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TECHNICAL SILICIFICATION OF WOOD MATERIALS

Техническое силикатирование древесины было проведено для улучшения ее свойств (сопротивление истиранию, влагопоглощение, прочность и др.) Экспериментальные исследования проводились с использованием двух сортов древесины (дуб и ель) и трех источников кремния, включая метасиликат натрия (Na_2SiO_3), коллоидную суспензию кремния (CSS) и тетраэтоксилан (TEOS). Эксперименты проводились в температурном диапазоне от 40 до 80 °C при нормальном давлении в стеклянных сосудах и при высоких температурах (до 138 °C) и давлении (до 12 бар) в автоклавах. Кроме микроскопического исследования (бинокулярное, поляризационная микроскопия, растровая электронная микроскопия, катодолюминесцентная микроскопия) были произведены измерения влагопоглощения и прочности. Катодолюминесцентная микроскопия оказалась наиболее эффективным методом обнаружения распределения SiO_2 внутри и на поверхности образцов древесины. Материал, силикатированный с применением коллоидной суспензии кремния и TEOS, поглощал на 40 % меньше влаги, чем необработанные образцы. Твердость по Бринеллю может быть увеличена на 100 % по сравнению с образцами из свежей древесины, благодаря стекловидным слоям кремния на поверхности образцов, образовавшимся в результате превращения золя в гель.

Technical silicification of wood was performed to improve the 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 three different sources of silica including sodium metasilicate (Na_2SiO_3), a colloidal suspension of silica (CSS), and tetraethoxysilane (TEOS). Experiments were done in the temperature range between 40 °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. Besides microscopic investigations (binocular, polarizing microscopy, SEM, cathodoluminescence microscopy), measurements of water absorption and hardness were performed. 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. Material silicified with colloidal silica and TEOS, respectively absorbed about 40 % less water than untreated specimens. Likewise, the Brinell hardness of treated samples could be increased by nearly 100 % compared to fresh wood samples, which is mainly caused by vitreous silica coatings (generated by sol-gel transformation) at the sample surface.

Introduction

Recently, different chemical und physical methods are being used to improve the structure of industrially used wood and to avoid damages caused by weathering. Most of these procedures use rather toxic chemicals such as chromated copper arsenate leading to certain environmental problems (Tanno et al. 1998). An appropriate silicification procedure would provide a new and harmless way to prevent the mechanical and chemical decay of wood materials.

In nature many examples are known where silica bearing solutions cause the permineralization of wood. Vitreous and crystalline silica minerals (opal, chalcedony, quartz) increase the hardness (up to Mohs 7) and improve the resistance against chemical, biological and weathering processes. The density of silicified wood is approaching 2,6 Mg/m^3. This fact leads to the conclusion that surface coating of wood may be suitable to obtain a new composite with moderate density.

Previous studies concerning the artificial silicification of wood were reported by Drum (1968 a, b), Leo & Barghoorn (1976), McCafferty (1992), Oehler & Schopf (1971), Saka & Tanno (1996) and Tanno et al. (1998). Their results show the general possibility of technical silicification. Drum (1968 a, b) for example

generated siliceous replicas of birch twigs and small pieces of plants by placing them in sodium metasilicate solutions. Saka & Tanno (1996) and Tanno et al. (1998) tried to «petrify» wood in a different way by using silicon-alkoxides (e.g. tetraethoxysilane TEOS). During sol-gel transformation these compounds hydrolyze to silicic acid $Si(OH)_4$. They found that the resistance against fungal attacks increases, and that treated samples absorbed significantly less water than untreated ones.

In this study more than 100 experiments with different silica sources (sodium metasilicate, colloidal silica suspension, tetraethoxysilane) were performed to silicify samples of oak and spruce wood by hydrothermal treatment, vacuum impregnation and by soaking with silica-containing solutions. Different analytical methods were used to estimate the degree of property enhancement.

Materials and methods

Cube-shaped samples (1 cm^3) were prepared from oak and spruce woods containing about 4 % moisture (25 °C) and volatile substances. Three distinct silicification methods were applied. Hydrothermal experiments at higher temperatures (100-138 °C) and pressures (1-12 bar) were realized in a PTFE-lined steel autoclave. In all experiments the degree of filling was 25 % and the reaction time about 3 hours. Sodium metasilicate solutions containing up to 2.5 wt % SiO_2 were used for this aim. The second method tested was vacuum impregnation of the specimens. The wood samples were penetrated by solutions under reduced pressure (≈ 100 mbar) at room temperature for about 10 minutes. In the third method the wood samples were placed in glass beakers containing silica-bearing solutions. These experiments were run in the temperature range between 40 °C and 80 °C at normal pressure.

The solutions were stirred (3h) and subsequently kept overnight to allow sol-gel transformation and diffusion processes. For the last two methods, TEOS solutions and a colloidal colloidal suspension of silica (only for impregnation tests) were prepared. TEOS contains about 30 wt % and CSS 40 wt % silica. All treated specimens were dried in an oven at 50 °C for at least 48 h. To evaluate the water absorption of the material, the samples were placed in distilled water for 6 days (at 25 °C and normal pressure). The Brinell hardness of selected samples was determined and the changes of mass through silicification measured. Microscopic methods (binocular and polarizing microscopy, SEM, CL) were applied to characterize the sample material.

Results and discussion

Aqueous solutions of sodium metasilicate solutions (Na_2SiO_3) have a high pH value (> 10) that causes damage and dissolution of the wood material, especially under high pressure and temperatures. Particularly, oak samples showed large loss of mass (up to 30 %)and spruce wood specimens decreased in mass by about 7 %. Additionally, water absorption and Brinell hardness of treated specimens were lower than those of fresh samples. These facts considerably avoid the further use of sodium metasilicate as silicification agent. Although the colloidal suspension of silica (CSS) behaves similar to Na_2SiO_3 solutions (pH value of about 10), the former contains much more silica (≈ 40 wt %). Nevertheless, wood samples placed for longer time (> 20 min) in CSS began to disintegrate. Therefore, only short time vacuum experiments were made with colloidal silica. On the other hand, organic TEOS solutions with alcohol and less diluted acetic acid caused no damage in wood.

Figure 1 illustrates comparable results of experiments in glass beakers (TEOS solution, 80 °C, normal pressure) and with the vacuum impregnation technique. In particular, the mass

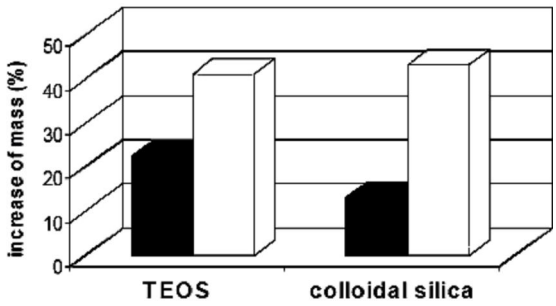

Figure 1. Increase of weight during silicification by TEOS in glass beakers and colloidal silica under vacuum (black = oak wood, white = spruce wood)

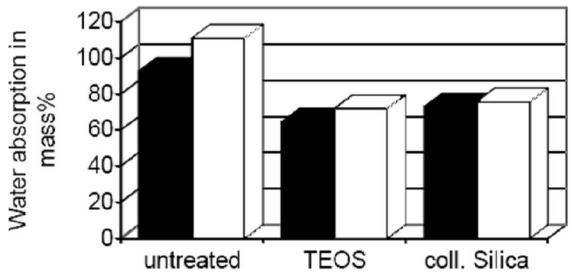

Figure 2. Water absorption of untreated and silicified wood samples (black = oak wood, white = spruce wood)

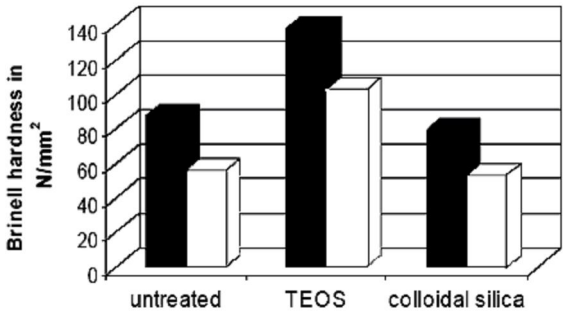

Figure 3. Brinell hardness of untreated and Silicified wood samples (black = oak wood, white = spruce wood)

of spruce wood increases during silicification up to 45 %. Less porous oak wood shows substantially lower mass gain (10-20 %). Significant differences could be detected for the formation of vitreous silica. The experiments in glass beakers (40-80 °C) lead to the deposition of silica coatings at the surface of the wood samples. In contrast to this, 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 resulted presumably from drying and preparation of the samples for microscopic examinations. Tetraethoxysilane (TEOS) hydrolyses during sol-gel transformation, followed by the formation of monosilicic acid which subsequently polymerizes. Hydrogen bonds can be formed between silicic acid and hydroxyl groups of cellulose (Tanno et al. 1998, Schultze-Lam et al. 1995). Several experiments with TEOS (80 °C, glass beaker) resulted in silica deposition not only in cell cavities but also in cell walls. Both wood samples of vacuum and glass beakers experiments with TEOS and CSS showed significantly decreased water absorption (up to 40 mass %) than untreated specimens (Figure 2).

The precipitated solid silica in the interior of the wood samples partially prevents the penetration of water. The silica coatings of samples produced in glass beakers show similar effects. Only cracks in the silica coatings enable the water to penetrate. The evaluation of the Brinell hardness shows significant differences. The evaluation of the Brinell hardness shows significant differences between samples from vacuum experiments and those treated in glass beakers (Figure 3). An increased hardness is likely caused by silica surface coatings. The experiments in glass beakers result in an increase of hardness of spruce wood of 100 %, in oak samples of about 60 %. In contrast, in samples impregnated under vacuum conditions nearly all silica was precipitated in the inner part. Therefore, no protecting coating with increased hardness develops at the wood surface.

Conclusions

The present study evaluated colloidal silica and TEOS as suitable sources for technical silicification. Wood samples of oak and spruce were impregnated under vacuum conditions and soaked in glass beakers containing TEOS solution.

The treatment at moderate temperature (40 to 80 °C and ambient pressure) in glass beakers and vacuum impregnation improve the weathering resistance by lowering water absorption. Furthermore, an increase of surface hardness of both oak and spruce wood (nearly 100 %) was observed for samples treated in glass beakers. On the surface of these specimens vitreous silica coatings (thickness up to 100 μm) could be detected resulting from sol-gel transformation processes. Methods that combine high alkaline solutions (pH > 10, e.g. sodium metasilicate solutions) with low silica content and temperatures above 100 °C are unable to silicify wood materials in short-time experiments (several days). Further studies are required to optimise experimental technique, chemical composition, drying procedures and other variables in order to generate a silica coating without cracks or other defects.

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