

Effect of Wood Surface Modification by Atmospheric-Pressure Plasma on Waterborne Coating Adhesion

Bernard Riedl,^a Costin Angel,^a Julien Prégent,^b Pierre Blanchet,^{a,*} and Luc Stafford^b

In this study, the effect of an atmospheric-pressure plasma treatment on the surface properties of sugar maple (*Acer saccharum* March.) and black spruce (*Picea mariana* (Mill.) was analyzed by contact angle measurement and a water-based coating pull-off testing. The plasma gases used were Ar, N₂, CO₂, and air. It was found that the wettability with water and the coating adhesion of maple and spruce can be highly influenced by the nature of the plasma gas used and the plasma treatment time. For example, in the case of sugar maple, coating adhesion increased by 66% after 1.5 s of exposure to argon plasma. Repetition of the contact angle measurement one and two weeks after the initial plasma treatment showed that the plasma-induced modification is not permanent. Improvements in wettability and adhesion were also obtained with simpler, cheaper air plasmas, a result promising for the development of advanced plasma reactors operating at atmospheric pressure, specially designed for the wood industry.

Keywords: Atmospheric-pressure plasmas; Sugar maple; Black spruce; Coating adhesion; Water contact angle; Pull-off test

Contact information: a: Renewable Materials Research Center, Department of Wood and Forest Sciences, Université Laval, Québec, Canada, G1V 0A6; b: Laboratoire d'Interactions Plasmas-Couches Minces et Plasmas-Nanomatériaux, Université de Montréal, Département of Physics, P.O. Box 6128, Succ. Centre-ville, Montréal, Québec, Canada, H3C 3J7; *Corresponding author: pierre.blanchet@sbf.ulaval.ca

INTRODUCTION

Plasma treatment has been used to modify the surface properties of many polymers, including some with complex chemistry and structure, such as those of textiles and wood. The treatment of these materials with plasma is a relatively new technology, and data reported from scientific papers are still sparse for both wood and textiles (Ibrahim *et al.* 2010a,b). Depending on the plasma reactor's design, the plasma gases used, and the plasma treatment parameters, the specific properties of polymers, such as their wettability, water repellence, and coating adhesion, can be improved. In terms of the final properties of the treated wood species, the plasma gas is likely one of the most important parameters to be considered, as it determines the nature of the active species (radicals, metastables, ions, and photons) interacting with the wood substrates. Inorganic plasma gases such as nitrogen, oxygen, carbon dioxide, air, argon, and others are generally used to alter surface properties such as wettability (Blanchard *et al.* 2009; Denes *et al.* 2005; Evans *et al.* 2007; Podgorski *et al.* 2002; Rehn *et al.* 2003), surface energy, and coating adhesion (Blanchard *et al.* 2009; Evans *et al.* 2007; Rehn *et al.* 2003). Plasmas generated from inorganic gases can alter the near-surface composition of

the wood surface by ion or atom interactions, cause etching of low-molecular weight species, and can modify their chemical structure following ultraviolet irradiation. On the other hand, organic gases such as ethane, hexamethyldisiloxane (HMDSO), polymethyldisiloxane (PMDSO), and those of fluorine compounds are often used in conjunction with inorganic carrier gases to deposit hydrophobic functional coatings onto the surface of wood *via* plasma-enhanced chemical vapor deposition (PECVD) (Kim *et al.* 2009; Levasseur *et al.* 2012; Manolache *et al.* 2008; Podgorski *et al.* 2001; Zanini *et al.* 2008).

Previously, several plasma-treated wood species have been investigated, including common northern species such as maple (Blanchard *et al.* 2009; Busnel *et al.* 2010), pine (Podgorski *et al.* 2001), spruce, poplar, and chestnut (Zanini *et al.* 2008) as well as more exotic species like coconut palm and eucalyptus (Blantocas *et al.* 2007). In addition to the wood species and the nature of the plasma gas, other variables of importance are the conditioning and finishing of the wood. Prior to plasma treatment, wood samples can be specifically conditioned and aged and either sanded to a specific degree or not sanded at all. It is important to account for sample finishing because sanding can remove extractives from the surface of the wood. The influence of the wood samples' preparation (sanded *vs.* not sanded) was evaluated by Wolkenhauer *et al.* (2009).

The effects of many other plasma parameters on wood modification dynamics have been investigated. These parameters include injected power and excitation frequency (Podgorski *et al.* 2000; 2001), operating pressure and gas flow rate (Blanchard *et al.* 2009; Podgorski *et al.* 2000; 2001), plasma exposure time (Podgorski *et al.* 2001), and cut orientation with respect to the grain direction of the wood (Evans *et al.* 2007). Given the highly complex composition of wood (which itself is composed of cellulose, hemicelluloses, and lignin), numerous mechanisms can take place following plasma exposure.

The effect of a specific plasma treatment is often characterized using contact angle analysis (Asandulesa *et al.* 2010; Blanchard *et al.* 2009; Busnel *et al.* 2010; Evans *et al.* 2007; Podgorski *et al.* 2000; 2001; 2001b; Rehn *et al.* 2003; Zanini *et al.* 2008) and adhesion tests (Blanchard *et al.* 2009; Busnel *et al.* 2010; Evans *et al.* 2007; Kim *et al.* 2009; Nussbaum 1999; Rehn *et al.* 2003). Regarding the effect of atmospheric air plasma treatment, Avramidis *et al.* (2012) found that there was little change in surface energy of pine wood, but that extractives were oxidized at the surface, according to XPS measurements. Thus water contact angle characterizations, are not as useful as one might think or like. In a general review on atmospheric plasma treatments of polymer surfaces, Williams and Hicks (2013) state that while surface wetting is necessary, it is not sufficient to determine whether a surface is optimally activated for adhesion. Other types of analyses include water droplet absorption tests (Blantocas *et al.* 2007; Manolache *et al.* 2008; Wolkenhauer *et al.* 2007), permeability tests (Chen and Zavarin 1990), X-ray photoelectron spectroscopy (XPS) (Avramidis *et al.* 2009; Busnel *et al.* 2010), and atomic force microscopy (Mahlberg *et al.* 1999). For example, using XPS, Klarhöfer *et al.* (2010) showed that dielectric barrier discharges (DBD) at atmospheric pressure in oxygen oxidized lignin, while those operated in argon reduced both lignin and cellulose.

All these analyses are not very good at making the difference between chemical species removed from the wood, such as water and extractives, by the plasma and

chemical species added by the plasma such as free radical species (due to UV emissions of some plasmas), and various grafted species on the surface. Thus better adhesion after plasma treatment could be due to changed surface energy, with better or worse wetting, but also specific chemical interactions and bonds between the adherent and substrate.

Plasma reactors can be generally classified as either vacuum (low-pressure) reactors or atmospheric pressure reactors. The differences between these types of reactors have been explained by numerous authors (Denes *et al.* 2005). Both types of plasma reactors have been used to alter the near-surface properties of wood. Low-pressure systems operate in closed enclosures in which the pressure (on the order of mTorr) must be achieved prior to and maintained during treatment. This usually involves expensive installations, time-consuming processes, and high operating costs. Further, since the space within the enclosure is limited, only relatively small quantities of wood can be treated at once. After a batch is treated, the reactor must be turned off and opened to replace the samples, operations which dramatically affect productivity. On the other hand, atmospheric-pressure plasma reactors operate in open environments, where samples can be inserted into or removed from the plasma at any time. From a practical standpoint, such reactors are advantageous in that they are highly productive and relatively inexpensive to operate. They could be installed within a continuous batch production line at a very low cost, allowing for the development of a new generation of wood products. The authors of this study consider that, even though vacuum plasma reactors are useful for creating some very high-value products such as medical prostheses and microchips, using atmospheric-pressure plasma reactors is the most suitable approach to treating low-value materials such as wood while still creating competitive products.

Of the reports regarding the plasma treatment of wood surfaces, reviews of those carried out under atmospheric conditions are particularly scarce. Rehn *et al.* (2003) used an atmospheric pressure DBD to improve the fracture strength and the water droplet uptake time on wood surfaces. The plasma gas used was atmospheric air, and the wood species investigated were *Robinia*, spruce, beech, teak, and oak. Another study involving a DBD operated in open air was conducted by Wolkenhauer *et al.* (2007). Samples consisted of wood-plastic composites, particle boards, and fibre boards. The authors found that the water contact angle on these surfaces decreased proportionally with plasma exposure time for all types of samples. Delamination tests have shown that coating adhesion increases after plasma treatment. Busnel *et al.* (2010) examined the effect of DBD treatments on sugar maple and black spruce. The plasma gases used were Ar, O₂, N₂, CO₂, and mixtures thereof. Depending on the gas composition, the contact angle and coating adhesion of both species were significantly modified. According to the data reported, a correlation between the plasma-induced improvement in the hydrophobic character of the wood samples and the corresponding improvement in wood-coating adhesion was proposed. The hydrophobic behaviour of wood was also investigated by Asanduleasa *et al.* (2010). The wood species studied were oak and beech, the plasma gas used was He, and the treatments were performed with a DBD tool. The wettability of the wood improved following the treatment, as shown by water contact angle analysis. Avramidis *et al.* (2009) also investigated how atmospheric-pressure plasma alters the hydrophilic characteristics of beech, oak, spruce, and pine.

Low-pressure or close-to-vacuum plasma treatments have been carried out by Podgorski *et al.* (2001), Evans *et al.* (2007), and Chen and Zavarin (1990). Podgorski *et al.* (2001) investigated the influences of plasma exposure time, power, sample-to-plasma distance, and aging time after treatment on fir samples. Another study, in which the effect of plasma energy and aging time on several eucalyptus species was monitored, was conducted by Evans *et al.* (2007). Chen and Zavarin (1990) investigated the effect of the plasma-induced permeability increase on white fir and Douglas fir.

According to the review presented, it is clear that plasma treatment at either low or atmospheric pressure is an effective way to alter the wettability and coating adhesion of wood. The effect of plasma exposure on wood depends on many parameters, such as the time of exposure, plasma gas usage, the time elapsed after treatment, and the wood species. While the influences of some of these parameters have been evaluated for low-pressure plasma treatments, there are little to no data available regarding treatment at atmospheric pressure. The objective of the present study was to contribute to the understanding of wood plasma treatment at atmospheric pressure by investigating the effects of several plasma factors on maple and spruce wood. This study is complementary to the work of Busnel *et al.* (2010) because the same wood species and plasmas were used; however, additional parameters, such as plasma exposure time and elapsed time after treatment, were investigated. The wood surface preparation was also different; wood samples were not sanded before plasma treatment.

EXPERIMENTAL

Black spruce (*Picea mariana* Mill.) and sugar maple (*Acer saccharum* March) wood blocks (3.5 in x 3.5 in x 0.5 in) were cut tangentially-longitudinally with respect to the wood grain direction. Four hundred specimens were made for each species. After cutting, all wood samples were randomized and conditioned at 20 °C and 50% RH for two weeks before undergoing the various plasma treatments. The plasma treatment apparatus (Fig. 1) consists of a custom made plane-to-plane dielectric barrier discharge opening to ambient air (Plasmionique; Quebec, Canada). In this system, the discharge was sustained between two metallic electrodes (285 cm²) covered with two 1.5-mm-thick quartz discharge plates.

The discharge gap was set to 1.4 mm. The system also has a gas inlet line, near the end of the electrodes, composed of several independent channels, allowing for the creation of plasmas with various gases (in this study, N₂, O₂, CO₂, and Ar). The electrical circuit used to power the plasma consists of several elements. The first is a function generator, which provides the reference signal. This signal is applied to the input of a linear power amplifier connected in series with the primary side of a step-up transformer. The discharge cell is connected to the transformer's secondary side, in series with a 50-Ω resistor, to measure the potential drop, and thus the current, using Ohm's law. For all gases investigated, the electrical stimulation was sinusoidal, with a frequency of 9 kHz. The peak-to-peak voltages and the resulting power absorbed or dissipated in the discharge for each gas investigated are shown in Table 1. After subtracting the capacitive current from the measured current (to obtain the discharge current) and the voltage drop

across the quartz dielectric plates from the applied voltage (to obtain the voltage applied to the gas), the power absorbed by or dissipated into the plasma was obtained using the approach described by Naudé *et al.* (2005).

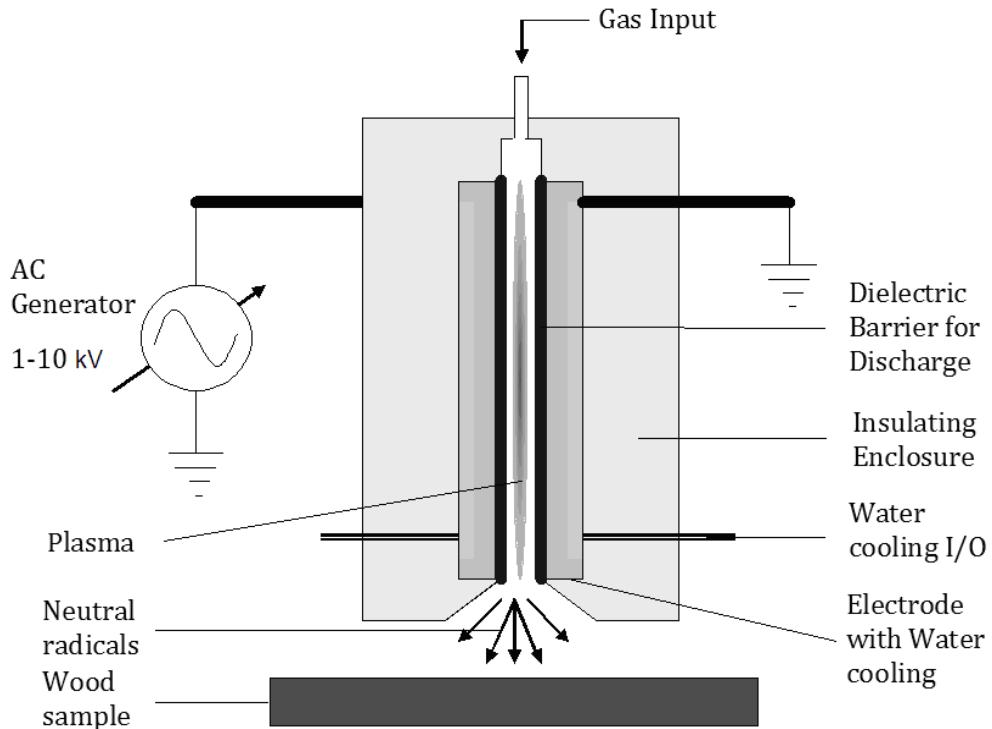


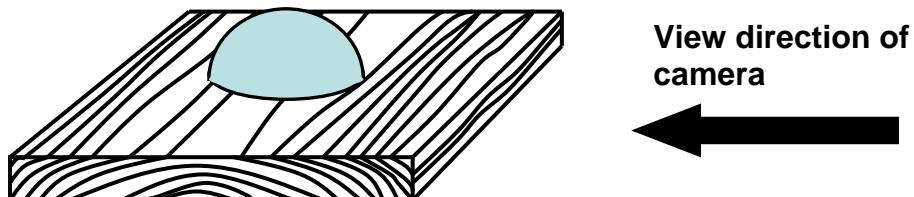
Fig. 1. Schematic of the flowing DBD apparatus used in this work; wood samples are moved on a conveyer along the plasma jet

One of the technical specifications of this reactor with respect to other atmospheric-pressure DBD units is that high gas flow rates (50 L/min) are passed between the two electrodes, where the plasma is sustained, such that the wood samples are exposed to the flowing afterglow, or the plasma jet. Depending on the wood's inherent roughness, the plasma-to-surface distance was in the range of 3 to 5 mm. In atmospheric pressure plasmas, a very large number of collisions leading to a loss of active species can occur on a very short distance. High flow rates are required to ensure that the flowing afterglow with active species reaches the surface. As such, no modification of the wood surfaces was observed for small gas flows (below about 1 L/min), which confirms that the observed change in wettability and adhesion reported below resulted from the exposure of the samples to a flowing afterglow or plasma jet and not to a coplanar surface discharge. To control the plasma exposure time, wood samples were placed on a treadmill on which the speed could be adjusted. In this work, a constant speed of 1.5 cm/s was used, which led to an estimated treatment time per pass of 0.1 s. For most experiments, multi-pass treatments were performed, allowing detailed investigations of the effects of plasma exposure time (between 0.1 and 1.5 s) on the wood surface modification dynamics. For all experimental conditions investigated, 10 to 15 repetitions were performed to account for random variation in the properties of the wood samples.

Table 1. Electrical Characteristics of the Discharge Used for Wood Treatments

Nature of the gas	Applied peak-to-peak voltage (kV)	RMS discharge current (mA)	Power absorbed or dissipated in the discharge (W)
Ar	3.5	8.4	4.0
N ₂	10	4.4	7.1
CO ₂	10	13	32
Dry air	10	18	37

Following each plasma treatment, two types of analysis were performed: contact angle measurements and coating pull-off tests. The wettability with water of plasma-modified wood samples was analyzed on the same day as the plasma treatment. The goniometer used was a First Ten Angstroms 200 Dynamic Contact Angle Analyser (Portsmouth, VA, USA). Contact angle values were recorded immediately after droplets were deposited on the wood sample surface. Because the water droplets spread asymmetrically with respect to the wood grain angle, the wood samples were placed such that the axis of the camera was always perpendicular to the wood grain direction, as shown in Fig. 2. Mean contact angles were determined by averaging data from several points of each sample. This was repeated for 10 replicate wood samples.

**Fig. 2.** View direction of the camera with respect to the direction of the wood grain

To examine the long-term stability of the plasma-modified wood samples following natural aging, contact angle measurements on uncoated samples were repeated after one and two weeks. During this natural aging period, the samples were kept in a conditioning chamber at 20 °C and 50% RH.

For each set of plasma conditions, 15 pull-off test repetitions were performed. Immediately after treatment, wood samples were covered with the same waterborne UV-curable polyurethane/polyacrylate coating used by Busnel *et al.* (2009). The coating was applied with a square applicator at a thickness of 0.1 mm. The coating was allowed to dry for 10 min at 60 °C. A second layer was then applied in the same way. All specimens covered with resin underwent UV curing (Sunkist mercury lamp; UVA = 53 J/m²). Once the resin cured, the pull-off test was performed according to ASTM D4541-02 (2002) standards. To accomplish this, metal dollies were glued onto the coating with an epoxy resin. After 24 h or more, the coating surrounding the dollies was sawn to separate it from the rest of the resin film, and the dollies were then pulled off with a hand machine made by Positest AT (DeFelsko; Ogdensburg, NY, USA). The maximum load, which occurred when the UV coating delaminated from the wood surface, was recorded. When significant wood failure was noticed, the measurement was eliminated from the statistics.

RESULTS AND DISCUSSION

In Fig. 3 the hydroscopic behaviors of sugar maple and black spruce wood samples following 1.5 s of exposure to various plasma gases are compared. It is apparent that nitrogen, argon, and air-based plasma jets dramatically decreased the mean contact angle of water in sugar maple. On the other hand, carbon dioxide did not significantly alter the wettability of maple (Fig. 3a). For black spruce, none of the four plasma gases investigated in this study significantly modified the mean contact angle of water, even at the maximum treatment durations (Fig. 3b). As discussed by Avramidis *et al.* (2012), part of the increase in the wood's surface energy, resulting in lower water contact angles following plasma exposure, can be attributed to the removal of hydrophobic extractives from the wood.

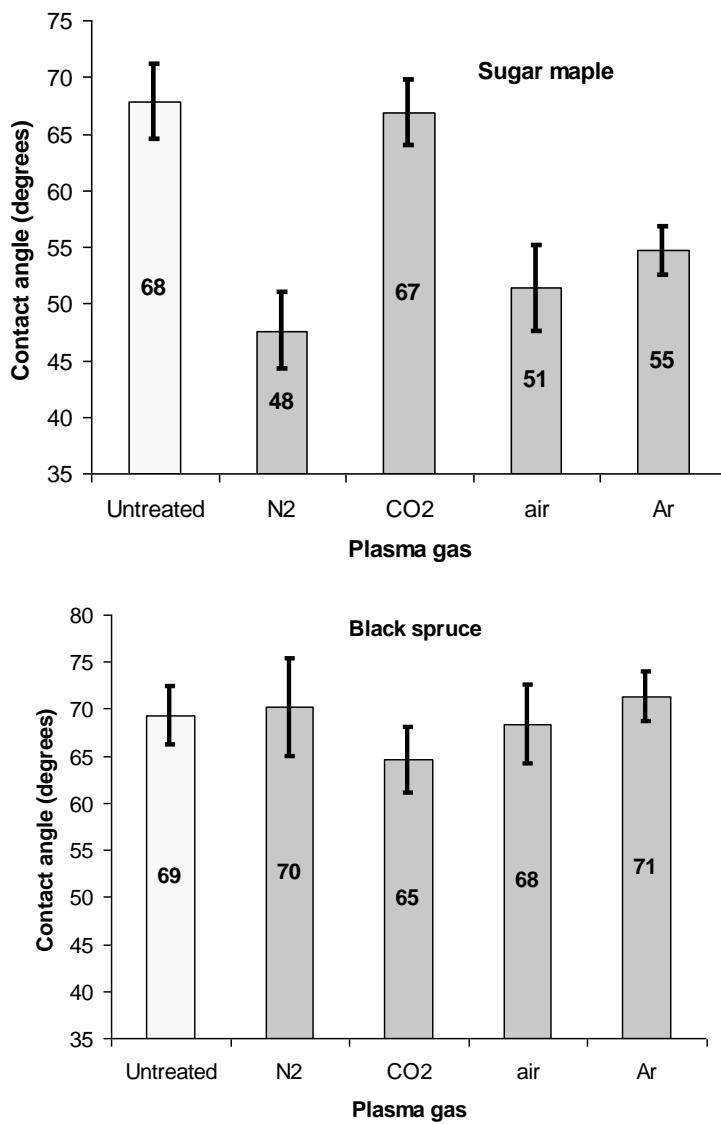


Fig. 3. Influence of plasma gas on the wettability with water of sugar maple (top) and black spruce (bottom) following 1.5 s of exposure to plasma

Given the highly porous nature of black spruce, one can expect a more rapid migration of wood extractives contained in the cell lumen toward the upper surface. For other similarly porous softwood species, even if some extractive removal occurs during plasma treatment, the outward diffusion of extractives is so rapid that the wood quickly returns to a pristine state as before plasma exposure; thus, the water contact angle does not change. Despite such little modification of the contact angle, improvements in adhesion may still be observed. Unlike in the simple removal of wood extractives by sanding, the wood surface can also undergo significant chemical, structural, and morphological changes in the presence of an active species in the plasma jet. These modifications are all likely to play a significant role in the evolution of the wood-coating adhesion properties.

Air-based plasma decreased the contact angle of water of sugar maple from 68 to 51° (25%) after only 1.5 s of treatment, a result very encouraging from a practical standpoint. Such results are a major step toward the development of atmospheric-pressure plasma reactors run with simple, cheap feed gases, which makes them more applicable to the wood industry. Such a reactor could operate using filtered ambient air instead of more expensive compressed gases. Because the formation of plasma jets such as those used in the present study consumes a very large amount of gas (flow rates greater than 50 L/min), air-based plasmas would be economical and therefore more suitable for wood producers.

The influence of plasma exposure time on the mean contact angle is shown in Fig. 4. For sugar maple, experimental results demonstrated that the mean contact angle loss was proportional to the plasma exposure time. This relationship was approximately linear. The exception was carbon dioxide, which failed to significantly modify the wettability of wood under any exposure time (Fig. 4a). For the black spruce, it was impossible to establish a relationship between the exposure time and the mean contact angle. Figure 5b shows that the values of the contact angles as functions of exposure times were randomly distributed above or under the control value (dotted line), so there was no measurable effect on the spruce wettability (*i.e.*, none that could be detected by contact angle analysis).

The stability of each plasma treatment for both wood species is illustrated in Fig. 5. As seen from the contact angle analysis, the effect of the active plasma species was not permanent for any plasma gas used. Repetition of the contact angle measurements after one and two weeks following the plasma treatment demonstrated that the mean contact angle values increased progressively during the period after treatment. In some cases, at low plasma exposure times, the initial contact angle value of the untreated specimens was reached after only one week. This was the case for argon and air treatments on sugar maple. For longer exposure times, such as 1 and 1.5 s, the initial plasma effects were strong enough to last more than two weeks in the case of sugar maple, but the trend was increasing for all exposure times (Figs. 5a, b, c, and d). It is likely that the mean contact angle values of high exposure durations would eventually reach the initial values after an aging period longer than two weeks. For black spruce, the effect of the elapsed time after plasma treatment was less obvious, likely because there was not an improvement in the first place (Figs. 5e and f). However, increasing contact angle values were observed for nitrogen at all exposure times and argon at all exposure times but 1.5 s. This relative

insensitivity of black spruce, may be due to its content, like many softwood resinous species, of resins and terpenes, which could be difficult to remove with plasma.

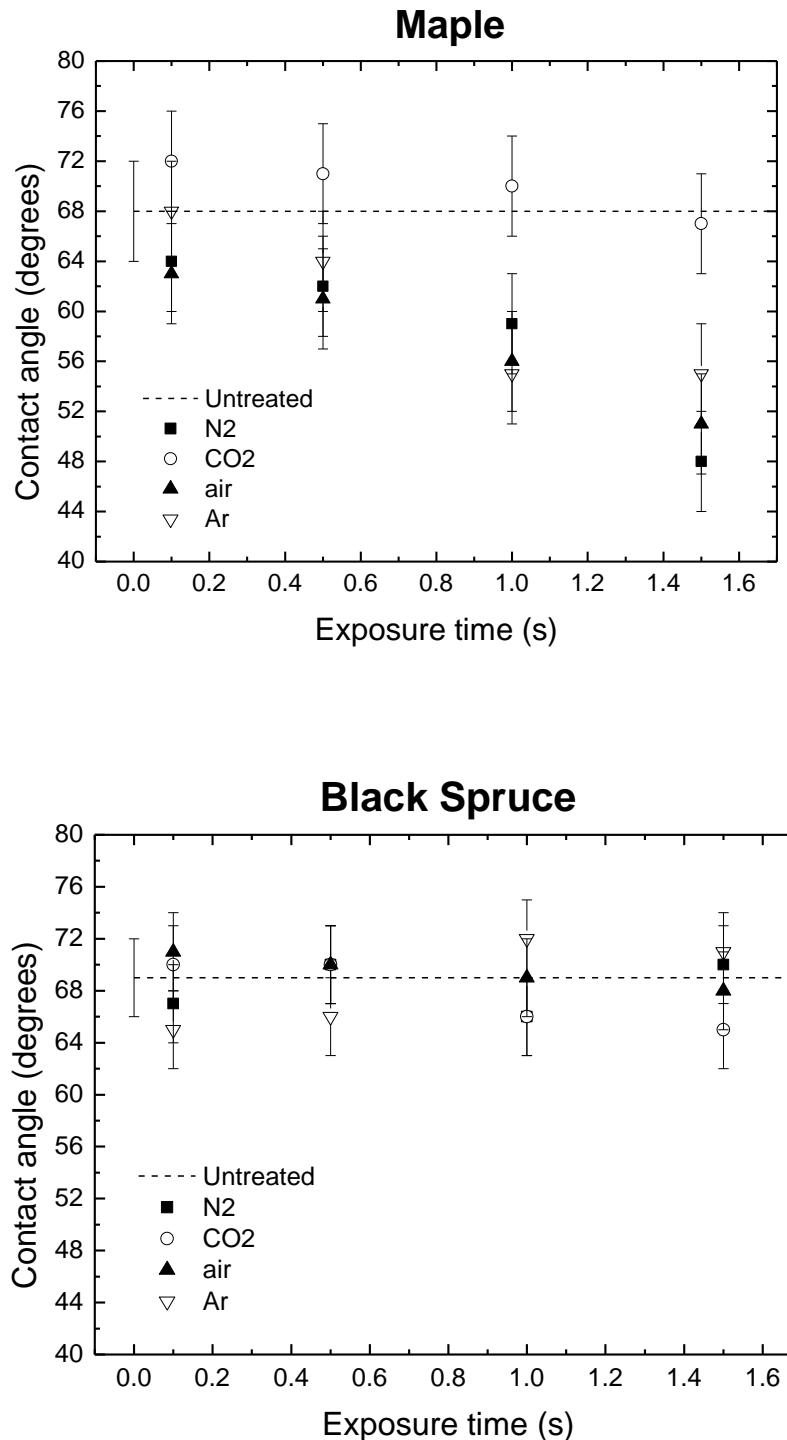


Fig. 4. Mean contact angles of water as a function of plasma exposure time for sugar maple (top) and black spruce (bottom). Dotted lines represent the values of the control samples

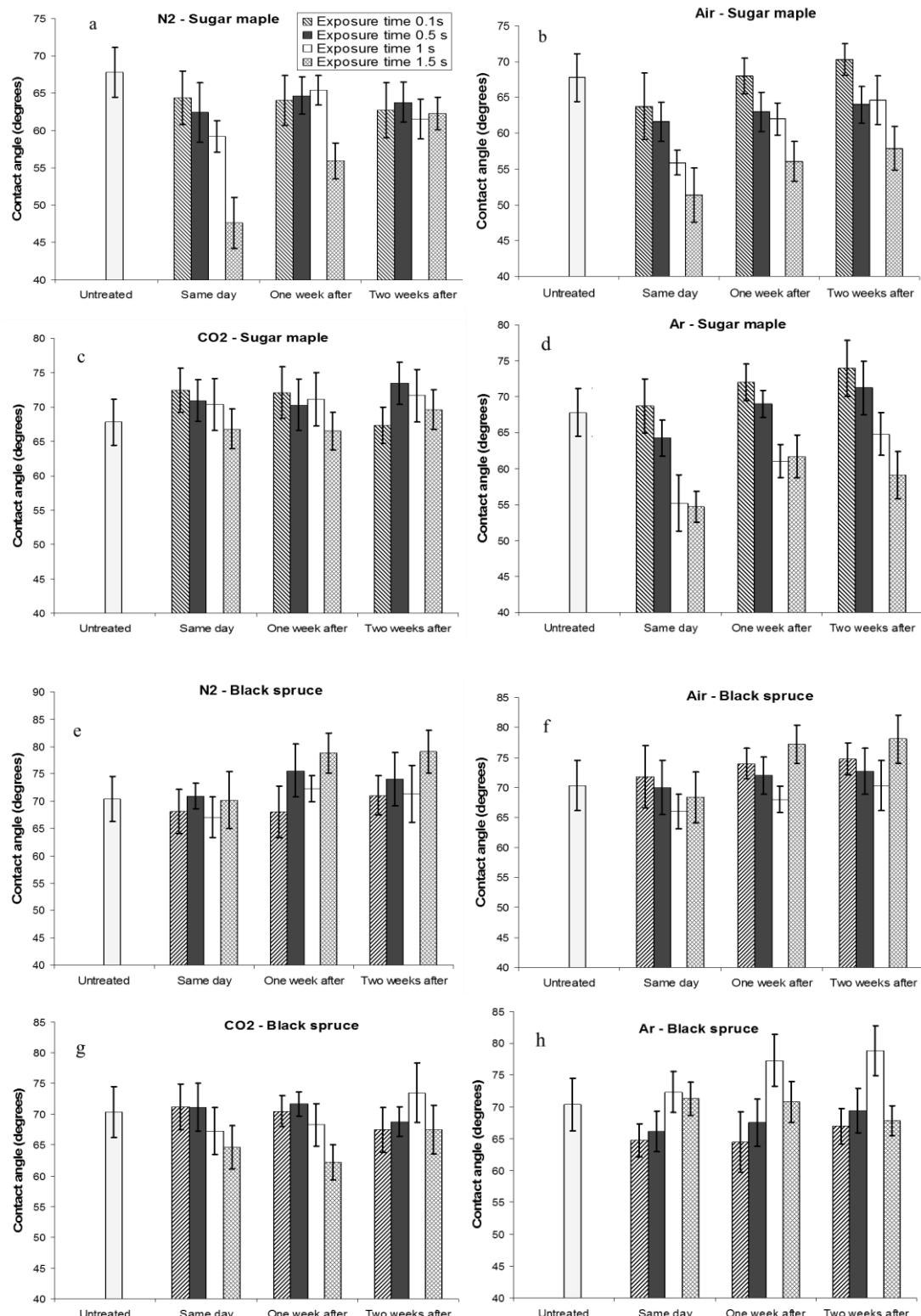


Fig. 5. Stability of plasma treatment of sugar maple (a to d) and black spruce (e to h)

The instability of the water contact angle may be due to the nature of the chemical changes to the wood surface. When wood is cut, contact angles with water vary with time due to the oxidation of and migration of extractives to the surface (Nussbaum 1999). Thus, the same thing is bound to happen following plasma treatment. Sakata *et al.* (1993), who carried out corona treatment of the wood surface, suggested that the changes in the surface energy of wood were due to the oxidation of hydrophobic extractives and the wood substance itself, as cellulose and lignin were not affected. Because this oxidized layer is generally quite thin, unreacted extractives in the unaffected wood may diffuse back into the surface and bring the surface energy back to its original values after a few weeks. Avramidis *et al.* (2012) also interpreted changes in the surface energy of the plasma-treated wood in terms of oxidation of extractives.

Regarding pull-off testing, statistical analysis revealed that the plasma treatment significantly increased the coating adhesion on black spruce for all plasma gases except for carbon dioxide (Fig. 6). This was true for almost all exposure times for black spruce, with the only exception being the air plasma treatment for 0.5 s.

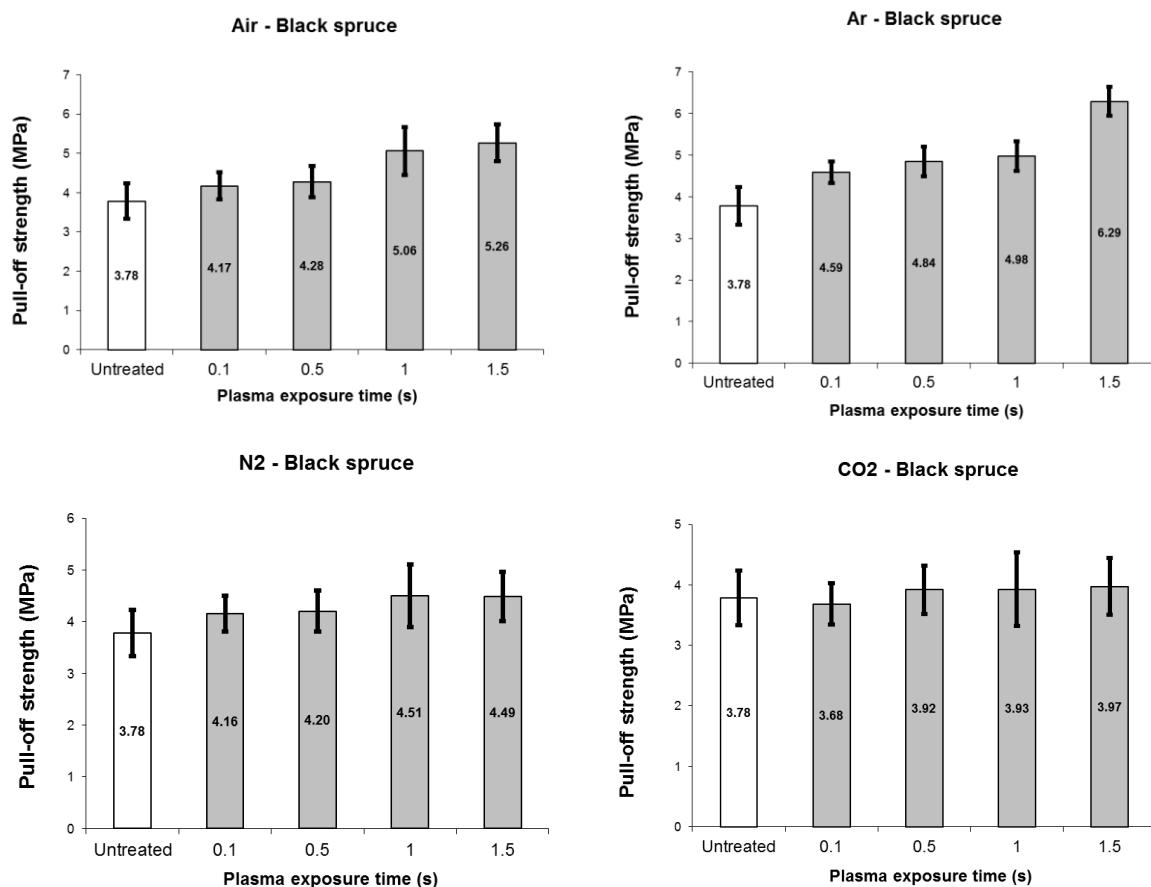


Fig. 6. Black spruce pull-off strength as a function of plasma exposure time

Carbon dioxide failed to improve the coating adhesion on spruce, regardless of the exposure time. For other gases, the improvement was dramatic in some cases, especially at high exposure times (66% increase in coating adhesion after 1.5 s of spruce exposure to argon plasma). The reason plasma improves the coating adhesion of waterborne resin but does not improve the wettability of black spruce is still unclear. One possible explanation is that, as pull-off tests were performed immediately after the plasma treatment and the contact angle analysis was conducted a few hours later, the plasma's effect on the spruce wood led to unstable surface species (such as free radicals) that were deactivated during the interim period. The creation of free radical species has previously been deemed the cause of the enhancement of adhesion in plasma-treated polyethylene by several authors (Bahners and Gutman 2011; Svorcik *et al.* 2006; Tahara *et al.* 2003). The wettability as measured by contact angle techniques is not necessarily sensitive to reactive or short lived species on the substrate: it only tells if it is less or more hydrophobic.

Pull-off tests on sugar maple samples also revealed that coating adhesion can be altered by most of the atmospheric-pressure plasmas examined, with the only exception being carbon dioxide plasma, which did not cause significant change with any exposure time investigated (Fig. 7). Carbon dioxide plasma usually increases the polymer's surface

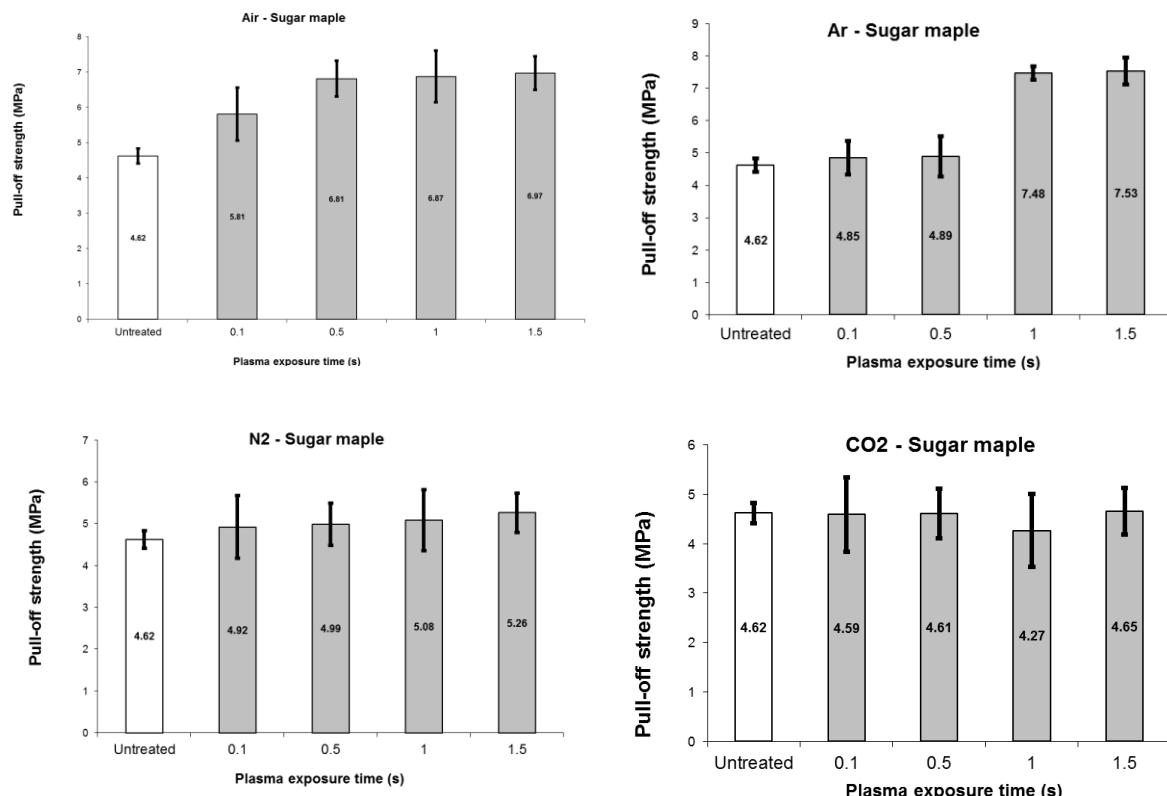


Fig. 7. Sugar maple pull-off strength as a function of plasma exposure time

acidity (Aouinti *et al.* 2003), which could be why neither wettability nor coating adhesion were improved by this plasma gas. Despite the higher power absorbed or dissipated by the CO₂ discharge with respect to other gases (Table 1), the overall plasma emission turned out to be much lower (not shown), which is an indicator of a much lower number density of charged particles. This reduces the number of active species formed during the discharge and reduces their availability for wood surface modification. On the other hand, nitrogen and argon plasmas significantly increased the adhesion following 1 and 1.5 s of plasma treatment. Changes induced by air plasma were statistically significant beginning with the lowest exposure time, 0.1 s. The most important modification of coating adhesion was obtained after 1.5 s of treatments with argon plasma (a 63% increase) and air plasma (a 51% increase). As detailed above, the performance of the flowing afterglow of the atmospheric pressure dielectric barrier discharges with dry air on the coating adhesion of both wood species is very promising. This is because such treatments could be cost-effective for the wood industry. In Blanchard *et al.* (2009), Raman confocal measurements were performed on sugar maple after plasma treatment and coating with polyacrylates. With plasma treatment, coating was found to penetrate more into plasma treated wood, thus giving better adhesion. Since the adhesion is measured by pulling off coating, if uncured coating penetrates further, the energy required to pull it off is higher since wood-coating adhesion surface is larger. This would thus relate better adhesion to a simple better 3D wicking of the paint into the substrate, due to better wetting.

Further analysis of the results presented in Figs. 3 to 7 indicates that in contrast with common beliefs, improved water wettability does not necessarily lead to improved wood-coating adhesion. This is because the surface energy (dispersive adhesion) and a number of other phenomena, including surface roughness (mechanical adhesion), the formation of chemical bonds (chemical adhesion), the formation of short-lived chemical moieties, the occurrence of electrical discharges (electrostatic adhesion), and the solubility of the coating (diffusive adhesion), drive adhesion dynamics. Given the diversity of the active species (ions, radicals, electrons, metastables, and photons) present in the flowing afterglow of Ar, N₂, CO₂, and dry air discharges at atmospheric pressure, such treatments can alter all of these phenomena through either surface texturing, polymer cross-linking, surface charges, surface oxidation, surface etching, or bond breakage.

At this point, further evidence is required to determine if the plasma treatment only removes the hydrophobic extractives from the surface or also induces chemical changes in the surface. In order to gain more insights on the plasma-wood surface modifications driving the wettability and adhesion improvements, future work will involve 1) an identification of the chemical active species in the plasma by a characterization of the plasma source and 2) an identification of the chemical components of wood (cellulose, lignin, extractives) affected by the treatment by characterization of the surface with Fourier Transform Infrared (FTIR) Spectroscopy and X-Ray Photoelectron (XPS) Spectroscopy, as well as, rather than use easy, but ambiguous techniques such as water contact angle determination, use of more specific techniques such as AFM with molecularly sensitive or even reactive tips, and detection of reactive short-lived species on wood surfaces such as free radicals, would be more constructive towards elucidation of adhesion mechanisms.

CONCLUSIONS

1. Atmospheric-pressure plasma treatment of sugar maple (*Acer saccharum* March.) and black spruce (*Picea mariana* (Mill.)) resulted in increased coating adhesion strength in both wood species. This was true for all plasma gases selected for this study, with the exception of carbon dioxide.
2. The precise reason why carbon dioxide failed to increase the coating adhesion remains unclear, although the low discharge currents point toward a low number density of active species over the range of experimental conditions investigated.
3. The wettability of maple by water was increased by plasma treatment, but this was not the case for spruce, regardless of the duration of the plasma treatment. A possible explanation could be the creation of unstable reactive species on the wood surface.
4. The study of the influence of plasma exposure time on maple wettability revealed that the loss of contact angle is directly proportional to the duration of the plasma treatment.
5. Repetition of the contact angle measurements after one to two weeks of natural aging demonstrated that the effect of atmospheric-pressure plasma treatment on wood wettability is not permanent: after treatment, the gain in wettability begins diminishing and in some cases reaches the control value within two weeks. Thus, it is important to take advantage of plasma-surface modification as soon as possible after treatment.
6. From a practical standpoint, the effect of air plasma on wood is highly important, as it could lead the way toward the development of industrial air plasma reactors for the wood industry operating at atmospheric pressure.
7. There is no direct correspondence between contact angle measurements and adhesion results.

ACKNOWLEDGMENTS

This work was supported by the Renewable Materials Research Center (Université Laval), FPInnovations, and the National Science and Engineering Research Council of Canada (NSERC).

REFERENCES CITED

- Aouinti, M., Bertrand, P., and Poncin-Épaillard, F. (2003). "Characterization of propylene surface after treatment in CO₂ plasmas," *Plasma Processes Polymers* 8(4), 225-236.
- Asandulesa, M., Topala, I., and Dumitrascu, N. (2010). "Effect of helium DBD plasma treatment on the surface of wood samples," *Holzforschung* 64(2), 223-227.

- ASTM D4541-02. (2002). *Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers*, American Society for Testing and Materials (ASTM).
- Avramidis, G., Hauswald, E., Lyapin, A., Militz, H., Viöl, W., and Wolkenhauer, A. (2009). "Plasma treatment of wood and wood-based materials to generate hydrophilic or hydrophobic surface characteristics," *Wood Mat. Sc. Eng.* 4(1-2), 52-60.
- Avramidis, G., Klarhöfer, L., Maus-Friedrichs, W., Militz, H., and Viöl, W. (2012). "Influence of air plasma treatment at atmospheric pressure on wood extractives," *Polym. Degrad. Stab.* 97(3), 469-471.
- Bahners, T., and Gutman, J. S. (2011). "Photo-initiated lamination of polyethylene (PE) and poly(ethylene terephthalate) (PET)," *J. Adhes. Sci. Technol.* 26(1-3), 121-130.
- Blanchard, V., Blanchet, P., and Riedl, B. (2009). "Surface energy modification by RF inductive and capacitive plasmas at low pressures on sugar maple: An exploratory study," *Wood Fib. Sci.* 41(3), 245-254.
- Busnel, F., Blanchard, V., Prégent, J., Stafford, L., Riedl, B., Blanchet, P., and Sarkissian, A. (2010). "Modification of sugar maple (*Acer saccharum*) and black spruce (*Picea mariana*) wood surfaces in a dielectric barrier discharge (DBD) at atmospheric pressure," *J. Adhes. Sci. Technol.* 24(13), 1401-1413.
- Chen, H. Y., and Zavarin, E. (1990). "Interaction of cold radio frequency plasma with solid wood," *J. Wood Chem. Technol.* 10(3), 386-400.
- Denes, F. S., Cruz-Barba, L. E., and Manolache, S. (2005). "Plasma treatment of wood," in: *Handbook of Wood Chemistry and Wood Composites*, R. M. Rowell (ed.), CRC Press, Boca Raton, FL, pp. 447-473.
- Evans, P., Ramos, M., and Senden, T. (2007). "Modification of wood using a glow-discharge plasma derived from water," *Proceedings of the Third European Conference on Wood Modification*, C. A. S. Hill, D. Jones, H. Militz, and G. A. Ormondroyd (eds.), Bangor, UK.
- Ibrahim, N. A., Hashem, M. M., Eid, M. A., Refai, R., El-Hossamy, M., and Eid, B. M. (2010a). "Eco-friendly plasma treatment of linen-containing fabrics," *Journal of Textile Institute* 101(12), 1035-1049.
- Ibrahim, N. A., Eid, B. M., Hashem, M. M., Refai, R., and El-Hossamy, M. (2010b). "Smart options for functional finishing of linen-containing fabrics," *Journal of Industrial Textiles* 39(3), 233-265.
- Kim, B. S., Chun, B. H., Lee, W. I., and Hwang, B. S. (2009). "Effect of plasma treatment on the wood flour for wood flour/PP composites," *J. Thermopl. Comp. Mat.* 22(1), 21-28.
- Klarhöfer, L., Viöl, W., and Maus-Friedrichs, W. (2010). "Electron spectroscopy on plasma treated lignin and cellulose," *Holzforschung* 64(3), 331-336.
- Levasseur, O., Stafford, L., Gherardi, N., Naudé, N., Blanchard, V., Blanchet, P., and Riedl, B. (2012). "Deposition of hydrophobic functional groups on wood surfaces using atmospheric-pressure dielectric barrier discharge in helium-hexamethyl-disiloxane gas mixtures," *Plasma Process. Polym.* 9(11-12), 1168-1175.
- Manolache, S., Jiang, H., Rowell, R. M., and Denes, F. S. (2008). "Hydrophobic wood surfaces generated by non-equilibrium, atmospheric pressure (NEAPP) plasma-enhanced coating," *Mol. Cryst. Liq. Cryst.* 483(1), 348-351.

- Naudé, N., Cambronne, J.-P., Gherardi, N., and Massines, F. (2005). "Electrical model and analysis of the transition from an atmospheric pressure Townsend discharge to a filamentary discharge," *J. Phys. D* 38(4), 530-538.
- Nussbaum, R. M. (1999). "Natural surface inactivation of Scots pine and Norway spruce evaluated by contact angle measurements," *Holz. als Roh- und Werk.* 57(6), 419-424.
- Podgorski, L., Bousta, C., Schambourg, F., Maguin, J., and Chevet, B. (2001). "Un nouveau revêtement imperméable pour le bois grâce au traitement plasma," *Double Liaison* 524, 39-46.
- Podgorski, L., Bousta, C., Schambourg, F., Maguin, J., and Chevet, B. (2001). "Surface modification of wood by plasma polymerisation," *Pigm. Resin Technol.* 31(1), 33-40.
- Podgorski, L., Chevet, B., Onic, L., and Merlin, A. (2000). "Modification of wood wettability by plasma and corona treatments," *Int. J. Adhes. Adhes.* 20(2), 103-111.
- Rehn, P., Wolkenhauer, A., Bente, M., Forser, S., and Viol, W. (2003). "Wood surface modification in dielectric barrier discharges at atmospheric pressure," *Surf. Coat. Technol.* 174-175, 515-518.
- Sakata, I., Morita, M., Tsuruta, N., and Morita, K. (1993). "Activation of wood surface by corona treatment to improve adhesive bonding," *J. Appl. Polym. Sci.* 49(7), 1251-1258.
- Svorcik, V. K., Slepicka, P., Blahova, O., Spirkova, M., Sajdl, P., and Hnatowicz, V. (2006). "Modification of surface properties of polyethylene by Ar plasma discharge," *Nucl. Instrum. Meth. B* 244(2), 365-372.
- Tahara, M., Cuong, N. K., and Nakashima, Y. (2003). "Improvement in adhesion of polyethylene by glow-discharge plasma," *Surf. Coat. Technol.* 174-175, 826-830.
- Williams, H. Y., and Hicks, R. F. (2013). "Atmospheric pressure plasma activation of polymers and composites for adhesive bonding: A review," *Rev. Adhes. Adhes.* 1(1), 46-87.
- Wolkenhauer, A., Avramidis, G., Hauswald, E., Militz, H., and Viöl, W. (2009). "Sanding vs. plasma treatment of aged wood: A comparison with respect to surface energy," *Int. J. Adhes. Adhes.* 29(1), 18-22.
- Wolkenhauer, A., Avramidis, G., Cai, Y., Militz, H., and Viöl, W. (2007). "Investigation of wood and timber surface modification by dielectric barrier discharge at atmospheric pressure," *Plasma Process. Polym.* 4(S1), 470-474.
- Zanini, S., Riccardi, C., Orlandi, M., Fornara, V., Donato, D. I., Legnaioli, S., and Palleschi, V. (2008). "Wood coated with plasma-polymer for water repellence," *Wood Sci. Technol.* 42(2), 149-160.

Article submitted: February 20, 2014; Peer review completed: April 22, 2014; Revised version received and accepted: June 3, 2014; Published: July 7, 2014.