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Improvement of dimensional stability of wood by silica nanoparticles

Miklós Bak [ID], Ferenc Molnár and Róbert Németh

Simonyi Károly Faculty of Engineering, Wood Sciences and Applied Arts, University of Sopron, Sopron, Hungary

ABSTRACT
The improving effect of nanoparticles on wood dimensional stability is barely known nowadays. The expected result of the research was the improvement of the dimensional stability through bulk hydrophobization, as a result of impregnation with hydrophobic SiO_2 nanoparticles. Two different wood species, beech (*Fagus sylvatica*) and scots pine (*Pinus sylvestris*) were investigated. Two different treatments with silica nanoparticles were used. One treatment was a pure emulsion of modified (hydrophobized) silica nanoparticles (carrier material: ethanol), and another one was modified (hydrophobized) silica nanoparticles in tetrahydrofuran carrier material in combination with polydimethylsiloxane (PDMS) as a bonding agent. PDMS was used to improve the bonding of the silica nanoparticles to the wood structure. The impregnation with nanoparticles was successful. Shrinking and swelling properties decreased by 17–33%, depending on wood species and treatment. Water uptake and equilibrium moisture content decreased significantly as a result of the treatments (40–58%). Application of PDMS did not provide better dimensional stability compared to the treatment without it, however, it resulted in lower equilibrium moisture content and water uptake compared to the basic nano-SiO_2 treatment.

Introduction

The improving effect of nanoparticles on wood dimensional stability is barely known nowadays. Contrarily, nanoparticles are commonly used in other industries because of their favourable properties. A lot of promising results were achieved with the use of silica nanoparticles in relation to the mechanical, combustion, hydrophobic and some other properties of different polymers, papers or textiles (Xue et al. 2009, Fanglong et al. 2016, Lee and Yoo 2016, Attiaa et al. 2017, Torun and Onses 2017, Yang et al. 2018). However, regarding the utilization of nanoparticles to improve the wood properties, some positive results are available as well. With the use of different nanoparticles the moisture uptake is reducible, UV-protection, mechanical properties and durability is improvable (Mahltig et al. 2008, Niemz et al. 2010, Sahin and Mantanis 2011, Yu et al. 2011, Rassam et al. 2012) In some cases fire resistance could be improved as well (Shabir Mahr et al. 2012).

There are some results available in the literature regarding the improving effect of silicon compounds on wood properties. These modification techniques are based on different organic or inorganic silicon formulations that affect wood properties mostly favourable. Beside some treatments showing serious drawbacks like increased moisture absorption and strength loss ("water glass" treatments), mostly improved dimensional stability, hydrophobicity, fire resistance and durability was reported (Mai and Militz 2004a, 2004b). Alkoxysilanes are among the most widely investigated silicon compounds to improve the wood properties, as the treatments of wood with them show favourable properties (decay resistance, hydrophobization) and they are non-toxic

(De Vetter et al. 2009, Panov and Terziev 2009, Terziev et al. 2009, Wang et al. 2011, Giudice et al. 2013, Broda and Mazela 2017). Among alkoxysilanes, tetraethoxysilane (TEOS) is a very commonly used compound, however using it as a pure agent provides low hydrophobic properties or dimensional stabilization for the wood material (Saka et al. 1992, Ogiso and Saka 1993, Saka et al. 2001). Therefore, it is used usually in a mixture of hydrophobizing compounds to improve water repellency of wood (Saka and Ueno 1997).

Beside the application of TEOS in a sol–gel process or in-situ polymerization for wood modification, it is also a precursor in the production of spherical silica nanoparticles with the Stöber method (Ibrahim et al. 2010). These nanoparticles are not hydrophobic initially, but it is possible to modify them to turn them hydrophobic (Cho et al. 2014, Ebrahimi et al. 2017, Hood et al. 2017). Such modified silica nanoparticles are used to create superhydrophobic wood surfaces with different techniques. These treatments show usually good water repellent performance, but usually they are lacking of wear resistance as there is only a weak bond between the wood surface and the nanoparticles, and these methods are only surface modifications. Bulk hydrophobization of wood could be the solution for this problem, but such methods are usually very complex, costly and time-consuming (Wang et al. 2013). To improve the bonding of hydrophobic nanoparticles to the wood surface, bonding agents are necessary.

In this study, silica nanoparticles were prepared by hydrolysis and condensation of TEOS at high pH. This step of preparing hydrophilic spherical nanoparticles was followed by a modification step with hexadecyltrimethoxysilane (HDTMS), resulting in the grafting of long-chain alkyl groups onto the

CONTACT Miklós Bak ✉ bak.miklos@uni-sopron.hu

surface of the nanoparticles to make them hydrophobic. To get better bonding to the wood surface, PDMS was used as a bonding agent between the HDTMS-coated silica nanoparticles and wood. The novelty of this research is the application of such nanoparticles not only as a surface coating, but a full cross-section impregnation, which utilization form in case of wood material was not investigated yet. The planned treatment will likely elongate the lifetime of the wood-based products, because the wood–water relations are essential at all utilization fields (Skaar 1988a). The expected positive effect of the investigated treatments is the improvement of the dimensional stability of wood as a result of impregnation with hydrophobic silica nanoparticles. The aim of this work was to improve the dimensional stability of wood material by the use of hydrophobized spherical silica nanoparticles. Another goal was to improve the effect of the treatment by the use of polydimethylsiloxane (PDMS) as the bonding agent between the nanoparticles and the wood surface.

Experimental

Materials

Tetraethoxysilane (TEOS) and hexadecyltrimethoxysilane (HDTMS) were obtained from Sigma-Aldrich Co. LLC, ammonium hydroxide (NH_4OH, 25%) from Reanal Kft., tetrahydrofuran (THF) from Scharlau Chemicals, ethanol were purchased from Merck KGaA. Polydimethylsiloxane (PDMS) and the required curing agent were supplied by Dow Corning (Sylgard 184 silicone elastomer kit). All chemicals were used as received without further purification. Wood samples of beech (*Fagus sylvatica*) and scots pine sapwood (*Pinus sylvestris*) were cut into blocks of 20 mm × 20 mm × 30 mm (radial × tangential × longitudinal) and 10 mm × 50 mm × 50 mm (radial/tangential × tangential/radial × longitudinal). All samples were cut from the same log in case of both wood species. The initial moisture content of the wood material used was $12 \pm 2\%$. Selection of wood species for the tests was based on their good permeability, because the investigated treatment is based on an impregnation process; on their importance in the wood industry; and to fulfil the goal to have a hardwood and a softwood species in the test.

Preparation of silica nanoparticles

As a first step, monodisperse silica sols were prepared by a typical Stöber method (Ibrahim et. al. 2010). 30 ml NH_4OH and 500 ml ethanol were mixed by continuous stirring using a magnetic stirrer (Witeg MS2DHS) for 30 minutes at 50°C to form a homogeneous solution. Thirty millilitre TEOS was then added dropwise into this solution while continuous stirring. Magnetic stirring at 50°C was continued for additional 2 hours to form a transparent silica sol. After that, 1% HDTMS was added to the prepared sol in order to modify the hydrophilic silica particles to hydrophobic. The reaction was continued for additional 2 hours while stirring at 50°C to form hydrophobic silica sol. After that, the sol was divided into 2 equal amounts. One part of this "base-sol" was used as the first type of treatment medium,

Table 1. Parameters of the treatments used for the tests.

| Treatment type	Nanoparticle used	Carrier material	Bonding agent
Nano-SiO$_2$	Hydrophobic SiO$_2$	Ethanol	–
Nano-SiO$_2$ + PDMS	Hydrophobic SiO$_2$	Tetrahydrofuran	PDMS

called later "nano-SiO$_2$". Particle size obtained was 40–80 nm with this method.

The other part of the initial sol was the base of the 2nd sol type, called later "nano-SiO$_2$+PDMS". In this case, hydrophobic SiO$_2$ nanoparticles were collected from the sol and washed three times in ethanol. Parallel to the preparation of the "base-sol", another solution of 11 g PDMS and 600 ml THF was prepared by magnetic stirring for 30 minutes at 50°C (solution "A"). Furthermore, a solution of 1.1 g curing agent and 600 g THF was prepared by magnetic stirring for 30 minutes at 50°C (solution "B"). Following, solution "A" and "B" were mixed by magnetic stirring for 30 minutes at 50°C. As the last step of the preparation of PDMS-improved silica nanosol, 22 g of hydrophobic SiO$_2$ nanoparticles were added and mixed by magnetic stirring for 30 minutes. Accordingly, the SiO$_2$:PDMS ratio of the nanosol was 2:1.

This way two different treatment was prepared (Table 1), where one treatment was based on a pure emulsion of modified silica nanoparticles (carrier material: ethanol), and another one was based on silica nanoparticles in tetrahydrofuran carrier material in combination with polydimethylsiloxane (PDMS) as the bonding agent (Figure 1).

Preparation of hydrophobic wood material

Wood blocks of 20 mm × 20 mm × 30 mm (radial × tangential × longitudinal) and 10 mm × 50 mm × 50 mm (radial/tangential × tangential/radial × longitudinal) were vacuum-impregnated with the prepared hydrophobic silica nanosols. On the one hand, altogether 80 pieces of wood blocks with the dimensions of 20 mm × 20 mm × 30 mm were impregnated, 20 pieces/treatment for both wood species. On the other hand, altogether 80 pieces of wood blocks with the dimensions of 10 mm × 50 mm × 50 mm were impregnated, 10 pieces/treatment for both wood species and annual ring orientation. Wood blocks were oven dried before the impregnation process at 105°C in a drying
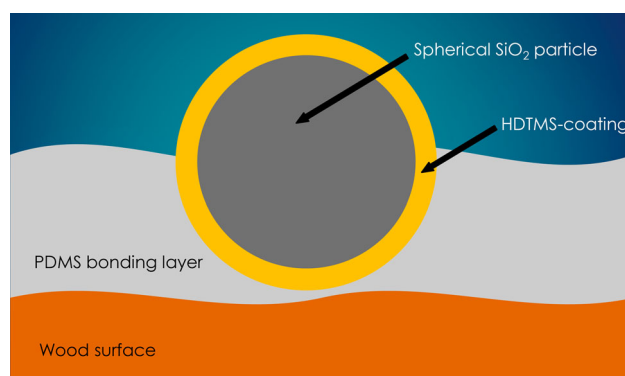
Figure 1. Schematic structure of the treatment system based on hydrophobic SiO$_2$ nanoparticles + PDMS bonding agent.

chamber (Memmert UP 500). The first step of the treatment was a 20-minute vacuum phase under 100 mbar pressure in a vacuum dryer (Memmert VO 400) at 25°C. This was followed by a 60-minute impregnation step under atmospheric pressure, by leaving the samples in the treatment solutions. After taking the samples from the sols, the treatment was finished with a 1 day long curing step in a drying chamber at 110°C.

Test methods

Retention

To determine retention, samples were weighed before the impregnation (dry weight), after the impregnation (wet weight), and after the curing step (dry weight). Retention was calculated according to the following equations:

$$R_w = \frac{m_{\text{wet}} - m_0}{V_0} \text{ (kg/m}^3) \tag{1}$$

where R_W is the wet retention, uptake of the nanoparticle suspension (kg/m^3); m_{wet} is the weight of samples after impregnation with nanoparticle suspension (kg); m_0 is the dry weight of samples before impregnation with nanoparticle suspension (kg) and V_0 is the volume of samples before impregnation (m^3).

$$R_D = \frac{m_{0\text{ imp}} - m_0}{V_0} \text{ (kg/m}^3) \tag{2}$$

where R_D is the dry retention, nanoparticle uptake of the samples (kg/m^3); $m_{0\text{ imp}}$ is the weight of samples after impregnation and curing (kg); m_0 is the dry weight of samples before impregnation with nanoparticle suspension (kg) and V_0 is the volume of samples before impregnation (m^3).

Anti-swelling-efficiency and swelling anisotropy

To determine swelling for the calculation of anti-swelling-efficiency (ASE), $20 \times 20 \times 30$ mm (radial × tangential × longitudinal) samples were used. There were 10 pieces from both treatment types investigated for both wood species. Ten pieces of untreated samples for both wood species served as the control. The samples were dried at 105°C until a constant mass and then the dimensions were measured in the radial and tangential directions. Thereafter, the samples were submerged into water for 10 days and finally, the dimensions were measured again in the radial and tangential directions. The swelling was determined according to the following equation:

$$S_{r,t} = \frac{l_u - l_0}{l_0} \text{ (%)} \tag{3}$$

where $S_{r,t}$ is the swelling, radial or tangential (%); l_u is the dimension at EMC under standard conditions (mm) and l_0 is the dimension in the dry state (mm).

ASE was determined according to the following equation:

$$\text{ASE}_{r,t} = \frac{S_{U,r,t} - S_{T,r,t}}{S_{U,r,t}} \text{ (%)} \tag{4}$$

where $\text{ASE}_{r,t}$ is the anti–swelling-efficiency, radial or tangential (%); $S_{U,r,t}$ is the swelling of untreated samples, radial or tangential (%) and $S_{T,r,t}$ is the swelling of treated samples, radial or tangential (%).

Swelling anisotropy was determined according to the following equation:

$$A_{sw} = \frac{S_t}{S_r} \tag{5}$$

where A_{sw} is the swelling anisotropy and $S_{r,t}$ is the swelling, radial or tangential (%).

Equilibrium moisture content

To determine equilibrium moisture content (EMC), $20 \times 20 \times 30$ mm (radial × tangential × longitudinal) samples were used; there were 10 pieces from both treatment types investigated for both wood species. Ten pieces of untreated samples for both wood species served as the control. Initially, the samples were stored in a drying chamber until constant mass at 105°C, and weighed. After that, the samples were stored in a climatic chamber under constant conditions (20°C and 65% relative humidity). During the climatization, the samples were weighed every week and the climatization was stopped when the difference between two following weighing was less than 1% in case of all sample groups (including control and treated samples). Accordingly, the last measurement was done after 10 weeks of climatization. EMC was determined according to the following equation:

$$\text{EMC} = \frac{m_u - m_0}{m_0} \text{ (%)} \tag{6}$$

where m_u is the wet weight of the samples after 10 weeks of climatization (g) and m_0 is the dry weight of the samples (g).

Water uptake

To determine water uptake, $10 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$ (radial/tangential × tangential/radial × longitudinal) samples were used. Additionally, samples were prepared with clear radial or tangential surfaces, to be able to determine the water uptake in clear anatomical directions. There were 10 pieces from both treatment types investigated for both wood species and anatomical directions (radial or tangential). Ten pieces of untreated samples for both wood species and anatomical directions served as the control. Water uptake in both radial and tangential direction was measured. After the impregnation and curing, the samples were climatized at 20°C and 65% relative humidity until constant mass. As the next step of the sample preparation, samples were sealed at the edges and at one radial/tangential surface and weighed. They were then immersed in distilled water with the unsealed surface and weighed after 72 hours. Water uptake was calculated according to the following equation:

$$W = \frac{m_u - m_0}{A} \text{ (g/m}^2) \tag{7}$$

where m_u is the mass of the samples after immersion in water (g); m_0 is the mass of the samples before immersion in water (g); A is the radial or tangential surface area of the samples (mm^2).

Total colour change (ΔE*)

Colour measurements were carried out with a colorimeter (Konica-Minolta 2600d). The CIELab colour coordinates were calculated based on the D65 illuminant and 10° standard observer with a test-window diameter of 8 mm. The relatively large window was chosen to measure the average colour of earlywood and latewood regions combined. The radial surfaces of the water uptake samples were used for colour measurement. The colour of randomly chosen 3 points was measured on each sample. Measurements on samples were carried out before and after impregnation, and the total colour change (ΔE*) was calculated according to the following equation:

$$\Delta E^* = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \, (g/m^2) \qquad (8)$$

where ΔL is the change in lightness as a result of the treatments; Δa is the change in red hue as a result of the treatments; Δb is the change in yellow hue as a result of the treatments.

Scanning electron microscope imaging

After nanoparticle treatments, the samples were investigated with scanning electron microscope (SEM) imaging to determine the location and distribution of the nanoparticles in the structure of the wood. The device used was a Hitachi S3400N scanning electron microscope. The surfaces were not gold coated with a sputter-coater machine before the imaging. Samples of 30 mm long and 20 mm wide for SEM imaging were used. Longitudinal (radial or tangential) sections were cut and investigated, to have an overview from the location and distribution of the nanoparticles.

Statistical analysis of the results

Distribution normality of the data was verified and statistical significance tests (ANOVA, LSD-test) were conducted for the effect of the different nano-SiO$_2$ treatments on the investigated material properties with the software Statistica 10.0 (Statsoft).

Results and discussion

Retention

Retention values for tested beech and pine specimens are shown in Table 2. There were significant differences in case of both dry and wet retention of the different wood species, while the type of nanoparticle treatment did not affect the retentions significantly. Pine samples showed lower retention values in all cases compared to the beech. The ratio of dry and wet retention was between 6.91% and 7.12% in case of all treatments, that shows the identical efficiency of the different investigated nanoparticles' penetration into the wood tissue. Thus, impregnation quality and quantity did not affected the results. This result indicates that the use of PDMS did not affect the retention negatively. However, the amount of silica nanoparticles penetrating the wood tissue must be lower in case of "SiO$_2$+PDMS" treatment, because dry retention is consisting only the amount of hydrophobic SiO$_2$ nanoparticles in case of "nano-SiO$_2$" treatment, while in case of the other treatment it consists of the amount of penetrated hydrophobic SiO$_2$ nanoparticles and PDMS together, with the ratio of SiO$_2$:PDMS = 2:1. It means, that in case of "SiO$_2$+PDMS" treatment, the amount of hydrophobic nanoparticles in wood is by 33% less compared to the "nano-SiO$_2$" treatment.

SEM imaging

Presence of the nanoparticles on the surface was stated by SEM imaging. Nanoparticles were distributed on the surface mostly evenly, and could be observed as small spherical particles (Figures 2–3). In case of using PDMS as the bonding agent, the nanoparticles were covered by the PDMS carrier layer. Beside the even distribution of the nanoparticles, larger deposits, agglomerations were found (Figure 4). This shows the susceptibility of the nanoparticles to agglomeration in the emulsion, followed by precipitation during the impregnation process. However, this kind of deposit in the cell lumen might increase the dimensional stabilization effect through the clogging of the lumens. A well visible difference could be observed between the structures of nanoparticle deposits of the two different treatment systems (Figure 5). In case of "nano-SiO$_2$" treatment, the deposit was amorphous and visibly porous, with loose structure, without any organization. While in case of "nano-SiO$_2$+PDMS" treatment, a closed structure was visible, with the spherical surface arrangement. This is because of the use of PDMS as the bonding agent in case of the "nano-SiO$_2$+PDMS" treatment.

ASE and swelling anisotropy

Shrinking and swelling properties decreased remarkably in case of both investigated wood species (Figure 6). The ASE was similar in the radial direction for both beech and pine wood in case of nano-SiO$_2$ treatment, with the ratio of

Table 2. Retention values of beech and pine samples in kg/m^3 in case of different nanoparticle suspension impregnations.

|	Beech				Pine			
	SiO$_2$		SiO$_2$+PDMS		SiO$_2$		SiO$_2$+PDMS	
	Dry retention (kg/m^3)	Wet retention (kg/m^3)	Dry retention (kg/m^3)	Wet retention (kg/m^3)	Dry retention (kg/m^3)	Wet retention (kg/m^3)	Dry retention (kg/m^3)	Wet retention (kg/m^3)
Mean	30.22	431.67	32.43	463.33	26.02	371.67	27.18	388.33
Min	29.75	425.00	31.50	450.00	20.42	291.67	23.33	333.33
Max	30.33	433.33	33.83	483.33	34.42	491.67	37.92	541.67
St. Dev.	0.26	3.73	0.98	13.94	6.68	95.49	6.04	86.32
Var. Coeff.	0.86%	0.89%	3.01%	3.09%	25.69%	24.16%	22.23%	21.44%
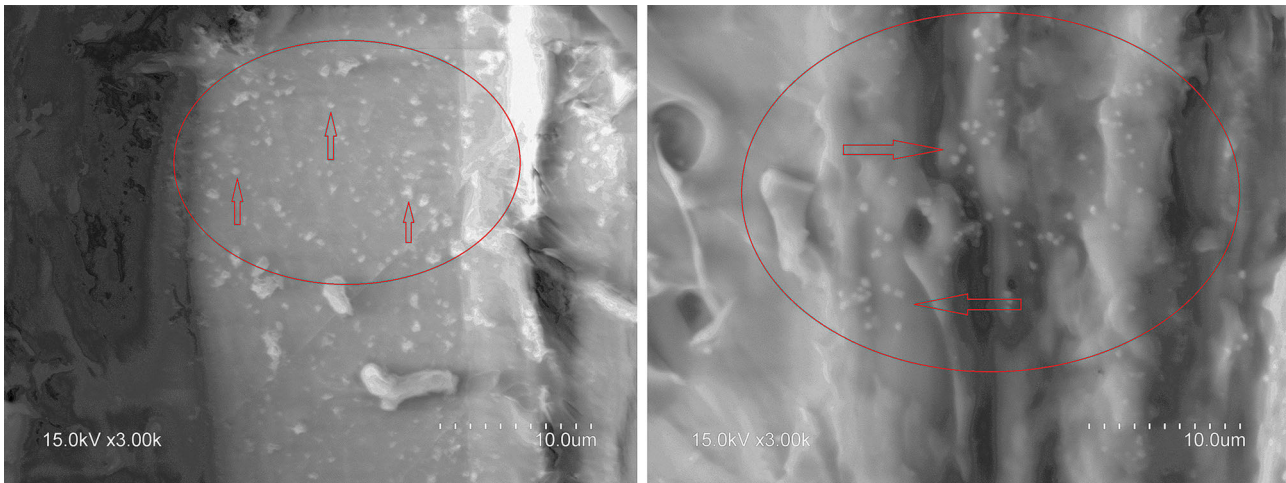
Figure 2. Nanoparticles' distribution on the surface of beech cell walls. Hydrophobic SiO_2 nanoparticles on the left, hydrophobic SiO_2 nanoparticles with PDMS bonding agent on the right.
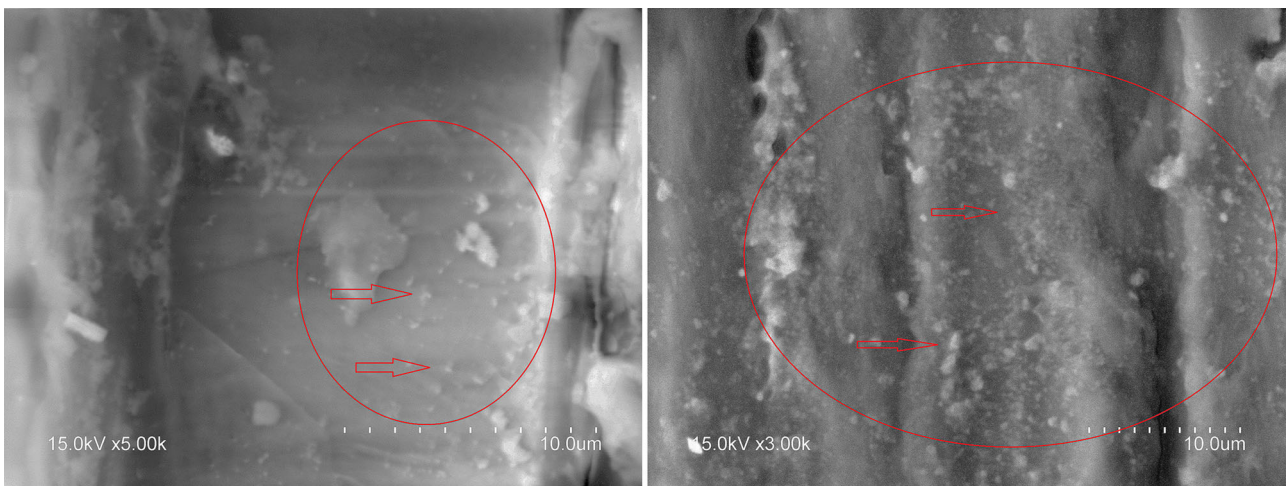
Figure 3. Nanoparticles' distribution on the surface of scots pine cell walls. Hydrophobic SiO_2 nanoparticles on the left, hydrophobic SiO_2 nanoparticles with PDMS bonding agent on the right.
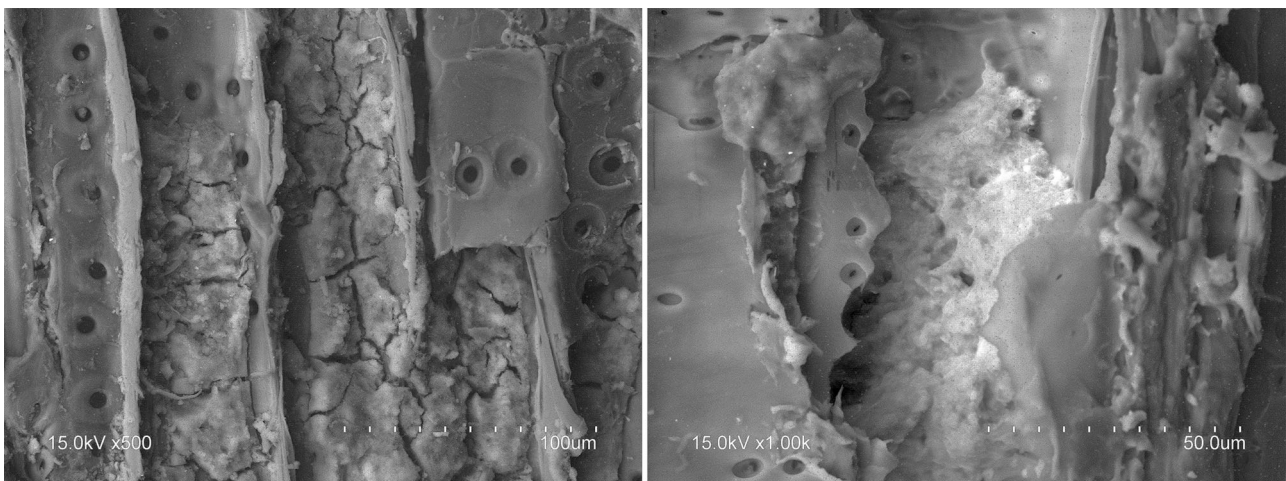
Figure 4. Nanoparticle deposition in the cell lumens. Hydrophobic SiO_2 nanoparticles on the left, hydrophobic SiO_2 nanoparticles with PDMS bonding agent on the right.
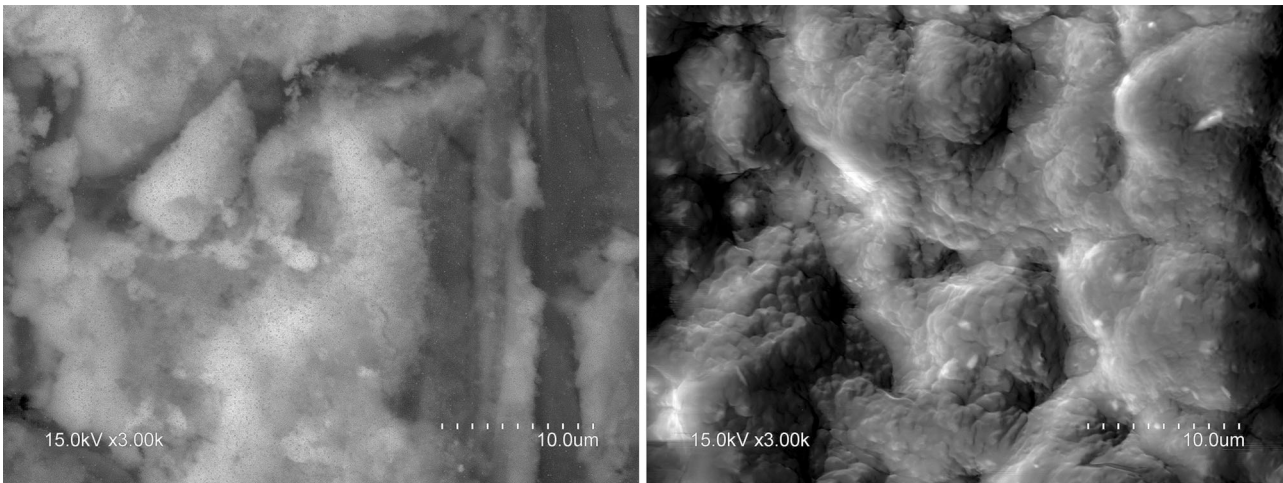
Figure 5. Surface of nanoparticle deposition in the cell lumens. Hydrophobic SiO$_2$ nanoparticles on the left, hydrophobic SiO$_2$ nanoparticles with PDMS bonding agent on the right.

30.09% and 33.04% respectively. Nano-SiO$_2$+PDMS treatment resulted in slightly, but significantly lower ASE in the radial direction in case of pine wood (25.79%), compared to beech (29.20%). ASE was significant also in tangential direction. Nano-SiO$_2$ treatment resulted in slightly, but significantly lower ASE in a tangential direction in case of beech wood (17.66%), compared to pine (23.58%). These results show that wood species has some effect on the efficiency of the investigated treatments. This is related to the differences in the anatomical structure that leads to the different permeability of beech and pine in the different anatomical directions. As hydrophobic nanoparticles caused bulking of the cell walls, the affinity of water for the cell wall decreased. As a result, dimensional stability increased due to less available space in the cell walls for water molecules (Wang et al. 2013). Additionally, lower retention values of pine were observed, as dry retention values were 30.22 and 32.43 kg/m^3 in case of beech, and 26.02 and 27.18 kg/m^3 in case of pine for the basic nano-SiO$_2$ treatment and nano-SiO$_2$+PDMS treatment, respectively (Table 2). These differences were not realized in the ASE of the treatments, as no correlation was found between the retention and ASE of the different treatments in radial and tangential direction.

In case of beech samples, application of PDMS did not provide significantly better dimensional stability compared to the treatment without it. However, in case of pine wood in both radial and tangential direction, a slight but significant decrease in the efficiency was observed as a result of using PDMS as the bonding agent in the system. However, in case of "SiO$_2$+PDMS" treatment the amount of hydrophobic nanoparticles is by 33% less compared to the "nano-SiO$_2$" treatment (nano-SiO$_2$:PDMS = 2:1), this did not result in 33% decrease in the ASE. It resulted in only a slight decrease, or similar result to the other treatment. This is explained by the effect of the polymerization of PDMS in the wood cell wall and cell lumen, which countervailed the lack of hydrophobic silica nanoparticles in terms of ASE through the hydrophobicity of PDMS itself, caused by the organic methyl groups in its structure (Mai and Militz 2004b). Thus, the use of PDMS did not result in relative higher ASE, but "SiO$_2$+PDMS" treatment showed similar dimensional stabilization already in the presence of lower amount of hydrophobic silica nanoparticles.
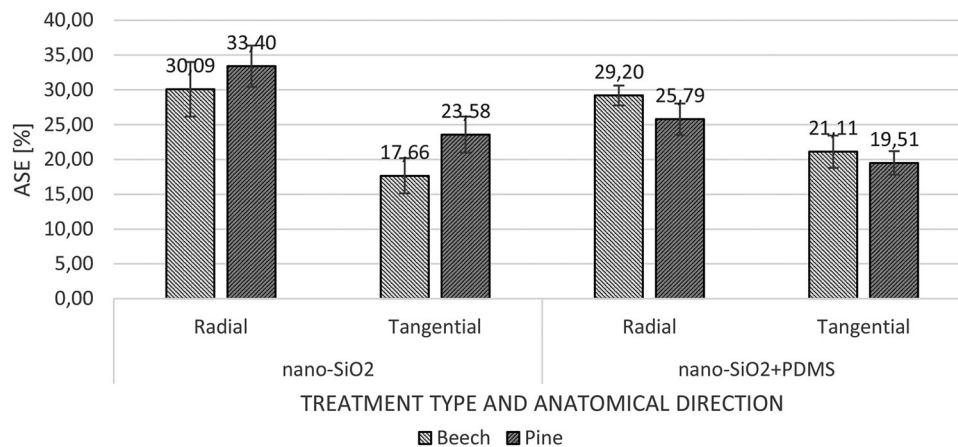
Figure 6. ASE of nano-silica treatments on beech and scots pine wood (whiskers showing standard deviation of the results).
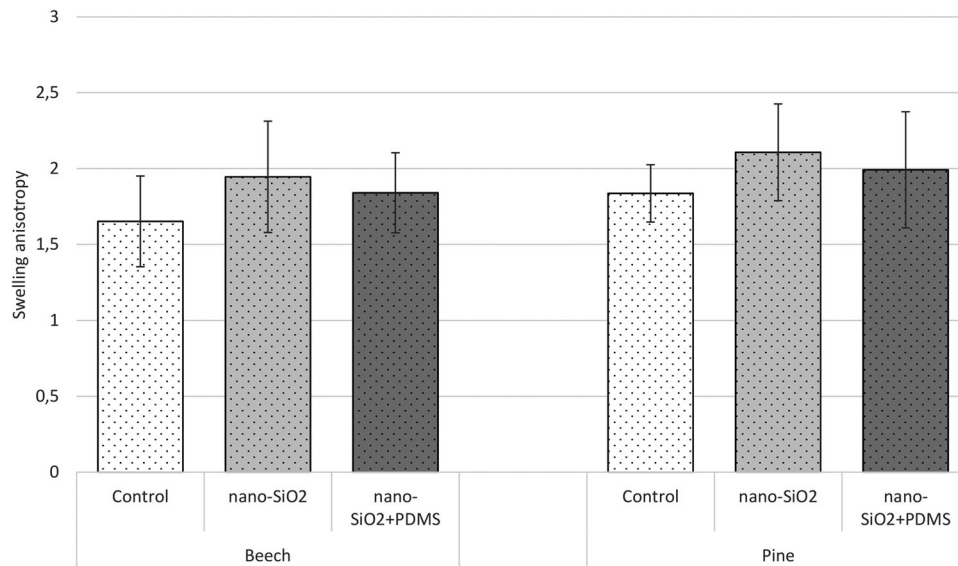
Figure 7. Effect of nano-silica treatments on the swelling anisotropy (whiskers showing standard deviation of the results).

Behind the result that, despite of the lower hydrophobic nanoparticle amount in wood while using PDMS as the bonding agent ASE is not decreasing, must be the reduced hygroscopicity of the treated wood material (Kumar et al. 2016). The sites that enable bonding of water molecules are replaced partly by PDMS layers. According to Donath et al. (2004) the treatment of wood with different alkoxysilanes (tetraethoxysilane, methyl triethoxysilane, propyl triethoxysilane) might result in 20–35% ASE, while other authors reported 8–69% ASE with other alkoxysilanes (ethyltriethoxysilane, diethyldiethoxysilane) at relatively high WPG values (16–65%). In our case, ASE values ranged between 17% and 33% as already reported, but only at 3.5% and 4.6% WPG in case of "nano-SiO$_2$" treatment for beech and pine respectively, furthermore, 3.75% and 4.72% WPG in case of "nano-SiO$_2$+PDMS" treatment for beech and pine, respectively.

Significantly higher ASE values were observed in the radial direction, compared to the tangential direction. Unfortunately, this effect increased the swelling anisotropy slightly, but statistically in an insignificant ratio (Figure 7). This phenomenon might lead to the increased capability of cracks, deformations and warping. However, the values of swelling anisotropy are in case of all treatments and both wood species under or only slightly over the value of 2, which is the theoretical limit for wood materials regarding the tending to the warping and deformations. Over the value of 2, the wood material is highly capable of warping and deformations related to the changes in the wood–water relations (Skaar 1988b).
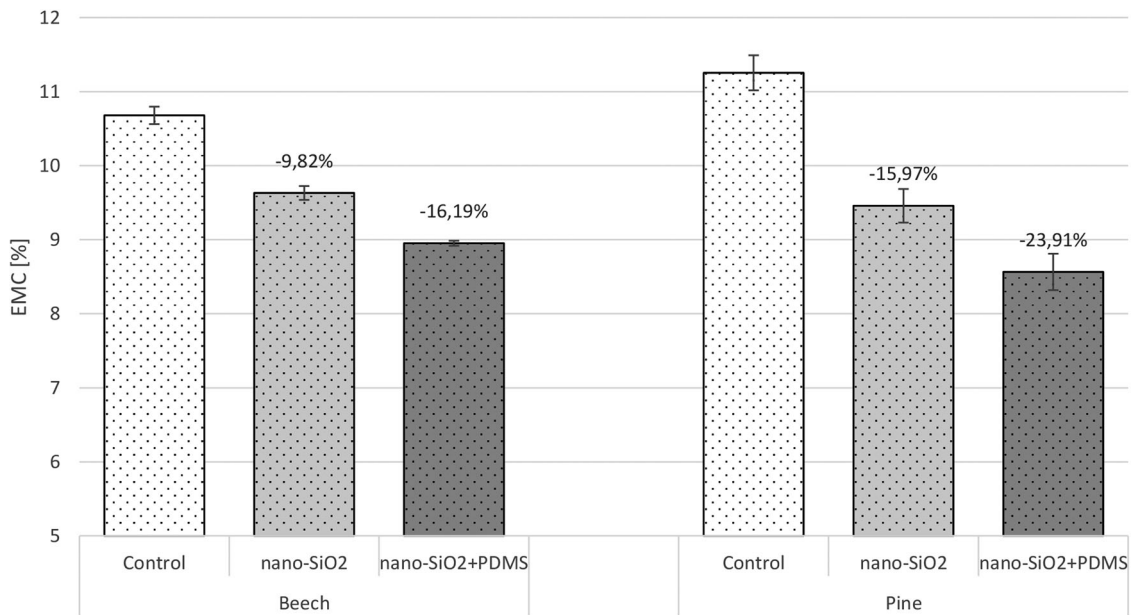
Equilibrium moisture content

EMC decreased significantly as a result of the different investigated nanoparticle treatments (Figure 8). With other words, the uptake of water vapour is decreased by the investigated treatments. This means that the investigated treatments did not only result in highly hydrophobic characteristic of surfaces of the treated wood, but decreased additionally the ability of

wood to absorb moisture (Kumar et al. 2016). In spite of the results of ASE, there is a significant difference between the effects of the investigated treatments, as the application of PDMS as the bonding agent for the hydrophobic silica nanoparticles resulted in lower EMC. This shows that the presence of polymerized PDMS decreases the moisture uptake beside the hydrophobation effect also by the exclusion of moisture from the cell wall pores and the cell wall surfaces (clogging effect). However, retentions were higher in case of beech, decrease of EMC was higher in case of pine wood. This might be related to the WPG, as in contrast to the retention, WPG was higher in case of pine (4.6% and 4.72% for the "nano-SiO$_2$" and the "nano-SiO$_2$+PDMS" treatment respectively), compared to the beech (3.5% and 3.75% for the "nano-SiO$_2$" and the "nano-SiO$_2$+PDMS" treatment, respectively).

Water uptake

Water uptake decreased significantly as a result of the treatments. In radial and also tangential direction, both nano-SiO$_2$ treatment and nano-SiO$_2$+PDMS treatment resulted in statistically significant decrease in case of beech and pine samples compared to the control (Figures 9–10). In addition, using PDMS as the bonding agent for the nano-SiO$_2$ particles resulted in a statistically significant lower water uptake compared to the "nano-SiO$_2$" treatment. These results indicated that a large amount of hydrophobic nano-silica particles successfully attached to the wood cell walls, impeding access of water to cell lumens in the treated wood samples (Wang et al. 2013). Thus, the presence of nanoparticles leads to lower water uptake capacity. Furthermore, the nanoparticles increasingly block the pits and micropores of the cell wall (Dong et al. 2015). The "nano-SiO$_2$+PDMS"-treated wood samples showed slightly lower water absorption compared to that of "nano-SiO$_2$"-treated wood samples, likely due to the additional water impeding effect of the hydrophobic PDMS bonding layer on the cell wall surfaces, which is due
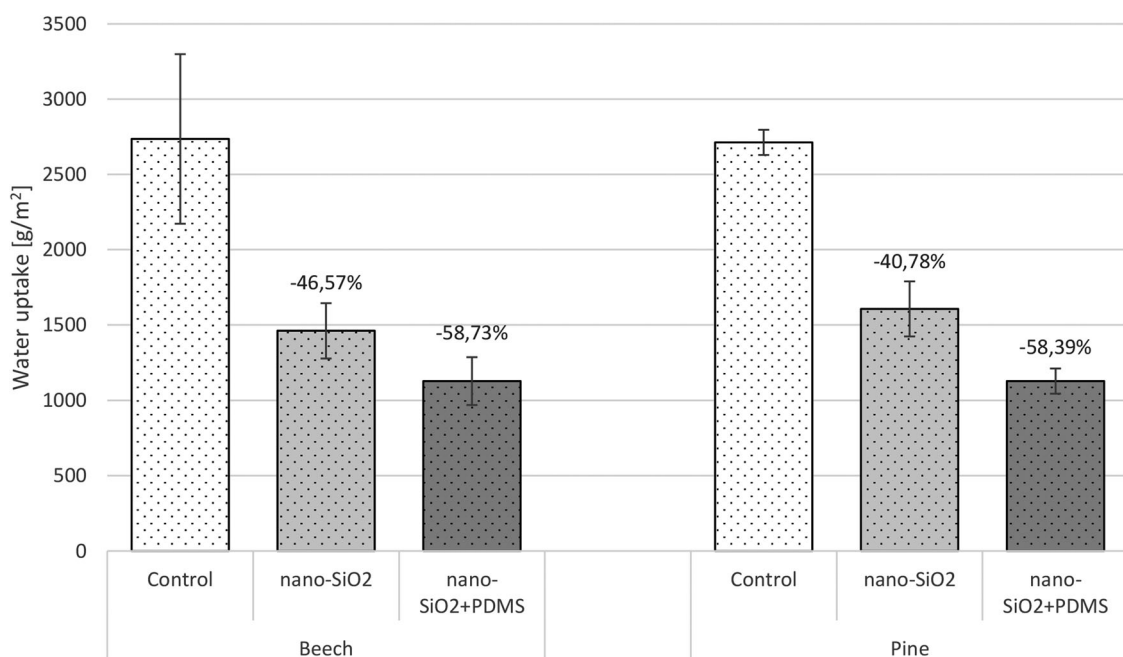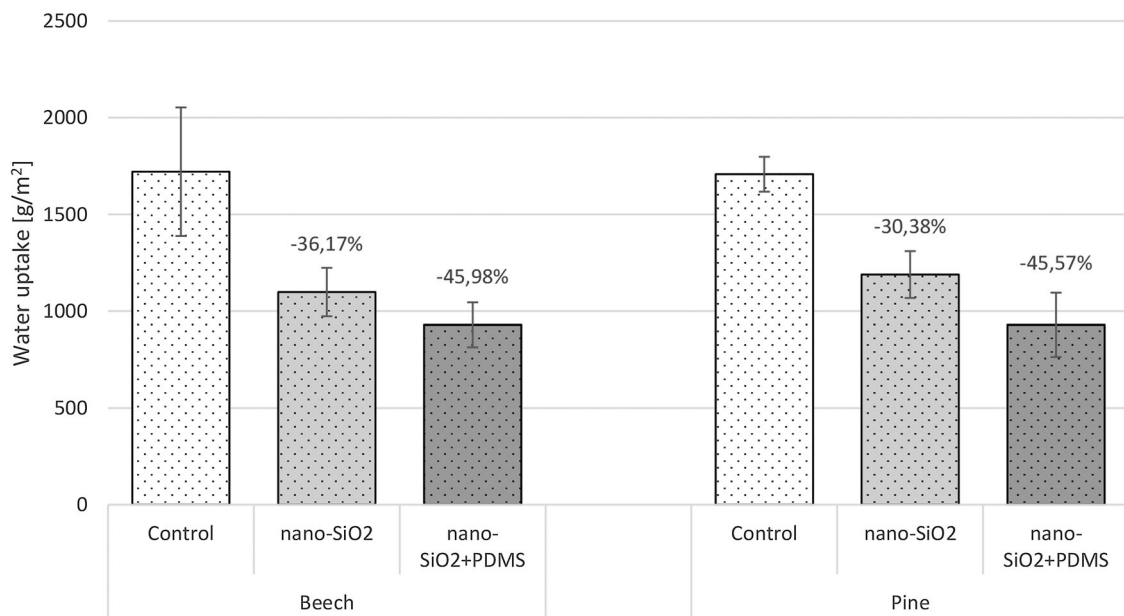
Figure 8. Effect of nano-silica treatments on the equilibrium moisture content of beech and scots pine wood (percentages showing the difference to the control and whiskers the standard deviation of the results).

to the polymerized PDMS that is filling the void spaces and blocking more effective the water absorption (Dong et al. 2015). The improved hydrophobicity could be explained by the combined effect of the hydrophobic nanoparticles and PDMS. Namely, the spherical nanoparticles are well-distributed on the cell wall surface (Figures 2–3), which improved the wood roughness. The PDMS polymerized in wood and covered the nanoparticles (Figure 5). As a result of that, a packed layer is deposited on the cell wall surface. Because of the roughness of this layer, the surface free energy is reduced (Dong et al. 2015). This is the so-called lotus effect

that is common in nature (Neinhuis and Barthlott 1997). Water uptake decreased in a much higher ratio compared to the water vapour uptake (EMC, Figure 8). The decrease of the EMC was between 9.82% and 23.91% depending on treatment type and wood species, while a decrease of the water uptake was between 30.38% and 58.73%, depending on treatment, wood species and anatomical direction. Highly decreased water uptake shows that besides a decreased ability of wood to absorb moisture, there is also a hydrophobization effect present, caused by the different investigated (hydrophobic) nanoparticle based treatments. This

Figure 9. Effect of nano-silica treatments on the water uptake of beech and scots pine wood in radial direction (percentages showing the difference to the control and whiskers the standard deviation of the results).

Figure 10. Effect of nano-silica treatments on the water uptake of beech and scots pine wood in tangential direction (percentages showing the difference to the control and whiskers the standard deviation of the results).
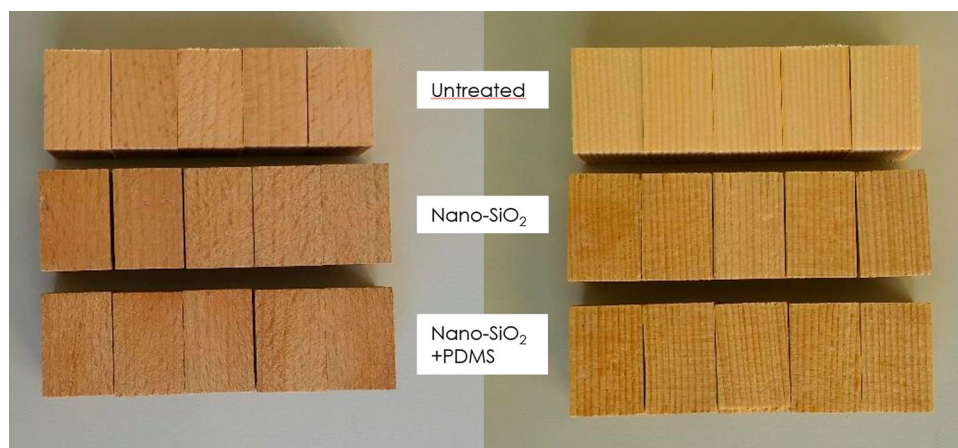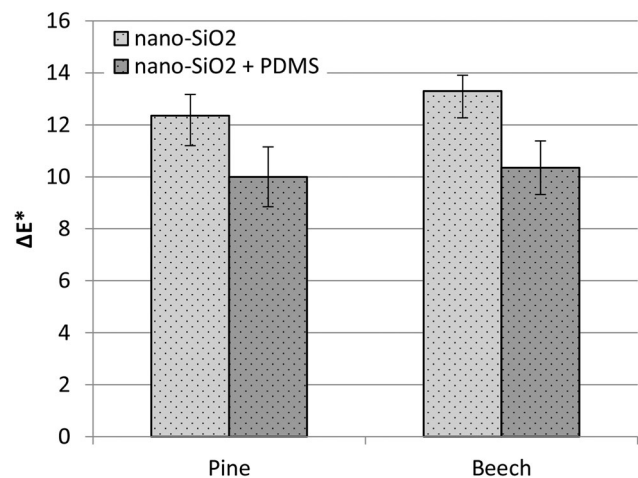

Figure 11. Colour change of beech (left) and scots pine (right) wood material as a result of different SiO_2 nanoparticle treatments.

hydrophobization effect of the used hydrophobic silica nanoparticles is responsible for the difference between the uptake of liquid water and water vapour. The improved hydrophobicity of the cell wall surfaces through the deposition of silica nanoparticles make the investigated treatments more effective against liquid water, compared to water vapour.

Colour change

As a side effect of the treatments, a well visible colour change in the form of darkening/fading was visible as well (Figures 11–12). The total colour change was significantly lower in case of "SiO_2+PDMS" treatment in case of both wood species. The value of total colour change was similar in case of both beech and pine. The reason for the colour change is on one hand the leaching effect of the organic solvents as carrier material (NH_4OH and THF), on the other hand the

Figure 12. Total colour change of beech and pine wood material as a result of different SiO_2 nanoparticle treatments (whiskers showing standard deviation of the results).

use of elevated temperature during the curing step of the treatments (Fan et al. 2010).

Conclusions

With the use of the modified hydrophobic silica nanoparticles (SiO_2), it is possible to improve the dimensional stability of wood. Shrinking and swelling properties decreased remarkably, depending on wood species and treatment type. The ASE was similar in radial and tangential direction for both beech and pine, however, a slight, statistically significant difference could be observed in the results between the different wood species. Application of PDMS did not provide better dimensional stability compared to the treatment without it, which is explained by the lower amount of hydrophobic nanoparticles in this case, but compensated by the hydrophobic properties of PDMS itself. Swelling anisotropy was increased slightly, but insignificantly as a result of the treatment, as slightly higher ASE was observed in the radial direction, compared to tangential. With the use of PDMS slightly lower EMC and highly lower water uptake compared to the basic "nano-SiO_2" treatment was observed. The improved hydrophobicity of the cell wall surfaces through the deposition of silica nanoparticles make the investigated treatments more effective against liquid water, compared to water vapour. SEM imaging showed that the distribution of the nanoparticles is mostly even on the cell wall surfaces, but some deposits and agglomerations were found as well. As a side effect of the treatments, a well visible colour change in the form of darkening/fading occurred.

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ORCID

Miklós Bak   http://orcid.org/0000-0003-4378-7838

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