

# Acetylation of wood in combination with polysiloxanes to improve water-related and mechanical properties of wood

Malte Pries · Roland Wagner · Karl-Heinz Kaesler ·  
Holger Militz · Carsten Mai

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**Abstract** Scots pine sapwood was acetylated with ethyltriacetoxysilane using acetic acid as a solvent and sulfuric acid as a catalyst. A weight percent gain (WPG) of 14 % and cell wall bulking of 7 % were obtained after 5 h of reaction time. Pine specimens were acetylated with acetic anhydride in the presence of 1 % ethyltriacetoxysilane, dihydroxy-functional siloxane, acetoxyl-functional siloxane, amino-functional siloxane and non-functional siloxane, respectively. Acetoxyl-functional siloxane induced the greatest reduction in water uptake with a water repellent effectiveness after 24 h of up to 62 % as compared to acetylated wood. WPG and cell wall bulking increased compared to solely acetylated wood with increasing concentrations of acetoxyl-functional siloxane in acetic anhydride; anti-shrink efficiency, however, did not increase. Fungal resistance of pine sapwood and beech as well as mechanical strength properties did not change when 20 % acetoxyl-functional siloxane was added to acetic anhydride compared to solely acetylated specimens.

## Introduction

Chemical modification has the potential to greatly improve properties of wood (Rowell 1983). The most studied process is by far the acetylation of wood which has undergone market introduction. Acetylation reportedly improved fungal resistance, photo-stability, dimensional stability and weathering performance of wood (Brelid et al. 2000; Chang and Chang 2001; Hill et al. 2005; Rowell 1983). The most

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M. Pries · H. Militz · C. Mai (✉)

Wood Biology and Wood Products, Burckhardt Institute, Georg-August-University Göttingen,  
Büsgenweg 4, 37077 Göttingen, Germany  
e-mail: cmai@gwdg.de

R. Wagner · K.-H. Kaesler

Momentive Performance Materials, Technology, Buildg. R20, 51368 Leverkusen, Germany

abundant reaction sites in wood, the hydroxyl groups, are acetylated in the process by use of acetic anhydride (AA) under release of acetic acid. Because of the greater volume of acetyl groups compared to hydroxyl groups, cell wall bulking is observed (Stamm 1964). Reduction in capillary water uptake, however, occurs only to a minor extent.

Silicones have experienced a widespread use in many industrial applications. They are widely used in the construction sector to improve water repellence of masonry (Mayer 1998) or to improve properties of textiles (Kim 2001). Silicones have been tested on wood to enhance water repellence and showed great effectiveness in reducing water uptake (Hager 1995; Lukowsky et al. 1997). Hager (1995) used silicone micro-emulsions to treat wood and found a reduction in capillary water uptake by 80 % as compared to the control after 24 h at 1 % silicone content in the emulsion. Lukowsky et al. (1997) tested the effectiveness of similar micro-emulsions and some additional silicone formulations and found water repellent effectiveness in a submersion test of up to 50 % after 24 h. Ghosh (2009) found high water repellence when wood was treated with a water solvent-based solution of amino-functional silicones. A water repellent effectiveness of approximately 50 % was reached after 24 h of water submersion with an amino-functional silicone comprised of 30 dimethyl siloxane units.

Silicones can therefore be used to hydrophobize wood; however, they are not easy to solubilize in water because of their strong water repellence. Real solutions can only be made by using high proportions of organic solvents in the solution which restricts the application in conventional impregnation plants. If emulsions are used, costs of emulsifiers have to be considered. In addition, the emulsifier will stay in the wood after impregnation and offset hydrophobation of the material by silicone. The micro-emulsions used by Hager (1995) and Lukowsky et al. (1997) solved this problem by using silanes and functionalized polysiloxanes as emulsifier or co-emulsifier, respectively. These emulsions, however, are not stable and a short solution stability of only approximately 24 h is obtained. This makes the use of these formulations not viable in impregnation plants (Lukowsky et al. 1997). Another possibility is the impregnation of solid wood with silicone using supercritical CO<sub>2</sub> as solvent (Eastman et al. 2009).

The acetylation procedure with acetic anhydride offers the opportunity to solve silicones directly in the acetylation reagent to impregnate wood without further treatment steps. Acetoxysilanes can acetylate hydroxyl groups via transesterification and releasing silanol compounds as leaving group; release of acetic acid from the silane is therefore omitted.

## Materials and methods

### Organo-silicon compounds

Ethyltriacetoxysilane (TAS) was used as silicon-based acetylation chemical. A short-chained silicone (Si 200 TP 3031), containing 70–100 % of  $\alpha$ - $\omega$ -functional polydimethylsiloxanediol with a mean of 6 dimethylsiloxane units (D6) and 0–30 %

of octamethylcyclotetrasiloxane was used as a siloxane backbone, which can easily be combined with ethyltriacetoxysilane. The silicone oils M5 and M100 are non-functional polydimethylsiloxanes (PDMS). M5 has a mean chain length of D6-7 and M100 of D80. Amino D9 and Amino D28 are  $\alpha$ - $\omega$ -functional diaminopolydimethylsiloxanes with a chain length of D9 and D28. All organo-silicon-compounds were supplied by Momentive Performance Materials GmbH (Leverkusen, Germany).

### Wood samples

Pine sapwood (*Pinus sylvestris* L.) blocks (defined as ASE specimens) measuring  $20 \times 20 \times 10 \text{ mm}^3$  ( $r \times t \times l$ ) were used to determine weight percent gain (WPG), cell wall bulking, anti-shrink efficiency (ASE) and water uptake. Blocks of beech wood (*Fagus sylvatica* L.) and pine sapwood (*P. sylvestris* L.) according to EN 113 (1996) were used for basidiomycete testing. Pine sapwood (*P. sylvestris* L.) stakes measuring  $10 \times 10 \times 180 \text{ mm}^3$  ( $r \times t \times l$ ) were used to determine bending strength and those measuring  $10 \times 10 \times 150 \text{ mm}^3$  ( $r \times t \times l$ ) to determine impact bending strength. Pine sapwood had an average density of  $0.51 \text{ g cm}^{-3}$ , while the beech wood showed a density of  $0.68 \text{ g cm}^{-3}$ .

### Acetylation of wood with ethyltriacetoxysilane

Acetylation with ethyltriacetoxysilane (TAS) was carried out with pure TAS and in a mixture with acetic acid serving as a solvent and swelling agent for wood (Mantanis et al. 1994). The mixture consisted of 30 % TAS mixed with 70 % acetic acid statically dried over molecular sieves (4 Å).

Acetylation was performed with and without catalyst. The reaction of pure TAS was catalyzed with 0.25 %  $\text{H}_2\text{SO}_4$  (w/w of TAS), while the following catalysts were used in the mixture of 30 % TAS with 70 % acetic acid:  $\text{MgCl}_2$  (0.8 % w/w), potassium acetate (KAc), triethylamine (1 % w/w) and  $\text{H}_2\text{SO}_4$  (0.07 % w/w). To apply KAc, the wood specimens were vacuum impregnated with 10 % (w/w) aqueous solution according to EN 113 and dried prior to the acetylation process at  $103 \text{ }^\circ\text{C}$  (Obataya and Minato 2008). The other catalysts were directly mixed into the treatment solution.

After impregnation with the acetylation reagent (according to EN 113), the specimens were heated in the solution to  $120 \text{ }^\circ\text{C}$  for 5 h, while protected against moisture by a  $\text{CaCl}_2$  tube. After the reaction, the specimens were extracted in a soxhlet extractor with acetic acid for 6 h under exclusion of moisture by  $\text{CaCl}_2$  and subsequently with ethanol for 6 h to remove acetic acid. The acetylation reaction was assessed by measuring WPG, cell wall bulking and recording IR spectra.

### Preparation of an acetoxy-functional polydimethylsiloxane

TAS was brought into a round-bottomed flask equipped with a reflux condenser and a dropping funnel, and Si 200 was added drop-wise until a ratio of 2 mol of TAS to 1 mol Si 200 was reached. During the addition, the temperature rose from

approximately 20–38 °C. After the addition, the product was confirmed by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$  on a 400 MHz spectrometer Bruker Avance 400 (Bruker, Bremen, Germany). A NMR diffusion experiment (DOSY) was applied to distinguish between ethyl groups (0.96–1.14 ppm) attached to a silane [diffusion coefficient from  $10^{-8.83} \text{ m}^2 \text{ s}^{-1}$  (monomer) to  $10^{-8.96} \text{ m}^2 \text{ s}^{-1}$  (dimer and trimer)] and attached to a polysiloxane backbone (diffusion coefficient from  $10^{-9.09}$  to  $10^{-9.17} \text{ m}^2 \text{ s}^{-1}$ ). After the reaction, no acetyl groups were left which were only attached to a silane. The structure of the product is depicted in Fig. 1.

### Acetylation of wood in the presence of organo-silicon compounds

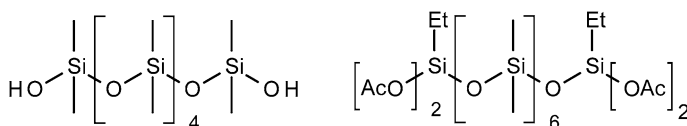
Impregnation of all wood specimens was done according to EN 113 (1996). The specimens were left in the solution and heated to 120 °C for 5 h. After the reaction, the samples were dropped into deionized water to quench the reaction. They were left in water for 2 days with a water change after 1 day. Subsequently, the specimens were dried at room temperature for 2 days and finally dried at 103 °C for 24 h. Eight ASE specimens at a time were treated with a solution of acetic anhydride (AA) and the following organo-silicon compounds:

1. 1 % acetoxy-functional silane (1st educt of No. 3).
2. 1 % Si 200 (2nd educt of No. 3).
3. 1 % acetoxy-functional siloxane (product of No. 1 and 2).
4. 1 % M5.
5. 1 % M100.
6. 1 % Amino D9.
7. 1 % Amino D28.

In another approach, the acetoxy-functional siloxane (No. 3) was mixed with AA in various ratios (1, 3, 6, 10 and 20 %). These solutions were used to impregnate 16 ASE specimens at a time and to determine WPG, cell wall bulking, water uptake and acetyl content. WPG and cell wall bulking were calculated according to Xiao et al. (2010).

### Infrared spectroscopy

Fourier-transform infrared (FT-IR) spectra were recorded of the cross-sections of the specimens by means of the attenuated total reflection (ATR) technique (DuraSamplIRII, SensIR Technologies, Warrington, UK), using a Vektor 22 spectrophotometer (Bruker, Bremen, Germany) (32 scans,  $4 \text{ cm}^{-1}$  resolution). Background spectra were collected with the empty ATR unit. Three spectra of each



**Fig. 1** Mean structure of Si200 (*left*) and idealized product (*right*)

specimen were normalized to an absorption of 2 absorption units at  $1,505\text{ cm}^{-1}$  (aromatic stretch vibration of lignin), baseline corrected using the rubber band method in the OPUS software (64 points, Bruker, Bremen, Germany) and subsequently averaged.

#### Water uptake test

Eight ASE specimens per treatment were submerged in approximately 300 ml water and weighted after 2, 4, 6 and 24 h of submersion. Water uptake and water repellent effectiveness (WRE) were calculated according to Donath et al. (2006).

#### Determination of the acetyl content

Eight ASE specimens were milled in a centrifugal mill (Retsch ZM100, Retsch, Germany) using a 0.5 mm sieve; the milled material was soaked in water and dried subsequently at  $103\text{ }^{\circ}\text{C}$  to remove acetic acid. Approximately 0.5 g of each material was weighted into a flat-bottomed flask and 10 ml of 75 % (v/v) ethanol–water mixture was added. This mixture was heated under agitation to  $50\text{ }^{\circ}\text{C}$  for 30 min. NaOH (25 ml,  $0.5\text{ mol l}^{-1}$ ) was added and the flasks were kept at  $50\text{ }^{\circ}\text{C}$  for 30 min. To neutralize the mixture 25 ml  $\text{H}_2\text{SO}_4$  ( $0.25\text{ mol l}^{-1}$ ) was added, the mixture was filtered and diluted with water to 250 ml.

The acetic acid content was determined with an HPLC equipped with an RI-detector (Waters 1525 pump, Waters 717<sup>plus</sup> auto sampler, Waters 2414 RI-detector, Waters Corporation, Milford, MA, USA) using 0.005 M  $\text{H}_2\text{SO}_4$  as solvent. The acetyl content was related to the weight of the specimen tested.

#### Fungal decay test

Resistance to basidiomycetes was assessed according to EN 113 (1996). Twenty pine sapwood specimens and 20 beech wood samples were impregnated either with acetic anhydride or with a mixture of acetoxy-functional siloxane (20 % w/w) in acetic anhydride as described above. Afterward the specimens were heated in the solution to  $120\text{ }^{\circ}\text{C}$ . Ten specimens of each kind were heated for 1 h and the other ten for 2 h. After the reaction time, the specimens were submersed into cold water and kept submerged to perform leaching according to EN 84 (1997).

After careful oven-drying ( $103\text{ }^{\circ}\text{C}$ ), weighing and conditioning (20 °C, 65 % RH), the specimens were incubated in kolle flasks with *Coniophora puteana* (BAM Ebw. 15) (pine sapwood) and *Trametes versicolor* (CTB 863 A) (beech wood) for 16 weeks. Two treated and two untreated control specimens, respectively, were incubated in one kolle flask according to CEN/TS 15083-1 (2004). After incubation, the mass loss was determined.

#### Bending and impact bending test

Bending strength and modulus of elasticity were assessed according to DIN 52186 (1978) with 9 replicates per treatment (Zwick/Z010, Zwick, Ulm Germany) and

impact bending strength according to DIN 52189 (1981) with 12 replicates per treatment (Resil Impactor, Ceast, Turin, Italy). The specimens were acetylated with pure acetic anhydride (AA) and with mixtures of 1, 5 and 10 % acetoxy-functional polysiloxane and AA for 6 h in the same way as described above. The reaction was quenched with water, and the WPG of the dry specimens was determined after 2 days of water leaching. Prior to testing, the specimens were conditioned at 20 °C and 65 % RH, and the equilibrium moisture content (EMC) was determined.

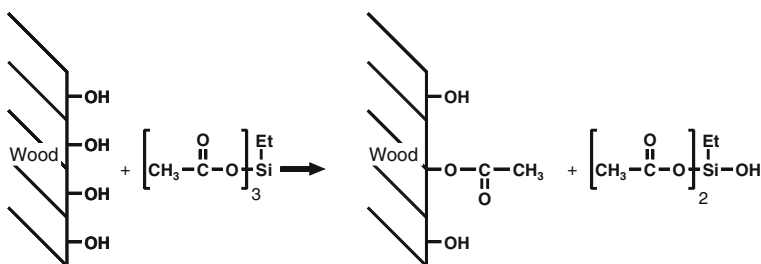
## Results and discussion

### Acetylation with ethyltriacetoxysilane (TAS)

Ethyltriacetoxysilane (TAS) can acetylate hydroxyl groups of wood via a transesterification reaction (Fig. 2). The resulting silanol groups produced from TAS can form siloxane groups upon dehydration and further generate a three-dimensional silicon dioxide network within the wood structure. In contrast to acetylation with acetic anhydride, this reaction principally does not release any acetic acid and the generated polysiloxane might further enhance the properties of the products.

The reaction of pure ethyltriacetoxysilane (TAS) with wood resulted only in negligible WPG and cell wall bulking. Soaking of ASE specimens in pure TAS revealed slight shrinkage (0.04 % of the cross-sectional area) after impregnation rather than swelling. This indicates that TAS does not penetrate into the cell wall and is therefore not able to react with the cell wall matrix. The minor shrinkage was probably due to complete dehydration of the specimens by the silane, which reacts with water upon formation of silanol groups and acetic acid.

The addition of  $\text{H}_2\text{SO}_4$  as a catalyst in TAS resulted in mean bulking of 1.3 % and WPG of 7.8 %. It therefore seems possible to acetylate wood without a solvent by using pure TAS, but effective acetylation in a reasonable time is not achievable. Swelling of the cell wall is indispensable (Rowell 1983) to acetylate wood more successfully with TAS. A 30 % solution of TAS in acetic acid caused swelling of the wood to an extent comparable to water and allowed the silane to enter the cell wall. In absence of a catalyst, no reaction of TAS with wood took place. Triethylamine and  $\text{H}_2\text{SO}_4$  induced noteworthy WPG and bulking, while magnesium



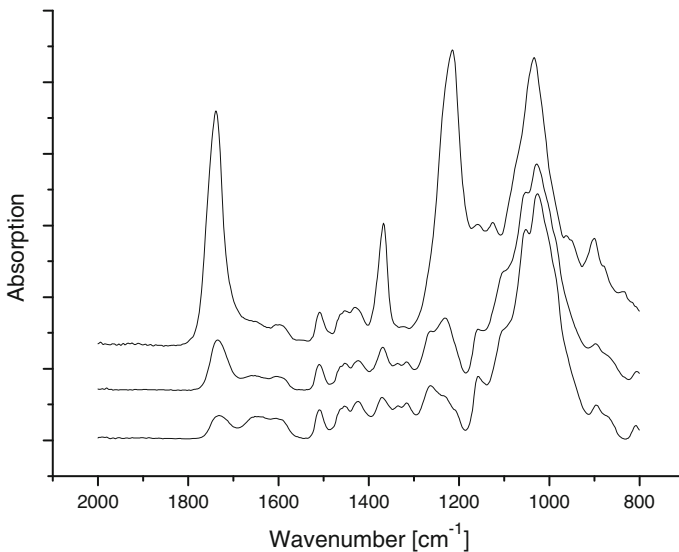
**Fig. 2** Reaction of wood with ethyltriacetoxysilane

chloride and potassium acetate did not. Using triethylamine, the treatment resulted in a WPG of 3.3 % and a bulking of 2.7 %; acetylation in the presence of  $\text{H}_2\text{SO}_4$  led to a WPG of 14 % and a bulking of 7 % after 5 h of reaction time.

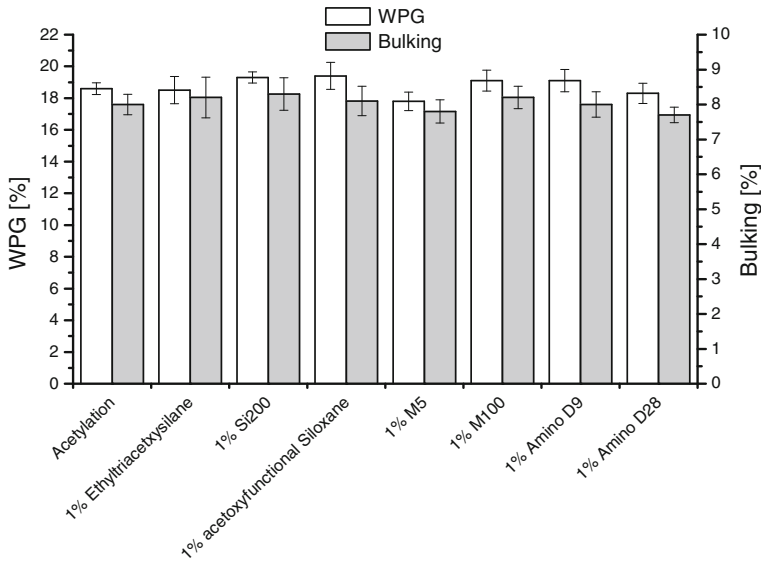
Infrared spectra revealed successful acetylation (Fig. 3). Absorption at  $1,740\text{ cm}^{-1}$  (C=O stretching),  $1,370\text{ cm}^{-1}$  (methyl vibration),  $1,220\text{ cm}^{-1}$  (C–O stretching) and  $897\text{ cm}^{-1}$  (methyl vibration) were strongly increased in the specimens acetylated with a mixture of TAS, acetic acid and  $\text{H}_2\text{SO}_4$  as compared to the control. The peak at approximately  $1,000\text{ cm}^{-1}$  (assigned to C–O stretch vibration in polysaccharides) probably increased due to the presence of silicon–oxygen bonds, which were formed despite of the extraction after treatment. Acetylation catalyzed with triethylamine resulted in much smaller WPG and cell wall bulking. A slightly increased absorption appeared at  $1,740$  and  $1,220\text{ cm}^{-1}$  assigned to acetyl groups. Other absorption peaks did not differ from those of the control.

**Bulking, WPG and water uptake after modification with various combinations of polysiloxane and acetic anhydride**

The two non-functional polydimethylsiloxanes (PDMS) (M5 and M100), especially M100, did not dissolve well in AA. The amino-functional siloxanes easily dissolved only in warm AA, while the other three materials, TAS, Si200 and acetoxy-functional siloxane, easily dissolved in cold AA. WPG and bulking of all treated specimens were very similar and did not differ from the solely acetylated specimens (Fig. 4).



**Fig. 3** FTIR spectra of control (*bottom*), triethylamine catalyzed acetylation (*middle*) and  $\text{H}_2\text{SO}_4$  catalyzed acetylation (*top*)

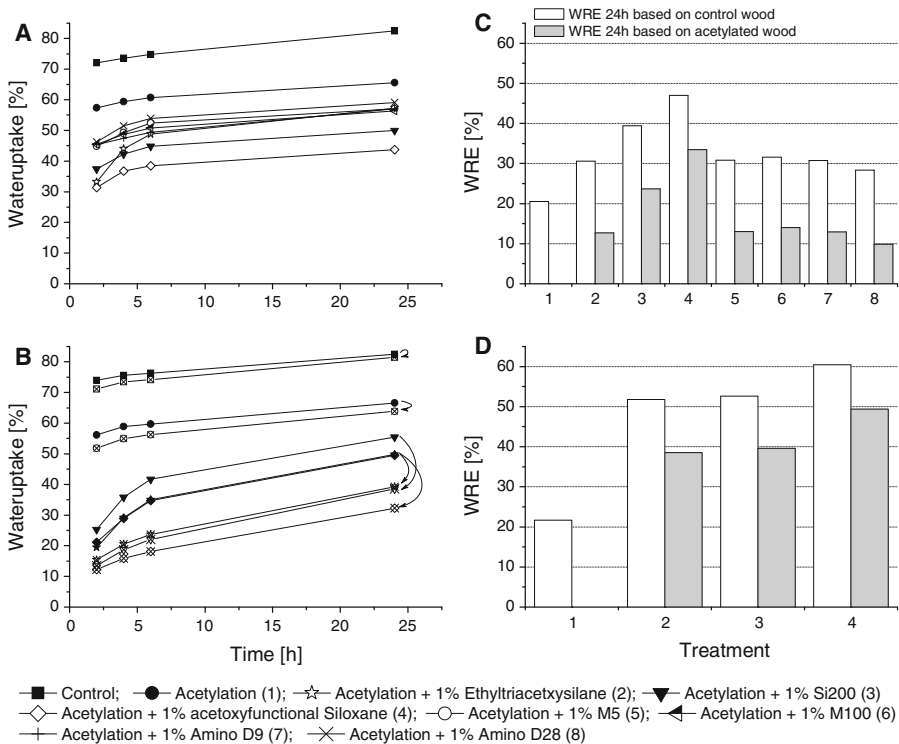


**Fig. 4** WPG and bulking values of wood treated with various siloxanes in combination with acetic anhydride, mean values and standard deviations

The non-functionalized siloxane (M5 and M100) as well as the amino-functional siloxane (D9 and D28) reduced water uptake only to a minor extent compared to the acetylated control. The acetoxy-functional siloxane, however, clearly reduced the water uptake to a greater extent than all other materials (Fig. 5a) with a WRE of 33 % related to acetylated wood. In subsequent water submersion tests, the two educts TAS, Si200 and their product, the acetoxy-functional siloxane, exhibited major changes. In the second test, TAS and acetoxy-functional siloxane did not differ, but in the third (not shown) and fourth tests the acetoxy-functional siloxane again reduced the water uptake more than both of its educts (Fig. 5b) with a WRE of 49 % as compared to the acetylated controls.

In general, water uptake of wood can be reduced through (a) blocking of penetration pathways for capillary water uptake and (b) altering of the surface properties of the wood in a way that hinders water uptake. The gradual decrease in water uptake from the first to the fourth experiment observed with the specimens treated with acetoxy-functional PDMS, TAS and Si200 suggests an alteration of the wood surface rather than pathway blocking. The reason for the reduction in water uptake in subsequent tests may be the increasing orientation of the siloxane chain due to several steps of wetting and high-temperature drying. Kim (2001) also found a strong increase in hydrophobation of textile materials after treatment with amino-functional siloxanes when the drying temperature was raised. The heat treatment is expected to increase the orientation of the siloxane in a way that the hydrophilic parts of the chain are facing toward the wood cell wall and the hydrophobic parts orient toward the lumens. This process is called activation (Kim 2001). In non-functional siloxane, the Si–O-backbone will mostly face toward the wood matrix





**Fig. 5** Water uptake of various siloxane-treated specimens. **a** First submersion test, **b** second and fourth submersion of control and specimens with treatment no. 1, 2, 3, 4, **c** WRE in first submersion test, **d** WRE in fourth submersion test

while the hydrophobic methyl groups are directed outwards (Kim 2001; Noll 1968). In contrast to previous studies (Ghosh 2009), the amino-functional siloxane did not cause strong hydrophobation. The previously found strong reduction in water uptake by amino-functional siloxane (which is a relatively hydrophilic material) was suggested to be due to pathway blocking which prevented capillary penetration of water (Ghosh 2009; Weigenand et al. 2007). In this study, the interaction of amino groups with the wood surface (as described for textiles by Bereck et al. 2001) might be weakened because of the introduction of acetyl groups. These might interfere with the interactions which are normally formed with hydroxyl groups. In addition, acetylation of amino groups can occur in the presence of acetic anhydride (Naik et al. 2004). The following studies focused on acetoxy-functional siloxane, because best results were obtained with this material.

WPG, bulking and acetyl content after modification with combinations of acetoxy-functional siloxane and acetic anhydride

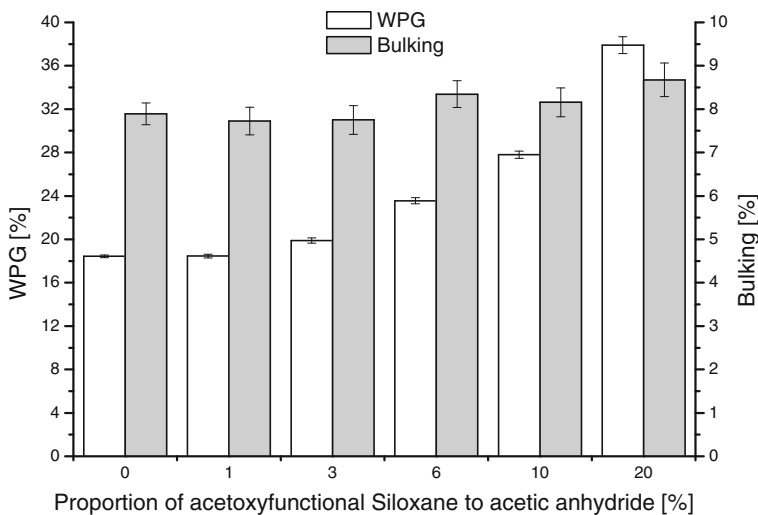
The WPG increased linearly with increasing content of the acetoxy-functional siloxane in AA (Fig. 6). Cell wall bulking increased slightly but significantly with

increasing siloxane content in AA (Fig. 6). Analysis of variance gave a  $p$  value of  $<0.0001$  indicating high significance. Bulking was significantly different from the control when 6, 10 and 20 % siloxane were added to AA.

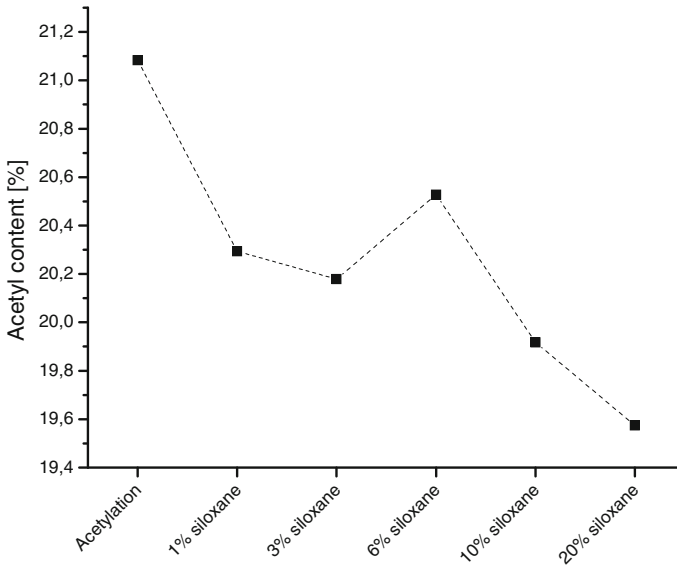
Bulking of acetylated wood is caused by acetyl groups introduced into the cell wall (Rowell 1983). Therefore, the acetyl content should increase with increasing bulking. Determination of the acetyl content, however, revealed that higher bulking was not attributable to a higher degree of acetylation in case of higher PDMS content in the mixture (Fig. 7). Obviously, the siloxane was able to penetrate the wood cell wall to a certain extent and to increase bulking. Ghosh (2009) treated wood with water solvent-based solutions of siloxanes with similar chain length as used here and found considerable bulking. This suggests that siloxanes are able to penetrate the cell wall despite their high molecular mass. While the ASE of the acetylated specimens was 48.4 %, that of the 20 % mixture amounted to 48.7 % and hence did not significantly increase. The reason for this unchanged ASE was a slight increase in maximum swelling in water as compared to the untreated control and the solely acetylated specimens which offset the greater bulking.

### Water uptake

The water uptake test revealed a strong hydrophobation of the wood treated with acetoxy-functional siloxane. The first submersion test still indicated differences between 1 % on the one hand and 3, 6, 10 and 20 % on the other hand (Fig. 8a, c). The specimens were soaked in water and dried two times at 103 °C prior to a second submersion. In this second test, the differences between the treatments nearly disappeared (Fig. 8b); the WRE ranged from 62 % (1 % siloxane) to 71 % (6 % siloxane) without showing a clear trend (Fig. 8d). Addition of 1 % acetoxy-



**Fig. 6** WPG and bulking induced through treatment with different acetic anhydride/siloxane mixtures, mean values and standard deviations

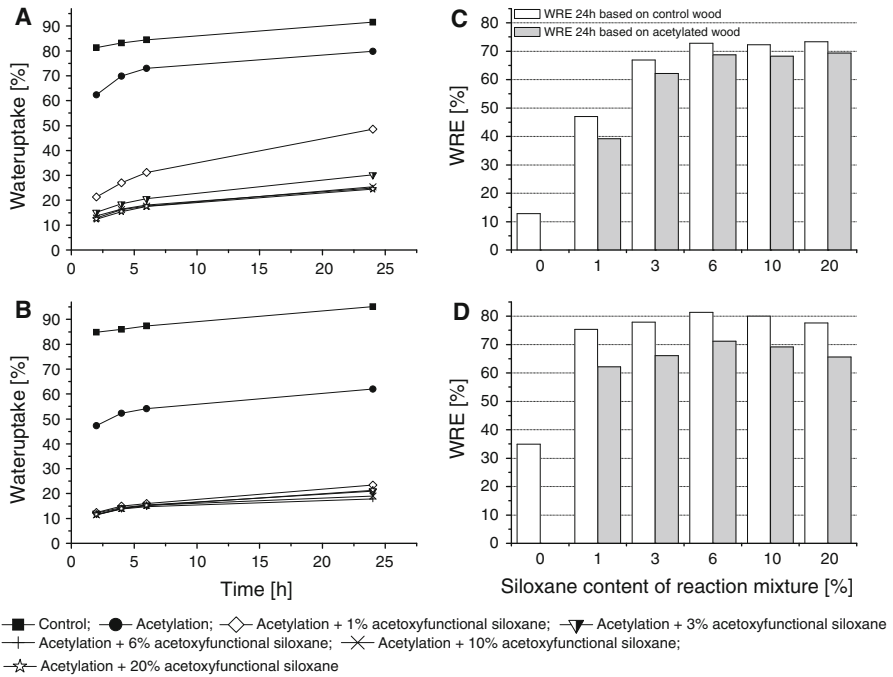


**Fig. 7** Acetyl content of various acetanhydride-siloxane mixtures

functional siloxane therefore appeared to be sufficient to decrease the water uptake to a maximum extent. This result indicates that pathway blocking is not the major reason for increased hydrophobation, because it can hardly explain increasing hydrophobation in subsequent water uptake tests. Furthermore, an increased concentration of the siloxane should lead to increased pathway blocking and thus enhance hydrophobation but this was not the case. It is therefore assumed that water uptake is reduced due to alteration of the (inner) wood surface; addition of 1 % siloxane seems to be sufficient for covering the inner surface of the wood. For maximum reduction in water uptake at 1 % siloxane concentration, however, a more intense activation process is needed, which encompasses extended heating to enhance the orientation of the siloxane chains.

### Fungal decay

In order to study the influence of the acetoxy-functional siloxane, a low degree of acetylation was established which still allowed fungal decay. The WPG of the specimens increased by addition of acetoxy-functional siloxane to AA, but the mass loss after fungal incubation was nearly the same (Table 1). A *t* test performed, respectively, on the pairs “acetylation (*x* h) and acetylation + 20 % siloxane (*x* h)” only revealed a different result between acetylation for 2 h in beech wood and acetylation with 20 % siloxane in beech wood for 2 h (Table 1). Thus, the resistance to fungal decay is exclusively attributable to the acetyl content and not to the presence of siloxane chains. The significantly higher mass loss in the case of beech (2 h acetylation) can be explained by a lower acetyl content which resulted



**Fig. 8** Water uptake of acetylated wood in combination with different ratios of acetoxy-functional siloxane: **a** first submersion, **b** fourth submersion, **c** WRE in first submersion, **d** WRE in fourth submersion

from the high amount of siloxane in the treatment solution (see above for the decrease in acetyl content).

Micro-pore blocking was previously discussed as the main reason for fungal resistance imparted by chemical modifications such as acetylation (Hill et al. 2005). Blocking of cell wall pores can reduce the availability of water as well as the penetration of enzymes (Papadopoulos and Hill 2002). A threshold value of approximately 20 % WPG was found to impart fungal resistance by acetylation,

**Table 1** WPG and mass loss in a fungal decay test after 16-week incubation with *C. puteana* (pine) and *T. versicolor* (beech) (mean values and, in brackets, standard deviations)

	Pine sapwood		Beech wood	
	WPG (%)	Mass loss (%)	WPG (%)	Mass loss (%)
Control	–	28.0 (9.8)	–	25.2 (1.9)
Acetylation 1 h	0.5 (0.1)	33.0 (3.1)	2.5 (0.4)	20.1 (1.6)
Acetylation + siloxane 1 h	8.6 (0.8)	35.5 (4.1)	5.5 (1.2)	21.5 (2.0)
Acetylation 2 h	4.5 (0.3)	26.0 (4.9)	10.2 (0.2)	<b>11.5 (0.9)</b>
Acetylation + siloxane 2 h	12.5 (0.4)	29.7 (10.4)	15.6 (0.9)	<b>14.2 (1.5)</b>

Bold values are significantly different from each other with 95 % confidence

which is accompanied with cell wall bulking of approximately 8 % in case of Scots pine sapwood (experimental results by the authors). A reduction in fungal decay has been reported previously for various functionalized siloxanes. Ghosh et al. (2012) attributed the effectiveness of siloxane treatment against fungal decay to the penetration of the siloxanes into the cell wall and micro-pore blocking as well as interaction with the cell wall. Treatment with amino siloxanes-induced fungal resistance to wood when a bulking value of approximately 4 % was reached (Ghosh 2009). Cell wall bulking of 4 %, however, cannot impart complete fungal resistance if the modification chemical is biologically inactive. It is therefore assumed that amino silicones used by Ghosh et al. (2012) exhibited a certain biological effectiveness in addition to micro-pore blocking. This effectiveness probably depends on the mobility of the siloxane chain, because higher effectiveness of the materials was found, when chain length decreased (Ghosh et al. 2012). In contrast to amino siloxanes used by Ghosh et al. (2012), acetoxy-functionalized siloxanes were applied in this study, which are able to undergo condensation and form a three-dimensional network within the wood. In this network, the siloxane chains are immobilised which is also evident in a completely stable WPG after severe leaching (data not shown). This immobility and the lack of functionality are the reasons why the siloxanes do not affect the physiology of decay fungi and do not prevent fungal decay. Many studies have previously shown the biological inertness of siloxanes with longer chain length (Ackermann and Damrath 1989; Noll 1968).

### Mechanical properties

Specimens treated with mixtures of AA and acetoxy-functional siloxane displayed a slightly greater maximum swelling in water than solely acetylated specimens. A similar result was found by Obataya et al. (2002), combining acetylation with a bulking treatment of glucose-pentaacetate. Greater swelling can be attributed to “solving” or weakening of lignin or to a distortion of the crystalline parts of cellulose. To investigate, if this has any effect on the mechanical properties, a bending test and an impact bending test were performed (Table 2).

Analysis of variance revealed that the bending strength and the modulus of elasticity did not exhibit any significant differences at a 5 % confidence level. The impact bending strength of acetylated wood was significantly higher than that of the

**Table 2** Results of mechanical tests (mean values and, in brackets, standard deviations)

	Bending strength (N mm <sup>-2</sup> )	Modulus of elasticity (N mm <sup>-2</sup> )	Impact bending strength (kJ m <sup>-2</sup> )	WPG (%)	Equilibrium moisture content at 20 °C/65 % RH (%)
Control	119 (11)	13,200 (1,276)	30,285 (7,855)	–	10.6 (0.1)
Acetylation	138 (22)	13,183 (1,510)	43,513 (9,992)	21.0 (0.3)	5.2 (0.1)
+1 % Siloxane	138 (25)	13,000 (1,669)	36,310 (9,733)	21.6 (0.3)	5.2 (0.1)
+5 % Siloxane	122 (26)	12,256 (1,516)	40,047 (7,381)	24.1 (0.2)	5.2 (0.1)
+10 % Siloxane	141 (17)	13,583 (1,164)	34,758 (11,945)	28.7 (0.4)	5.2 (0.0)

control specimens with 95 % confidence. There were, however, no differences between the solely acetylated wood and acetylated wood combined with siloxane.

## Conclusion

Combining acetylation with polysiloxane treatment can enhance the water repellence of acetylated wood without any apparent drawbacks. ASE, mechanical properties and fungal resistance were not changed by the treatment. Small amounts of siloxane are sufficient to reduce water uptake to a great extent, because only the inner surfaces of the wood need to be covered by the siloxane. Fungal resistance of acetylated wood is solely brought about by the acetyl content; fungal resistance is not increased by introduction of acetoxy-functional siloxane probably because of the immobility of the condensed siloxane in the wood.

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