Performance Enhancement of Wood Surfaces Used in Outdoor Applications: The Effect of Sol-gel Treatment on the Weathering Performance of Solid Wood-polymer Composites

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Keywords: colour, hardness, sol-gel, weathering, wood-polymer composites

ABSTRACT

Although wood remains the building material of choice in residential construction, it has the deleterious properties of poor durability and dimensional instability. For above-ground exterior applications such as deck flooring, important properties include hardness and weathering resistance. To improve these properties, wood was modified with acrylic polymers to slow the moisture sorption and improve its hardness and with a hybrid inorganic-organic thin film to improve its photostability. Modification of the wood was accomplished by *in situ* polymerization of acrylic monomers in the lumens and voids of the wood. Deposition of the hybrid inorganic-organic thin film in the cell walls of the outer layers of the wood was accomplished by sol-gel deposition from a water-borne sol of silsesquioxane oligomers. The weathering behaviour, including weight and colour changes of the coated and non-coated modified wood specimens under exposure to accelerated weathering conditions was performed in a Weather-Ometer™ (Atlas Material Testing Technology, LLC, Chicago, Illinois).

INTRODUCTION

Wood exposed outdoors is susceptible to degradation from sunlight, moisture, and microbial colonization. Sol-gel modification of the wood cell wall, based on surface deposition of multifunctional alkoxysilanes, has been shown to improve moisture resistance and photostability of wood substrates (Tshabalala *et al.* 2003a, 2003b, Tshabalala *et al.* 2007). Evans (2009) has observed (that modification technologies designed to impart photostability to wood are most likely to be successful when used as surface treatments.

In situ polymerization of monomers (such as acrylates and methacrylates) in the voids or lumens of solid wood can produce a water resistant and harder material. It does not make the wood dimensionally stable, but can improve resistance of the wood to water sorption by filling the voids with polymer and impeding moisture movement.

Various acrylic monomers have been evaluated for dimensional stability, ability to exclude water vapor and liquid water, and hardness (Ellis and O'Dell 1999, Ibach and Ellis 2005). Different combinations of hexanediol diacrylate (HDDA), hydroxyethyl methacrylate (HEMA), hexamethylene diisocyanate (Desmodur N75, DesN75), and maleic anhydride (MAn) were polymerized *in situ* in solid pine, maple, and oak wood. The rate of water vapor and liquid water absorption was slowed, and the rate of swelling was less than that of unmodified wood specimens, but the dimensional stability was not permanent (Ellis and O'Dell 1999).

Crosslinking agents are generally used to increase reaction rate and improve the physical properties of wood–polymercomposites (WPCs) (Kenaga 1970). Some of the crosslinking agents frequently used with methyl methacrylate (MMA), styrene, or other vinyl monomers are trimethylolpropane triacrylate, trivinyl isocyanurate, trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, trimethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and divinylbenzene. WPCs with only MMA show a void space at the interface between cell wall and polymer (Kawakami *et al.* 1977). With addition of crosslinking esters such as di- and tri-methacrylate, the shrinkage (and hence void spaces) of the polymer during polymerization increases. On the other hand, in the WPCs containing polar esters having hydroxyethyl and glycidyl groups, the voids caused by the shrinkage of polymer were found to form inside the polymer itself, suggesting better adhesion of the polymer to the inner surface of cell wall (Kawakami *et al.* 1981).

WPCs made with birch and pine and impregnated with MMA or styrene-acrylonitrile were more resistant to surface checking than untreated wood when exposed to accelerated weathering in a Weather-Ometer™ (Atlas Material Testing Technology, LLC, Chicago, Illinois) for 1,000 h (Desai and Juneja 1972). The styrene-acrylonitrile treatment performed better than MMA. A combination of cell wall-modifying treatments (butylene oxide or methyl isocyanate) with MMA lumen-filled treatments showed improved resistance to the degradative effects of accelerated weathering in a Weather-Ometer™. The use of MMA in addition to the cell wall-modifying chemical treatments provides added dimensional stability and lignin stabilization and has a significant effect on weatherability (Rowell *et al.* 1981).

The objective of this study was to explore the effect of hybrid inorganic-organic sol-gel deposits on weathering properties of solid wood-polymer composites.

EXPERIMENTAL

Materials and Methods

Wood specimens were prepared from western red cedar *(Thuja plicata)* boards in the form of wafers, 51.3 mm × 0.8 mm × 15.8 mm (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. 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. This dilution afforded the longest time before onset of gelation. Hexanediol dimethacrylate (HDDMA) was from Sartomer Company, West Chester, Pennsylvania. Triinethylolpropane trimethacrylate (TMPTM) was from Aldrich Chemical Company, Milwaukee, Wisconsin. 2,2'-azobis(2-methylbutanenitrile) (VAZO 67G), was from DuPont Specialty Chemicals, Wilmington, Delaware.

Specimens were divided into 18 treatment groups as summarized in Table 1. Each treatment group, except P and PWC, consisted of five replicates.

In situ, void filling polymerization

The wood specimens were dried at 105°C for 24 h to remove moisture and then weighed. The wood specimens were placed in a glass crystallizing dish and weighted down with glass weights to hold them under the solution. A vacuum (0.7 to 1.3kPa) was applied to the wood for 30 min. The monomer solution containing HDDMA, 0.5% VAZO 67G catalyst, and 5% TMPTM (if added) crosslinker was introduced into the container. The vacuum was maintained for 5−10min to remove air from the monomer. The vacuum was then released, and the chamber returned to atmospheric conditions. The wood and solution were allowed to stand for 30 min. The treated wood was removed from the solution, wiped to remove excess chemical from the outside of the specimens, wrapped in aluminum foil, placed in a hot oven, and heated at 105 °C for 20 h. Aluminum foil was then removed, specimens were weighed again, and percentage weight gain calculated. Some polymer was on the surface ofthe wood and was left on.

Surface modification

The treatments are described below in Table 1. Each group of specimens was coated by placing in separate reaction vials filled with 40-mL of the appropriate WSA sol. The reaction vials were then placed on a horizontal shaker to react for 24 h at room temperature. After reaction, the specimens were placed in an oven to dry for 6 h at 65° C, and to cure for 24 h at 105°C.

Table 1: Description of surface treatment specimens

Specimen ID	Treatment	Replicates
C	Control	5
P	Void filling polymerization	10
PWC	Void filling polymerization w/crosslinker	10
W6	WSA-6511	5
W6+P	WSA-6511 followed by void filling polymerization	5
W6+PWC	WSA-6511 followed by void filling polymerization w/crosslinker	5
P+W6	Void filling polymerization followed WSA-6511	5
PWC+W6	Void filling polymer w/crosslinker followed by WSA-6511	5
W7	WSA-7021	5
W7+P	WSA-7021 followed by void filling polymerization	5
W7+PWC	WSA-7021 followed by void filling polymerization w/crosslinker	5
P+W7	Void filling polymerization followed by WSA-7021	5
PWC+W7	Void filling polymer w/crosslinker followed by WSA-7021	5
W9	WSA-9911	5
W9+P	WSA-9911 followed by void filling polymerization	5
W9+PWC	WSA-9911 followed by void filling polymerization w/crosslinker	5
P+W9	Void filling polymerization followed by WSA-9911	5
PWC+W9	Void filling polymer w/crosslinker followed by WSA-9911	5

Accelerated weathering

For accelerated weathering studies, three replicates from each treatment group were exposed for a total of 240 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 at a rate of 0.2 L/min). The light source was a Xenon arc lamp with borosilicate inner and outer filters, and its irradiance was controlled at 0.35 $W.m^{-2}$ at 340 nm. During the light and spray cycle, the black panel temperature (BPT) was 50±5 °C; and RH was 80±5%.

Colour measurements

The colour of each specimen was measured at three contiguous spots with a Konica Minolta CR-400 Chroma Meter (Minolta Co., Ltd., Osaka, Japan).

Colour measurements were determined according 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 exposure in the Weather-Ometer™. These values were used to calculate the resulting colour change, qE*, and chromaticity change, qC* according to the following equations:

$$qL^* = L^*_{(t)} - L^*_{(i)} \quad (1)$$
$$qa^* = a^*_{(t)} - a^*_{(i)} \quad (2)$$
$$qb^* = b^*_{(t)} - b^*_{(i)} \quad (3)$$
$$qC^* = \{qa^{*2} + qb^{*2}\}^{1/2} \quad (4)$$
$$qE^* = \{qL^{*2} + qa^{*2} + qb^{*2}\}^{1/2} \quad (5)$$

qL*,qa*, and qb* are differences between the initial (i) and exposure time (t) values.

RESULTS AND DISCUSSION

The average weight percentage gain and standard deviations of the *in situ* polymerized specimens are summarized in Table 2.

Table 2: Average weight gain of specimens after in situ polymerization

Specimen ID	Treatment	WPG (STDEV)
P	Void filling polymerization	68.31 (9.84)
PWC	Void filling polymerization w/crosslinker	63.82 (8.79)
W6+P	WSA-6511 followed by void filling polymerization	64.95(6.73)
W6+PWC	WSA-6511 followed by void filling polymerization w/crosslinker	57.39(3.58)
W7+P	WSA-7021 followed by void filling polymerization	72.94 (3.54)
W7+PWC	WSA-7021 followed by void filling polymerization w/crosslinker	67.15(7.09)
W9+P	WSA-9911 followed by void filling polymerization	68.63 (4.37)
W9+PWC	WSA-9911 followed by void filling polymerization w/crosslinker	59.62(7.83)

The specimens were evaluated for weight loss and colour changes caused by weathering.

Weight loss

As shown in Figure 1, specimens treated with either the polymer or with polymer with crosslinker or with sol-gel showed less weight loss compared to the non-treated control specimens. This suggests that the polymer or the sol-gel or a combination of both the polymer and the sol-gel improved the resistance of the wood to erosion under accelerated weathering conditions. Improved resistance to erosion increased in the order sol-gel < polymer ≈ polymer with crosslinker < sol-gel with polymer ≈ sol-gel with polymer+crosslinker.

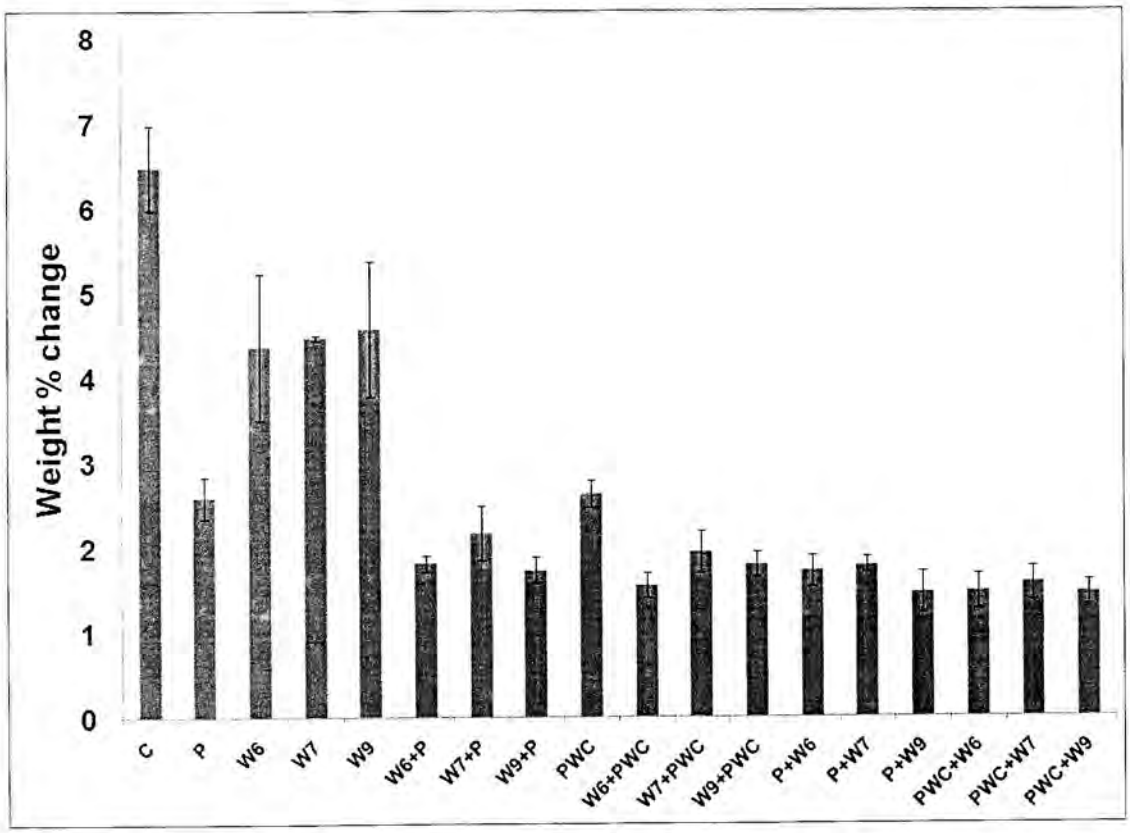

Figure 1: Average weight percentage change of specimens after 240-h exposure in Weather-Ometer™

Colour change measurements

Figure 2 shows the average lightness change, ΔL^* of the specimens after exposure for 240 h in the Weather-Ometer™. Except for those specimens treated with the sol-gel followed by polymer with crosslinker, there was little difference in lightness change between the treated and the control non-treated specimens. However, compared with control non-treated specimens, average chromaticity changes, ΔC^*, were generally lower for those specimens treated with sol-gel, WSA6511 in combination with either the polymer or polymer with crosslinker. (See Figure 3).

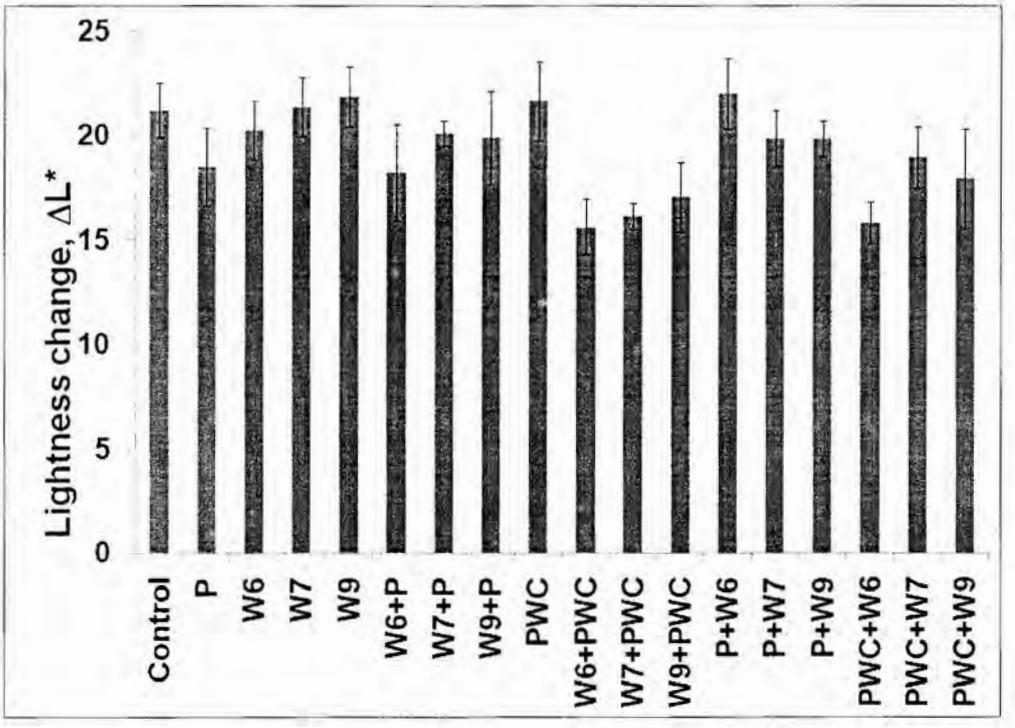

Figure 2: Average lightness changes of specimens after 240-h exposure in Weather-Ometer™

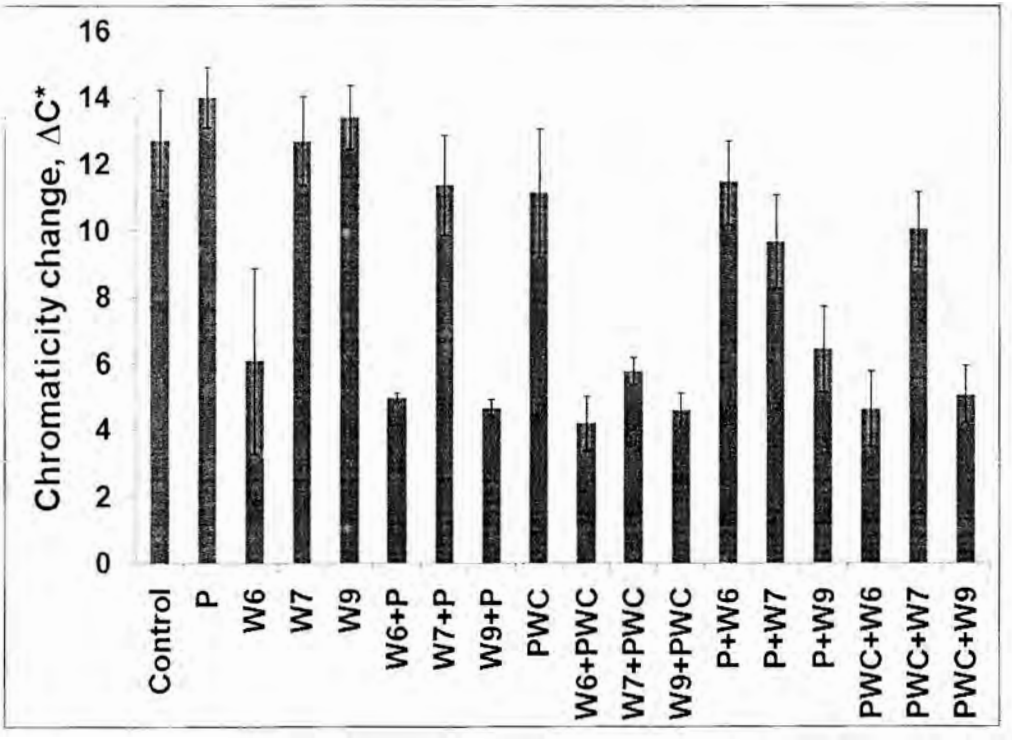

Figure 3: Average chromaticity changes of specimens after 240-h exposure in Weather-Ometer™

Average colour changes of the specimens after 240-h exposure in the Weather-Ometer™ are shown in Figure 4. Specimens treated with sol-gel followed by polymer with crosslinker showed the greatest resistance to colour change compared with the non-treated control specimens. It is also interesting to note that the average colour changes, ΔE*, followed a similar pattern to the average lightness changes as illustrated in the plot of ΔE* versus ΔL* in Figure 5.

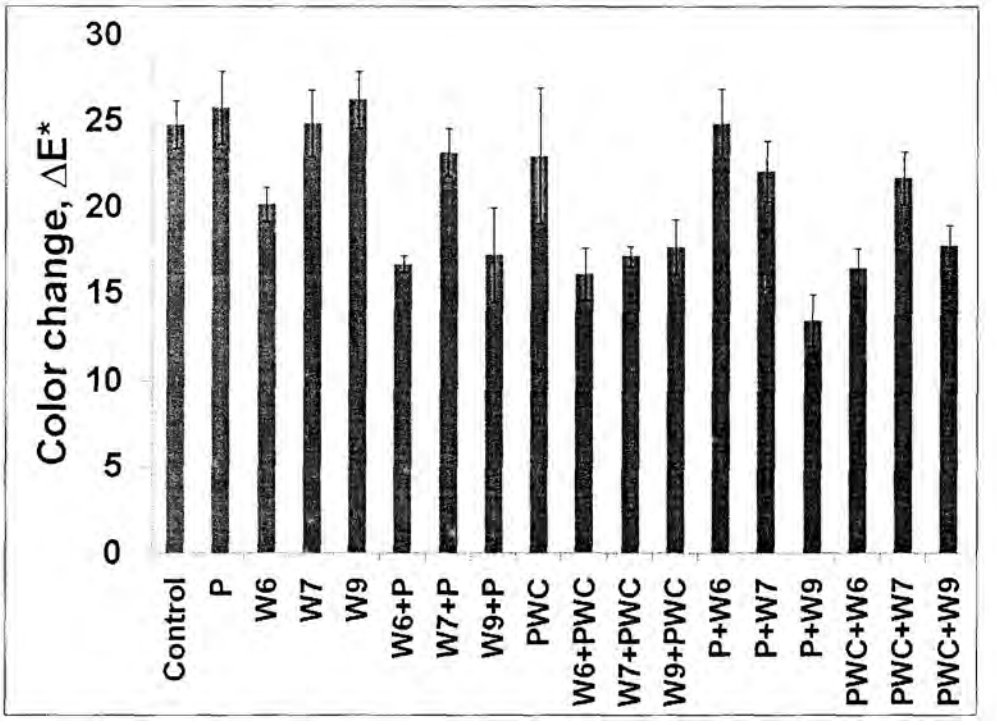

Figure 4: Average colour changes of specimens after 240-h exposure in Weather-Ometer™

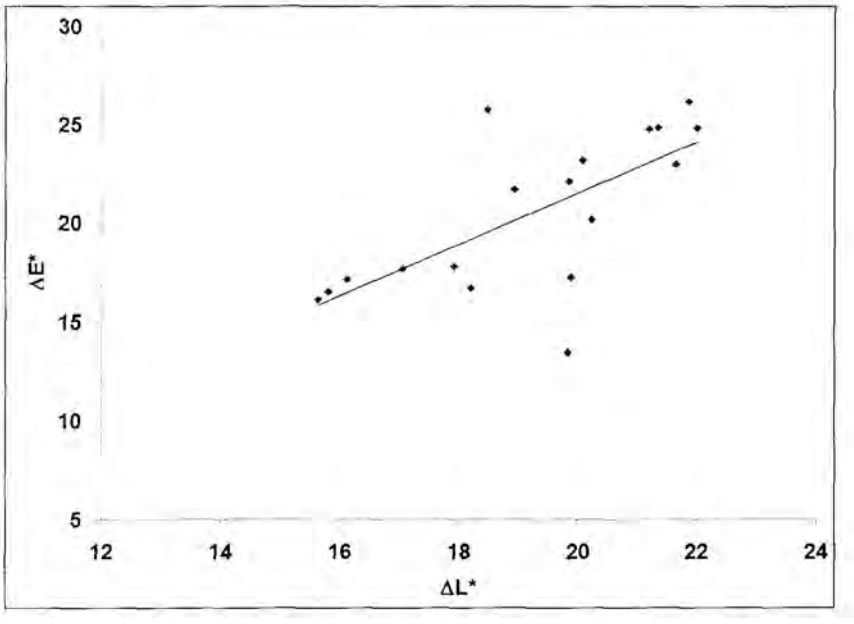

Figure 5 Plot of ΔE* versus ΔL*, with trend line indicating a linear correlation between these two parameters

CONCLUSIONS

These results indicate that some sol-gel systems (for example WSA6511) have the potential to improve colour stability of wood-polymer composites. In addition, the order of treatment appeared to be important. For example, specimens that were treated with sol-gels before *in situ* polymerization with polymer or with polymer and crosslinker appeared to show better resistance to weathering in terms of resistance to weight loss and colour stability.

Weathering exposure on these specimens continues. Future research is required to optimize the sol-gel deposition conditions in addition to understanding the influence of the chemistry of the sol-gel systems on weathering performance of wood polymer composites.

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Edited by C.A.S. Hill, H. Militz and B. Andersons

Riga, 2010