Water vapor plasma processing of wood

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Abstract

Cold plasma processes are simple dry procedures that can effectively modify the surface of materials and produce desirable properties for specific applications. The surface properties of wood can be modified using plasma treatments. In this research we use water vapor plasma to modify wood and examine the effect of plasma on the micro-structure and physical and chemical properties of wood. We also examine whether plasma treatment can alter the permeability of wood and remove fungal blue stain from wood. Several hardwoods and softwoods, including blue-stained pine, as well as isolated fungal hyphae, were exposed to glow discharge plasma. Microscopy and chromatic confocal profilometry were used to examine etching of wood surfaces and hyphae. Wet chemical analysis, FTIR and XPS were employed to analyze the chemical changes at treated wood surfaces. The effect of plasma treatments on the color of wood was evaluated using spectrophotometry. Plasma etched wood cell walls and created new microstructures. Plasma increased cell wall porosity by creating small voids within secondary walls leaving the middle lamella less affected. Longer exposure to plasma created more voids at wood surfaces by destroying pit apertures and intervening cell walls. We quantified the erosion of cell walls and cellulose and lignin models using confocal profilometry, and found that there is a strong relationship between plasma treatment time and etching of cell walls and their polymeric constituents. Plasma oxidized wood surfaces and preferentially degraded wood's carbohydrates. Lignin was more resistant to plasma etching than cellulose and hemicelluloses. Plasma was able to remove blue stain from wood, and it also improved the effectiveness of hypochlorite bleach at removing blue stain from wood. These effects can be explained by the ability of plasma to increase wood's permeability and degrade fungal hyphae. We discuss the implications of our findings and the potential applications of plasma processing in the field of wood preservation, and development of new treatments to remove fungal discoloration from wood.

i. Introduction

Plasma is an exited gas, which consists of atoms, molecules, ions, electrons and metastable species (Boenig 1982). Plasma is considered to be the fourth state of matter because it is more highly activated than solid, liquid or gaseous states (Inagaki 1996). Plasma can be produced in the laboratory by raising the energy of a gas regardless of the nature of the energy source. “The easiest way to continuously inject energy into a system is using electrical energy” and for this reason electrical discharges are commonly used to produce most plasmas (Denes et al. 2004). Plasma generated by electrical discharge can be classified as either cold or hot. An example of a naturally occurring high temperature plasma is lightning. A natural cold plasma is created during the phenomena known as Aurora Borealis or Northern Lights (Denes et al. 2004). A low temperature plasma generated under reduced pressure is a glow discharge plasma. Low temperature plasmas can also be generated at atmospheric pressure, using air or a mixture of other gases. These plasmas are called dielectric barrier or corona discharge plasmas.

The excited species in plasmas can etch or erode polymers (Flamm et al., 1989), deposit a thin layer of material on a substrate (Chapman 1980), or substitute atoms at the surface of polymers with the ones from the plasma (Inagaki 1996). These classes of reactions are being exploited commercially for the processing of materials and today, many industries such as the biomedical, automotive, textile, electronics and lighting industries are using plasmas to modify the surface of materials (BMBF, 2001). For example, the capacity of plasma to etch materials is being used by the semiconductor industry to clean silicon, and the same sector employs plasma deposition processes to coat silicon wafers (Boenig 1982). The capacity of plasma to functionalize surfaces is being used to increase the surface energy of plastics to make them easier to finish with liquid coatings (Inagaki 1996). Plasma modification of wood and other lignocellulosic materials is seen as being important because it can enhance some important surface properties. However, there have been relatively few studies of the use of plasma to treat wood in comparison to its use to modify polymers. Most studies of the plasma modification of wood have been confined to the laboratory, and commercial applications of the technology for wood processing have not occurred (Chen et al. 1990, Podgorski et al. 2000, Evans et al. 2007, Wolkenhauer et al. 2007, Avramidis et al. 2009).

In the surface science laboratory at UBC we have examined the effect of a water vapor plasma on the surface properties of wood and on cellulose and lignin in particular. Table 1 lists the wood species that have been exposed to plasma and examined for changes in their surface micro-structure or chemical properties.

Table 1: Wood species treated with glow discharge plasma and examined in surface science laboratory at UBC

Species	Scientific name	Wood type	Family
Redwood	*Sequoia sempervirens* (D. Don) End.	Normal	Taxodiaceae
Actinostrobus	*Actinostrobus arenarius* (Gardner)	Normal	Cupressaceae
Yellow cedar	*Chamaecyparis nootkatensis* (D. Don) Spach	Normal/compression	Cupressaceae
Radiata pine	*Pinus radiata* D. Don	Normal	Pinaceae
Lodgepole pine	*Pinus contorta* Dougl. ex Loud	Normal/blue stained	Pinaceae
Hybrid poplar	*Populus* sp.	Normal	Salicaceae
Rose gum	*Eucalyptus grandis* W. Hill ex Maiden	Normal	Myrtaceae

Wood specimens were modified with a glow discharge plasma derived from water in the glass chamber of a plasma reactor (Fig. 1). Plasma was produced in the chamber under vacuum (19.998 ± 1.33 Pa) by capacitively coupling a high voltage radio frequency signal (1 kV at 135 kHz) through a ring electrode (diameter 480 mm) on the exterior of the chamber into the low pressure interior of the reactor chamber (Fig. 1). All internal stainless steel components were grounded. The power output of the radio frequency generator to the chamber was adjusted to 150 W. The duration of treatment varied from 0.5 to 22 minutes. After treatment, the chamber was vented to atmosphere, and samples were removed from the chamber, taking care to avoid touching and contaminating their upper surfaces.

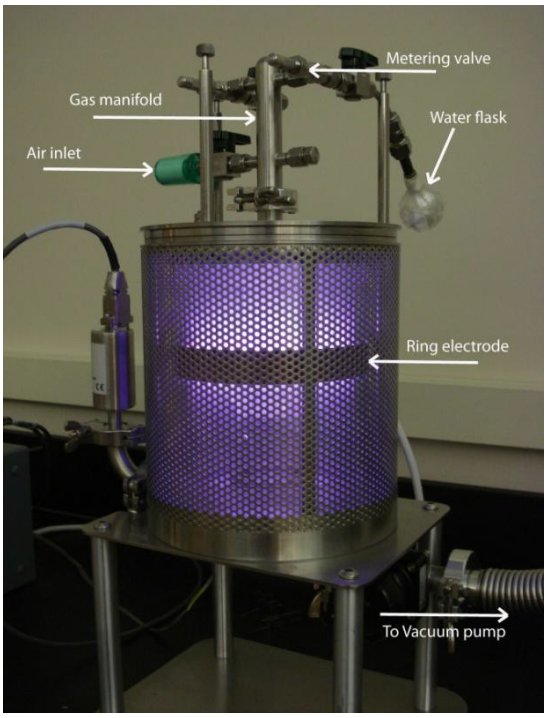

Figure 1: Plasma reactor used to modify wood samples

ii. Effects of plasma on etching of wood walls and cellulose and lignin

We used scanning electron and light microscopy to examine plasma treated wood surfaces. Radial longitudinal, tangential longitudinal or transverse surfaces of untreated (control) and plasma treated samples were examined using either a variable pressure scanning electron microscope (Hitachi S-2600 N) or a field emission scanning electron microscope (Hitachi S-4700).

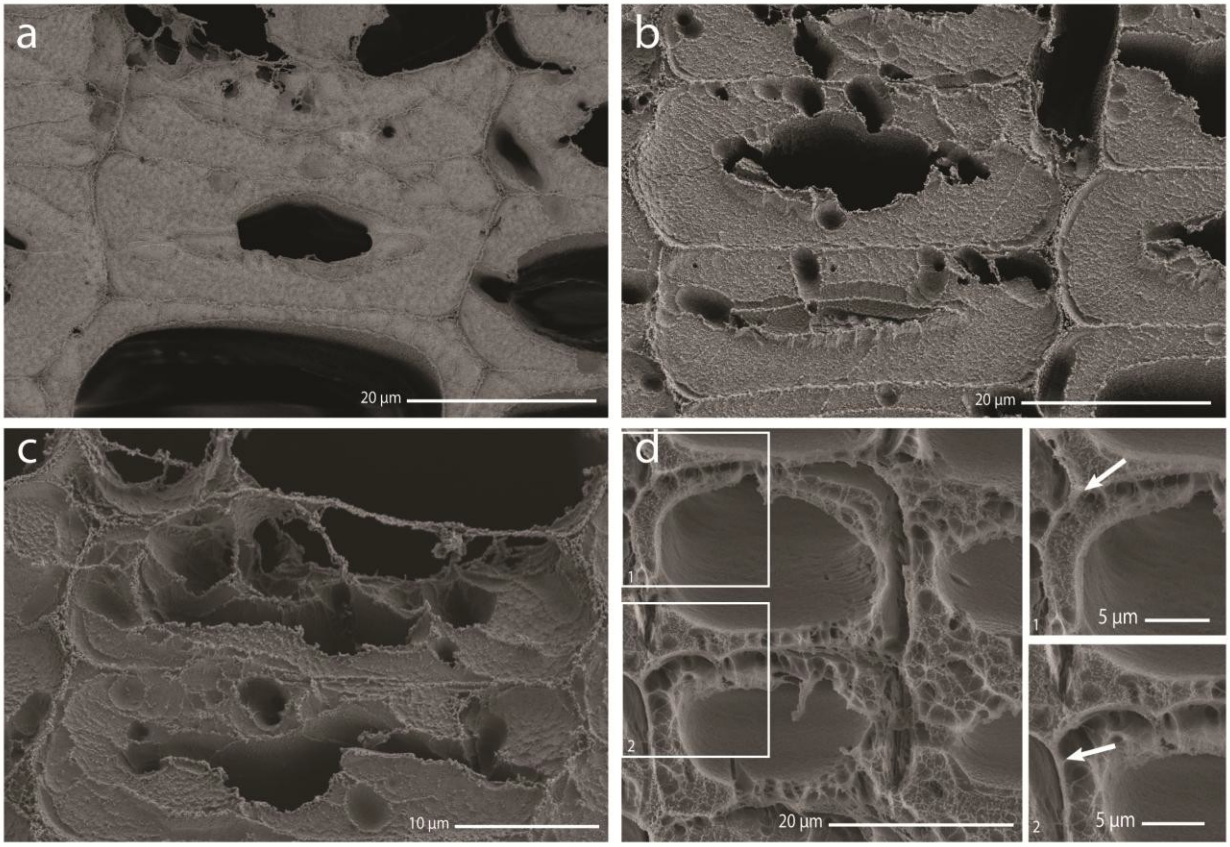

Figure 2: SEM photomicrographs of transverse surfaces of plasma treated latewood tracheids in redwood: (a) tracheids exposed to plasma for 33 s, note creation of a micro-roughened surface and small cavities in the cell walls; (b) tracheids exposed to plasma for 333 s, note further erosion of the secondary cell walls and formation of ridges created by the middle lamella at the surface; (c) tracheids exposed to plasma for 667 s, showing a rough surface with enlarged voids and (d) tracheids subjected to plasma for 1333 s, showing pronounced etching of secondary wall; split-screen enlarged images showing middle lamella (arrowed) and thin lamellae radiating from the middle lamella to the tertiary wall layer

Examination of plasma treated samples showed that the degree of etching of wood cell walls was related to the time samples were exposed to plasma. We observed differential etching of the cell walls by plasma and found that the middle lamella, which contains a high concentration of lignin (Fergus et al. 1969), was more resistant to etching than the secondary wall (Fig. 2). This observation suggested that lignin is less susceptible to etching by plasma than cellulose, in accord with observations of the greater resistance of aromatic polymers to plasma etching compared to aliphatic polymers (Pederson 1982, Egitto 1990).

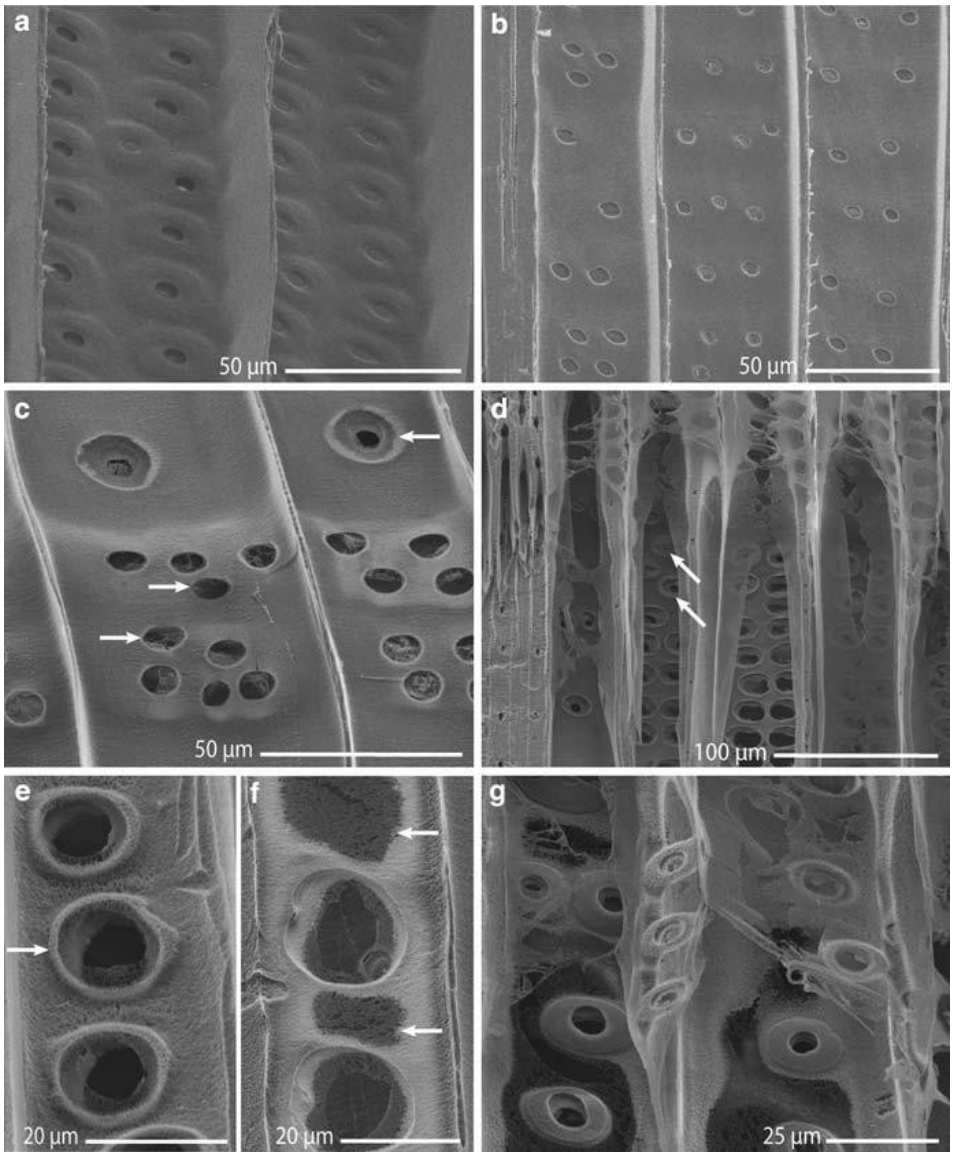

Figure 3: Radial longitudinal surfaces of redwood before and after plasma treatment: (a) untreated earlywood showing bordered pits in tracheids with bi- and triseriate arrangement of pits, note intact pit membranes; (b) untreated earlywood showing taxodioid cross-field pits, note intact pit membranes; (c) earlywood tracheids subjected to plasma treatment for 667 s, note etching of bordered and half-bordered cross-field pit membranes (arrowed left of centre) and etching of the raised border of a bordered pit (arrowed top right); (d) earlywood and latewood (far left) subjected to plasma treatment for 1,333 s, note complete degradation of upper cell walls of earlywood tracheids and etching of bordered pits in sub-surface tracheids (arrowed centre); (e) latewood tracheid subjected to plasma treatment for 1,333 s showing etching of borders on both sides of bordered pits, note roughening of cell wall and outer collars of bordered pits remaining at the surface (arrowed left); (f) latewood tracheid subjected to plasma treatment for 1,333 s showing etching of cell wall material separating bordered pits (arrowed right) and (g) earlywood tracheids subjected to plasma treatment for 1,333 s showing heavily etched tracheid cell walls, note that in this case the borders of pits resisted etching and are suspended at the surface by a thin web of cell wall material

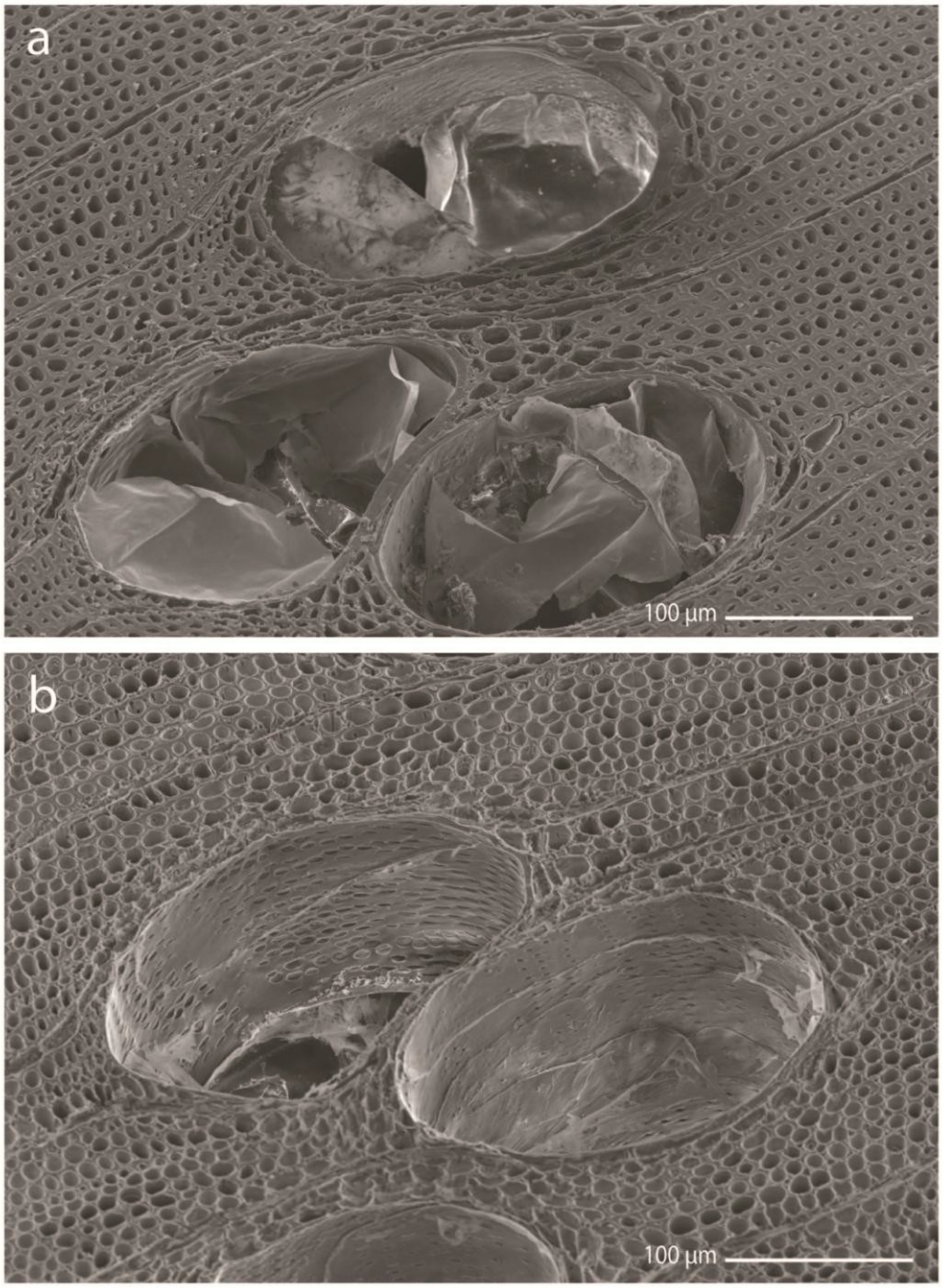

Figure 4: SEM photomicrographs of transverse surface of rose gum (*E. grandis*): (a) untreated surface showing cross-cut fibers and three vessels occluded with tyloses and (b) surface subjected to plasma for 1333 s showing etching of fibers and removal of tyloses from two vessels

Plasma created large voids at radial longitudinal surfaces by eroding pits. Microstructural changes became more pronounced with increasing exposure to plasma. There was complete removal of cell walls from the surface of specimens exposed to plasma for prolonged periods of time (Fig. 3). We also observed that tyloses, which are sac-like intrusions into the lumen of vessels or ray parenchyma in eucalyptus and many other hardwood species (Foster 1967, Sachs et al. 1970), were etched from vessels during prolonged plasma treatment (Fig. 4).

We also used chromatic confocal profilometry to quantify etching and follow changes in the surface micro-structure of yellow cedar and poplar exposed to plasma. Plasma treatment etched cell walls and hence reduced their volume as can be seen in the figure below (Fig. 5).

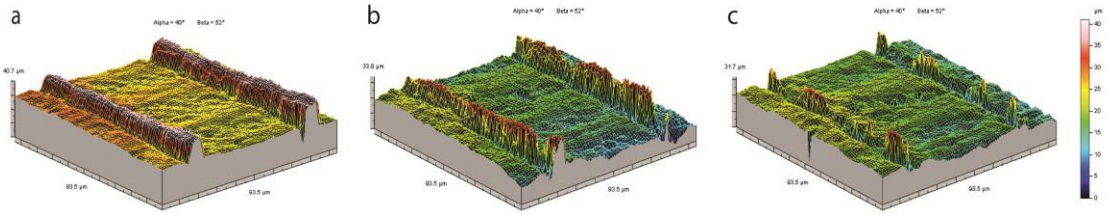

Figure 5: Topographical images of cell walls on a radial longitudinal surface of yellow cedar before and after plasma treatment: (a) untreated early wood tracheid showing tangential cell walls of tracheid and bordered pits; (b) the same earlywood tracheid shown in Fig. 5a after exposure to plasma for 333 s, note thinning of cell walls and decreases in height of tangential cell walls in places and (c) the same earlywood tracheid shown in Fig. 5a–b after exposure to plasma for 667 s, note pronounced thinning and decreases in height of tangential cell walls and etching of bordered pits and the residual of middle lamella in between tracheids

Statistical analysis revealed highly significant effects of treatment time on the ratio of cell wall material remaining after treatment to that present before treatment. Figure 6 shows the effect of plasma treatment on the etching of wood cell walls in yellow cedar and poplar. The effect of species type (yellow cedar vs. poplar) or wall type (radial vs. tangential) on volume of cell wall material etched from specimens was not statistically significant.

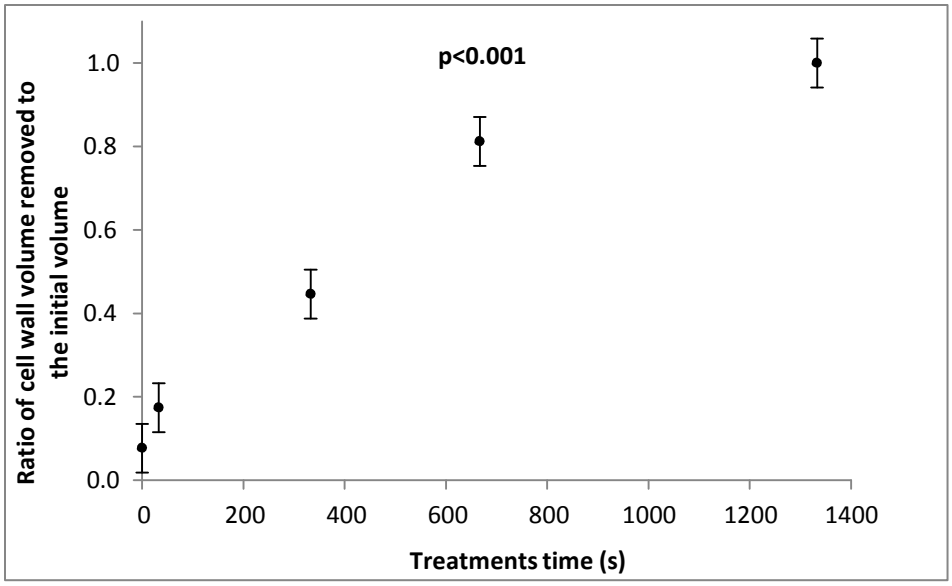

Figure 6: Effect of plasma treatment time on the mass loss in yellow cedar and poplar specimens (results are averaged across species and cell walls [radial and tangential])

We also used chromatic confocal profilometry to quantify the etching of cellulose and lignin by plasma. Observation of plasma treated cellulose and lignin pellets revealed that cellulose was more susceptible to degradation than lignin, however etching of both polymers was positively correlated with plasma treatment time (Fig. 7).

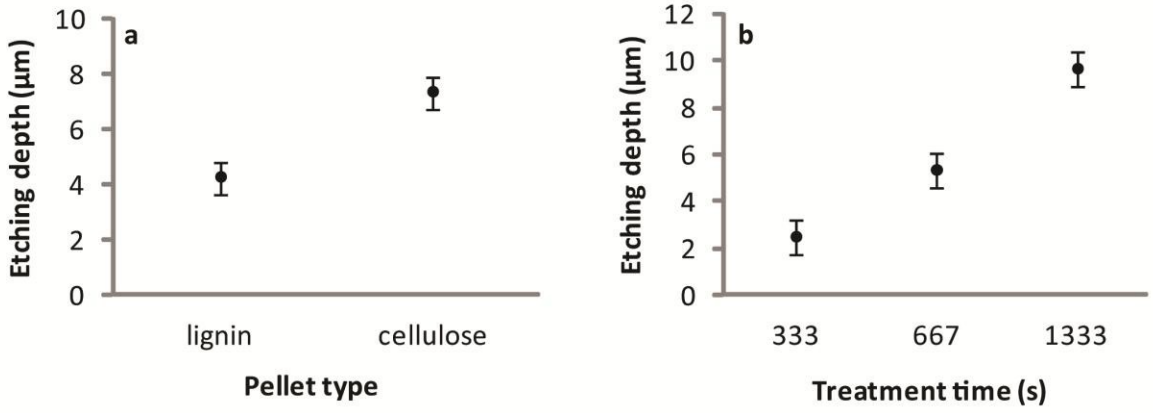

Figure 7: Plasma etching of lignin and cellulose pellets (results averaged across plasma treatment time) (a), and treatment time (averaged across pellet type) (b) on the depth of etching of the pellets during plasma treatment

iii. Effects of plasma etching on wood and surface chemistry

Wet chemical techniques, Fourier transform infra-red spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to examine chemical changes at wood surface following plasma treatment.

Wet chemical analysis showed that plasma treatment reduced the carbohydrate content of wood. This decrease in the carbohydrate derived sugar content was accompanied by proportional increases in the lignin content of wood. Figure 8 shows the amount of lignin and sugars in untreated and plasma treated poplar and lodgepole pine. From this figure it can be seen that degradation of sugars and the increases in lignin content were higher in plasma treated poplar compared to those in lodgepole pine.

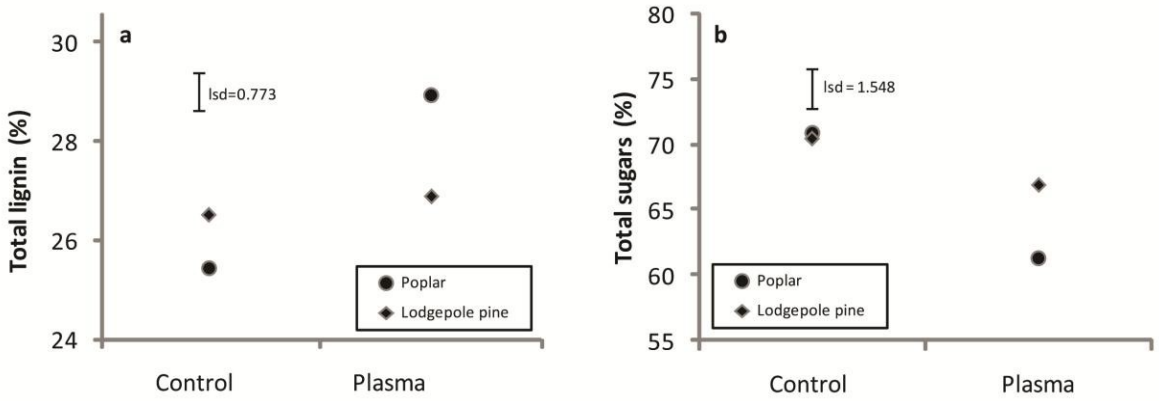

Figure 8: Effect of plasma treatment (667 s) on lignin and sugar contents of thin veneers of lodgepole pine wood. Specimens exposed to vacuum acted as a control.

FTIR spectroscopy revealed increases in lignin related bands and decreases in the bands related to the carbohydrates in lodgepole pine as a result of plasma treatment. The increase in lignin and decrease in carbohydrates was positively correlated with the length of time that samples were exposed to plasma (Table 2).

Table 2: Effects of plasma treatment on the chemical composition of lodgepole pine wood. Figures in the body of the table show ratios of the bands associated with lignin (wavenumber 1510) and carbohydrates (wavenumbers 1160 and 1110)

Treatment time (s)	Area under peak (A. cm^{-1})			Relative area under aromatic peak at 1510 to the carbohydrate peaks	
	Lignin	Carbohydrate			
	1510	1160	1110	1510/1160	1510/1110
0 (Control)	29.01	57.66	33.73	0.50	0.86
333	37.08	62.01	24.19	0.60	1.53
667	43.30	59.84	15.06	0.72	2.87
1000	41.30	55.69	13.68	0.74	3.02
1333	42.27	49.18	10.77	0.86	3.92

Results of XPS analysis of plasma treated surfaces indicated oxidation of wood surfaces during plasma treatment resulting in an increase in the ratio of atomic concentration of oxygen to carbon.

iv. Plasma etching and bleaching to remove blue-stain from lodgepole pine

We exposed blue-stained lodgepole pine wood to plasma and examined the wood for changes in color. We also measured the permeability of the treated wood to an aqueous solution of sodium hypochlorite, and analyzed the effectiveness of the combination of plasma treatment and bleaching at changing the color of blue-stained wood using CIE Lab space (CIE, 1976). We collected hyphae from the blue-stain fungus *Grosmannia clavigera* and examined the effects of plasma on the structure of fungal hyphae.

Plasma treatment removed the blue color from blue-stained wood. Increases in yellowness (b*) of samples (i.e. decrease in blueness) were positively correlated with the length of plasma treatment (Fig. 9). Plasma treatments of 1000 s and longer significantly increased the yellowness of blue-stained wood, resulting in a significant change in the total color (ΔE) of the modified

wood (Fig. 9). Plasma treatments for longer than 33 s significantly increased the bleach uptake by wood compared to that in untreated samples (Fig. 10).

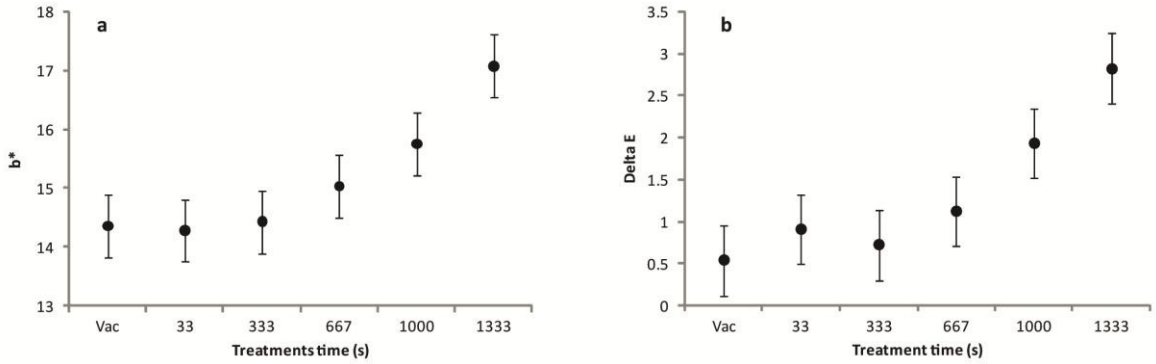

Figure 9: Effect of plasma treatments on the yellowness (b*) (a), and total color change (delta E) of blue-stained lodgepole pine wood (b)

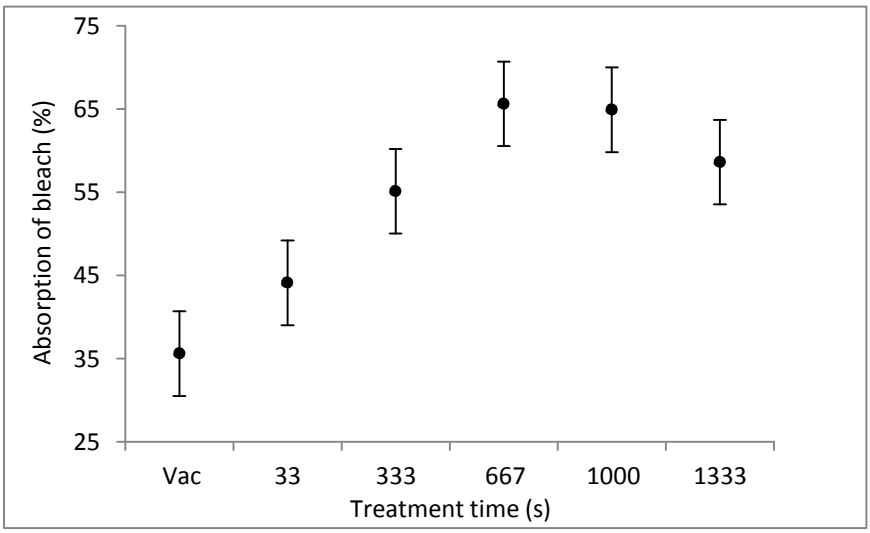

Figure 10: Effect of plasma treatments on the absorption of bleach by blue-stained lodgepole pine wood

The combination of plasma treatment and bleaching had a significant effect ($p<0.01$) on redness (a*), yellowness (b*), lightness (L*) and color change (ΔE) of the bleached samples. Plasma treatment increased a* and b* but reduced the L* (Fig. 11). The total color change of the plasma treated wood was significantly greater than untreated control (Fig. 11). These changes in

CIE Lab parameters indicate that the wood is becoming less blue (therefore redder and yellower) and slightly darker.

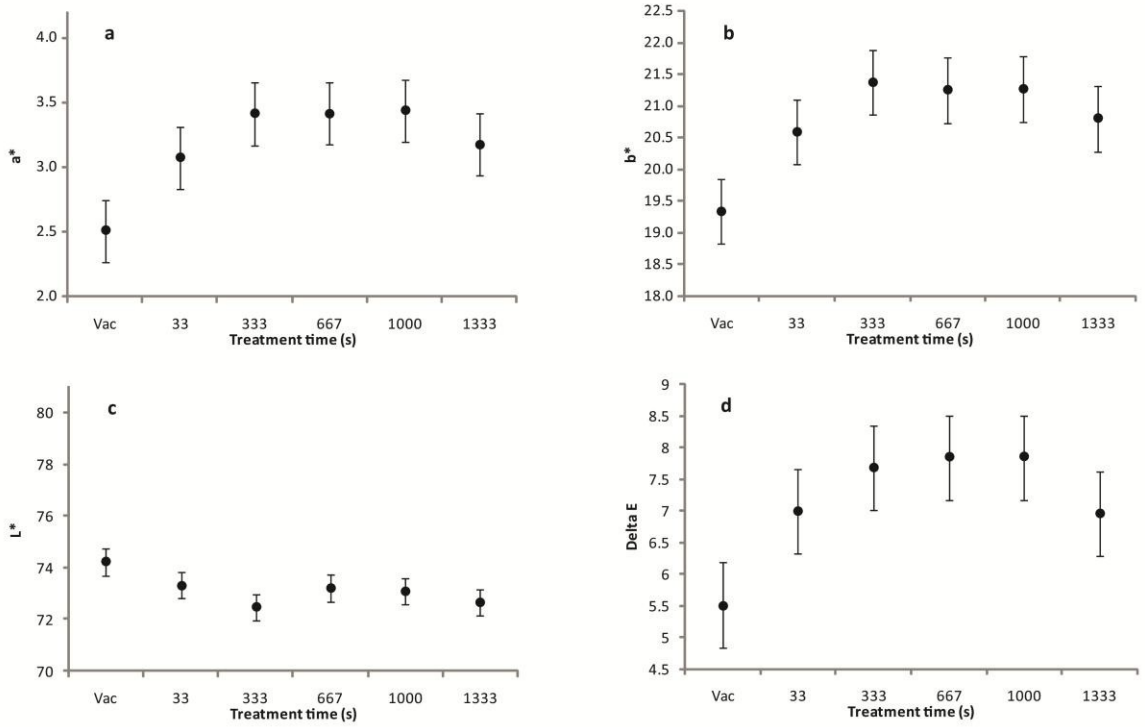

Figure 11: Effect of the combination of plasma pretreatments of different durations with bleaching on the redness (a*), yellowness (b*), lightness (L*) and total color change (delta E) of blue-stained lodgepole pine wood

Hyphae within tracheids were etched by plasma, but remnants of hyphae remained in the wood cells of plasma treated wood (Fig. 12a-b).

Scanning electron microscopy (SEM) images of a hyphal mat before and after plasma treatment are shown in Figure 12c-f. Untreated hyphae have a rough warty surface (Fig. 12e). Plasma etched the walls of hyphae at the surface of the hyphal mat. Plasma removed the walls of hyphae and opened up the hyphal tubes (compare Fig. 12e and 12f). The plasma degraded the hyphal mat to the depth of a few hyphae's thicknesses and removed small fragments and debris from the surfaces of the mat. The density of the warts on the hyphae's wall appears to be lower in plasma treated hyphae (compare Fig. 12e and 12f). The surface porosity of cell walls in lodgepole pine wood increased because plasma opened up bordered pits and etched cell walls (Fig. 12g-h).

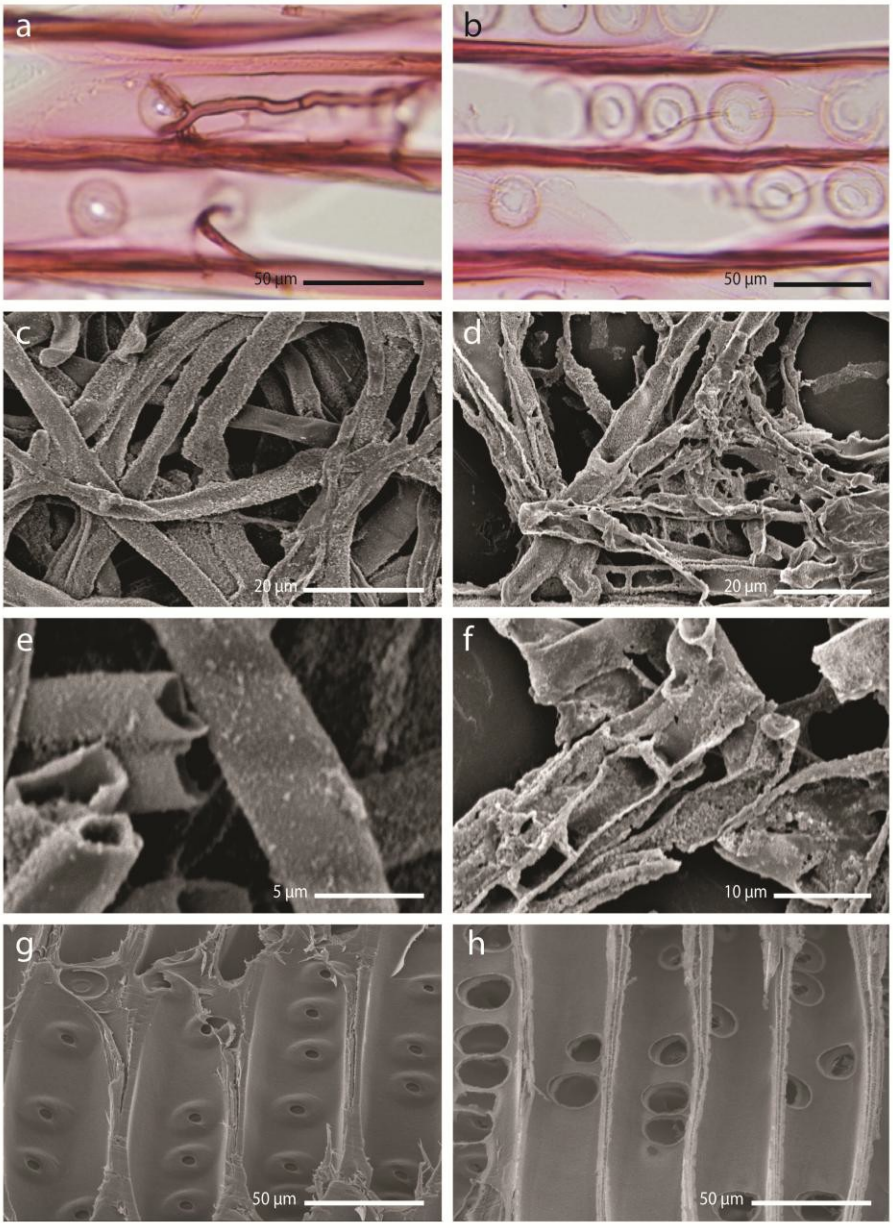

Figure 12: (a-b) Transmitted light microscopy of blue-stained lodgepole, (a) untreated radial longitudinal section showing fungal hyphae penetrating into bordered pits; (b) radial longitudinal surfaces exposed to plasma for 333 s, showing etching of cell walls and hyphae, note that hyphae are much lighter as a result of plasma treatment; (c-f) SEM photomicrographs of hyphal mat of *Grosmannia* claviger, which was grown for 3 weeks: (c) untreated hyphae showing warty surfaces; (d) hyphae exposed to plasma for 667 s showing degradation of hyphae and exposure of the internal hyphal walls; (e and f) higher magnification photograph of untreated hyphae (e) and after exposure to plasma for 667 s (f); (g-h) radial longitudinal earlywood tracheids in lodgepole pine's sapwood before (e) and after exposure to plasma for 667 s (f) showing etching of bordered pits in tracheids and creation of voids on the surface

v. Concluding remarks

Glow discharge plasma was able to etch and completely remove cell walls at the surface of softwoods and hardwoods. Plasma initially created voids in cell walls of softwood by etching pit membranes and then pit borders and intervening cell wall material. The creation of these large voids allowed etching of sub-surface layers to occur. Therefore, it is concluded that plasma can etch sub-surface cells if the plasma can penetrate wood's porous microstructure.

All of wood's cell wall polymers can be degraded by plasma even though cell wall layers in wood that are rich in lignin were etched more slowly than other parts of the cell wall. Examination of the etching of lignin and cellulose revealed that lignin was more resistant to etching than cellulose and accordingly there was less etching of lignin rich cell wall layers and compression wood. The morphology of plasma treated wood resembled that of wood attacked by soft rot fungi which preferentially degrade cell wall layers that are rich in cellulose. Chemical analysis showed that plasma preferentially degraded carbohydrates (cellulose and hemicelluloses) and hence the lignin content of wood increased (like brown-rotted wood). Overall, our results clearly show that lignin is more resistant to etching by plasma than cellulose.

Plasma treatment increased the wettability and permeability of blue-stained lodgepole pine sapwood and removed some of the blue-discoloration from the wood. Bleaching of blue-stained wood by sodium hypochlorite bleach was significantly improved by a plasma pre-treatment. The effectiveness of plasma pretreatment at removing blue stain was influenced by the length of time samples were exposed to plasma treatment. Plasma treatment etched hyphal walls of a blue-stain fungus and degraded melanin. Therefore we conclude that plasma treatments are able to remove the discoloration from blue-stained wood and increase the effectiveness of a bleaching agent because they degrade and remove blue/black fungal hyphae and bordered pits, and enable more of the bleach to be absorbed by the blue-stained wood.

Plasma is being used in many industries to treat materials, for example plastics and silicon. However, plasma treatment of wood has been limited to the laboratory research using either low-pressure or atmospheric pressure devices (Evans et al. 2007, Avramidis et al. 2011). Our findings on the ability of water vapor plasma to etch pits and increase the porosity of wood could have potential applications in the field of wood preservation. The ray cells and bordered pits between tracheids in gymnosperms have been recognized as flow paths between cells (Buro et al. 1959).

In wood preservation treatment processes, preservative penetration and uptake is partially determined by the availability of open flow paths between cells (Wardrop et al. 1961). Therefore, the ability of plasma to etch wood and create open flow paths could create opportunities to use plasma to improve the treatability of refractory Canadian species. Plasma treatments may also be useful in removing fungal stains from wood, and increasing the performance of coatings. We employed a low-pressure plasma to treat wood samples. However, atmospheric pressure processes may be more attractive for the wood industry because of their lower cost, higher throughput and ability to operate in-line without vacuum systems (Tino et al. 2011).

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