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# Plasma-chemical surface engineering of wood

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# Manufacturing and processing

# <u>ABSTRACT</u>

**Purpose:** Wood infiltrated with nano-silica hydrosol forms a "weak", irregular composite of components bound with hydrogen bonds only. The purpose of this study was to investigate the influence of low-energy ions bombardment on the structure and properties of the surface of this composite. The aim of these investigations was to produce a shallow "buried" layer of a dense wood-ceramic composite on a wood surface.

**Design/methodology/approach:** D.c. glow-discharge in N2/H2 (9:11) atmosphere under a pressure of 4hPa was the source of ions. A beech plate was placed on the cathode. The temperature of wood was 200°C. The material collected from the wood-silica composite surface was investigated with FTIR spectroscopy and SEM observations. The surface energy was determined with the use of contact angle measurements.

**Findings:** The ions influenced silica only. The nano-particles underwent sintering changing its medium size twice and a small I.R. peak of N2 trapped in SiO2 suggest the possibility of silica nitriding. A buried, continual surface layer of sintered silica did not form. The surface energy of the "wood-silica" plate was slightly decreased after plasma treatment.

**Research limitations/implications:** The results proved the possibility of plasma treatment of wood even in a d.c. glow-discharge under low pressure. Silica sintering, a difficult process which in a thermal way has to be carried out at a temperature of 1000°C, taking place in a plasma at a temperature of 200°C showed the very special nature of an influence of ions.

**Originality/value:** The plasma surface treatment of wood in the d.c. glow-discharge (GD) under reduced pressure has not been investigated. There are only publications about glow-dielectric-barrier-discharge (GDBD) at atmospheric pressure applications for wood surface modification. The energy of ions in GDBD is much smaller than that of ions in GD and therefore the application of glow discharge under reduced pressure to wood surface treatment can be more efficient.

Keywords: Surface Treatment; Ion nitriding; Wood; Nano-silica

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# **1. Introduction**

Protective modifications of wood surface with the use of additional materials e.g. varnishes are well known and has been used for a long time. A new type of varnishes utilizes supplements of nanoparticles for example scratch resistant lacquer "Addler-UV-AC-Walzdecklack" which contains nanosilica particles (1). However if the coating material includes flammable polymers the paint does not improve the fire retardance of wood. The best solution is ceramic coating. T.Harada et al. (2) developed the fireproof material CRB-90 paint made up of undergoing hydrolysis and condensation polymer and alkoxy metal salts that together make a hydrophobic, shielding glass film on the wood surface. The major components of CRB-90 are nano-SiO<sub>2</sub> and nano-Ag. Pure nanosilica deposited on wood from a hydrosol demonstrates good adhesion, even chemisorption to wood but the deposit consist of nanoparticles not linked together (3). Sintering nanosilica is difficult, the process is controlled by viscous flow and therefore it has to be carried out quickly at temperature of 1000°C (4). These conditions are inapplicable for wood.

Nonisothermal plasma creates conditions of relatively low atmosphere temperature and high energetic ionic treatment. Glow dielectric barrier discharge at atmospheric pressure (GDBD) which produces nonisothermal plasma has been applied for wood surface modification (5,6). The plasma treatment was able to remove the chemical and mechanical weak boundary layer caused by e.g. mechanical treatment of wood. The surface properties and increase of fracture strength were achieved. Action of ions of GDBD plasma seems to be to weak for nanosilica sintering. The ions of a diode discharge under reduced pressure bombarding the cathode surface are much "stronger", one can appreciate their energy as 100-500 eV. The aim of this work was to investigate the influence of d.c. discharge at reduced pressure on the nanosilica deposited on wood.

#### 2. Experimental

The material under examination was beech wood in form of plates of thickness of 2 mm. The electric conductivity of the dry wood was  $10^{-16} \Omega$  cm. Wood plates were immersed in a silica hydrosol during 8h in order to penetrate it with nano SiO<sub>2</sub>. Nano SiO<sub>2</sub> powder (Orisil Ltd., Kalush, Ukraine) was produced by SiCl<sub>4</sub> hydrolysis in flame. The chemical composition of wood surface material was analyzed with FTIR spectroscopy (Genesis Mattson). The sizes and shapes of nanosilica deposit on the wood surface and under the wood surface were observed in Scanning Electron Microscope (Supra). The water wetability of the specimens was measured with the use of contact angle measurement method.

The ion treatment was performed in the d.c. glow discharge process in a  $N_2/H_2$ -9:1 gas at the pressure of 4 hPa at the temperature of 200°C during 1 h. The silica coated wooden plate was located on the metallic cathode. The glow shine surrounded the wooden plate.

# **3. Results and discussion**

FTIR spectra of the silica-infiltrated wood material collected from the surface before and after plasma treatment are presented in Figs. 1 a,b.



Fig. 1. FT-IR spectrum: a) wood, b) wood infiltrated with SiO<sub>2</sub>, c) wood infiltrated with SiO<sub>2</sub> after plasma treatment

Although the color of wood changed, the spectrum obtained for wood did not show any differences due to plasma treatment. In the spectrum silica in modified material the peak for about 480 cm<sup>-1</sup>, derived from rocking mode was strongly higher and the peak about 1120 cm<sup>-1</sup> derived from Si-O asymmetric stretching mode was more narrow.

It seems that plasma influenced on the silica deposit only. The appearance of silica on the wood surface before and after plasma treatment is shown in Figs. 2a,b,c. The size distribution function of  $SiO_2$ -nanoparticles on the surface before and after plasma

treatment is shown in Figs. 3 a,b. As can be seen the particles undergo sintering changing its medium size twice.

SiO<sub>2</sub>-nanoparticles introduced into wood formed separated groups. This "SiO<sub>2</sub>-islands" near the surface also enlarged their medium sizes after plasma treatment but did not form a "buried" continual layer of sintered silica.

The results of water wetability, shown in Fig. 4 are surprising. Water wetted wood infiltrated with nano SiO2 completely, what is characteristic for both materials. After plasma treatment the modified surface became slightly water repellent . The only explanation of the observation is that some small chemical changes appeared in silica and wood ( cellulose) , most probably it was nitriding. Although there is no clear evidence of the Si-N streching vibration mode at 800-900 cm-1 (7) in the FTIR spectrum. However the small broad peak at 2337 cm-1 may be ascribed to (Si-N2) trapped nitrogen, observed in plasma nitrided SiO<sub>2</sub>(8).



b)

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Fig. 2. Nano-  $SiO_2$  particles on the wood surface: a) before plasma treatment, b)after plasma treatment





Fig. 3. Size distribution of nano-  $SiO_2$  particles on the wood surface: a) before plasma treatment, b) after plasma treatment



Fig. 4. Water wetability

### 4. Conclusions

The investigations of plasma treatment of wood infiltrated with  $SiO_2$  in a d.c. glow discharge under reduced pressure in N2 showed appearance of first stages of silica sintering and nitriding athough the material is electrically isolating. The temperature of

the cathode was 526 K so the effects may be explained only as a result of ions bombardment. The results underline the role of ions and their specific functionality in the surface engineering processes.

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