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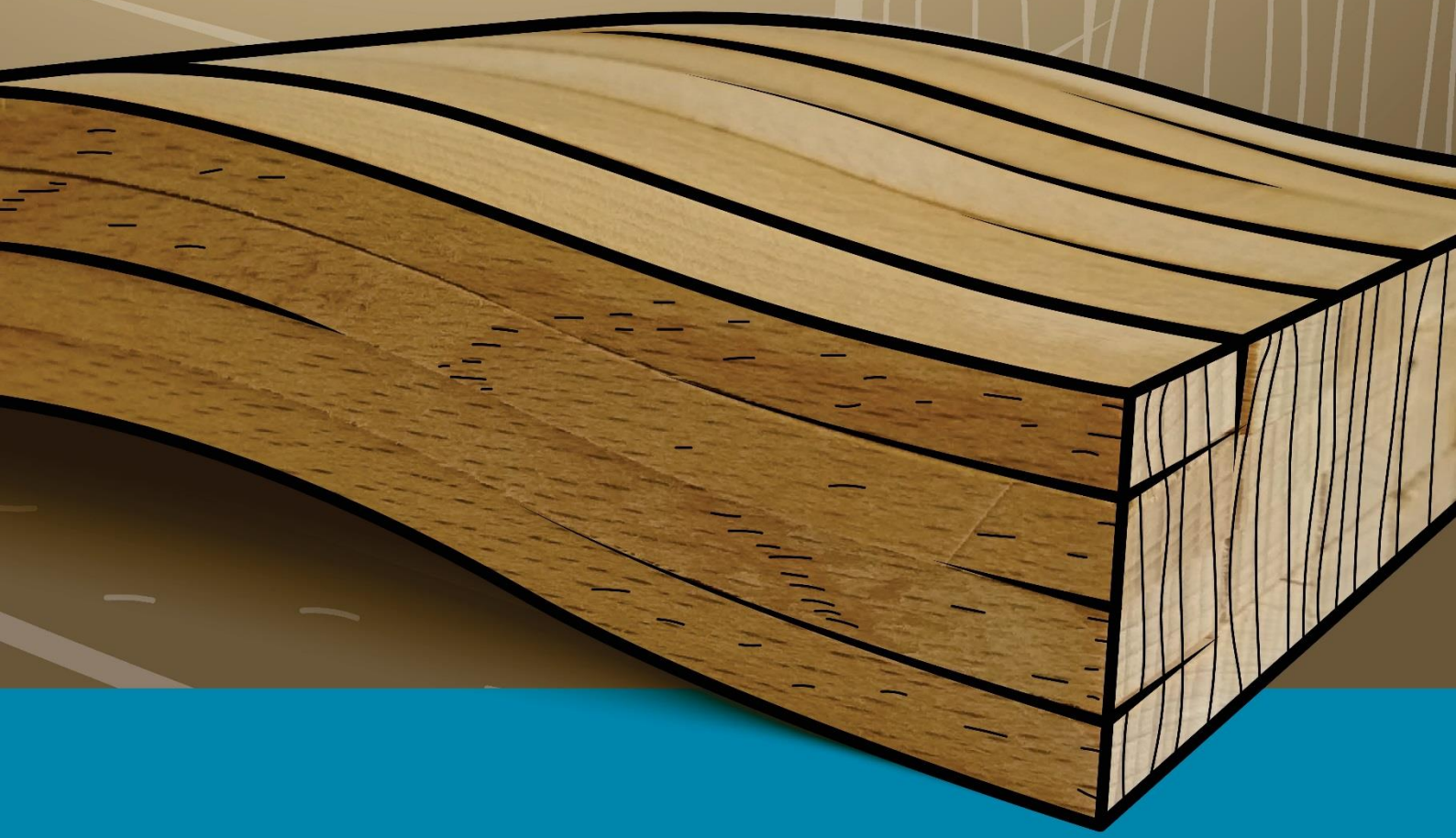

WOOD KPLUS

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10TH HARDWOOD CONFERENCE PROCEEDINGS

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Cover image based on the beech specimens of Radim Rousek and Mátyás Báder by Miklós Bak, 2021

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Dimensional stabilization of wood by using microporous silica-aerogel

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ABSTRACT

The expected result of the research was the improvement of the dimensional stability through bulk hydrophobization, as a result of impregnation with microporous SiO_2 aerogel. Two different wood species, beech (*Fagus sylvatica*) and scots pine (*Pinus sylvestris*) were investigated. Silica aerogel was prepared in situ in the wood tissue via a sol-gel process. The impregnation with silica aerogel was successful, as shrinking and swelling properties decreased by 25-40%, depending on wood species, beside a low weight percent gain (6.9-9.4%). Water uptake and equilibrium moisture content decreased significantly as a result of the treatments (30-60%). Beside some changes in the permeability, high hydrophobization effect was observed as one of the main reasons for the improved dimensional stabilization of the treatment. The treatment resulted in an obvious colour change as well. FT-IR measurements proved a chemical bonding of the silica aerogel to the cellulose structure of wood, that indicates a long-lasting effect of the treatment.

INTRODUCTION

Investigating the improving effect of nanoparticles and structures on wood dimensional stability is an emerging topic nowadays. Furthermore, regarding the utilization of nanostructures to improve various wood properties, some positive results are available as well (Niemz et al. 2010; Mahltig et al. 2008; Sahin and Mantanis 2011). Recently, the aim of using silica aerogels in combination with cellulosic materials at nano and micro scale is to synthesize high-performance insulation materials to produce new generation building solutions (Demilecamps et al. 2015; Zhao et al. 2015; Sedighi Gilani et al. 2016). However, studies on wood modification using "nano- SiO_2" coating techniques on the cell walls are well known (Wang et al. 2013; Ebrahimi et al. 2017) there is only a limited knowledge so far about the use of microporous silica aerogels made in-situ within the wood cell structure. Existing studies deal rather with the cell wall modification of wood material with silica.

The motivation for this work was to improve dimensional stability, by incorporation of functional materials such as microporous silica aerogel inside the lumens. The planned treatment will likely elongate the lifetime of the wood-based products because the wood-water relations are essential at all utilization fields. The expected positive effect of the investigated treatment is the improvement of the dimensional stability of wood through a decreased moisture or water adsorption as a result of covering the cell wall surfaces and filling the cell lumens with silica aerogel. The adhesion of silica aerogel to the cellulose structure of wood was tested on paper samples by a leaching process, using FT-IR spectroscopy.

EXPERIMENTAL METHODS

Wood samples of beech (*Fagus sylvatica* L.) and scots pine sapwood (*Pinus sylvestris* L.) 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). Tetraethoxysilane (TEOS) and hydrochloric acid (HCl, 36-38%), ethanol (ET, 99.99%) and distilled water was used for the preparation of the treatment.

The SiO_2 aerogel with porous network structure was prepared by sol-gel method. The TEOS/ET/H_2O mixture with a molar ratio of 1 : 5 : 8 was added into the reaction system. To promote the hydrolysis process, HCl was added until the pH value reached the value of 3. The mixture solution was stirred at 50°C for 60 minutes, while the initially opaque solution turned clear.

Wood blocks were vacuum impregnated with the prepared silica nano solution. Wood blocks were oven dried at 105 °C in drying chamber before the impregnation process for 24 hours. The next step of the treatment was a 1 h long vacuum phase under 100 mbar pressure in a vacuum dryer at 25°C. This was followed by a 2 h long impregnation step under atmospheric pressure, by leaving the samples in the treatment suspension. The impregnated specimens were then placed in an oven at 60°C for 24 h, and at 105°C for another 24 h to age the gels until SiO_2 aerogel formed in the cell lumens of wood.

To determine WPG, samples were weighed before the impregnation (m_0), and after the curing step ($m_{0,\,imp}$). WPG was calculated according to Eqn. (1):

$$WPG_{W/D} = \frac{m_{wet/0,imp} - m_0}{m_0} \ [\%] \quad (1)$$

FT-IR measurements were performed on the tangential surfaces of wood samples using a Shimadzu IRAffinity^{-1} spectrometer equipped with the HATR 10 total reflection accessory kit. The spectra were recorded in the wavenumber range of 4000-670 cm^{-1} with a spectral resolution of 1 cm^{-1} using the Happ-Genzel apodisation. All the spectra were corrected by the background spectra at ambient conditions and the registered spectra were derived as the means of 49 scans.
To determine swelling for the calculation of anti-swelling-efficiency (ASE), 20×20×30 mm (radial × tangential × longitudinal) samples were used. There were 20 pieces for both wood species and treatment types used. 20 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. Thereafter, the samples were submerged into water for 10 days and finally the dimensions were measured again. ASE was determined using radial or tangential swelling of untreated (SU,r,t) and treated (ST,r,t) samples according to Eqn. (2):

$$ASE_{r,t} = \frac{S_{U,r,t} - S_{T,r,t}}{S_{U,r,t}} \cdot 100 \ [\%] \quad (2)$$

To examine water repellency, contact angle (CA) of deionized water (surface tension: 3.2 mN/m) was evaluated as the ability of the resulting wooden surfaces to repel water. An optical goniometer (68-76 PocketGoniometer PGX+) was used to measure the CA of droplets on the prepared surfaces. Each droplet was dropped to the sample surface by vibrating the syringe. The volume of the droplet was controlled at around 4μL. CA was measured at intervals of 120 ms for the 1st s and at 5, 10, 20, 30, 60, 120, 240, 360, 480 and 570 sec. 20 CA determinations were made at different locations on the surface for each specimen.

RESULTS AND DISCUSSION

Weight percent gain

WPG values for tested beech and pine specimens are shown in Table 1. There were significant differences in case of both dry and wet WPG of the different wood species. Variation coefficients of beech samples' WPG-s were significantly lower. This result shows a more even impregnation of beech material. However, mean value of pine samples' WPG was higher. Ratio of dry and wet WPG was 8.71 and 9.29% in case of beech and pine respectively. This shows the identical efficiency of the investigated silica-sol's penetration into the wood tissue of the different wood species. Thus, impregnation quality did not affect the results. The WPG reached with this treatment is rather low, compared to some other silica-based modification methods, where usually 20-60% WPG is reported (Donath et al. 2004). The ratio of TEOS in the silica-sol was only 7.14%, thus the achieved WPG corresponded to the expectations.

Table 1: WPG values of beech and pine samples as a result of porous silica aerogel treatment

	Beech		Pine	
	WPG_{wet} [%]	WPG_{dry} [%]	WPG_{wet} [%]	WPG_{dry} [%]
Mean	79.22	6.90	101.14	9.40
Min	65.61	5.53	71.38	6.00
Max	94.82	9.01	130.50	11.99
St. Dev.	7.94	1.03	20.17	2.25
Var. Coeff.	10.02%	14.92%	19.94%	23.89%

FT-IR analysis

ATR reflection spectrometry allows rapid and non-destructive examination of wood. The light absorption originates from the surface of the sample, therefore ATR-FTIR method requires that the sample be in close contact with the ATR crystal. The standard normal variate (SNV) transformation was applied in order to reduce unwanted spectral variability caused by surface roughness, inhomogeneity and scattering effects.
The FTIR spectra indicate the change in the chemical property of the wood surface after modification. The SNV transformed FTIR spectra of the control and treated wood samples are depicted in Fig. 1. The absorption peaks in the spectrum of treated wood observed at 1079 and 789 cm^{-1} correspond to the asymmetric stretching vibration and bending mode of Si–O–Si. (Gwon et al. 2010, Fu et al. 2016, Yue et al. 2019). These ones can reflect that the TEOS on the wood surface was hydrolysed, then, during the polycondensation reaction, a cross-linked gel was formed with the formation of siloxane bonds.

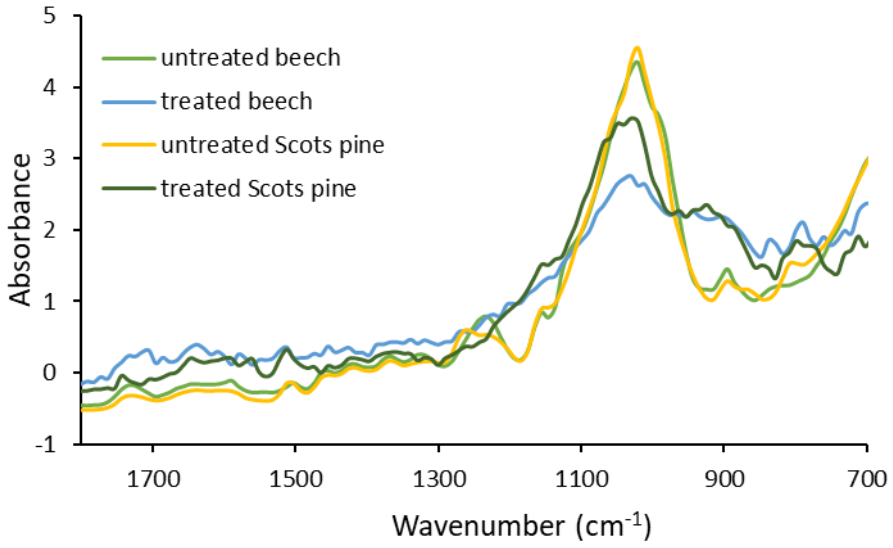

Figure 1: SNV transformed FT-IR spectra of untreated and treated Scots pine sapwood and beech wood

Anti-Swelling-Efficiency (ASE) and swelling anisotropy

Shrinking and swelling properties decreased remarkably in case of both investigated wood species (Table 2). Silica aerogel treatment resulted in slightly, but significantly lower ASE in both radial and tangential direction in case of pine wood (35.17% and 23.10% respectively), compared to beech (39.64% and 26.49% respectively). 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 different permeability of beech and pine in the different anatomical directions. As silica aerogel 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, aerogel covered the cell wall surface, that delays and prevents the penetration of water molecules to the cell wall as well. Furthermore, higher WPG values of pine were observed, as dry WPG values were 6.90 % in case of beech, and 9.40% in case of pine (Table 1). This difference was not realized in the ASE of the treatments, as no correlation was found between the WPG and ASE of the treated beech and pine samples in radial and tangential direction. Higher ASE values were observed in the radial direction, compared to the tangential direction. Unfortunately, this effect increased the swelling anisotropy slightly.

Table 2: Effect of silica aerogel treatment on ASE in beech and Scots pine wood

	Radial		Tangential	
	Mean	SD	Mean	SD
Beech	39.64	2.58	26.49	1.04
Pine	35.17	2.12	23.10	0.91

Equilibrium moisture content

EMC decreased significantly as a result of the investigated silica aerogel treatment (Table 3). With other words, the uptake of water vapour is decreased by the investigated treatment. This means that it did not only result in highly water-resistant characteristic of surfaces of the treated wood but decreased additionally the ability of wood to absorb moisture (Kumar et al. 2016). This shows that the presence of silica aerogel 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). Decrease of EMC was higher in case of pine wood, which was in accordance with the different WPG values for the wood species.

Table 3: Effect of silica aerogel treatment on the equilibrium moisture content of beech and scots pine wood

		Mean	SD	Decrease (%)
Beech	Control	10.68	0.12	
	SiO_2 aerogel	7.64	0.09	-28.46%
Pine	Control	11.25	0.24	
	SiO_2 aerogel	7.15	0.24	-36.44%

Water repellence

Results showed high hydrophobization effect as a result of the investigated silica-based treatment (Fig. 2). The initial contact angle (at time = 0 s) of the untreated wood material was around 65-70° for both wood species. In contrast to that, significantly higher contact angles were observed for the SiO_2 aerogel treated wood surfaces, between 130-135°. This is close to the superhydrophobic region (>150°). The treatments are not only providing high hydrophobicity for wood, but they also provide long lasting effect, as the contact angle is only slightly decreasing with time. Thus, the microporous silica aerogel treatment is a stable treatment. These results are supporting the conclusions taken related to the dimensional stabilization and water-uptake decreasing effect of the investigated treatments. One of the main reasons, why these treatments are improving these properties of wood is the long-lasting hydrophobization effect of the treatments.

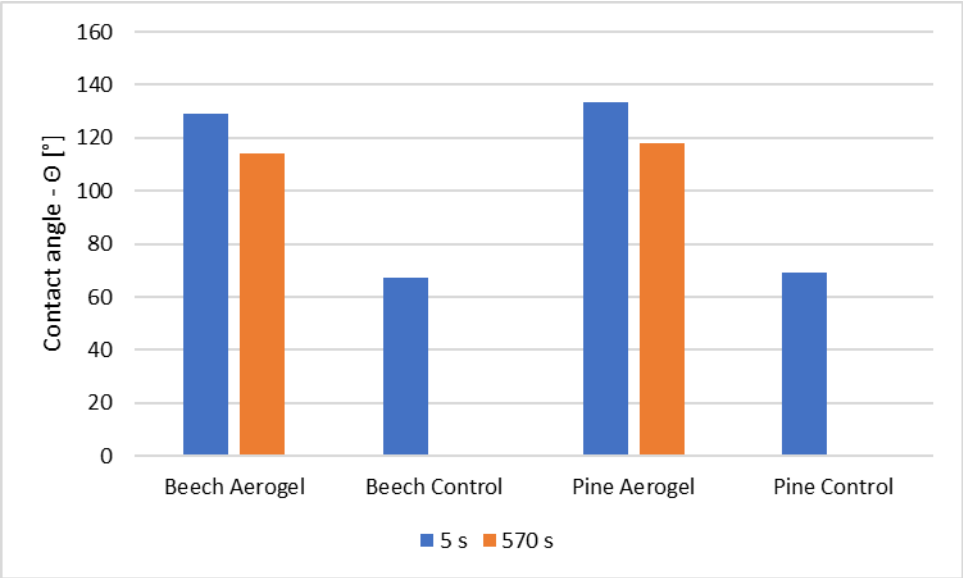

Figure 2: Effect of silica aerogel treatment on the contact angle of beech and scots pine wood

CONCLUSIONS

With the use of the microporous silica aerogel, it is possible to improve dimensional stability of wood. Shrinking and swelling properties decreased remarkably, depending on wood species and anatomical direction. 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. Swelling anisotropy was increased slightly, but significantly as a result of the treatment, as remarkably higher ASE was observed in radial direction, compared to tangential. The improved hydrophobicity of the cell wall surfaces through the deposition of silica aerogel makes the investigated treatments more effective against liquid water, compared to water vapour. FT-IR measurements proved a chemical bonding of the silica aerogel to the cellulose structure of wood, that indicates a long-lasting effect of the treatment. As a side effect of the treatments, an explicit colour change in the form of darkening occurred.

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