General paper

TOPOCHEMISTRY OF SiO₂ WOOD-INORGANIC COMPOSITES FOR ENHANCING WATER-REPELLENCY

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Abstract: Methyltrimethoxysilane (MTMOS) was used to prepare the SiO₂ wood-inorganic composites. To enhance the properties of these composites, 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) as a property enhancer was added to this reaction system for SiO₂ wood-inorganic composites. To elucidate the mechanism for enhancing the water-repellent property in the HFOETMOS-SiO₂ wood-inorganic composites, the composites with various weight percent gains (*WPGs*) were prepared, and the prepared composites with the lower *WPG* revealed the better property in water-repellency, whereas those with the higher *WPG* could not attain the high water-repellent property. SEM-EDXA analysis on these composites revealed that the HFOETMOS-derived residues were concentrated on the boundary between the cell wall and cell lumen in both composites with the lower and higher *WPGs*, while SiO₂ gels were almost uniformly distributed within the cell walls in the composites with lower *WPG*. SiO₂ gels in the composites with higher *WPG* were distributed in a similar manner but slightly higher in its concentration at the boundary between the cell wall and cell lumen. From these results, it was assumed that for the composites with lower *WPG*, the cell wall would be covered with the long hydrophobic alkyl residue of the HFOETMOS, whereas for the composites with higher *WPG*, SiO₂ gels formed in the cell lumen would have prevented HFOETMOS-derived residues from being exposed uniformly over the surface of cell wall. This may be why the different water-repellent properties were shown between the composites with higher and lower *WPGs*. These results suggest that the topochemical effects of the SiO₂ gels and HFOETMOS-derived residues exist for the enhancement of water-repellent property.

Key words: *Wood-inorganic composites, Sol-gel process, Topochemistry, Property-enhancement, Water-repellency, SiO₂ gels, HFOETMOS*

1. INTRODUCTION

To enhance the properties of wood, a sol-gel process has been applied to prepare wood-inorganic composites [1-11], and inorganic substances were found to be distributed differently in wood as different metal alkoxides were used with moisture-conditioned wood or water-saturated wood [1,2,4,6].

In SiO₂ wood-inorganic composites from alkoxy-silane with moisture-conditioned wood, SiO₂ gels were found to be formed selectively within the cell walls with retaining the porous structure characteristic of wood. However, in SiO₂ wood-inorganic composites with water-saturated wood, mainly the cell lumens were filled with SiO₂ gels. From a comparative study for these two types of composites, it was revealed that the SiO₂ gels within the cell walls were more effective for property-enhancement of wood with a very small weight percent gain (*WPG*) of the gels, compared with the SiO₂ gels formed in the cell lumens. Therefore, it was concluded that a topochemical effect of the SiO₂ gels exists for the property-enhancement of wood in dimensional stability, combustibility and some other wood properties.

For adding water-repellent property to wood, we have applied 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) to the reaction system for various wood-inorganic composites [8-10]. It was consequently revealed that HFOETMOS-added binary SiO₂-P₂O₅ and SiO₂-B₂O₃ wood-inorganic composites from tetraethoxysilane

(TEOS) and trimethylphosphite (TMP) or trimethylborate (TMB) could attain the high water-repellent property. With this property enhanced, these composites could have prevented P₂O₅ or B₂O₃ gels from leaching out and maintained their high fire-resisting property after severe weathering test [8]. It was also found that HFOETMOS-added various SiO₂ composites with fire-resisting agents could have maintained their fire-resisting property [9].

As some other trials, 3-(trimethoxysilyl)propyl-octadecyl ammonium chloride (TMSAC) was recently applied to the reaction system to prepare the antimicrobial wood-inorganic composites from TEOS. While the obtained TMSAC-SiO₂ composites revealed some antimicrobial activities, the use of HFOETMOS could provide water-repellent property to the composites which has, furthermore, improved its activities against both white-rot and brown-rot fungi [10].

However, a mechanism of their property-enhancement for these wood-inorganic composites with HFOETMOS has not been confirmed yet. In this study, therefore, various HFOETMOS woods and HFOETMOS-SiO₂ wood-inorganic composites (HFOETMOS-SiO₂ composites) were prepared to elucidate the mechanism of water-repellent property enhancement. By evaluating their water-repellency and the fluorine distribution from HFOETMOS in these composites by scanning electron microscopy coupled with an energy-dispersive X-ray analysis (SEM-EDXA) [12], the topochemistry of the HFOETMOS-SiO₂ wood-inorganic composites were

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studied for enhancing water-repellency of wood.

2. EXPERIMENTAL

2.1. Wood Specimens

The specimens [30 (R) × 30 (T) × 5 (L) mm] obtained from the sapwood portions of western hemlock (*Tsuga heterophylla* Sarg.) were extracted with acetone for 24h and subsequently with water for another 24h in a Soxhlet apparatus. Extracted wood specimens were then oven-dried, and their oven-dried weights were measured. To prepare the wood specimens with 20 to 25 % moisture content, oven-dried specimens were placed in a desiccator for three weeks at 20°C in which the relative humidity was controlled to be 98 % with a saturated salt solution of K₂SO₄.

2.2. Preparation of Various HFOETMOS-SiO₂ Wood-Inorganic Composites

Solutions were prepared with a molar ratio of 1:1:0.01 in tetraethoxysilane [(TEOS), Si(OC₂H₅)₄] or methyltrimethoxysilane [(MTMOS), CH₃Si(OCH₃)₃], ethanol or methanol and acetic acid for preparing two kinds of SiO₂ wood-inorganic composites from TEOS or MTMOS. To these solutions, property-enhancer, 2-heptadecafluorooctylethyltrimethoxysilane[(HFOETMOS), CF₃(CF₂)₇CH₂CH₂Si(OCH₃)₃] was added with a molar ratio of 0.05, 0.01, 0.004 and 0.001 to TEOS or MTMOS to prepare HFOETMOS-SiO₂ wood-inorganic composites from TEOS or MTMOS. TEOS, MTMOS and HFOETMOS were provided from Shin-Etsu Chemical Co., Ltd.

Furthermore, solutions were prepared with a molar ratio of 0.03, 0.01, 0.006 or 0.001 of MTMOS in the 1 : 0.01 : 0.004 molar ratio of methanol, acetic acid and HFOETMOS to prepare the HFOETMOS-SiO₂ wood-inorganic composites with various weight percent gains (WPGs). To achieve the same weight concentration of HFOETMOS in these reaction medium, MTMOS was displaced at an equal weight with methanol, as its molar ratio was decreased. Just for comparison, HFOETMOS-treated woods were also prepared with several solutions of HFOETMOS in methanol and acetic acid with 0.03, 0.01, 0.004, 0.001 or 0.0005 of HFOETMOS in the 1 : 0.01 molar ratio of methanol and acetic acid.

Subsequently, into moisture-conditioned specimens, the prepared solutions above were impregnated at 20°C under a reduced pressure (15 mmHg) for three days. The impregnated specimens were then placed in an oven controlled to be 60°C for 24h and 105°C for another 24h for aging of the gels. For each treatment, four specimens were prepared.

2.3. Evaluation of Wood-Inorganic Composites

The weight percent gain (WPG) of the composites was determined, on an oven-dried weight basis, by measuring the oven-dried weights of the extractive-free untreated specimens and the composite specimens. The bulking coefficient (B) was also determined for all prepared composites.

The fluorine content in the obtained composites was determined by using fluorine ion selective electrode after decomposing the composites by oxygen flask combustion method [13]. From the determined fluorine content in the

composites, the amount of fluorine added-on ($F_{\text{added-on}}$) was calculated, on an oven-dried weight basis, which can show the amount of fluorine added on to the non-treated wood basis.

To evaluate the water-repellent property of the composites, the specimens were placed in distilled water with weights under a normal pressure at 20°C, and changes in the weights of the prepared composites (W_1) due to water absorption were measured every other day. After 14 days, the untreated specimens were soaked further with distilled water under a reduced pressure for three days. The water content in such a water-saturated wood specimen (W_2) was considered to be maximal. The water absorption ratio (WAR) was then computed by the following formula :

$$WAR = W_1 / W_2 . \quad (1)$$

The contact angle (°) of the droplet over the prepared composites was measured from a photograph taken one minute after 2μl of water dropped over the cross section of the specimens.

For an energy-dispersive X-ray analysis, oven-dried specimens [0.7(R) × 0.7(T) × 3(L) mm] were soaked overnight in Spurr low viscosity epoxy resin consisting of a mixture of vinylcyclohexene dioxide, diglycidyl ether of polypropyleneglycol, nonenyl succinic anhydride, and dimethylaminoethanol (10:6:26:0.4 in weight ratio) and then cured in the usual way. The embedded specimens were subsequently sectioned with a glass knife, and the obtained transverse sections of 0.5μm in thickness were placed on a carbon-coated formvar film covered over single hole carbon grid. The sections were then studied with a scanning electron microscope (JEOL JSM-5800) coupled with an energy dispersive X-ray spectrometer (EDAX PHOENIX) (SEM-EDXA), based on the method described by Saka [12]. The accelerating voltage was set at 15 kV. Additional variable conditions such as the distance of the X-ray detector from the specimens, the tilting angle of the specimens holder (0°), take-off angle, and working distance were all held constant throughout the entire study.

3. RESULTS AND DISCUSSION

3.1. HFOETMOS-SiO₂ Wood-Inorganic Composites from TEOS or MTMOS

Table 1 shows the weight percent gain (WPG) and bulking coefficient (B) for various HFOETMOS-SiO₂ wood-inorganic composites prepared from TEOS. The WPGs of these composites were found to increase slightly

Table 1. Weight percent gain (WPG) and bulking coefficient (B) for various HFOETMOS-SiO₂ wood-inorganic composites from TEOS.

Composites	Molar ratio [HFOETMOS]/[TEOS]	WPG (%)	B (%)
SiO ₂	0 / 1	7.6	4.0
HFOETMOS-SiO ₂	0.001 / 1	7.9	4.3
	0.004 / 1	8.0	4.3
	0.01 / 1	8.1	4.2
	0.05 / 1	10.1	4.0

Fig. 1. Change of water absorption ratios for various HFOETMOS-SiO₂ composites from TEOS with different molar ratio of HFOETMOS to TEOS.

Fig. 2. Change of water absorption ratios for various HFOETMOS-SiO₂ composites from MTMOS with different molar ratio of HFOETMOS to MTMOS.

Table 2. Weight percent gain (*WPG*) and bulking coefficient (*B*) for various HFOETMOS-SiO₂ wood-inorganic composites from MTMOS.

Composites	Molar ratio [HFOETMOS]/[MTMOS]	WPG (%)	B (%)
SiO ₂	0 / 1	29.8	11.6
HFOETMOS-SiO ₂	0.001 / 1	27.5	10.8
	0.004 / 1	27.8	10.9
	0.01 / 1	27.8	10.9
	0.05 / 1	25.9	10.8

Table 3. Weight percent gain (*WPG*), bulking coefficient (*B*), amount of fluorine added-on (*F_{added-on}*) and contact angle of water for various HFOETMOS woods.

Composites	Molar ratio [HFOETMOS]/[MeOH]	WPG (%)	B (%)	<i>F_{added-on}</i> (%)	Contact angle (°)
HFOETMOS	0.0005 / 1	2.0	0.1	0.8	140
	0.001 / 1	2.6	0.0	1.5	142
	0.004 / 1	8.4	0.0	4.8	143
	0.01 / 1	22.8	0.0	12.8	142
	0.03 / 1	32.3	0.1	16.4	142

with increasing in the molar ratios of HFOETMOS to TEOS in a reaction medium. However, the bulking coefficient (*B*) was found to be almost constant. Presumably, the increase in the *WPG* would be due to an increase in the HFOETMOS incorporated. For these composites, water absorption ratio (*WAR*) was measured as shown in Fig. 1. Although untreated wood specimens and SiO₂ composites from TEOS were saturated with water after soaking for several days, HFOETMOS-SiO₂ composites absorbed water to a much lesser extent. Therefore, HFOETMOS-SiO₂ composites prepared from TEOS could attain high water-repellent property, especially for these with the molar ratios of HFOETMOS to TEOS being 0.004, 0.01 and 0.05.

Table 2 shows the *WPG* and *B* for various HFOETMOS-SiO₂ wood-inorganic composites prepared from MTMOS. Compared with the results in Table 1, the *WPG*s of these composites from MTMOS were found to be higher and constant to be above 25%. The *B* was also higher than that of the composites from TEOS (Table 1). This is because MTMOS has the higher hydrolysis and subsequent polycondensation rate than TEOS during sol-gel reaction, having resulted in the higher deposition of the SiO₂ gels. However, as shown in Fig. 2, the composites from MTMOS absorbed water as much as untreated wood specimens and the high water-repellent property could not be attained. This fact is different from the composites from TEOS in Fig. 1. To elucidate such a

Fig. 3. Scanning electron micrograph of the 0.5 μm thin section of HFOETMOS woods (upper) and obtained distributions of Si-Kα and F-Kα X-rays emitted along the line across the double cell walls (lower).

difference in the water-repellency between HFOETMOS-SiO₂ wood-inorganic composites prepared from TEOS and MTMOS, HFOETMOS woods and HFOETMOS-SiO₂ wood-inorganic composites from MTMOS with various *WPG*s were prepared and studied on their water-repellency.

3.2. HFOETMOS Woods and Their Water-Repellency

Table 3 shows the *WPG*, *B* and *F_{added-on}* of the prepared

Fig. 4. A relationship between molar ratio of HFOETMOS to methanol and water absorption ratio of the HFOETMOS wood after five days soaking.

Table 4. Weight percent gain (*WPG*), bulking coefficient (*B*), amount of fluorine added-on (*F_{added-on}*) and contact angle of water for various HFOETMOS-SiO₂ wood-inorganic composites.

Composites	Molar ratio [MTMOS]/[MeOH]*	WPG (%)	B (%)	<i>F_{added-on}</i> (%)	Contact angle (°)
HFOETMOS-SiO ₂	0.001 /1	10.5	1.6	5.4	146
	0.006 /1	11.2	2.3	5.0	145
	0.01 /1	11.6	2.8	4.9	146
	0.03 /1	17.6	4.4	4.6	144

* The molar ratio of HFOETMOS to MeOH is 0.004 for all composites prepared.

HFOETMOS woods in which the *WPG* and *F_{added-on}* were found to increase with the increase in the molar ratios of HFOETMOS to methanol in a reaction medium. However, the *B* was found to be constant to be nearly 0%. Since only substances present in the cell walls can contribute to the bulking of the specimens, HFOETMOS molecules would not be impregnated into the cell walls. To ensure this concept, the distribution of HFOETMOS-derived residues in the HFOETMOS woods was studied by SEM-EDXA analysis.

Figure 3 shows the obtained scanning electron micrograph of the 0.5 μm thin section of HFOETMOS wood over which the distributions of fluorine and silicon were studied by SEM-EDXA along the line across the double cell walls. It is apparent that, although Si-Kα X-rays emission is detected with little concentration across the double cell walls, F-Kα X-rays are not uniform but concentrated at a boundary between the cell wall and cell lumen. This high concentration of F-Kα X-rays at the boundary must be due to the deposition of HFOETMOS-derived residues. Perhaps long hydrophobic fluorinated alkyl chain of HFOETMOS would have prevented its molecules from being impregnated into rather hydrophilic cell walls, and during the sol-gel reaction, the hydrolyzed HFOETMOS must be dehydrated to bind covalently each other at the surface of the cell lumens, with long fluorinated hydrophobic alkyl chains exposed. This would have enhanced water-repellent property of HFOETMOS woods.

Fig. 5. Changes of water absorption ratio for various HFOETMOS-SiO₂ wood-inorganic composites with different molar ratios of MTMOS to methanol.

Fig. 6. A relationship between *WPG* and water absorption ratio for various HFOETMOS-SiO₂ wood-inorganic composites after their five days soaking.

For these HFOETMOS woods, the contact angle of water droplet and water absorption ratio (*WAR*) of the specimens were measured to evaluate their water-repellency. The obtained contact angles on the prepared HFOETMOS woods are shown in Table 3. The contact angle on the untreated specimens could not be measured because the water drops were penetrated into the specimens as soon as they were dropped. However, all of the HFOETMOS woods showed the high contact angles above 140°.

Figure 4 shows a relationship between the molar ratio of HFOETMOS to methanol and the *WAR* of the HFOETMOS woods after five days soaking. HFOETMOS woods resulted in much less *WAR*, compared with untreated specimens ([HFOETMOS]/[MeOH]=0), indicating that HFOETMOS woods could have attained the enhanced water-repellent property. Furthermore, although the *WAR* decreased up to the molar ratio of about 0.004, it became constant afterward. This indicates that the optimum of its molar ratio must exist near 0.004 for the property enhancement of water-repellency.

Fig. 7. Scanning electron micrograph of the $0.5\mu\text{m}$ thin section of HFOETMOS-SiO₂ wood-inorganic composites (upper) and obtained distributions of Si-K α and F-K α X-rays emitted along the line across the double cell walls (lower).

3.3. HFOETMOS-SiO₂ Wood-Inorganic Composites with Various WPGs and Their Water-Repellency

Table 4 shows the WPG , B and $F_{\text{added-on}}$ for the various HFOETMOS-SiO₂ wood-inorganic composites. The WPG of the obtained composites was found to increase with increasing in the molar ratio of MTMOS to methanol. The value of B was also found to increase with increasing in the molar ratio of MTMOS to methanol. However, these composites show almost the same $F_{\text{added-on}}$, because the molar ratio of HFOETMOS to methanol was 0.004 for all composites prepared. Therefore, SiO₂ gels formed within the cell walls would increase with increasing in the molar ratio of MTMOS to methanol.

For these composites, the contact angles measured (Table 4) were all to be above 140° , as in HFOETMOS woods. However, the changes of WAR in Fig. 5 are quite different among various HFOETMOS-SiO₂ composites. This result suggests that the degree of achieved water-repellency is different among these composites. Although not clear after 1 day soaking, it was obvious after 3 days soaking that the HFOETMOS-SiO₂ composites with molar ratio of 0.001:1 in MTMOS to methanol have the lowest WAR and thus highest water-repellent property compared with other composites.

To study this difference in water absorption ratios among various HFOETMOS-SiO₂ composites, the relationship between WAR after five days soaking and WPG was studied as in Fig. 6 for HFOETMOS-SiO₂ wood-inorganic composites. Consequently, the WAR was found to increase with increasing in the WPG of the HFOETMOS-SiO₂ composites. Although $F_{\text{added-on}}$ in the obtained HFOETMOS-SiO₂ composites is almost the same as that in Table 4, the composites with the higher WPG s show the lower water-repellent property.

For the HFOETMOS-SiO₂ wood-inorganic composites with the higher and lower WPG s, therefore, SEM-EDXA

Fig. 8. Schematic illustration of HFOETMOS-SiO₂ wood-inorganic composites with the lower and higher WPG s. (The size of HFOETMOS, MTMOS, SiO₂ sol, SiO₂ gel and cell wall do not necessarily demonstrate the real scale in the composites.)

analysis was made to study the distribution of SiO₂ gels and HFOETMOS-derived residues in the HFOETMOS-SiO₂ wood-inorganic composites. Figure 7 shows the scanning electron micrographs of HFOETMOS-SiO₂ wood-inorganic composites with the higher and lower WPG s and the obtained distributions of Si-K α and F-K α X-rays emitted along the line across the double cell walls. It is apparent that fluorine is concentrated at the boundary between the cell wall and cell lumen in both composites, as in HFOETMOS woods (Fig. 3). On the other hand, silicon in the composites with the lower WPG is almost

uniformly distributed within the cell walls with certain concentrations. Silicon in the composites with the higher *WPG* was found to be distributed in a similar manner but slightly higher in its concentration at the intercellular layers and the boundary between the cell walls and cell lumens. These distributions of silicon in both composites would correspond to the distribution of SiO₂ gels from MTMOS because the Si-K α from HFOETMOS-derived residue were detected with little concentration as shown in Fig. 3.

From these results, HFOETMOS-derived residues must be distributed at the boundary between the cell wall and the cell lumen, whereas MTMOS would be mostly impregnated into the cell walls and deposited within the cell walls as SiO₂ gels through the sol-gel reaction. This speculation can be well supported by the fact that the value of *B* of HFOETMOS-SiO₂ composites decreases with the decrease in the molar ratio of MTMOS to methanol, as shown in Table 4.

3.4. Mechanism of Water-Repellent Property in HFOETMOS-SiO₂ Wood-Inorganic Composites

Based on the results mentioned above, possible models of the HFOETMOS-SiO₂ composites with the lower and higher *WPGs* were schematically proposed in Fig. 8 to elucidate the mechanism of water-repellent property added to HFOETMOS-SiO₂ composites.

For the case of the lower *WPG* (Fig. 8(A)), HFOETMOS molecules would be impregnated into the cell lumens with reaction medium, but not into the cell walls due to its hydrophobic nature. During drying process, HFOETMOS molecules with high molecular weight (*M.W.*=568) would be deposited on the surface of the cell wall without being vaporized, whereas MTMOS molecules with low molecular weight (*M.W.*=136) could be readily vaporized. The surface of the cell walls would, thus, be covered with the long hydrophobic alkyl residue of the HFOETMOS, covalently bound with each other or with SiO₂ gels in the cell walls. Therefore, HFOETMOS-SiO₂ composites with the lower *WPGs* could attain the high water-repellent property.

For the case of the higher *WPG* (Fig. 8(B)), HFOETMOS molecules would be deposited on the surface of the cell wall in a similar manner. However, some of the SiO₂ sols tend to be formed in a reaction medium present in the cell lumens owing to the higher concentration of MTMOS. These sols with high molecular weight

as in HFOETMOS molecules could not be vaporized and would be deposited over the surface of the cell walls during drying process. Therefore, some of SiO₂ gels derived from these SiO₂ sols would be distributed at the boundary between cell walls and cell lumens. A slightly higher concentration of silicon at the boundary in Fig. 7(B) can support this concept, and these gels would prevent HFOETMOS-derived residues from being exposed uniformly over the surface of wood cells as proposed in Fig. 8(B). Therefore, the composites with the higher *WPG* could not have attained the high water-repellent property as in the composites with the lower *WPG*.

Consequently, for achieving the high water-repellency, it is important that HFOETMOS molecules distribute uniformly over the surface of cell walls and that the long hydrophobic alkyl chain of the HFOETMOS molecules cover the surface of cell walls. This suggests that the topochemical effect of HFOETMOS molecules exists for enhancement of properties in wood-inorganic composites.

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