

Wood surface modification by in-situ sol-gel deposition of hybrid inorganic–organic thin films

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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 nonresidential construction, researchers all over the world are investigating new

technologies for enhancing durability and service life of wood-based construction materials. At the USDA Forest Service Forest Products Laboratory (FPL) we are studying 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

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Experimental

Certain instruments or materials are identified in this paper in order to adequately specify experimental

details. In no case does it imply endorsement by USDA or NIST or imply that it is necessarily the best product for the experimental procedure.

Materials and methods

Methyltrimethoxysilane (MTMOS) and 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 mm × 15.8 mm × 51.3 mm (tangential, radial, and longitudinal), from air-dried loblolly pine (*Pinus taeda* L.) boards.

Preparation of aluminum oxide sol

AIP and 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 at the boiling point of IPA (82°C) 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 at 82°C 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 in a Weather-Ometer[®] to a filtered Xenon arc lamp equipped with inner and outer borosilicate glass filters, 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 300–400 nm wavelength range. 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 LEO EVO40 scanning electron microscope and by laser scanning confocal microscopy (LSCM) on a Zeiss LSM510 reflection laser scanning confocal microscope. For SEM characterization, the specimens were cut with a razor blade and mounted on aluminum specimen mounts using silver paste. For LSCM characterization, the specimens were analyzed without additional preparation, and surface roughness measurements were obtained from more than five locations on the specimen surface.

Surface chemical composition of the specimens was characterized by energy dispersive X-ray analysis (EDXA) and by Fourier transform infrared spectroscopy (FTIR). For EDXA specimens were mounted on carbon specimen mounts using double stick carbon tape, and EDXA performed on the LEO EVO40 scanning electron microscope with attached Vantage EDXA Analyzer. For FTIR analysis, small portions of treated and control wood specimens were ground with potassium bromide powder and pressed into transparent disks. Infrared spectra were obtained by transmission at 4 cm⁻¹ resolution.

Leaching characteristics of sol-gel deposit

At the end of the liquid water sorption experiment, specimens were left in deionized water for an additional 830 h. At the end of this period, the volume of water was determined before it was analyzed by

inductively coupled plasma (ICP) for the 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. Figure 1 shows SEM micrographs of the radial surfaces of control and treated wood specimens. The sol-gel deposit appears as a thin xerogel film with sickle-shaped microstructures on the surface of the wood specimen (see Fig. 1b). Figure 2 shows LSCM images of the surfaces of control and treated wood specimens presented in three-dimensional profiles along with the corresponding root-mean-square

(rms) roughness values of the surfaces. It should be noted that the rms roughness values of control earlywood and latewood surfaces were quite different at (14.90 ± 0.71) and (10.46 ± 0.50) μm , respectively. By contrast, the rms roughness values of treated earlywood and latewood surfaces were practically the same at (17.22 ± 0.67) and (16.58 ± 0.72) μm , respectively. Thus the thin xerogel film deposit had the effect of minimizing the difference in morphology between earlywood and latewood surfaces by increasing the rms roughness value of the latewood surface to a greater extent compared to the earlywood surface.

Surface chemistry of wood specimens

The elemental composition of the surface of the wood specimens before and after sol-gel treatment is shown

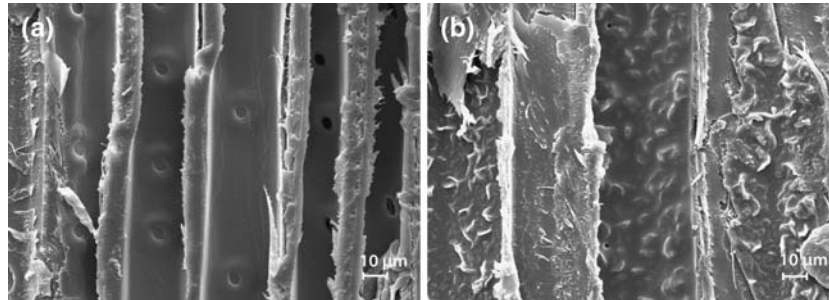


Fig. 1: SEM micrographs of radial surface of (a) control and (b) sol-gel treated wood specimens

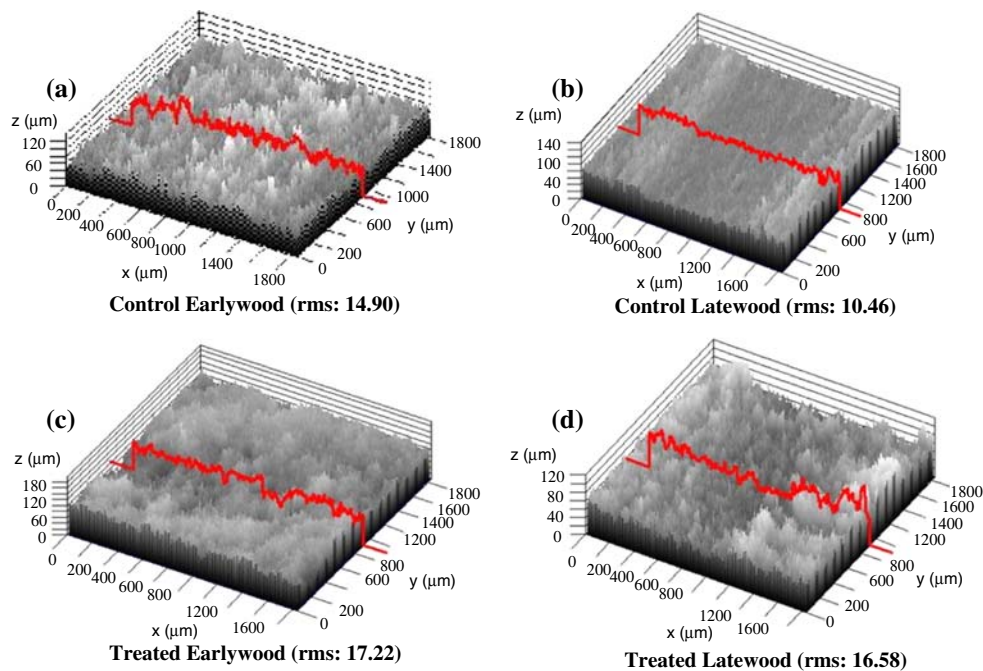


Fig. 2: LSCM micrographs of control earlywood (a) and latewood (b), and sol-gel treated earlywood (c) and latewood (d) surfaces of wood specimens

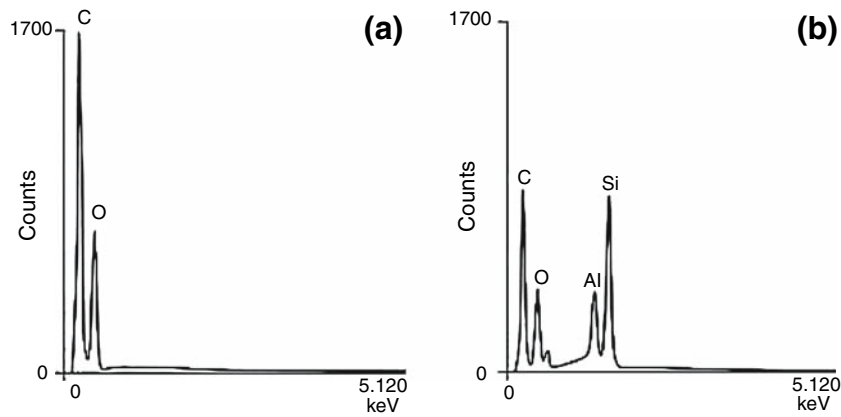


Fig. 3: EDXA spectra of radial surface of (a) control and (b) sol-gel treated wood specimens

in the EDXA spectra presented in Figs. 3a and 3b, respectively. The strong peaks at 1.484 and 1.739 keV in Fig. 3b confirmed the presence of aluminum and silicon, the major inorganic constituent elements 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 presented in Fig. 4. The sol-gel treated wood showed a band at 3432 cm^{-1} , which was attributed to O–H stretch of hydrogen bonded hydroxyl groups or adsorbed water.^{9,10} The peaks at 2926, 2855, and 1672 cm^{-1} were attributed to CH_3 asymmetric, CH_2 symmetric stretch and O–H bending mode of adsorbed water, respectively.^{11,12} The peaks at 1468, 1272, and 1219 cm^{-1} were attributed to C–H deformation and Si– CH_3 stretch, respectively.^{13,14} The peaks at 1134, 1036, 778, 588, and 488 cm^{-1} were tentatively attributed to Si–O–Si, Si–O–Al, Si–O–C, Al–O–C, and Si–O–C vibrations, respectively.

Thus EDXA and infrared spectra of the wood specimens after sol-gel treatment support the hypoth-

esis that the surface was covered with a thin metaloxane xerogel whose chemical composition consisted of aluminum–silicon oxides ($\text{Al}_2\text{O}_3\text{--SiO}_2$) attached to hydrocarbon chains.

Moisture sorption

Water vapor and liquid water sorption behaviors of wood specimens before and after sol-gel treatment are shown in Figs. 5 and 6, respectively. The thin xerogel film deposit decreased the amounts of both water vapor and liquid water uptake by approximately 60% and 80%, respectively. The improved resistance to moisture sorption by the sol-gel treated wood specimens correlates well with their surface chemical composition, which according to the EDXA and infrared spectra consists of hydrophobic hydrocarbon chains attached to aluminum oxide–silicon oxide networks. The observed differences in water vapor uptake between the treated specimens, 1–4 in Fig. 5 may be

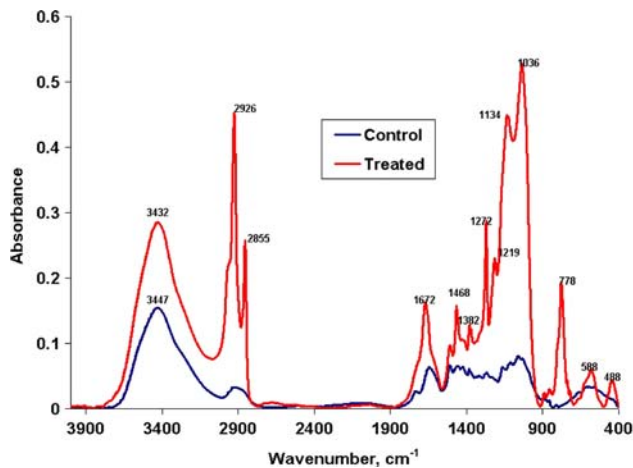


Fig. 4: FTIR spectra of control (bottom trace) and sol-gel treated (top trace) wood particles

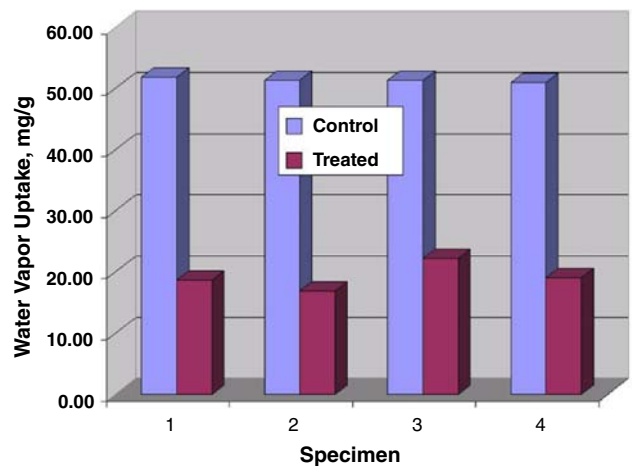


Fig. 5: Water vapor uptake of control and sol-gel treated wood specimens at 65% relative humidity, 27°C

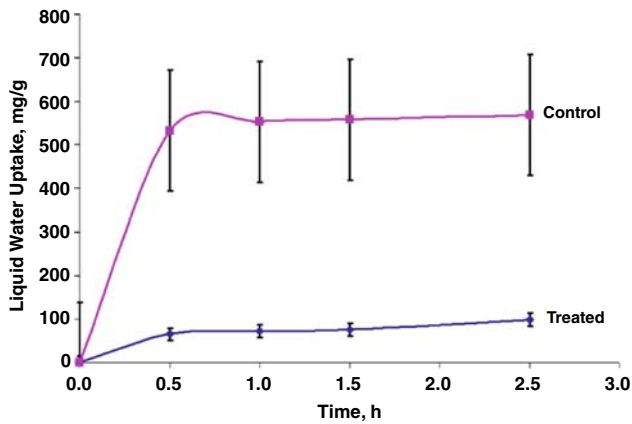


Fig. 6: Liquid water uptake of control and sol-gel treated wood specimens

attributable to surface morphological differences between specimens prepared from different boards or from different areas of the same board. Such morphological differences in the substrate could conceivably result in differences in the nanostructure of the thin xerogel film deposit, which does not appear to be uniform, according to the LSCM micrographs.

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 constituted less

than 0.25% of the mass of the sol-gel deposit. This indicates that the thin xerogel film deposit on the wood specimens was quite resistant to water leaching.

Effect of ultraviolet radiation

There was a noticeable difference in the surface morphology of the treated and control specimens after exposure to a nominal radiant dosage of 220 MJ/m², as shown in the LSCM and SEM micrographs in Figs. 7 and 8, respectively. The LSCM micrographs indicate that the rms surface roughness values of the treated specimens showed a significant decrease, from 17.22 to 11.76 μm, while that of the control specimens remained practically the same, or increased very slightly (14.90–15.74 μm) within limits of experimental error. The slight increase in the rms surface roughness values for the control specimens and the significant decrease in the rms roughness values for the treated specimens are consistent with their respective SEM micrographs which show that the surface of the control specimens suffered severe erosion after a nominal radiant dosage of 220 MJ/m², as evidenced by the complete degradation of tori, delamination of the warty membrane and appearance of additional micro-fissures in the middle lamellae. By contrast, the SEM micrographs of the treated specimens show that the thin xerogel film deposit remained intact, and actually became smoother. In addition there was little or no evidence of degradation of tori or the warty membrane in the underlying wood cell wall.

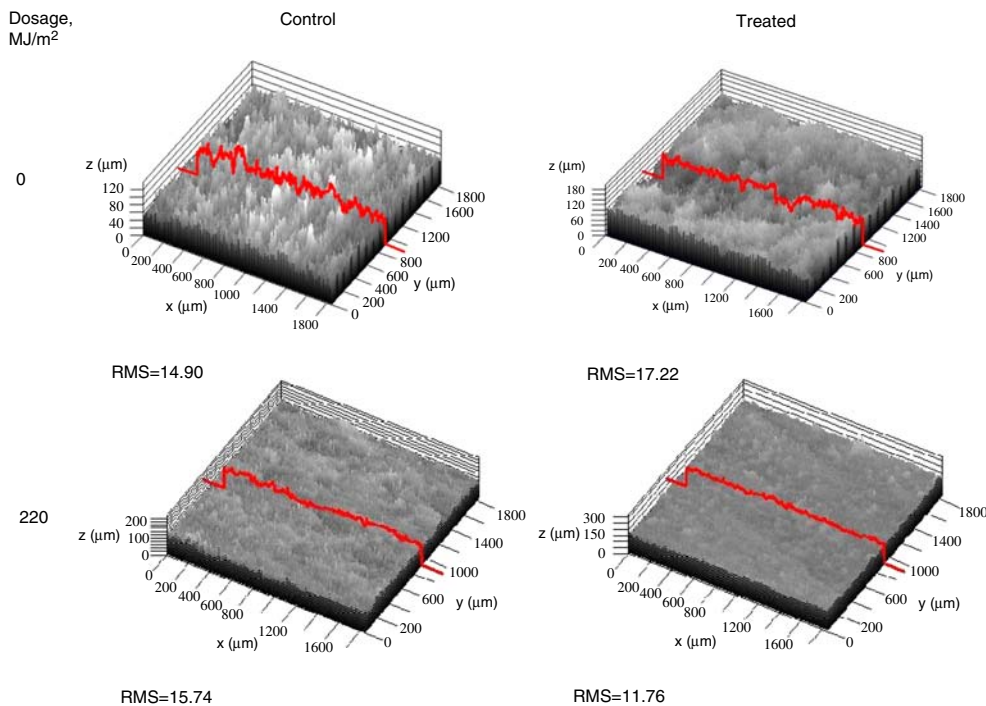


Fig. 7: LSCM micrographs of control and treated wood specimens before and after exposure to a nominal radiant dosage of 0 and 220 MJ/m²

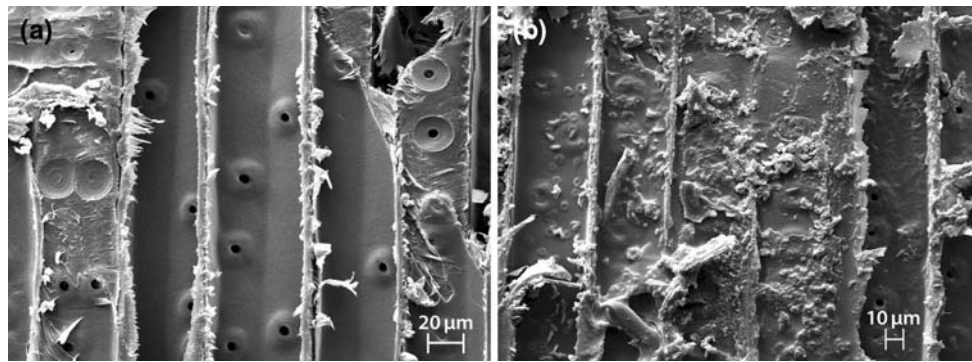


Fig. 8: SEM micrographs of radial surface of (a) control and (b) sol-gel treated wood specimens after exposure to a nominal radiant dosage of 220 MJ/m²

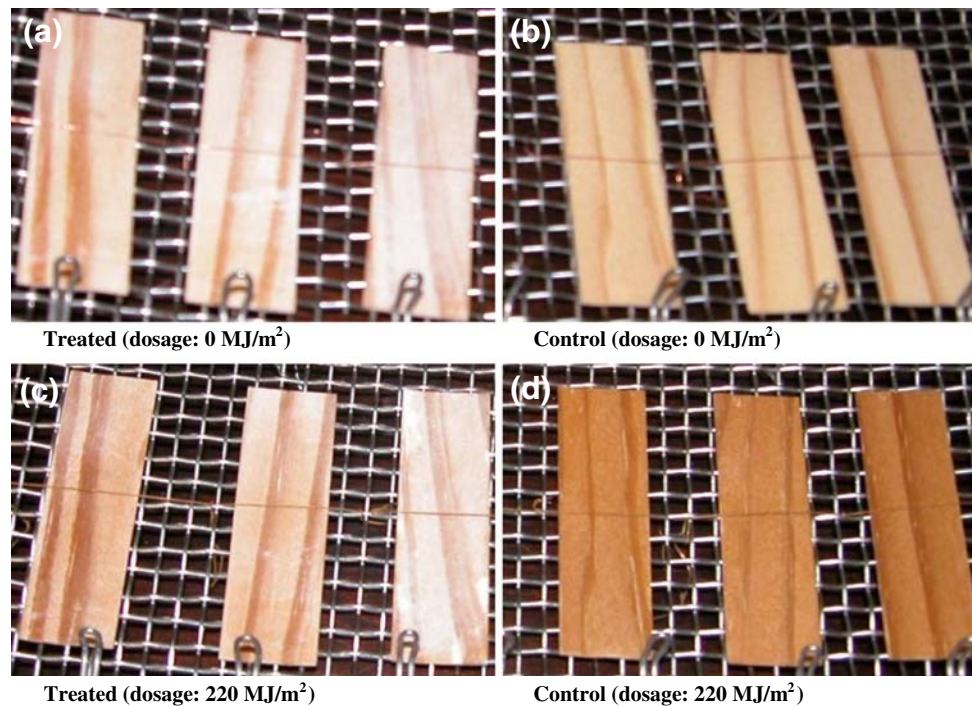


Fig. 9: Color stability of sol-gel treated [(a) and (c)], and control [(b) and (d)] wood surfaces before and after exposure to UV radiation

There was also a noticeable difference in the surface color of the treated and control specimens after exposure to a nominal radiant dosage of 220 MJ/m², as shown in Fig. 9. The surface color of the treated wood specimens remained stable while that of the control specimens changed from light yellow to brown. Apparently the thin xerogel film deposit on the surface of the treated specimens preserved the original surface color by preventing UV radiation from reaching the wood substrate.

It is also important to note that the thin xerogel film deposit was strongly bound within the wood cell wall as confirmed by the presence of strong Al and Si peaks in the EDXA spectra of treated specimens even after

water leaching and exposure to a nominal radiant dosage of 220 MJ/m² (see Fig. 10). However, as shown in Fig. 11 both the treated and control specimens showed some weight loss as a function of nominal radiant dosage. The observed differences in weight loss between the treated and control specimens suggest that the origins of the weight loss were also different. For the control specimens, the observed weight loss appears to be consistent with liberation of volatile products of photodegradation of lignin in the wood substrate. These products may include carbon dioxide, carbon monoxide, hydrogen, methanol, formaldehyde, and moisture.¹⁵ For the sol-gel treated wood, loss of such volatile products was somewhat retarded due its

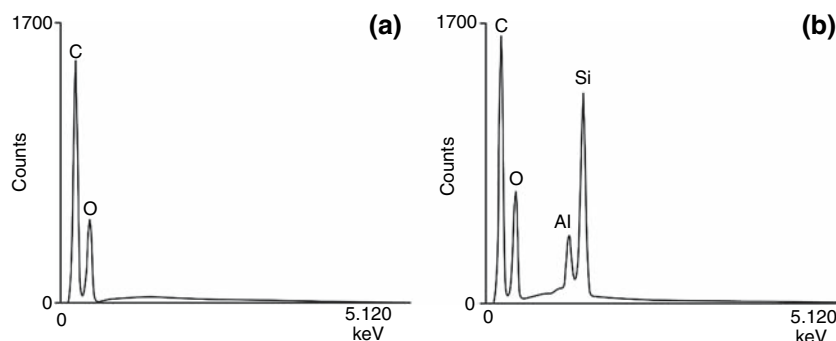


Fig. 10: EDXA spectra of radial surface of (a) control and (b) sol-gel treated wood specimens after exposure to a nominal radiant dosage of 220 MJ/m²

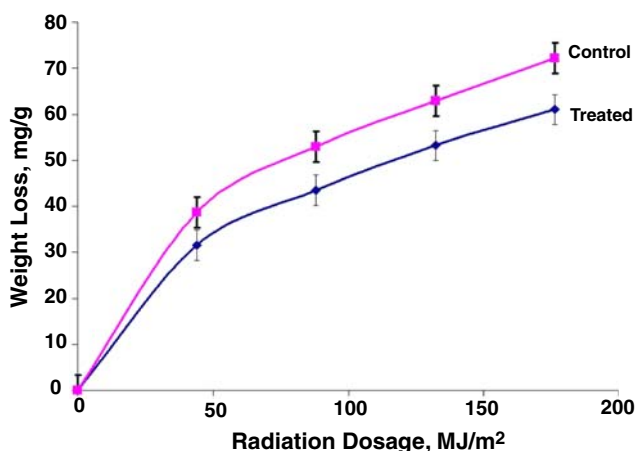


Fig. 11: Weight changes of control and sol-gel treated wood specimens after exposure to UV radiation in a Weather-Ometer

changed surface chemistry and morphology. It is also very likely that weight loss of the treated specimens resulted from evaporation of the by-products of the sol-gel deposition process, isopropanol, trifluoroacetic acid esters, and water. It is interesting to note that the EDXA peak intensity ratios (see Table 1) of surface elements on treated and control specimens changed in different ways after exposure to UV radiation. The O/C peak intensity ratio for the control specimens

decreased from 0.41 to 0.32, while that for the treated specimens remained practically constant or increased very slightly (0.37–0.40) within limits of experimental error.

The observed decrease in the O/C peak intensity ratio may be attributed to either a decrease in surface concentration of oxygen atoms or an increase in surface concentration of carbon atoms. Since photodegradation of lignin in the wood substrate is accompanied by liberation of oxygenated compounds such as carbon dioxide, carbon monoxide, methanol, formaldehyde, and moisture, which in aggregate contain more oxygen atoms than carbon atoms, it is likely that the decrease in the O/C peak intensity ratio for the control specimens is attributable to a decrease in the surface concentration of oxygen atoms. By contrast, the treated specimens showed a very slight change in the O/C peak intensity ratio because the surface was covered with the thin xerogel film, which because of the high oxygen content in its Al₂O₃–SiO₂ composition; either masked any oxygen losses arising from lignin photodegradation, or because of its optical properties protected the lignin from photodegradation. This supports our hypothesis that the photodegradation pathways of treated and control specimens are probably different. The observed decreases in the peak intensity ratios; Al/C, Si/C, Si/O, and Al/O are consistent with water leaching characteristics of the treated specimens as discussed in the paragraph on “leaching characteristics” above.

Table 1: EDXA peak intensity ratios of surface elements in control and treated wood specimens

Peak ratio	Before water leaching and exposure to UV radiation		After water leaching and exposure to UV radiation	
	Control	Treated	Control	Treated
O/C	0.41	0.37	0.32	0.40
Al/C	0.00	0.38	0.00	0.20
Si/C	0.00	1.22	0.00	0.94
Si/O	0.00	3.32	0.00	2.36
Al/O	0.00	1.05	0.00	0.50

Conclusion

Using a mixture of AOS, MTMOS, and HDTMOS, a transparent thin xerogel film was deposited on wood substrates. The thin film deposit was strongly bound to the wood cell wall and remained practically intact even after water leaching and exposure to UV radiation as indicated by the SEM–EDXA results. In addition to decreasing the tendency of the wood substrate to absorb moisture, the thin film deposit protected the wood surface from discoloration caused

by UV radiation. The mechanism of how this transparent thin xerogel film protected the wood surface from photo discoloration is not yet precisely known.

In a study on thin oxide films deposited on a fused silica substrate by reactive sputtering, it was shown that an Al₂O₃ film with an optical thickness of 900 nm had a high extinction coefficient (2.91×10^5 – 1.19×10^5) for UV radiation in the wavelength range 200–300 nm.¹⁶ It has also been shown that total integrated surface light scattering of a thin film is proportional to the rms roughness, and inversely proportional to the fourth power of the radiation wavelength.¹⁷ Thus a hybrid Al₂O₃–SiO₂ thin film with a high refractive index can scatter UV radiation more intensely than visible light radiation. Therefore, it is reasonable to expect that the thin xerogel film can prevent UV radiation from reaching the wood substrate by a combination of absorption and scattering mechanisms. However, as shown by the LSCM results the rms roughness was lower for the treated specimens compared to the control specimens. The question then remains: to what extent does surface roughness of the thin xerogel film contribute to the scattering losses of the incident UV–visible radiation? This and other related questions such as the thickness of the xerogel film and its microstructure and nanostructure are the subject of future research.

It is generally believed that the most useful strategy for wood surface protection from photodegradation will involve compounds and treatments that stabilize lignin.¹⁸ This study has demonstrated that sol-gel derived hybrid inorganic–organic thin film deposits on wood surfaces can be tailored to protect wood surfaces from moisture intrusion and photo discoloration by UV radiation.

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