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Surface engineering of wood substrates to impart barrier properties: a photochemical approach

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Abstract

In this study, sugar maple and white pine, two species of wood commonly used in indoor and outdoor applications, were treated by photo-initiated chemical vapour deposition (PICVD) to impart barrier properties. After treatment, wood wettability decreased significantly, as evidenced by water contact angle measurements (from 50° to 113° for sugar maple, 87° to 172° for white pine). Further, beyond being able to repel water, the coating shows the ability to breathe, evidenced by standardized vapour sorption tests. However, accelerated weathering via ASTM G155 testing determined that the treatment could not protect the wood from photo-degradation, or retain its properties post-weathering. This treatment could therefore be best suited for wood pre-treatment in combination with other coatings.

Introduction

Industry-wide research and development agencies, such as FPInnovations, are working with wood manufacturers to enable them for example to build and supply their products more effectively, but more importantly, to implement innovative technologies that can improve the performance, durability and resistance of value-added wood products while keeping its aesthetic qualities (FPInnovations 2016). One such approach is to bring about new characteristics to wood by engineering its surface. The need for this kind of technology results from the desire to develop materials with functions beyond their intrinsic properties. Although it is *prima facie* perfect for construction applications primarily because of its abundance, its weight in relation to its sturdiness, the fact that it can be easily shaped and its capacity to provide good insulation, wood can easily be affected by external elements such as solar radiation and especially by water because of the presence of functional groups characterized by its three lignocellulosic constituents, lignin, cellulose, and hemicellulose, the latter being responsible for the hydrophilic and hygroscopic behaviour of its surface due to the abundance of hydroxyl groups -OH (Denes et al. 1999). For example, wood can swell or shrink depending on its moisture level and can change color under solar exposition. To improve upon these features, advanced surface modification approaches are being developed to provide functions such as protection against water and moisture or more complex properties such as self-cleaning (FPInnovations 2016). Superhydrophobicity of wood can be an indicator of improvement for these desired features. Wood treated to become superhydrophobic however tends to exhibit decreased performance over time, primarily because the degradation of their microstructures and low surface energy layers that can get readily be removed by organic solvents (Cai et al. 2015). Some recent studies have nonetheless demonstrated that it is possible to obtain stable and durable superhydrophibic surfaces on wood. Indeed, it has been reported that samples treated via a sol-gel process would retain their superhydrophobicity over two months of storage in air and water (Wang et al. 2011), that superhydrophobic surfaces obtained by mussel-inspired dopamine chemistry and electrodeless deposition showed excellent stability under harsh environments such as strong acid/base exposition, organic solvent exposition and ultrasonic washing (Wang et al. 2017) and that silica-polymer nanocomposites could be used to produce superhydrophobic surfaces on wood with stability over 60 days in a high temperature, high humidity environment (Chang et al. 2015).

Surface modification can be conducted through two main streams, either by physical adsorption or chemical functionalization. In the case of wood, physical adsorption surface treatments can be accomplished through varnishes, paints, lacquers or even polishing wax imparting features such as resistance to deformation, protection against moisture, and solar radiation. Despite their widespread use, these kind of coatings face major drawbacks such as adhesion and thermal desorption issues, and health and safety risks for those who apply them (inhalation of toxic fumes, strong unpleasant odors). Moreover, to ensure good coating quality, several layers must be applied, which can lead to extensive curing times (Petric 2013), (Presutti 2009), (Bulian and Graystone 2009), (Baysal 2008).

The second approach, chemical functionalization, allows for the formation of strong covalent bonds between the functional groups formed during the process and the surface, thus making it a much more stable treatment (Qin and Coulombe 2007). It can be performed by many means such as liquid-phase methods and thermal methods (torrefaction of wood) or by gas-phase methods. The liquid-phase method come unfortunately with some hindrances: due to the porous nature of wood, reagent uptake is significant and treatment must be performed with excess reagents. As these are usually toxic and corrosive, post-treatment and removal costs are high (Levasseur et al. 2012). In the case of thermal methods, the main limitation is the negative effects we can observe on mechanical properties after treatments: bending and compressive strengths for example can be greatly weakened depending on treatment intensity and thermal processing conditions. They can also significantly increase the speed of color change of wood which is an undesirable property for outdoor applications (Candelier et al. 2016), (Esteves and Pereira 2009), (Kocaefe et al. 2008). The gas-phase methods, compared with the other two, is a much more interesting technique as it has the ability to modify near-surface regions of substrates without affecting their bulk properties. Because of its solvent-free approach, meeting of environmental and safety requirements is also much more easier (Busnel et al. 2012).

With this in mind, the present study focuses on the surface functionalization of wood performed with an alternative gas-phase method, photo-initiated CVD (PICVD). This low-cost process can be applied to several types of substrate and is flexible enough to be easily implemented in projects of larger scope, without the mechanical limitations imposed by heat treatments (Dorval Dion and

Tavares 2013). Moreover, PICVD has demonstrated the ability to form a thin film with tuneable wettability on a wide variety of substrates, a potential indicator of desirable barrier properties (Dorval Dion et al. 2014), (Farhanian et al. 2014), (Bérard et al. 2016), (Labonté et al. 2016), (Farhanian et al. 2017). The present investigation aims to determine if PICVD can be used as a finishing treatment for indoor and outdoor timber to be resistant to solar radiation, to repel water and prevent moisture absorption.

Materials and methods

Sugar maple (*Acer saccharum*, representative of indoor applications) and white pine (*Pinus strobus*, outdoor applications) samples were provided by FPInnovations in 4 geometries: (A) 15 mm x 15 mm x 8 mm small squares, (B) 30 mm x 15 mm x 5 mm small rectangles, (C) 5 mm x 5 mm x 5 mm small cubes, and (D) 65 mm x 65 mm x 17 mm large squares. Geometries C and D were used for the accelerated UV exposure and vapour sorption tests, respectively. Prior to treatment, each sample was carefully polished using a 3M pneumatic orbital sander at 12,000 RPM with sandpaper P150. The PICVD reactor employed argon (HP +), carbon monoxide (CO - Pure T-44) and hydrogen (H2 - UHP T-30), all supplied by Air Liquide. Hydrogen peroxide (H_2O_2 - 50% w/w solution), purchased from Fisher Scientific, was used as a photo-initiator.

Prior to treatment, polished wood samples were conditioned in an Electro-Tech Systems 5503-11 environmental chamber (Cole-Parmer) at a relative humidity of (50± 2%) for a minimum period of 3 days (or until stabilization of their mass); conditioning temperature was set between 23 °C and 26 °C. Conditioned samples of geometries A or C were placed in a 920 mm long, 25 mm ID quartz tube PICVD microreactor, while types B or D were treated in a 920 mm, 75 mm ID quartz tube PICVD reactor. Both reactors are illuminated by two germicidal UVC lamps (Cole-Parmer,VL-230-G, emitting at 253.7 nm with a power density of 0.01 W/cm^2 at 45 mm, measured using an International Light Technologies ILT 1700 Research Radiometer equipped with a SED240 probe) (Figure 1).

Treatment parameters were based on previous PICVD work, in conditions known to yield hydrophobic (water repelling) conditions (Bérard et al. 2016). These parameters include sample

position, gas mixture precursor ratio, operating pressure, treatment duration and photo-initiator feed rate. Sample position was set to 850 mm from the gas inlet for all experiments in this study because it is believed that the wettability can decrease as the distance between samples and the source of the treatment increases (Bérard et al. 2016). The samples are firstly inserted horizontally into the reactor with one face exposed to UV light, as seen in Figure 1, item 3. After insertion, the reactor is sealed by means of two plates installed on each end, and purged with argon for 3 minutes to remove any traces of oxygen. CO and H_2 gas flow was controlled by two I-series Brooks 5850 mass flow controllers, and the H_2 / CO molar ratio was varied from 0.10 to 4 (total gas flow values were calculated to maintain the residence time between both reactor configurations roughly within the same order of magnitude, 45 s vs. 69 s). A three-way solenoid proportional valve is installed at the outlet of the reactor to regulate treatment pressure, from slightly under vacuum (91 kPa), to atmospheric pressure (101 kPa) or slight overpressure (111 kPa). The pressure is adjusted using a differential pressure sensor (± 25 kPa) purchased from RobotShop (Model RB-Phi-159). The treatment time is fixed at 60 min while H_2O_2 is fed to the reactor with a syringe pump at a rate of 1 mL/h (Dorval Dion et al. 2014). After each experiment, the reactor is purged once again with argon for 3 minutes. Treated samples are then removed cautiously from the reactor for analysis.
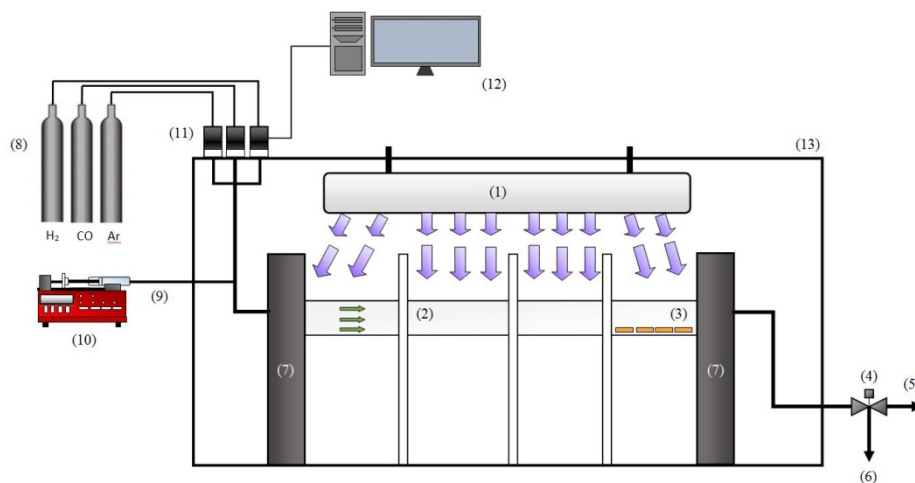

Figure 1 - Layout of experimental setup: (1) UV Source, (2) Quartz tube reactor, (3) Treated samples, (4) solenoid proportional valve, (5) ventilation, (6) vacuum, (7) sealing plates, (8) Syngas & Argon, (9) Hydrogen Peroxide [H_2O_2], (10) Syringe pump, (11) Mass flow controllers, (12) Computer, (13) protective box

Sample analysis

Contact angle

Water contact angle measurements were taken on type A and B samples, before and immediately after treatment, using a FDS OCA DataPhysics TBU 90E tensiometer. A 2 µL water droplet is deposited on the surface to measure the sessile contact angle (measurements taken between 1 and 3 seconds after drop deposition). Five measurements are taken on the same surface, from which an average is calculated.

Dynamic vapor sorption (DVS)
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DVS analysis is a technique for measuring the amount of water a sample of wood can absorb and desorb by varying the vapor concentration surrounding it and by recording changes in mass (Surface Measurement System 2016). These tests were conducted using type C samples, by applying a protocol similar to ASTM D5229 - *standard test method for moisture absorption properties and equilibrium conditioning of polymer matrix composite materials* (ASTM International 2014). Samples are first inserted into a VTI-SA+ vapor sorption analyzer from TA Instruments. They are then dried until their mass is stabilized. At this point, the test begins: the relative humidity (R.H.) of the analysis chamber increases incrementally starting at 0%, all the way up to 95%. Relative humidity is then scaled back down using the same increments until reaching 0%. The increment changes occur when the mass percentage of the sample varies less than 0.0003% over a 5-minute period or the increment time exceeds 180 minutes. The temperature during the tests is kept constant at 25 ° C.

Accelerated UV exposure

Accelerated UV exposure tests are carried out following ASTM protocol G155 - *standard practice for operating xenon arc light apparatus for exposure of non-metallic substrates* (ASTM International 2005) and are used to simulate the effect of the damage occurring during an exposure to full-spectrum sunlight and rain. An initial colorimetric measurement is taken at five different

areas on the surface of the samples to be analyzed. Samples are then placed in a Q-Lab Q-SUN Xe-3 Xenon conditioning chamber (Q-Lab 2016) where they are subjected to a cycle that repeats itself over 1000 h. The cycle depends on the type of exposition to be simulated (interior or exterior) (**Table 1**). The test is interrupted at 250 h, 500 h, 750 h and 1000 h, to take further color measurements.

Table 1- Cycle used during UV exposure test

Cycle	Irradiance (W/m^2.nm)	Wavelength (nm)	Exposure cycle	
Exterior wood (white pine)	0.35	340	!	102 min light at 63°C (black panel temperature)
			!	18 min light and water spray (Temp. not controlled)
Interior wood (sugar maple)	1.10	420	!	3.8 h light, 35% R.H., at 63°C (black panel temperature)
			!	1 h dark, 90% R.H., at 43 °C

Dimensional analysis

Samples were placed in a chamber, according to the tangential-longitudinal orientation. They then successively underwent three conditioning steps: 20°C and 50% R.H., 20°C and 20% R.H. and 20°C and 80% R.H.. Each conditioning step lasts 7 days, with the first step used to ensure sample stability. Spatial dimensions, namely length, width and thickness of the samples are recorded throughout the test.

Results and discussion

Effect of treatment parameters on wettability

Treatments were first conducted on sugar maple, with a native water contact angle (polished and conditioned) of 50° ± 6°. In a previous study, it was demonstrated that it was possible to vary the wettability of a metallic substrate simply by using pressure (Dorval Dion et al. 2014). Consequently, operating pressure was varied to validate this hypothesis with wood samples and optimized to obtain contact angle values above 90° (hydrophobic) (**Figure 2**). The wettability of wood increases at low operating pressure (91 kPa) (the contact angle decreases to 25° ± 6°), is unchanged at atmospheric pressure and decreases at increased pressure (111 kPa) (the contact angle increases by 70% to 85° ± 6°). At higher operating pressure, it is posited that the precursor

molecules react preferentially in the gas phase, forming higher molecular weight products that will deposit on the surface. At lower pressures, molecules in the gas will tend to be adsorbed onto the surface and then begin to react (Choy 2003), (Dorval Dion and Tavares 2013). The film created by PICVD can be considered a form of oligomer (Labonté, et al., 2016). Given the desire to pursue conditions of low wettability, subsequent experiments will focus on higher pressure treatments, more precisely at an operating pressure of 111 kPa.
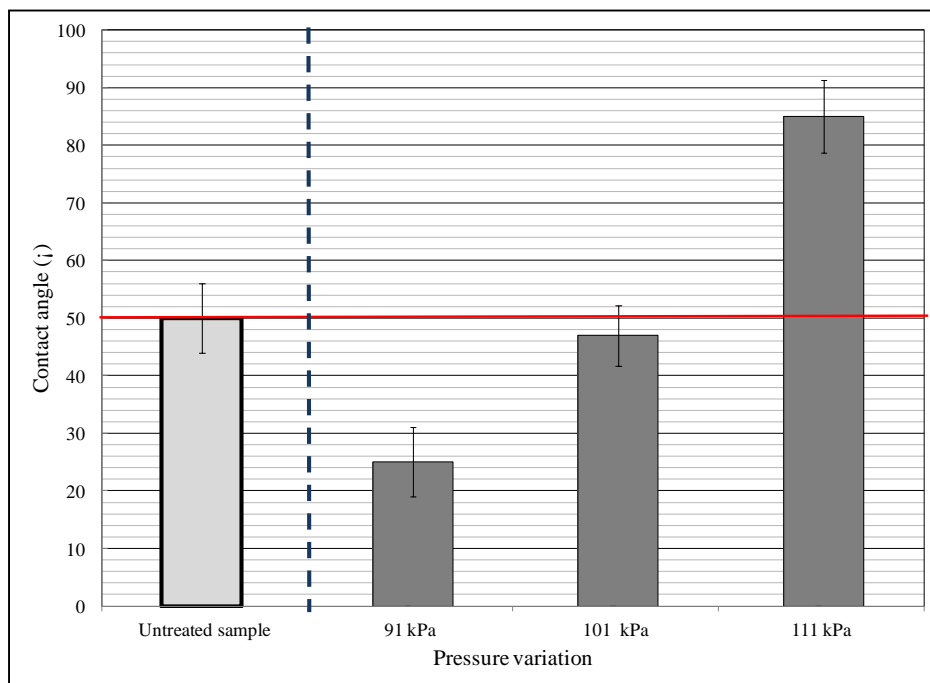

Figure 2 - Water contact angle measurements on sugar maple as a function of treatment pressure

Despite a favorable 70% increase in contact angle at higher operating pressure, it may be possible to further decrease wettability by varying the precursor molar ratio (**Table 2** and **Figure 3**) (Dorval Dion et al. 2014). Wettability generally increases as a function of molar ratio. At $H_2/CO = 0.12$, the contact angle increased to an average of $113° \pm 5°$, 126% over the untreated sample contact angle of sugar maple, and a maximum value of $121°$ was observed.

Table 2 - Gas ratios used during experiments

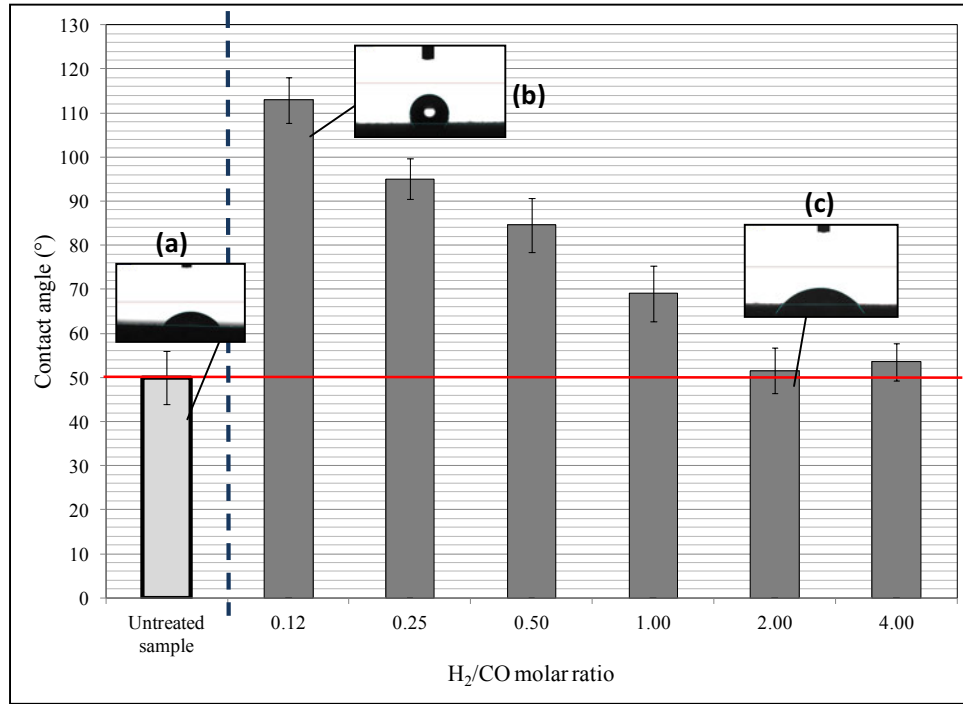| H$_2$ flowrate (mL/min)	CO flowrate (mL/min)	H$_2$/CO ratio
75	525	0.12
138	462	0.25
224	376	0.50
326	274	1.0
423	177	2.0
495	105	4.0

Figure 3 - Water contact angle measurements on sugar maple as a function of H$_2$/CO molar ratio. Illustrated contact angles of (a) 53¡ for the untreated sample (b) 120¡ for the ratio of 0.12 (c) 48¡ for the ratio of 2.

Treatments were then conducted on white pine to see whether it would have similar behaviour to maple. Hence, operating pressure was kept at 111 kPa, while molar ratio was varied as per treatments conducted on maple **(Table 2)**. The untreated sample contact angle of white pine, after polishing and conditioning, is 87 ° ± 5 °. **Figure 4** shows that each of the tested ratios allow for a

substantial increase in water contact. At the best conditions ($H_2/CO = 0.12$), the average value is $172\degree \pm 6\degree$, an increase of almost 100%, while the maximum angle observed is $180\degree$.
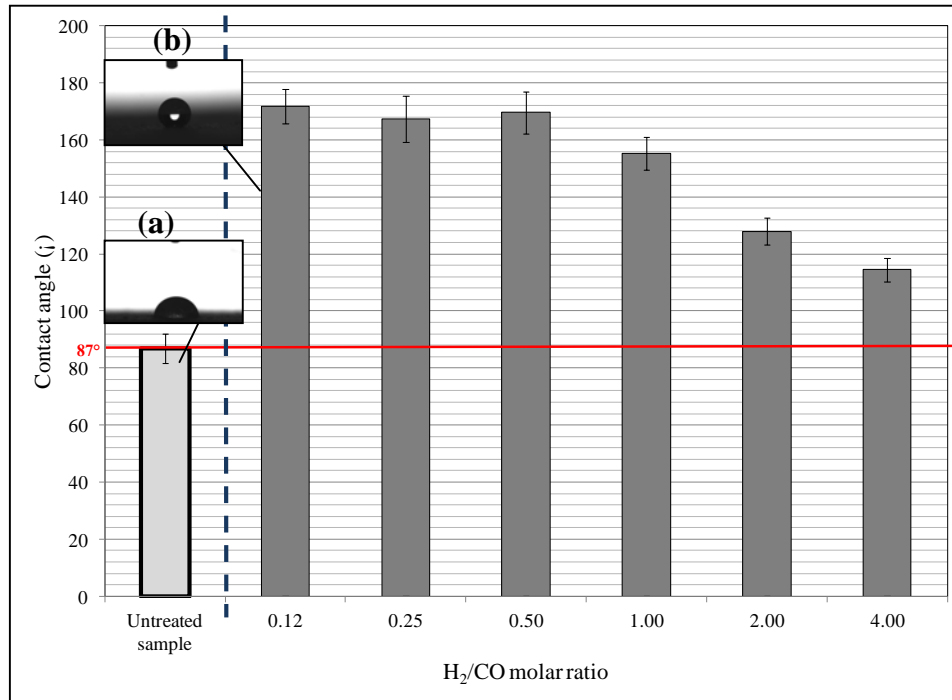

Figure 4 - Water contact angle measurement on white pine as a function of H_2/CO ratio. Illustrated contact angle of (a) 89¡ for the untreated sample (b) 179¡ for the molar ratio of 0.12

After PICVD treatment, it was believed that treated samples were totally coated, potentially protecting them completely from exterior conditions. However, dynamic contact angle analysis revealed that this may not be the case (**Figure 5**). After treatment, a drop of water on either wood samples will retain its shape for an extended period compared to a drop on an untreated surface. It will nonetheless eventually be absorbed by the surface, but at a much slower rate (droplet will shrink over time). In other words, the wood, even when "trapped" behind a barrier, can still breathe, which is a desirable feature to avoid moisture retention-related problems like mold, and can affect dimensional stability and cracks (Coxworth 2012). This feature is hypothesized to be the result of island-like deposits formed as a result of PICVD, as shown in previous works (Dorval Dion et al. 2014), (Bérard et al. 2016), (Labonté et al. 2016), (Farhanian et al. 2017), which would affect wettability without completely sealing the wood's pore structure.
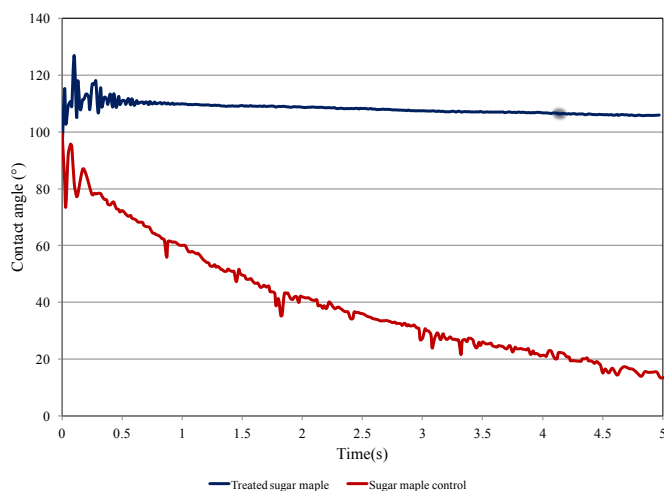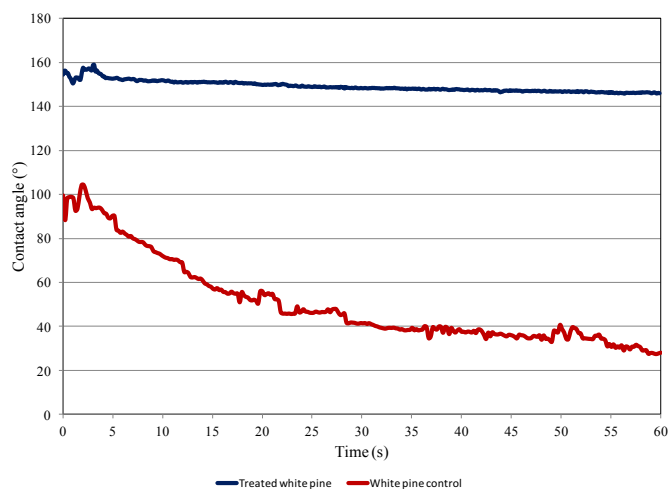
a)   b)

Figure 5 - Contact angle decrease in time: a) Sugar maple, b) White pine

Dynamic vapor sorption

One of the well-known drawbacks of wood is its low resistance to humidity variations leading to dimensional instability of its structure. A barrier-like protection against water could solve this problem and increase its lifespan. DVS analysis seeks to assess how well a sample can absorb or desorb water. Unlike contact angle analyses, which require only one treated surface, samples for DVS analysis must be "encapsulated", meaning that all surfaces need to be treated. This was accomplished by using a 203 mm x 13 mm x 8 mm support built to hold 20 samples at the same time (**see supplementary information**). The PICVD treatment was run for a total of six hours and the surface exposed to UV was systematically changed after one hour to ensure a uniform coating of the entire sample. **Figure 7** shows that PICVD treatment does impart barrier properties to sugar maple, as the average weight gain as a function of relative humidity is significantly and systematically lower for treated samples. For example, at R.H. = 95%, the weight gain is 15% lower for the treated maple sample. It is hypothesized that this barrier effect may increase as a function of film thickness (i.e. as a function of treatment time).
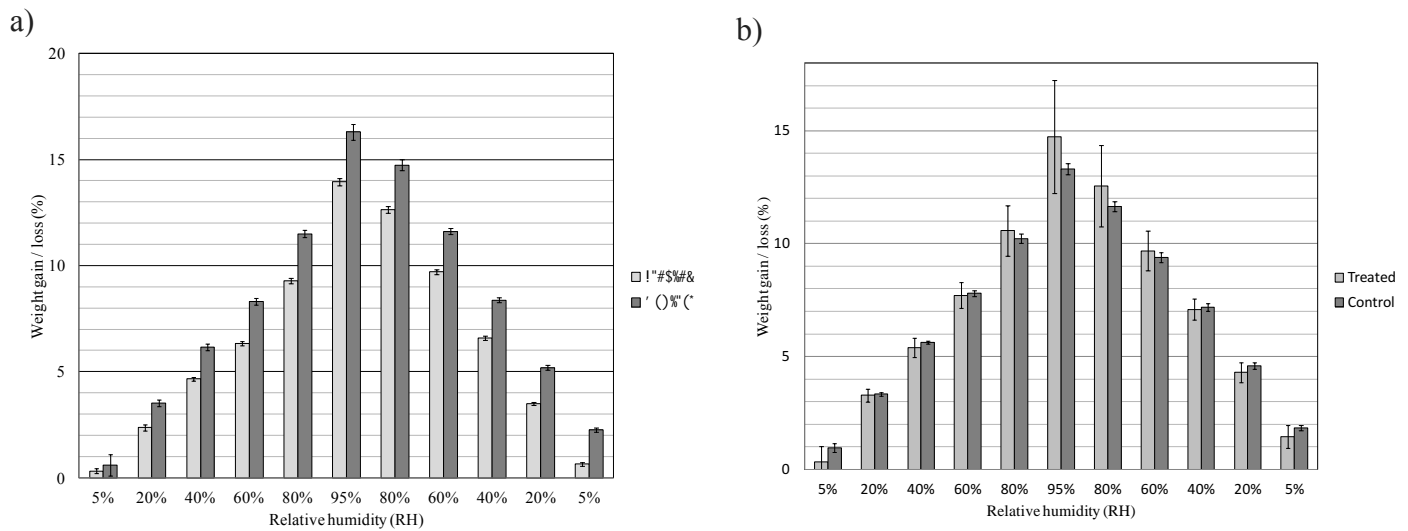
!!

Figure 6 - Dynamic vapour sorption analysis of treated: a) sugar maple, b) white pine

Water vapor sorption in the cell wall of wood has been compared to a film forming by water molecules binding to active sorption sites, mainly from amorphous cellulose and hemicelluloses. This is called cell wall unbound water. However, this is not the only state water can adopt in wood - it can also be observed as water vapor and as cell wall bound water (Hill et al. 2010). Bound water, which is refers to a monolayer of water, represents the molecules closely associated with the hydroxyl group present in the cellulose and hemicelluloses. Unbound water on the other hand, refers to multilayer water, occupying the space in the cell wall, the transient microcapillary network and is not strongly linked to hydroxyl groups (Hill et al. 2009). These forms affect the sorption curves of woods according to the relative humidity (RH). For values of RH ranging from 0 to 15%, monolayer adsorption is the dominant process. Between 15% and 70%, multilayer water formation occurs and for values higher than 70%, it is possible to see capillary condensation, which will dominate with increasing RH. (Hill et al. 2009). By converting surface hydroxyl groups to less hydrophilic groups through binding with PICVD-derived species, as well as bulking up the cell wall with the deposition of these chemical, the space for water molecules is reduced and we can decrease the water vapor sorption (Zaihan et al. 2009), (Hosseinpourpia et al. 2016). This is exactly what we observe in the case of sugar maple. In the case of white pine, despite a significant increase in water contact angle, dynamic vapor sorption tests (Figure 7) showed no compelling differences between treated and control samples. This apparent lack of change from white pine might probably be the result of the nature of the wood and its interaction with the PICVD treatment

– the film structure may have been more porous than in the case of sugar maple. As stated previously, this could potentially be improved through a longer treatment time (because of the coating's previously described Volmer-Weber / island growth mechanism).

Dimensional stability

Dimensional analyses were performed only on treated sugar maple, as no conclusive differences were identified for white pine during dynamic vapor sorption analysis. As illustrated in **Figures 7 a and b**, dimensional stability analyses demonstrated no major differences between treated and untreated samples. It is suggested that this is due to an inadequate distribution of reacted chemicals in water-accessible regions of the wood (Rowell 1983). An adequate distribution is defined as a uniform and systematic distribution of the reacted chemical throughout the wood samples, which would minimize the hydrophilic sites present and diminish water absorption.
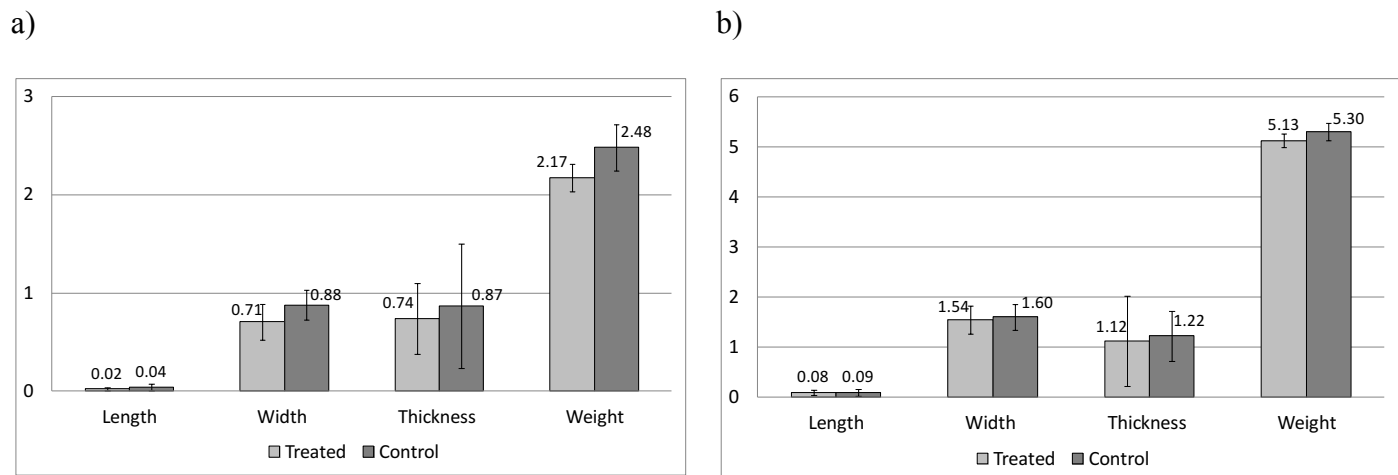
a)   b)

Figure 7 - Average difference percentage of size before and after: a) 20/20 conditioning, b) 20/80 conditioning

Accelerated aging

The exposure of wood to sunlight may cause degradation of its surface, which can be observed by a change in its color because of its ability to absorb all wavelengths of solar radiation (Deka and Petric 2008). Depending of the type of wood and its composition, the color may change to white, orange, yellow and even brown (Hansmann et al. 2006), (Kamdem and Grelier 2002). Accelerated UV exposure tests (such as those proposed in ASTM G155) coupled with color measurements can

assess these long-term effects over a decreased period. Color levels are assessed five times over the course of 1,000 h. The color change is then evaluated by the CIE L * a * b * system (**Figure 8**). In this coordinate system, the a and b axes represents a color dimension, red-green and blue-yellow respectively, and L is the brightness (Mischke et al. 2010). The total color difference (ΔE_{ab}) of a sample can be quantified through equation 1 (Mischke et al. 2010).

$$\Delta E_{ab^*} = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (1)$$
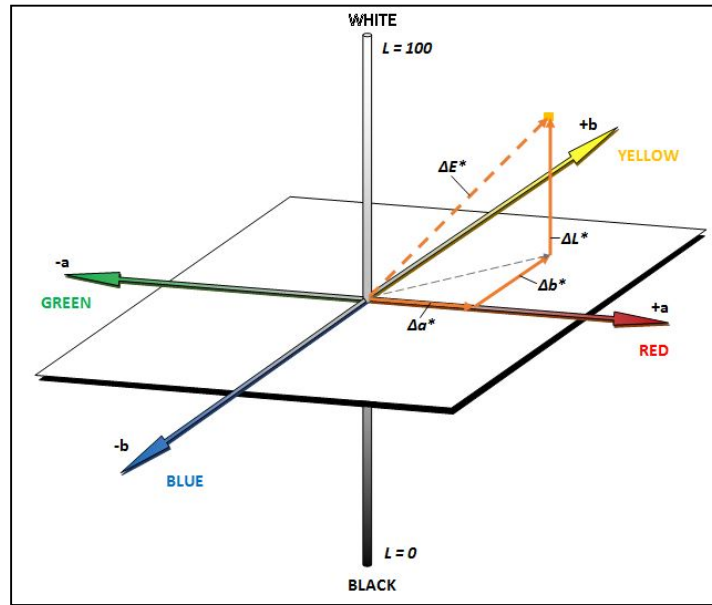

Figure 8 - Schematic showing the L*a*b* coordinate system

where ΔL, Δa and Δb represents the difference in color between a reference sample (at 0 h) and a treated sample (at 250 h, 500 h and 1,000 h). **Figure 11 (supplementary information)** shows the average of ΔE_{ab^*} as a function of exposure time for sugar maple and white pine respectively, while **Figure 9** illustrates the color change over 1,000 h (10 samples compared to 2 controls). In both cases, there is no statistically significant difference in color change following accelerated aging between the treated and control samples. Post-exposure contact angle measurements reveal that the hydrophobic behavior acquired by the wood was also lost. The contact angle decreased to an average of 53°± 4 in the case of sugar maple and an average of 90°± 5 for white pine. In all

likelihood, the thickness of the PICVD generated film (of the order of 50 to 120 nm (Farhanian, 2017 #17)) was insufficient to block or attenuate UV light attaining the surface and the wood started to decay resulting in the loss of the enhanced properties given by the surface modifications (Deka and Petric 2008).
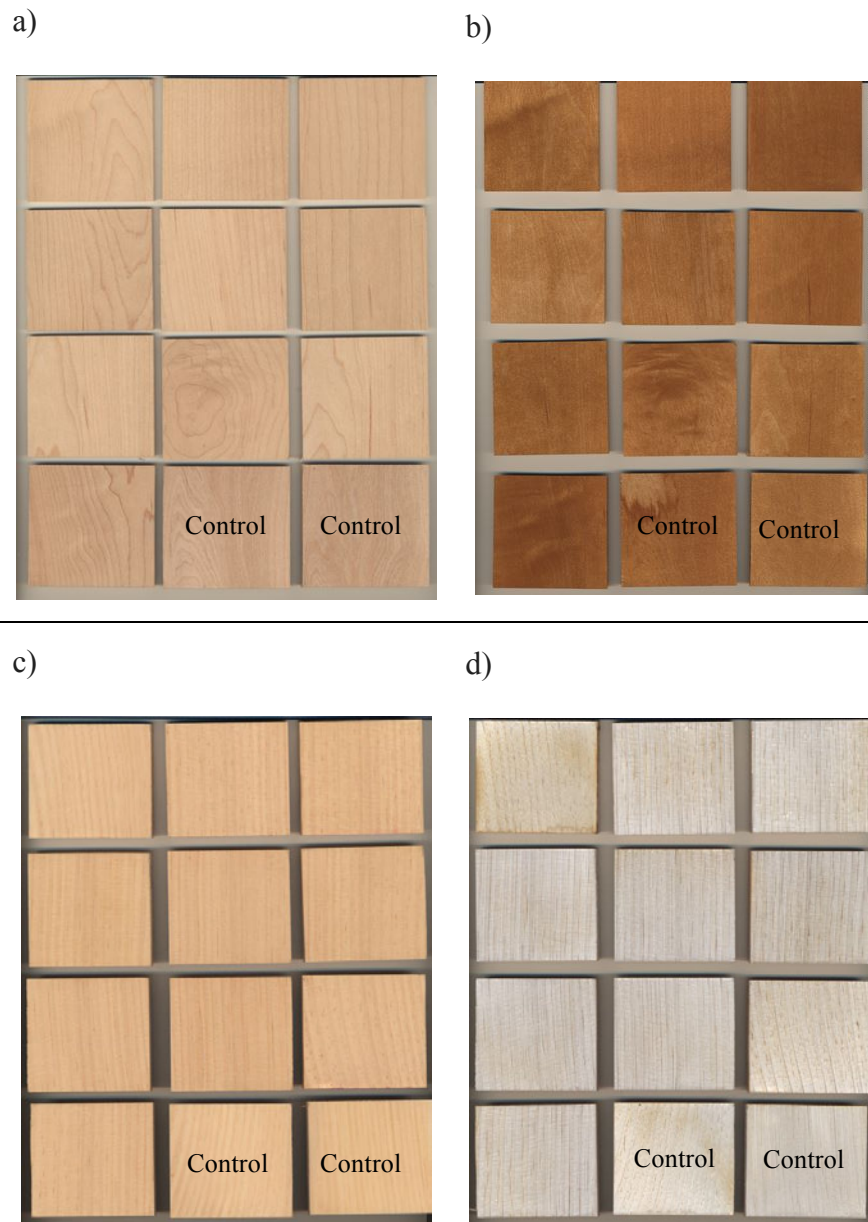
a)

b)

c)

d)

Figure 9 - Picture of maple samples and white pine taken at: a), c) 0 h and b), d) 1000 h during UV exposure tests

Conclusion

This study expands upon Canada's expertise in secondary wood transformation, focusing on the behavior of two types of wood (representative of indoor and outdoor applications) to a new treatment technology: photoinitiated chemical vapor deposition (PICVD). The main objective was to assess this treatment's ability to give to wood new properties to slow down its deterioration and thus extend its life. Contact angle measurements showed that PICVD treatments led to a substantial decrease in wettability for both wood types. Moreover, interior wood showed interesting behavior in terms of water intake, being able to absorb 15% less water than an untreated sample. However, in the case of exterior wood, it was determined that the PICVD treatment did not alter water intake behavior, though increasing treatment time may improve this. Despite these improvements, PICVD treatment was not able to protect wood from weathering and has no effects on its dimensional stability, likely because of the small thickness of the coating surrounding the wood. Nonetheless, the results presented in this study show that PICVD has great potential and opens the door for ongoing and future research. Namely, we will seek to determine if the treatment can be applied as a finishing technique to either replace or act in concert with (as a pre-treatment) paint and varnishes.

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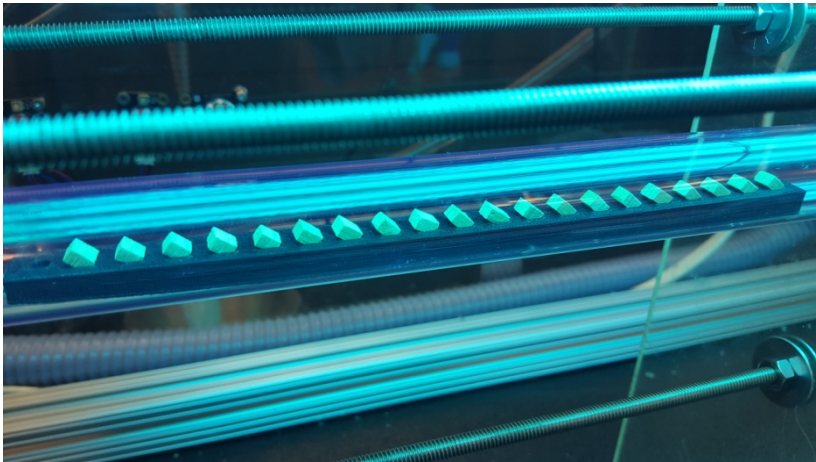Supplementary informations

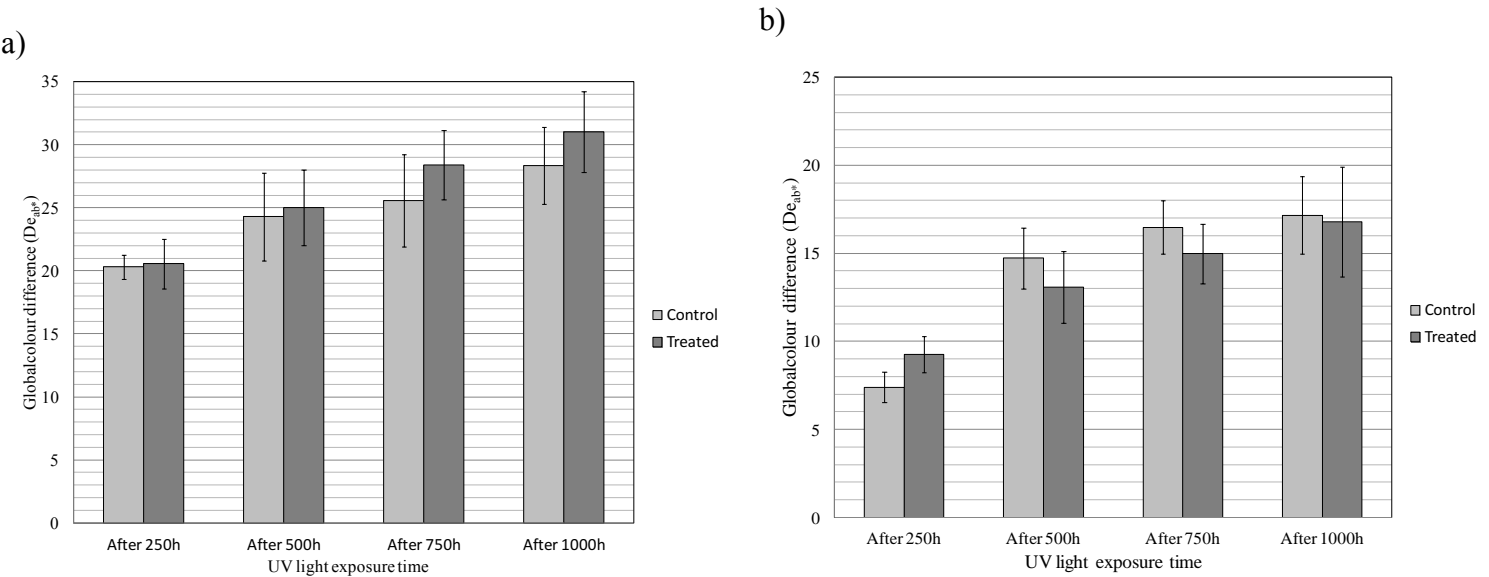**Figure 10 - Support for samples treated for dynamic vapor sorption analysis**

a)

b)

Figure 11 - Global colour differences during aging tests of: a) sugar maple, b) white pine