

Wood Surface Modification by In-situ Sol-gel Deposition of Hybrid Inorganic-Organic Thin Films

Mandla A. Tshabalala, USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53726-2398

ABSTRACT

Interest in the use of nanoparticles of iron, titanium, aluminum, and zinc oxides in transparent coatings for wood is increasing. Such nano-composite coatings have the potential of not only preserving the natural color of the wood but also stabilizing the wood surface against the combined degradative effects of sunlight and moisture. The nanoparticles can be used as additives to coating formulations or deposited directly as thin films on a substrate. Thin film deposition can be accomplished by plasma-enhanced chemical vapor or by sol-gel deposition. This paper describes sol-gel deposition of a hybrid inorganic-organic thin film on wood using a mixture of metal-organic precursors and its effect on weathering properties of the wood surface.

Keywords: Sol-gel, wood, surface, thin film, moisture, weathering

INTRODUCTION

Motivated by growing environmental concerns, growing demand for sustainable use of natural resources, and the changing nature of the wood resource and its use in residential and non-residential construction, researchers all over the world are investigating new technologies for enhancing durability and service life of wood-based construction materials. In our laboratories we are researching new methods of depositing thin barrier films on wood surfaces to enhance their moisture and ultraviolet (UV) radiation resistance properties, thus enhancing the durability and service life of wood and wood composites in outdoor applications.

Hybrid inorganic-organic thin films deposited on wood substrates have been shown to lower the rate of moisture sorption by wood [1, 2]. Deposition of such thin films can be accomplished by cold plasma chemical vapor deposition or by sol-gel deposition processes. Using hexamethyldisiloxane and zinc oxide as precursors, weather-resistant thin films were deposited on wood substrates by cold plasma chemical vapor deposition process [3, 4]. This paper describes sol-gel deposition of moisture- and UV-resistant thin films on wood substrates using methyltrimethoxysilane (MTMOS), hexadecyltrimethoxysilane (HDTMOS), and aluminum isopropoxide (AIP) as precursors.

The sol-gel process allows room-temperature deposition of hybrid inorganic-organic thin films on a wide range of substrates, including wood. Some of these thin films exhibit high barrier properties with respect to permeation rates of oxygen, water vapor, and volatile organic compounds [5]. Studies by other researchers have shown that sol-gel thin films deposited on wood, paper, or textiles enhanced water or fire-resistance properties or improved leaching stability of dyes bound to the thin films [6-7]. Our studies have shown that sol-gel

deposits can be tailored to enhance not only moisture and UV resistance but also color stability of wood surfaces [8].

EXPERIMENTAL

Materials and methods

Methyltrimethoxysilane (MTMOS), hexadecyltrimethoxysilane (HDTMOS), were purchased from Fluka (Buchs, Switzerland). Isopropanol (IPA) and aluminum isopropoxide (AIP) were purchased from Sigma-Aldrich (Milwaukee, Wisconsin). Trifluoroacetic acid (TFA) was purchased from GFS Chemicals (Powell, Ohio).

Wood specimens were prepared in the form of small thin wafers, 0.8 × 15.8 × 51.3 mm (tangential, radial, longitudinal), from air-dried loblolly pine (*Pinus taeda* L.) boards.

Preparation of aluminum oxide sol: AIP, IPA in the molar ratio, 1:40 respectively were added to a 500-mL three-neck round-bottom flask containing a magnetic stir bar and equipped with a water condenser and a thermometer. The mixture was heated for 15 min with vigorous stirring. TFA, in the molar ratio 1:3 relative to AIP, was added drop-wise to the mixture, and heating to the boiling point with vigorous stirring was continued until the mixture was clear. The clear AIP sol (AOS) was allowed to cool to room temperature with gentle stirring.

Preparation of sol mixture: AOS, MTMOS and HDTMOS were mixed by gentle stirring at room temperature in the volume ratio, 2:2:1 respectively. The sol mixture was stored in a capped brown bottle at room temperature until required for sol-gel deposition experiments.

Sol-gel deposition on wood specimens: Six replicates of the wood specimens were preconditioned at 65-68% RH, 27°C before placing in the sol mixture. Sol deposition was initiated by adding 2 mL TFA to the reaction vessel. The specimens were left in the closed reaction vessel at room temperature for 24 h. At the end of this period the specimens were removed from the reaction vessel and placed in an oven to dry at 70°C for 6 h. To cure the sol-gel deposit, the specimens were conditioned for 8 h in an oven at 105°C.

Water vapor sorption: Specimens were transferred to the 30% RH room where their weights were recorded at convenient intervals over a period of approximately 30 h. Thereafter they were transferred to the 65% RH room, where their weights were recorded at convenient intervals over a period of 1680 h.

Liquid water sorption: Specimens were placed in 500 mL deionized water in a covered trough in the 65% RH room, and their weights were recorded at 30-min intervals over a period of 2.5 h.

UV radiation exposure: Specimens were exposed to a filtered xenon arc lamp in a WeatherOmeter® and their weights were recorded at intervals of 240 h over a period of 1200 h. A radiometer was used to measure the irradiance in the 300- to 400-nm wavelength range. The radiation dosage was estimated by multiplying the measured irradiance with exposure time in hours.

Specimen surface characterization: Surface morphology of specimens was characterized by scanning electron microscopy (SEM) on a Jeol JSM-840 scanning electron microscope, and by laser scanning confocal microscopy (LSCM) on a Zeiss LSM510 reflection laser scanning confocal microscope. Surface chemistry was analyzed by energy dispersive X-ray analysis (EDXA) on a Tracor Noran TN-5500 energy dispersive X-ray analyzer.

Leaching characteristics of sol-gel deposit: At the end of the liquid water sorption experiment, the specimens were left in deionized water for an additional 830 h. At the end of this period the water was analyzed by inductively coupled plasma (ICP) for presence of aluminum and silicon, the major inorganic constituent elements of the sol-gel deposit.

RESULTS AND DISCUSSION

Sol-gel deposit

Sol-gel uptake on the wood specimens was 400.0 ± 60.9 mg/g. As shown in Figure 1(b), the sol-gel deposit appears as a thin film with sickle-shaped microstructures on the surface of the wood specimen. Representative EDXA spectra of the surface of the wood specimens before and after sol-gel deposition are shown in Figure 2. The strong peaks at 1.484 keV and 1.739 keV in Figure 2(b) confirmed the presence of aluminum and silicon, the major inorganic constituent elements of the sol-gel deposit on the wood specimens.

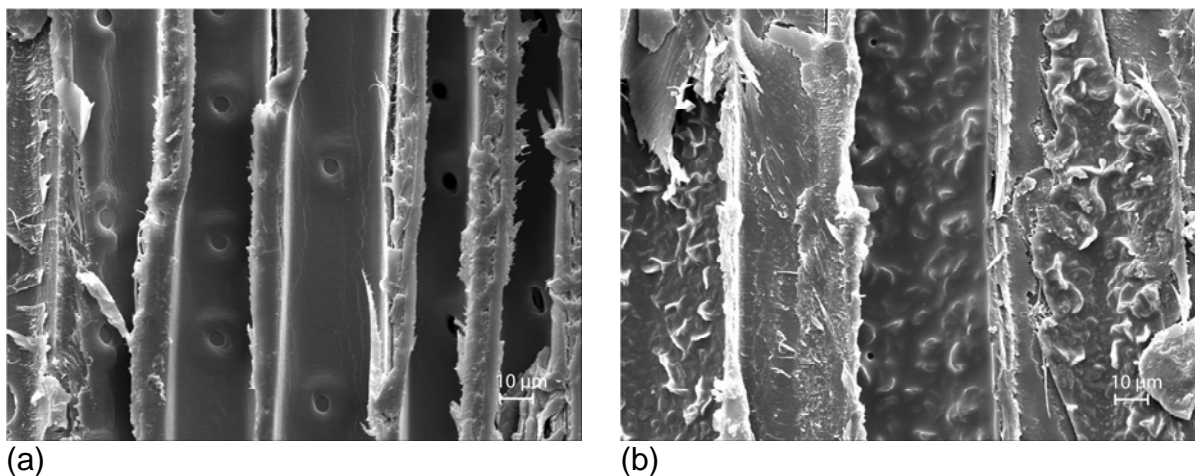


Figure 1 SEM micrographs of radial surface of (a) control and (b) treated wood specimens

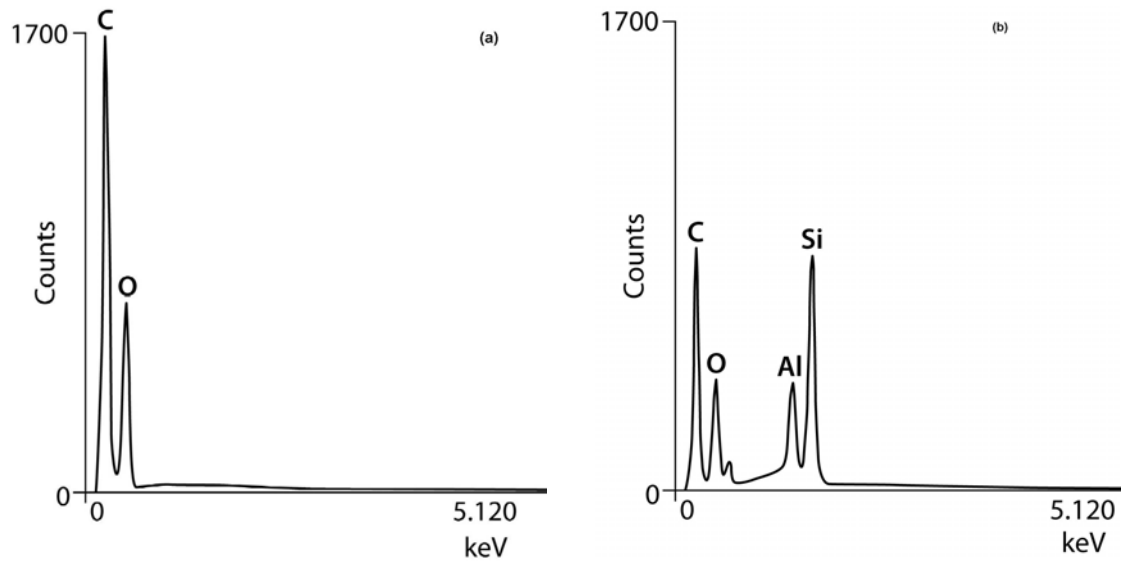


Figure 2 EDXA spectra of radial surface of (a) control and (b) treated wood specimens.

Moisture sorption

Water vapor and liquid water sorption behaviors of wood specimens before and after sol-gel deposition is shown in Figures 3 and 4 respectively. The sol-gel deposit decreased the amounts of both water vapor and liquid water uptake by approximately 60% and 80% respectively.

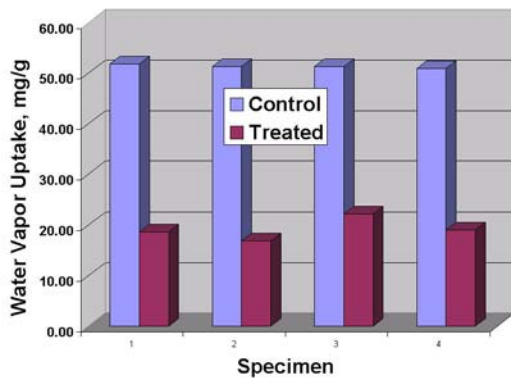


Figure 3 Water vapor uptake of control and sol-gel treated wood specimens

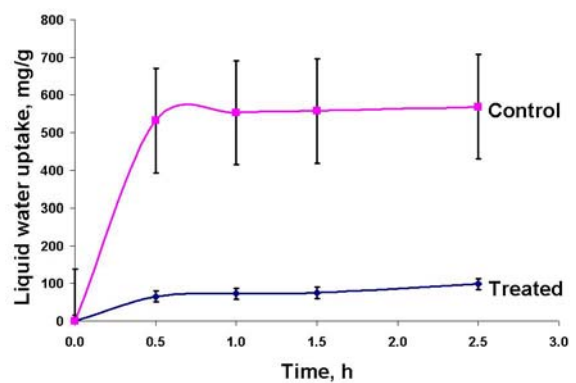


Figure 4 Liquid water uptake of control and sol-gel treated wood specimens





Leaching characteristics

Only trace amounts of aluminum, 0.814 mg/g, and silicon, 0.213 mg/g were detected in the leachate. These losses sustained over a period of 800 h suggest that the major constituents of the sol-gel deposit were quite resistant to water leaching.

Effect of ultraviolet radiation

As shown in Table 1 the surface color of the treated wood specimens remained stable even after a radiation dosage of 220 MJ/m², whereas that of the control specimens changed from light yellow to brown. Figure 5 shows weight loss of the specimens as a function of radiation dosage. Weight loss of treated specimens was less than that of control specimens by approximately 15%, and may be the result of liberation of volatile products of photodegradation of the wood substrate, such as methanol, carbon monoxide, carbon dioxide and hydrogen [9].

Table 1 Color stability of wood surfaces exposed to UV radiation

Dosage, MJ/m ²	Treated	Control
0		
220		

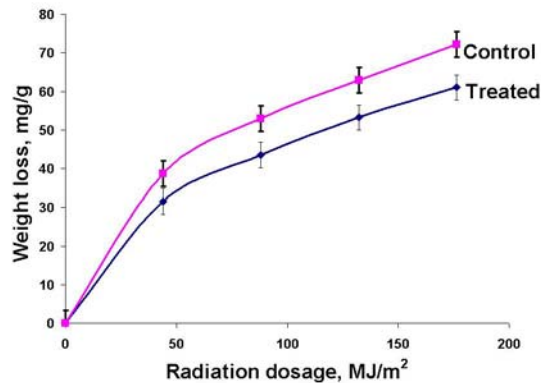


Figure 5 Weight loss of specimens after exposure to UV radiation in a WeatherOmeter

CONCLUSION

Sol-gel deposition of hybrid inorganic-organic thin film on wood substrate using AIP, MTMOS and HDTMOS as precursors decreased the tendency of the wood substrate to absorb moisture. Although the sol-gel deposit improved resistance of the wood substrate to color change, it did not completely impede the photodegradation process.

REFERENCES

1. Tshabalala, Mandla A., Kingshott, Peter, VanLandingham, Mark R., Plackett, David, Surface Chemistry and Moisture Sorption Properties of Wood Coated with Multifunctional Alkoxysilanes by Sol-Gel Process. *J. Appl. Polym. Sci.*, Vol. 88, 2828-2841 (2003).
2. Tshabalala, Mandla A. and Gangstad, John E., Accelerated Weathering of Wood Surfaces Coated With Multifunctional Alkoxysilanes By Sol-Gel Deposition. *J. Coat. Technol.*, Vol. 75(943); 37-43 (2003).
3. Denes, Agnes R., Tshabalala, Mandla A., Rowell, Roger, Denes, Ferencz and Young, Raymond A., Hexamethyldisiloxane-Plasma Coating of Wood Surfaces for Creating Water Repellent Characteristics. *Holzforschung*, Vol. 53(3); 318-326 (1999).
4. Denes, Agnes R. and Young, Raymond A., Reduction of Weathering Degradation of Wood through Plasma-Polymer Coating. *Holzforschung*, Vol. 53(6); 632-640 (1999).
5. Amberg-Schwab, A. and Hoffman, M., Inorganic-Organic Polymers with Barrier Properties for Water Vapor, Oxygen and Flavors. *J. Sol-Gel Sci. Technol.*, Vol. 1(2); 141-146 (1998).
6. Saka, S. And Ueno, T., Several SiO₂ Wood-Inorganic Composites and Their Fire-Resisting Properties. *Wood Sci. Technol.* 31; 457-466 (1997)
7. Trepte, J. and Böttcher, H., Improvement in the Leaching Behavior of Dye-Doped Modified Silica Layers Coated onto Paper or Textiles. *J. Sol-Gel Sci. Technol.*, 19; 691-694 (2000)
8. Mandla A. Tshabalala, Sol-Gel Deposition of Inorganic Alkoxides on Wood Surfaces to Enhance Their Durability Under Exposure to Sunlight and Moisture, Chapter 27 in "Service Life Prediction Challenging the Status Quo", Edited by Jonathan W. Martin, Rose A. Ryntz, Ray A. Dickie, Federation of Societies for Coatings Technology, Blue Bell, PA. pp 385-391 (2005)
9. Kalnins, M.A., Photochemical Degradation of Wood in Surface Characteristics of Wood as they Affect Durability of Finishes, U.S. Forest Service Research Paper, FPL 57; 23-60 (1966)

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Author: Dr Mandla A Tshabalala

Presented by: Dr Mandla A Tshabalala
Research Chemist

Company: USDA Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison
Wisconsin 53726-2398
USA

Tel: +1 608 231 9505

Fax: +1 608 231 9262

e-mail: mtshabalala@fs.fed.us

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