

SILICIFICATION OF WOOD IN THE LABORATORY

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Silicification of wood was performed in the laboratory to improve the physical properties (e.g. wear resistance, water absorption, hardness) of the material. Experimental studies were carried out using two types of wood (oak and spruce) and five different sources of silica including sodium metasilicate (Na_2SiO_3), a colloidal suspension of silica, tetraethoxysilane (TEOS), a mixture of TEOS with methyltriethoxysilane (MTEOS), and silica sol with three different particle sizes. Additionally, TEOS mixed with the alkoxides tetrapropyl zirconate (TPOZ) and tetrabutyl orthotitanate (TBOT), respectively was tested. Experiments were performed in the temperature between 20°C and 80°C under normal pressure in glass beakers and at higher temperatures (up to 138°C) and pressures (up to 12 bar) in autoclaves. A special experimental setup with vacuum impregnation was developed to increase the penetration depth of the silica into the wood material. The properties of the impregnated wood were investigated using different analytical techniques. Besides microscopic investigations (binocular, polarizing microscopy, SEM, cathodoluminescence), XRD analysis, FTIR spectroscopy and measurements of water absorption and hardness were performed. XRD studies revealed that the silica coatings completely consist entirely of X-ray amorphous silica (opal-A similar to hyalite). CL microscopy proved to be the most effective method to reveal the distribution of SiO_2 within and on the surface of the wood samples. FTIR studies showed that deposited silica may contain organic residues of the source materials. The technical properties of wood could significantly be improved by the silicification. Material silicified with colloidal silica and TEOS, respectively absorbed up to 40% less water than untreated specimens. Likewise, the Brinell hardness of treated samples could be increased by nearly 100% compared to untreated samples. This is mainly caused by vitreous silica coatings (generated by sol-gel transformation) at the sample surface.

INTRODUCTION

Wood materials are widely used in various industrial applications because of their excellent physical, chemical and visual properties. The disadvantages of utilizing wood in many applications relate to its low hardness and high water uptake. Therefore, several attempts have been made to improve the structure of industrially used wood and to reduce damage caused by weathering. Unfortunately, many of these physical and chemical procedures use rather toxic chemicals such as chromated copper arsenate leading to certain environmental problems [1]. An appropriate silicification procedure could provide a new and environmentally less harmful way to prevent the mechanical and chemical decay of wood materials and allow preservation of its visual appearance.

In nature, permineralization of wood by silica-bearing solutions as well as by other mineral substances (e.g. fluorite, carbonate) is well known. Silicification by vitreous and crystalline silica minerals (opal, chalcedony, quartz) increases wood hardness (up to MOHS hardness 7) and improves resistance against chemical,

biological and weathering processes. Therefore, permineralized wood can persist for millions of years in the environment without damage [2]. The density of completely silicified wood, however, approaches 2.6 g/cm³. This fact leads to the conclusion that surface coating of wood may be a more suitable process allowing the creation of a new composite material with moderate density.

Several authors investigated the general possibility of artificial silicification of wood (e.g. [3, 4, 5, 6, 7]). Drum [3, 4] generated siliceous replicas of birch twigs and small pieces of plants by placing them in sodium metasilicate solutions. Oehler & Schopf [5] examined the artificial permineralization of blue-green algae in silica gel at 165°C and 3000 bar. This appears to be a relevant experiment since the chemical surface structure of algae and wood are comparable in terms of terminating OH-groups. Hydrogen bondings between silica and the OH-groups are considered to cause the preservation of these algae filaments [8]. McCaferty [7] impregnated wood by soaking in a solution containing silicon and aluminium compounds. However, no conclusions about the properties of the wood-ceramic were drawn except an increase of hardness (up to 120%).

Most researchers since the 1990s kept focus on coating wood surfaces in different ways by using multi-functional silicon-alkoxides like tetraethoxysilane (TEOS, e.g. [9, 10]), methyltrimethoxysilane (MTMOS, e.g. [9, 11]), methyltriethoxysilane (MTEOS, e.g. [10, 12]) and others. These compounds hydrolyze to silicic acid $\text{Si}(\text{OH})_4$ during sol-gel transformation, a common form of silica source in nature. Tanno et al. [1] and Saka & Tanno [13] examined only a few properties of silicified specimens. They found that the resistance against fungal attacks increases, and that treated samples absorbed significantly less water than untreated ones. The absorption of water is an excellent index for the quality of the coating, since it represents the coating's impermeability. Water repulsion, and therefore limited weathering effects, is one of the main targets of coating wooden materials [9, 11, 12, 14].

There has been increased interest in the topic in the last recent years. Sol-gel processes have proved to be an effective method to impregnate wooden material. Saka & Ueno [9] added fire-resistant agents to SiO_2 composites and additionally conducted experiments with MTMOS silica precursor and compared results to those of TEOS. MTMOS was also used by Tshabalala et al. [14]. They carried out extensive investigations concerning the coating structure by using AFM, ATR-FTIR, XPS and SEM/EDX. De Vetter et al. [15] combined SEM/EDX analysis with micro-CT investigation and found these methods to be a useful tool to characterize silicon coatings on wooden substrates. Donath et al. [12, 16] tried additional types of precursors, but the method of sol-gel-process still remained the same. Investigation on both artificial [11] and natural [16] weathering revealed that the resistance of impregnated wood is largely increased, although some problems occurred concerning the colour stability. To prevent these problems, UV light stabilizing agents have to be added to the coating [16]. A review about modifications of wood by treatment with silicon compounds was given by Mai and Militz [17].

The present study aimed to investigate the technical silicification of wood materials (oak and spruce) using different sol-gel precursors as well as sodium metasilicate solutions and colloidal suspensions, mainly to increase hardness of wooden surfaces in addition to weathering resistance. The experiments were conducted under varying conditions and included hydrothermal treatment, vacuum impregnation and soaking with silica-containing solutions. A combination of different analytical methods (XRD, CL microscopy and spectroscopy, FTIR spectroscopy) were used afterwards to characterize the treated materials, especially the spatial distribution and structural state of the silica.

EXPERIMENTAL

Sample material

Cube-shaped samples (1 cm^3) of oak and spruce wood were prepared for the experiments (Figure 1). The raw material contained about 4% moisture (25°C) and volatile substances. Therefore, most of the samples were immersed in acetone for 24 h and afterwards oven-dried (50°C , 24 h). Some experiments were run with untreated samples to compare the results. In Table 1, density and hardness of spruce and oak wood are compared. Considering the lower density (higher porosity) of spruce wood, a faster and probably better silicification could be expected. On the other hand, the inter-connectivity of open spaces (e.g. connection of gymnosperm tracheids by bordered pits) has also to be taken into account for the experiments.

Table 1. Selected properties of spruce and oak wood (hardness after [22]).

Kind of wood	Density (g/cm^3)	Brinell hardness (N/mm^2)
Spruce	0.45	< 35
Oak	0.65	60-65

Silica sources

In a first step, three different sources of silica were used. Sodium metasilicate solutions containing up to 2.5 wt.% SiO_2 (ALDRICH) were prepared for hydrothermal experiments and soaking experiments in glass beakers. Colloidal suspensions of silica (LUDOX, ~40 wt.% SiO_2 , pH ~10, particle size 1-1000 nm) were applied during vacuum impregnation and in glass beaker experiments. Furthermore, tetraethoxysilane (TEOS, FLUKA and LUDOX, other used alkoxysilanes supplied by FLUKA) was tested as silica source, which was initially treated with isopropanol to set up the favoured concentration, and therefore, control the speed of the following reaction. TEOS and a suspension of colloidal silica (SCS) contain about 30 and 40 wt.% silica, respectively. Their solutions were applied in glass beakers (only TEOS) and under vacuum conditions (both silica sources).

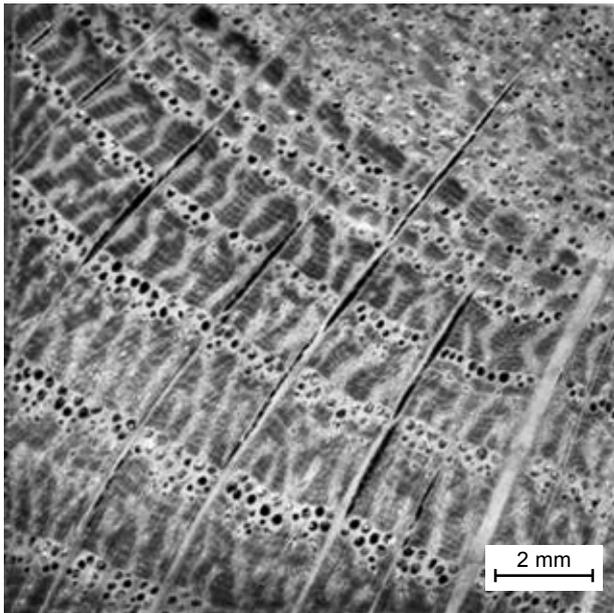
In a second step, 0.8 mol TEOS were combined with 0.2 mol methyltriethoxysilane (MTEOS) to compensate strain within the prepared silica coatings and increase their thickness. Commercial silica sols Köstrosol 0730, 1530, 3530 distributed by CWK BAD KÖSTRITZ with three different particle sizes (average particle size of 7 nm, 15 nm and 35 nm, respectively) were added. The TEOS/MTEOS (60 % SiO_2) was prepared with each silica sol (40 % SiO_2) under different experimental parameters according to [18].

Furthermore, TEOS was combined with tetrapropyl zirconate (TPOZ) and/or tetrabutyl orthotitanate (TBOT) to increase the surface resistance of the coatings. The last two experiments (TEOS/MTEOS/silica sol and TEOS/TPOZ/TBOT) were performed under differing conditions to those with pure TEOS with lower oxide contents (about 5 wt.%) of the precursor solutions.

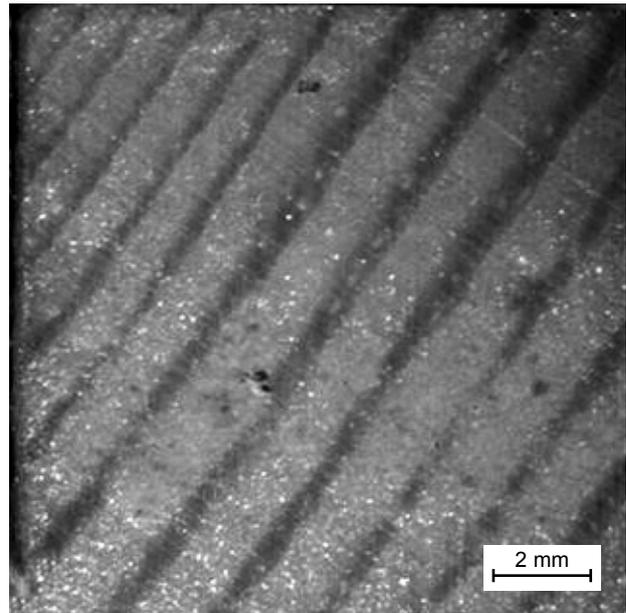
During the experiments the general applicability of these different silica precursors should be tested, including handling and quality of the resulting coatings.

Silicification experiments

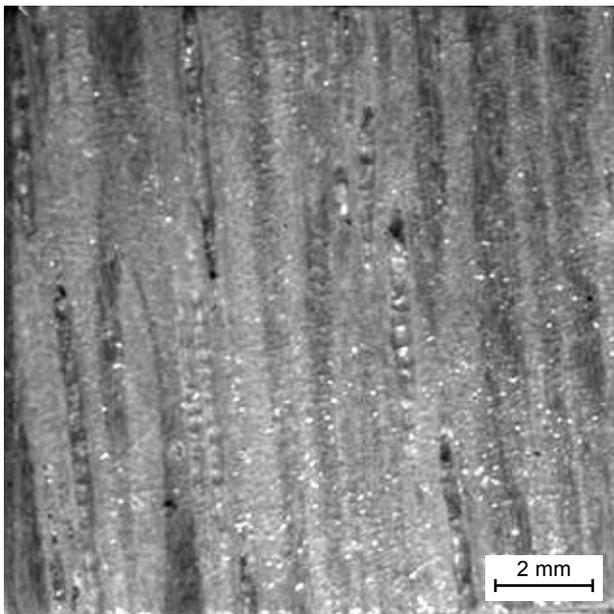
Three distinct silicification methods were applied. In most of the experiments the wood samples were placed in glass beakers containing silica-bearing solutions. These experiments were run in the temperature range between 20°C and 80°C at normal pressure. The solutions were stirred (3 h) and subsequently kept overnight to allow sol-gel transformation and diffusion processes. Hydrothermal experiments at higher tempe-



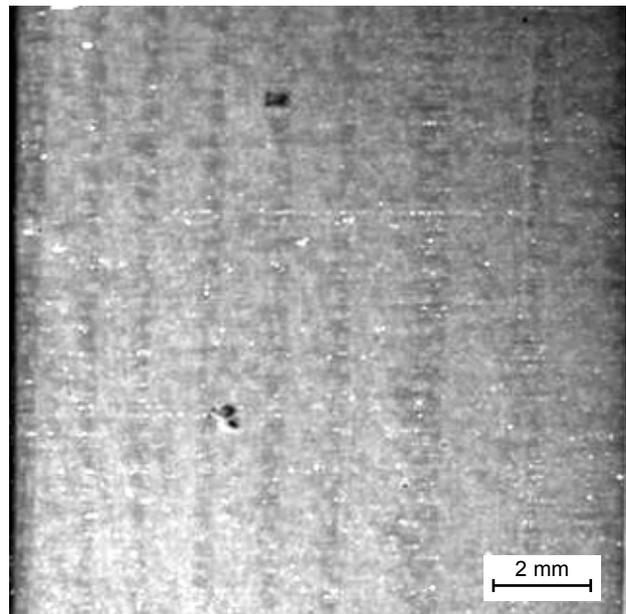
a)



b)



c)



d)

Figure 1. Cubes of oak (left) and spruce wood (right) with surface cuts transversely (a,b) and parallel (c,d) to the long axis of vessels and tracheids, respectively. The sample of oak wood shows deformation and cracking (a) due to treatment with Na_3SiO_3 solution; a thin layer of silica is developed at the surface of the spruce sample after silicification with TEOS (b,d).

atures (100–138°C) and pressures (1–12 bar) were conducted in a PTFE-lined steel autoclave. In all experiments the degree of filling was 25 % and the reaction time about 3 hours. The third method used was vacuum impregnation of the specimens. For these experiments, a modified equipment for the impregnation of thin sections with epoxy resin was designed. The wood samples were penetrated by solutions under reduced pressure (~100 mbar) at room temperature for about 10 minutes. Treated specimens were dried for 1–2 days on air and afterwards in an oven at 50°C (48 h). Preliminary tests with 1 cm³ raw wood samples using different temperatures (30–105°C) and times (48–72 h) have shown the best results under these conditions.

Analytical methods

Different analytical methods were used to characterize the silica-coated wood samples. After initial macroscopic investigation of samples with a binocular microscope (ZEISS Stemi 2000-C), samples were selected for preparation of polished thin sections (30 µm thick). These were first analyzed in polarized transmitted light using a ZEISS Axio Imager A1m. Details of the samples were additionally studied by SEM (JEOL 6400 with EDX detector).

Cathodoluminescence (CL) investigations were performed on carbon-coated, polished thin sections using a "hot cathode" CL microscope HC1-LM (see [19]). The system was operated at 14 kV accelerating voltage and a current density of about 10 µA/mm². Luminescence images were captured "on-line" during CL operations using a peltier cooled digital video-came-

ra (KAPPA 961-1138 CF 20 DXC). CL spectra in the wavelength range 380 to 900 nm were recorded with an Acton Research SP-2356 digital triple-grating spectrograph with a Princeton Spec-10 CCD detector that was attached to the CL microscope by a silica-glass fibre guide.

Infrared (IR) absorbance measurements were undertaken by using a FTS 40A (fourier-transform spectrometer) by BioRad with data range of 400–4000 cm⁻¹ and 2 cm⁻¹ resolution. KBr tablets including 1 wt.% ground sample material were pressed under pressure of 8 bar for measurements.

To evaluate the water absorption of the material, the samples were placed in distilled water for 6 days (at 25°C and normal pressure) or in the second experimental series in tap water (20°C, 48h). Mass gain was determined by weighing the samples before and after coating experiments. The Brinell hardness of selected samples was determined with a HP 250 (WPM Leipzig) device.

RESULTS AND DISCUSSION

Sodium metasilicate solutions

First silicification experiments were run with aqueous solutions of Na₂SiO₃ with varying concentrations (8–410 mmol/l) and at different temperatures (Table 2). The high pH value (>11) caused damage and dissolution of the wood material, especially under elevated temperature and pressure. A significant loss of mass (up to 30 %) was especially observed for oak samples, whereas the mass of spruce wood decreased only ca. 7 %.

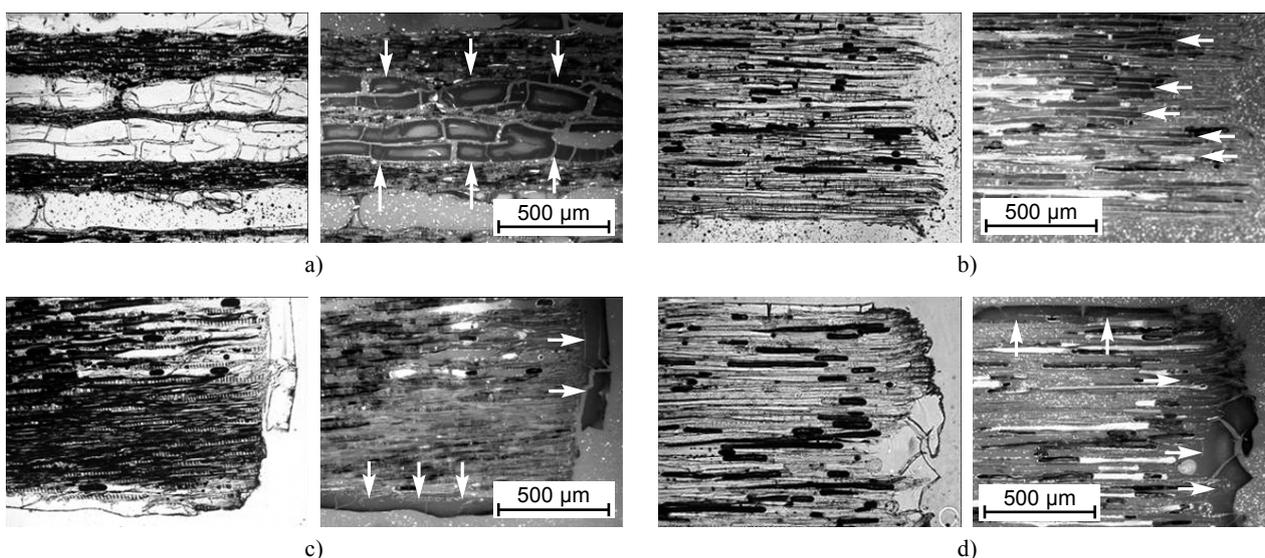


Figure 2. Transmitted light (left) and cathodoluminescence (right) image pairs of silicified wood samples. The SiO₂ is clearly visible under CL because of its characteristic blue luminescence colour. Micrographs of oak (a) and spruce (b) after vacuum impregnation with colloidal silica solution; the oak sample shows silicification of large tracheides, whereas the spruce is almost completely silicified. Micrographs of oak (c) and spruce (d) after treatment with TEOS in glass beakers; both samples show a remarkable silica coating at the wood surface.

Additionally, water absorption and Brinell hardness of the treated specimens were lower compared to those of fresh samples. These facts considerably limited the further use of sodium metasilicate as a silicification agent.

Table 2. Parameters of silicification experiments with sodium metasilicate solution.

Method	T (°C)	time (h)	SiO ₂ (wt.%) at 25°C	pH
Hydrothermal 1	138	3	0.5	11.0
Hydrothermal 2	138	3	2.5	11.8
Glass beaker 1	25	3	0.05	11.6
Glass beaker 2	50	3	0.05	11.6
Glass beaker 3	70	3	0.05	11.6
Glass beaker 4	90	3	0.05	11.6

Suspension of colloidal silica (SCS)

Experiments dipping the wood samples into a glass beaker containing commercial SCS (~ 40 wt.% SiO₂) resulted in similar effects as those with Na₂SiO₃ solutions. The relatively high pH value (about 10) caused again disintegration and decolourization of the wood samples after longer immersion times (>20 min). Therefore, only short-time vacuum experiments were made with colloidal silica.

The advantages of vacuum impregnation are a deeper penetration of the silica bearing suspension into the wood structure and therefore, a higher degree of silicification. The results illustrate, that the samples treated with acetone before silicification, showed the highest mass gain (oak: +13 %, spruce: +43 %). The pre-treatment probably opens the void space for the penetrating silica. The differences in the degree of silicification between oak and spruce wood are clearly visible under CL. In oak wood, mostly large vessels are filled with SiO₂, whereas the spruce wood is almost completely

filled (Figure 2a,b). This is due to the more or less homogeneous tracheid-size distribution of spruce and connectivity between vessels (oak).

Measurements of the water uptake confirm these results. The water uptake of oak wood is ca. 18% less than that of untreated samples, whereas the decrease in water uptake of spruce wood is ca. 30% (Figure 3). However, the hardness of the wood surface could not be improved because of the lacking silica layer on the wood surface (Figure 4).

In nearly all experiments that were performed with dipping the wooden cubes into solutions, we observed that the coatings are much thicker on the surface areas cut transversely to the vessels and tracheids than on surface areas cut parallel to the long axis (see Figure 2c,d). This may be due to the filter cake effect or to the fact that the transversely cut surface is rougher and therefore more material will be deposited here.

Tetraethoxysilane (TEOS)

Most silicification experiments were realized with organic TEOS solutions in alcohol and diluted acetic acid (Table 3), since no damage of the wood material was observed. Tetraethoxysilane (TEOS) hydrolyses during sol-gel transformation, followed by the formation of monosilicic acid, which subsequently polymerizes (formula 1). Hydrogen bonds can be formed between silicic acid and hydroxyl groups of cellulose ([1, 8]). By heating these hydrogen-bonded polysilanolols, they release water and produce covalent bonds with the wooden surface and build up a three-dimensional SiO₂-network (simplified in formula 2, in this case R-OH represents cellulose on the wood surface).

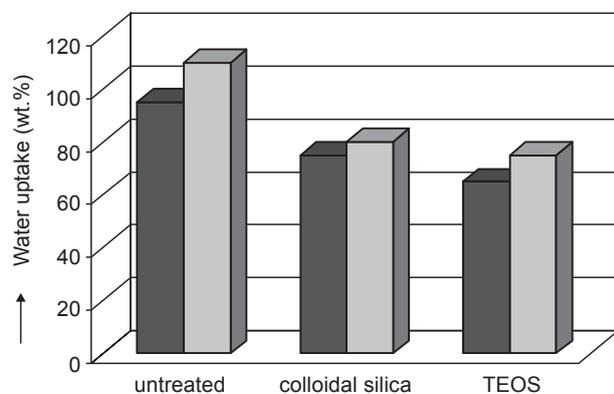
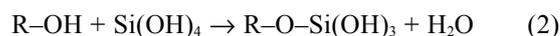
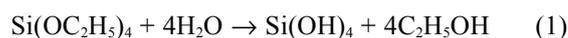


Figure 3. Comparison of water uptake between untreated wood with samples silicified with colloidal silica and TEOS, respectively (black = oak wood, grey = spruce wood).

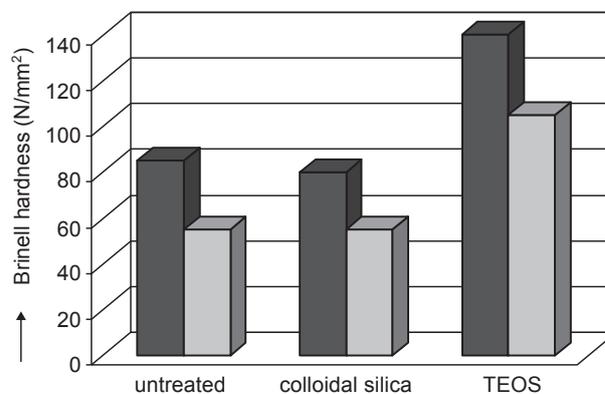


Figure 4. Comparison of Brinell hardness of untreated wood with samples silicified with colloidal silica and TEOS, respectively (black = oak wood, grey = spruce wood).

Table 3. Parameters of silicification experiments with TEOS.

Method	T (°C)	time (min)	TEOS (mol/l)	C ₃ H ₇ OH (mol/l)	CH ₃ COOH (mol/l)	NH ₃ (mol/l)	SiO ₂ (wt.%)
Glass beaker 1	25	180	0.41	10.07	-	3.73	3.07*
Glass beaker 2	25	180	2.71	3.54	0.32	-	17.75
Glass beaker 3	80	180	2.71	3.54	0.32	-	17.75
Vacuum	25	5	2.71	3.54	0.32	-	17.75

* pH 10.9 at 25°C

The treatment with TEOS (80°C, glass beaker) resulted in silica deposition not only in cell cavities but also on the wood surface (Figures 1 and 2c,d). Similar to the experiments with SCS, vacuum impregnation caused a deeper penetration of the silica-bearing solutions into the wood resulting in silicification of inner parts of the wood material. Visible cracks and mechanical damage of the solid silica coatings are probably caused by drying and preparation of the samples for microscopic examinations.

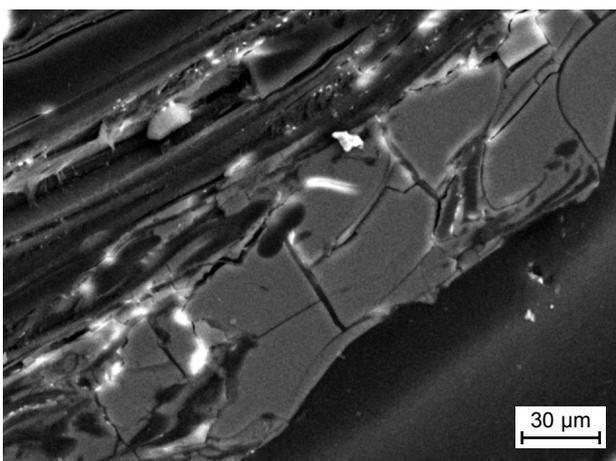


Figure 5. SEM micrograph of a silica coating on spruce wood prepared by a mixture of TEOS, MTEOS and silica sol (15 nm).

Both vacuum impregnation and glass beaker experiments with TEOS showed significantly decreased water uptake (up to 40 wt.%) compared to untreated specimens (Figure 3). The precipitated silica in the interior of the wood material prevents the penetration of water. Similar effects are caused by the silica surface coatings prepared in glass beakers. Only cracks in the silica coatings enable the water to penetrate.

The measurements of the Brinell hardness revealed significant differences between samples from vacuum experiments and those silicified in glass beakers (Figure 4). Only silica surface coatings improve the hardness of the wood material. The experiments in glass beakers result in an increase of hardness of spruce wood of 100%, in oak samples of about 60%. In contrast, no protecting surface coating with increased hardness was observed during vacuum impregnation.

TEOS combined with methyltriethoxysilane (MTEOS) and silica sols

Silicification experiments of wood with a mixture of TEOS, MTEOS and different silica sols were exclusively run in glass beaker experiments in order to develop silica coatings on the wood surface. Investigations by binocular and polarization microscopy revealed that the coatings are transparent and colourless. SEM studies showed that the coatings have a thickness of 10-100 μm and often contain numerous micro-cracks (Figure 5).

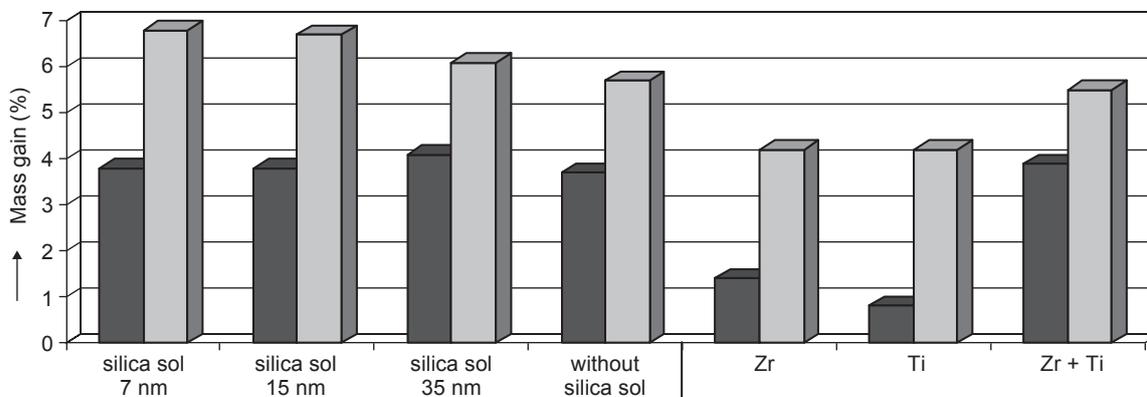


Figure 6. Mass gain of wood samples after silicification in a glass beaker with a mixture of TEOS and MTEOS and silica sols of different particle size as well as mixtures of TEOS/TPOZ/TBOT (black = oak wood, grey = spruce wood).

Figure 6 shows the increase of weight after coating with TEOS and MTEOS as well as different sized silica sols. It can be concluded that the mass gain by combined coating with TEOS/MTEOS and silica sol is much less than with the former experiments. This can probably be related to the lower oxide content (5 wt.%) in the solutions. It is noticeable that there are no significant differences between the various coatings.

Comparison of raw and silicified samples illustrates that only the treatment of spruce wood resulted in a significant decrease of water uptake (Figure 7). Curiously, there is virtually no significant effect by coating oak wood, whereas impregnating of spruce wood with the same precursors was successful. The particle size of the silica sols did not influence the results. Hardness measurements were not possible due to the low thickness of the silica coatings. It is assumed that the values are similar to those detected for the pure TEOS treatment.

TEOS combined with tetrapropyl zirconate (TPOZ) and/or tetrabutyl orthotitanate (TBOT)

The experiments with the Zr- and Ti-bearing alkoxides tetrapropyl zirconate $Zr(OC_3H_7)_4$ and tetrabutyl orthotitanate $Ti(OC_4H_9)_4$ were performed as attempts to increase the hardness of the coatings (Table 4). The coatings, especially those containing Ti, have light yellow colours, which might be disadvantageous in many applications.

Optical examinations of the coated samples by binocular microscopy revealed structurally quite intact coatings, although some cracks appeared. Investigations by polarizing and CL microscopy (Figure 8) however, show large unsilicified parts on the surface of the coating prepared by combined TEOS, TPOZ and TBOT on spruce wood. This may be due to problems occurring during preparation of thin sections because of the differences in hardness of the weak wood substrate and the surface layer. On the other hand, the micrograph reveals that the solution was able to penetrate deeply into cells (up to 300 μm) and silicify inner parts of the wood as well.

Table 4. Experimental parameters for wood silicification in glass beakers using mixtures of TEOS and Ti- and Zr-alkoxides.

Mixture (mol:mol)	H ₂ O (mol)	T (°C)	pH at 25°C
TEOS =1.0	2.0	25	1-2
TEOS:TBOT = 0.5:0.5	1.5	25	3-5
TEOS:TPOZ = 0.5:0.5	1.5	25	5-7
TEOS:TBOT:TPOZ = 0.5:0.25:0.25	1.5	25	4-6

Figure 6 illustrates that the mass gain after impregnation with TEOS and alkoxides is rather low due to the low oxide content. The more porous structure of spruce wood results in higher material uptake, and the coating prepared with TEOS and both alkoxides reaches the highest value and seems to be the most effective way. The water uptake for oak wood is lowered from 61 wt.% of the raw material to 41 wt.% of the impregnated samples. In spruce samples, the value decreases from 46 wt.% to 43, 38 and 37 wt.% for TEOS/TPOZ, TEOS/TBOT and the mixture of both, respectively. Because of the rather thin coatings, hardness measurements were carried out on remaining material from the glass beakers, which was treated in the same way as the coated samples. The MOHS hardness was around 4, which is higher than that of untreated samples, but much lower than in naturally silicified wood. This may be due to incompletely hydrolyzed parts of the coating (see below).

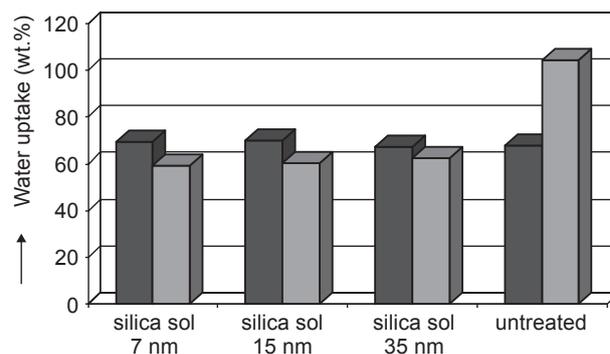


Figure 7. Comparison of water uptake of untreated wood samples with those of wood silicified with different TEOS/MTEOS-silica sol mixtures (black = oak wood, grey = spruce wood).

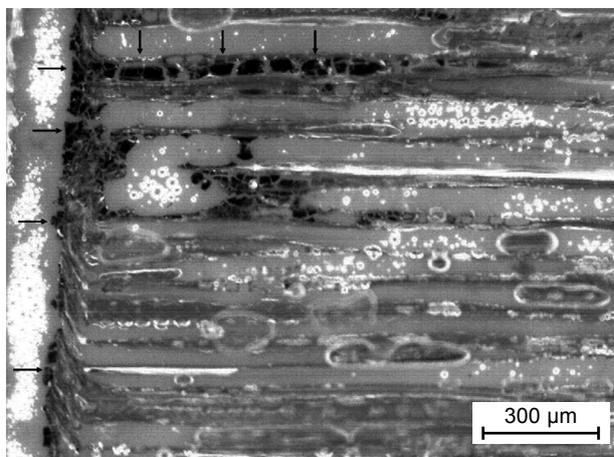


Figure 8. CL micrograph of silicified spruce wood (TEOS + TPOZ + TBOT) with massive cracks and partly missing coating on the surface (arrows indicate the deposited silica).

Characterization of the deposited silica

Additional analyses by XRD, CL spectroscopy and FTIR measurements were performed to obtain more information about the phase composition and structural state of the silica coatings. Analyses of different coatings by XRD revealed that the coatings exclusively consist of X-ray amorphous silica, similar to opal-A. Figure 9 presents a comparison of three layers prepared by TEOS and a mixture of TEOS with two different silica sols (particle size of 35 and 7 nm), respectively. The coatings show identical patterns, which are very similar to a sample of hyalite (opal-A) that was analysed for comparison.

These results were confirmed by CL spectroscopic analyses of the silica coatings. All investigated samples show a broad emission band with a maximum around 500 nm (Figure 10). This emission band was also found

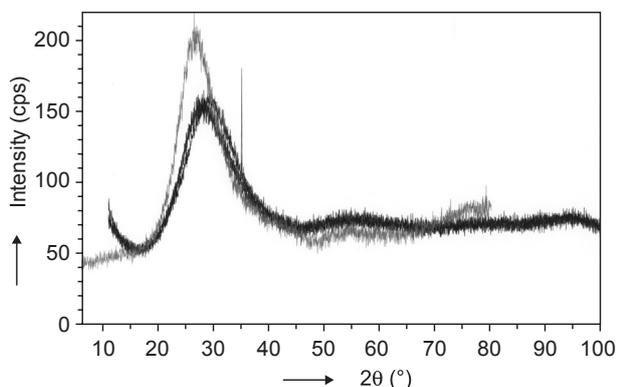
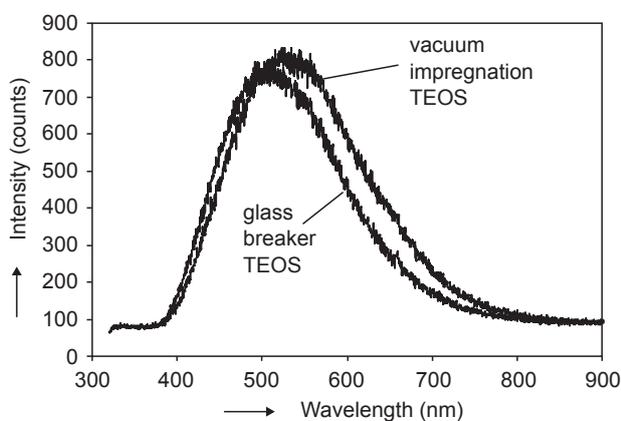


Figure 9. X-ray diffractograms of certain silica coatings produced by TEOS and mixtures of TEOS with silica sols of different particle size; the material exclusively consists of X-ray amorphous silica similar to hyalite (grey curve, the sharp peak is due to a carbonate impurity).



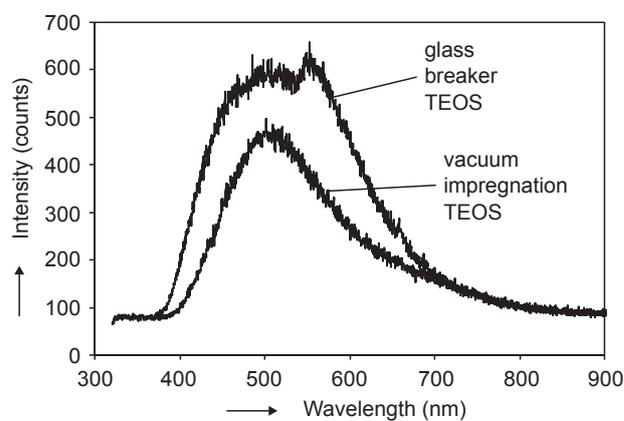
a) Oak

in amorphous silica of natural origin [20]. Only one sample (spruce, TEOS treatment in glass beaker) has an additional emission band around 580 nm. This CL emission was reported from microcrystalline quartz with high defect density [20]. Probably, we can find here a first step of crystallization from a complete non-crystalline precursor to a low crystalline SiO₂ structure.

The infrared spectroscopic studies additionally revealed that some organics and water from the silica precursors remained in the oven-dried samples. The absorption bands of Si-C bonds at around 840 and 1280 cm⁻¹ in the IR spectra of MTEOS (Figure 11) are characteristic, because of a direct bonding between Si and CH₃ groups. Peaks at ca. 1300-1400 cm⁻¹ can be related to some organic end groups with similar range of wave numbers [21]. Figure 12 shows infrared spectra of coating material indicating lots of infrared active organic end groups remaining within the layers. These derive from organic solvents (e.g. the peaks between 1350-1500 cm⁻¹ belong to ethylacetoacetate), which were only used in coatings containing TPOZ and TBOT, and thus could be identified very easily. Therefore, we assume that the process of hardening of the layers was not completely performed and has to be improved. Nevertheless, the peaks between 800 and 1250 cm⁻¹ indicate the formation of a well-developed three-dimensional network of SiO₂, ZrO₂ and TiO₂ (for line 1, Figure 12) and moreover, a good combination of the precursors.

CONCLUSION

In the present laboratory study, different methods were tested to impregnate wood samples by coating with siliceous material. These were performed to improve several properties of the wood including



b) Spruce

Figure 10. CL spectra of silica coatings on spruce and oak wood prepared by TEOS; the spectra show a broad band with a maximum at ca. 500 nm, which is similar to the spectra of opal.

mechanical and chemical resistance, reduced water uptake and increased surface hardness. The results demonstrate that precursors, especially those with high silica contents (at least 30 wt% SiO₂), such as TEOS and/or colloidal silica are suitable sources for an artificial silicification in the laboratory. Precursors with alkaline pH (sodium metasilicate) or low silica contents did not provide successful results. The use of additional silica sol, TPOZ, TBOT to precursor solutions caused differing results but might be a worthwhile alternative in future investigations.

The silicification experiments with spruce wood often yielded better results than those with oak wood due to the higher amount of large tracheids and the associated higher uptake of silica into the internal structure. The comparison of different silicification procedures showed that the high temperatures and pressures during

hydrothermal experiments damage the wood material. In contrast, treatment at moderate temperatures (20 to 80°C and ambient pressure) in glass beakers and vacuum impregnation improve the weathering resistance by lowering water uptake. Furthermore, an increase of surface hardness could be observed for samples treated with solutions of high SiO₂ contents.

A significant difference was detected for the formation of silica during the experiments in glass beakers or with vacuum impregnation. Whereas the latter one resulted in an impregnation of the wood material without the development of a surface layer, dipping caused the formation of dense silica coatings (thickness up to 100µm) resulting from sol-gel transformation processes. Further studies should combine experiments in glass beakers with the vacuum impregnation technique to use the advantages of the two methods.

XRD measurements and CL spectroscopy indicate that deposited silica is X-ray amorphous. However, IR measurements revealed that there are still some residues of solvents remaining in the layers after drying, indicating that the process of drying and hardening was incomplete. Therefore, further studies are required to optimize variables like chemical composition, drying procedures and different additives to precursors in order to generate a silica coating without cracks or other defects and to increase the hardness of the protecting layers.

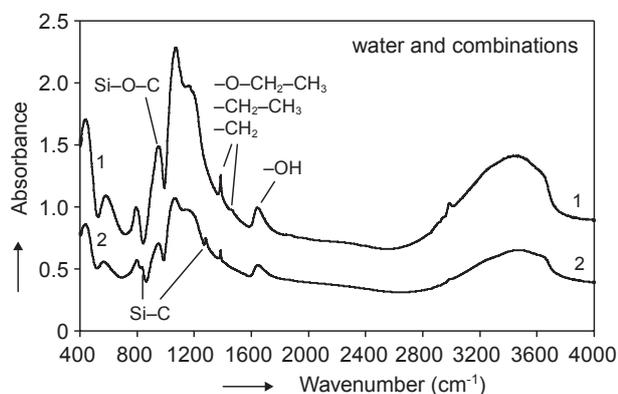


Figure 11. Infrared spectra of silica coatings produced by TEOS (1) and TEOS/MTEOS (2), respectively. Several absorption bands can be assigned to residual organic compounds; the absorption bands related to either SiO₂ or water are not indicated.

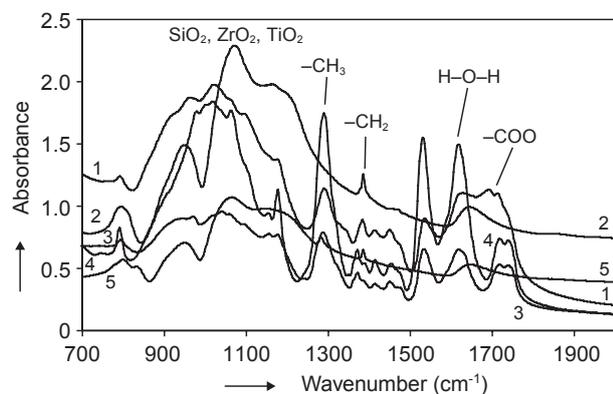


Figure 12. IR spectra of different coatings prepared with precursors of TEOS (2), TEOS/MTEOS (5), TEOS/TPOZ (4), TEOS/TBOT (3) and TEOS/TPOZ/TBOT (1), respectively; several absorption peaks are indicated, which can be related to the different precursors.

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KŘEMÍKOVÁNÍ DŘEVA V LABORATOŘI

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V laboratoři bylo provedeno křemíkování dřeva pro zlepšení fyzikálních vlastností materiálu (např. odolnost proti otěru, nasákavost vodou, tvrdost). Experimentální studie byly provedeny na dvou druzích dřeva (dub a smrk) s pěti různými zdroji oxidu křemičitého včetně metakřemičitanu sodného (Na_2SiO_3), koloidní suspenze oxidu křemičitého, tetraethoxysilanu (TEOS), směsi TEOS s methyltriethoxysilanem (MTEOS) a koloidního roztoku kyseliny křemičité se třemi různými velikostmi částic. Kromě toho byl zkoušen TEOS ve směsi s alkokidy tetrapropylzirkoničitanem (TPOZ) a tetrabutylortotitančitanem (TBOT). Pokusy probíhaly v teplotním rozmezí od 20°C do 80°C za normálního tlaku ve skleněných kádinkách a za zvýšených teplot (až 138°C) a tlaků (až 12 bar) v autoklávech. Bylo navrženo zvláštní uspořádání pokusu s vakuovou impregnací pro zvýšení hloubky penetrace oxidu křemičitého do hmoty dřeva. Vlastnosti impregnovaného dřeva byly zkoumány pomocí různých analytických technik. Kromě mikroskopického zkoumání (binokulární, polarizační mikroskopie, SEM, katodoluminiscence) byla provedena i analýza XRD (rentgenovou difrakcí), spektroskopie FTIR (Fourierova transformace v IR oblasti) a měření absorpce vody a tvrdosti. Studie XRD odhalily, že křemičité povlaky se skládají zcela výhradně z rentgenamorfního oxidu křemičitého (opálu A podobného hyalitu). Nejefektivnější metodou odhalení distribuce SiO_2 uvnitř a na povrchu vzorků dřeva se ukázala být katodoluminiscenční (CL) mikroskopie. Studie FTIR prokázaly, že nános oxidu křemičitého může obsahovat organické zbytky z výchozích surovin. Technické vlastnosti dřeva mohou být křemíkováním výrazně vylepšeny. Materiál ošetřený koloidním oxidem křemičitým nebo TEOS absorboval až o 40 % méně vody než neošetřené vzorky. Podobně lze u ošetřených vzorků zvýšit tvrdost podle Brinella o téměř 100 % v porovnání se vzorky neošetřenými. To je způsobeno hlavně nánosem křemičitého skla (vznikajícím sol-gelovou transformací) na povrch vzorku.