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Effect of short-chain silicones bearing different functional groups on the resistance of pine (*Pinus sylvestris* L.) and beech (*Fagus sylvatica* L.) against decay fungi

Abstract: Blocks of pine sapwood and beech wood were treated with water-based emulsions containing short-chain silicones with different α - ω -bonded functional groups, such as diamino, carboxyl and carbonyl, betain, and epoxy groups. The weight percent gain upon treatment of the pine wood specimens was relatively high (10%–20%), but their cross-sectional bulking was low (1%–2.5%). Thus, the anti-shrink efficiency (ASE) due to the treatment was also low. The first water-submersion tests revealed some hydrophobation of the treated wood. A second submersion test, however, revealed successful hydrophobation only for betain-functionalised material. The carboxylated silicone even increased the speed of water uptake as compared to the controls. The samples treated with silicones bearing epoxy, diamino, and carboxy functionalities showed a distinct reduction in mass loss compared to the control samples after 16 weeks of incubation with the fungi *Coniophora puteana* and *Trametes versicolor* according to EN 113 and CEN/TS 15083-1, whereas the betain-functionalised silicone did not enhance fungal resistance. All silicones tested lowered the mass loss in a soft rot test according to ENv 807. The mode of action of the silicones is discussed.

Keywords: amino silicone, carboxy silicone, epoxy silicone, short-chain silicone, wood modification

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Introduction

Wood in outside applications, when directly exposed to weathering, needs to be protected either by preservative treatment or by coating. In conventional impregnation, biocides in the treatment liquids prevent fungal growth. However, alternatives to biocides are sought due to environmental concerns. Less toxic preservatives and wood modification without biocides are preferable alternatives (Evans 2003).

In this context, organosilicon compounds were tested, especially silanes and polydimethylsiloxanes (silicones) (Mai et al. 2003; Hill et al. 2004; Donath et al. 2006a,b). Silanes are usually reactive via silanol groups and can form a polymer inside the wood. Silicones, however, are mostly unreactive and are brought into the wood as a pre-synthesised polymer.

Silicones are used as water repellents for masonry (Mayer 1998) and can improve the properties of textiles (Kim 2001). Water repellence of wood was improved by the treatment with silicones (Hager 1995; Lukowsky et al. 1997). Weigenand et al. (2008) treated Scots pine sapwood with an amino silicone microemulsion bearing a chain length of 300–400 dimethylsiloxane (DMS) units. At higher concentrations they found improved dimensional stability and high decay resistance of the treated wood to white and brown rot fungi.

Silicone applied as a microemulsion penetrated the cell wall to a higher extent than as a macroemulsion (Weigenand et al. 2007). Silicones bearing functional groups – amino groups, quaternary ammonium groups, and simple alkyl functional groups – proved to be effective in water-based formulations; especially the first two functionalities imparted increasing resistance to *Trametes versicolor* and *Coniophora puteana* when applied in higher concentrations (up to 15%). Intermixing of silicones with agar resulted in a growth reduction of the incubated fungi for all three types of silicone; this effect

15 min. Then the silicone emulsions were injected and the vacuum was released. The specimens remained in the solution for 2 h and were subsequently weighed and predried for 1 week at 20°C and 65% relative humidity (RH); then the temperature was slowly increased up to 103°C over a period of 3 days.

WPG, cell wall bulking

The weight (W) of the dry specimens was determined and the WPG was calculated:

$$WPG (\%) = 100[(W_{\text{after treatm.}}/W_{\text{before treatm.}})-1] \quad (1)$$

A theoretical WPG was also calculated on the basis of the emulsion (Em) uptake:

$$WPG_{\text{theor.}} (\%) = 100(Em_{\text{uptake}} \times \text{conc. of } Em/W_{\text{before treatm.}}) \quad (2)$$

Cross-sectional bulking was calculated:

$$\text{Bulking} (\%) = 100[(\text{cross-sect. area}_{\text{after treatm.}}/\text{cross sect. area}_{\text{before treatm.}})-1] \quad (3)$$

The specimens were leached according to EN 84 (1997). WPG and bulking were measured before and after leaching.

Water uptake

After leaching and subsequent drying, pine sapwood ASE specimens were immersed in approximately 300 ml of water and the weight was determined after 2, 4, 6, 24, 48, and 72 h. Thereafter, a vacuum of approx. 40 hPa was applied for 1 h. The specimens were kept in water for one more day to establish maximum water uptake. The water uptake was related to the oven dry weight of the specimens prior to the silicone treatment.

Microorganisms

The brown rot fungus *C. puteana* (Schum.: Fr.) Karst. strain BAM Ebw. 15 (DSM No. 3085), and the white rot fungus *T. versicolor* (Linneus) L. Quélet strain CTB 863 A (DSM No. 3086) were obtained from the German Collection of Microorganisms and Cell Cultures. The cultures of *C. puteana* and *T. versicolor* were maintained on 4% malt extract agar medium at 22°C; subculturing was done in intervals of 4 weeks.

Resistance to white and brown rot fungi

The wood specimens were conditioned at 20°C and 65% RH until they reached equilibrium moisture content and were then sterilised by γ -irradiation (25 kGy, Isotron, Ede, The Netherlands). Then the samples were inoculated on 4% malt and 1.5% agar in Kolle flasks according to EN 113 (1996). Two treated or two untreated specimens were inoculated together in one flask as described in the standard CEN/TS 15083-1 (2004). Ten replicates were tested per treatment. Treated and untreated specimens were tested with *C. puteana* (Scots

pine) and with *C. puteana* and *T. versicolor* (European beech). WPG effectiveness was calculated on the basis of mass loss (ML):

$$WPG_{\text{effect.}} = (\text{mean } ML_{\text{control}} - ML_{\text{sample}})/WPG_{\text{EN84}} \quad (4)$$

Soft rot test

Soft rot testing was performed according to ENv 807 (2001). Six samples per treatment were leached according to EN 84 (1997), dried, and conditioned at 20°C and 65% RH. Forest soil with a water-holding capacity of 61% (w/w) based on dry mass was used. The soil moisture was adjusted to 95% of the water-holding capacity before incubating the specimens randomly distributed within the box; incubation time was 32 weeks.

Analyses of variance (ANOVA) of the fungal test

For basidiomycete testing, the mean mass loss of the two specimens incubated together in each Kolle flask was used as a single value; in the soft rot test, the mass loss of each sample was regarded as one value. The normality and homogeneity of the variance was checked visually on the normal probability plot of the studentized residuals and the plot of predicted values versus the studentized residuals. When the ANOVA gave a significant P value of <0.05, least significant differences (LSD) bars were calculated to distinguish significant differences (Anderson and Whitcomb 2007).

$$LSD = t_{\text{critical}} \times s_{\text{pooled}} \times \sqrt{\frac{\sum_{i=0}^k \frac{1}{n_j}}{k-1}} \quad (5)$$

where t_{critical} = the critical t value for the specific degree of freedom; s_{pooled} = square root of the mean value of the treatment variances; j = number of samples per treatment; k = number of treatments. The values are significantly different with 95% confidence when the LSD bars in the resulting plots do not overlap.

Results and discussion

WPG

The WPG of most specimens was higher than the theoretical WPG based on the solution uptake and the respective silicone concentration (Figure 2). This is attributable to the emulsifiers, which were taken up by the wood and contributed to the WPG. After leaching, the WPG was equal to the theoretical WPG because of leaching of the emulsifiers. The WPG of the specimens treated with betain-functional silicone was lower than the theoretical WPG, probably because this type of silicone had been filtered out by the wood ("chromatographic effect"). The carboxy- and carboxyl-type

Figure 2 WPG and theoretical WPG of (a) beech and (b) Scots pine specimens (both EN 113 samples) and (c) ASE samples before and after leaching.

Mean values and standard deviations.

silicone, however, caused higher WPGs than those calculated from the solution uptake.

Initially, all WPGs of the ASE samples were higher than those of the EN 113 samples. After leaching, the WPGs of the ASE specimens were below the theoretical values. Leaching of the ASE samples was more severe than that of the EN 113 specimens because they were smaller and exhibited a greater cross-sectional area in relation to the total volume. Fixation was lowest with the carboxy-functional silicone; only approximately 34% of the theoretical WPG remained after leaching. The carboxy-functional silicone is very hydrophilic because of the formation of carboxylate ions, which offset the hydrophobic properties of the silicone backbone.

Cell wall bulking

All treated specimens had low cell wall bulking, which did not induce noteworthy dimensional stabilization of the wood. Bulking, however, remained more stable towards leaching than WPG. Carboxy silicone with the highest leaching rate (approx. 78% reduction in WPG), showed reduction in bulking by only approximately 26% due to leaching. Accordingly, the material is fixed after entering the cell wall, but when located in the lumens it will eventually be leached out. Other materials, such as the epoxy-functional silicones D30 and D10, exhibited minor

reduction in bulking, although the WPG showed a considerable loss (Figure 3).

Weigenand et al. (2007) found minor penetration of silicone emulsions into the cell wall and corresponding bulking values. It can be concluded that bulking is higher when wood is treated with a microemulsion instead of a macroemulsion. However, the emulsion particles are not able to penetrate the cell wall because the nanopores in it are 10-fold smaller in diameter (Hill and Papadopoulos 2001).

Figure 3 Bulking of pine sapwood before and after leaching according to EN 84 (1997).

Mean values and standard deviations.

Hence, it is more likely that the emulsion particles break during the impregnation and the material released penetrates the cell wall. The diameter of the emulsion particles can merely influence the penetration into the capillary system of wood.

Bulking values with silicones bearing amino and quaternary ammonium groups (Ghosh 2009) were in the same order of magnitude but somewhat higher for the same WPG level than those observed in the present study. The silicones in the quoted study, however, were dissolved in a mixture of water and organic solvent.

Obviously, the molecular mass of the silicones is still too high (approx. 1000 g mol^{-1}) to allow cell wall penetration. Hill et al. (2005) found a significant reduction in cell wall penetration with molecules $>500 \text{ g mol}^{-1}$. Still, Weigenand et al. (2007) reported considerable penetration of silicones consisting of 300–400 DMS units ($>20,000 \text{ g mol}^{-1}$) into the cell wall, but the influence of the emulsifiers was not assessed. Thus, it cannot be ruled out that the emulsifiers and not the silicones caused most of the bulking. This might also explain the higher bulking of the microemulsion than that of the macroemulsion. The former exhibited approximately 20% higher emulsifier content based on the silicone (Weigenand et al. 2007).

Water uptake

Compared to the control, water uptake was reduced by the treatments, but the magnitude depended on the functional group (Figure 4a).

A second submersion test performed with the same specimens reduced the difference between the controls and the treated samples (Figure 4b). The carboxy-functional silicone even induced a higher water uptake than the controls. Betain-functional silicone caused the slowest water uptake in both tests. It was also the only material that significantly reduced the water uptake for longer than 24 h at the second submersion.

The water uptake clearly depended on the functionality of the material. Usually, the silicone chain is hydrophobic, but when the chain becomes shorter, the influence of the functional group increases. Both, the carboxy and the amino functional group are hydrophilic and make the whole molecule hydrophilic. The epoxy functional group is hydrophobic as long as the oxirane ring is closed. Ring opening due to hydrolysis in the presence of acid forms a hydrophilic dihydroxy functionality. Ghosh (2009) found much greater reductions in water uptake compared to our results with amino functional silicones of different chain length. Because the silicone material and the concentrations are

Figure 4 Water uptake of pine sapwood treated with different polysiloxanes.

a) First water uptake, b) second water uptake.

comparable, these differences can be attributed to the altered formulation of the silicone material: water-based emulsions vs. solutions based on water and organic solvents.

Surface properties of textiles are frequently modified with amino functional silicones. Bereck et al. (2001) assumed that the amino groups interact with the textile surface via dipole-dipole and hydrogen bonding. The amino groups were strictly oriented towards the fiber surface as revealed by X-ray photoelectron spectroscopy measurements, thus exposing the hydrophobic polysiloxane chains towards entering water. Emulsifiers are easily removed from textile fibers by washing. In wood, however, intensive leaching is necessary because emulsifiers are entrapped in the tissue. These might offset the hydrophobing impact of the silicone.

The effect of chain length was apparent with the epoxy functional silicones. The longer epoxy functional silicone (D127) reduced water uptake to a higher degree than those with shorter chain length. This can be attributed to more effective blocking of cell lumens by long-chain silicones. The two amino silicones tested did not induce differences in water uptake; both chains, however, were very short (D5 and D10) and should not have different effects on blocking of cell lumens. Ghosh (2009) also found a greater reduction in water uptake with increasing chain length of amino silicones.

Fungi test

Basidiomycetes

A clear reduction in mass loss (*ML*) due to fungal attack was observed depending on the functionality and chain length of the silicones (Figure 5a–c). ANOVA gave a highly significant *P* value of <0.0001 for all three combinations of fungi and wood species. The normal probability plot and the variance of residuals confirmed the underlying assumptions of the ANOVA.

Figure 5 Mass loss of pine sapwood (a) and beech wood (b, c) after 16 weeks of incubation with *C. puteana* (a, b) and *T. versicolor* (c) as well as mass loss of pine sapwood specimens due to soft rot decay after 32 weeks of incubation (d).

Mean values and LSD bars are shown. If LSD bars do not overlap, the two treatments can be regarded as statistically different at a confidence level of 95%.

Wood blocks treated with betain functional silicone even increased the *ML* as compared to the untreated controls. All other functionalities reduced the *ML* but to different extents. Among the D10 silicones the carboxy functional silicone brought about the most pronounced *ML* reduction; in two cases the mean *ML* was below 3% (*T. versicolor* on beech; *C. puteana* on pine). Beech wood blocks treated with epoxy functional silicone showed significantly lower *MLs* caused by *C. puteana* than those treated with amino functional silicone. Amino functional silicone never induced significantly lower *MLs* as compared to the other two effective functionalities.

In most cases, short-chain silicones exhibited higher effectiveness in reducing *ML* than those with longer chains. Specimens treated with short-chain epoxy functional silicones (D10) underwent lower *MLs* than those treated with the corresponding long-chain compounds (D127) during incubation with *C. puteana*, whereas the results obtained with *T. versicolor* did not show a clear tendency.

The diamino functional silicone with chain length D5 imparted significantly higher resistance to beech wood to both fungi than the respective long-chain material (D10).

With regard to the epoxy functional silicone (D127), the *ML* was lower with higher treatment concentration, i.e., with higher WPG. The *ML* of the beech and pine control specimens incubated with *C. puteana* was comparable; *ML* reduction of all treated specimens, however, was much lower with beech than with pine. This is attributable to the higher density of the former, which entails a lower WPG after treatment.

WPG effectiveness (Table 2), which considers the effect of the WPG, revealed the same order as the preceding statistical analysis, but it takes into account that, e.g., the high efficiency of carboxy functional silicone on pine sapwood was accomplished with the highest WPG of all treatments (Figure 2).

Functionality and chain length	WPG _{eff.} with <i>C. puteana</i>		WPG _{eff.} with <i>T. versicolor</i>	WPG _{eff.} average
	Pine	Beech	Beech	
Betain	-0.93	-1.03	-0.86	-0.94
Epoxy, D127	1.45	1.55	1.54	1.51
Epoxy, D30	2.07	1.86	1.25	1.73
Epoxy, D10	2.75	2.61	1.63	2.33
Diamino, D10	2.62	1.27	1.26	1.72
Diamino, D5	3.0	2.73	1.76	2.5
Carboxy, D10	2.53	3.21	2.02	2.59

Table 2 Mean WPG effectiveness [see Eq. (4)] of the functionalised silicones against two fungi.

In the work of Ghosh et al. (2008), the alkyl-modified silicone did not exhibit any effect on wood-decaying fungi, whereas the amino and quaternary ammonium silicones reduced *ML*. Amino silicones with decreasing chain length caused higher decay resistance (Ghosh et al. 2012). Amino groups are supposed to play a crucial role in the inhibition of fungal growth (Donath et al. 2006b; Weigenand et al. 2008) but this supposition was not confirmed (Ghosh et al. 2012). The findings of the present study do not support the importance of amino groups regarding fungal resistance either. Dihydroxy functionality (derived from epoxy) and carboxy functionality were more effective in this regard. Ghosh et al. (2012) ascribed the effectiveness of silicones to penetration of the cell wall and blocking of its micropores as well as interaction of the siloxane chains with the cell wall polymers.

Micropore blocking as the mode of action has been discussed for other types of chemical modification (Hill et al. 2005). This reduces the availability of water and the penetration of fungal decay agents in the cell wall (Papadopoulos and Hill 2002). The minor cell wall bulking found in this study, however, makes the micropore blocking theory implausible.

The amino group is positively charged, whereas the opposite is true for the carboxy group. The epoxy group, which can be hydrolyzed to a dihydroxy functionality, is expected to be uncharged. The positive charge of the amino group was considered to be responsible for the effectiveness of the amino group against fungi (Donath et al. 2006b; Ghosh et al. 2008). The present study does not support the assumptions that the charges of the functional groups are relevant for the effectiveness against decaying fungi.

The physical or chemical interaction of the silicones with the cell wall can also be ruled out as the main reason for high effectiveness. A silicone type that strongly interacts with the cell wall is unlikely to be leached out by water. However, carboxy silicone, which was highly susceptible to leaching, exhibited the highest effectiveness against fungi. Obviously, the leachable carboxy functionalised silicone does not interact with the cell wall as strongly as the amino group. Amino and particularly ammonium groups can form ionic pairs with anionic moieties such as carboxylic groups in hemicelluloses or phenolate groups in lignin, whereas respective cationic groups, which could ionically interact with carboxy silicone, are not present in the cell wall.

Hydrophobation of the wood substrate can clearly be excluded as the main reason for the effectiveness against decaying fungi. All three effective silicones (carboxy, amino and epoxy silicone) did not impart a high degree of

hydrophobation; they even increased water uptake during the second submersion (Figure 4).

Most likely the mobility of the silicones is important for the effectiveness against fungal decay, and silicones can directly affect fungal physiology. This effect is restricted, when the silicone is long chained or interacts strongly with the wood cell wall. The effect on fungal physiology is most likely caused by the siloxane chain itself because it occurs with different functionalities. The siloxane chain probably interferes with the fungal cell membranes, whereas the functionality has an important influence on the mobility of the siloxane chain.

Soft rot decay

After 32 weeks of exposure to soft rot fungi, all silicone-treated specimens showed significantly reduced *MLs* compared to the control (Figure 5d). ANOVA confirmed the significance of the differences with a *P* value <0.0001. The normality and homogeneity of variance was checked on the studentized residual plots.

Different from the basidiomycete test, the betain functional silicone caused reduced decay compared to the control but was still the least effective compound. Comparing the same chain length (D10) of the other silicones, the *MLs* did not differ significantly. A chain length effect is visible only in case of the diamino functional silicone; the *ML* of specimens treated with D5 was significantly lower than that of D10-treated ones.

A characteristic decay feature of soft rot fungi is the formation of cavities within the S_2 layer of the cell wall, whereas decay by basidiomycetes starts from the cell lumens and proceeds to the middle lamellae (Eriksson et al. 1990). Thus, soft rot fungi are less susceptible to chemicals mostly located in the lumina, as is the case for the silicones tested. The results of soft rot decay are in line with those reported for silicones bearing functional groups of amino, quaternary ammonium, and alkyl type (Ghosh et al. 2008). These compounds reduced the *ML* but did not impart full decay resistance to wood.

Conclusion

Although water uptake was not reduced by most short-chain silicones tested, mass loss due to basidiomycete attack was considerably decreased. Hence, there is no direct relation between hydrophobation caused by the siloxanes and resistance to fungal attack. The most effective

compound in the fungal test, the carboxy functional silicone, even enhanced water uptake in a submersion test. Fungal resistance in general increased with shorter chain lengths. Functionality also influenced fungal decay: carboxy groups imparted somewhat higher decay resistance than epoxy and amino groups. As carboxy groups are not assumed to have a detrimental effect on fungal physiology, it can be concluded that the siloxane chain itself seems to be effective against fungal decay. However, effective silicone compounds must be mobile, a requirement

that is easier to achieve with shorter chain length and with functional groups that enhance the solubility in water but do not cause strong fixation to the cell wall matrix.

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