

EFFECT OF THE PASSIVE CHEMICAL MODIFICATION
OF WOOD WITH SILICON DIOXIDE (SILICA) ON ITS
PROPERTIES AND INHIBITION
OF MOULDS

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ABSTRACT

This work investigates how wood modification with silicon dioxide affects its selected physical and mechanical properties and resistance to moulds. Silicon mineralization can improve some of the technical properties of wood and extend the service-life of wooden structures. Silicon, which is contained in inorganic and organic-inorganic substances that are used for artificial wood mineralization or is the main component at natural wood mineralization, was used in the form of colloidal silicon dioxide and its various concentrations for pressure impregnation of beech (*Fagus sylvatica*) and Silver fir (*Abies alba*) wood samples. Following, physical, mechanical and biological properties of such modified woodswere tested together with waterlogged fir wood stored in water over a long period. Silicon-dioxide did not significantly improve properties of beech and fir woods, probably due to the hypothesis, that none covalent bonds between the silicon and the OH- groups of cellulose, hemicelluloses or lignin could be created in the cell-walls of the silicon-modified woods.

KEYWORDS: Beech, fir, silicon-dioxide, chemical modification, mineralization, physical and mechanical properties, moulds.

INTRODUCTION

People have learned to use wood despite its dimensional instability depending on the water content of the wood (Mantanis et al. 1994). Wood may be degraded by various microorganisms or burn or decompose from ultraviolet radiation (Stamm 1964, Rowell 1983, Reinprecht 2016). With growing awareness of environmental vulnerability and the need for long-term durability of wood products, new technologies have been developed to increase wood durability without the use of toxic chemicals (Militz 1991, Westin 1996, Hill 2006, Rowell et al. 2009, Rowell 2012, Gérardin 2016).

Improved technical properties of wood, and thereby also the durability of wood structures, can be achieved by mineralization based on the principle of chemical modification. Mineralization means the partial or total saturation of organic matter with mineral particles, and it can take place under completely natural conditions (petrification), or even during artificial overburdening of the wood with silicates. Agents based on silicon dioxide SiO_2 and silicic acid H_4SiO_4 are used most often for this purpose, but other suitable chemicals may also be used. From the point of view of the nature of the effect, this can consist of artificial or natural modification.

The mineral solution penetrates into the wood where it remains in the lumens, or it penetrates the cell walls where it can chemically react with certain components (Hill 2006). The silicon dioxide plant tissue impregnation process is generally considered to be one of the most common and most enduring fossilization processes.

Furuno et al. (1986a) created a four-stage wood mineralization model where minerals begin to fill lumens in the first stage. The storage in lumens continues in the second stage and the decomposition of individual cell wall components begins. In the third stage, individual cell wall components are replaced by minerals, which results in a change in the physical and mechanical properties of the wood. In the fourth and final stage, the significant and complete replacement of organic wood substances with minerals occurs.

The differences between active and passive modifications are shown in Fig. 1. Active modification changes the chemical nature of the wood material, while the passive modification does not change the chemical nature of the wood material. The active modification is usually connected with reaction of the agent with the hydroxyl groups in wood cell walls.

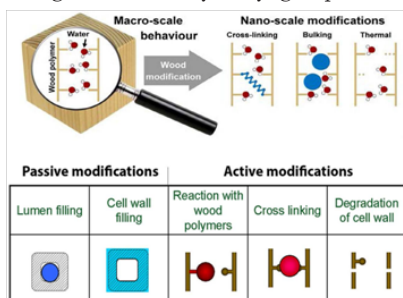


Fig. 1: Schematic diagram illustrating the effect of chemical active and passive modification (Sandberg et al. 2017).

The natural process of wood mineralization is described by Selmeier (1990), Furuno et al. (1986a, 1986b, 1988). It takes millions of years to fully mineralize wood, and the mineralization takes place under the surface of the earth with the help of silicic acid (H_4SiO_4) that infiltrates the cell walls. The silicic acid gel formed by poly-condensation is further converted to crystal

(chalcedony) and opal (wood opal). For comparison, some tropical woods contain a high percentage of silicon that exceeds the amount of calcium in the wood (Hillis and de Silva 1979).

Samples treated with a silicon dioxide colloidal solution absorb up to 40% less water than untreated samples. Similarly, according to Brinell, hardness can be increased by almost 100% in treated samples compared to untreated ones, which is mainly due to the deposition of siliceous glass (resulting from a sol-gel transformation) on the surface of cell walls (Götze et al. 2008).

The basis of the polysiloxane function is the inorganic chemical bond between silicon and oxygen atoms, which is much more resistant to the effects of natural influences (including UV radiation) than the bonding of carbons used in conventional organic paints such as epoxies or polyurethanes.

Mechanical properties (strength, toughness) were not significantly improved, with the exception of the use of a 5% silicic acid monomer solution. For hydrophobicity and non-shrinkage ability, the highest values were measured after treatment with a 5% silicic acid monomer solution (about 40% hydrophobization and 20% non-shrinkage). The shrinkage values were also to the same extent for tetraethoxysilane (TEOS ethyl citrate – ortho-silicate), with which other samples were impregnated (Saka et al. 1992). In all other cases, the shrinkage values were less than 20%.

Amino-silicone macro-emulsion (AminoSiMaE) reduces mould growth to the highest extent with the increasing concentration of silicone. Quaternary ammonium silicone micro-emulsion (QuatSiMiE) also reduces mould growth, but when using a silicone macro-emulsion with the alkyl-modified side of the group (AlkylSiMaE), no mould growth resistance was achieved. Resistance to mould growth is attributed primarily to the AminoSiMaE and QuatSiMiE group of silicones. AlkylSiMaE does not contain amino groups and as a result does not completely reduce the mould colonies. Donath et al. (2006b) investigated the amino effect of the silane of the oligomer against the decomposition of wood by mould and discovered the anti-mould effect of the amino groups, whereas the alkyl groups played a smaller role in decomposition resistance. Similarly, Weigenand et al. (2008) found a mild anti-mould effect in the amino silicone emulsion attributed to the negative effects of propyl-amino groups on mould physiology. Reinprecht et al. (2016) documented that activity of moulds on wood surfaces suppressed also the mixture of methyltrimethoxysilane (MTMS) and benzalkoniumchloride (BAC). Silicone emulsions have great potential to be used commercially for wood preservation. Weigenand et al. (2007) and Reinprecht et al. (2013) also presented that silicones can cause water repellency and, in part, shape stability of wood. The amino-silicone emulsion showed an improvement in wood resistance against the fungus of the basidiomycete genus (Weigenand et al. 2008, Ghosh et al. 2008).

The analysis of the literature shows that in recent years, various silicone-based materials are being used for wood modification requiring correct application, which is a guarantee of changes in the physical and mechanical properties of wood and resistance to moulds and fungi. To this time, silicone dioxide was not essentially used for wood impregnation. Most of the authors dealt with the impregnation method and fixation on the wood substance. Therefore, we consider relevant the measurement of the changes in the physical and mechanical properties of such treated samples from industrially-processed wood species of the Czech Republic. The main benefit of the study is that a pressure impregnation of the colloidal silicon dioxide solution was used to accelerate the process of depositing minerals in wood samples. Wood naturally mineralizes either partially, which can take several hundred years, or completely, which lasts for several million years, as via diffusion, the minerals get into cell-walls of wood and gradually replace its individual components until the wood is completely transformed into stone.

MATERIAL AND METHODS

Wood for the production of samples was used from planks of European beech (*Fagus sylvatica* L.), which represented hardwoods, and it was without a false core and other defects. The European silver fir (*Abies alba* Mill.) was selected as the representative of conifers. Fir wood does not contain resin, and its impregnation is more difficult than in beech. Naturally mineralized samples were made of a fir beam that originated from Central Bohemia (Kostelec nad Černými Lesy). The beam was from approximately the 16th century located under the stone pavement in a cellar built in clay and served as drainage for the removal of surface water. Prisms measuring approximately 25 mm x 25 mm x 1300 mm were always manipulated from the planks in order to maintain the parallelism of the samples. These prisms were then shortened to nominal dimensions. Physical properties (swelling and water absorption) were investigated on samples measuring 20 mm x 20 mm x 30 mm (thickness x width x longitudinal). Samples with dimensions of 20 mm x 20 mm x 300 mm (thickness x width x longitudinal) were used for mechanical tests (static and dynamic modulus of elasticity, bending strength, impact strength and hardness), and mould tests were carried out on samples measuring 5 mm x 10 mm x 50 mm (tangential x radial x longitudinal).

Silicon dioxide (SiO₂) was selected from different silicates due to its inertness. Wood samples were impregnated with 0%, 1%, 5% and 10% colloidal solutions of SiO₂ in Technical University of Zvolen, Slovak Republic, in a VTIZ pressure impregnation device, manufacturer: VYVOS spol. s.r.o., Uherský Brod, Czech Republic, (production year 2009), whilst using pressure at 0.8 MPa for 1 hour and at a temperature of 20°C. Crushed silicon dioxide was used for impregnation so that the individual particles would be able to penetrate not only into the lumens of the cells. Such particles are used in the standard technology process in the rubber industry.

The samples modified with SiO₂ were then dried naturally (short-term weak fixation was carried out) and in the final phase they were air-conditioned to a moisture content of approximately 12% under conditions of relative moisture content of 65% and a temperature of 20°C inside a CLIMACELL 707 conditioning chamber (BMT Medical Technology Ltd., Czech Republic).

Determining the quantity of silicon in wood

The State Geological Institute of Dionýz Štúr (Slovak Republic) conducted a test to determine the amount of silicon in wood and in the extraction from both natural and impregnated samples. The samples were burned after drying and the silicon quantity was subsequently analysed from the ash. The inductively coupled plasma atomic emission spectroscopy (AES-ICP) method was used. An internal regulation (IR) was used during the tests. Enhanced uncertainty for individual measurements was relative combined standard uncertainty with a coverage coefficient of k=2.

The images were photographed using the MIRA 3 electron microscope. Manufacturer: TESCAN, Brno, Czech Republic. An elemental analysis was carried out using software from BRŮCKNER. The accelerating voltage (SEM HV) was 15.0 kV, and only 10.0 kV was used in Fig. 7. A secondary electron (SE) was used as a detector (DET). The working distance (WD) and magnification (SEM MAG) were different for each picture.

Determination of physical properties

All physical properties were measured on wood samples air-conditioned at 20°C and 65% humidity, it means at their approximately 12% absolute moisture content.

In order to calculate density at 12% moisture content, the formula specified in ČSN 49 0108 was used:

$$\rho_{12} = \frac{m_{12}}{V_{12}} \quad (1)$$

where: ρ_{12} – wood density at 12 % moisture content ($\text{kg}\cdot\text{m}^{-3}$),
 m_{12} – weight of the wood at 12 % moisture content (kg),
 V_{12} – wood volume at 12 % moisture content (m^3).

The conventional wood density was determined from the formula:

$$\rho_k = \frac{m_0}{V_{\max}} \quad (2)$$

where: ρ_k – basic wood density ($\text{kg}\cdot\text{m}^{-3}$),
 m_0 – weight of the wood in an oven dry state (kg),
 V_{\max} – wood volume at a moisture content above the fibre saturation point (m^3).

Volume swelling was calculated according to the formula specified in ČSN 49 0126 standard:

$$\alpha_{V_{\max}} = \frac{V_{\max} - V_{\min}}{V_{\min}} \cdot 100 \quad (3)$$

where: $\alpha_{V_{\max}}$ – maximum volumetric swelling (%),
 V_{\max} – volume of the specimen at a moisture content at or above the fibre saturation point (cm^3),
 V_{\min} – volume of the specimen in an oven dry state (cm^3).

Determination of mechanical properties

Samples with 12% equilibrium moisture were tested on a tensile testing machine with a maximum force of 50 kN, manufactured by TIRA GmbH (Germany). The distance of the supports was 240 mm, which is 12 times the sample width. The bending strength calculation was carried out according to ČSN 49 0116.

$$\sigma_{\text{pohw}} = \frac{3 \cdot F_{\max} \cdot l_0}{2 \cdot b \cdot h^2} \quad (4)$$

where: σ_{pohw} – bending strength (MPa),
 F_{\max} – the force corresponding to the breaking strength (N),
 l_0 – the distance between the supports (mm),
 b – the width of the specimen (mm),
 h – the height of the specimen (mm).

The modulus of elasticity was calculated from the formula according to standard ČSN 49 0115:

$$E_{\text{ohw}} = \frac{\Delta F \cdot l_0^3}{4 \cdot b \cdot h^3 \cdot \Delta y} \quad (5)$$

where: E_{ohw} – the modulus of elasticity (MPa)
 F – the force difference between the upper and lower load threshold (N),
 l_0 – the distance between the supports (mm), b , h is the width and height of the specimen (mm),

- b – the width of the specimen (mm),
- h – the height of the specimen (mm),
- Δy – bend of the test specimen in a zone of pure bending equal to the difference in bend values corresponding to the upper and lower load threshold (mm), (Desch and Dinwoodie 1996).

The dynamic modulus of elasticity was measured using the UltraSonic Timer device, manufacturer FAKOPP (Hungary) with pressure probes, where the time of the ultrasound signal passing through the sample was measured at different probe distances from one another. In calculating the dynamic modulus of elasticity, the formula for calculating the velocity was first used:

$$v = \frac{d}{t} \quad (6)$$

- where: v – wave velocity ($m \cdot s^{-1}$),
d – the distance between the probes (m),
t – the ultrasonic wave time, needed for passage through the two probe (s).

The dynamic modulus of elasticity was then calculated from the following relationship:

$$E_{\text{dyn}} = v^2 \cdot \rho_w \quad (7)$$

- where: E_{dyn} – the dynamic modulus of elasticity (Pa),
 ρ_w – the wood density ($kg \cdot m^{-3}$),
v – the wave velocity ($m \cdot s^{-1}$).

The determination of toughness was carried out using a Charpy hammer with energy of up to 50 J. The test was carried out according to ČSN 49 0117, where the test specimens are broken by the impact on the centre of the radial surface on supports spaced 240 mm apart from each other. Impact toughness is calculated from the following formula:

$$A_w = \frac{Q}{b \cdot h} \quad (8)$$

- where: A_w – impact strength ($J \cdot cm^{-2}$)
Q – work necessary to the breaking strength (J),
b – the width of the specimen (cm),
h – the height of the specimen (cm), (Lokaj 2010).

The Brinell method, ČSN EN 1534, was used to determine the hardness of the samples. During the test, a steel ball with a diameter of 10 mm was pushed by the appropriate force (250 N for fir and 500 N for beech). The resulting hardness was calculated according to the following formula:

$$HB = \frac{2 \cdot F}{\pi \cdot D \cdot (D - \sqrt{D^2 - d^2})} \quad (9)$$

- where: HB – wood hardness (MPa),
F – the force applied to the bullet (N),

- D – bullet diameter (mm),
d – diameter of callous areain the wood(mm).

Hardness was measured on a Duravision 30 (Struers, Austria) device, where the hardness was measured on both radial and both tangential surfaces.

Mould test

The anti-mould resistance test against the microscopic fungi *Aspergillus niger* and *Penicillium purpurogenum* was based on the EN 15457 (2014) with some changes in the sterilization process and the shape of wood samples. UV light sterilized samples 50 mm x 10 mm x 5 mm (L x R x T) were placed into Petri dishes with a diameter of 120 mm filled with 3 - 4 mm thick layer of the malt-agar (3 pieces of the same tested series and 1 reference untreated piece perpendicular thereto), and then inoculated with the spore suspension of the given species of mould. Incubation of wood samples in thermostats lasted 4 weeks at a temperature of $24 \pm 2^\circ\text{C}$ and a relative moisture content of 90 – 95%. The growth activity of moulds (GAM) on the top surfaces of samples was evaluated in the 7th, 14th, 21st and 28th day by these criteria: 0 = no growth on the top surface, 1 = growth $\leq 10\%$, 2 = growth $\leq 30\%$; 3 = growth $\leq 50\%$; 4 = growth $> 50\%$.

Statistical evaluation

An analysis of variance (ANOVA) was used to determine the relationship between different properties, i.e. whether they are statistically insignificant or not. A qualitative number – the ratio between strength and density – (Požgaj et al. 1993) was used to more accurately express the properties of the tested wood samples.

RESULTS AND DISCUSSION

Silicon dioxide dust used for pressure impregnation of wood accelerated the process of its partial mineralization (see Fig. 2).

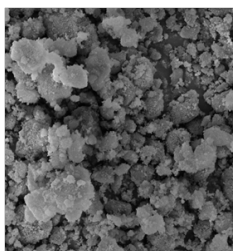


Fig. 2: Enlarged grain of SiO_2 dust used during impregnation.

Legend:WD is 26.07 mm, SEM MAG is 4500.

Although pressure impregnation was used, due to the impregnation of the samples across the entire cross-section, the silicon dioxide did not sufficiently get into the cell walls, but remained in the lumens and intercellular spaces, which is best seen in Fig. 4.

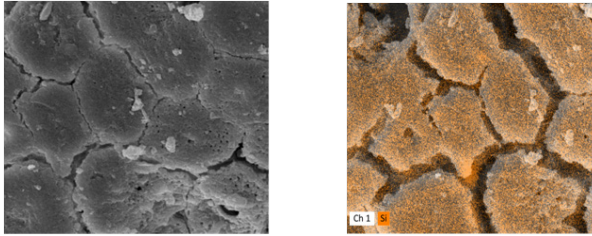


Fig. 3 and 4: Enlarged cross section of beech with 10% concentration of colloidal solution SiO_2 , where the presence of silicon is displayed in orange. Legend: WD is 14.08 mm, SEM MAG is 4500 x.

The silicon dioxide was only scattered; it should properly form individual clumps caused by covalent bonds of silicone to wood. No or only very weak covalent linkages between silicon and cell walls (via the OH group with hemicelluloses cellulose or lignin) were formed to subsequently more significantly affect the physical and mechanical properties. Here, the silicon dioxide likely also only got into the lumens, see Figs. 5 and 6.

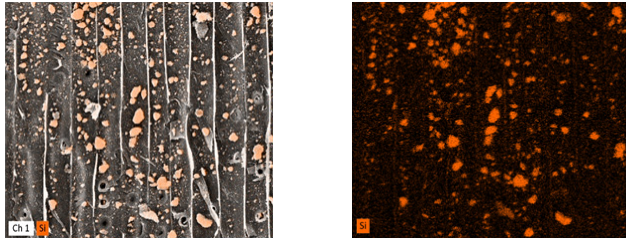


Fig. 5 and 6: provide a colour representation of the presence of Si in an enlarged sample of mineralized fir in the longitudinal section. Legend: WD is 15.1 mm, SEM MAG is 4500 x.

It can be deduced from a four-stage model of wood mineralization (Furuno et al. 1986a) that the first, or at most the second stage was achieved using artificial impregnation of colloidal silicon dioxide solution. The same applies to naturally mineralized fir wood. In the artificially mineralized fir sample, the same irregular distribution of silicon throughout the specimen as with mineralized fir can be clearly seen, with the difference being a lesser representation of silicon, see Fig. 8.

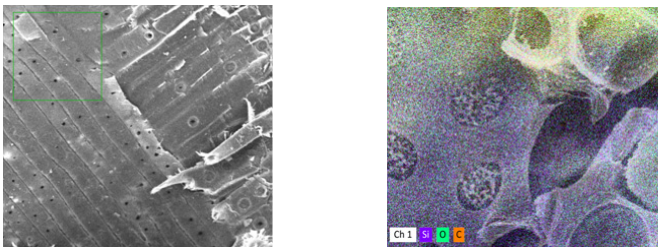


Fig. 7 and 8: Reference fir sample in the longitudinal section. Colour representation of the presence of silicon, oxygen and carbon in the artificially modified fir sample.

Legend: Fig.7 WD is 14.9 mm, SEM MAG je 499 x, Fig.8 WD is 15.6 mm, SEM MAG is 6232 x.

The natural process of partial wood mineralization may take tens to hundreds of years. Adversely, complete mineralization, wherein the complete replacement of organic wood components with inorganic substances takes place, may last several million years. Everything is dependent on abiotic factors in the surrounding environment where the wood is found, in particular on the amount of mineral substances contained in lake water, peat bogs or swamps, and on hydrostatic pressure or on ground pressure where a set of shear surfaces is formed in the soil. For this reason, the old fir beams were not naturally sufficiently mineralized, as they were likely not in the water during the mineralization period, and even surface water contains a small quantity of mineral substances.

Tab. 1 shows that in the naturally mineralized fir wood, the silicon was only a maximum of 9.2% higher than in the reference wood samples. With regard to the 10% SiO₂ impregnation, there for fir wood the silicon was 31 times higher and for beech wood it was 6 times higher than in the reference wood samples.

Tab. 1: Quantity of silicon in the samples and in the infusion determined by the laboratory method.

Lab No.	Sign of	(Si mg·kg ⁻¹)	(Si mg·kg ⁻¹)	Method	Methodical	Examination
	sample	in water leach	in samples		recipe	
16-004923	Referential beech	0.83	138	AES-ICP	IP 2.12, IP 2.1	A
16-004924	Referential fir	0.83	109	AES-ICP	IP 2.12, IP 2.1	A
16-004925	Impregnated 10% SiO ₂ - beech	18.0	716	AES-ICP	IP 2.12, IP 2.1	A
16-004926	Impregnated 10% SiO ₂ - Fir	25.2	3386	AES-ICP	IP 2.12, IP 2.1	A
16-004927	Mineralized fir	1.78	111	AES-ICP	IP 2.12, IP 2.1	A
16-004928	Impregnated 10% SiO ₂ - beech	-	817	AES-ICP	IP 2.12	A
16-004929	Impregnated 10% SiO ₂ - fir	-	3390	AES-ICP	IP 2.12	A
16-004930	Mineralized fir	-	120	AES-ICP	IP 2.12	A

From results in Tab. 1 is evident that Si used as 10% SiO₂ colloidal solution did not infuse, or only minimally, into the fir and beech wood samples at the used impregnation process.

Tab. 2 shows the basic physical and mechanical properties and their statistics for beech wood at individual tests. There are no significant differences between the series at concentrations of SiO₂ from 1% to 10%. There is only an ascending trend for hardness when using a qualitative number. In terms of maximum absorption, the value increases with increasing concentration. According to Brinell, hardness increased by a maximum of 12% in beech samples treated with 10% colloidal silicon dioxide solution. Götze et al. (2008) indicates that the hardness may increase up to 100%.

Tab. 2: Basic statistics for the properties of beech wood.

Property	Solution of SiO ₂ (%)	Valid N	Mean	Minimum	Maximum	Std.Dev.	Coef.Var. (%)
Oven-dry density (kg·m ⁻³)	0	30	690	632	768	38	5.5
	1	30	668	617	731	31	4.7
	5	30	688	638	762	41	5.9
	10	30	662	643	709	19	2.9
Basic wood density (kg·m ⁻³)	0	30	563	523	609	25	4.4
	1	30	568	508	614	26	4.6
	5	30	566	526	635	32	5.7
	10	30	538	523	572	13	2.5
Density for MOR (kg·m ⁻³)	0	30	712	673	788	31	4.3
	1	30	691	660	713	13	1.8
	5	30	709	666	772	23	3.3
	10	30	705	646	763	32	4.5
Density for IBS and H (kg·m ⁻³)	0	30	719	674	779	32	4.4
	1	30	719	672	765	23	3.2
	5	30	730	677	773	25	3.5
	10	30	703	655	771	33	4.6
Volumetric swelling (%)	0	30	22.5	19.5	26.3	1.8	8.0
	1	30	23.4	19.0	28.7	2.1	9.0
	5	30	21.5	11.3	24.6	2.3	10.7
	10	30	23.0	21.3	25.3	1.1	4.7
Maximum water absorption (%)	0	30	102.7	82.5	121.4	12.0	11.7
	1	30	103.3	84.8	131.3	10.8	10.5
	5	30	105.3	86.0	121.1	11.3	10.7
	10	30	114.8	97.5	121.5	7.0	6.1
Modulus of rupture - bending strength (MPa)	0	30	116.3	70.1	161.1	19.7	16.9
	1	30	87.3	57.6	111.1	12.0	13.8
	5	30	118.1	100.9	135.0	9.7	8.2
	10	30	103.0	40.7	130.9	21.8	21.2
Dynamic modulus of elasticity (MPa)	0	30	16855	13125	22026	2359	14.0
	1	30	12429	9134	16299	1771	14.3
	5	30	16080	8912	20450	2447	15.2
	10	30	12800	8503	21690	2622	20.5
Static modulus of elasticity (MPa)	0	30	12103	10110	14559	1201	9.9
	1	30	8794	7552	11148	755	8.6
	5	30	12618	8986	14288	995	7.9
	10	30	10255	7529	12575	1623	15.8
Toughness - impact bending strength (J·cm ⁻²)	0	30	8.8	5.3	12.3	2.3	25.6
	1	30	9.4	3.6	12.9	2.3	24.1
	5	30	9.8	6.9	12.5	1.5	15.8
	10	30	8.0	3.6	11.6	2.2	27.7

Hardness R/T (MPa)	0	30	58.1	42.8	69.5	6.2	10.7
	1	30	56.9	43.0	68.3	5.9	10.3
	5	30	60.6	52.0	70.8	4.1	6.7
	10	30	64.2	55.3	74.8	5.7	8.8
Qualitative number - MOR / Density (km)	0	30	163.6	91.5	232.9	28.1	17.2
	1	30	126.4	84.7	162.3	17.9	14.1
	5	30	166.5	137.2	185.3	11.4	6.8
	10	30	146.5	57.8	182.9	31.6	21.6
Qualitative number - Hardness / Density (km)	0	30	80.9	63.3	98.1	8.0	9.9
	1	30	79.0	62.9	89.3	6.8	8.6
	5	30	83.0	71.2	92.8	5.0	6.0
	10	30	91.2	81.9	100.4	5.1	5.6

Note: The moisture content of the test samples was app. 12 %, i.e. conditioning in the air relative moisture content of 65 ± 5 % and temperature of 20 ± 2 °C.

Tab. 3 shows the basic physical and mechanical properties and their statistics for natural and mineralized fir wood in individual tests. There are no significant differences between the series at concentrations of SiO₂ from 1% to 10%. Mechanical properties of artificially mineralized fir wood usually increased (except of the modulus of elasticity) with increasing of SiO₂ concentration. However, the highest mechanical properties were achieved for the naturally mineralized fir wood. In terms of maximum absorption of water, the mineralized fir samples had 26% lower values than the untreated samples, whereas Götze et al. (2008) indicates a value of as much as 40%.

Tab. 3: Basic statistics for the properties of fir wood.

Properties	Solution of SiO ₂ (%)	Valid N	Mean	Minimum	Maximum	Std.dev.	Coef.var. (%)
Oven-dry density (kg·m ⁻³)	0	30	333	283	392	29	8.6
	1	30	343	314	392	20	5.8
	5	30	329	293	371	20	6.2
	10	30	344	304	389	24	6.9
	M	30	434	381	527	43	10.0
Basic wood density (kg·m ⁻³)	0	30	296	257	341	21	7.2
	1	30	301	275	333	17	5.6
	5	30	301	268	342	19	6.2
	10	30	304	271	339	19	6.1
	M	30	372	328	444	35	9.4
Density for MOR (kg·m ⁻³)	0	30	362	331	432	28	7.9
	1	30	351	294	395	27	7.7
	5	30	378	242	446	40	10.5
	10	30	372	308	414	25	6.7
	M	30	458	416	543	31	6.8

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Density for IBS and H (kg.m ⁻³)	0	30	366	309	439	39	10.8
	1	30	379	334	409	25	6.7
	5	30	369	335	406	22	5.9
	10	30	354	296	395	26	7.4
	M	30	448	369	557	38	8.4
Volumetric swelling (%)	0	30	12.1	7.7	15.9	1.9	15.3
	1	30	14.3	10.9	17.7	1.6	11.5
	5	30	12.5	10.3	15.1	1.3	10.3
	10	30	13.1	10.9	15.3	1.2	9.4
	M	30	16.7	14.8	18.8	1.1	6.6
Maximum water absorption (%)	0	30	252.4	191.2	289.3	31.1	12.3
	1	30	233.4	208.4	264.2	16.3	7.0
	5	30	233.6	192.8	261.9	18.2	7.8
	10	30	229.6	189.2	262.7	20.0	8.7
	M	30	188.0	147.5	223.0	20.7	11.0
Modulus of rupture - bending strength (MPa)	0	30	57.8	35.3	79.8	10.9	18.9
	1	30	57.6	40.2	69.5	7.1	12.4
	5	30	26.9	23.4	32.1	2.5	9.2
	10	30	60.2	43.9	76.8	8.6	14.4
	M	30	77.3	61.2	96.3	7.4	9.6
Dynamic modulus of elasticity (MPa)	0	30	10809	7807	16599	2403	22.2
	1	30	10221	6418	13923	1982	19.4
	5	30	8681	6843	14086	1502	17.3
	10	30	8708	4938	13136	1930	22.2
	M	30	14581	11215	23150	2393	16.4
Static modulus of elasticity (MPa)	0	30	6830	5440	9357	1168	17.1
	1	30	6475	4563	7554	775	12.0
	5	30	6980	5020	8971	918	13.2
	10	30	6819	5080	8730	1047	15.4
	M	30	9304	7205	10923	896	9.6
Toughness - impact bending strength (J.cm ⁻²)	0	30	2.4	1.0	5.5	1.0	43.0
	1	30	2.6	1.3	4.6	1.0	36.8
	5	30	3.2	1.7	4.5	0.8	25.2
	10	30	2.4	1.3	3.9	0.6	27.4
	M	30	4.1	1.6	5.9	0.9	20.8
Hardness R/T (MPa)	0	30	13.9	5.8	21.3	2.7	19.5
	1	30	14.4	11.0	23.7	3.0	20.8
	5	30	13.1	10.0	18.3	2.1	15.6
	10	30	13.4	11.3	15.0	1.3	9.4
	M	30	17.5	11.5	35.5	6.5	37.4
Qualitative number - MOR / Density (km)	0	30	158.8	98.6	190.6	20.1	12.7
	1	30	163.5	134.9	179.4	12.1	7.4
	5	30	71.8	59.8	99.1	7.5	10.4
	10	30	161.2	129.0	189.4	15.0	9.3
	M	30	168.6	147.2	184.8	9.6	5.7

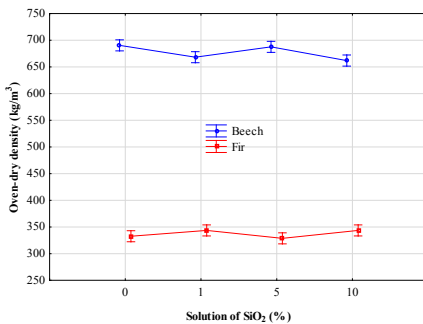
Qualitative number - Hardness / Density (km)	0	30	38.3	16.6	65.2	8.6	22.4
	1	30	38.0	28.8	62.9	7.2	18.9
	5	30	35.6	28.5	46.9	5.0	14.1
	10	30	37.8	31.9	43.9	3.0	8.1
	M	30	38.5	27.6	67.2	11.3	29.3

Note: The moisture content of the test samples app. at 12 %, i.e. conditioning in the air relative humidity of 65 ± 5 % and temperature of 20 ± 2 °C. M = naturally mineralized.

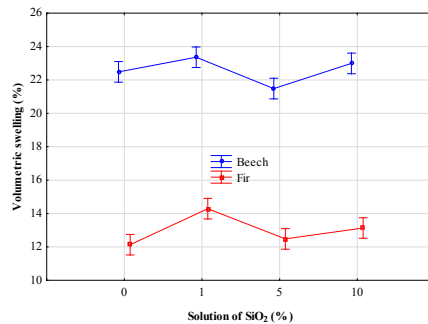
Generally, it is evident from the results and their statistical analyses (Tabs. 2 and 3) that the differences between the individual series of mineralized wood are minimal. The relationships between the individual properties occurred statistically insignificant. This was likely due to the fact that the variability of wood properties, which may be even more than 10%, was higher than the effect of SiO₂ on the measured and achieved results.

As can be seen from the graphs in Fig. 9, the relationships between some series of modified samples are statistically significant, and this is particularly evident for the 5% SiO₂ concentration. However, for mineralized fir wood, the hardness value was higher than for the reference samples, but when using a qualitative number (by eliminating the effect of density), this difference decreased. However, the overall trend for individual properties is that they are statistically insignificant.

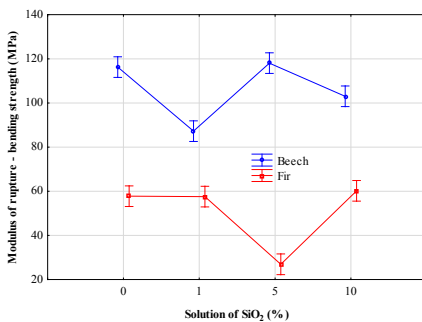
A)



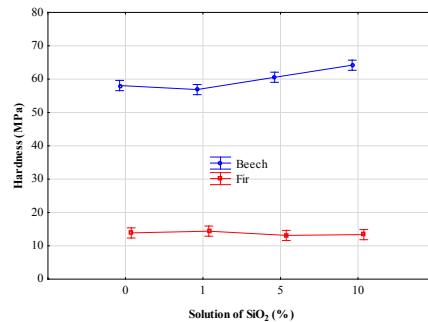
B)



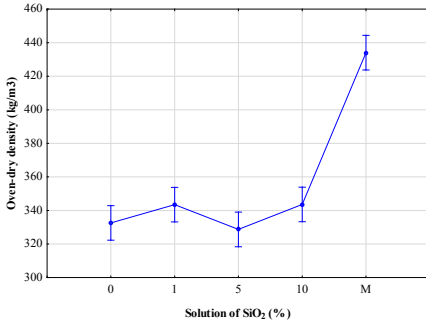
C)



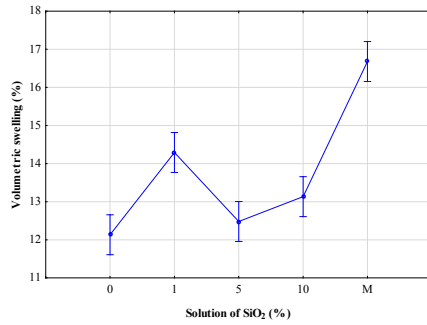
D)



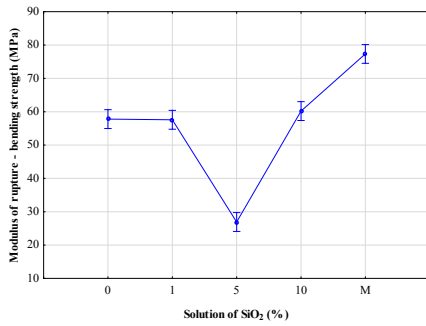
E)



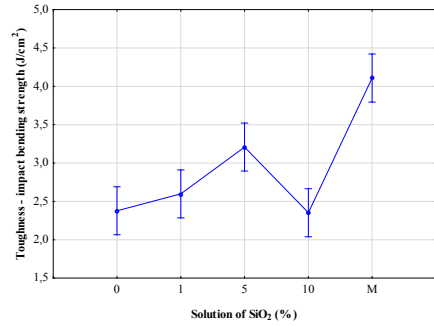
F)



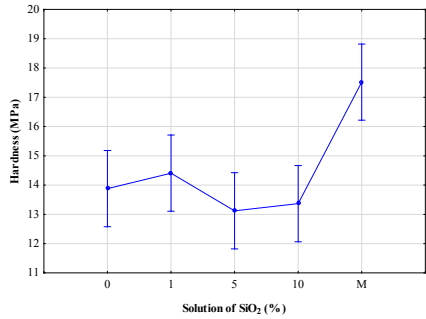
G)



H)



CH)



I)

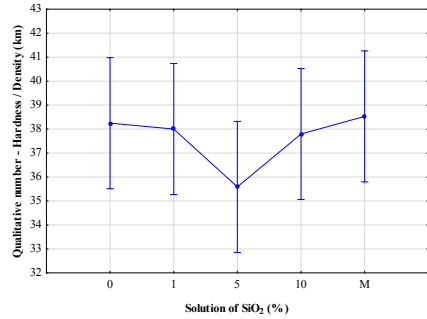


Fig. 9: Graphical representation of course of individual tests: A) density of absolutely dry fir and beech wood, B) volume swelling of fir and beech, C) bending strength of fir and beech, D) hardness of fir and beech, E) density of absolutely dry fir wood, F) volume swelling of fir, G) bending strength of fir, H) impact toughness of fir, Ch) hardness of fir, I) qualitative number of fir, axis x- M mineralized fir.

The silicon dioxide (silica) had none or in the first days of the mould test only a minimal inhibition effect against the growth activity of moulds (GAM) on the top surfaces of modified beech and fir woods (Tabs. 4 and 5, Figs. 10 and 11).

Tab. 4: Growth activity of the mould *Aspergillus niger* (GAM, from 0 to 4) on the top surfaces of the reference and with SiO₂ modified beech and fir samples.

Silicon dioxide (%)	Growth activity of <i>A. niger</i> from 7 th to 28 th day (0-4)							
	Beech				Fir			
	7	14	21	28	7	14	21	28
0 (Reference)	4.0	4	4	4	3.5	4.0	4.0	4
1	3.5	4	4	4	3.5	3.5	4.0	4
5	3.83	4	4	4	3.17	3.5	3.5	4
10	3.17	4	4	4	3.0	3.17	3.83	4

Note: Mean values are from 12 replicates.

Tab. 5: Growth activity of the mould *Penicillium purpurogenum* (GAM, from 0 to 4) on the top surfaces of the reference and with SiO₂ modified beech and fir samples.

Silicon dioxide (%)	Growth activity of <i>P. purpurogenum</i> from 7 th to 28 th day (0-4)							
	Beech				Fir			
	7	14	21	28	7	14	21	28
0 (Reference)	4	4	4	4	3.5	3.5	4	4
1	4	4	4	4	3.5	3.58	4	4
5	3.5	4	4	4	3.17	3.5	3.83	4
10	3.5	4	4	4	3.17	3.33	3.5	3.5

Note: Mean values are from 12 replicates.



a) 10% SiO₂/ beech



b) 10% SiO₂/ fir

Fig. 10: Beech and fir samples (in Petri dish 3 modified with SiO₂ + 1 reference) attacked by the mould *A. niger* (black colonies at sporulation) in the 28th day.



a) 1% SiO₂/ beech



b) 5% SiO₂ / beech

Fig. 11: Beech samples (in Petri dish 3 modified with SiO₂ + 1 reference) attacked by the mould *P. purpurogenum* (yellow-green colonies at sporulation) in the 28th day.

Similarly, only a negligible or none inhibition effect against moulds had some other silicone compounds used in concentrations less than 10%, e.g. methyl-tripotassiumsilanol in Lukofob 39 (Reinprecht et al. 2013), or MTMS – methyltrimethoxysilane, VTMS – vinyltrimethoxysilane, PTMS – propyltrimethoxysilane, and APTMS – 3-aminopropyltrimethoxysilane (Reinprecht and Grznárik 2015).

CONCLUSIONS

The pressure impregnation was possible to accelerate the process of depositing silicon dioxide into cell lumens of wood and accelerated its partial mineralization. However, presence of silicon dioxide in wood structure had only a minimum positive effect on the tested physical, mechanical and bio-resistance properties of the artificially mineralized beech and fir wood samples.

Silicon dioxide essentially only got into the lumens of cells, and that is why it did not significantly affect physical and mechanical properties of modified wood. Covalent bonds of silicon dioxide with cellulose, hemicelluloses or lignin (cell wall components) were not formed, or were formed only slightly, which only corresponds to the first or second stage of mineralization of wood according to Furuno et al. (1986a). Silicone crystals have not yet formed in fir which had been in contact with surface water since the approximately the 16th century and was probably not underwater the entire time; these crystals would replace the individual components of the cell walls and more significantly influence the tested properties of wood. In commercially available preparations, an inhibitor that should guarantee the formation of this covalent bond is usually part of the solution, and thus further research will also focus on affixing silicon to the cell wall. However, it is not a guarantee for some commercially produced wood-based substances that mineralization will be achieved throughout the wood specimen, but rather only on the surface.

Silicon dioxide did not show anti-mould efficiency, via the testing of its 1 – 10% solutions on the top surfaces of beech and fir woods.

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REFERENCES

1. ČSN 49 0108, 1993: Drevo. Zisťovanie hustoty (Wood. Determination of the density). Czech Standards Institute: Prague, Czech Republic.
2. ČSN 49 0115, 1979: Drevo. Zisťovanie medze pevnosti v statickom ohybe (Wood. Determination of ultimate strength in flexure tests). Office for Standardization and Measurement: Prague, Czech Republic.
3. ČSN 49 0116, 1982: Drevo. Metóda zisťovania modulu pružnosti pri statickom ohybe (Wood. Determination of the modulus of elasticity in static bending). Office for Standardization and Measurement: Prague, Czech Republic.
4. ČSN 49 0117, 1980: Drevo. Rázová húževnatosť v ohybe (Wood. Impact strength in flexure). Office for Standardization and Measurement: Prague, Czech Republic.
5. ČSN 49 0126, 1989: Skúšky vlastností rastlého dreva. Metóda zisťovania napúčavosti (Test of wood properties. Method of swelling determination). Office for Standardization and Measurement: Prague, Czech Republic.
6. ČSN EN 1534 (492124), 2011: Dřevěné podlahoviny - Stanovení odolnosti proti vtisku - Metoda zkoušení (Wood flooring - Determination of resistance to indentation - Test method). Czech Office for Standards, Metrology and Testing: Prague, Czech Republic.

7. Desch, H. E., Dinwoodie, J. M., 1996: Timber structure, properties, conversion and use. (7th ed.). Macmillan Press Ltd. 306 pp.
8. Donath, S., Miltz, H., Mai, C., 2006: Treatment of wood with aminofunctional silane for protection against wood destroying fungi, *Holzforschung* 60(2): 210–216.
9. EN 15457:2014. Paints and varnishes Laboratory method for testing the efficacy of film preservatives in a coating against fungi.
10. FAKOPP Ultrasonic Timer user's guide. (Available online: <http://fakopp.com/docs/products/ultrasonic/UltrasonicGuide.pdf>, accessed on 22/08/2018).
11. Furuno, T., Watanabe, T., Suzuki, N., Goto, T., Yokoyama, K., 1986a: Microstructure and silica mineralization in the formation of silicified woods. 1. Species identification of silified woods and observations with a scanning electron microscope, *Mokuzai Gakkaishi* 32: 387–400.
12. Furuno, T., Watanabe, T., Suzuki, N., Goto, T., Yokoyama, K., 1986b: Microstructure and silica mineralization in the formation of silicified woods. 2. Distribution of organic carbon and the formation of quartz in the structure of silified woods, *Mokuzai Gakkaishi* 32: 575–583.
13. Furuno, T., Suzuki, N., Watanabe, T., 1988: Microstructure and silica mineralization in the formation of silicified woods. 3. The role of resinous content in silification, *Mokuzai Gakkaishi* 34: 87–93.
14. Gérardin, P., 2016: New alternatives for wood preservation based on thermal and chemical modification of wood. A review, *Annals of Forest Science* 73: 559–570.
15. Ghosh, S.C., Miltz, H., Mai, C., 2008: Decay resistance of treated wood with functionalised commercial silicones, *BioResources* 3(4): 1303–1314.
16. Götze, J., Möckel, R., Langhof, N., Hengst, M., Klinger, M., 2008: Silicification of wood in the laboratory, *Ceramics-Silikáty* 52(4): 267–277.
17. Hill, C. A. S., 2006: Wood modification: Chemical, thermal and other processes. Chichester: John Wiley & Sons, Ltd. 260 pp.
18. Hillis, W.E., de Silva, D., 1979: Inorganic extraneous constituents of wood, *Holzforschung* 33: 47–53.
19. Lokaj, A., Vavrušová, K., 2010: Proceedings of the scientific work of the Mining University, Technical University Ostrava 10(1): 27–32.
20. Mantanis, G., Young, R. A., Rowell, R. M., 1994: Swelling of wood. Part 1. Swelling in water, *Wood Science and Technology* 28:119–134.
21. Miltz, H., 1991: The improvement of dimensional stability and durability of wood through treatment with non-catalysed acetic acid anhydride, *Holz als Roh- und Werkstoff* 49(4):147–152.
22. Požgaj, A., Chovanec, D., Kurjatko, S., Babiak, M., 1993: Wood structures and properties (Štruktúra a vlastnosti dreva), *Príroda Bratislava*, 486 pp (in Slovak).
23. Reinprecht, L., 2016: Wood deterioration, protection and maintenance. John Wiley & Sons, Ltd, Chichester, UK, 357 pp.
24. Reinprecht, L., Pánek, M., Daňková, J., Murínová, T., Mec, P., Plevová, Z., 2013: Performance of methyl-tripotassium silanol treated wood against swelling in water, decay fungi and moulds, *Wood Research* 58(4): 511–520.
25. Reinprecht, L., Grznárik, T., 2015: Biological durability of Scots pine (*Pinus sylvestris* L.) sapwood modified with selected organo-silanes, *Wood Research* 60(5): 687–696.
26. Reinprecht, L., Vacek, V., Grznárik, T., 2017: Enhanced fungal resistance of Scots pine (*Pinus sylvestris* L.) sapwood by modification with methyltrimethoxysilane and benzalkonium chloride, *European Journal of Wood and Wood Products* 75(5): 817–824.

27. Rowell, R. M., 1983: Chemical modification of wood: A review, Commonwealth Forestry Bureau, Oxford, England, No. 6, Pp 363-382.
28. Rowell, R. M., Ibach, R. E., Mc Sweeney, J., Nilsson, T., 2009: Understanding decay resistance, dimensional stability and strength changes in heat treated and acetylated wood. *Wood Material Science and Engineering* 1-2:14-22.
29. Rowell, R. M., 2012: *Handbook of wood chemistry and wood composites*, 2nd Ed., CRC Press, Taylor and Francis Group, Boca Raton, Florida, USA, 703 pp.
30. Selmeier, A., 1990: Anatomische Untersuchungen an verkieselten Hölzern, *Holz Roh- und Werkstoff* 48:111-115.
31. Saka, S., Sasaki, M., Tanahashi, M., 1992: Wood-inorganic composites prepared by sol-gel processing. 1. Wood-inorganic composites with porous structure, *Mokuzai Gakkaishi* 38:1043-1049.
32. Sandberg, D., Kutnar, A., Mantanis, G., 2017: Wood modification technologies - a review, *Forest* 10: 895-908.
33. Stamm, A. J., 1964: *Wood and cellulose science*, Roland Press, New York, USA, 549 pp.
34. Weigenand, O., Humar, M., Daniel, G., Militz, H., Mai, C., 2008: Decay resistance of wood treated with amino-silicone compounds, *Holzforschung* 62(1): 112-118.
35. Weigenand, O., Militz, H., Tingaut, P., Sebe, G., de Jeso, B., Mai, C., 2007: Penetration of amino-silicone micro- and macro-emulsions into Scots pine sapwood and the effect on water related properties, *Holzforschung* 61(1): 51-59.
36. Westin, M., 1996: Development and evaluation of new alternative wood preservative treatments. Final report to The Swedish Council for Forestry and Agri. Res. (SJFR), Pp 1-25.

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