Modification of the Wood Surface Properties of _Tsoongiodendron odorum_ Chun with Silicon Dioxide by a Sol-gel Method

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A sol-gel method was employed to improve wood surface properties by generating SiO_2 with tetraethoxysilane and methyl triethoxysilane as co-precursors. The effect of SiO_2 on the wood surface properties was studied by the analysis of size stability, ultraviolet radiation aging resistance, and contact angle of the modified wood. The improvement mechanism was explored using scanning electron microscopy (SEM), energy dispersive X-ray (EDAX), and Fourier transform infrared spectroscopy (FT-IR). The results showed that the water absorption and the hygroscopic expansion rate of the modified wood were less than those of the control samples. The discoloration resistant properties were improved 1.5 times more than that of the control samples. The thickness of SiO_2 on the wood surface was approximately 60 μm, and the silicon content increased as the dipping time increased. The contact angle of modified wood showed that it was more hydrophobic than that of the control sample, and this increased as the dipping time increased. The variation in contact angle of the modified wood was less than that of the control sample before and after aging. The anti-aging performance of the modified wood surface was also improved.

Keywords: Sol-gel; Silicon dioxide film; Surface modification

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INTRODUCTION

Tsoongiodendron odorum Chun is one of the most important wood species in tropical and subtropical areas of China (Song _et al_. 2001). Because of its compact structure, straight texture, and good workability, this type of wood is widely used in the wood product industry as well as in costly furniture. However, poor dimensional stability and light aging resistance limit the utilization of _T. odorum_; some modifications, especially the surface functional modifications, are needed to improve the surface properties of wood (Fu and Zhao 2007). Many methods have been used to improve the surface properties of wood, namely wood dyeing, wood bleaching, wood painting, wood preservation, surface strengthening, surface chemical decoration, plasma polymerization, surface activation, _etc_. (Schmalzl _et al_. 1995; Podgorski _et al_. 2002; Rehn _et al_. 2003; Fu _et al_. 2012). For wood samples, moisture absorption on the surface of wood has serious impact on dimensional stability. Anti-aging performance has great influence on the color change of wood (Fu _et al_. 2006).

To maintain good dimensional stability and light aging resistance of wood, the service time of wood should be extended. Many scholars have a variety of related research on wood surface functional modifications with SiO_2, TiO_2, ZnO, and other oxides by

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physical, chemical, and other treatment methods (Miyafuji *et al.* 2004; Li *et al.* 2010; Sun *et al.* 2012). Through the above surface modifications, the modified wood materials are expected to be extensively applied in outdoor structure, interior decoration, flooring construction, and many other applications (Li *et al.* 2015).

Many promising results on wood modifications with SiO_2 have been obtained by the sol-gel method. Saka *et al.* (1992), Ogiso and Saka (1993, 1994), and Saka and Tanno (1996) have prepared wood/SiO_2 composites by the sol-gel method by dipping hinoki cypress into alkoxy silane. Their results indicated both the dimension stability and flame retardance of wood were improved after the modification. Liao *et al.* (2001) have also studied the properties of wood samples modified by the sol-gel method. These studies focused on the wood modification by generating SiO_2 inside the lumen or the void of cell wall. The dimensional stability of wood could be improved by silicon compounds, and the light stability could also be improved due to the existence of silicon functional groups (Qiu and Li 2005; Fu *et al.* 2006). Recently, Lu *et al.* (2014) developed an ultrasonic-assisted sol-gel method to conduct wood surface modification. Tetraethoxysilane (TEOS) has been used to undergo the sol-gel process for wood surface modification in most of the studies. However, there are many free hydroxyl groups on the surface of SiO_2 that are prepared by the hydrolysis of TEOS, which limits the surface hydrophobicity of the wood. Therefore, a precursor that will not introduce free hydroxyl groups on the surface is required to produce the SiO_2 surface with the sol-gel process. Herein, both TEOS and methyl triethoxysilane (MTES) were used as co-precursors to solve this problem.

This study aimed to improve the surface properties and application of *Tsoongiodendron odorum* wood and provide a theoretical basis for its scientific and reasonable utilization by studying the surface modification of *T. odorum* wood with the sol-gel method. In this study, SiO_2 film was produced on the wood surface to improve the hydrophobicity and anti-aging performance of the wood surface by sol-gel process with TEOS and MTES. The microcosmic structures, wood surface hydrophobicity, and anti-aging performance were all studied to explore the generation mechanism and function of silicon dioxide film.

EXPERIMENTAL

Experimental Materials and Reagents

Wood specimens from air-dried wood (*Tsoongiodendron odorum*) were cut into a size of $20 \times 20 \times 20$ mm and $95 \times 65 \times 5$ mm (longitudinal, tangential, and radial). The chemicals, including TEOS (($C_2H_5)_4SiO_4$), MTES ($C_7H_{18}O_3Si$), ethanol (CH_3CH_2OH), and acetic acid (CH_3CHOOH) were supplied by the Guangxi Songyuan Chemical Co. Ltd., Nanning City, China.

Experimental Method

In the sol-gel method, ethyl orthosilicate, methyltriethoxysilane, ethanol, acetic acid, and water, which were mixed with a ratio of 1:1:1:0.01:0.1, served as the ceramic precursor, coupling agent, solvent, catalyst, and initiator, respectively. Air-drying samples were immediately dipped in the mixed solution after its preparation for different periods of 0.5, 1, 2, 4, and 6 h. The samples were aged at the room temperature for 5 days after the dipping treatment. This was done so that the silica film was formed on the wood surface. The samples were oven-dried at 120 °C until they were dry and then at 150 °C for 6 h to

dehydrate the silicon dioxide film and eliminate its free hydroxyl groups. The samples were then ready for the subsequent characterizations.

Characterizations

Dimensional stability measurement

The silica modified samples were put on the partition in the dryer with distilled water at the bottom after they were oven-dried. The weight, moisture absorption, and dimensions of the samples were measured. Five replicates were used in the measurements. The measurements of the 5 samples were completed every 6 h (Chen *et al*. 2008). The moisture uptake was determined using Eq. 1,

$$\Delta m = \frac{m_1 - m_0}{m_0} \times 100\%$$
(1)

where Δm was the moisture uptake, m_1 was the weight of the sample after moisture absorption, and m_0 was the weight of the oven dried sample. The hygroscopic expansion rate was calculated using Eq. 2,

$$\Delta L = \frac{L_1 - L_0}{L_0} \times 100\%$$
(2)

where ΔL was the degree of hygroscopic expansion, L_1 was the size (length, width, and thickness) of the sample after moisture absorption, and L_0 was the size (length, width, and thickness) of the oven-dried sample.

Accelerated aging measurement

An artificial accelerated aging test was carried out on the wood surface using a QUV/SPRAY (SPRAY type) ultraviolet aging instrument (Q-Lab Corporation, Shanghai, China) with the tube type of UVA-340, light intensity of 0.89 w/m^2, a temperature of 60 °C, and the condensation temperature of 50 °C. The test cycle was 8 h illumination, 15 min spray, and then 3.45 h of condensing. The international standard lighting committee CIE1976 system was used and the chromaticity coordinates of each sample including L^* (lightness), a^* (red and green index), and b^* (yellow blue index), was measured by the ADCI-60-C automatic color difference instrument (Chentaike Instrument Technology Co., Ltd., Beijing, China) after the aging time of 0, 2, 4, 8, 12, 24, 48, 72, 96, and 120 h, respectively. Three samples in each group were measured. Five points were measured on each sample, and the mean value was calculated. Through the formula of $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$, the changes of the sample surface color differences before and after aging were calculated (Dang 2007).

Microstructure of wood surface

By slicing with a blade, the film thickness, morphology, and structure of the wood surface were studied with the S-3400N scanning electron microscope (SEM; Hitachi Ltd., Tokyo, Japan). An energy dispersive X-ray spectrometer (EDAX; Hitachi Ltd., Tokyo, Japan) was used to observe the morphology of silica and their distribution on the wood surface. The chemical structure of silicon dioxide in the oxidation film and the combination with the wood surface were analyzed by the Nexus470 Fourier transform infrared spectrophotometer (FTIR; Thermo Fisher, Waltham, MA, USA).

Contact Angle Measurement

A KRUSS contact angle instrument (KRÜSS, DSA100S, Germany) was used to measure the contact angles of distilled water on the wood surfaces before and after the aging tests. The contact angles on both tangential and radial surfaces of each sample were measured and averaged.

RESULTS AND DISCUSSION

The Influence of Dipping Time on Dimensional Stability

The effect of dipping time on moisture uptake

The moisture content increased with the increase of dipping time from 0 to 120 h. The moisture uptake increased with the increase of moisture absorption time within 30 h. However, after a hygroscopic period of 30 h, the moisture uptake began to increase slowly. Moreover, moisture content at that time was close to saturation. Figure 1 shows that the moisture uptake of modified wood was smaller than that of the controlled one, and the moisture uptake decreased with the increase of dipping time. These results show that silicon dioxide film reduced hydroxyl groups on the surface of the treated wood, and moisture absorption capacity was prevented. The thicker the silicon dioxide film, the longer dipping time, which helps to prevent the presence of water in the wood.
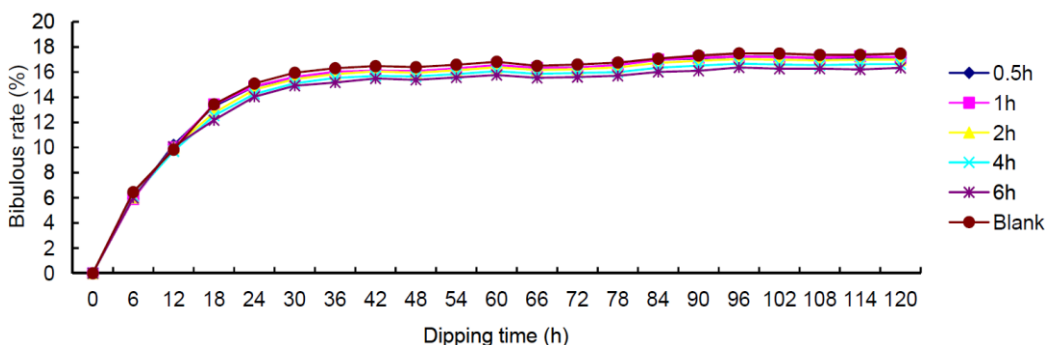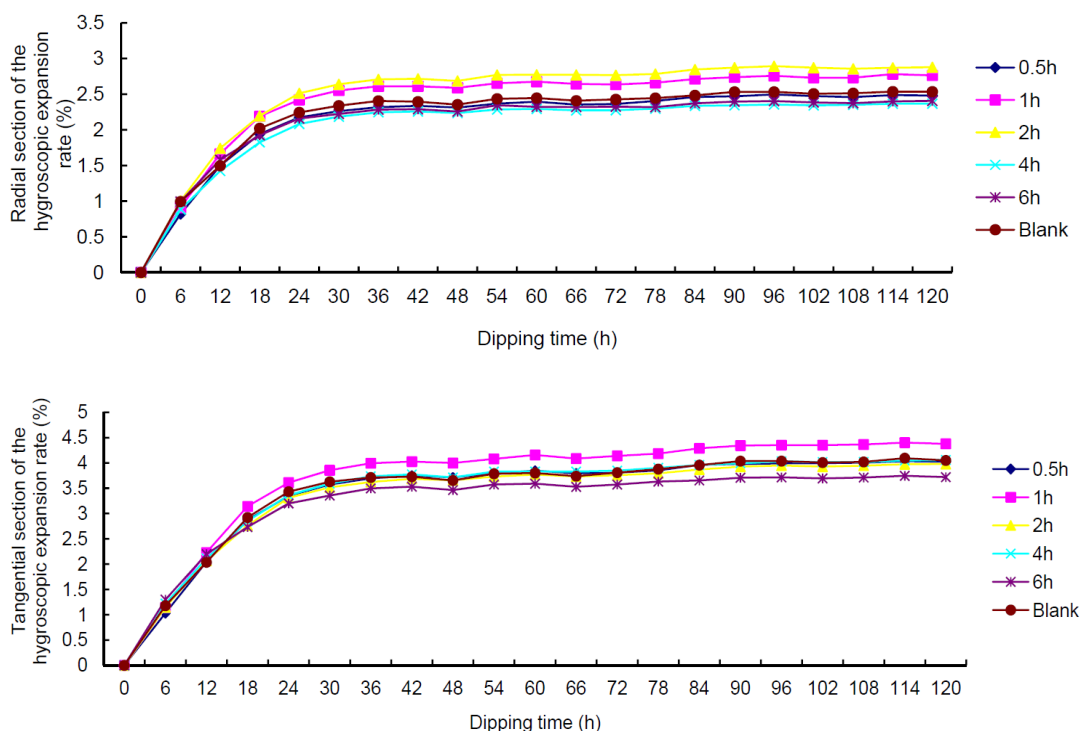

Fig. 1. Changes in moisture uptake under different moisture absorption times with different dipping times

The effect of dipping time on the hygroscopic expansion rate

After the dipping, moisture content increased with the increase of moisture absorption time from 0 to 120 h. The moisture uptake increased with the increase of moisture absorption time to within 24 h. Nevertheless, after a hygroscopic period of 24 h, the moisture uptake began to slowly increase. Moreover, the moisture content was close to saturation at that time. Figure 2 shows that the hygroscopic expansion rate of modified wood was smaller than that of the control samples, except for the samples with dipping times of 1 and 2 h. Moreover, the silicon dioxide film prevented moisture absorption in wood. In addition, the hygroscopic expansion rate of tangential section was close to twice as much as the radial section, which was consistent with the hygroscopicity of lumber. The hygroscopic expansion rate increased initially and then decreased with increased dipping time. Wood inclusions were dissolved, and the silica content on the wood surface was low within 0 to 2 h. Therefore, the hygroscopic expansion rate of modified wood increased. Silica film on the wood surface increased with the increase of dipping time when dipping time was extended to a certain stage. Silica was distributed on the wood surface or

combined with hydroxyl groups on the wood surface, which limited the moisture absorption of hydroxyl groups in the wood. The adsorption ability of water molecules was weakened, which caused the moisture absorption rate to decrease.

Fig. 2. Changes in hygroscopic expansion rate under different moisture absorption times with different dipping times

Aging Resistance Analysis of Silica Modified Wood

The ultraviolet aging test was conducted on modified wood and control wood simultaneously. The samples prepared in different dipping times were tested with different aging times (light, spray, condensing) of 2, 4, 8, 12, 24, 48, 72, 96, and 120 h. The changes in surface lightness (ΔL) and total color difference (ΔE) are shown in Fig. 3. The color changes of ultraviolet aging were based on the color before aging. For both the modified wood and the control wood lightness, ΔL basically decreased, while the ΔE presented an initial increase, a following decrease, and then a final increase after the artificial accelerated ultraviolet aging test. Aging treatment remarkably lowered the lightness and increased the total color difference of the wood. Also, the color of the silica modified wood surface was relatively stable, and the changes detected were remarkably less than those of the control samples, which indicated that the silicon dioxide had a strong ability for ultraviolet absorption. The absorption, reflection and refraction of ultraviolet can take place in the nanometer silicon dioxide (Yu *et al.* 1998; Zhang *et al.* 2002), which may enhance the ultraviolet resistance of the modified wood. The wood had the effect of ultraviolet aging resistance because the silica were generated on the wood surface through a sol-gel process.

The influence of different dipping times on the sample's ultraviolet aging resistance can be observed in Fig. 3. Surface lightness and total color difference of modified wood were less than those of the control samples. With the increase of dipping time, the change in lightness ΔL that was present decreased and then increased. Also, the modified sample impregnated for 2 h had the least change; moreover, ΔE decreased with the increase of

dipping time. The wood with 2 h impregnation had the minimum lightness change. Longer dipping times resulted in lower total color difference. After an ultraviolet aging of 120 h, the average value of the total color difference of modified wood was 25.6, and that of the control samples was 38.3. The surface light discoloration resistance of modified wood was 1.5 times that of the control.
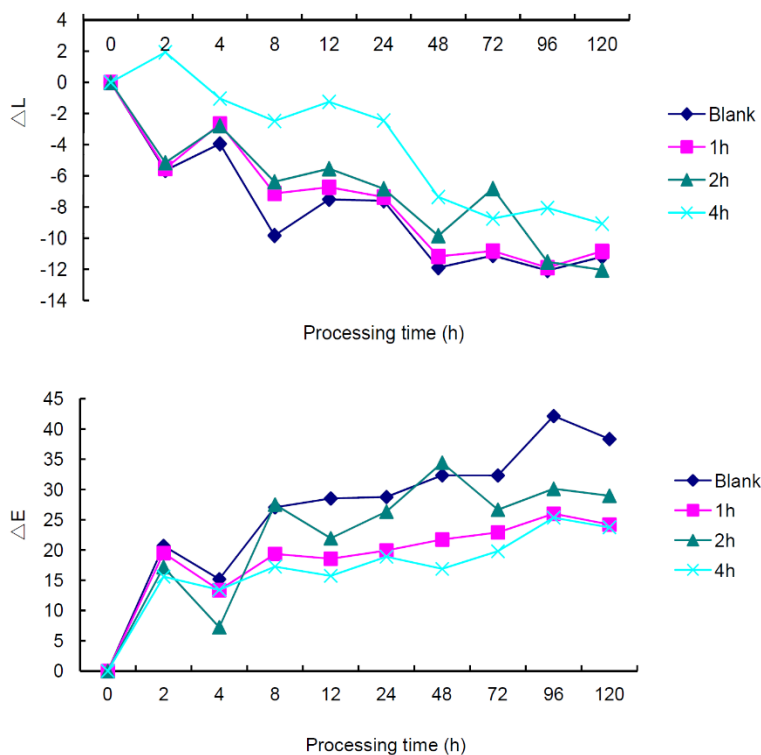
Fig. 3. ΔL and ΔE variation in the process of aging

SEM, EDAX, and FTIR Analysis of Modified Wood

SEM analysis of silica modified wood in different dipping times

Figures 4 through 6 show the SEM analysis of the control wood sample and the modified wood on the cross section, tangential section, and radial section, respectively under 200× magnification. The cells on the wood surface had obvious changes, including a layer of white crystal that appeared in the cell wall and cell lumen of the wood surface. The white solid material was silica particles, which were generated after the hydrolysis and polycondensation reaction.
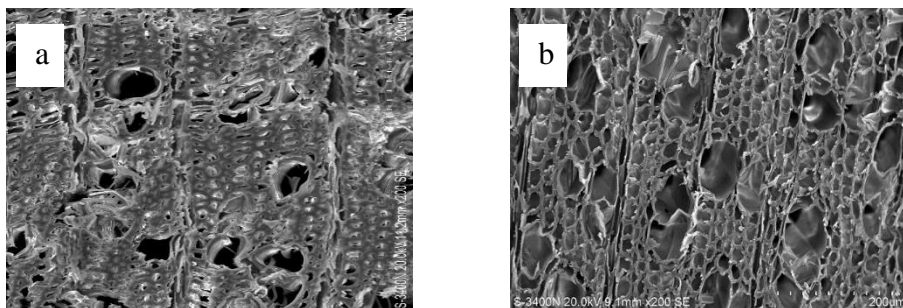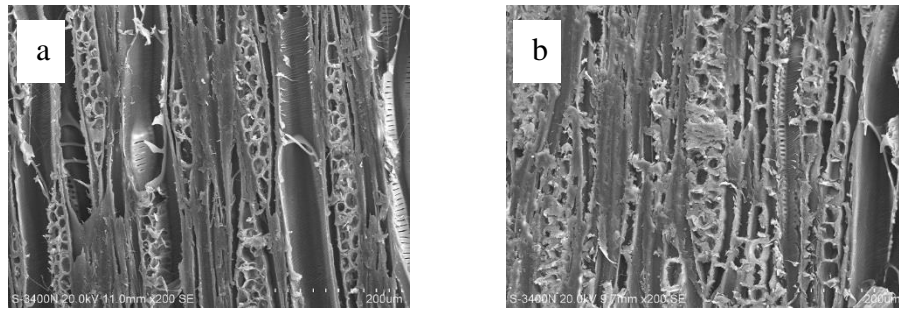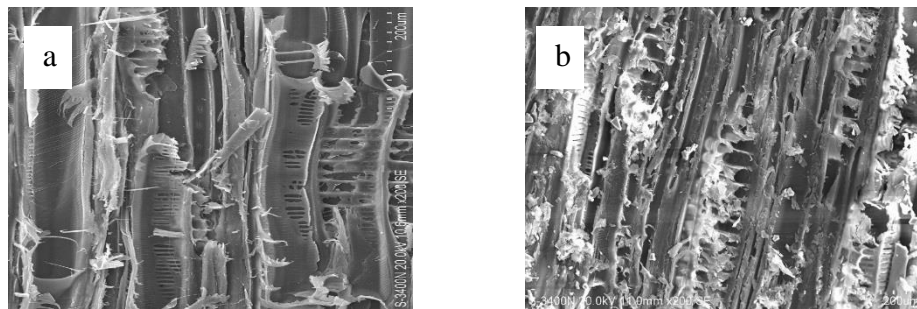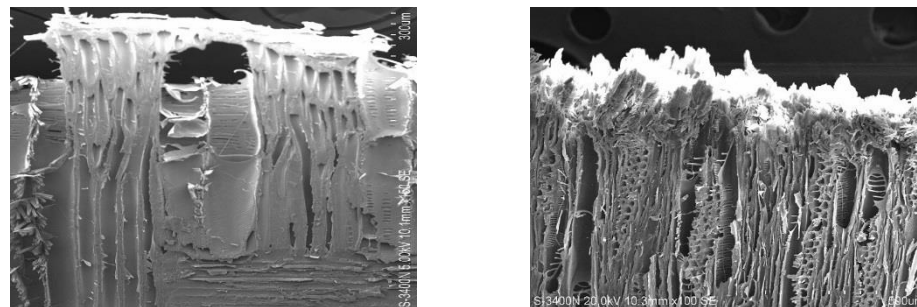

Fig. 4. SEM analysis of the control and modified wood in the cross section (a: control; b: modified wood)

Fig. 5. SEM analysis of the control and modified wood in the tangential section (a: control; b: modified wood)

Fig. 6. SEM analysis of the control and modified wood in the radial section (a: control; b: modified wood)

Fig. 7. Thickness of the silica generated on the wood surface

Figure 7 shows the SEM analysis of the thickness of the silica modified wood. A layer of white silica was shown at the top of Fig. 7, and the chart showed that the thickness was about 60 μm.

EDAX and scattergram analysis of modified wood in different dipping times

Figure 8 displays the EDAX elemental content analysis of samples with different dipping times. There was little silicon in the control samples, but an obvious amount of 2.4% in the modified wood, which was revealed through the presence of silicon dioxide on the wood surface. Silica content increased remarkably from 0.79% to 2.4% with a dipping time increase from 1 to 2 h, which showed that the longer dipping time resulted in more silica generated.
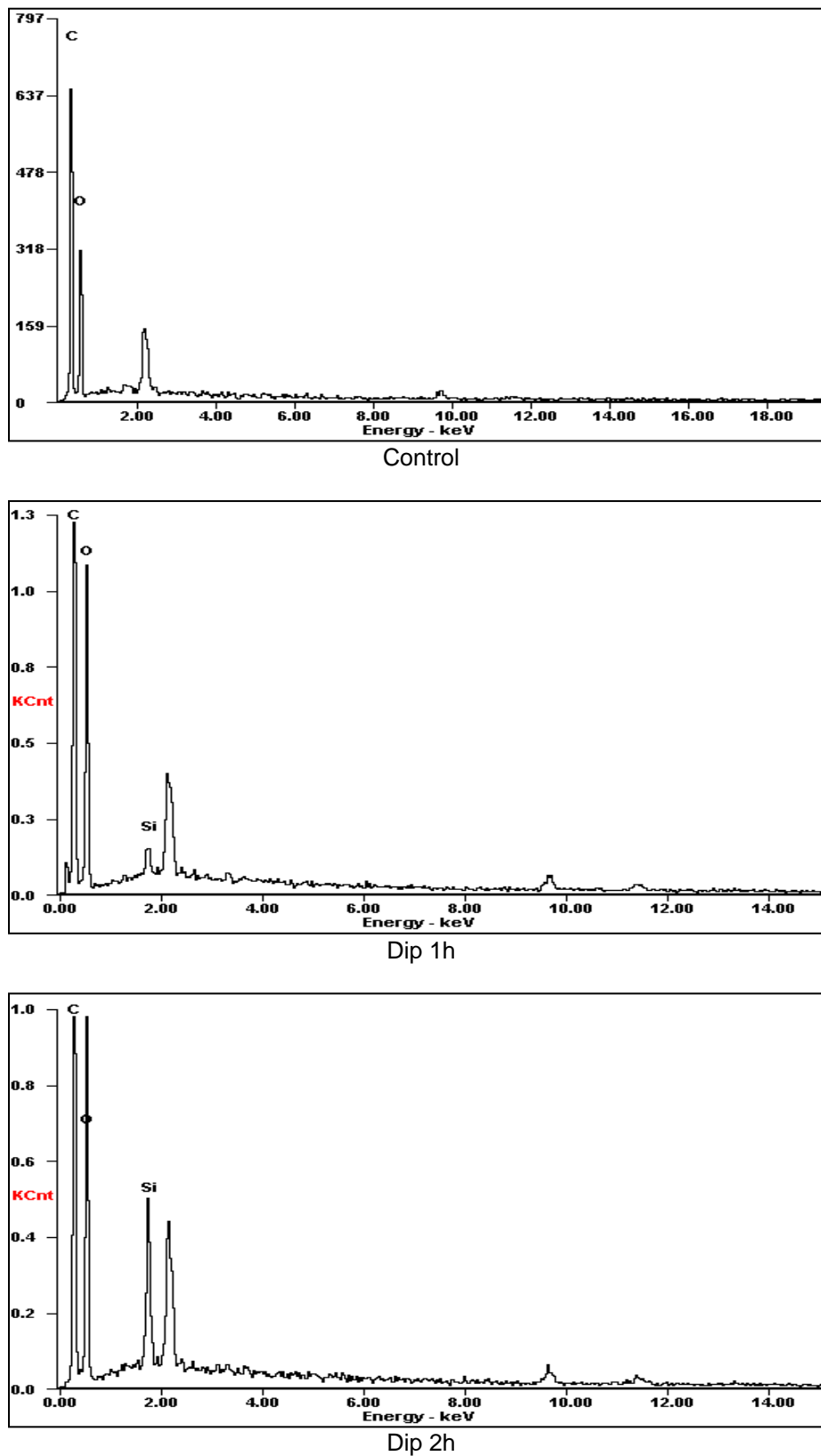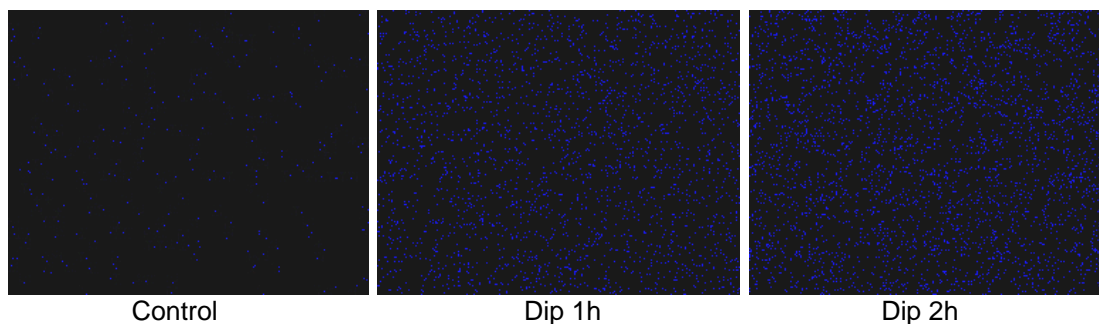
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Fig. 8. EDAX analysis of blank and modified wood

| Control | Dip 1h | Dip 2h |

Fig. 9. Topographic map of silica modified wood in different dipping times

Figure 9 presents a topographic map of silicon atoms on the cross section of wood. Many silicon atoms were observed in the silica modified surface, while fewer were present in the control sample. Moreover, with the increase of dipping time, the silicon atoms increased and distributed uniformly. Most silicon atoms were distributed in the cell wall, and a few were present in the cell lumen.
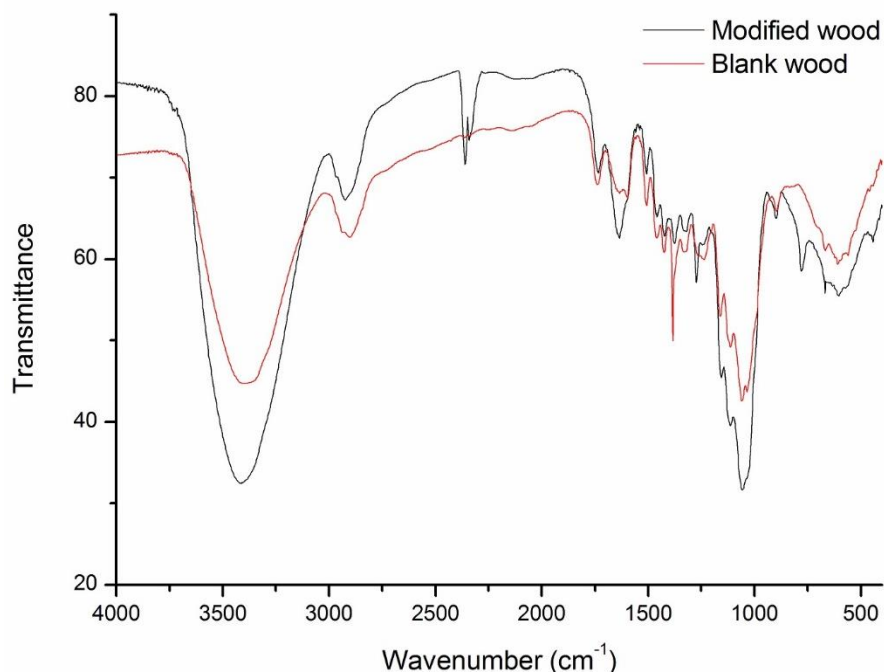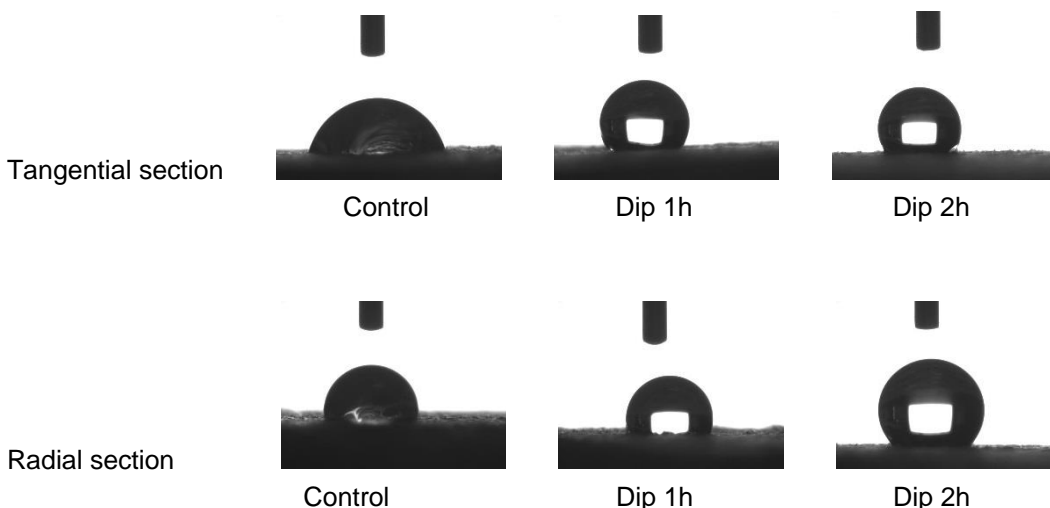

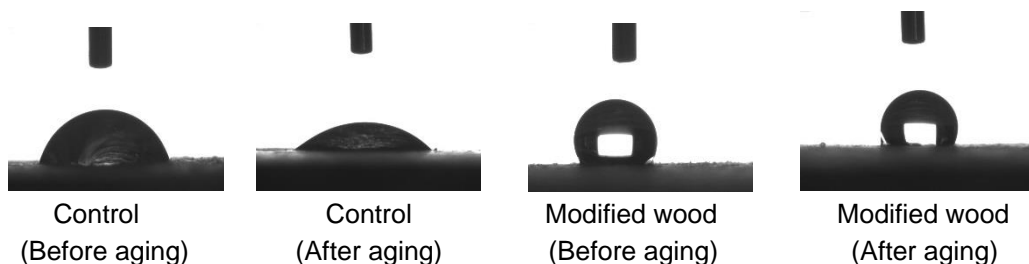**Fig. 10.** FTIR analysis of silica modified wood and blank wood

FTIR analysis of silica modified wood and blank wood

FTIR analysis of silica modified wood is shown in Fig. 10, and the characteristic peaks can be assigned to the corresponding groups (Kim 1997; Pu *et al*. 1997; Kim *et al*. 2000). In the range of approximately 3408 to 3425 cm^{-1}, the stretching vibration absorption peak intensity of the hydroxyl groups (O–H) decreased. Also, there were strong aliphatic functional group absorption peaks of C=O around 1730 cm^{-1}. The peak intensity of the aliphatic functional group (C-O-C) vibration remarkably increased near 1265 cm^{-1} in modified wood, which illustrated that a large number of non-polar functional groups were generated, and that polar hydroxyl groups decreased by silica modification treatment. The hydroscopicity of wood decreased and the hydrophobicity strengthened, by which the

expected effect of hydrophobicity was achieved. A Si-O-Si stretching vibration peak appeared near 1125 cm^{-1} and a Si-(CH$_3$)$_3$ characteristic peak appeared near 1265 cm^{-1}, which confirmed the modification mechanism of silanization to wood. Thus, silanization made some oxygen-containing groups into oxygen-silicon groups. Methyltriethoxysilane served as coupling agent. Si-(CH$_3$)$_3$ groups and the condensation product of organic silicon compounds reduced hydroxyl groups on the wood surface and increased hydrophobicity.

Fig. 11. Comparison chart of contact angle of modified wood and blank wood

Fig. 12. Comparison chart of contact angle before and after aging

Hydrophobicity Analysis of Silica Modified Wood

The comparison of contact angles before and after modified wood is shown in Fig. 11. The contact angles before and after aging are shown in Fig. 12. The results showed that the contact angle of silica modified wood was larger than that of control wood. Moreover, the contact angle increased with increased dipping time. The contact angle increased from 84° to 125° and from 68° to 125° in the radial and tangential sections, respectively. The hydrophobicity of wood was improved, and the effect of super-hydrophobicity was achieved. The contact angle of the wood was smaller after aging, and the reduction was not obvious for modified wood. However, the result was opposite for wood without modification, which showed a contact angle of 35° before aging and 2° after aging. The anti-aging property of silica modified wood was more effective than that of the wood without modification. Because of the silica distribution on the wood surface and/or combination with hydroxyl groups on the wood surface, the moisture absorption of the

hydroxyl groups was limited. A layer of super-hydrophobic silica film formed on the wood surface, which caused the contact angle to greatly increase and the hydrophobicity to improve.

CONCLUSIONS

1. The moisture uptake of silica-modified wood was smaller than that of the control sample. The moisture uptake also decreased as the dipping time increased. Longer dipping time resulted in better dimensional stability of the wood. The moisture absorption rate of silica-modified wood was smaller than that of the control sample. The hygroscopic expansion rate in tangential direction was nearly 2 times greater than that in the radial direction. Nevertheless, as the dipping time elapsed, the hygroscopic expansion rate initially increased and then decreased.

2. Lightness (ΔL) of both the modified wood and the control sample showed a decreasing trend, while the total color difference (ΔE) showed an initial increase, followed by a decrease, and then an increase after aging for 120 h. Modification with SiO_2 improved the photochromic resistance of the modified wood. The surface light discoloration resistance of modified wood was 1.5 times higher than that of the control sample.

3. The thickness of silica generated on the wood surface was about 60 μm. There were limited silicon in the control samples, but the silica content in the modified wood was 2.4%. The silica content increased as the dipping time increased. The $Si\text{-}(CH_3)_3$ groups on modified wood surface and the condensation of organic silicon compounds reduced the number of hydroxyl groups, which led to increased hydrophobicity. This was made clear by the increased contact angle for the silica modified wood surface. Furthermore, the change of contact angle of the modified wood before and after the aging test was less than that of the control sample, which indicated that the modified wood had better anti-aging performance.

ACKNOWLEDGMENTS

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