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Weathering Characteristics and Moisture Uptake Properties of Wood Coated with Water-Borne Sol-Gel Thin Films

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Abstract

In this study, wood specimens were coated with water-borne silsesquioxane oligomers by an in situ sol-gel deposition process. The effect of these water-borne sol-gel thin films on weathering characteristics and moisture-uptake properties of the wood specimens were investigated. The weathering characteristics were investigated by exposure of the specimens to artificial weathering conditions in a Weather-Ometer™. Water vapor uptake properties were determined by equilibrating the specimens in controlled humidity chambers, and liquid water uptake properties were determined by immersing the specimens in water over a period of 28 days. After exposure to artificial weathering conditions, subtle differences were observed between the erosion patterns of the sol-gel-coated and the non-coated specimens. Compared with the noncoated controls, the sol-gel coated specimens showed lower weight losses. There were also differences in lightness, chromaticity, and color changes of the sol-gel coated compared with the non-coated specimen surfaces. Moisture-uptake properties of both coated and non-coated specimens were practically similar.

Keywords

Weathering, water-borne silsesquioxane oligomers, sol-gel thin films, coating systems, wood surface

Introduction

The need to enhance performance properties of wood products in aboveground exterior applications has motivated research and development of sol-gel coating systems for wood. Sol-gel coating systems are hybrid inorganic-organic thin films whose properties can be tailored to different requirements such as ultraviolet (UV) blocking and moisture-resistance properties. Wood weathering outdoors is induced by solar radiation, UV, visible (Vis)), infrared (IR), moisture (dew, rain, snow, and humidity), and temperature and oxygen. Of these factors, the UV portion of solar radiation is the most damaging and is responsible for the primary photochemical degradation of wood surfaces[1].

Contemporary approaches to protecting wood from photodegradation rely on use of organic UV absorbers to block UV radiation from reaching the wood surface and on hindered amine light stabilizers (HALS) for scavenging radicals formed from lignin photolysis reactions[2]. In recent years, there has been increased interest in the use of inorganic UV-blocking nanoparticles for photostabilization of wood surfaces. The inorganic nanoparticles can be incorporated in wood clear coatings, where they block UV radiation from reaching the wood surface by scattering and absorption mechanisms, while remaining transparent to visible light[3]. Inorganic UV blockers can also be deposited within the cell wall of the outer layers of the wood surface by sol-gel process, where they form a thin film of metaloxane gels[4-7]. Because of their zero or very low VOC levels compared with traditional coatings, water-borne sol gel systems are emerging as a new class of versatile coating systems that combine the flexibility of organic polymers and the strength and durability of inorganic polymers[8].

In previous studies, we reported on weathering characteristics of wood specimens coated with solvent-borne sol-gel systems[9-11]. The objective of the current study was to evaluate the weathering characteristics of wood surfaces coated with water-borne silsesquioxane oligomers, a new class of water-borne sol-gel systems that can be used as primers for promoting adhesion of polymeric sealant, adhesive, and coating systems to a wide variety of substrates including glass, metal, concrete and plastics[12, 13]. No studies have so far been reported on their use on wood substrates.

Experimental

Materials and Methods

Wood specimens were prepared from western redcedar (Thuja plicata) boards in the form of mini-blocks, 25.4mm x 25.4mm x 6.25mm (longitudinal, tangential and radial directions). The specimens were placed in a controlled humidity room to condition at 65% relative humidity (RH), 26.7°C to a constant weight before coating.

Concentrated sols of water-borne silsesquioxane oligomers, WSA-9911, WSA-7021, and WSA-6511, containing Aminopropyl, Aminoethylaminopropyl, and Aminopropyl, vinyl functional groups, respectively, were purchased from Gelest, Morrisville, Pennsylvania. According to the supplier, the molecular weight distributions of WSA-9911, WSA-7021, and WSA-6511 oligomers were 270-550, 370-650, and 250-500, respectively. The weight percentage content of WSA-9911 in the concentrated sol was 22–25% and for WSA-7021 and WSA-6511, it was 25–28%.

Sols for coating the wood specimens were prepared in separate containers by diluting one part by volume of each concentrated sol with 63 parts by volume of deionized water to yield nominal weight percentage contents of 1.66 for WSA-9911, 1.72 for WSA-7021, and 1.73 for WSA-6511, The dilution factor was selected on the basis of preliminary experiments, which indicated that the time to gelation increased with increase in the dilution factor. The initial pH values of the coating sols were determined to be 10.65 for WSA-9911, 10.39 for WSA-7021, and 10.40 for WSA-6511. Properties of the water-borne coating sols are summarized in Table 1.

Table 1: Water-borne silsesquioxane coating sols

Sol ID	Pendant group	Molecular weight	Weight % in solution	PH
WSA6511	Aminopropyl, vinyl	250-500	1.73	10.40
WSA7021	Aminoethylaminopropyl	370-650	1.72	10.39
WSA9911	Aminopropyl	270-550	1.66	10.65

The specimens were coated by placing six replicates in separate jars containing each of the coating sols. Each container was tightly capped and placed on a horizontal shaker to allow the sols to react with the specimens for 24 h. At the end of this period, the specimens were removed from the jars and allowed to air dry. The specimens were then placed in an oven to dry for 6 h at 65°C before curing for 24 h at 105°C.

For accelerated weathering studies, the specimens were exposed for a total of 960 h in a Ci-65 Weather-Ometer™ (Atlas Material Testing Systems, Chicago, Illinois) using Program 1, which consisted of a 2-h cycle (102-min UV radiation only followed by 18-min radiation and water spray). The light source was a Xenon arc lamp with borosilicate inner and outer filters. During the light-only cycle, the black panel temperature (BPT) was 65 ± 2°C; the relative humidity (RH) was 48 ± 5%, and during the light and spray cycle, the BPT was 50 ± 5°C and RH was 80 ± 5%. Specimens were removed from the Weather-Ometer at 240-h intervals, preconditioned first at 65% RH and then at 30%, weighed, subjected to surface color measurements, and returned to the Weather-Ometer for further exposure.

Surface color measurements were performed with a Technidyne Micro S-5 Brightimeter (Technidyne Corporation, New Albany, Indiana). Surface erosion was assessed visually with a Wild Heerbrugg Photomakroskop M400 light microscope (Wild Heerbrugg AG, Gais, Switzerland).

For water vapor uptake studies, the specimens were equilibrated in controlled humidity chambers. Water vapor uptake was measured after each exposure interval in the Weather-

Ometer. For liquid water uptake studies, non-weathered specimens were immersed in deionized water over a period of 28 d, during which time they were occasionally removed from the water and weighed.

Semi-quantitative determination of water leaching of the film deposit was performed by EDXA of the specimens before and after immersion in water for 28 d. EDXA was performed on the LEO EVO40 scanning electron microscope with attached Vantage EDXA Analyzer (Thermo Noran, Madison, Wisconsin). Spectra were collected for 100 sec at 15.0005 KeV.

Results and Discussion

The specimens were evaluated for surface erosion, surface checking, and color change and moisture-uptake properties.

Figure 1: Micrographs of specimen surfaces at 0 h and after 960-h exposure in the Weather-Ometer (semidetached fibers after 960-h exposure of the control specimen are highlighted in white).

Surface erosion and weight loss

Surface erosion of the specimens was evaluated by both microscopic visualization and weight change after exposure in the Weather-Ometer. Figure 1 shows microscopic images of the surfaces of representative specimens at 0-h and after 960-h exposure in the Weather-Ometer. There were subtle differences between erosion patterns of non-coated control specimens and the coated specimens. While the latewood in the non-coated control

specimens showed a substantial number of semi-detached fibers after 960-h exposure in the Weather-Ometer, the coated specimens did not show any such damage to the latewood. There were also some differences between weight changes of non-coated control specimens and the coated specimens. As shown in Figure 2, after 240-h exposure, both noncoated and coated specimens initially showed different extents of weight gain. All the coated specimens, except for those coated with WSA6511, showed greater weight gains compared with the non-coated control specimens. These initial weight gains were followed by relatively steep weight losses by both the coated and non-coated specimens. There were very small differences in the rates of weight loss between the non-coated control and coated specimens. All the coated specimens, except for those coated with WSA6511, showed lower weight losses compared with the non-coated control specimens. Evidently, at the initial stages, the rate of moisture uptake was higher than the rate of weight loss because of surface erosion, but after 240-h exposure, weight losses from surface erosion progressed at a comparatively higher rate than the rate of moisture uptake.

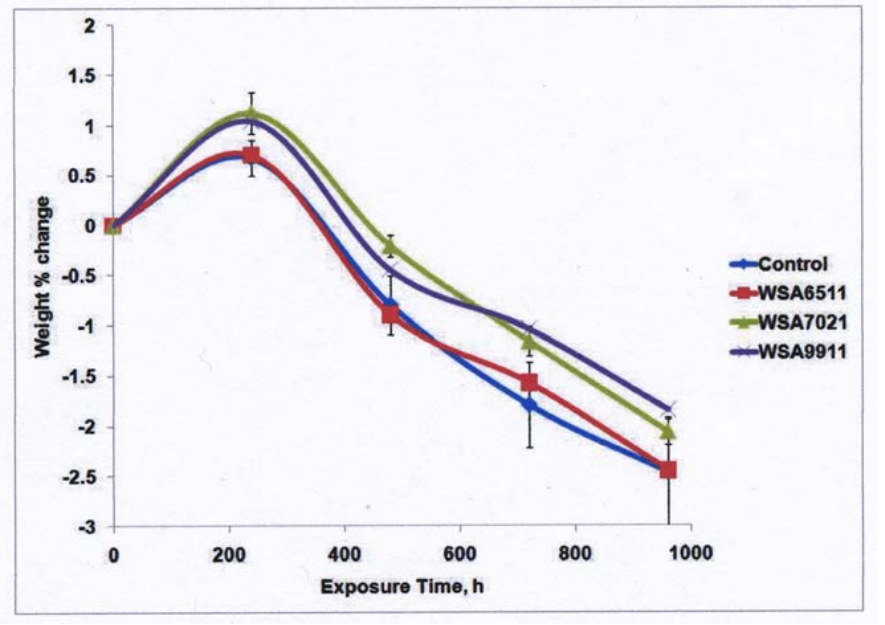

Figure 2: Weight percentage changes of specimens with exposure time in the Weather-Ometer (error bars represent standard deviation of six replicates).

Color change measurements

Color measurements were determined according to the CIE L*a*b* system of three parameters. The L* axis represents the lightness and varies from 100 (white) to zero (black). The a* coordinates represent chromaticity with +a* for red and -a* for green; and the b* coordinates represent chromaticity with +b* for yellow and –b*for blue. L*, a* and b* were measured before and after 240-h, 480-h, 720-h and 960-h exposure in the Weather-Ometer. These values were used to calculate the resulting color change, ΔE^*, and chromaticity change, ΔC^* according to the following equations:

$$\Delta L^* = L^*_{(t)} - L^*_{(i)} \quad (1)$$

$$\Delta a^* = a^*_{(t)} - a^*_{(i)} \quad (2)$$

$$\Delta b^* = b^*_{(t)} - b^*_{(i)} \quad (3)$$

$$\Delta E^* = \{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\}^{1/2} \quad (4)$$

$$\Delta C^* = \{\Delta a^{*2} + \Delta b^{*2}\}^{1/2} \quad (5)$$

ΔL^*, Δa^*, and Δb^* are differences between the initial (i) and exposure time (t) values. Average initial L* values of the specimens before exposure in the Weather-Ometer are summarized in Table 2. It should be noted that the non-coated control specimens had higher initial lightness values compared to the coated specimens.

Table 2: Average L* values of the specimens before exposure in the Weather-Ometer

Specimen	Average L* ± STDEV (n=6)
Non-coated control	55.17±0.87
Coated with WSA6511	54.94±1.25
Coated with WSA7021	52.75±1.90
Coated with WSA9911	53.83±3.31

Figure 3 shows lightness changes, ΔL^* after a total of 960-h exposure in the Weather-Ometer. Specimens coated with WSA7021 showed the highest rate of lightness change, followed by specimens coated with WSA9911 and WSA6511. Non-coated control specimens showed the lowest rate of lightness change. Since the thin sol-gel deposit turned darker in appearance after curing for 24 h in an oven at 105°C, the higher rate of lightness changes of the coated specimens may have been due to the bleaching of the thin film solgel surface coating. Such an effect would be particularly apparent for the thin WSA7021 coating, which because of its higher molecular weight precursor oligomers, may have concentrated on the surface rather than within the cell wall of the outer layers of the wood specimens. By comparison, bleaching of the non-coated control specimens was the result of bleaching of the wood substance itself.

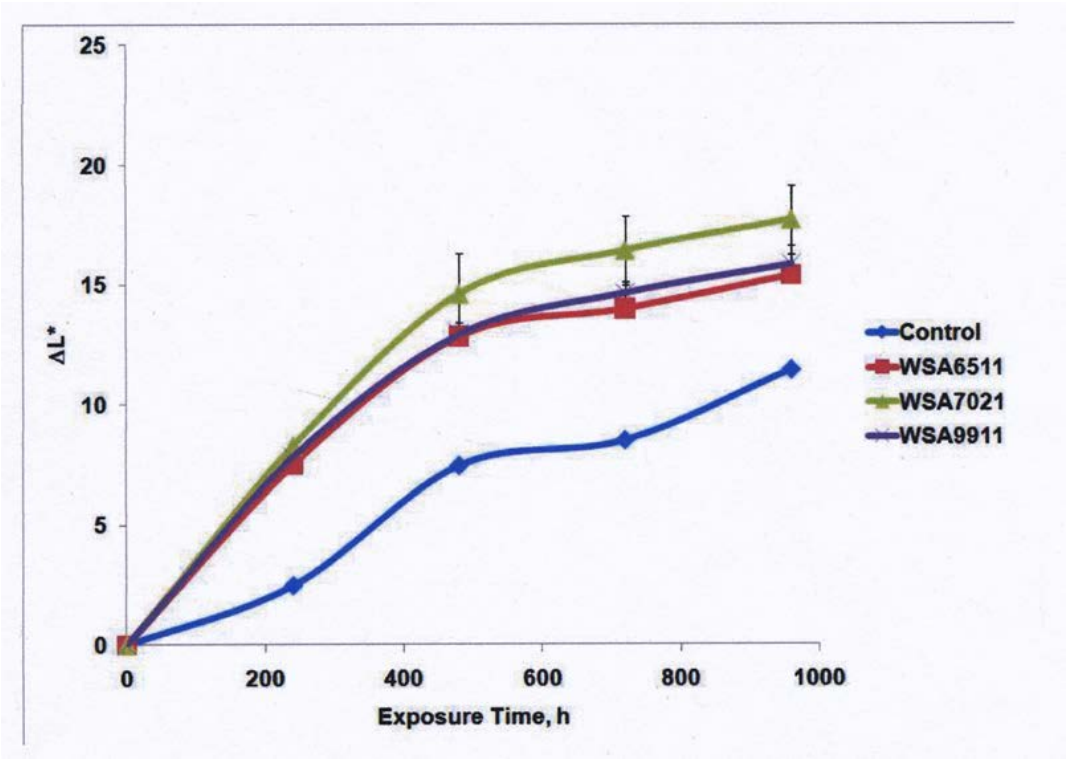

Figure 3: Lightness changes of specimens with exposure time in the Weather-Ometer (error bars represent standard deviation of six replicates; and in some cases the error bars are obscured by the markers).

Figure 4 shows chromaticity changes, ΔC* after a total of 960-h exposure in the Weather-Ometer. During the initial stages of artificial weathering (0 to approximately 700 h), specimens coated with WSA9911 showed the lowest rate of chromaticity change. The next lowest rate of chromaticity change was shown by non-coated control specimens. If an assumption is made that chromaticity changes are strongly influenced by the surface chemistry of the wood specimens, then it is reasonable to assume that solgel precursors that are deposited within the cell wall of the outer surface layers of the wood specimens are likely to influence chromaticity changes more than deposits that are concentrated on the cell wall of the outer surface layers of the wood specimens. Apparently, WSA9911 precursors penetrated the cell wall farther than WSA7021. Based exclusively on molecular weight, WSA6511 precursors should have behaved similarly to WSA9911. However, because of the presence of vinyl in addition to aminopropyl pendant groups in the WSA6511 oligomers, specimens coated with WSA6511 showed anomalous behavior with respect to chromaticity change.

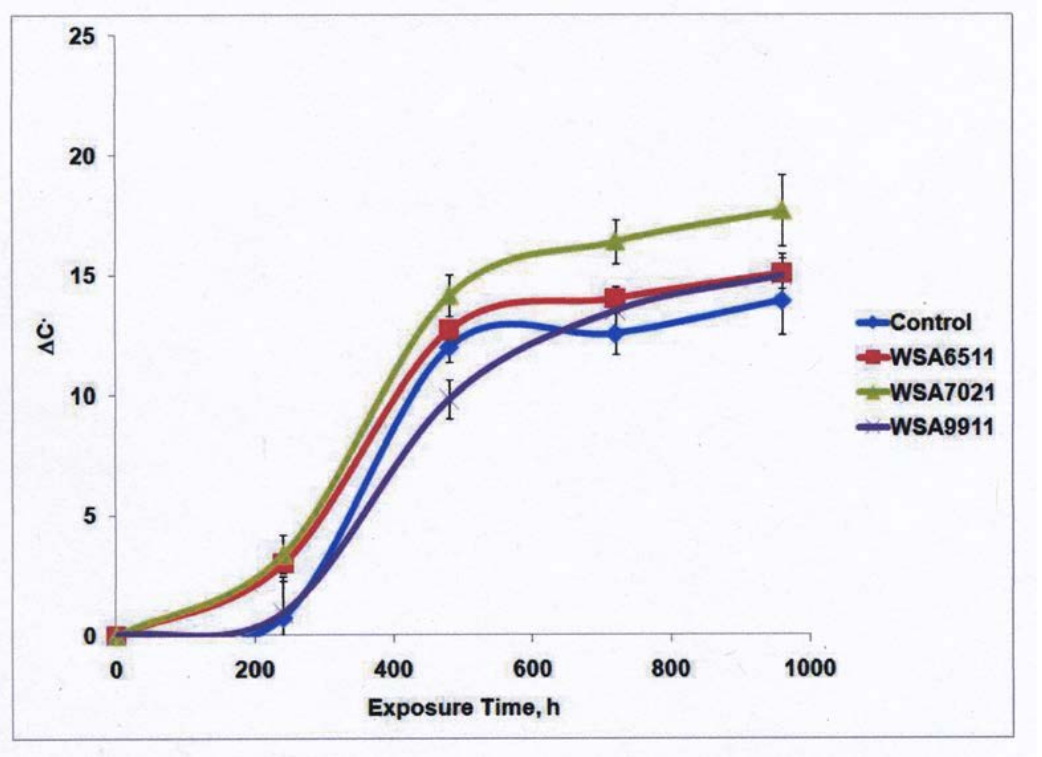

Figure 4: Chromaticity changes of specimens with exposure time in the Weather-Ometer (error bars represent standard deviation of six replicates).

Figure 5 shows color changes, ΔE* after a total of 960-h exposure in the Weather-Ometer. It is clear that color change was dominated by lightness changes. In photo-induced discoloration of sapwood, radiation over 390nm gives rise to lightening, and radiation under 390nm brings about darkening. The wavelength range for lightening or bleaching is considered to be between 390 and 580nm[14]. Since the filtered Xe arc radiation emits UV and Vis radiation between 285nm and 800nm similar to solar radiation, it is reasonable to assume that the photo-induced discoloration of western red cedar was due to degradation and washing away of lignans, plicatic acid, and plicatin, which are believed to be responsible for its surface color[15].

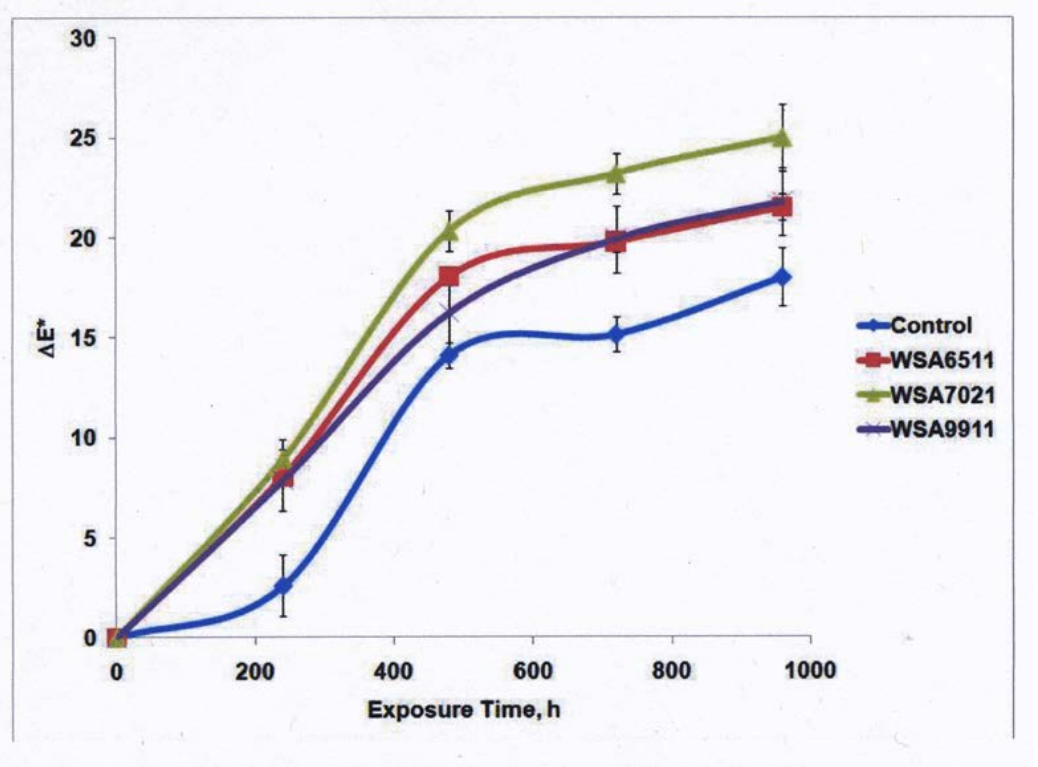

Figure 5: Color changes of specimens with exposure time in the Weather-Ometer (error bars represent standard deviation of six replicates).

Moisture-uptake properties

Moisture-uptake properties of both sol-gel-coated and non-coated control specimens were practically the same. Figure 6 shows water vapor uptake of the specimens at 65% RH before and after exposure in the Weather-Ometer for 240 h, 480 h, 720 h, and 960 h. Figure 7 shows liquid water uptake of the specimens immersed in deionized water for a total of 28 d.

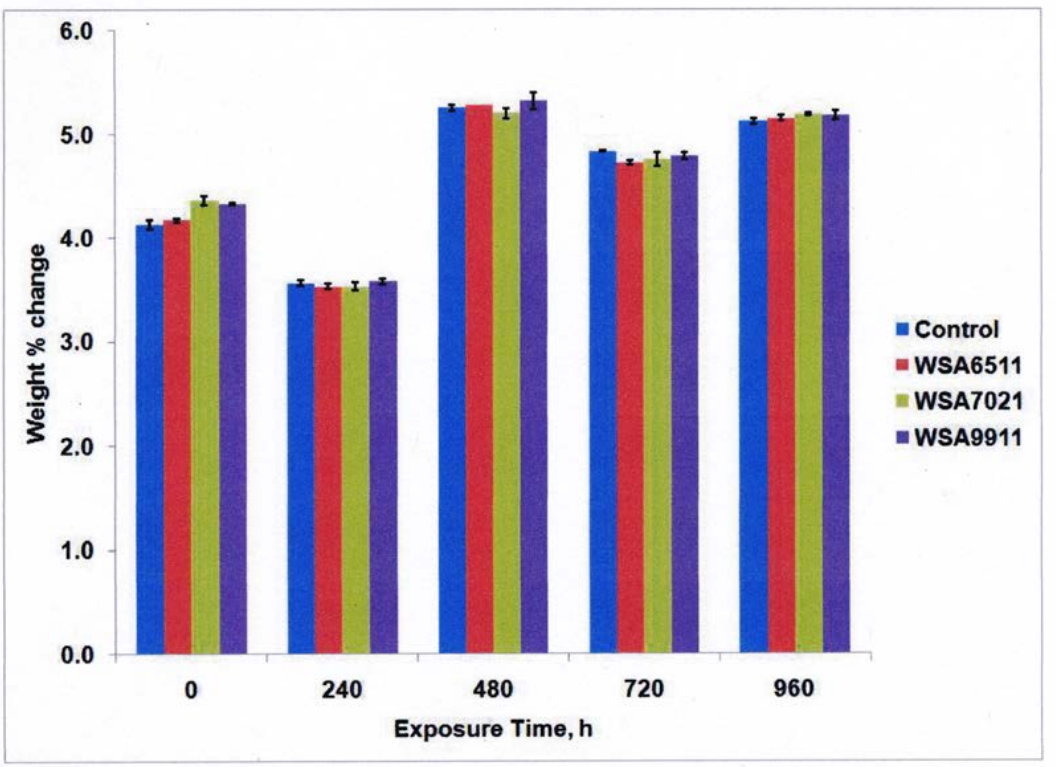

Figure 6: Water vapor uptake of specimens at 65% RH after exposure in Weather-Ometer (error bars represent standard deviation of six replicates).

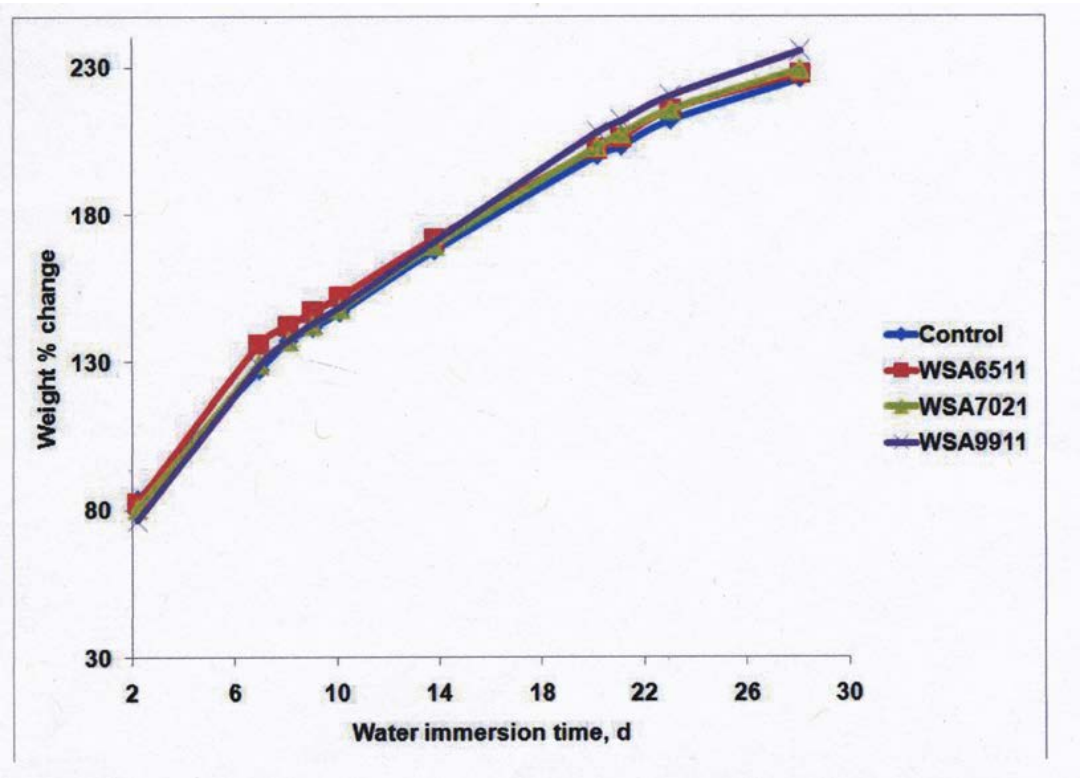

Figure 7: Liquid water uptake of specimens after immersion for 28 d in deionized water (Each weight measurement was an average of six replicates. Error bars are obscured by the markers).

Water leachability of the sol-gel deposits

Figure 8a shows representative EDX spectra of the specimens coated with WSA6511 before and after immersion in water for a total of 28 d. Using the intensity of the Si (K_α) peak as a measure of retention of the sol-gel deposit on the wood specimen, leachability of the sol-gel deposit appeared to be less for WSA9911 compared with WSA6511- or WSA7021-coated specimens (see Figure 8b). This behavior appears to be consistent with the molecular weight and the nature of the pendant functional groups contained in these precursor oligomers. Because of its lower molecular weight compared to WSA7021, WSA9911 may have penetrated farther into the cell walls of the outer surface layers of the wood. And because it contains aminopropyl pendant groups, WSA9911 may have formed stronger hydrogen bonds with the wood substrate, compared with WSA6511, which contains vinyl pendant groups that cannot form hydrogen bonds with the wood substrate.

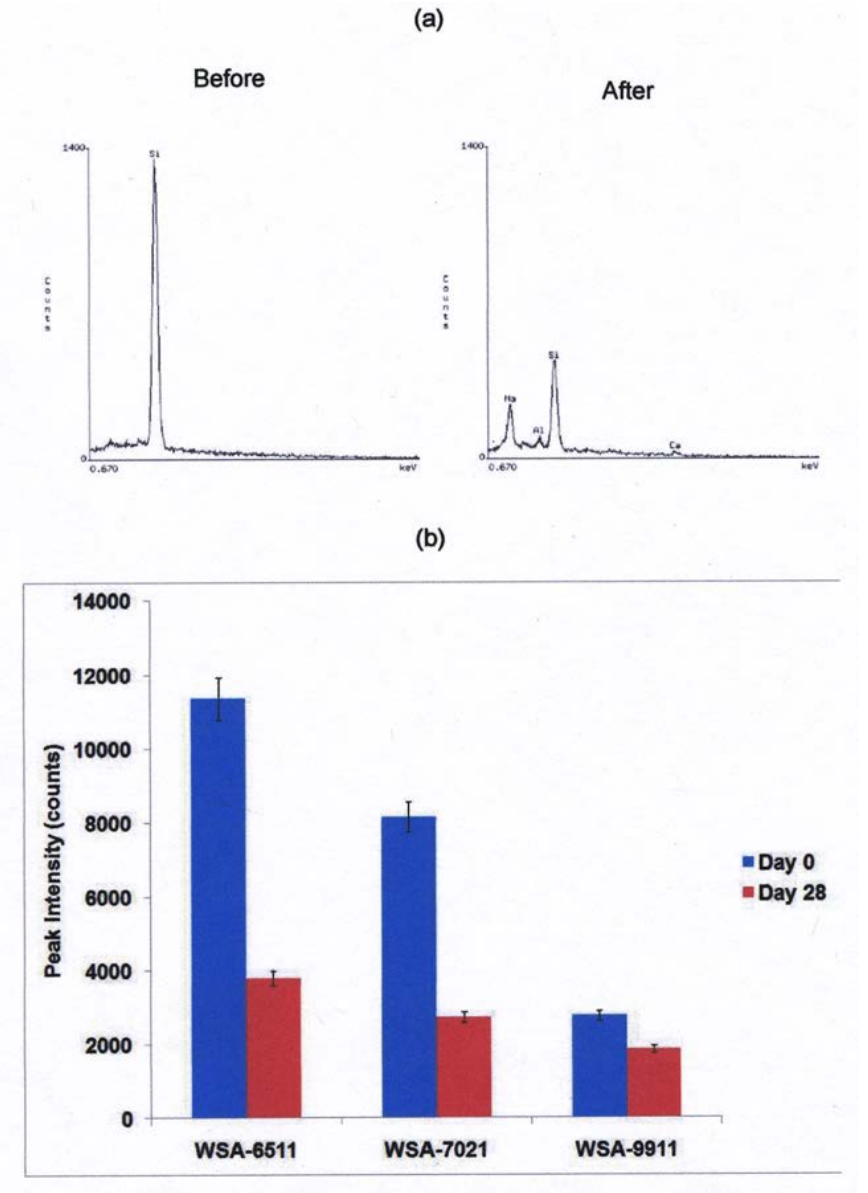

Figure 8: (a) Representative EDX spectra of specimen surface; (b) Peak intensities of Si(K_α) on specimen surfaces before and after immersion in deionized water for 28 d.

Conclusions

Thin films deposited by the sol-gel process from water-borne silsesquioxane oligomers used in this study had an effect on weathering characteristics of wood specimens. Unlike non-coated control specimens, erosion patterns of the coated specimens did not show any semi-detached latewood fibers. Rates of lightness changes of the coated specimens were higher than non-coated control specimens. Specimens coated with WSA9911 showed the lowest rate of chromaticity changes during the initial stages of artificial weathering. The overall color changes of the specimens were dominated by lightness changes, primarily due to washing away of the surface color. Moisture-uptake properties of the coated specimens were practically similar to non-coated control specimens.

Further research is needed to develop waterborne silsesquioxane oligomers that have improved moisture resistance and weatherability properties for protecting wood in exterior above-ground applications.

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