The Effect of Atmospheric Pressure Plasma on Paper and Pulps

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The increased functionality of cellulose fiber based paper products is of high interest, as researchers are investigating methods to replace petroleum-based products with modified paper products. In this study, fully bleached wood pulps were treated with atmospheric pressure plasma, made into paper handsheets, and then tested for surface and other physical properties. Paper handsheets after formation were also treated with plasma to induce surface modifications. The plasma was generated using helium with fractions of either O_2, CF_4, or C_3F_6 to determine the effect of the nature of the gas. Drying methods had a greater effect on strength properties and density than plasma treatment. Plasma treatments on previously made paper increased the surface roughness, but plasma treatments on pulps prior to papermaking did not cause any roughness changes in the resulting paper. X-ray photoemission spectroscopy (XPS) revealed small increases in the oxygen to carbon ratios of oxygen enhanced plasmas for both pulp and paper treated samples. The plasma treatment showed evidence of surface fluorine in paper treated with CF_4 containing plasma, but not in pulps treated with CF_4 containing plasma and then made into paper.

Keywords: Paper; Pulp; Plasma; Surface Treatment

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INTRODUCTION

Plasma is the fourth state of matter, occurring when electrons in a gas obtain sufficient energy to separate from their respective nuclei, resulting in charged particles that can be manipulated by electric and magnetic fields. Substrates exposed to plasmas undergo changes to surface chemistry (Zhang *et al.* 2017) and surface topography (Wielen *et al.* 2005).

'Cold,' laboratory plasmas are generated at ambient conditions and consist of electrons, ions, excited atoms and molecules, neutral gas species, and UV radiation (Lieberman and Lichtenberg 2005). Historically, plasma treatment has been carried out in high vacuum, low-pressure devices (Hochar *et al.* 2003). This leads to large mean free paths as well as very energetic ions and electrons capable of rapid and extreme surface modification (Mori *et al.* 1994).

Disadvantages related to vacuum systems include expensive vacuum equipment, long pump-down and treatment times, and a restriction to batch processing. The application of plasma for the treatment of paper products is challenging due to the high throughput of paper product, the continuous nature of the processing, and the relatively low value of conventional paper. However, the advent of atmospheric pressure plasma processing has reopened the potential for the industrial use of plasmas and for plasma companies such as APJeT®, Plasmatreat®, and Molins® (based on Dow Corning technology) that are now offering commercial devices. Atmospheric plasma treatment provides both a fiscal and environmental benefit (Nema and Jhala 2015; Roth *et al.* 2007). The cost of plasma treatment is lower than other treatment methods, and plasma treatment rarely produces byproducts or significant quantities of waste. Environmental concerns are strong within the paper industry, and today approximately 50% of fibers are made from recycled materials (Pelache *et al.* 2016). Plasma treatment offer the potential for paper and pulp chemical modification with a green technology.

Atmospheric pressure plasma has almost all the kinetic processes and potential for surface activation as vacuum plasma, but requires different gases and parameters (Shenton and Stevens 2001). Atmospheric pressure plasma also offers benefits over corona discharge due to broader substrate treatment capabilities, longer-lived effects, and the capacity to treat thicker substrates (Wolf 2004).

Plasma also allows substrate modification without harsh chemicals or effluent generation. Wood-based pulp fibers have been treated to increase water absorption by oxygen-plasma and improve wettability by oxidizing extractives and lignin (Carlsson and Strom 1994; Carlsson and Strom 1995) in pulps. Pulps high in these contaminants wet similarly to carbohydrate rich pulps after a plasma exposure as short as five seconds.

The treatment of paper has also been investigated with atmospheric pressure plasma devices. Pure air and nitrogen plasmas generated at atmospheric pressure modified the surface structure of ground wood (lignin rich) paper by introducing C-O bonds along with C=O and nitrogen moieties (Toth *et al.* 2007). Maximum oxidation has been rapidly achieved after only two seconds of plasma exposure. This increase in oxygen functional groups improved the wettability of bleached kraft paper as well as the wet strength (Vander Wielen *et al.* 2006). Wet stiffening was also observed at high plasma intensities and attributed to a covalent cross-linking mechanism.

Increased wettability and moisture properties observed for vacuum and atmospheric pressure plasma treatment of pulp and paper are subject to aging effects (Pykonen *et al.* 2008). Although the oxidation level remains unchanged, decay in surface energy was observed for conventionally pigment coated and surface sized paper substrates treated in atmospheric pressure plasma and corona discharges. Decay was most significant in the first few weeks of storage, but leveled off after 12 weeks to an energy level still higher than untreated samples. Reduction of surface energy was attributed to the rotation of polar groups into the bulk of the substrate as well as partial re-contamination by atmospheric impurities.

Most atmospheric pressure plasma treatments focus on increased hydrophilicity, but hydrophobic plasma treatments have also been investigated. In one study the plasma treatment was applied to slices of spruce wood (Bente *et al.* 2004) using methane, ethane, or silane/nitrogen plasma to produce hydrophobic surfaces. Silane/nitrogen plasma created the most hydrophobic surface with a contact angle of 145°, which was an increase of 73° over an untreated reference. Ageing effects were also observed, but limited to a 2° to 6° decrease in contact angle over a period of six months.

Plasma treatment is a surface treatment, modifying only a few micrometers of a substrate (Levalois-Grutzmacher and Tsafack 2007). This prevents direct alteration of bulk properties, which is desirable in some applications, but a limitation in others. Plasma may affect paper bulk properties indirectly by affecting the surface properties of the pulp fibers prior to papermaking. In this study, the properties of handsheets treated with plasma as well as pulps treated with plasma and subsequently made into handsheets were examined to investigate potential differences produced by treating paper surfaces *versus* complete fiber surfaces. It was expected that pulps have more surface area and are less dense than paper, permitting better penetration and increasing potential for alteration by plasma. Additionally, it was expected that the plasma modifications would be uniformly distributed throughout the bulk of the pulp-treated handsheets rather than limited to the surface.

EXPERIMENTAL

Three different fully bleached wood pulps were prepared for experimentation: an ethanol dried pulp (MEP), a liquid carbon dioxide dried pulp (CD), and an untreated pulp.

Softwood Disintegration and Refining (All Pulps)

NIST fully bleached softwood sheet (NIST SS) was used to prepare all pulps. The NIST SS was tested for moisture content and mixed in a TAPPI disintegrator with sufficient de-ionized water to prepare the pulp to a 3% final consistency. After full disintegration, which took about 5 min, the pulp was transferred to a PFI mill and subject to 15 min of refining. The refined pulp was pressed using cheesecloth to remove excess water, and an aliquot was taken to determine the consistency, which was 10%.

Ethanol Exchange

Ethanol was added to the 10% pulp-water mixture for solvent exchange to obtain a 5% solid to liquid consistency. The mixture was allowed to soak for at least 4 h, and then the pulp was pressed once again, using cheesecloth, to about a 10% consistency. This solvent exchange process was repeated once more.

Carbon Dioxide Dried Ethanol Pulps (CD Pulps)

A portion of the ethanol-pulp slurry was submitted to liquid carbon dioxide drying using a Parr Reactor Assembly Model 4082 (Moline, IL, USA). The pulps were extracted twice at 2000 psi and room temperature with a ratio of 150 g CO_2 to 30 g pulp slurry.

Force Air Dried Pulps (CD and MEP Pulps)

The ethanol-pulp slurry and the CO_2-pulp slurry were subject to forced-air evaporation at 20 °C and 50 °C, respectively for 48 h at atmospheric pressure. Due to clumping, pulp was subsequently milled using a Wiley Mill (Swedesboro, NJ, USA) with 3-mm mesh holes. The average fiber length of the milled and unmilled samples was determined using an OpTest Fiber Quality Analyzer (Hawkesbury, USA).

Handsheet Preparation

After pulp disintegration and refining, a set of handsheets was prepared according to the TAPPI T205 standard (2012). These handsheets, the CD pulps, and the MEP pulps were dried at 100 °C to measure a dry weight and subsequently submitted to plasma

treatment. After plasma treatment, the CD and MEP pulps were also made into handsheets according to the TAPPI T205 standard (2012). The steps in processing for each paper method, including conventional handsheets, MEP handsheets, and CD handsheets, are detailed in Table 1.

Table 1. Summary of Pulp Treatments

Conventional Handsheets	MEP Handsheets	CD Handsheets
Fibers dispersed in water	Fibers dispersed in water	Fibers dispersed in water
Fibers refined	Fibers refined	Fibers refined
Handsheet made, dried in air at 20 °C	2 exchanges with ethanol	2 exchanges with ethanol
Heated to 100 °C	Air-dried at 20 °C	2 exchanges with CO_2 at 50 °C
0 or 1 min plasma treatment	Wiley Milled	Air-dried at 50 °C
Analytical Testing	Heated to 100 °C	Wiley Milled
	0 or 1 min plasma treatment	Heated to 100 °C
	Handsheet made, dried in air at 20 °C	0 or 1 min plasma treatment
	Analytical Testing	Handsheet made, dried in air at 20 °C
		Analytical Testing

Atmospheric Pressure Plasma Treatment

Pulps and handsheets were plasma-treated using the NCAPS, North Carolina Atmospheric Pressure System, located on Centennial Campus at North Carolina State University (Raleigh, NC, USA). The NCAPS device has been used for the plasma treatment and chemical grafting of various polymers and vinyl monomers (Borcia *et al.* 2003; Virk *et al.* 2004; Wafa *et al.* 2006; Cornelius 2007).

The device is a dielectric barrier discharge plasma (DBD), composed of two 0.258 m^2 copper electrodes encased in a garolite dielectric. The gap between the two electrodes can be manually adjusted, but a distance of 3.8 cm was maintained for these experiments. The electrodes were powered by 4.8 kW direct current power supplies oscillated by a function generator in the audio frequency range. A frequency of 5 kHz was chosen for these experiments.

The device consisted of two chambers (Fig. 1), an internal chamber and an external chamber, both made of Lexan polycarbonate. The inner chamber housed the electrodes and a removable cell for batch treatment. The cell within the inner chamber maintained the 3.8 cm gap and reduced the quantity of gas needed to run batch samples. Inside the cell, a nylon mesh was suspended equidistant from the electrodes for sample placement. The pulps and handsheets were placed on top of this nylon mesh for plasma treatment. Approximately 3 grams of the Wiley milled pulp was spread uniformly across the mesh for each plasma treatment. Care was taken to keep the thickness of the pulp to 1.5 cm or less to prevent direct contact with the electrode. For treatment of the handsheets, each handsheet was suspended on the mesh and individually exposed to plasma.

The gas within the machine was regulated to generate the plasma at atmospheric conditions. Helium was always used as the primary gas, with optional small fractions of additional gases. Oxygen (O_2), carbon tetrafluoride (CF_4), and hexafluoropropylene (C_3F_6) were all used as test gases for this experiment. Gas flow was regulated by flow controllers and was supplied at 1% by mass for the test gases with a constant 10.00 L/min flow rate of

helium gas. Each sample was placed individually within the system and treated with the specified gas mix for exactly 1 min.

Online monitoring of the plasma system was conducted using a LabVIEW® system (Austin, TX, USA). The LabVIEW® system monitored voltage, current, temperature, impedance, and electron number density in real time. The LabVIEW® program for this system calculates electron number density as approximately 10^{12}/ m^3 using a complex electrical circuit model (Cornelius 2007). The electron number density obtained from this complex electrical circuit model is in close agreement with the electron number density of other researchers using more complex techniques, including neutral Bremsstrahlung and H_∞ line broadening of the using optical emission spectroscopy on similar atmospheric pressure plasmas (Greim 1978; Henins *et al.* 2000).

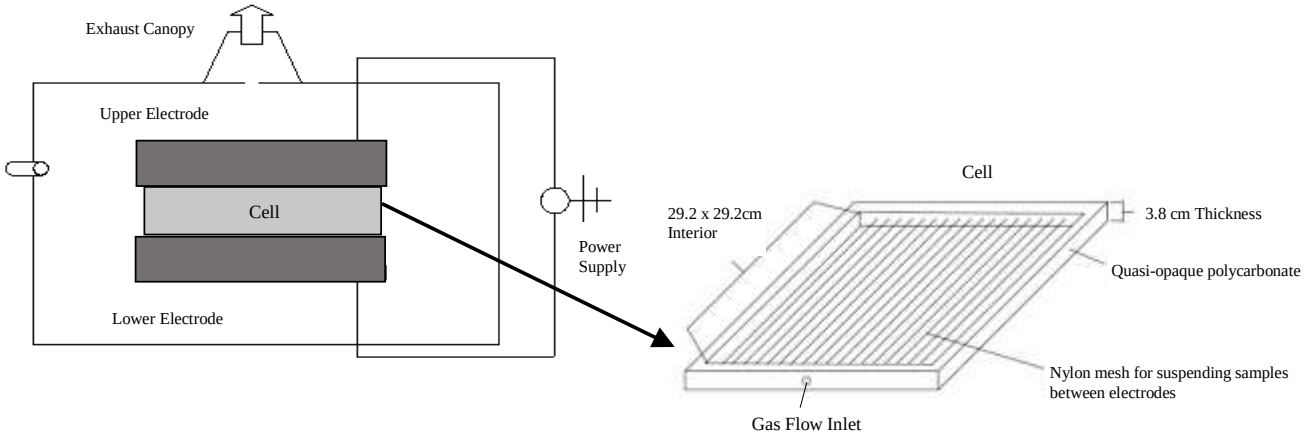


Fig. 1. Atmospheric pressure plasma device and cell

Fourier Transform Infrared Spectroscopy

A Nicolet Nexus® 470 Fourier transform infrared spectrometer (Madison, WI, USA) device was used in conjunction with a Nicolet® Omnisampler. The FTIR was used to evaluate changes in the surface functionalities of the treated paper samples.

Surface Roughness

An ABB L&W PPS Tester™ SE 115 (Zurich, Switzerland) was used to evaluate roughness of the samples.

Tensile Testing

Tensile index (TI) was determined using a Mullen Tester Model C (Chicopee, MA, USA) and the following equation,

$$TI = TS/G \quad (1)$$

where *TI* is tensile index (N-m/g), *TS* is tensile strength (N/m), and *G* is grammage (g/m^2).

Burst Index

Burst index (BI) was determined using a Mullen Tester Model C (Chicopee, MA, USA) and the following equation,

$$BI = BS/G \quad (2)$$

where *BI* is burst index (kPa-g/m^2), *BS* is bursting strength (kPa), and *G* is grammage (g/m^2).

Tear Index

Tear index (TI) was determined using the Mullen Tester Model C (Chicopee, USA) and the following equation,

$$TI = TS/G \quad (3)$$

where *TI* is tear index (N-m/g), *TS* is tear strength (N/m), and *G* is grammage (g/m^2).

X-ray Photoelectron Spectroscopy (XPS)

A Riber XPS device (Bezons, France) at 12 kV, 14 mA, and spot size of 1 mm was used to characterize the sample. The resolution of the XPS device was 0.3 eV to 4 eV with an acceptance solid angle of 6% of 2π.

Vertical Wicking

The wettability of plasma-treated handsheets and handsheets prepared from plasma-treated pulps was evaluated using vertical wicking. Samples were cut into 2.5 cm × 20.3 cm strips and clipped vertically to a stationary beam. Due to the stiff nature of the strips, no weight was needed to keep the strips vertical. A beaker of room temperature (20 °C) water was elevated beneath the strip just until the strip penetrated the surface. The height of the water in the strip was measured every 15 s for 8 min. Two samples were evaluated for each experimental condition.

RESULTS AND DISCUSSION

Milling of Forced-Air Dried Pulps

Images of the MEP pulps before and after milling are shown in Fig. 2. Milling of the pulps resulted in a less compacted pulp with greater surface area. Because atmospheric pressure plasma treatment is a surface process, increased surface area in the relatively unbonded pulp was expected to increase plasma effects for a given density of pulp relative to bonded handsheets.

(a) (b)

Fig. 2. Photographs of (a) forced-air dried ethanol pulps and (b) forced-air dried and milled ethanol pulps.

Fiber Length of Milled and Unmilled Pulps

The average fiber length of the milled and unmilled samples is displayed in Table 2. Measurements were taken as an arithmetic mean, as well as length- and weight-weighted. The fibers subject to milling did not show a considerable difference in fiber length over unmilled pulps. Differences in fiber length of the MEP/CD milled pulps *vs*. the conventional handsheets were therefore not expected to play a significant role in handsheet properties.

Table 2. Fiber Mean Lengths of Unmilled and Milled Ethanol Pulps

Sample	Fiber Mean Length (mm)		
	Arithmetic	Length-Weighted	Weight-Weighted
Unmilled 1	1.394	2.302	2.760
Unmilled 2	1.357	2.268	2.719
Average	**1.376**	**2.285**	**2.740**
Stdev	**0.026**	**0.024**	**0.029**
Milled 1	1.298	2.279	2.746
Milled 2	1.296	2.286	2.797
Average	**1.297**	**2.283**	**2.772**
Stdev	**0.001**	**0.005**	**0.036**

Density of Handsheets

The density of the final handsheets was evaluated for the MEP, CD, and conventional handsheets (Fig. 3). As expected, the drying history of the pulps made a noticeable difference in their packing and density, with the handsheets dried from water being tightly packed due to the surface tension forces of the water promoting consolidation. In addition, MEP and CD pulps were dried at 100 °C prior to the formation of handsheets. These effects of hornification may have contributed to the reduced density of the MEP and CD handsheets compared to the conventional handsheets (Diniz *et al.* 2004; Luo and Zhu 2011; Kose *et al*. 2016).

In general, plasma treatment decreased the density of the treated pulps, but did not remarkably change the density of the treated handsheets. Atmospheric plasma in a dielectric barrier system does not have deep penetration beyond the outer surface of a material. Therefore plasma treatment of the handsheets resulted in only surface modification, and a change in density was not expected. The structure and density of the handsheets were fixed during the paper making process. In contrast, plasma treatment of the pulps modified the entire fiber surfaces, which in turn modified the compaction of the fibers during papermaking and thus the bulk density of the handsheets.

The nature of the gas was not significant for the MEP handsheets, causing a similar reduction in handsheet density for O_2, CF_4, and C_3F_6 plasma treatments. There was not a clear trend in density with the CD handsheets. Samples treated with CF_4 and C_3F_6 were expected to undergo some oxidation, due to the 99% helium discharge and oxygen contamination from the air and atmospheric conditions, but with the potential for fluorination as well. Optical emission spectroscopy of the CF_4 plasma in similar conditions indicated the presence of excited F atoms that could interact with the pulps (Cornelius 2006). Introduction of fluorine atoms on the pulp could alter fiber packing and increase stiffening of the surface due to the electronegativity of the fluorine atoms.

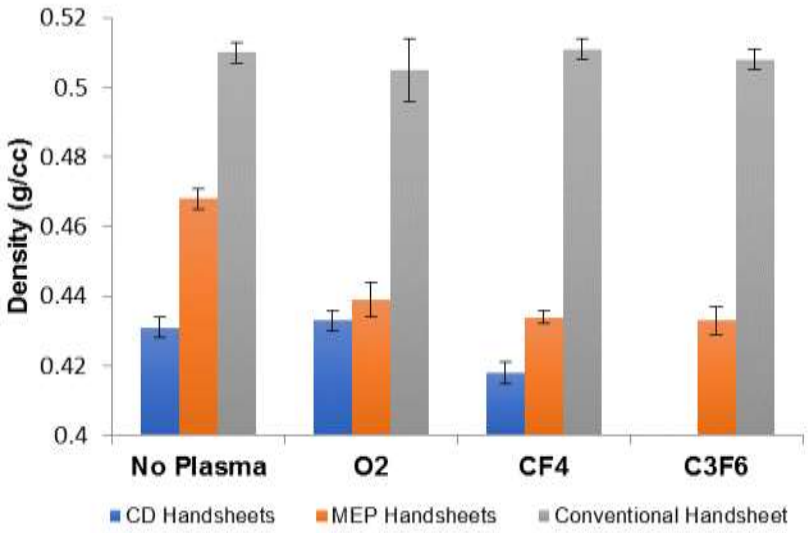


Fig. 3. Effect of plasma treatment on handsheet density (error bars represent standard deviation)

Tensile, Burst, and Tear Indices

Tensile, burst, and tear indices were assessed for the plasma-treated handsheets and the handsheets prepared from the MEP and CD plasma-treated pulps (Figs. 4 through 6). For these properties, the drying history was much more influential in determining handsheet properties than plasma treatment. Conventionally prepared handsheets prepared from pulp not subject to heating and drying, had a noticeably greater tensile, burst, and tear indices than the MEP or LCF handsheets.

Plasma treatment of the conventional handsheets caused little change in comparison to an untreated control for O_2 and CF_4 gas mixtures, and only slight reductions in tear and burst strengths for the C_3F_6 gas. Because tensile, burst, and tear index are all bulk properties and plasma treatment is a surface phenomenon, major changes were not expected for the plasma-treated handsheets, as their bonding structure was set prior to plasma treatment.

For the CD and MEP pulps, the effect of plasma was noticeable. In general, tensile, burst, and tear index decreased when the pulp was treated by plasma. The fact that plasma-treatment of pulps prior to papermaking has more impact on strength properties than plasma treatment of previously made paper is in accordance with the expectation that plasma treatment of pulps impacts bonding and plasma treatment of paper does not. Thus, plasma treatment of previously produced paper can modify exposed surface chemistry and at the same time can avoid the decreased strength seen with pulps.

It was hypothesized that the oxygen plasmas would cause oxidation of the pulps and would increase paper strength due to increased intermolecular interactions, including hydrogen bonding. The C_3F_6 and CF_4 plasmas were expected to cause fluorination, reducing hydrogen bonding and weakening the handsheets due to the presence of the electronegative fluorine atom. The observed data indicate a reduction in strength properties for all plasma compositions, and the reasons are unknown. Atmospheric pressure plasma has been known to cause chain scission and a reduction in molecular weight for polymers (Hwang *et al.* 2004; Matthews *et al.* 2004). This damage to the polymer chain might cause a reduction in tensile properties. It is likely that chain scission, oxidation, and fluorination will be occurring simultaneously and that strength properties reflect the combined effects of these processes.

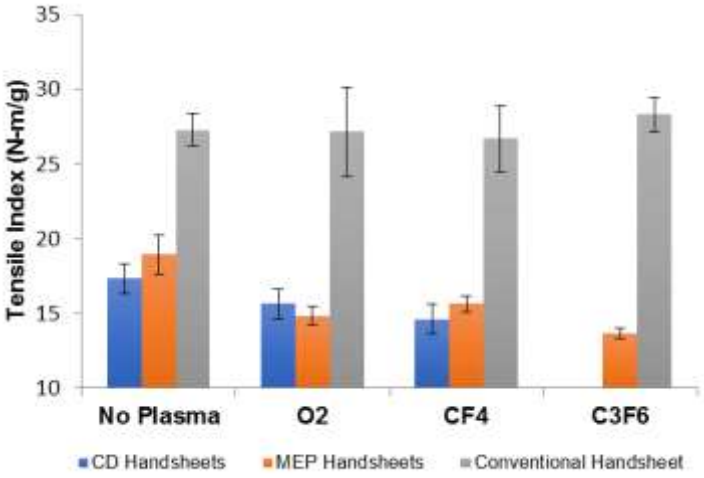


Fig. 4. Tensile index of plasma-treated handsheets and handsheets made from plasma-treated MEP and CD pulps (error bars represent standard deviation)

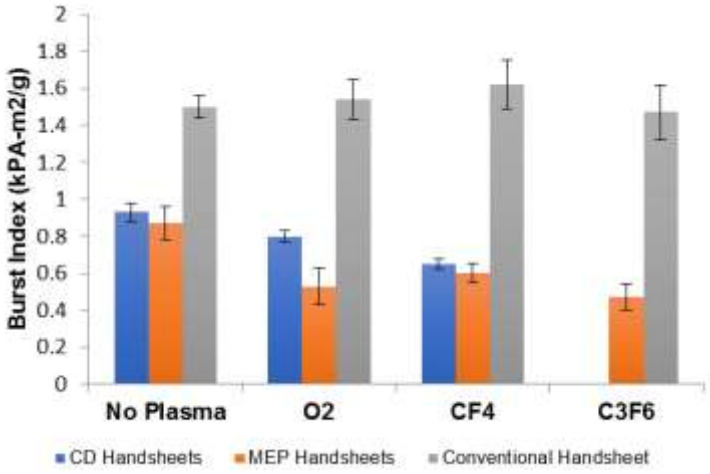


Fig. 5. Burst index of plasma-treated handsheets and handsheets made from plasma-treated MEP and CD pulps (error bars represent standard deviation)

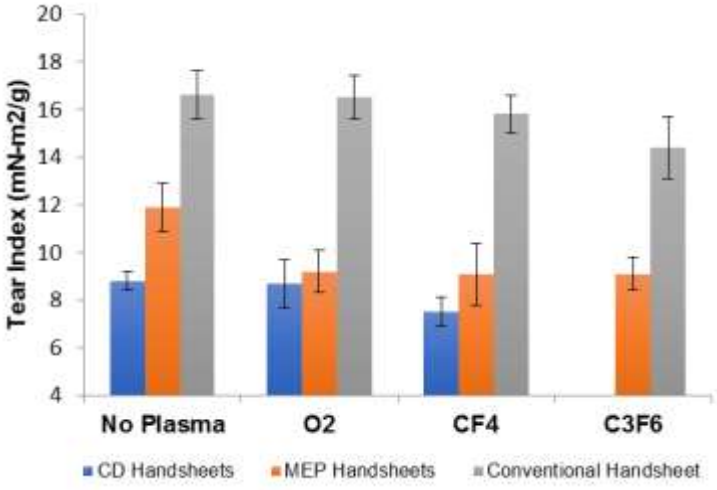


Fig. 6. Tear index of plasma-treated handsheets and handsheets made from plasma-treated MEP and CD pulps (error bars represent standard deviation)

Tensile Index and Density Correlation

Density is expected to correlate strongly with tensile properties. As the density of paper increases, the fibers are more closely packed and have increased bonded area. The expected correlation is shown below (Figs. 7 through 9). This indicates that the consolidation of the paper fiber network, reflected by density, was not affected in a significant way through plasma treatment.

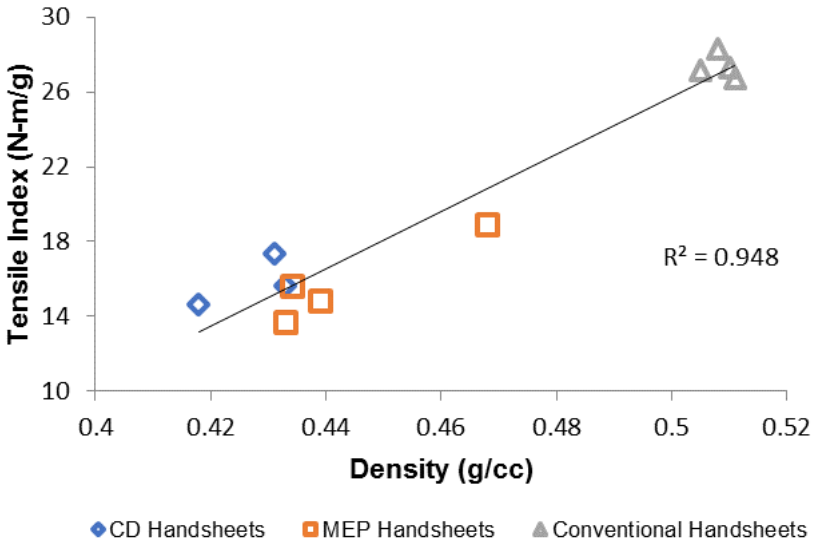


Fig. 7. Tensile index versus density for CD, MEP, and conventional handsheets (error bars represent standard deviation)

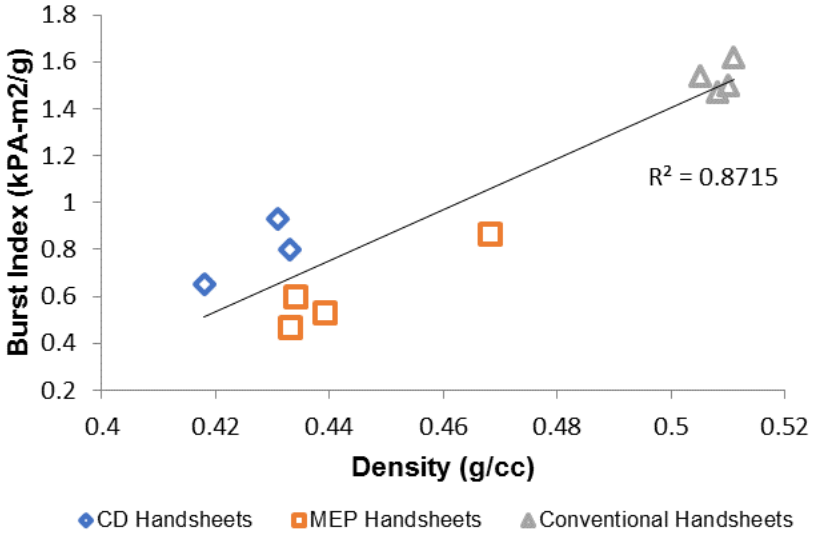


Fig. 8. Burst index versus density for CD, MEP, and conventional handsheets (error bars represent standard deviation)

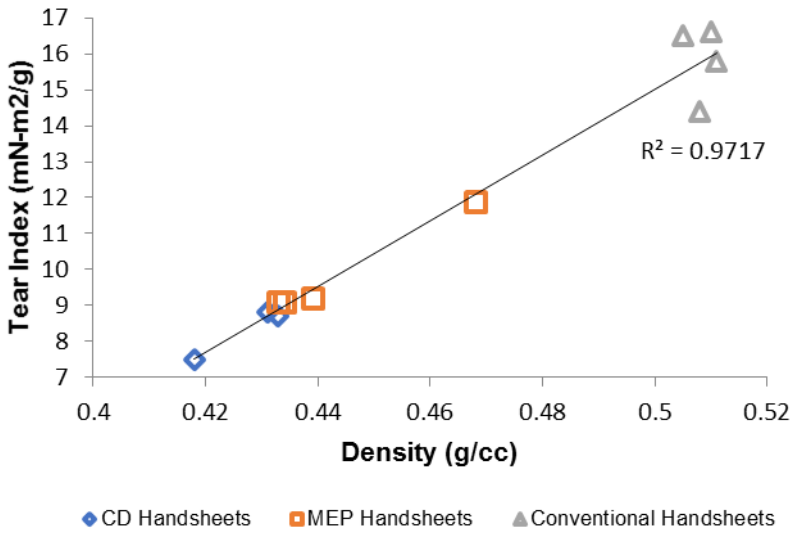


Fig. 9. Tear index versus density for CD, MEP, and conventional handsheets (error bars represent standard deviation)

Surface Roughness

Surface roughness was evaluated for the MEP, CD, and conventional handsheets. As a surface property, the effect of plasma treatment was expected to be more significant on the plasma-treated handsheets than on the plasma-treated pulps, and this was observed (Fig. 10). However, neither CD handsheets nor MEP handsheets were noticeably affected by the plasma treatment.

The surface roughening of paper at the nanometer scale has been observed by AFM on bleached kraft paper and thermomechanical pulp sheets treated at low energy dielectric barrier plasma (Van der Wielen *et al.* 2005). Roughening can be attributed to physical etching processes caused by the nonreactive helium gas (Chapman 1980), and chemical reactions from the oxygen and fluorinated gases (Matthews *et al.* 2005). It is suggested that the etching that occurs with plasma treatment on the various pulps does not survive the wetting and drying process during subsequent papermaking.

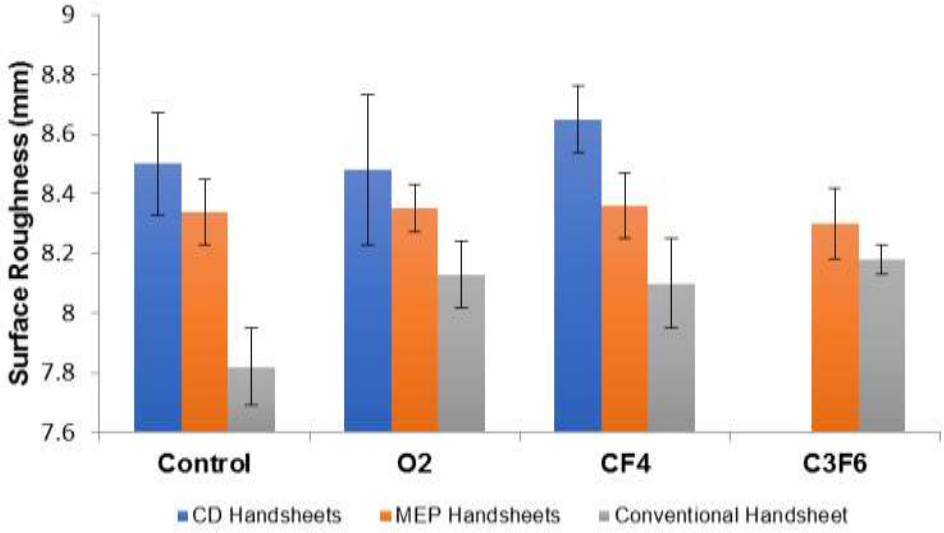


Fig. 10. Surface roughness of plasma-treated handsheets and handsheets made from plasma-treated milled and CD dried pulps (error bars represent standard deviation).

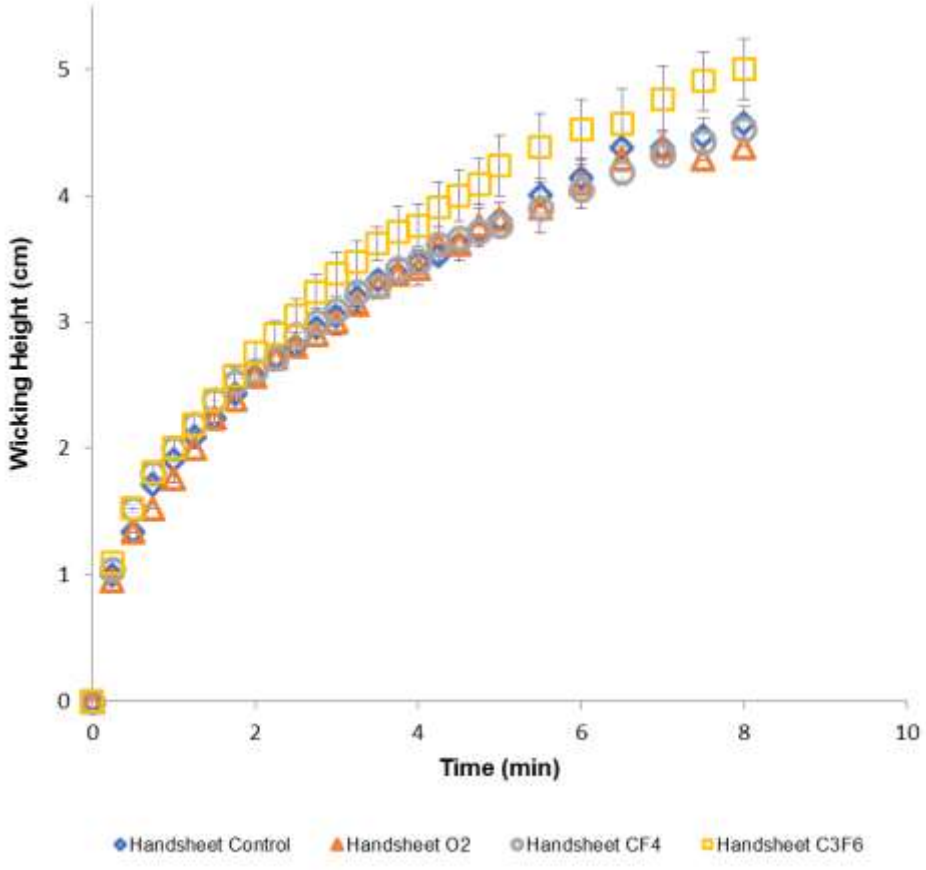
Contact Angle

Contact angles of the MEP, CD, and conventional handsheets were measured to identify any changes in surface functionalities, such as the theorized oxygen or fluorine functional groups. All samples exhibited high surface tension and absorbed or spread all applied liquids before a contact angle could be measured. Thus, the contact angle test was not sensitive enough to measure changes in hydrophilicity. Also, the test did not indicate the presence of fluorine atoms in concentrations high enough to affect a noticeable increase in contact angle.

Wicking

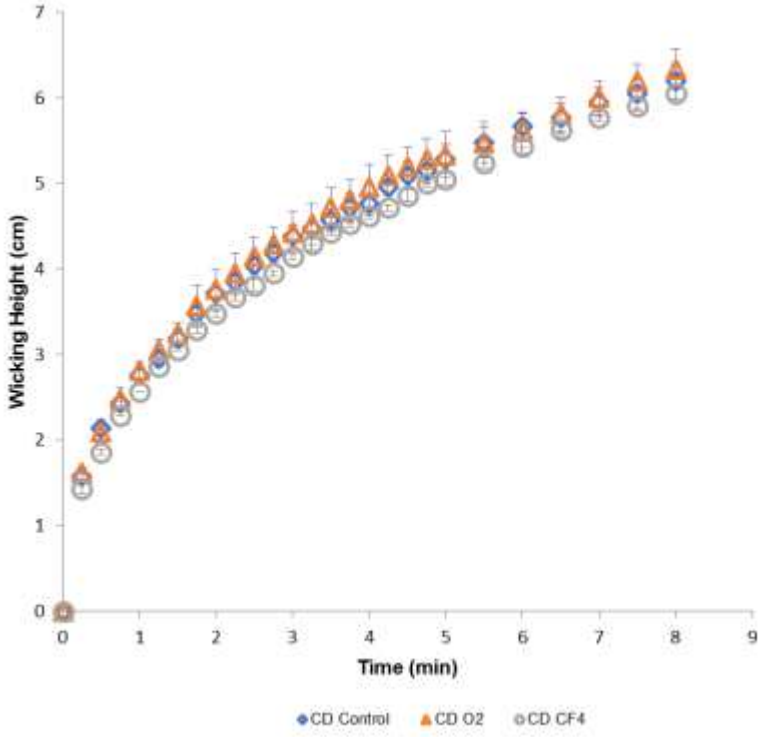
Wickability of the handsheets was also examined to observe changes due to plasma treatment and pulp processing conditions. Graphs of the wicking for each pulp processing treatment are shown below (Fig. 11).

The nature of the gas was significant for each individual pulp processing condition. C_3F_6 plasma had the greatest effect on wicking, increasing wickability considerably for both the conventional and MEP handsheets. Plasma treatment by the O_2 and CF_4 plasma increased wicking equally for the MEP and CD handsheets, but was indistinguishable from the control for the conventional handsheets.



(a)

Fig. 11 (a). Wicking of (a) plasma-treated handsheets, (b) handsheets made from plasma-treated CD pulps, and (c) handsheets made from plasma-treated MEP pulps (error bars represent standard deviation)



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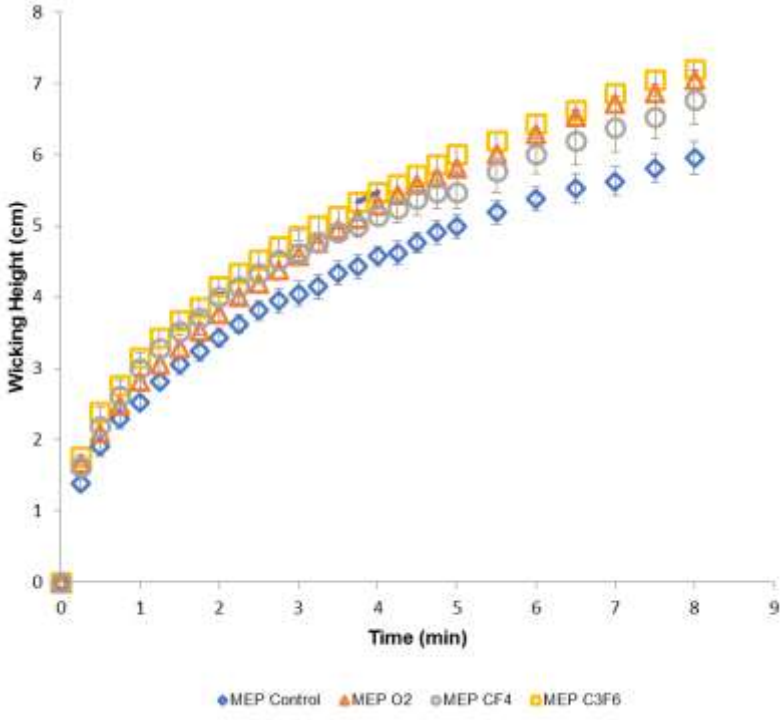

(c)

Fig. 11. Wicking of (a) plasma-treated handsheets, (b) handsheets made from plasma-treated CD pulps, and (c) handsheets made from plasma-treated MEP pulps (error bars represent standard deviation)

Pulp preparation was more significant in modifying wicking properties than plasma treatment. The average values for wicking height and initial slope for the various pulp preparations is shown in Table 3. Conventionally prepared handsheets wicked significantly slower than the CD and MEP handsheets. MEP handsheets wicked marginally better than the CD handsheets, with a slightly higher initial slope and maximum wicking height.

Wicking Height and Density Correlation

Wickability is the ease in which water can migrate between interfiber capillaries. Washburn's equation, generally used for wicking applications, indicates that larger capillaries will transport water more rapidly,

$$L^2 = \frac{\gamma D t}{4\eta} \cos\theta \quad (4)$$

where L is the depth of penetration (m), η is the viscosity of the penetrating liquid (mPa.s), γ is the surface tension (N/m), D is the average pore diameter (m), $\cos\theta$ is the contact angle between liquid and solid (radians), and t is the time required for penetration (s).

In contrast, researchers in the textile industry have found that smaller capillaries of cellulosic fibers may wick more rapidly than predicted by Washburn's Equation. This is attributed to the 'holding' capacity rather than 'transporting' capacity of the capillary radii (Raheel and Giz 1985).

For this experiment, the density of the handsheets was inversely proportional to the wickability (Fig. 11). This suggests that Washburn's equation applies for this set of data if the pore size and density are inversely related.

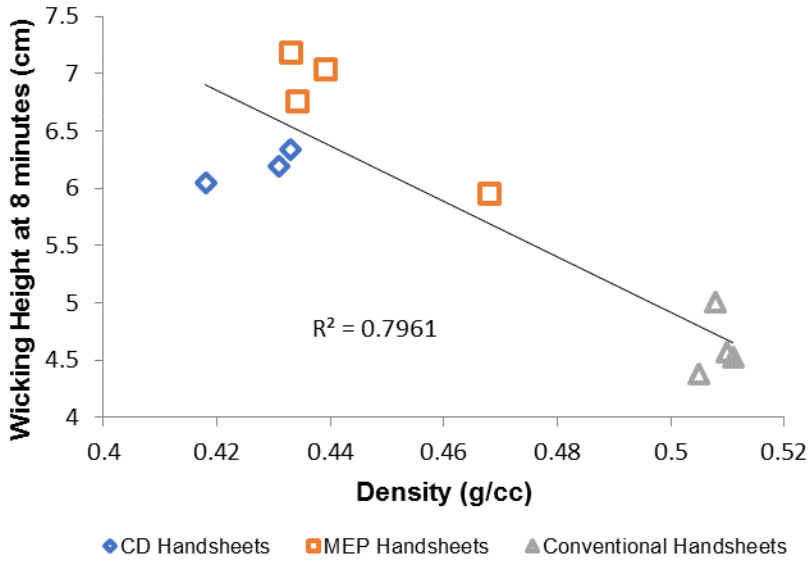

Fig. 12. Wicking height at 8 min *versus* density for CD, MEP, and conventional handsheets

X-ray Photoelectron Spectroscopy (XPS)

XPS was conducted on selected plasma-treated conventional handsheets as well as handsheets created from the MEP pulp (Table 4). Treatment by O_2, CF_4, or C_3F_6 plasma altered the oxygen to carbon concentration for both MEP and conventional handsheets. The MEP handsheets were made from plasma-treated pulp, and therefore the surface

distribution of elements revealed by XPS should be representative of the fiber surfaces throughout the bulk of the paper. In contrast, conventional handsheets treated with plasma after handsheet formation should have altered surfaces primarily.

Oxygen plasma treatment increased the oxygen content of the MEP handsheets and the conventional handsheets by about 2% and 3%, respectively. This indicates the generation of oxygen functionalities such as –OH, C=O, and –COOH that has been observed by other researchers (Toth *et al.* 2007; Kamel *et al.* 2011; Zhang *et al.* 2017). Replacement of the O_2 gas by CF_4 reduced the O/C ratio in the handsheet samples but increased it for the MEP samples. This can be attributed to air impurities present in the plasma due to atmospheric pressure processing conditions.

Although no surface fluorine was observed on the MEP samples, the plasma-treated conventional handsheets treated with CF_4 revealed a fluorine content of 2.7%.

Table 4. Relative Intensities of Chemical Composition of the MEP and Conventional Handsheets (HS)

Sample	C 1s Percent	O 1s Percent	N 1s Percent	F 1s Percent	O/C
HS Control	*62.62*	*37.38*	*0.00*	*0.00*	*0.60*
HS O_2	*60.79*	*39.21*	*0.00*	*0.00*	*0.65*
HS CF_4	*61.87*	*35.23*	*0.20*	*2.71*	*0.57*
MEP Control	*56.89*	*43.11*	*0.00*	*0.00*	*0.77*
MEP O_2	*54.71*	*45.29*	*0.00*	*0.00*	*0.83*
MEP CF_4	*55.52*	*44.48*	*0.00*	*0.00*	*0.80*
MEP C_3F_6	*57.17*	*42.83*	*0.00*	*0.00*	*0.75*

CONCLUSIONS

1. Despite changes observed in the handsheets due to plasma treatment, pulp processing conditions (drying directly from water, ethanol exchange, super critical carbon dioxide exchange, and heating) impacted properties more significantly in all cases than did plasma treatment.
2. Plasma treatment of fully bleached wood pulps prior to papermaking modified bulk and surface properties in paper, whereas plasma treatment of handsheets affected surface properties more significantly.
3. Pulp preparation methods, *i.e.*, ethanol exchanged, CO_2-ethanol exchanged, or standard processing including drying directly from water, contributed significantly to tensile properties, density, and wicking.
4. The density and tensile index of paper made from plasma treated pulps was lower than for paper made from untreated pulp. Treatment of already formed paper with plasma did not change the density or tensile index of the paper.

REFERENCES CITED

Bente, M., Avramidis, G., Forster, S., Rohwer, E. G., and Viol, W. (2004). "Wood surface modification in dielectric barrier discharges at atmospheric pressure for creating water repellent characteristics," *Holz Roh Werkst* 62, 157-163. DOI: 10.1007/s00107-004-0475-0

Borcia, G., Anderson, C. A., and Brown, N. M. D. (2003). "Dielectric barrier discharge for surface treatment: Application to selected polymers in film and fibre form," *Plasma Sources Science and Technology* 12(3), 335-344. DOI: 10.1088/0963-0252/12/3/306/meta

Carlsson, C., and Strom, G. (1994). "Improved wettability of chemithermomechanical pulp by oxygen plasma treatment," *Nordic Pulp and Paper Research* 9(1), 72-75. DOI: 10.3183/NPPRJ-1994-09-02-p072-075

Carlsson, C., and Strom, G. (1995). "Water sorption and surface composition of untreated or oxygen plasma-treated chemical pulps," *Nordic Pulp and Paper Research* 10(1), 17-23. DOI: 10.3183/NPPRJ-1995-10-01-p017-023

Chapman, B. (1980). "Plasma etching," in: *Glow Discharge Processes: Sputtering and Plasma Etching*, John Wiley and Sons, Hoboken, NJ, USA.

Cornelius, C. E. (2007). *Atmospheric Plasma Characterization and Mechanisms of Substrate Surface Modification*, Ph.D. Dissertation, North Carolina State University, Raleigh, North Carolina, USA.

Diniz, J., Gil, M., and Castro, J. (2004). "Hornification: Its origin and interpretation in wood pulps," *Wood Science and Technology* 37, 489-494. DOI: 10.1007/s00226-003-0216-2

Henins, P., Herrmann, H., and Selwyn, G. (2000). "Neutral bremsstrahlung measurement in an atmospheric-pressure radio frequency discharge," *Physics of Plasmas* 7(8), 3141-3144.

Hochar, F., De Jaeger, R., and Levalois-Grutzmacher, J. (2003). "Graft-polymerization of a hydrophobic monomer onto PAN textile by low-pressure plasma treatments," *Surface and Coatings Technology* 165(2), 201-210. DOI: 10.1016/S0257-8972(02)00577-7

Hwang, Y. J., Matthews, S., McCord, M., and Bourham, M. (2004). "Surface modification of organic polymer films treated in atmospheric plasmas," *Journal of the Electrochemical Society* 151,C495-C4501. DOI: 10.1149/1.1756891

Kamel, M. M., Zawahry, M. M., Helmy, H. H., and Eid, M. A. (2011). "Improvements in the dyeability of polyester by atmospheric pressure oxygen plasma treatment," *The Journal of the Textile Institute* 102(3), 220-231. DOI: 10.1080/00405001003672366

Kose, R., Yamaguchi, K., and Okayama, T. (2016). "Preparation of fine fiber sheets from recycled pulp fibers using aqueous counter collision," *Cellulose* 23, 1393-1399. DOI: 10.1007/s10570-016-0874-5

Lieberman, M. A., and Lichtenberg, A. J. (2005). "Introduction," in: *Principles of Plasma Discharges and Materials Processing* (2nd ed.), John Wiley and Sons, Hoboken, NJ, USA.

Luo, X., and Zhu, J. (2011). "Effects of drying-induced fiber hornification on enzymatic saccharification of lignocelluloses," *Enzyme and Microbial Technology*, 48, 92-99. DOI: 10.1016/j.enzmictec.2010.09.014

Matthews, S. R., Hwang, Y. J., McCord, M. G., and Bourham, M. A. (2004). "Investigation into etching mechanism of polyethylene terephthalate (PET) films

treated with helium and oxygenated helium atmospheric plasmas," *Journal of Applied Polymer Science* 94(6), 2383-2389. DOI: 10.1002/app.21162

Matthews, S. R., McCord, M. G., and Bourham, M. A. (2005). "Poly(vinyl alcohol) desizing mechanism via atmospheric pressure plasma exposure," *Plasma Process Polymers* 2(9), 702-708. DOI: 10.1002/ppap.200500056

Mori, M., Uyama, Y., and Ikada, Y. (1994). "Surface modification of polyethylene fiber by graft polymerization," *Journal of Polymer Science: Part A Polymer Chemistry* 32(9), 1683-1690. DOI: 10.1002/pola.1994.080320910

Nema, S., and Jhala, P. (2015). "12.4.1 World status" in: *Plasma Technologies for Textiles and Apparel*, CRC Press, Boca Raton, FL, USA.

Pelache, M., Delgado-Aguilar, M., Alcala, M., Puig, J., Blanco, A., and Mutje, P. (2016). "New strategy for the production of packaging from recycled fibers." *Cellulose Chemistry and Technology* 50(3-4), 449-454.

Pykonen, M., Sundqvist, H., Kaukoniemi, O. V., and Tuominen, M. (2008). "Ageing effect in atmospheric plasma activation of paper substrates," *Surface & Coating Technology* 202(16), 3777-3786. DOI: 10.1016/j.surfcoat.2008.01.035

Raheel, M., and Giz, E. C. (1985). "Effect of fabric geometry on resistance to pesticide penetration and degradation," *Archives of Environmental Contamination Toxicology* 14(3), 273-279. DOI: 10.1007/BF01055403

Roth, R., Nourgostar, S., and Bonds, T. (2007). "The one atmospheric glow discharge plasma (OAUGDP)-a platform technology for the 21st century," *IEEE Transactions on Plasma Science* 35(2), 233-250. DOI: 10.1109/TPS.2007.892711

Shenton, M. J., and Stevens, G. C. (2001). "Surface modification of polymer surfaces: Atmospheric plasma versus vacuum plasma treatments," *Journal of Physics D: Applied Physics* 34(18), 2761-2768. DOI: 10.1088/0022-3727/34/18/308/pdf

Toth, A., Cernakova, L., Cernak, M., and Kunovska, K. (2007). "Surface analysis of roundwood paper treated by diffuse coplanar surface barrier discharge (DCSBD) type atmospheric plasma in air and in nitrogen," *Holzforschung* 61(5), 528-531. DOI: 10.1515/HF.2007.080

Tsafack, M. J., and Levalois-Grutzmacher, J. (2007). "Towards multifunctional surfaces using the plasma-induced graft-polymerization (PIGP) process: Flame and waterproof cotton textiles," *Surface and Coatings Technology* 201(12), 5789-5795. DOI: 10.1016/j.surfcoat.2006.10.027

Vander Wielen, L. C., Elder, T., and Ragauskas, A. J. (2005). "Analysis of the topochemical effects of dielectric-barrier discharge on cellulosic fibers," *Cellulose* 12, 185-196. DOI: 10.1007/s10570-004-2785.-0

Vander Wielen, C. L., Ostenson, M., Gatenholm, P., and Ragauskas, A. J. (2006). "Surface modification of cellulosic fibers using dielectric-barrier discharge," *Carbohydrate Polymers* 65(2), 179-184. DOI: 10.1016/j.carbpol.2005.12.040

Virk, R. K., Ramaswamy, G. N., Bourham, M. A., and Bures, B. (2004). "Plasma and antimicrobial treatment of nonwoven fabrics for surgical gowns," *Textile Research Journal* 74(12), 1073-1079. DOI: 10.1177/004051750407401208

Wafa, D. M., Breidt, F., Gawish, S. M., Matthews, S. R., Donohue, K. V., Roe, R. M., and Bourham, M. A. (2006). "Atmospheric plasma-aided biocidal finishes for nonwoven polypropylene fabrics. II. Functionality of synthesized fabric," *Journal of Applied Polymer Science* 103(3), 1911-1917. DOI: 10.1002/app.24042

Wolf, R. (2004). "Plasma treatment boosts adhesion," (http://www.adhesivesmag.com/articles/84478-plasma-treatment-boosts-adhesion),

Accessed 28 February 2017.
Zhang, C., Zhao, M., Wang, L., Qu, L., and Men, Y. (2017). "Surface modification of polyester fabrics by atmospheric pressure air/He plasma for color strength and adhesion enhancement," *Applied Surface Science* 400, 304-311. DOI: 10.1016/j.apsusc.2016.12.096

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