Effect of quat- and amino-silicones on fungal colonisation and decay of wood

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Abstract

Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus sylvatica* L.) wood samples treated with quaternary (quat)- and amino-silicone (QS and AS) solutions of different chain lengths were tested against brown-rot and white-rot fungi as well as with regard to blue stain colonisation. The treatment with short-chained silicones bearing quat and amino functional group reduced the mass loss (ML) by decay fungi at 15% treatment concentration. The release of metabolic heat by decayed samples determined in a microcalorimeter corresponded with the ML of the samples, i.e., samples with high ML produced more heat indicating higher fungal activity. Short-chain ASs reduced the blue staining more strongly than long-chain ones. However, the opposite was true in the case of QS. It was assumed that the combined effect of hydrophobation, cell wall bulking and change of the wood surface energy are responsible for a successful performance of silicone compounds as wood preservatives.

Keywords: amino-silicone; blue stain; brown rot; microcalorimetry; quat-silicone; white rot.

Introduction

Treatment with emulsions of silicones (polydimethylsiloxanes) bearing amino and quaternary ammonium (quat) groups enhances the resistance of solid wood against decay and staining fungi, while an alkyl-modified silicone formulation is not effective in this regard (Ghosh et al. 2008, 2009; Weigenand et al. 2008). Ghosh et al. (2008, 2009) reported that emulsions of silicones bearing primary amino groups are more effective

in preventing wood decay and staining than those bearing quat groups. This is unexpected, as quat ammonium compounds are conventionally utilized as wood preservatives (Preston et al. 1987; Urbanik et al. 1997; Pernak et al. 1998, 2004; Thang and Ruddick 2000; Matejuk et al. 2004). The tested products were commercial ready-to-use formulation with different-sized emulsion particles and emulsifiers, which could have unknown effects on fungal physiology and on wood properties. The emulsion particle size could have a crucial influence on the durability of wood because it influences the penetration of silicone into the wood cell wall. From the studies of Ghosh et al. (2008, 2009), it can be assumed that the reduction of water uptake alone cannot increase wood durability. Deposition of silicone within the cell wall might reduce moisture absorption and prevent the access of agents that are involved in the decay of cell wall polymers (Hill 2006). Probably, chemical modification hinders penetration of low-molecular weight diffusible agents required for fungal degradation into the cell wall via cell wall bulking and micropore blocking (Papadopoulos and Hill 2002; Hill et al. 2005). Amino-silicone (AS) microemulsions penetrated the cell walls of Scots pine better than the corresponding macroemulsions (Weigenand et al. 2007). Silicones have the property of spreading on various surfaces and of forming a thin layer (Noll 1968). Because of their high zeta potential, ASs might also form a closed layer on the inner surfaces of the cell lumens and prevent fungal colonisation due to surface effects.

With respect to organo-silicone compounds, mainly silane systems were applied to improve resistance to fungi; systems bearing primary amino groups and quat ammonium groups were particularly effective against basidiomycetes. Donath et al. (2006) showed that the antifungal behaviour is due to primary amino groups, while in alkyl groups, by influencing mainly the water uptake play a secondary role.

Isquith et al. (1972) reported on the antimicrobial activity of 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (Si-QAC). The treated wood was tested against bacterial and mixed spore suspension with respect to staining and soft-rot fungi. Si-QAC was applied in combination with an oligomeric silane system for incorporating quat ammonium sites into a SiO₂ matrix via a sol-gel process. This combined treatment enhanced the decay resistance of pine wood against *Coniophora puteana* significantly (Donath et al. 2006). The decay resistance against basidiomycetes was significantly enhanced by adding low proportions of the amphoteric quat ammonium compound 3-(trimethoxysilyl)-propyl (carboxymethyl) decylmethyl ammonium hydroxide inner salt (TMSAH) to tetraethoxysilane for impregnation of wood. A further increase in decay resistance was achieved by additional application of the water repellent 2-heptadecaflu-

oroctylethyl-trimethoxy-silane (HFOETMOS) to this silane mixture (Tanno et al. 1998).

Fungal activity in wood can be assessed by measuring the mass loss (ML) of the infected wood (Wälchli 1970), the respiration, i.e., production of carbon dioxide (Smith 1967; Weigenand et al. 2008), production of ATP, ergosterol (Bjurman 1992, 1994), total esterase (Kerem et al. 1992; Bjurman 1993) or immunodiagnostics (Clausen 1996; Clausen and Green 1996, 1998).

Isothermal microcalorimetry is useful to measure the metabolic activity of chemical reactions or of the metabolic activity in a living organism. Determination of metabolic heat (energy) in a microcalorimeter is a non-destructive, reproducible method that has been applied for the determination of fungal activity in a number of studies (Criddle et al. 1991; Xie et al. 1997; Bjurman and Wadsö 2000). Verma et al. (2008) evaluated the activity of white- and brown-rot fungi in chemically modified wood by this method. The total (net) heat output measured in a calorimeter is equal to the metabolic enthalpy change and can be subdivided into a catabolic and an anabolic part (Dermoun and Belaich 1980). The released heat is proportional to the consumption of nutrients as long as the mode of metabolism does not change (Xie et al. 1997). Catabolic metabolism, however, constitutes the main part of metabolism in terms of heat (energy) release.

The present study focusses on the effects of water-based solutions of ASs and quat-silicones (QSs) with respect to resistance improvement of wood against fungal colonisation and decay. Microcalorimetric observation of the metabolic activity and ML measurement will be the main methods applied for evaluation of the silicones' effectiveness.

Materials and methods

Chemicals

Silicones or polydimethylsiloxanes bearing amino and quat ammonium groups were supplied by Momentive Performance Materials GmbH (Leverkusen, Germany). The chain length, i.e., the number of dimethylsiloxane units (D) and the structures of the functional groups are given in Table 1. QSs were supplied in 50% isopropanol

Table 1 Chemical properties of QSs and ASs; [M]=R₃SiO_{1/2}, [D]=R₂SiO_{2/2}.

Chemical name	Chain length	N content (mmol g ⁻¹)	Structure of functional group
QS	10	2.7	R ¹ R ² N ⁺ CH ₃ -R ³
QS	30	0.9	R ¹ R ² N ⁺ CH ₃ -R ³
AS	7	3.0	M-amino-D7-M-amino, amino=CH ₂ CH ₂ CH ₂ NH ₂
AS	9	2.4	M-amino-D9-M-amino, amino=CH ₂ CH ₂ CH ₂ NH ₂
AS	26	0.96	M-amino-D26-M-amino, amino=CH ₂ CH ₂ CH ₂ NH ₂
AS	30	4.2	M-D25-(Damino) ₅ -M, amino=CH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NH ₂

in 1:1 (w/w), and the ASs were supplied as 100% silicone. The ASs were diluted (1:1 w/w) in isopropanol to make comparable solutions as QSs. All solutions were further diluted with water to reach the desired silicone concentration. For solubility enhancement of ASs, 1.25 ml acetic acid was added for 1.0 g of silicone.

White- and brown-rot decay

Mini wood blocks 5×10×30 mm³ (R×T×L) of Scots pine sapwood (*Pinus sylvestris* L.) and European beech wood (*Fagus sylvatica* L.) were vacuum pressure impregnated at 100 mbar (1 h) and 12 bar (1 h) with 5% and 15% of the aqueous silicone solutions. Subsequently, the specimens were dried gradually from 40°C to 103°C and weighed. All treated specimens were subjected to an accelerated leaching procedure according to the European standard EN 84 (1997) and dried again gradually from 30°C to 103°C for determination of the dry mass. The absolute weight gain (kg m⁻³) and the weight percent gain (WPG) were calculated from the dry masses before and after treatment. Fifteen replicates were made per treatment; three of the replicates were submitted to microcalorimetry. The specimens were then stored in a climate chamber at 20°C and 65% RH for about 2 weeks.

Resistance of wood treated with silicone solutions to basidiomycete decay was evaluated according to Bravery (1978). Treated and untreated beech wood (*F. sylvatica* L.) was tested with *Trametes versicolor* (CTB 863 A) and pine sapwood (*P. sylvestris* L.) with *C. puteana* (BAM Ebw. 15). After conditioning (20°C, 65±5% RH) and sterilisation through γ-irradiation (25 kGy, Isotron, Netherlands), the specimens were inoculated on 4% malt agar (Scharlau, Spain) in Kolle flasks. In each Kolle flask, three treated samples were exposed together with three control specimens. Fifteen treated and untreated replicates were tested per treatment over an exposure time of 12 weeks. After incubation, the specimens were oven dried to determine the ML.

Microcalorimetry

The measurement temperature was 25°C, and the microcalorimeter (Thermal Activity Monitor 2277, Thermometric, Jarvalla, Sweden) was located in a climatic chamber (Verma et al. 2008). Internal calibration was carried out at 3000 μW in the static mode. The detection limit was ±9 μW, and baseline stability over 6 h was ±15 μW. The ampoules (25 ml each) of every channel were allowed to equilibrate for 1 h in the standby position before heat production data were recorded at 300 s intervals over 6 h.

After a 12-week decay, the mini-blocks were removed from the Kolle flask, cleaned off the mycelia and put into the measuring ampoule as described previously. For measurements, three samples for each treatment and test fungi were taken from three different Kolle flasks. Three replicates were made per treatment. One ampoule filled with an untreated and undecayed sample served as reference. After measurement, the samples were oven dried at 103°C and weighed for

Table 2 Ranking of blue stain colonisation.

Rank	Description, st. areas
0	No st. at all
1	Beginning of st., single annual rings are st.
2	Up to 20% area is st.
3	More than 20% to 50% area is st.
4	More than 50% up to 75% area is st.
5	More than 75% area is st.

Table 3 Absolute weight gain and WPG of QS- and AS-treated Scots pine and European beech wood after EN 84. All values (n=15) represent mean values±standard deviation (SD).

Treatment (Concentration)	Absolute weight gain (kg m ⁻³)		WPG (%)	
	Scots pine	Beech	Scots pine	Beech
QS D10 (5%)	17.5±1.2	22.2±2.4	4.9±0.9	1.9±0.6
QS D30 (5%)	10.8±1.0	12.7±1.3	5.1±0.7	2.2±1.0
AS D7 (5%)	9.8±1.0	9.0±2.1	3.6±0.6	1.8±0.7
AS D9 (5%)	11.0±0.3	11.5±2.0	5.1±0.8	2.5±0.7
AS D26 (5%)	10.5±1.1	10.9±3.5	4.4±0.8	2.6±0.9
AS D30 (5%)	4.4±1.0	6.6±1.6	3.5±0.6	1.1±0.5
QS D10 (15%)	55.2±4.0	67.2±5.8	14.2±3.0	11.6±1.1
QS D30 (15%)	18.5±2.0	26.8±2.7	17.3±3.6	10.0±1.5
AS D7 (15%)	11.7±1.0	14.4±2.4	16.6±2.2	8.9±1.2
AS D9 (15%)	20.1±1.0	20.9±2.2	15.6±3.0	10.6±0.9
AS D26 (15%)	7.5±0.8	8.9±2.8	14.6±4.2	8.7±1.8
AS D30 (15%)	9.6±1.2	10.9±2.2	15.9±2.5	9.9±5.8

the calculation of ML. Cumulative energy production (E_{total}) [J] was calculated from the following equation, $E_{total} = \sum Q_i \times t$, where, Q_i is the heat (W) produced per time interval, t is the time interval (300 s).

Blue stain test

Scots pine samples measuring 5×40×40 mm³ (R×T×L, growth rings oriented at 45° with the tangential face) treated with 5% and 15% aqueous silicone solutions were subjected to accelerated leaching

as described in EN 84 (1997). The samples were then conditioned in the climate chamber (20°C, 65% RH). The sterilized samples (γ -irradiation, 25 kGy, Isotron, Netherlands) were dipped in mixed spore suspension of *Aureobasidium pullulans* (de Barry) and *Sclerophoma pithyophila* (Corda) and placed on the stainless steel wire mesh over a vermiculite media inoculated with 20 ml mixed spore suspension. Untreated samples of the same dimensions served as a control. Two samples of each treatment were placed in one Kolle flask; eight replicates were made per treatment. The inoculated samples were incubated for 8 weeks in a climate chamber at 20°C and 65% RH. The blue-stained (st.) area was analysed by means of an Epson Expression 10000XL scanner (Epson, UK) and the GIMP image processing software (GNU General Public Licences, developed online). The st. area was ranked from 0 to 5 (Table 2) on both surfaces.

Statistical analysis

Software: OriginLab 8.0 (OriginLab Corporation, Northampton, MA, USA). The data were first tested for normal distribution (Shapiro-Wilk test), and the mean values were compared by one-way ANOVA (Tukey test).

Results and discussions

Mini block test

Pine and beech wood samples had similar absolute weight gains after treatment with 5% and 15% concentration of QSS and ASs (Table 3). The WPG for the respective treatment concentrations was always lower in beech wood, due

Figure 1 Absolute ML of Scots pine sapwood due to decay by *C. puteana* (a, b) and of European beech wood due to decay by *T. versicolor* (c, d); 5% (a, c) and 15% (b, d) treatment concentration. (n=15, mean values±SD). Significantly different mean values (P<0.05) are denoted with different letters.

Table 4 Relative ML of Scots pine sapwood due to decay by *C. puteana* and of European beech wood due to decay by *T. versicolor* (n=15, mean values±SD).

Treatment (Concentration)	ML (%)	
	Pine with <i>C. puteana</i>	Beech with <i>T. versicolor</i>
AS D7 (5%)	33.9±6.1	34.3±7.6
QS D10 (5%)	36.3±5.6	19.6±4.7
AS D9 (5%)	46.4±8.6	31.9±4.6
AS D26 (5%)	46.7±3.5	39.6±8.2
QS D30 (5%)	44.5±8.7	23.8±5.1
AS D30 (5%)	48.9±11.0	43.3±8.7
AS D7 (15%)	1.0±0.7	7.2±3.0
QS D10 (15%)	4.6±1.1	6.4±3.3
AS D9 (15%)	1.6±0.7	11.8±4.6
AS D26 (15%)	24.4±6.7	17.9±3.8
QS D30 (15%)	29.0±11.4	15.4±6.7
AS D30 (15%)	23.0±6.9	26.0±6.3
Untreated control	44.8±11.8	56.2±9.5

to the higher density of this hardwood (Table 3). Samples treated with 5% silicone solution were totally overgrown by the respective brown-rot (*C. puteana*) or white-rot (*T. versicolor*) fungus after 12 weeks incubation. The MLs of these samples were considerably higher and, in some cases, similar to those of the untreated controls (Figure 1a, c). Treatment with 15% silicone solution reduced the ML noticeably for both fungi compared to the untreated controls (Figure 1b, d). Among the pine samples, none of the silicone treatments was able to inhibit surface colonisation by *C. puteana*, while the

treatment with short-chain QSs and ASs reduced the growth of surface mycelium of *T. versicolor* on the beech specimens until the end of the test duration. With both fungi, short-chain QS (QS D10) and ASs (AS D7, AS D9) reduced the ML to a higher degree than the longer-chain silicones (QS D30, AS D26, AS D30). In the case of pine wood, the ML of samples treated with AS D7 and AS D9 was below 3% (which is the acceptable threshold according to EN 113, 1996), while the respective beech specimens exceeded the threshold (Table 4). Also, the absolute MLs of these samples were lower than those of the respective beech wood samples (Figure 1b, d). This indicates that the higher percentage ML of beech specimens treated with AS D7 and AS D9 is not only attributable to a higher density of this wood but also to a higher activity of *T. versicolor* compared to *C. puteana* in pine wood.

The effect of amino groups in polysiloxanes, i.e., in condensed silanes and in silicones on decay protection, has been reported previously (Donath et al. 2006; Ghosh et al. 2008; Weigenand et al. 2008). Silicone emulsions with quat-, amino- and alkyl-functional groups inhibited mycelia growth in agar media. However, only QS and ASs led to ML reduction in decay tests, while alkyl-silicones were ineffective (Ghosh et al. 2008). The inhibition of wood decay through ASs was attributed to the effect of cationic amino group on fungal physiology (Donath et al. 2006; Weigenand et al. 2008). All studies on ASs and QSs reported on aqueous emulsions with different emulsion particle sizes and emulsifiers (Ghosh et al. 2008; Weigenand et al. 2008). In the present study, pure solutions of short- and long-chained silicones were used. A detrimental effect of emulsifiers on fungal physiology can thus be ruled out. The results show that QSs and ASs of shorter-chain lengths are more effective in preventing wood decay

Figure 2 Energy production (J h^{-1}) by *C. puteana* on pine sapwood (a: 5% conc. and b: 15% conc.) and *T. versicolor* on beech wood (c: 5% conc. and d: 15% conc.). (n=3).

Figure 3 Energy (J h^{-1}) produced within 3 h and respective ML after 12 weeks incubation with *C. puteana* (a) and *T. versicolor* (b). Three samples decayed by the test fungi were tested per treatment.

than those of longer-chain length. This is attributable mainly to two effects. Probably, the shorter chains are assumed to be able to penetrate into the cell wall and effectuate cell wall bulking and microvoid blocking. Micropore blocking might prevent penetration of enzymes and diffusible agents with low molecular weight, which are required for fungal degradation of the cell wall (Papadopoulos and Hill 2002; Hill et al. 2005). The shorter the chain length of the silicones, the higher is the amino or quat content, respectively, of the silicones (Table 1). The higher nitrogen content in the short-chained silicones should cause higher fungal resistance, if the mode of action of the tested silicones is mainly based on the effect of the amino or quat groups on fungal physiology. The branched AS D30, however, exhibits the highest content of primary and secondary amino groups on its side chains, but caused the lowest decay resistance. This is a demonstration of the crucial

role of the penetration of the ASs into the cell wall and of the interaction of the silicone with the cell wall matrix in terms of decay resistance.

Microcalorimetry

The heat-energy production (average of three samples) of the decay fungi in wood was measured in a microcalorimeter after 12 weeks incubation (Figure 2). Overall, the energy production of both fungi reflected the ML of the wood samples caused by fungal decay (Figure 3). The heat produced by *T. versicolor* and *C. puteana* was very similar within the control samples and revealed similar fungal activity, i.e., a similar degree of colonisation in untreated pine and beech wood. For both wood species, the lowest-energy production rate was found for samples treated with short-chained QSs and ASs (QS D10, AS D7, AS D9) at 15% concentration. Energy production from infected wood treated with long-chained silicones (QS D30, AS D26, AS D30) was clearly higher revealing a higher degree of colonisation. The highest degree of colonisation in both treated wood species was found in the samples treated with chemicals with the highest nitrogen content (AS D30). Obviously, the presence of the highest proportion of amino groups did not cause the most effective prevention of fungal colonisation.

In the case of *C. puteana*, the lowest energy production was found in pine wood treated with the shortest-chained AS (AS D7), while *T. versicolor* produced the lowest energy in beech wood treated with the shortest-chained QS (QS D10). In general, the activity of *T. versicolor* in beech wood was higher for a given silicone treatment than that of *C. puteana* in pine; this observation is also reflected by the higher ML of treated beech samples. Overall, the total energy production of both the brown- and the white-rot fungus tended to increase with the increase of ML (Figure 3a, b). These results are in agreement with data reported on the energy production of *C. puteana* and *T. versicolor* in pine and beech wood treated with 1,3-dimethylol-4,5-dihydroxyethyl urea (Verma et al. 2008).

Table 5 Mean area of staining of Scots pine sapwood with SD and their corresponding ranking of treated and untreated wood (rank 0–5) ($n=8$, mean values $\pm$ SD).

Treatment	Mean area of staining (%)		Mean rank	
	Front	Reverse	Front	Reverse
5% QS D10	5.1 $\pm$ 5.0	28.6 $\pm$ 13.3	1	3
5% QS D30	2.8 $\pm$ 2.5	13.2 $\pm$ 7.6	1	2
5% AS D7	4.2 $\pm$ 2.9	5.6 $\pm$ 2.2	1	1
5% AS D9	13.6 $\pm$ 7.3	12.8 $\pm$ 5.7	2	2
5% AS D26	13.7 $\pm$ 3.8	13.8 $\pm$ 6.1	2	2
5% AS D30	16.6 $\pm$ 7.1	20.5 $\pm$ 10.3	2	2
15% QS D10	6.5 $\pm$ 8.6	45.2 $\pm$ 12.7	1	3
15% QS D30	0.7 $\pm$ 0.3	13.8 $\pm$ 9.5	1	2
15% AS D7	2.1 $\pm$ 1.6	4.6 $\pm$ 0.8	1	1
15% AS D9	5.5 $\pm$ 3.5	7.9 $\pm$ 3.1	1	1
15% AS D26	11.8 $\pm$ 5.1	8.8 $\pm$ 5.4	2	1
15% AS D30	5.9 $\pm$ 5.2	6.4 $\pm$ 4.9	1	1
Untreated control	74.3 $\pm$ 8.0	75.5 $\pm$ 6.5	5	5

Figure 4 Images of Scots pine specimens after 8 weeks incubation with a spore suspension of the blue stain fungi *A. pullulans* and *S. pithyophila* (surfaces in vermiculite contact). (a) control, (c) treated with 15% AS D7 and the corresponding image analysis by GIMP (b, d).

Blue stain test

All QSs and ASs caused a reduction of the blue-st. area on the wood surfaces compared to that of untreated controls after 8 weeks of incubation (Table 5). Regardless of the silicone type, a clear effect of concentration was observed on the staining intensity. Higher treatment concentration (15%) resulted in less-st. area. Among the QSs, the long-chain compounds (QS D30) were more effective in preventing surface colonisation than short-chain compounds (QS D10). This is due to the inhibited penetration of the long-chained QS, which results in higher concentration of the silicone on the wood surface.

Among the ASs, however, the short-chained AS, AS D7, exhibited the highest efficacy to reduce staining at both concentrations. The differences between the ASs, however, were low compared to those with the control specimens (Figure 4).

The high resistance to blue staining caused by short-chain ASs might be attributed to changes in surface properties of wood, reduced moisture sorption and an adverse effect of amino groups on fungal growth as described above with regard to decay resistance. These results show that the increased staining resistance reported for commercial ready-to-use QS and AS emulsions (Ghosh et al. 2009) are predominantly due to the silicone constituents and not due to emulsifiers or other additives in the formulations.

Conclusions

Treatment of wood with solutions of QSs and ASs was performed to evaluate the effect on fungal colonisation and decay. The treatment with pure silicone solutions (in contrast to silicone emulsions) decreased fungal colonisation and increased the decay resistance of wood. Thus, QSs and ASs are mainly responsible for the improved durability performance rather than emulsifiers or other additives in commercial ready-to-use emulsions. For both quat and amino compounds, the decay resistance decreased with the increasing chain length of the silicones. This cannot be explained with a higher nitrogen content of the shorter-chain length alone, as the longest-chained AS (AS D30), which exhibited

the highest nitrogen content, imparted the lowest decay resistance. Accordingly, the primary causes of increased durability are due to cell wall bulking and micropore blocking, reduction of moisture content as well as the covering of inner surfaces. QSs and ASs have a high potential as protecting agents for wood in hazard class 3 according to the European standard EN 335-1 (2006).

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