Surface Modification of Wood by Alkoxysilane Sol–Gel Deposition to Create Anti-mold and Anti-fungal Characteristics

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Abstract

Hybrid inorganic/organic thin films deposited on wood substrates have been shown to lower the rate of moisture sorption of the wood. Deposition of such thin films can be accomplished by sol–gel deposition or by plasma-enhanced chemical vapor deposition. This paper describes *in situ* sol–gel deposition of hybrid inorganic/organic thin films on wood substrates using methyltrimethoxysilane (MTMOS) as precursor and trifluoroacetic acid as catalyst. MTMOS has desirable performance characteristics such as substrate penetration and water repellence.

The surface chemistry of wood specimens coated with these thin films was characterized by Fourier transform infrared (FTIR) spectroscopy and energy dispersive X-ray analysis (EDXA). Surface morphology was characterized by scanning electron microscopy (SEM).

The effect of sol–gel-deposited thin films on mold growth and fungal colonization on wood surfaces was investigated. These thin films were shown to inhibit growth of mixed mold spores and decay fungi, *Trametes versicolor* and *Gloeophyllum trabeum*, on wood surfaces. Moisture resistance properties of the sol–gel thin film deposit may be the single most important contributor to the anti-mold and anti-fungal properties of the sol–gel-treated wood surfaces.

Keywords

Sol–gel deposition, alkoxysilanes, wood surface modification, hybrid inorganic–organic thin films, anti-mold, anti-fungal

1. Introduction

Residential construction accounted for 57% of all wood products consumed in the United States in 2003 [1–5]. Growing concerns over sustainable construction mean

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that wood products will likely continue to dominate the proportion of non-wood products used in residential construction. Wood is the world's most sustainable resource. It is renewable and environmentally friendly. In a study on environmental performance of renewable building materials in the context of residential construction, Perez-Garcia *et al.* [6] found that above-grade wood wall subassemblies had superior environmental performance indexes compared with those of steel or concrete wall subassemblies. However, wood is susceptible to degradation caused by moisture, ultraviolet (UV) radiation from the sun, or wood-colonizing microorganisms, including wood-decay fungi and mold, which can severely limit the service life of wood products in residential construction. To prolong the service life of wood products in residential construction, the durability of wood to the degradative effects of moisture, UV radiation, or wood-colonizing microorganisms needs to be improved.

Various approaches have been developed over the centuries to improve the durability of wood for use under different environmental conditions. To protect wood from damage caused by moisture, wood has been treated with waxes, resins, paints, and coatings that help exclude moisture absorption by the wood. To protect wood from damage caused by wood-destroying fungi or wood-staining mold, wood has been impregnated with toxic chemicals that prevent wood decay or mold colonization. To protect wood from damage caused by weathering, wood surfaces have been covered with stains or paints that prevent UV radiation and moisture from penetrating the wood cell wall. Although these approaches have been successful in improving the durability of wood in service under different microenvironments encountered in a structure, their environmental sustainability has come under increasing scrutiny. Reports have emerged indicating that production, treatment, and waste management of wood-protection chemicals might have had a negative impact on the environment [7]. Consequently, intensive research is required to develop new environmentally sustainable technologies for improving the durability of wood for use in residential construction.

The durability of wood can be improved by surface modification without compromising its intrinsic mechanical properties, including tensile strength. Surface modification of wood can be accomplished by plasma-enhanced chemical vapor deposition (PECVD) methods. Denes *et al.* [8], Denes and Young [9] and Podgorski *et al.* [10] modified wood surfaces with polysiloxanes under cold plasma conditions to create water-repellent characteristics and to attenuate damage caused by weathering. Lukowsky and Hora [11] reported use of atmospheric plasma, corona treatment and fluorination on wood to improve the wet adhesion of waterborne acrylic dispersions. Rehn *et al.* [12] reported that plasma pretreatment of wood surfaces with a dielectric barrier gas discharge at atmospheric pressure under an average process gas temperature of 35°C increased the fracture strength of glued wood. Recently,

Bente *et al.* [13] reported plasma treatment of wood surfaces with a mixture of silane/nitrogen gases to create water-repellent characteristics using a dielectric barrier gas discharge at atmospheric pressure. The advantages of PECVD methods are that they are intense and efficient. Furthermore, they are dry processes and are confined only to the outermost layers of the wood surface. One disadvantage of PECVD methods is their requirement for expensive vacuum systems. However, dielectric barrier gas discharge at atmospheric pressure may change that situation if simple equipment is developed that can maintain a good homogeneous gas discharge for plasma treatment of wood.

Surface modification of wood can also be accomplished by sol–gel deposition methods. Brebner and Schneider [14] modified wood by sol–gel deposition of alkoxysilanes to decrease its hygroscopicity and improve its anti-swelling efficiency (ASE). Tanno *et al.* [15] reported sol–gel treatment of wood with a mixture of 3-trimethoxysilyl-propyl-carboxymethyl-decylmethyl ammonium hydroxide (TMSAH) inner salt and 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) to improve its antimicrobial resistance. Donath *et al.* [16] compared the properties of wood specimens impregnated with either monomeric or oligomeric silane solutions and found that cell wall bulking effect, ASE, moisture resistance, and durability against white-rot fungi were more significantly improved in wood specimens treated with monomeric silanes than in specimens treated with oligomeric silanes. In our laboratories, we have demonstrated that sol–gel deposition of thin barrier films using a mixture of multifunctional alkoxysilanes on wood can be tailored to improve not only its moisture resistance properties [17] but also its color stability under exposure to accelerated weathering conditions [18]. In a recent study, Donath *et al.* [19] observed that water uptake was considerably diminished in wood treated with sol–gel deposits of multifunctional water-borne silane systems containing both hydrophilic and hydrophobic groups. They concluded that such sol–gel deposits could be applied as a component in complex preservative formulations for wood. In such formulations, the silane, applied at low concentrations, could protect wood against water and prevent leaching of antimicrobial reagents. One major advantage of sol–gel deposition methods is that they allow low-temperature surface modification of wood using non-toxic metal alkoxides of silicon, aluminum, titanium, or zirconium.

This paper deals with *in situ* sol–gel deposition of hybrid inorganic/organic thin films on wood substrates with the objective of creating anti-mold and anti-fungal characteristics. Because such hybrid inorganic/organic thin films can have high barrier properties with respect to permeation rates of oxygen and water vapor [20], they could be useful as non-toxic anti-mold or anti-fungal treatments on wood.

2. Materials and Methods[1]

2.1. Materials

Wood specimens, approximately 24 mm long, 20 mm wide and 6 mm thick, were prepared from green southern yellow pine sapwood obtained from a sawmill in Mississippi. The specimens were stored in a freezer until required for experimentation. Methyltrimethoxysilane (MTMOS) was purchased from Fluka (Buchs, Switzerland). Isopropyl alcohol (IPA) was purchased from Acros Organics (Geel, Belgium). Trifluoroacetic acid (TFA) was purchased from GFS Chemicals (Powell, OH). Disposable Petri dishes (15 by 100 mm) were purchased from BD Biosciences (San Jose, CA). Three mold fungi were evaluated: *Aspergillus niger* 2.242, provided by the University of Virginia; *Penicillium chrysogenum* PH02, obtained from the Forest Products Laboratory, Madison, WI; and *Trichoderma viride* ATCC 20476, grown on 2% malt agar (Difco, Becton, Dickinson & Company, Sparks, MD) for 2 weeks. Spore suspensions of test fungi were prepared by washing the surface of each malt agar plate with 10–15 ml of sterile deionized water (DI) according to ASTM standard D 4445-91 [21]. In this test, a mixture of three mold spore suspensions was transferred to a spray bottle and diluted to 100 ml with DI water to yield 3×10^7 spores/ml. The spray bottle was adjusted to deliver 1 ml inoculum per spray. Decay fungi, *Gloeophyllum trabeum* and *Trametes versicolor* were obtained from the Forest Products Laboratory, Madison, Wisconsin, and were maintained on 2% malt agar.

2.2. Methods

2.2.1. Sol–Gel Treatment

Wood specimens were removed from the freezer and soaked in IPA for 96 h to displace air and adsorbed water from the lumens. At the end of this period, the specimens were allowed to dry to a constant weight in a controlled-humidity room at 30% relative humidity (RH) and 27°C. The specimens were divided into two groups of triplicates. One group was placed in a reaction vial and reacted with 12:1 molar ratio of MTMOS and TFA for 72 h with gentle agitation on an oscillating shaker. At the end of this period the treated specimens were allowed to air-dry for 1 h and then placed in an oven to dry at 65°C for 6 h and to condition at 105°C for 24 h. The other group of specimens that was not subjected to the sol treatment served as the non-treated control specimens. All specimens were allowed to equilibrate at 30% RH, 27°C to a constant weight.

[1] Certain commercial instruments and materials are identified in this article to adequately describe the experimental procedure. In no case does such identification imply endorsement by the U.S. Department of Agriculture of any product or service, nor does it imply that the instruments or materials are necessarily the best available for the purpose.

2.2.2. Specimen Surface Characterization

Surface morphology of specimens was characterized by scanning electron microscopy (SEM) on a LEO EVO40 scanning electron microscope.

Surface chemical composition was characterized by energy dispersive X-ray analysis (EDXA) and by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. EDXA was performed on a LEO EVO40 scanning electron microscope with attached Vantage EDXA Analyzer. For ATR-FTIR spectroscopy, a zinc selenide internal reflection element was used to sample the outermost 5-μm layers of the specimens.

2.2.3. Microorganism Growth Test

Sol–gel-treated and non-treated control specimens were placed on three layers of blotting paper saturated with 10 ml deionized water and supported on polyethylene mesh spacers in sterile disposable Petri dishes.

For the mold growth test, sol–gel-treated and non-treated control specimens were sprayed with 1 ml of the mixed mold spore inoculum sealed in polyethylene bags to prevent drying and incubated at 27^{o}C and 70% RH. Following incubation, specimens were evaluated for mold growth on weeks 1, 4, 8 and 12 and rated on a scale of 0–5, with 0 indicating no growth and 5 indicating heavy mold growth.

For the decay fungal growth test, specimens were inoculated with 5- by 5-mm malt-agar-grown *G. trabeum* or *T. versicolor*. Specimens were incubated and evaluated on weeks 1, 4, 8 and 12 as described above. A separate weight loss study by the soil block culture bottle test (American Wood Preservers' Association E-10-06) is still in progress.

2.2.4. Moisture Resistance Properties

Water vapor resistance properties of the wood specimens were determined by measuring the weight change of wood specimens after equilibration at 30% RH, followed by equilibration at 65% RH.

To determine liquid water resistance, wood specimens were immersed in DI water for a period of 7 days and the weight change resulting from water uptake was measured.

3. Results and Discussion

3.1. Sol–Gel Deposit

Sol–gel uptake on the wood specimens was 88.31 ± 13.89 mg/g. Figure 1 shows representative SEM images of the cell walls of non-treated control and sol–gel-treated wood specimens. Although somewhat difficult to discern, some differences in surface morphology were apparent between cell walls of the sol–gel-treated and non-treated control samples. Surfaces of the sol–gel-treated wood cell walls appeared to have a smoother texture than the non-treated control.

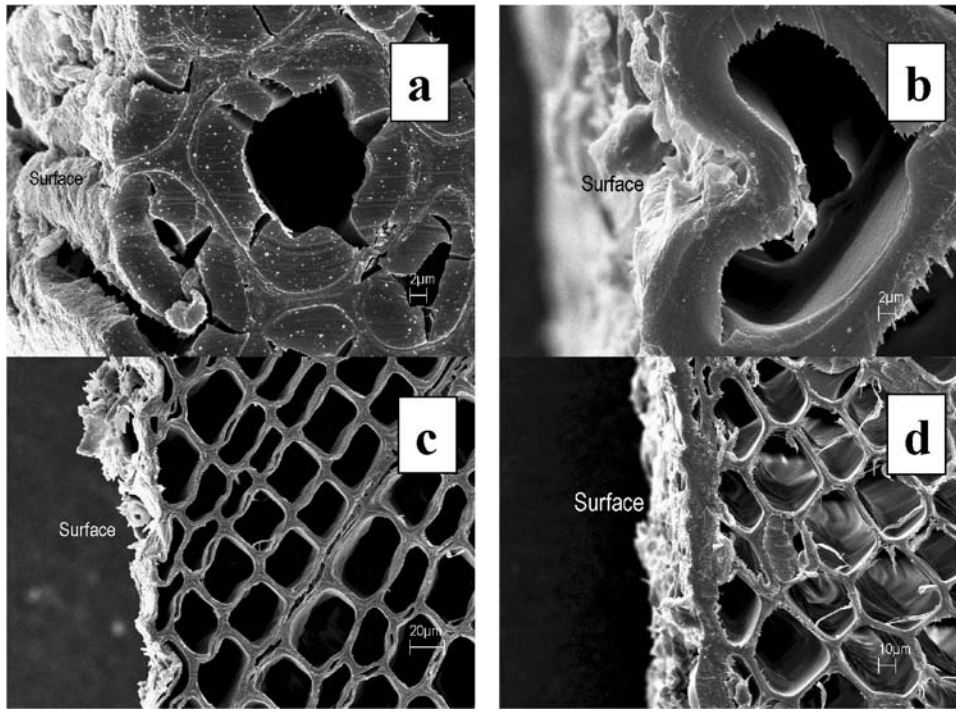

Figure 1. SEM images of cell wall of (a, c) non-treated control and (b, d) sol–gel-treated wood specimens.

3.2. Surface Chemistry of Wood Specimens

The elemental composition of the surface of wood specimens before and after sol–gel treatment is shown in the EDXA spectra (Fig. 2a and 2b, respectively). The strong peak at 1.737 keV in Fig. 2b confirmed the presence of silicon, the major inorganic constituent element of the sol–gel deposit on the wood specimens.

The functional group composition of the surface of the wood specimens before and after sol–gel treatment is shown in the infrared spectra (Fig. 3). The non-treated control wood specimens showed a broad peak around 3376 cm^{-1}, which is assigned to bonded OH stretch vibrations, and peaks at 1274 cm^{-1} and 1010 cm^{-1}, which are assigned to CO stretch vibrations in wood [22]. The peak at 778 cm^{-1} is assigned to skeletal deformation of aromatic rings in lignin [23]. In contrast, the sol–gel-treated wood showed a broad peak around 3354 cm^{-1} and a shoulder at 910 cm^{-1}, which represent Si–OH stretching vibrations. The peaks at 2926 cm^{-1} and 1267 cm^{-1} were attributed to Si–CH_3 asymmetric and symmetric bending vibrations respectively. The peak at 2868 cm^{-1} was attributed to Si–OCH_3 stretching vibrations. The peaks at 1035 cm^{-1} and 809 cm^{-1} were tentatively attributed to Si–O–Si and Si–O vibrations, respectively [24].

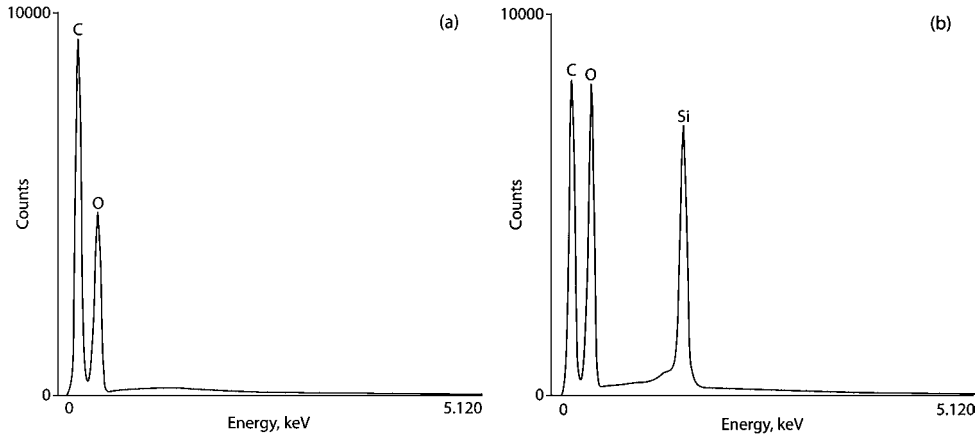

Figure 2. EDX spectra of (a) non-treated control and (b) sol–gel-treated wood specimens.

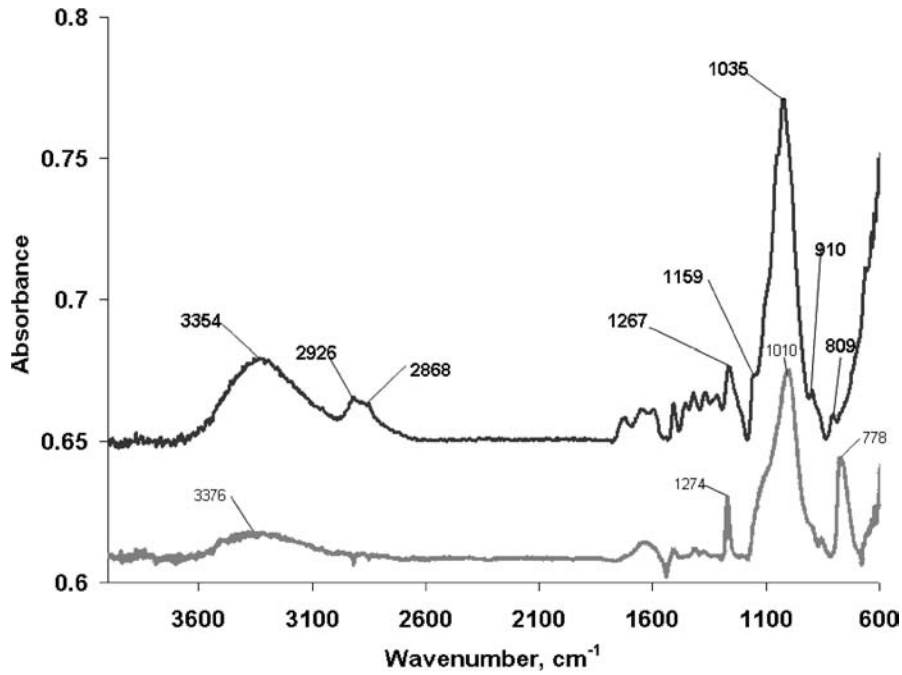

Figure 3. FTIR spectra of sol–gel-treated (MTMOS) (top trace) and non-treated control (bottom trace) wood specimens.

3.3. Mold Growth

No mold growth was observed on the sol–gel-treated specimens even after 12 weeks of incubation. By contrast, non-treated control specimens showed mold growth by week 1 of incubation, and by week 12, mold growth was characterized as fully

grown. Mixed mold growth ratings are summarized in Table 1, and the progression of mold growth during the course of 12 weeks is shown in Fig. 4.

3.4. Fungal Growth

As in the case of mold growth, no fungal growth was observed on the sol–gel-treated specimens even after 12 weeks of incubation. Note that fungal growth appeared to be slower than mold growth on the non-treated control specimens, and only about 60% growth was observed at week 1 of the incubation period. However, by week 12, fungal growth was also characterized as fully developed. Fungal growth ratings are summarized in Table 2. The progression of *G. trabeum* and *T. versicolor* growth during the course of 12 weeks is shown in Figs 5 and 6 respectively.

3.5. Moisture Resistance Properties

The average amounts of water vapor uptake of sol–gel-treated and non-treated control wood specimens, 37.26 ± 1.34 mg/g and 42.24 ± 0.52 mg/g, respectively, were significantly different at the 95% confidence level ($P = 0.05$).

The average amounts of liquid water uptake of sol–gel-treated and non-treated control wood specimens, 501 ± 27.0 mg/g and 1004 ± 123.0 mg/g, respectively, were also significantly different at the 95% confidence interval ($P = 0.05$).

Figure 7 shows liquid water uptake of the non-treated control and sol–gel-treated wood specimens during 7 days of immersion in DI water.

Thus, we conclude that sol–gel treatment improved the moisture resistance properties of the wood specimens. Improved moisture resistance can be attributed to the changed surface chemistry of the sol–gel-treated specimens. In addition to the appearance of an intense Si peak in the EDX spectrum of the sol–gel-treated wood specimens, the O/C peak intensity ratio of the treated specimens was much higher than that of the non-treated control specimen (Table 3). Increase in the O/C peak intensity ratio may be attributed to an increase in surface concentration of oxygenated groups or a decrease in surface concentration of carbon atoms. Because the infrared spectra of the treated specimens indicated presence of Si–CH_3 groups that were not detected in the non-treated control specimens, the increase in the O/C peak intensity ratio for the treated specimens can be reasonably attributed to an increase in surface concentration of oxygenated groups such as Si–O and Si–OCH_3. All three of these surface groups are capable of restricting moisture movement by hydrophobicity, in the case of Si–CH_3; or hydrogen-bonding, in the case of Si–O; or hydrolysis, in the case of Si–OCH_3.

4. Conclusion

Growth and proliferation of mold or fungi require certain essential physical and chemical conditions, including satisfactory temperature, adequate moisture, sufficient oxygen, proper pH, and essential nutrients [25]. Lack of any of these requirements may prevent mold or fungal growth on wood substrates. Wood moisture

Table 1.
Mold growth scores

Time (weeks)	Sol–gel-treated specimen	Non-treated control specimen[a]
1	0	4
4	0	5
8	0	5
12	0	5

[a] Mold and decay fungi growth rating scale: 0, no growth; 1, 20%; 2, 40%; 3, 60%; 4, 80%; 5, 100% coverage.

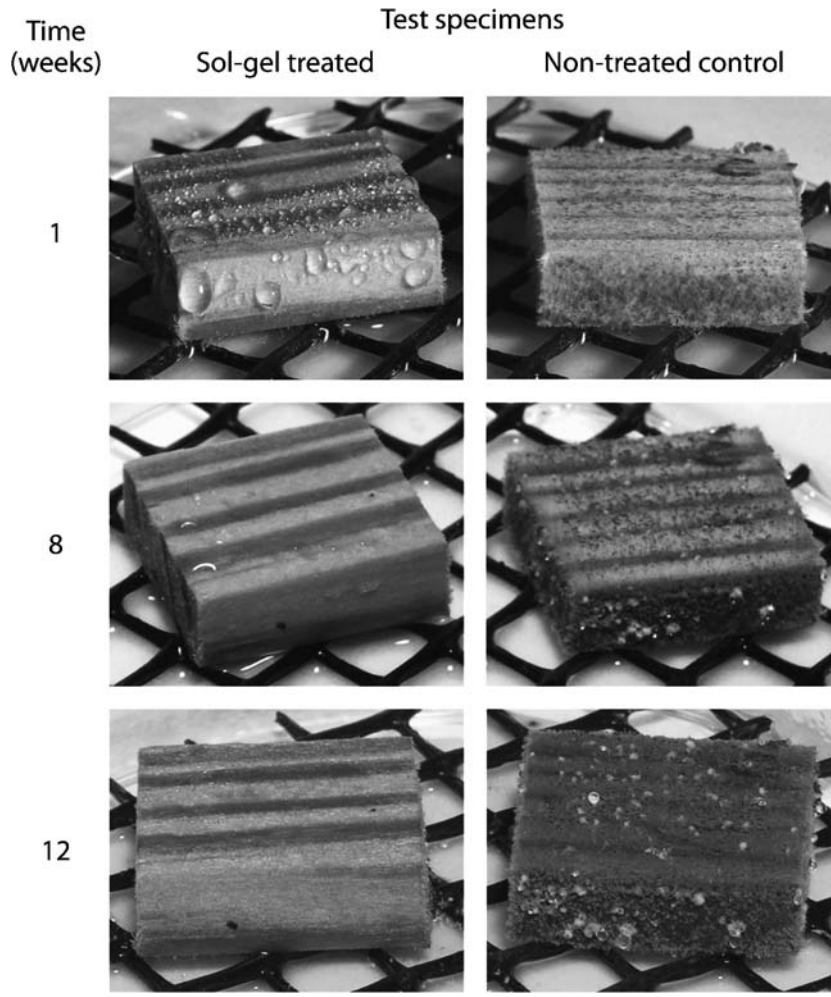

Figure 4. Progression of mixed mold growth during the course of 12 weeks.

Table 2.
Fungal growth scores

Time (weeks)	Sol–gel-treated specimen	Non-treated control specimen[a]	
		G. trabeum	*T. versicolor*
1	0	3	3
4	0	4	3
8	0	5	4
12	0	5	5

[a] Mold and decay fungi growth rating scale: 0, no growth; 1, 20%; 2, 40%; 3, 60%; 4, 80%; 5, 100% coverage.

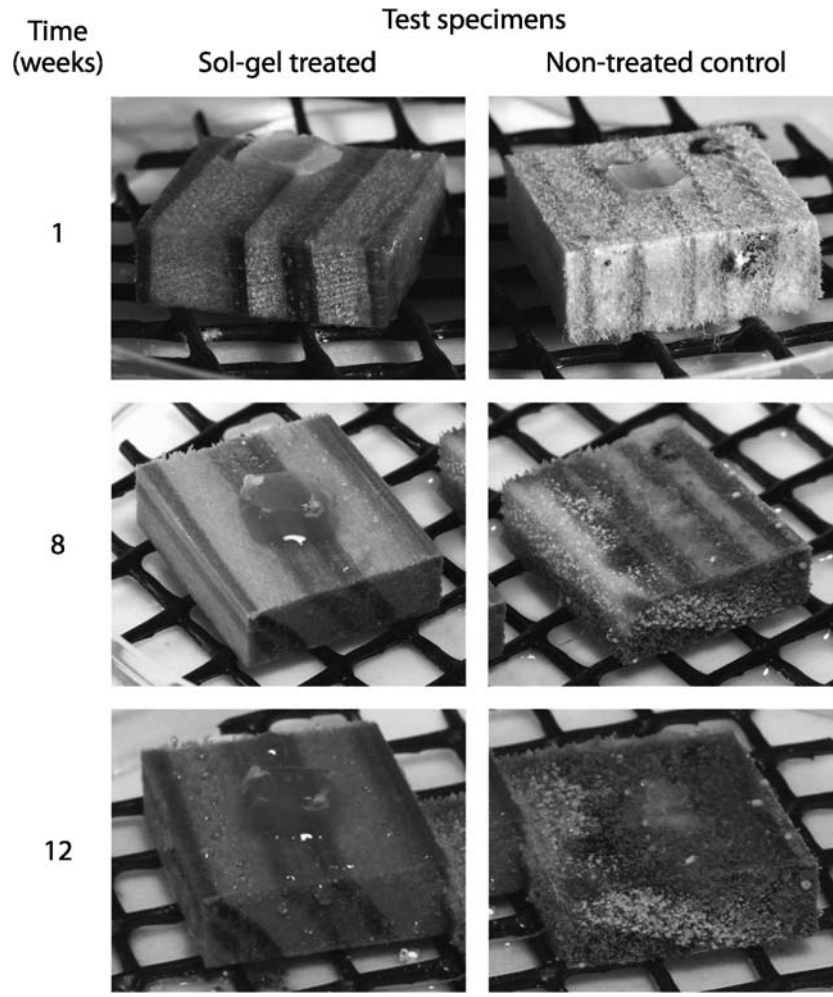

Figure 5. Progression of fungal (*G. trabeum*) growth during the course of 12 weeks.

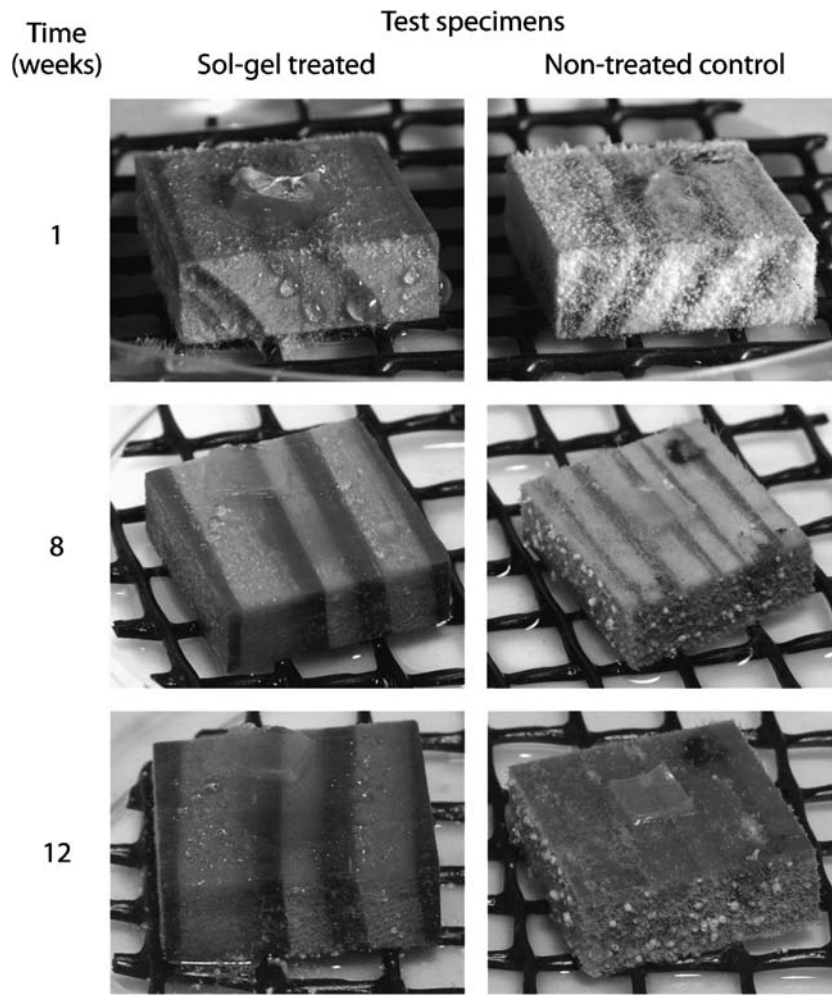

Figure 6. Progression of fungal (*T. versicolor*) growth during the course of 12 weeks.

content, which depends on air humidity, precipitation, and water uptake by means of ground contact or leakage, has been identified as the main critical factor for colonization of wood by decay fungi [26, 27]. Optimum wood moisture content for most fungal growth is generally accepted to be between 40% and 70% [27].

In our current study, sol–gel-treated specimens showed improved resistance to moisture absorption compared with non-treated controls, which most likely resulted in wood substrate moisture content that was well below the optimum for fungal or mold growth. Although the thin sol–gel deposit evidently restricted adequate supply of moisture to the wood substrate for the mold or fungus to grow, it may have also decreased the rate of oxygen diffusion into the wood substrate. This latter possibility remains a subject for future research.

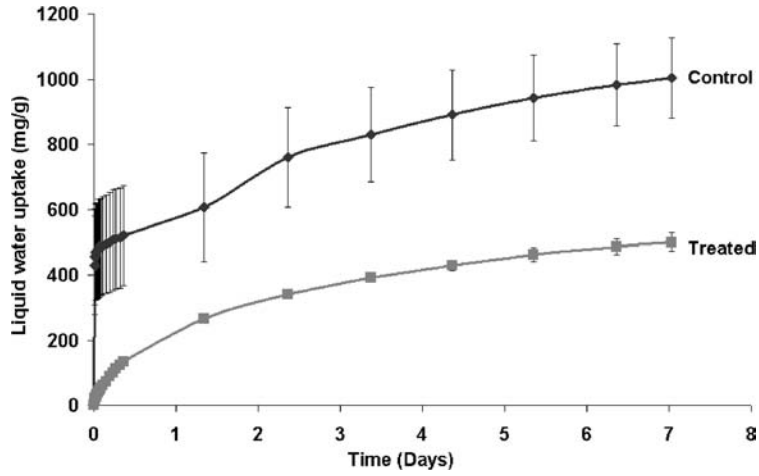

Figure 7. Liquid water uptake of non-treated control and sol–gel-treated wood specimens.

Table 3.
EDX peak intensity ratios of surface elements in non-treated control and treated wood specimens

Peak intensity ratio	Non-treated control	Sol–gel-treated
O/C	0.52	0.96
Si/O	0.01	1.01
Si/C	0.005	0.98

This study has demonstrated the possibility of using sol–gel treatment to prevent mold or fungal growth on wood substrates. The advantage of sol–gel treatment over conventional wood preservatives is the use of non-toxic, environmentally sustainable ingredients based on alkoxysilanes. One disadvantage of sol–gel deposition on wood substrates is the evolution of volatile organic by-products by the deposition reactions, which may result in unacceptable levels of volatile organic compounds (VOC) in the atmosphere.

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References

1. C. Adair, Regional production and market outlook for structural panels and engineered wood products, 2004–2009. APA Economics Report E170. APA–The Engineered Wood Association, Tacoma, WA (2004).

2. J. L. Howard, U.S. timber production, trade, consumption, and price statistics 1965 to 2002, Research Paper FPL-RP-615. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI (2003).
3. J. L. Howard, U.S. timber production, trade, consumption, and price statistics 1965 to 2005. Preliminary draft. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI (2006).
4. Wood Products Council, Wood products used in new residential construction in the U.S. and Canada — 2003. APA–The Engineered Wood Association, Tacoma, WA (2005).
5. Wood Products Council, Wood products used in residential repair & remodeling in the U.S. and Canada — 2003. APA–The Engineered Wood Association, Tacoma, WA (2005).
6. J. Perez-Garcia, B. Lippke, D. Briggs, J. B. Wilson, J. Bowyer and J. Meil, *Wood Fiber Sci.* **37**, 3–17 (2005).
7. E. Larnøy, S. Dantz, M. Eikens and H. Militz, *Wood Mater. Sci. Eng.* **1**, 59–68 (2006).
8. A. R. Denes, M. A. Tshabalala, R. Rowell, F. Denes and R. A. Young, *Holzforschung* **53**, 318–326 (1999).
9. A. R. Denes and R. A. Young, *Holzforschung* **53**, 632–640 (1999).
10. L. Podgorski, C. Bousta, F. Schambourg, J. Maguin and B. Chevet, *Pigment Resin Technol.* **31**, 33–40 (2001).
11. D. Lukowsky and G. Hora, *Macromolecular Symposia* **187**, 77–85 (2002).
12. P. Rehn, A. Wolkenhauer, M. Bente, S. Förster and W. Viöl, *Surface Coatings Technol.* **174–175**, 515–518 (2003).
13. M. Bente, G. Avramidis, S. Föster, E. G. Rohwer and W. Viöl, *Holz als Roh- und Werkstoff* **62**, 157–163 (2004).
14. K. I. Brebner and M. H. Schneider, *Wood Sci. Technol.* **19**, 75–81 (1985).
15. F. Tanno, S. Saka, A. Yamamoto and K. Takabe, *Holzforschung* **52**, 365–370 (1998).
16. S. Donath, H. Militz and C. Mai, *Wood Sci. Technol.* **38**, 555–566 (2004).
17. M. A. Tshabalala, P. Kingshott, M. R. Van Landingham and D. Plackett, *J. Appl. Polym. Sci.* **88**, 2828–2841 (2003).
18. M. A. Tshabalala and J. E. Gangstad, *J. Coatings Technol.* **75**(943), 37–43 (2003).
19. S. Donath, H. Militz and C. Mai, *Holzforschung* **60**, 40–46 (2006).
20. A. Amberg-Schwab and M. Hoffman, *J. Sol–Gel Sci. Technol.* **1**, 141–146 (1998).
21. ASTM D 4445-91, Standard test method for fungicides for controlling sapstain and mold on unseasoned lumber (laboratory method).
22. K. K. Pandey and K. S. Theagarajan, *Holz als Roh- und Werkstoff* **55**, 383–390 (1997).
23. U. P. Agarwal in: *Advances in Lignocellulosic Characterization*, D. S. Argyropoulos (Ed.). TAPPI Press, Atlanta, GA (1999).
24. H. El Rassy and A. C. Pierre, *J. Non-crystalline Solids* **351**, 1603–1610 (2005).
25. S. S. Block, *Appl. Environ. Microbiol.* **1**, 287–293 (1953).
26. A. M. Harju, M. Venäläinen, S. Anttonen, H. Viitanen, P. Kainulainen, P. Saranpää and E. Vapaavuori, *Trees* **17**, 263–268 (2003).
27. C. Brischke, R. Bayerbach and A. O. Rapp, *Wood Mater. Sci. Eng.* **1**, 91–107 (2006).