Natural Weathering of Scots Pine (*Pinus sylvestris* L.) Wood Modified by Functionalized Commercial Silicone Emulsions

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ABSTRACT

Quat-silicone micro emulsion (<40 nm), amino-silicone macro emulsion (110 nm) and alkyl modified silicone macro emulsion (740 nm) were used to modify Scots pine (*Pinus sylvestris* L.) sapwood. Treated and uncoated panels were exposed to natural weathering for one year along with water treated controls according to EN 927-3. The results of colour measurement done according to the CIELab system showed that the silicone emulsions did not improve the colour stability. Treatment with amino-silicone emulsions gave yellowish appearance of the wood surface before weathering, evident from the higher chroma value compared to that of other treatments and the untreated controls. The amino-silicone treated specimens were found less overgrown by staining fungi than the other treated samples, but to a similar extent as the controls. Surface cracking of the treated and untreated specimens was analyzed by measuring the surface roughness. Quat- and amino-silicone treated specimens showed reduced surface roughness compared to the alkyl modified silicone treated as well as to the untreated control specimens.

INTRODUCTION

Photo-degradation, surface roughness, and surface checking or cracking are the major weathering phenomena of wood used for outdoor applications (Chang *et al.* 1982). The surface weathering is attributed to the photosensitivity and consequential deterioration of almost all wood cell wall components (Gellerstedt and Petterson 1977) by ultraviolet light of solar irradiation that usually penetrates up to 75 µm of wood surface (Hon and Feist 1980). Photo-degradation is initiated by the depolymerization of lignin due to rapid oxidation (Hon 1981). This results in the formation of chromophores due to free radical reactions (Lin and Kringstad 1970). The degradation products of lignin are washed out by water, which also opens up new areas for photo-degradation (Feist 1982). Moreover, the change of wood dimensions due to different moisture content leads to the formation of cracks and checks in wood (Chang *et al.* 1982). The development of checks and cracks facilitates the colonization of wood by insects, bacteria and fungi (Kamdem and Grelier 2002). The colonization of *Aureobasidium pullulans*, the most common fungal strain and able to metabolize the photo-degraded lignin, holocellulose and derived sugars (Schoeman and Dickinson 1997), gives a grey hue to the weathered surface (Xie *et al.* 2008a). Photo-degradation and surface roughening along with fungal colonization drastically affects wood appearance and this is why protection from weathering is of significant economic importance.

Silicones are polydimethysiloxanes and have been reported to impart hydrophobicity as well as improve dimensional stability of wood (Weigenand *et al.* 2007; Ghosh *et al.* 2008a). Studies also show that functional silicones can reduce the growth of blue stain and mould fungi on wood surfaces (Ghosh *et al.* 2008a) and increase resistance to decay fungi (Weigenand *et al.* 2008; Ghosh *et al.* 2008b). Treatment of wood with water repellents can reduce coating failure by reducing water accumulation in the wood substrate, but they result in poor spreading and adhesion of water-borne finishes on wood surface (Lukowsky *et al.* 1997). This is why uncoated Scots pine wood treated with commercial silicones with different functional groups were exposed outside to study the weathering performance in terms of colour change, crack formation and infestation of staining fungi on the wood surfaces.

MATERIALS AND METHODS

Chemicals

Quat-silicone micro-emulsion (QuatSiMiE, <40 nm particle size), amino-silicone macro-emulsion (AminoSiMaE, 110 nm) and alkyl-modified silicone macro-emulsion (AlkylSiMaE, 740 nm) were supplied by Momentive GmbH, Leverkusen, Germany (Table 1). In order to adjust the treatment concentration, the stock solutions were diluted with demineralised water considering the silicone content (Ghosh *et al.* 2008a).

Table 1: Name and chemical properties of silicone emulsions tested

Formulation	**Emulsion particle (nm)**	**Silicone content (%)**	**N-content (mmol g^{-1})**	**Structure of functional group**
Quat silicone micro-emulsion (QuatSiMiE)	<40	35	0.25	quaternary ammonium, R^1-$N^+(CH_3)_2$-R^2
Amino silicone macro-emulsion (AminoSiMaE)	110	35	0.25	Amino, $(CH_2)_3$-NH_2
Alkyl modified silicone macro-emulsion (AlkylSiMaE)	740	35	0	Alkyl modified, (-CH_{12}-C_{14})

Anti-swelling efficiency (ASE) and capillary water uptake

The anti-swelling efficiency (ASE) of treated wood blocks was calculated between the oven dried and water saturated state and was expressed as the ratio of the volumetric swelling coefficients of treated and untreated specimens (Donath et al. 2004). Capillary water uptake along three directions (longitudinal, tangential and radial) was tested according to the standard DIN 52617 (1987). Wood specimens for longitudinal uptake (20 x 20 x 200 mm^3, R x T x L) and for tangential and radial uptake (40 x 40 x 40 mm^3, R x T x L) were treated with silicone emulsions (15% silicone). Five replicates were used; water impregnated specimens served as a control. The specimens were sealed along four faces keeping only the cross sections, the radial or the tangential faces open to test longitudinal, tangential and radial water uptake. The specimens were set on a water saturated sponge so that the wood specimens took up water only through the face in contact with the sponge. The test was terminated when water reached the face opposite to that in contact with the saturated sponge. The water uptake coefficient was calculated for all three directions considering the uptake data of the first 24h using the equation, $w_t = \Delta W_t \, \Delta t^{-0.5}$, where w_t is the water uptake coefficient (kg m^{-2}h$^{-0.5}$), ΔW_t is the mass of water uptake per area (kg m^{-2}); and t is the time (h).

Natural weathering

Scots pine (*Pinus sylvestris* L.) sapwood (75 x 15 x 150 mm^3, R x T x L, 5 specimens per treatment) impregnated (100 mbar vacuum 1h, 12 bar pressure 1h) with 5% and 15% of the three silicone emulsions were cured from 30 to 103 °C. Water impregnated and subsequently cured specimens served as controls. Following the instructions of EN 927-3, the specimens were placed on weathering racks in the test field of Georg-August Universität, Göttingen for 12 months (August 2007 to August 2008). Every three months, colour change and surface roughness were determined after conditioning the specimens at 20 °C and 65% RH for one week.

Colour measurement

The colour of the specimens was determined with a spectrophotometer CM500, equipped with a standard illuminant D65 (Minolta, Japan) using the CIE-Lab system (Eqn. 1, 2, 3, 4, 5).

$$\Delta L_t^* = L_t^* - L_i^* \qquad (1)$$

$$\Delta a_t^* = a_t^* - a_i^* \qquad (2)$$

$$\Delta b_t^* = b_t^* - b_i^* \qquad (3)$$

$$\Delta E_t^* = [(\Delta L_t^*)^2 + (\Delta a_t^*)^2 + (\Delta b_t^*)^2]^{1/2} \qquad (4)$$

$$C = [a_t^{2*} + b_t^{2*}]^{1/2} \qquad (5)$$

Where, L^* is the lightness (ranging from 0 or black to 100 or white), a^* and b^* are the chromaticity coordinates (+*a* refers to red, –*a* refers to green colouration, while +b and –b respectively denote yellow and blue), the subscripts i and t are the initial time and the time after weathering (*e.g.* t = 3, 6, 9, 12 weeks), ΔL_t^*, Δa_t^* and Δb_t^* are changes of lightness and the colour coordinates, ΔE^* is the colour change due to weathering, and C is the chroma. In order to assess the effect of weathering on the macroscopic appearance, the panel surfaces were scanned before and after weathering using an Epson Expression 10000XL scanner (Epson, UK).

Surface roughness

A Perthometer S4P (Feinprüf Perthen GmbH, Germany), operating with stylus method, was used to measure surface roughness. Following surface roughness measurement values of R_a, R_z and R_{max} were recorded for each surface, which are commonly used parameters for surface characterization (Hiziroglu 1996). The average roughness (total 20 measurements, 4 measurements on each specimen surface) is denoted by R_a, which represents the average deviation of the roughness profile, but it does not differentiate between the peaks and valleys of a surface profile (Maldas and Kamdem 1998). In addition, R_z (mean of peak-to-valley height) and R_{max} (maximum roughness depth) were also used for surface roughness characterization. The relative roughness (R′) for all parameters *e.g.*, R_a', R_z' and R'_{max} of all surfaces were calculated using the Eqn. 6,

$$R = R_t/R_0 \qquad (6)$$

Where, R_t is the roughness parameter of wood after natural weathering and R_0 is the value of the respective specimen before weathering.

RESULTS AND DISCUSSIONS

Anti-swelling efficiency (ASE) and capillary water uptake

All treated and untreated specimens showed the highest water uptake in the longitudinal direction due to the longitudinal orientation of the tracheids. The water uptake was reduced in all three directions due to silicone treatment (Figure 1A), but the most pronounced reduction was found for longitudinal uptake. The macro-emulsions (AminoSiMaE, AlkylSiMaE) caused greater reduction in water uptake along all three directions than the micro-emulsion QuatSiMiE. This might be due to deposition of greater amounts of silicone in the lumens of tracheids and rays as the main flow paths. SEM-EDX studies revealed that silicone of macro-emulsions partly filled tracheid lumens of both earlywood and latewood cells completely, while silicone of micro-emulsions covered only the inner lumen surface of tracheids (Weigenand *et al.* 2007). QuatSiMiE induced 21.8% ASE, whereas AminoSiMaE and AlkylSiMaE brought about 19.0% and 5.4% ASE (Figure 1B). This trend coincides with previous findings that micro-emulsion caused greater ASE than macro-emulsions (Weigenand *et al.* 2007).

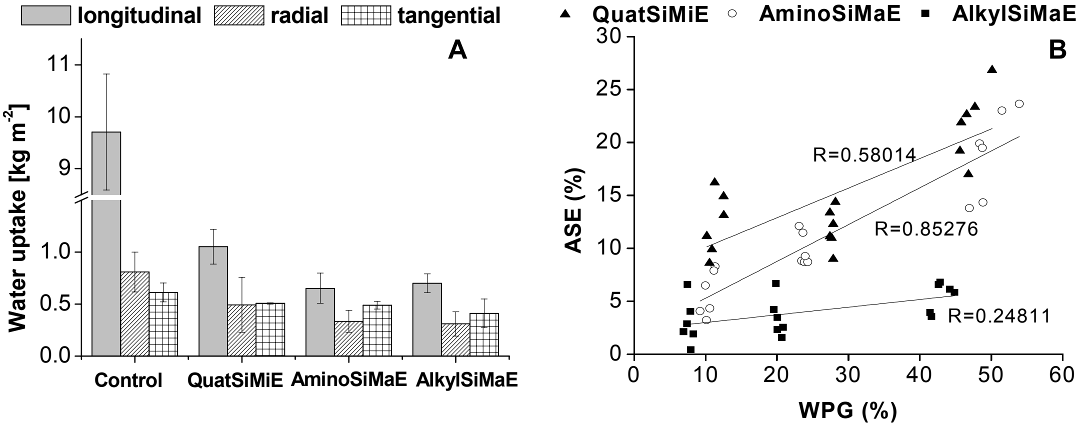

Figure 1: Water uptake coefficient of Scots pine wood treated with 15% QuatSiMiE, AminoSiMaE, AlkylSiMaE and of the controls (A), anti-swelling efficiency (ASE) of Scots pine sap wood treated with the silicone emulsions (B)

Colour measurement

Independent from weathering, the treatment of wood with silicone emulsions changed the colour parameters compared to water treatment (controls). Lightness was reduced (Figure 2A), while the chroma increased (Figure 2B, see values before weathering, t = 0 month). Changes of lightness and chroma were higher at higher silicone content. This phenomenon can be attributed to functional groups of the silicones. Treatment with amino-silicone (AminoSiMaE) caused the greatest shift in the chroma attributable to higher Δb-value, i.e., a yellowing of the panels. After weathering, the panels treated with quat- (QuatSiMiE) and amino-silicone emulsions (AminoSiMaE) displayed similar colour changes (ΔE) as the controls, while the specimens treated with alkyl-modified silicone (AlkylSiMaE) showed a higher ΔE-value after weathering (Table 2). The colour changes (ΔE) of the AlkylSiMaE-treated panels were mainly caused by the change in lightness (ΔL), which is attributable to the colonization of the wood surface by staining fungi (Table 2, also see below).

Table 2: Colour components of Scots pine specimens after 12 months of natural weathering (values in brackets show standard deviation)

Treatment	WPG (%)	Colour components			
		ΔE^*	ΔL^*	Δa^*	Δb^*
QuatSiMiE	8.3(0.9)	35.8(3.1)	27.6(4.0)	5.0(1.0)	22.1(1.1)
AminoSiMaE	6.5(0.9)	36.1(2.5)	22.4(4.0)	5.8(1.7)	27.3(2.7)
AlkylSiMaE	7.8(0.4)	38.6(3.8)	31.2(3.9)	4.2(1.6)	22.1(3.1)
QuatSiMiE	16.4(1.9)	31.9(1.4)	22.2(2.0)	5.5(0.5)	22.2(1.3)
AminoSiMaE	15.3(4.3)	37.5(2.0)	20.7(3.1)	6.5(1.2)	30.4(2.0)
AlkylSiMaE	16.3(1.3)	45.7(3.3)	39.4(3.7)	3.5(0.8)	22.5(3.5)
Control	-	36.2(2.8)	28.1(3.3)	4.4(0.9)	22.3(1.2)

Accordingly, AminoSiMaE-treated panels exhibited the lowest ΔL-value, i.e. the lowest degree of fungal colonization. Recently results from laboratory experiments revealed that AminoSiMaE was the most effective and AlkylSiMaE the least effective formulation in preventing blue stain infestation (Ghosh *et al.* 2008a). The relatively high ΔE-value of the AminoSiMaE-treated panels is attributable to the high Δb-value which indicates yellowing of the surfaces and might be caused by oxidation of the amino-groups in the silicone (Xie *et al.* 2008b). Maximum reduction in lightness and chroma occurred during the first three months of weathering in treated and control panels (Figure 2) and diminished afterwards at a more or less similar velocity.

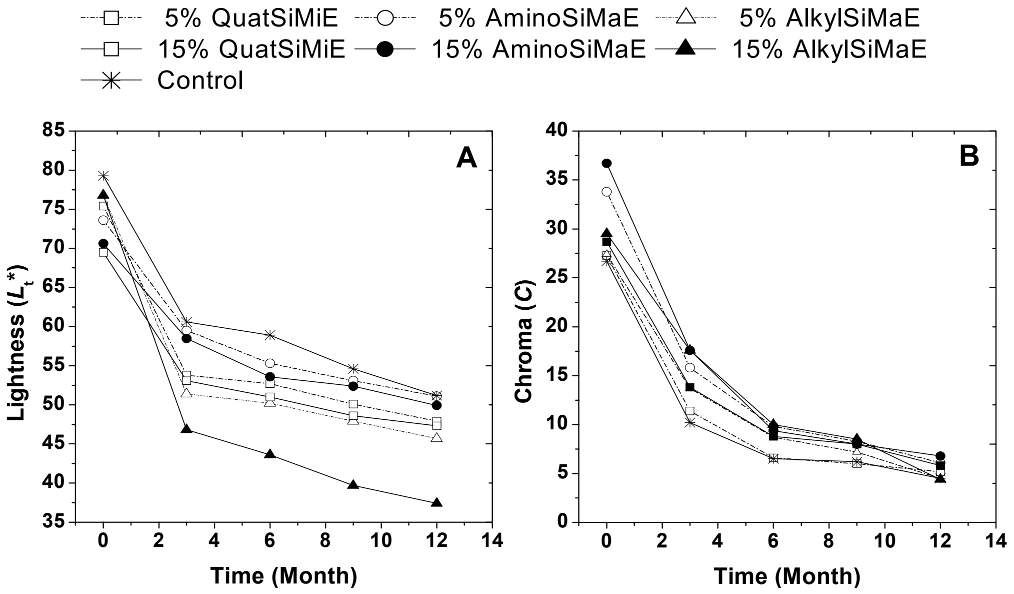

Figure 2: Change of lightness (L_t*) and Chroma (C) of silicone-treated and untreated Scots pine panels

This decrease is due to the degradation and wash-out of chromophoric lignin at the initial phase of exposure and due to fungal colonization (Donath *et al.* 2007). Depolymerization of lignin and other wood components is mainly caused by the UV light of solar irradiation within the region ranging from 300 to 550 nm (Hon and Chang 1985). The reduction of lightness and chroma of silicone treated Scots pine ensures that the treatment cannot protect lignin from photo-degradation. The finding is in agreement with Ghosh *et al*. (2008a) reporting the breakdown of lignin in artificially weathered Scots pine treated with the same silicones.

Macroscopic surface appearance

The macroscopic appearance of untreated and treated specimen surfaces after weathering (front) showed the evidence of photodegradation (Figure 3). The front face of control specimens appeared to be dark grey, while QuatSiMiE and AminoSiMaE treatment at low and high treatment concentrations showed similar appearance. But the specimen surfaces of AlkylSiMaE treatment appeared to be darker at both low and high treatment concentrations. The appearance of the reverse faces of both treated and control specimens gave the evidence of the growth of staining fungi. Least growth intensity of staining fungi was found in case of AminoSiMaE treated specimens at both treatment concentrations followed by AlkylSiMaE, QuatSiMiE and untreated controls.

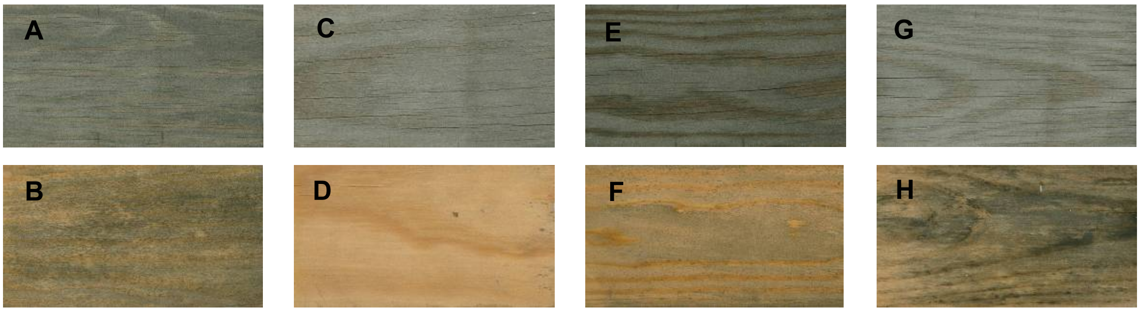

Figure 3: Appearance of wood surfaces after 12 months of natural weathering treated with QuatSiMiE front (A) and back (B), AminoSiMaE front (C) and back (D); AlkylSiMaE front (E) and back (F), water treated control front (G) and back (H)

Ghosh *et al.* (2008a) found that AminoSiMaE could strongly reduce the growth of staining and mould fungi in the laboratory tests. The resistance of specimens treated with QuatSiMiE was lower than that of AminoSiMaE-treated specimens, while AlkylSiMaE-treated specimens showed no resistance. With respect to the reverse surface, the treatment with AlkylSiMaE appeared to be more effective in reducing fungal staining than that with QuatSiMiE. This might be due to the more hydrophobic nature of the alkyl-modified silicone compared to the quat-silicone (Ghosh *et al.* 2008a). As a consequence, AlkylSiMaE might prevent the penetration of rain water through the panels more efficiently than QuatSiMiE and, thus, reduces the availability of moisture for the staining fungi on the reverse, indirectly exposed surface.

Surface roughness

The relative roughness parameters R′ of both untreated and silicone treated wood specimens are given in Table 3.

Table 3: Relative surface roughness parameters of silicone emulsion treated and untreated wood.

Treatment	WPG	R'a	R'z	R'max
QSMiE	8.3(0.9)	3.3(0.7)	3.6(0.8)	3.3(1.1)
ASMaE	6.5(0.9)	3.4(0.7)	3.7(1.1)	3.4(0.4)
AmSMaE	7.8(0.4)	3.5(1.0)	3.8(1.8)	3.5(0.9)
QSMiE	16.4(1.9)	2.1(0.5)	1.9(0.6)	2.1(0.6)
ASMaE	15.3(4.3)	2.5(0.8)	2.4(0.5)	2.5(1.0)
AmSMaE	16.3(1.3)	3.3(0.6)	3.1(0.7)	3.3(0.6)
Control		3.8(0.9)	3.9(1.1)	3.8(1.7)

R´ values close to 1 indicates little to negligible changes of the wood surface roughness (Kamdem and Grelier 2002). The different R´values of treated and untreated wood specimens indicate that the 12 months natural weathering resulted in the formation of rough surfaces. The treatment of wood with silicone emulsions at low concentration (5%) performed similar to the control samples (Table 3). Nevertheless, treatment with higher concentration (15%) resulted in reduced R´ values indicating smoother surfaces or fewer cracks, which was restricted to only QuatSiMiE and AminoSiMaE treatment. Control specimens of Scots pine were found to form more and wider cracks on the exposed surface. The cracking can be attributed to the dimensional changes of wood responding to moisture conditions. The results from Figure 1 reveal that the particle size of silicone emulsions influenced the anti-swelling efficiency of treated Scots pine. QuatSiMiE and AminoSiMaE having comparatively smaller particle size resulted in higher ASE than AlkylSiMaE. The reduced roughness of the panels treated with QuatSiMiE and AminoSiMaE (15%) can be attributed to this higher ASE. The ASE imparted by AlkylSiMaE was clearly lower, but it induced higher hydrophobicity than QuatSiMiE and AminoSiMaE. This reveals that dimensional stabilization seems to be more crucial in terms of cracking reduction than hydrophobation.

CONCLUSIONS

The silicone emulsions used in this study were not able to reduce the discolouration of surfaces directly exposed to natural weathering. While the panels treated with AminoSiMaE displayed comparable greying than the controls, those treated with QuatSiMiE and AlkylSiMaE turned even darker. These results show, on the one hand, that the used silicones cannot protect the lignin from photo-degradation. On the other hand, the efficacy of silicones against fungal staining under long-term natural weathering conditions is much lower than that observed in laboratory tests (Ghosh et al. 2008a). In contrast, all silicones reduced the staining of the reverse, indirectly weathered sides of the panels. This effect can be attributed to hydrophobation of the entire panel which inhibits the migration of moisture from the front to the reverse surface. The QuatSiMiE and AminoSiMaE reduced surface cracking to a higher degree than AlkylSiMaE. The effect is mainly attributed to a higher dimensional stabilization imparted by the amino- and quat-silicone rather than to hydrophobation.

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