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Photostability and moisture uptake properties of wood veneers coated with a combination of thin sol-gel films and light stabilizers

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Abstract

In recent years, there has been increased interest in the use of inorganic UV blocking nanoparticles for photostabilization of wood surfaces. Photostability and moisture uptake properties of wood veneers coated with a combination of hybrid inorganic-organic thin sol-gel films and organic light stabilizers was investigated. The light stabilizers were applied by brushing, and the thin sol-gel films were deposited on the wood surface by dipping in a sol prepared from a mixture of methyltrimethoxysilane, hexadecyltrimethoxysilane, and aluminum isopropoxide precursors. Although the sol-gel film improved the moisture resistance of the wood veneers, it showed mixed results on photostability. Under light and spray conditions in a Weather-Ometer™, specimens treated with a combination of sol-gel thin film and a UV absorber, tris-resorcinol triazine and an acrylic self-crosslinking binder, or treated with lignin stabilizer/tris-resorcinol triazine/acrylic self-crosslinking binder showed good overall weathering performance. Under permanent light conditions in the Weather-Ometer™, specimens treated with a combination of sol-gel thin film, a lignin stabilizer, and a water soluble UV absorber – namely: (2-hydroxyphenyl)-benzotriazole – revealed a good overall weathering performance. This study has demonstrated the feasibility of using a combination of organic light stabilizers and sol-gel deposits of hybrid inorganic-organic thin films to improve weathering resistance of softwood substrates.

Keywords: hybrid inorganic-organic thin films; light stabilizers; lignin stabilizer; moisture; photostability; sol-gel precursors; UV absorber; weathering; wood coatings.

Introduction

Although sol-gel surface coatings for application to polymer substrates were first reported more than 22 years ago, it is only in the past 7 years that we have witnessed significant advances in the development of hybrid inorganic-organic sol-gel systems for wood coatings.

Lin and Falleroni (1988) developed an organoalkoxysilane/alumina sol-gel formulation for application on polycarbonate and acrylic substrates to improve abrasion resistance. The authors also demonstrated that such formulations could comprise a pigment or blend of pigments to form a nonporous durable paint that could be applied by conventional methods and cured conveniently at temperatures as low as 80°C.

Kissel (1991a,b) developed sol-gel polymer surface coatings that were useful for gloss enhancement and tannin block enhancement on wood substrates. These sol-gel polymer surface coatings were prepared by adding a sol-gel composition containing a salt to a polymer binder. The salt in the sol-gel composition was added in sufficient amounts to increase both the specular gloss and the tannin block properties.

Tanno et al. (1998) investigated application of sol-gel formulations in wood to enhance its dimensional stability and its resistance against termites and fire, and developed a sol-gel system that also enhanced fungal resistance of the wood. The sol-gel system was composed of tetraethoxysilane (TEOS) precursor mixed with small amounts of 2-heptadecafluorooctyl trimethoxysilane and 3-(trimethoxysilyl)-propyl-(carboxymethyl)-decylmethyl ammonium hydroxide.

However, to control the barrier and protective properties of sol-gel coatings on wood substrates against weathering and moisture uptake, a deeper understanding of the surface chemistry and morphology of sol-gel deposited thin films in wood substrates is needed. To address this gap in knowledge, Tshabalala et al. (2003) investigated the surface chemistry and moisture sorption properties of wood substrates that had been treated with a sol-gel system that contained a mixture of low and high molecular weight precursors, methyltrimethoxysilane (MTMOS) and hexadecyltrimethoxysilane (HDTMOS), respectively. They concluded that the low molecular weight MTMOS apparently penetrated the outer surface layers of the wood and was fixed via hydrogen bonding with hydroxyls that might not be readily accessible to the higher molecular weight HDTMOS. Once attached to such sites, it was reasonable to assume that some of the surface derivatives of MTMOS also reacted with other molecules of MTMOS and the high molecular weight HDTMOS formed a hydrophobic polysiloxane network in the cell wall of the outer surface layers of the wood substrate. In a subsequent study, Tshabalala and Gangstad (2003) evaluated performance of sol-gel coated wood surfaces under acceler-

ated weathering conditions and observed that wood specimens coated with a combination of MTMOS and HDTMOS by the sol-gel process exhibited good resistance to liquid water sorption and photochemical degradation. In a recent study, Tshabalala and Sung (2007) described sol-gel deposition of a hybrid inorganic-organic thin film on wood using a mixture of metal-organic precursors.

Donath et al. (2004) compared performance properties of wood specimens impregnated with three different sol-gel precursors, namely: TEOS, methyl triethoxysilane, and propyl triethoxysilane. They observed that wood properties – such as cell wall bulking, anti-swelling efficiency, moisture uptake, and durability – improved significantly in wood specimens treated with the monomeric sol-gel precursors compared to those specimens that were treated with oligomeric sol-gel particles. Apparently, the high molecular weight oligomeric particles did not penetrate the cell wall as effectively as the monomeric precursors.

Sèbe et al. (2004) demonstrated that n-propyl-trimethoxysilane reacted by alcoholysis with available hydroxyl groups in the wood substrate. The authors studied the effect of both weak acid and weak base catalysts on the extent of fixation of silane molecules to the wood substrate, and observed that in the presence of low concentrations of either acetic acid or ethylamine catalysts, the amount of silane bonded to the wood substrate was measurably higher than in the absence of a catalyst. This study also demonstrated that, despite the sensitivity of the C-O-Si bond to hydrolysis, a significant amount of silane remained in the wood even after 14 days in water.

Bonding between sol-gel deposited silicon dioxide and the wood cell wall was recently further confirmed by Fu and Zhao (2007). By measuring change of dielectric relaxation time of methylol groups (-CH_2OH) in the amorphous region of the wood cell wall treated with increasing amounts of TEOS sol-gel precursor, they concluded that methylol groups were involved in the hydrolysis and condensation reactions that result in bonding of silicon dioxide to the wood cell wall.

As understanding of the bonding mechanism between sol-gel precursors and wood cell wall components has improved, so has the increase in the number of new applications of sol-gel systems to improve the performance properties of wood (Mahltig et al. 2008) and wood-plastic composites (Mishra and Luyt 2008).

Coating of wood with sol-gel polymers is only one of the strategies to improve the wood/water relationship and photostability. Selected examples from recent literature – concerning surface modifications with organosilicons (De Vetter et al. 2010) and amino-silicon micro- and macro-emulsions (Weigenand et al. 2007) and silanes (Donath et al. 2006), impregnation with wax (Scholz et al. 2010a,b), plasma treatment (Wolkenhauer et al. 2008; Asandulesa et al. 2010), chemical modification with organic (Bryne and Wålinder 2010; Xiao et al. 2010) and inorganic components (Klarhöfer et al. 2007) – show that the sol-gel approach could be competitive with other processes.

The objective of this study was to evaluate the effect of thin sol-gel films in combination with light stabilizers (UV absorber and/or lignin stabilizer) on the weathering performance of pine wood veneers. It is well-known that softwood species such as pine require a double protection strategy as given by the lignin stabilizer concept. This concept is based on a combination of a UV absorber to screen out harmful UV-A and UV-B radiation, which causes lignin decomposition and the use of a lignin stabilizer to protect lignin from the impact of visible light that is not screened by UV absorbers (Schaller and Rogez 2007). The sol-gel thin films were deposited on the wood specimens from a mixture of MTMOS, HDTMOS, and aluminum isopropoxide (AIP) precursors.

Materials and methods

Pine (*Pinus radiata* Don.), Monterey pine, wood veneer specimens were supplied by Ciba AG, Basel, Switzerland (Table 1). Chemicals, MTMOS and HDTMOS, were from Fluka. AIP, trifluoroacetic acid (TFA), and isopropanol (IPA) were from Sigma-Aldrich. All reagents were used as received.

The sol for treating the wood specimens was prepared according to the procedure described by Tshabalala and Sung (2007) by means of MTMOS, HDTMOS, and AIP as precursors, and TFA as catalyst. Deposition of a thin sol-gel film on the surface of each specimen was accomplished by dipping in the sol for 24 h. The treated specimens were allowed to air-dry at room temperature for 1 h before placing them in a forced-air oven to dry at 65°C for 6 h. At the end of this period, the specimens were cured for 24 h in an oven at 105°C to fix the gel. The cured specimens were allowed to equilibrate in the 30% relative humidity (RH) room at 27.6°C for 24 h before recording their individual weights. The specimens were kept in the 30% RH room for further studies.

Accelerated weathering and surface color measurements

For accelerated weathering studies, sliced veneer specimens, 2 mm×76 mm×102 mm (tang.×long.×rad.), were divided into

Table 1 Specimen description.

Code	Treatment	Method of application
B1-C	Control (non-treated)	None
B2-C	Lignin stabilizer+(2-hydroxy-phenyl)-benzotriazole[a]	Brush at 100 gm^{-2}
B3-C	10% tris-resorcinol triazine (20% active)/10% acrylic self-crosslinking binder[b]	Brush at 100 gm^{-2}
B4-C	1% lignin stabilizer/10% tris-resorcinol triazine (20% active)/10% acrylic self-crosslinking binder[b]	Brush at 100 gm^{-2}
B1-T	B1-C treated with sol-gel	Dipping 24 h
B2-T	B2-C treated with sol-gel	Dipping 24 h
B3-T	B3-C treated with sol-gel	Dipping 24 h
B4-T	B4-C treated with sol-gel	Dipping 24 h

[a]Water soluble UV-absorber; [b]UV absorber and binder in water.

two groups, labeled Set 1 and Set 2. Set 1 consisted of quadruplicate, and Set 2 consisted of duplicate control and sol-gel-treated specimens. Set 1 was exposed in the Ci65 Weather-Ometer™ (Atlas, Chicago, IL, USA) to Program 1, which consisted of a 2-h cycle (102 min UV radiation only followed by 18 min radiation and water spray at 0.2 l min^{-1}. Set 2 was exposed in the Weather-Ometer™ to Program 0, which consisted of permanent UV radiation only. The light source was a Xenon arc lamp with borosilicate inner and outer filters, and its irradiance was controlled at 0.35 Wm^{-2} at 340 nm. For Program 0, the black panel temperature (BPT) was 65±2°C, and RH was 30±5%. For Program 1, the light-only BPT was 65±2°C; RH 48±5%, and the light and spray BPT was 50±5°C; RH 80±5%.

Accelerated weathering experiments in the Weather-Ometer™ were terminated when the first visible signs of discoloration of the specimens became apparent. That occurred during 240 h of exposure.

The color of each specimen was measured with a Technidyne Micro S-5 Brightimeter (Technidyne Corporation, New Albany, IN, USA).

Color measurements were determined according to the CIE*Lab* system of three parameters (Goktas et al. 2008). 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.

The L^*, a^*, and b^* values for each specimen were measured at four contiguous spots (Figure 1) on the surface of each specimen before and after exposure in the Weather-Ometer™. The resulting color differences (ΔE^*) were calculated based on the average values:

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

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

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

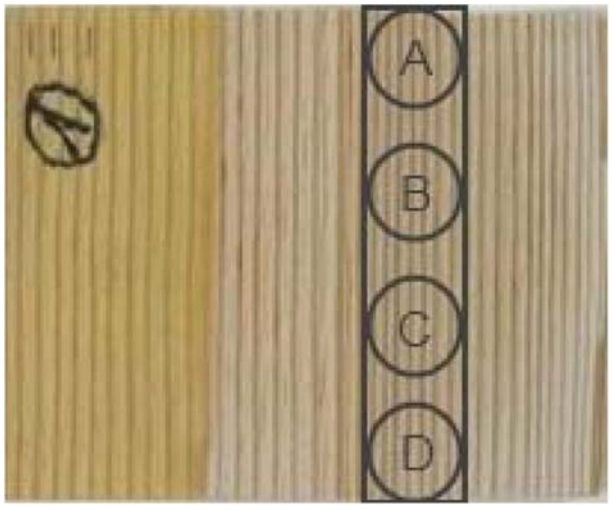

Figure 1 Illustration of the four contiguous spots on the sapwood where color measurements were made. The darker shading on the left-hand side is the area of the specimen that was shielded by the specimen holder from irradiation. It is actually the original color of the specimen before exposure to Program 1 in the Weather-Ometer™.

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

where ΔL^*, Δa^*, and Δb^* are the changes between the initial (i) and final (f) values. Higher values of ΔE^* represent greater discoloration.

Water vapor and liquid water uptake

The measurements of water vapor and liquid water uptake were performed in duplicate. The former was determined by measuring weight gain of each specimen at 65% RH relative to its equilibrium weight at 30% RH. Liquid water uptake was determined by keeping the specimens submerged under deionized (DI) water for a period of 10 days. On the first day of water immersion, the weight of each specimen was recorded hourly, and on subsequent days it was recorded only once a day at the same time.

Results and discussion

Color change

Figure 2a shows average color change values, ΔE^*, for control and sol-gel treated specimens in Set 1 after 240-h exposure to Program 1, and Figure 2b illustrates ΔE^* for Set 2

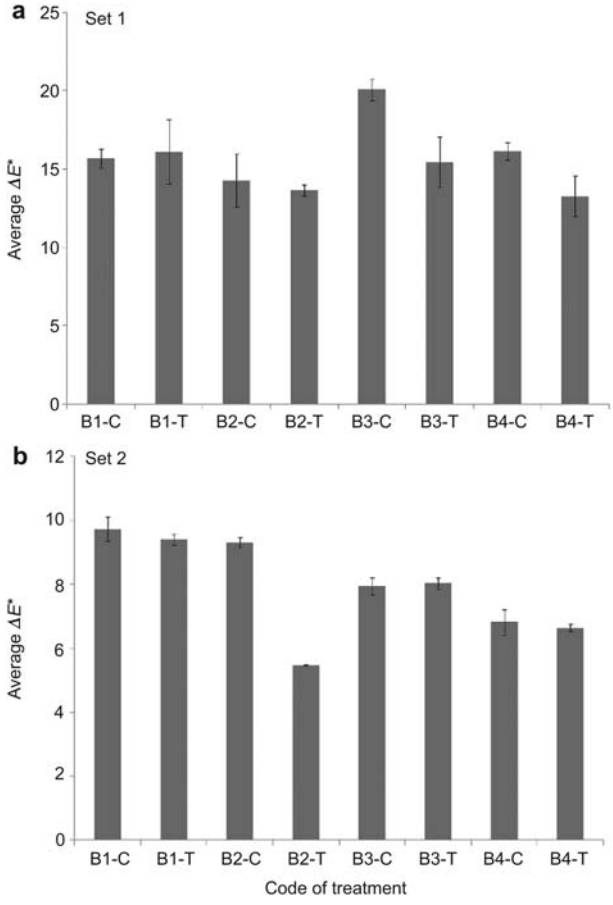

Figure 2 Average color change values, ΔE^*, for control and treated specimens after 240 h exposure in the Weather-Ometer™ (a) to Program 1 (light and spray) and (b) to Program 0 (light only).

Table 2 Color change statistics for Set 1 and Set 2 specimens.

	Set 1 specimens (light+spray)			Set 2 specimens (light only)		
Code	Average ΔE^* (n=4)	SD	P-value	Average ΔE^* (n=2)	SD	P-value
B1-C	15.70	0.62	0.7221	9.72	0.37	0.4312
B1-T	16.11	2.05		9.40	0.17	
B2-C	14.25	1.69	0.5463	9.31	0.16	0.0180
B2-T	13.68	0.35		5.47	0.01	
B3-C	20.07	0.67	0.0062	7.93	0.27	0.6847
B3-T	15.44	1.62		8.03	0.17	
B4-C	16.14	0.58	0.0150	6.82	0.40	0.6273
B4-T	13.29	1.30		6.63	0.12	

n, number of replicates.

exposed to Program 0 for the same time in the Weather-Ometer™.

To evaluate the effect of sol-gel treatment on weathering characteristics, the ΔE^* data from sol-gel treated specimens was compared to that of the corresponding control specimens, based on P-values determined by the Welch two sample t-test. A P-value <0.05 represents a test that is statistically significant at the 0.05 significance level, and corresponding values below 0.01 indicate significance at the 0.01 significance level. Set 1 and Set 2 statistics are summarized in Table 2. Thus, for Set 1, the average color change for the sol-gel treated specimens, B3-T, was different from the average change for control specimens, B3-C, at the 0.01 significance level. The average color change for B4-T was different from the average change for B4-C at the 0.05 significance level. The average color changes for B1-T and B2-T were not significantly different from those for B1-C and B2-C, respectively. Thus, under light and spray weathering conditions in the Weather-Ometer™ sol-gel treatment resulted in improvement of the photostability of those specimens that had been pretreated with a UV absorber, tris-resorcinol triazine, and an acrylic self-crosslinking binder, or with lignin stabilizer/tris-resorcinol triazine/acrylic self-crosslinking binder.

For Set 2, the average color change for the sol-gel treated specimens, B2-T, was different from the change for the control specimens, B2-C, at the 0.05 significance level. The average color changes for B1-T, B3-T, and B4-T were not significantly different from those for B1-C, B3-C, and B4-C, respectively. Thus, under light only weathering conditions in the Weather-Ometer™ sol-gel treatment resulted in improvement of the photostability of those specimens that had been pretreated with a lignin stabilizer and a water soluble UV absorber, (2-hydroxyphenyl)-benzotriazole.

Water vapor uptake

Sol-gel treatment resulted in considerable improvement in resistance of the specimens to water vapor uptake. As shown in Figure 3, water vapor uptake at 65% RH and 27.6°C of the sol-gel treated specimens (B1-T, B2-T, B3-T, and B4-T) decreased by approximately 80% relative to the control specimens (B1-C, B2-C, B3-C, and B4-C).

Liquid water uptake

Sol-gel treatment also decreased the initial liquid water uptake of the specimens to a considerable extent. As shown in Figure 4, after submersion for 10 days in distilled water in a controlled temperature room, sol-gel treated specimens showed lower liquid water uptake values of 670–750 mg g^{-1} compared to the specimens without sol-gel treatment, which showed twice as much liquid uptake values of 1265–1340 mg g^{-1}. Based on these results, it is very clear that sol-gel treatment and not the light stabilizers is responsible for improving resistance to liquid water uptake.

Conclusions

Sol-gel treatment improved resistance to liquid water and water vapor uptake, but the results were not always unambiguous with regard to improving the photostability of the wood veneer specimens. Under light and spray conditions in a Weather-Ometer™, good overall weathering performance was observed for specimens treated with a combination of sol-gel thin film and a UV absorber, tris-resorcinol triazine, and an acrylic self-crosslinking binder, or treated with lignin stabilizer/tris-resorcinol triazine/acrylic self-crosslinking

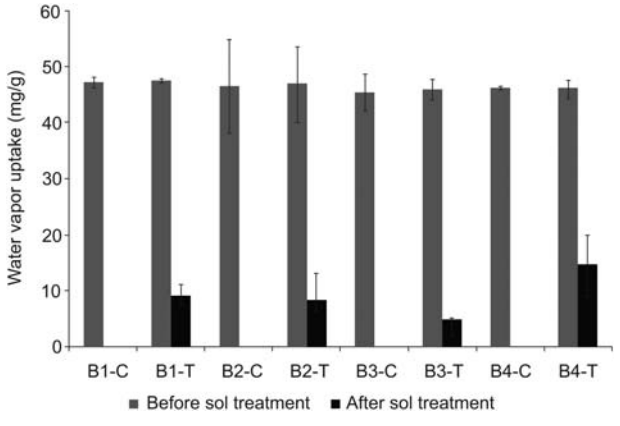

Figure 3 Water vapor uptake (at 65% RH, 27.6°C) of specimens with sol-gel treatments (B1-T, B2-T, B3-T, B4-T) and without sol-gel treatments (B1-C, B2-C, B3-C, B4-C).

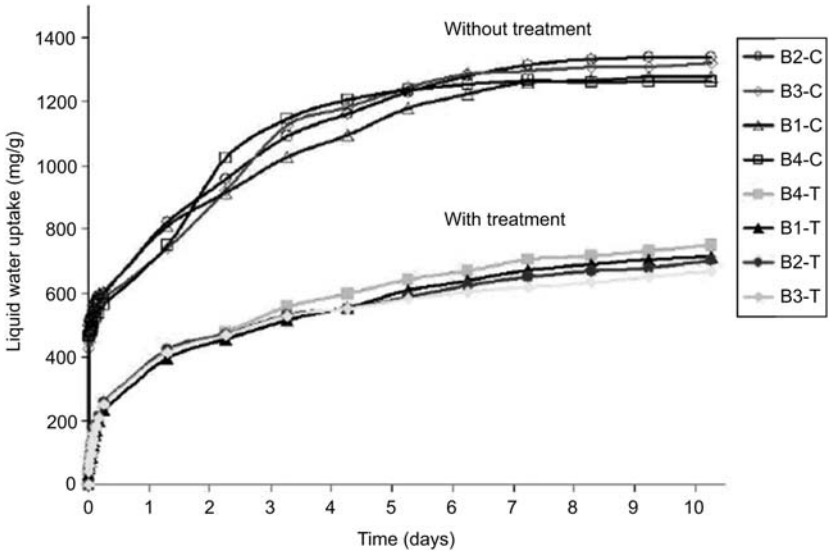

Figure 4 Liquid water uptake of specimens with sol-gel treatments (B1-T, B2-T, B3-T, B4-T) and without sol-gel treatments (B1-C, B2-C, B3-C, B4-C).

binder. Under permanent light only conditions in the Weather-Ometer™ specimens resulted in a good overall weathering performance, when treated with a combination of sol-gel thin film, a lignin stabilizer, and a water soluble UV absorber, i.e., with (2-hydroxyphenyl)-benzotriazole. Accordingly, the feasibility was demonstrated that the weathering resistance of softwood substrates can be improved by means of a combination of organic light stabilizers and sol-gel deposits of hybrid inorganic-organic thin films.

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