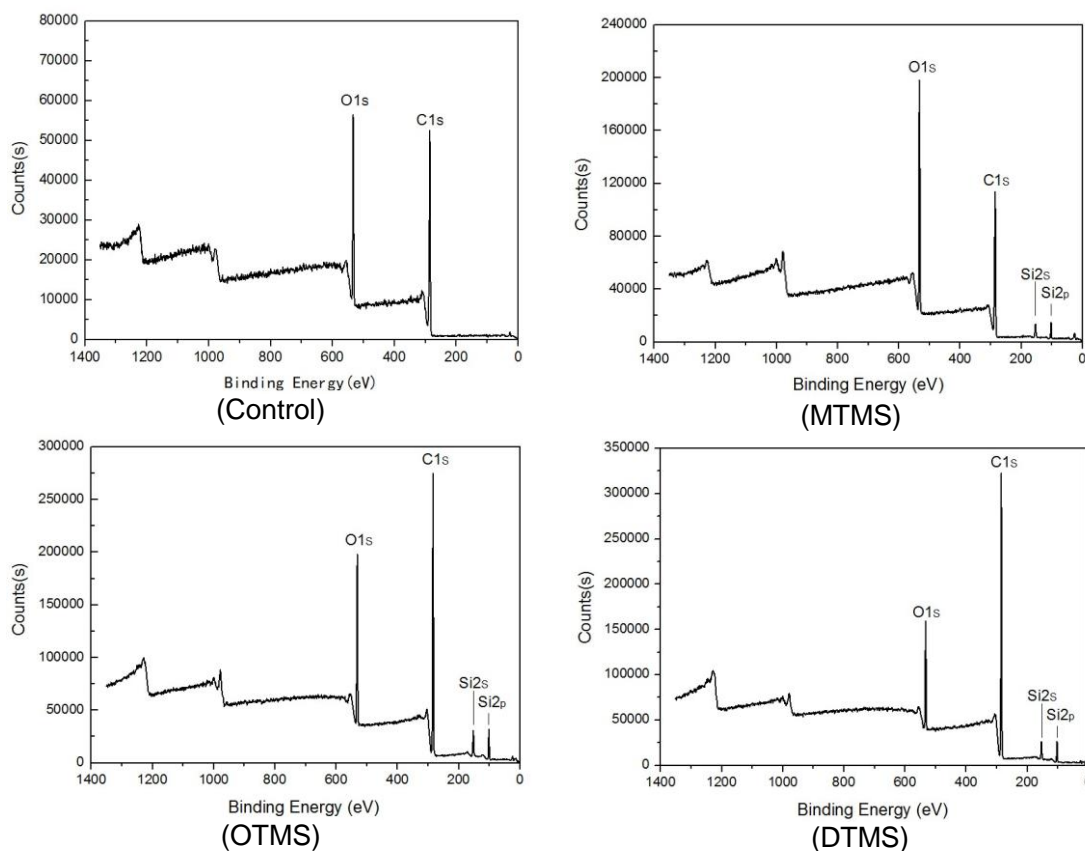


Fig. 7. XPS spectra of wood fibers unmodified or modified by different silanes

Figure 8 shows the representative XPS high-resolution $\text{C}1s^*$ spectra of control and modified wood fibers. The binding energy of the $\text{C}1s^*$ peak comprised of four different carbon types attributed to C1, C2, C3, and C4. C1 is assigned to carbon linked to hydrogen or carbon ($-\text{C}-\text{H}$ or $-\text{C}-\text{C}$), C2 to carbon linked to one oxygen ($-\text{C}-\text{O}$), C3 to carbon linked to two noncarbonyl oxygen atoms ($-\text{O}-\text{C}-\text{O}-$), or one carbonyl oxygen ($-\text{C}=\text{O}$), and C4 to carbon linked to both carbonyl and noncarbonyl oxygen ($\text{O}=\text{C}-\text{O}-$) (Girones *et al.* 2007; Liu *et al.* 2013). The XPS elemental composition of the specimens is summarized in Table I. These data confirmed that the sol-gel deposition of silane on the wood fibers led to significant changes in their surface chemistry.

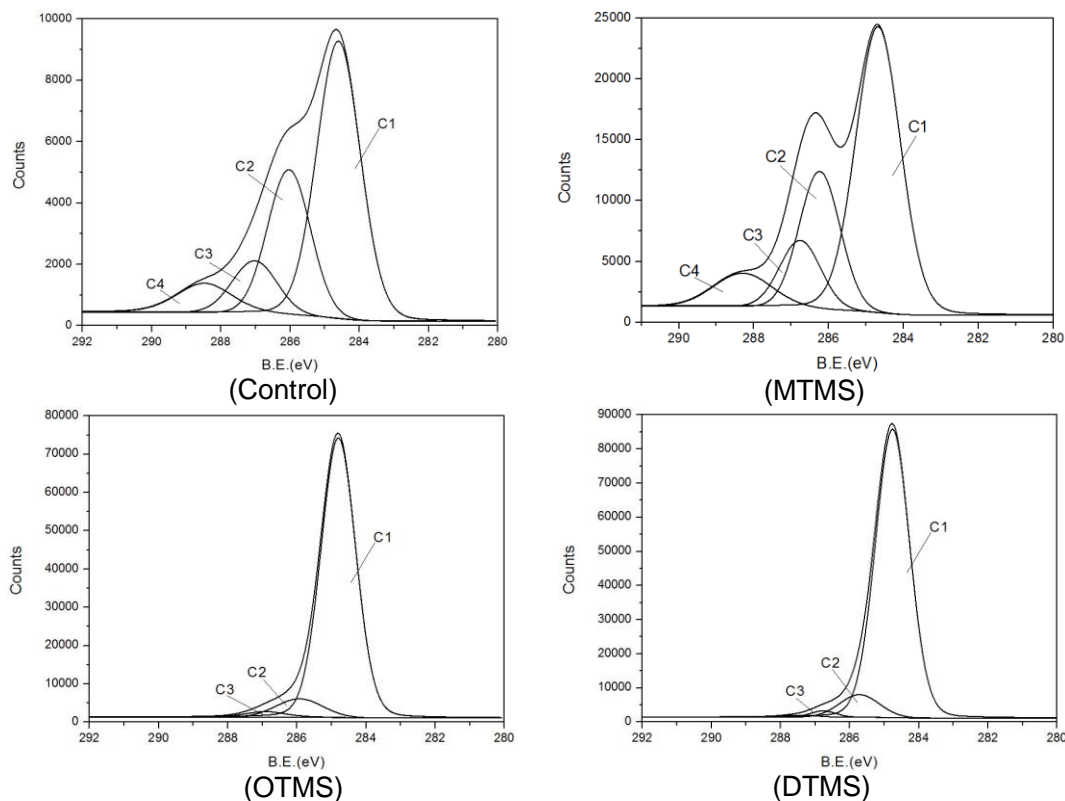


Fig. 8. High resolution C1s* spectra of wood fibers unmodified or modified by different silanes

Being modified by three different kinds of hydrolyzed silane, the C1 fraction of wood fibers surface increased to 56.59%, 89.97%, and 90.26%, respectively from 54.83% for the control. This increment was caused by the alkyl chains of silanes anchoring on wood fiber surface, which blocked the formation of hydrogen bonds between water molecules and wood fibers, therefore reducing the hygroscopicity of wood fiber surface. The MTMS with short chain length showed the least increment among all three treated groups, indicating the least residue on the fiber surface, which was in agreement with the results of SEM observation.

Compared with the control group, the binding energy of the C2 component of treated groups shifted from 284.03eV to 286.26 eV, 285.93 eV, and 285.72 eV respectively, which confirmed the presence of a carbon atom linked to an oxygen and a silicon atom (C-O-Si) (Tshabalala *et al.* 2007). The C2 fraction of wood fiber surface decreased to 23.71%, 7.57%, and 7.80%, respectively from 27.07% for the control. The C2 fraction can serve as a detector of hydroxyl groups. Lower value represents reduced number of hydroxyl groups on the fiber surface. This reduction was most likely due to the formation of the hydrogen bonds *via* polycondensation between the hydroxyl groups on both polysilanol and wood fiber surface. Compared with OTMS and DTMS, MTMS-treated fibers showed the least decline of C2 fraction, corresponding to the least reduction of hydroxyl groups on fiber surface. Therefore, one can speculate that the reduction in moisture adsorption and increasing contact angle for MTMS-modified fiber are mainly due to the penetration of MTMS into fiber cell wall and reaction with cell wall components. In addition, the restrained hygroscopicity and increased surface hydrophobicity of OTMS and DTMS modified fibers principally resulted from the

polymerization reaction on the fiber surface, as the hydrophobic long alkyl chains hindered the penetration of silanol.

The C4 fraction diminished and the C3 fraction became extremely low in OTMS- and DTMS-treated fibers, which can be attributed to their undetectable surface concentration after coating with silanes with long hydrocarbon chain. Similar results were also reported by Tshabalala *et al.* (2007).

Table 1. Analysis of High Resolution C1s Peaks of the Samples

Sample	Control		MTMS		OTMS		DTMS	
	Binding energy (eV)	Surface concentration (%)	Binding energy (eV)	Surface concentration (%)	Binding energy (eV)	Surface concentration (%)	Binding energy (eV)	Surface concentration (%)
C1	284.60	54.83	284.64	56.59	284.80	89.97	284.76	90.26
C2	286.03	27.15	286.26	23.71	285.93	7.57	285.72	7.80
C3	287.03	10.21	287.03	11.58	286.91	2.46	286.77	1.38
C4	288.48	7.81	288.39	8.12	-	-	287.45	0.57
Si	-	-	102.52	100.00	102.47	100.00	102.47	100.00

CONCLUSIONS

Selected alkoxy silanes (MTMS, OTMS, and DTMS) reduce moisture adsorption and increase contact angle of wood fibers. In addition, chain length affects the distribution of alkoxy silane in wood fibers, thereby affecting wood fiber performance. MTMS with short chain length penetrates most easily into the fiber cell wall and reacts with cell wall components, demonstrating the best performance in both the extent of polycondensation and hydrophobic improvement. Although the OTMS and DTMS have longer and more hydrophobic alkyl chains, these chains block their entrance into wood fiber. This restricts their reaction with the hydroxyl groups in the fiber cell wall and ultimately only achieves similar hydroscopicity as the MTMS modification. Future research on the influence of silane concentration on modification is necessary to ascertain the optimal condition in which to produce MDFs.

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