SOLID WOOD TREATED BY PLASMA JET

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Abstract

Cold plasmas were produced by electric glow discharges in a gas medium at reduced pressure and low frequency. A new technique called plasma jet was used to improve the deposition rate on solid wood. The treatment caused the solid softwood surface to become hydrophobic. The water contact angle was used to evaluate surface hydrophobicity. Although the surface plasma treatment resulted in water repellence, permeability to water vapor remained. The ability of the plasma jet technique to coat the surface of wood orifices was investigated using a mixture of tetraethyl orthosilicate vapor (TEOS) and oxygen (O_2).

Keywords: solid wood, glow discharge, plasma polymerization, hydrophobic surface

Introduction

Solid wood is a natural polymer composite that can be subjected to a wide variety of treatments to render it suitable for specific technical applications. The greatest disadvantage of solid wood, however, is its hygroscopicity. Moist wood is vulnerable to attack by fungi and termites and loses its dimensional stability. The most widely used treatments for solid wood are impregnation [1-2] and coating with paints and varnishes [3-4]. A promising future technique for solid wood surface coating is a plasma treatment with a glow discharge. Chen Hy and Zavarin [5] treated solid wood with radio frequency plasma and studied the permeability along the grain. Cho and Sjöblom [6] used several gases (CH_4, C_2F_4, hexamethyldisiloxane, O_2, acrylic acid) to control the hydrophobicity of solid wood surfaces and to improve paint adhesion. Denes *et al.* [7] have also used hexamethyldisiloxane-plasmas to produce water repellent surfaces. Recently, Denes and Young [8] have studied the improvement of solid wood weathering resistance through plasma treatment. Although these authors worked with high frequency plasma, they did not investigate the ability of the plasma technique to deposit inside wood capillaries.

Two different techniques – known as capacitive coupled plasma and plasma jet – were tested in this study. Both these techniques appear promising in view of the low vacuum level, low frequency power supply required, the lack of pollutants, and the use of industrial chemicals.

The study reported on here involves the modification of moisture absorption and water repellence of solid wood surfaces through the deposition of plasma-polymer films of 1-butene and TEOS vapor, using a homemade reactor operated at 60 Hz, 200 kHz and a plasma jet. Using low energetic plasmas, the deposited film can be polymer-like with a less crosslinked structure.

Experimental Procedure

The gases were supplied by Air Liquid do Brasil and the tetra ethyl orthosilicate (TEOS) from DATIQUIM Produtos Químicos Ltda (Brasil). The rest of the chemicals were supplied by Aldrich Chemical Company Inc.

Two substrates were used: B270 1-cm thick optic glasses and flat grained solid *Pinus caribaea hondurensis* softwood.

The glasses were immersed for 1 hour in a sulfuric acid / hydrogen peroxide 70/30 volume solution, after which they were washed with pure water and dried with dry nitrogen. Having become clean and hydrophilic after the above treatment, these glasses were used as substrate for the plasma treatments.

Defect-free pine (*Pinus caribaea hondurensis*) was sawed into blocks with a 2.0x2.0x1.0 cm nominal size in the radial, tangential and longitudinal directions, respectively. Flat-grained boards with a nominal dimension of 0.5x2.0x2.0 cm were sawed and sanded with 220-grit sandpaper. The blocks and boards were oven-dried at 100°C for 24 hr, plasma treated, and then used for water absorption measurements in a controlled environment. After being plasma treated, the boards were used for contact angle measurements along the grain.

The film growth rates were calculated after measuring the film thickness on 1-mm thick glass substrate using a Tyle Step Hudson stylus profilometer.

Static advancing water contact angle measurements were taken at room temperature by the sessile drop method, using optical microscopy (MM Optics, Inc. Brazil) and digitizing the image taken by a CCD (LG Honeywell) camera. The photographs were enlarged on a computer screen, providing a clear picture of the contact between the droplet and the substrate surface. About 9 contact angle measurements were measured on different parts of one wood sample for each reported averaged value of the angle in the parallel and perpendicular directions of the wood surface grains. The standard deviation of the contact angle was less than 2 degrees for glass substrates and less than 8 degrees for wood substrates.

SEM (scanning electron microscopy) micrographs and Si mappings were made using a Zeiss 960 microscope equipped with an EDS Analytical Link QX 2000 analyzer.

Before deposition of the plasma-polymerized film, the reactor chamber was evacuated to a base pressure of 9.33 Pa and flushed three times with argon. A glow discharge with Ar at 53.33 Pa was then applied for 15 min to clean the surfaces, after which the reactor was again evacuated to the base pressure.

The next step was the admission of the reactive gas, with the control valve adjusted to set the pressure in the chamber to 106.66 Pa before the glow discharge was switched on.

TEOS was vaporized into the interior of the reactor using an appropriate apparatus with heating and Ar bubbling.

The capacitive coupled plasma reactor is described elsewhere [9].

To deposit the plasma jet, an ion beam was built (fig.1) and operated attached to the plasma chamber window. The plasma jet consists of a cylindrical aluminum tube into which the 1-butene gas is admitted at one end, while three metallic grids with three different electric potentials are mounted at the other end to generate and accelerate the plasma through the substrate. The first grid operates at 260 VAC, 60 Hz, the second one at minus 5 KVDC, and the third at 15 KVAC, 60 Hz. Permanent ring magnets are fixed around the external aluminum cylinder. Thus, the magnetic field (1,200 Gauss) is applied parallel to the cylinder's axis. Electrons repelled from the cathodes are attracted to the anode but the magnetic field constrains the electrons to follow helical trajectories, increasing their path length and enhancing ionization efficiency.

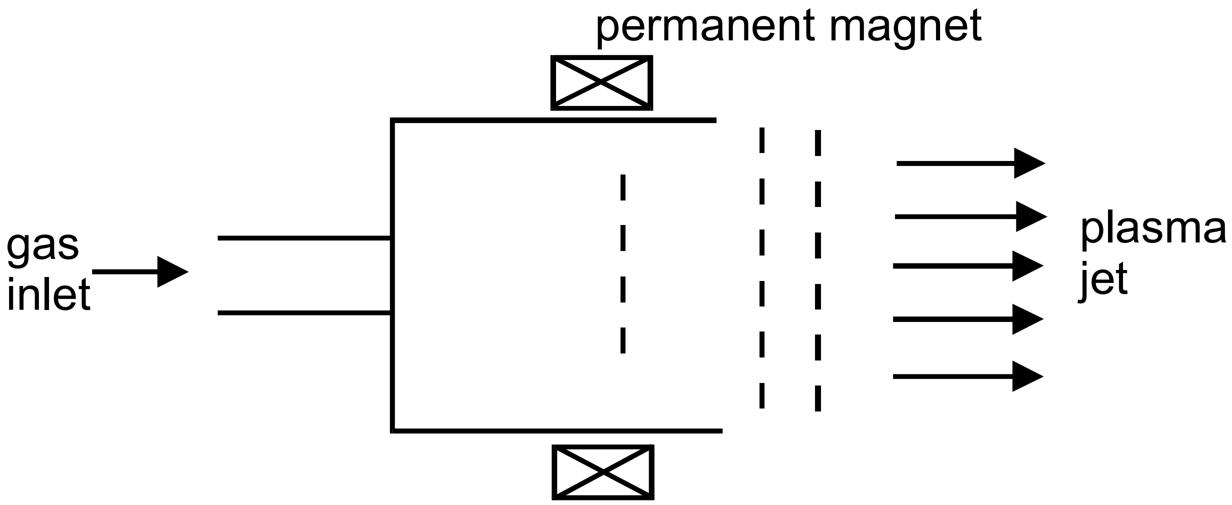

Figure 1. Diagram of the plasma jet

Since film deposition by plasma jet does not depend on substrate thickness, this technique is highly efficient to coat solid wood surfaces.

Results

Deposition rate

Table 1 shows the rate and uniformity of the film deposited on a common glass substrate with two thicknesses for different treatment conditions. Depending on the thickness of the substrate, the distinct deposition rate observed for capacitive coupled plasma suggests a much lower deposition rate for the wood substrate. Deposition uniformity is the same for all treatments and can be improved by modifying the homemade equipment to increase the gas flow symmetries. The deposition rate in the capacitive coupled plasma with the 2-mm substrate on the cathode is twice that of the deposition rate using the plasma jet. Nonetheless, the plasma jet technique is useful in solid wood treatment because surface roughness and porosity are readily covered, regardless of the substrate thickness.

Table 1. Deposition rate and uniformity of the film

Deposition rate (nm/min)	**60 Hz**		**200 kHz**	**Plasma jet**
	on an anode	**on a cathode**	**on a cathode**	
1 mm thick glass	1,6	1,3	64	24
2 mm thick glass	-	-	48	24
Uniformity (%)	-	-	10%	10%

Morphology

Figure 2 shows the morphology of the longitudinal tracheid cell wall before and after 1-butene-plasma treatment. Figures 2A, B, and C show, respectively, the external cell wall of untreated wood, wood treated by capacitive coupled plasma, and wood treated by plasma jet. Figures 2D, E, and F show the internal cell wall of untreated wood, capacitive plasma-treated wood, and plasma jet-treated wood, respectively. Figure 2A illustrates the wood before treatment, showing the random cellulose microfibrillar orientation of the primary cell wall. The S3 layer of the lumen's internal wall, with the microfibril nearly normal to the fiber's axis, is depicted in the electron micrography of figure 2D. Exposure of the wood to 1-butene plasma caused the morphologies of both the external and internal cell wall surfaces to change to a rougher texture.

The plasma jet-treated surface (fig. 2F) was rougher than that treated by capacitive coupled plasma (fig. 2E). The principal difference between capacitive and jet plasmas is that the plasma jet coats exposed orifices and channels more effectively than the capacitive arrangement did.

TEOS/O_2 mixture was used as reactive gas in the plasma jet in order to deposit SiO_x films on the solid wood surface. The deposited film was characterized by Si EDX mapping.

Figures 3 and 4 show SEM micrographs of solid wood surfaces exposed to the TEOS/O_2 plasma jet.

Figure 3A illustrates the morphology of the SiO_x deposited film, showing that the deposit is as rough as the woody substrate. However, the coating concealed the ultrastructure of the solid wood surface. Figure 3B shows the Si mapping, revealing white dots spread over the entire surface, which confirms the complete coating of the wood surface.

Figures 4A and 4B show, respectively, SEM micrographs and Si mapping of the surface of the 1.0-mm wide, 3.0-mm deep slit opened in the solid wood. These micrographs demonstrate that the plasma jet coated orifices which capacitively-coupled plasma was barely able to coat.

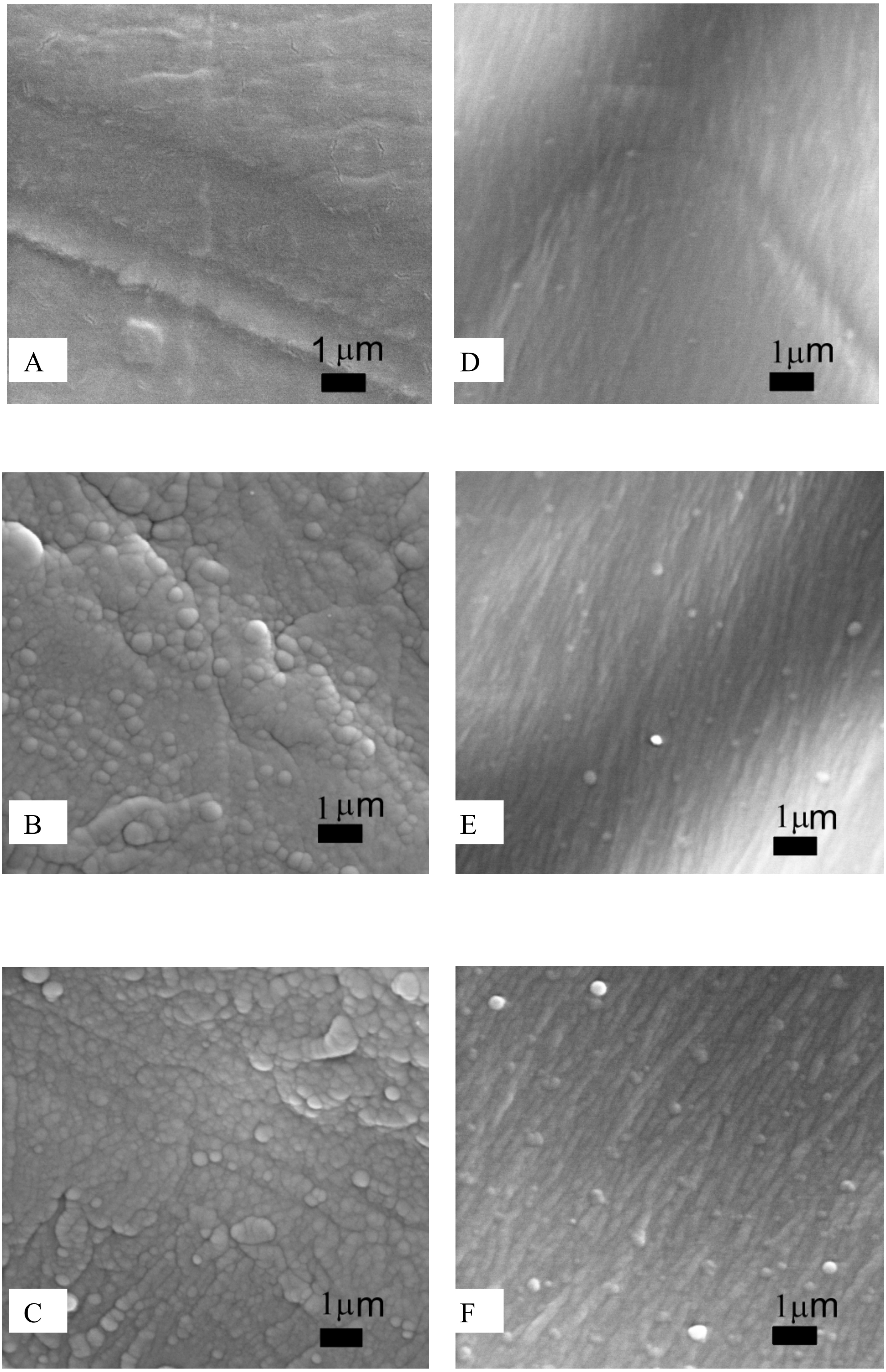

Figure 2. A: primary cell wall before treatment; B: primary wall exposed to capacitive plasma; C: primary wall after plasma jet. D: S3 layer before treatment; E: S3 layer exposed to capacitive plasma; F: S3 layer exposed to plasma jet. Magnification: 10,000X

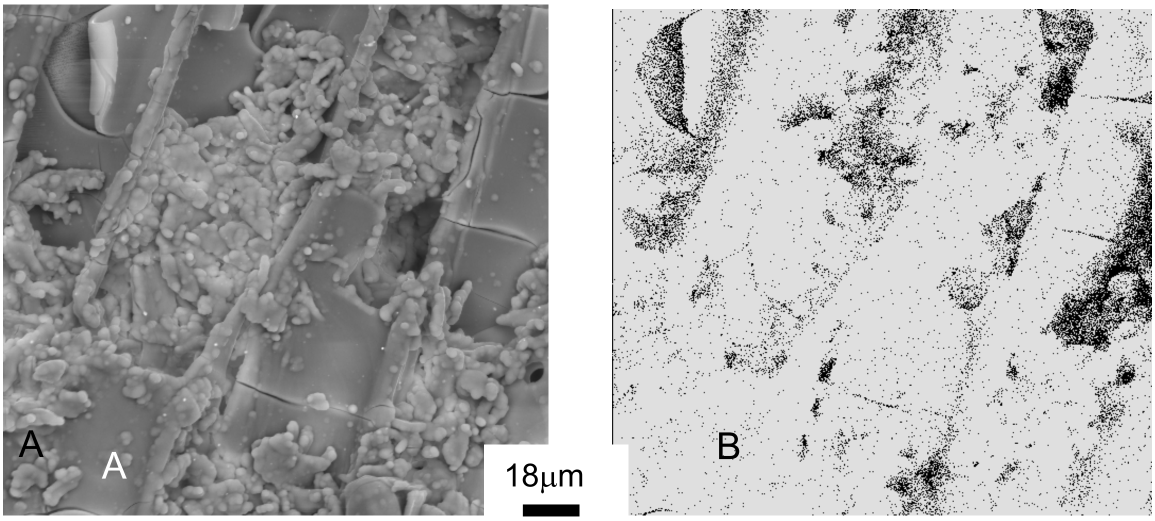

Figure 3. Solid wood surface along the grain coated with SiO_x by plasma jet. A) SEM using secondary electrons and B) Si mapping of the same region. Magnification: 500X

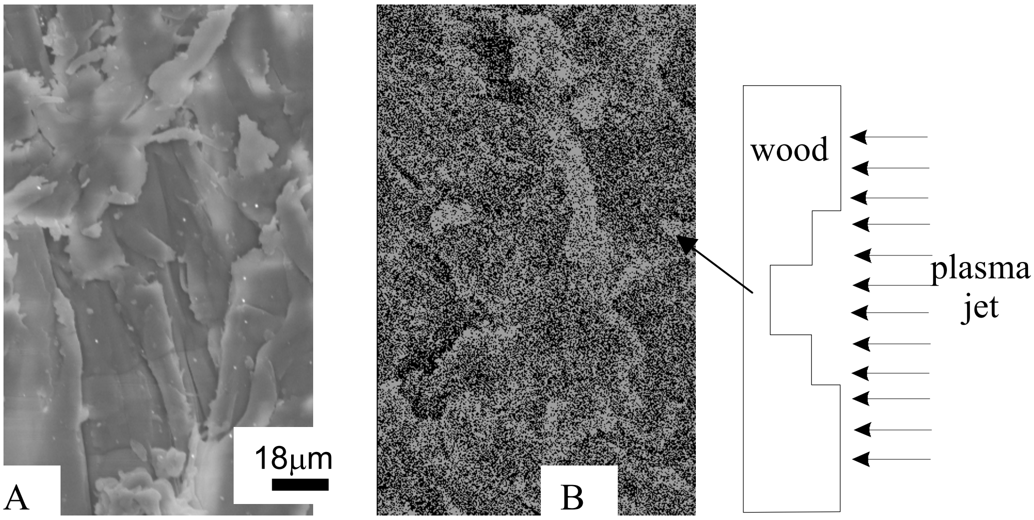

Figure 4. Surface of the slit opened in the solid wood and exposed to $TEOS/O_2$ plasma jet. A) SEM, and B) Si mapping of the same region

Contact angle

The cross section perpendicular to the fibres of untreated solid softwood exposed to the ambient air showed cell lumens with a diameter of approximately 40 µm, facilitating water absorption by capillarity. Water droplets were readily absorbed into the structure of the wood substrate, rendering it difficult to take an accurate reading of contact angle values.

The softwood surface treated by plasma film deposition presented a distinct behaviour after 1-butene-plasma deposition. Table 2 shows the contact angle of water droplets on plasma-treated wood and common glass under different conditions. The plasma treatment affected the entire wood surface along and across the grain, rendering it hydrophobic. The dissimilar surface contact angle values along and across the grain were attributed to uneven surface roughness. The glass substrate remained hydrophilic after plasma treatment, although the contact angle increased by over 55 degrees.

Table 2. Contact angle on wood and glass surfaces under different plasma conditions.

	Along the grain	Cross section	Glass
Without treatment	Absorbs the water droplet	Absorbs the water droplet	Small
200 kHz	115°	126°	75°
60 Hz	115°	140°	76°
Plasma jet	117°	132°	80°

Since the plasma jet penetrates solid wood orifices more efficiently than does the capacitively-coupled plasma, new experiments with 1-butene as precursor were conducted to evaluate water vapor exclusion. Wooden blocks and boards were used as substrates, with the cross section and the flat-grained surface, respectively, exposed to the plasma jet. Each wood surface was exposed to the plasma twice owing to the plasma jet's small (2 cm) diameter. Only the two largest surfaces of the wood samples were directed coated by the plasma jet; the other four faces were treated indirectly.

The treated and untreated samples were cyclically exposed to a humid and dry environment and their weight monitored at regular intervals. Figure 5 shows graphs of the water vapor absorption of the 1-butene treated and untreated solid wood. Although the plasma jet treatment provided efficient protection from liquid water, it proved ineffective against water vapor (humidity).

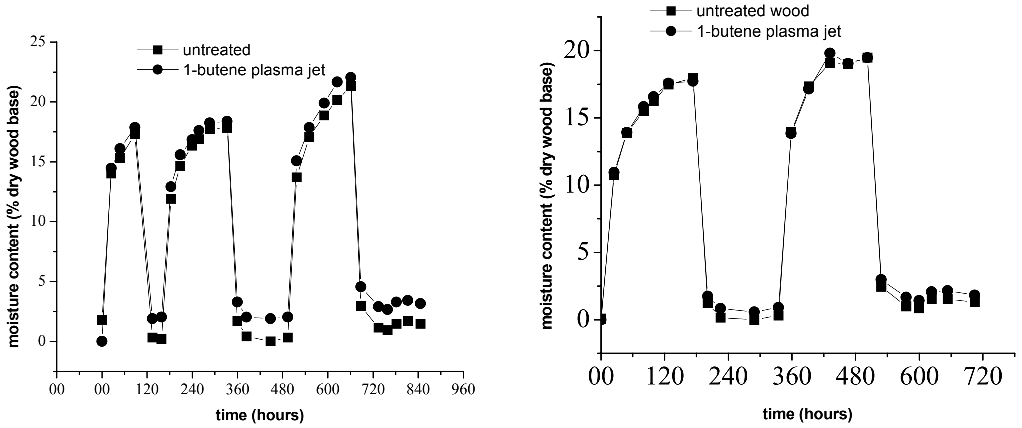

Figure 5. Change in moisture content of Caribbean pine finished with 1-butene plasma jet coat and exposed to alternating cycles of 95 and 22 percent relative humidity at room temperature, compared with untreated wood. Left: boards with nominal dimensions of 0.5 (R) x2.0 (T) x2.0 (L) cm. Right: blocks with nominal dimensions of 2.0 (R) x2.0 (T) x0.5 (L) cm.

The plasma jet penetrated inside the 1-mm slits but barely coated shadow areas, as illustrated in figure 6.

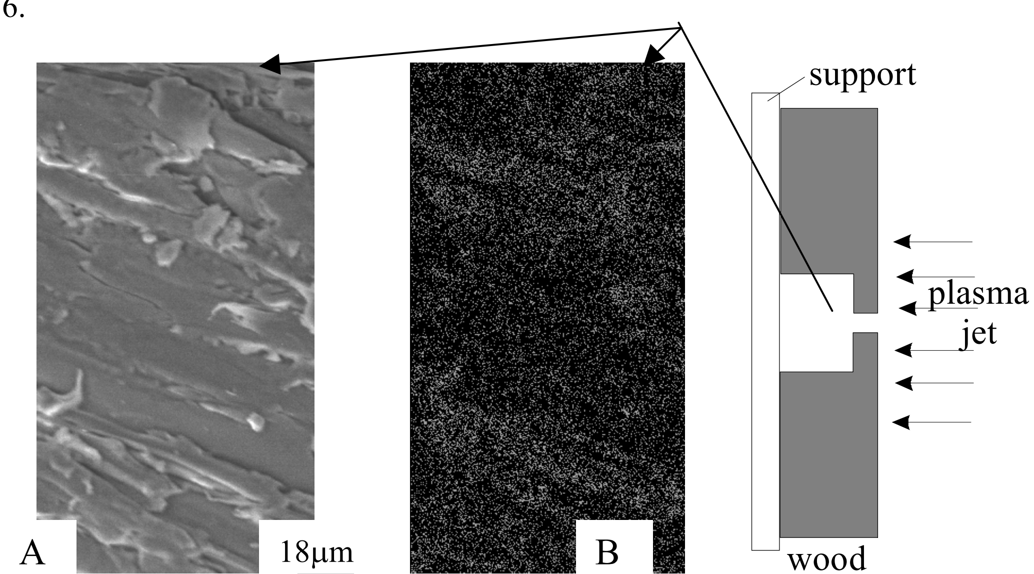

Figure 6 - A) Micrograph of the area not directly exposed to the TEOS/O_2 plasma jet, see diagram at right. B) Si mapping of the same region of A); white dots correspond to Si deposition.

Although the plasma jet easily penetrates 1-mm size slits, deposition inside the cell lumen is very difficult. Figures 7 and 8 show that, when the jet's incidence was not aligned with the longitudinal cell axis, internal coating of the cell wall was very difficult to achieve. Moreover, wood powder and debris adhered to the surface after the wood was sanded and machined, serving as a shield that prevented the capillaries from being coated.

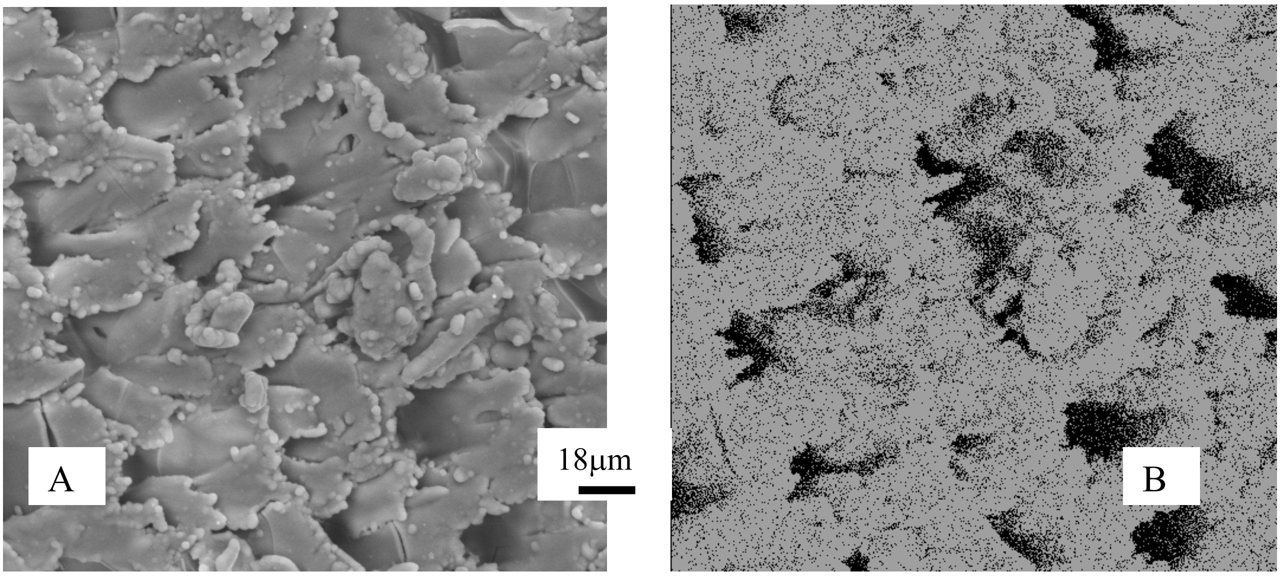

Figure 7. A) Micrograph of a wood surface slanted in relation to the cell axis after TEOS/O_2 plasma jet coat, showing uncoated orifices. B) Si mapping of the same region of A). The film was not continuous.

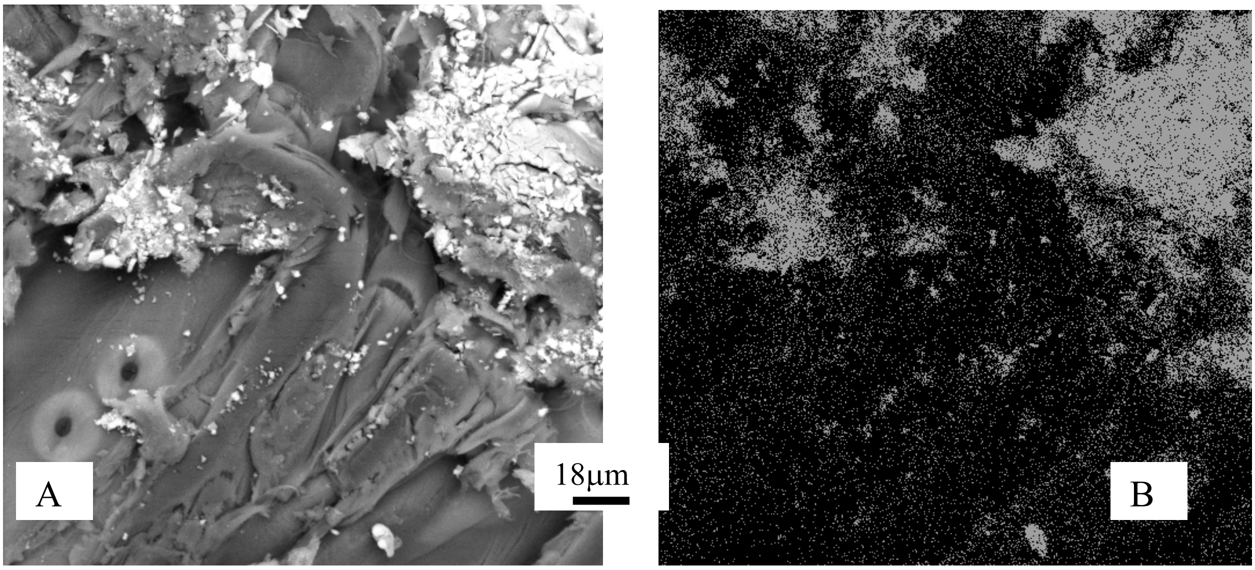

Figure 8. A) Micrograph of the longitudinal cut in the cell lumen, showing internal cell walls after TEOS/O_2 plasma jet coating. B) Si mapping of the same region as A). The treatment did not coat the cell wall efficiently.

Conclusions

A thin solid film deposited by 1-butene-cold plasma successfully coated solid softwood. The wood surface became hydrophobic after the plasma treatment. Plasma jet treatment is more effective to coat wood surfaces than capacitive coupled plasma treatment. The plasma-deposited film was unsuccessful in preventing water vapor absorption and desorption because the technique proved inadequate to coat wood capillaries.

Acknowledgment

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