Effects of Atmospheric Pressure Plasma Activation on Inkjet Print Quality

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Abstract

This work concerns the suitability of atmospheric plasma activation for the modification of paper and polymer surfaces and its ability to improve inkjet print quality of conventional non-inkjet printing papers and polymer films.

In this work pigment coated and surface sized papers, PE and PP films were modified using two kinds of atmospheric plasma equipment; one at the pilot scale and one at the laboratory scale. The pilot scale plasma activation was also compared to conventional corona treatment. The changes in the surface chemistry were measured using X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance infrared spectrometry (FTIR-ATR). In addition, the surface energy was estimated by contact angle measurements. The topographical changes were measured using atomic force microscopy (AFM). The substrates were printed with different ink types with an inkjet printing system simulating industrial production and print quality and rub resistance were measured. Furthermore, the correlation between surface property changes and inkjet print quality are presented and discussed.

The treatments oxidized the surface of the substrates increasing the base and the polar components of the surface energy. The conventional corona treatment gave higher surface energy and oxidation level than the nitrogen and helium plasma activations. The laboratory scale plasma activation was the most efficient one, because of the longest treatment time. Inkjet print quality of PE film clearly improved due to treatments. On the contrary, print quality of PP film worsened. Treatments for the paper substrates lead to relatively small changes.

Introduction

Plasma is a state of ionized gas, consisting of excited atomic, ionic, molecular, and free-radical species. Atmospheric plasma treatment has raised interest in recent years, because non-thermal industrial plasma processing provides a possibility to develop a new dry surface modification method based on roll-to-roll processing. The plasma modifies only the outermost atomic layers without affecting bulk properties, such as mechanical strength and optical response. Plasma activation changes the surface chemistry of a substrate by adding or forming molecular fragments. Plasma parameters, such as power, duration, pressure, temperature and flow rate of gases, all influence the final plasma treatment result [1, 2].

The current trend in plasma processing is to develop atmospheric plasma sources, because vacuum processing increases the capital cost and requires batch processing [2]. Few literature references consider the effects of atmospheric pressure plasma treatment on inkjet printability, although the option for corona treatment already exists in some industrial inkjet printing presses. Currently, corona treatment is mostly exploited for polymer surfaces. The drawbacks of the corona treatment, such as the treatment's low uniformity and occurrence of undesired back side effects, are emphasized by porous and rough paper substrates. Plasma activation is believed to yield more uniform treatment than corona. Both corona treatment and plasma activation increase surface energy and hydrophilicity of a substrate, whereas with plasma deposition it is also possible to create hydrophobic surfaces [1]. Ivutin et al. [3] plasma-etched papers, which were coated by modified calcium carbonate pigments. Plasma-etching increased the hydrophilicity, and did not change the porous structure. The surface chemical modification was suggested to improve image quality with water based inks in inkjet printing [2]. Lahti [4] investigated the effects of corona treatment on electrophotographic printability. Surface energy and toner adhesion measurements demonstrated that corona treatment improves the printability of extrusion coated paperboards. The impact of corona treatment and plasma activation has also been studied for flexographic printing [e.g. 5–7]. For example, Mesic et al. [5] found that corona treatment improves printability and had significance on rub resistance of extrusion coated PE board with water based inks.

The surface properties of printing substrates, such as surface energy, charge, roughness and porosity, are important elements in inkjet print quality [8]. However, it is the interactions between the ink and the substrate that define the final print quality [9]. Spreading of the ink droplets on the surface of the substrate depends predominantly on the surface chemistry and energy in relation to the surface tension of the ink [10]. Therefore, modifying the surface properties by plasma activation is expected to influence both the affinity and ink absorption in inkjet printing. The objective of the current work was to understand which chemical changes occur on plastic and paper substrates when treated with atmospheric plasma, and furthermore understand the influence of the changes on inkjet printability.

Experimental work

A number of substrates were treated with corona and atmospheric plasma in pilot and laboratory scales. The surface energy, surface chemistry and surface topography as well as inkjet print quality were measured within one week from the treatments.

Substrates and Surface Treatments

Commercially available pigment coated and surface sized papers, and polyethylene and polypropylene films were treated with both conventional corona treatment and with novel plasma activation in pilot scale. The parameters of the treatment equipment are given in table 1. In plasma activation, gas (here, nitrogen and helium gases were used) is fed to an electric field between the electrodes being arranged above a web. The gas ionizes after which the created plasma is blown onto the substrate surface. In the conventional corona treatment plasma state occurs between two electrodes, in which the other is a grounded metal roll under the web. In corona treatment no feed gases are used.

The paper substrates were also treated with a laboratory scale atmospheric dielectric barrier discharge plasma apparatus, the parameters of which are given in table 1. The created plasma was blown from the apparatus onto the paper surface with pressured air.

Table 1. Parameters of plasma equipment.

Parameter	Pilot scale treatments	Lab. scale plasma treatment
Treatment power	2 kW	300 W
Voltage	22.5–25 kV	1kV
Frequency	21.5–25 kHz	16–20 kHz
Flame temperature	–	~250 ºC
Treatment width	370 mm	10–35 mm
Air gap	2 mm	10 mm
Treatment speed	20 m/min	0.45 m/min

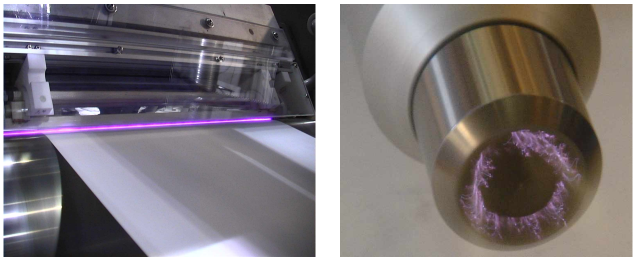

Figure 1. *Pilot and laboratory scale plasma equipment.*

Surface Energy and tension

Contact angle measurements were performed using a KSV CAM 200 Optical Contact Angle Meter at controlled atmosphere (50% RH, 20ºC) with probe liquids shown in table 2. Results are given as an average value of at least three measurements. The surface energy of the substrates, including dispersive and polar components, were calculated using the Fowkes equation. Acid and base properties were determined with the van Oss equation. The surface tension of inkjet inks was measured with a Sigma 70 Tensiometer using the Du Nouy ring method.

Table 2. Surface tension components (mJ/m²) for probe liquids at 20ºC. Surface free energies were determined using all liquids and probe liquids marked with asterisk were used for determination of acid and base components.

Probe liquid	γ	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}
Water*	72.8	21.8	51	25.5	25.5
Ethylene glycol*	48	29	19	1.92	47
Tricresyl phosphate	40.9	39.2	1.7	–	–
Formamide*	58	39	19	2.28	39.6
Diiodomethane	50.8	50.8	≈0	–	–

Surface Chemistry by XPS and FTIR-ATR

The changes in chemical composition of the substrate surfaces due to treatments were determined with XPS using a Physical Electronics Quantum 2000 ESCA instrument, equipped with a monochromatic Al $K\alpha$ X-ray source, operated at 25 W of power. Three different spots were measured in each sample. The pass energy for the survey spectra was 184 eV, and the measurement time was five minutes. For high resolution C1s spectra the pass energy was 23.5 eV and measurement time 10 minutes. The high resolution spectra were measured only from paper substrates. Curve fitting (deconvolution) of high resolution C1s peaks was performed using a Shirley background, Gaus-Lorentzian character and full width at half-maximum (FWHM) of 1.3-1.7 eV. Binding energy (BE) of all spectra was related to C1 (C-C, C-H) at 285 eV. The following chemical shifts relative to the C1 position were employed for the respective groups; 1.7 ± 0.2 eV for C2 (C-O), 3.1 ± 0.3 eV for C3 (C=O, O-C-O), 4,6 ± 0,3 eV for C4 (O=C-O) and 5 eV for C5.

FTIR-ATR measurements of the paper substrates were performed using a Perkin–Elmer Spectrum instrument. FT-IR spectrometer equipped with deuterated trygline sulfate detector and coupled to a DuraSample diamond crystal accessory was used. The spectral resolution was 4 cm^{-1} and the number of scans was 32. A minimum of three different spots were analyzed on each sample.

Surface Topography by AFM

The AFM images were recorded with a Nanoscope IIIa AFM (Digital Instruments Veeco Metrology Group, Santa Barbara, CA). All the images were recorded in tapping mode using silicon cantilevers with a resonance frequency between 320 and 340 kHz. The scan rate was typically 0.3 – 1 Hz. The free tapping amplitude was set to 70±5 nm, and a damping ratio between 0.65-0.85 was used. The Scanning Probe Image Processor (SPIP, Image Metrology, Denmark) software was used for the surface roughness analysis of the images.

Inkjet Printability

Inkjet printing was carried out with industrial piezoelectric printheads having an 80 pL drop volume, at 360 dpi resolution and a printing speed of 0.05 m/s. The inkjet printing equipment is shown in figure 2. Three black inks were used on the paper substrates: solvent based pigment ink, solvent based dye ink and water based pigment ink. The polymer films were printed using the two solvent based inks.

The samples were analyzed for their visual print quality and rub-off resistance. Visual print quality was analyzed by measuring properties of the printed lines (line width, edge raggedness) and properties of the 100% black compact areas (optical density, unevenness). Rub-off resistance was tested with a Taber Rotary

Platform Abraser (CS-10F abrasive wheels, 40 revolutions, and 2 x 150g counterweights). Rub-off resistance was quantified as a difference in optical density of the printed pre- and post-test samples.

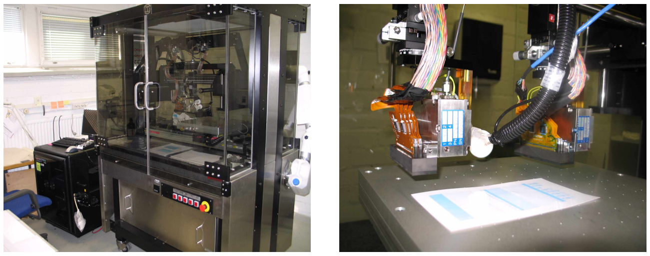

Figure 2. *Inkjet printing equipment.*

Results

Surface Properties

Corona treatment and plasma activation increased the surface energy of the samples. The polar component increased as shown in figures 3-6, and the increase of the polar component was mainly due to the base component. The treatments hence rendered the surface of the substrates more hydrophilic and increased the ink-substrate polar interactions, especially regarding inks being acidic in nature. For paper samples, the conventional corona treatment was found to cause a larger surface energy and polarity change than the novel plasma activation. However, the laboratory scale plasma activation yielded the largest changes, most probably due to the longest treatment time. Furthermore, the paper samples differed in that the pigment coated paper was most dependent on the treatment method whereas for the sized paper both plasma treatments yielded a similar result. For the polymer films the change in surface chemistry was independent on the plasma treatment method, but the helium plasma treatment yielded the largest change in the base component. In general, the impact of all treatments on surface energy was weaker with polymer films than with paper substrates. It may hence be concluded that the surface composition of the substrate influences the effectiveness of the treatment.

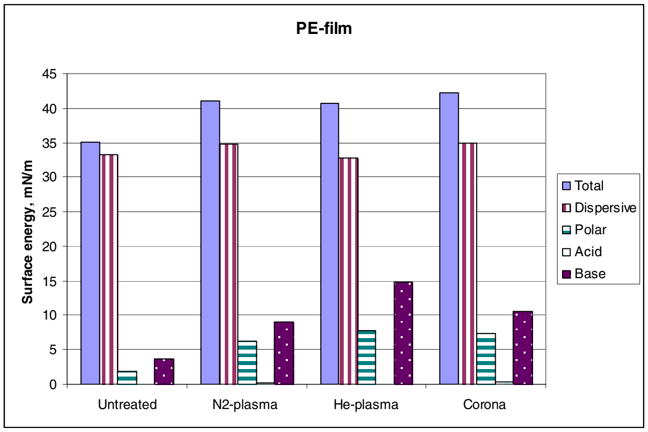

Figure 3. *Surface energy components for the PE film.*

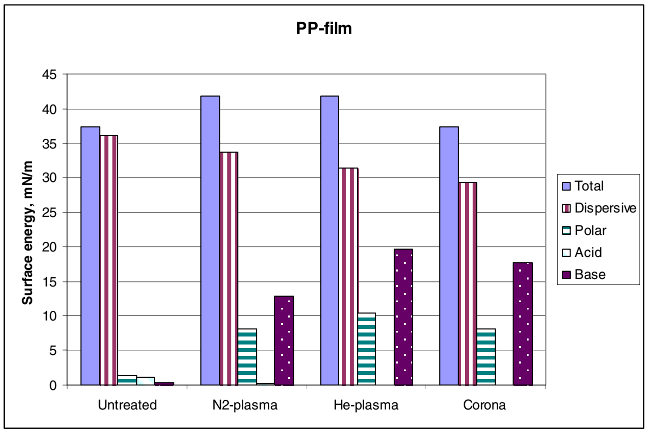

Figure 4. *Surface energy components for the PP film.*

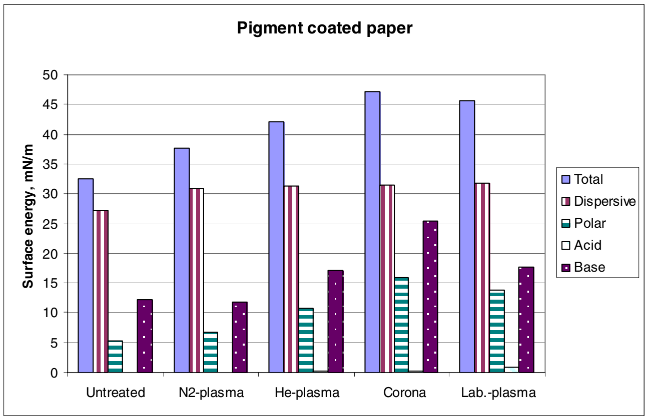

Figure 5. *Surface energy components for the pigment coated paper.*

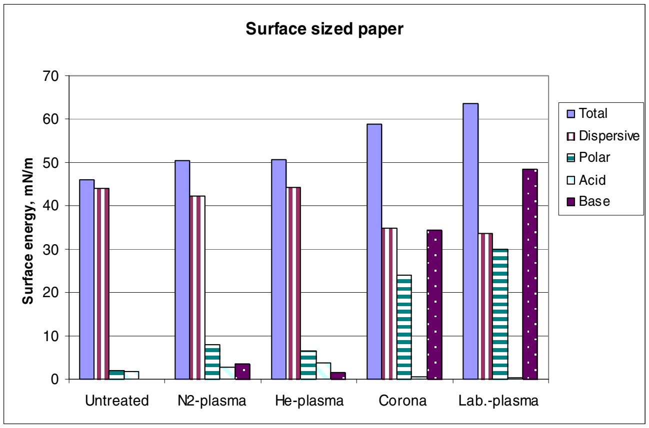

Figure 6. *Surface energy components for the surface sized paper.*

It is a well-known fact that surface energy of a substrate to be printed should be about 10 mN/m higher than that of the ink to achieve good affinity between the substrate and the ink [e.g. 5, 6]. For this reason the surface tension of water based inks is typically reduced with surfactants. The surface tension of the inks used here was between 22 mN/m and 27 mN/m (table 3). The surface energy of the untreated PE film was 35 mN/m and that of the PP film 37.5 mN/m, both values are higher than those reported in literature (30–

31mN/m and 29–31 mN/m respectively [4]). Part of these differences may arise from differences in determining the surface energy, or be explained by different pretreatment of the polymer films. Anyhow, since the surface energy of already the untreated substrate was higher than the surface tension of all the studied inks, hence fulfilling the basic energetic requirement set for the paper-ink compatibility, the plasma treatment was expected to rather enhance the inkjet printability than enable it.

Table 3. Surface tension of the inks.

Ink type	Surface tension, mN/m	Stdev.
Solvent based dye ink	22.1	0.1
Solvent based pigment ink	24.1	0.1
Water based pigment ink	26.8	0.02

XPS results showed that all treatments oxidized the surface as can be seen in figure 7. The corona treatment was the most powerful treatment in the pilot scale. However, the laboratory scale plasma activation with the longest treatment time caused the largest changes in the O/C ratio. The oxidation of the paper surfaces was more pronounced compared to the polymer films. According to the survey spectra, the nitrogen content was not increased by the treatments. The increase of the molecular groups arising from the feed gas ingredients is typical in low-pressure plasma treatments. However, in atmospheric treatments oxygen in the air seems to be more reactive and preferentially reacts with the surface. This may explain why there were no significant differences between the helium and nitrogen plasma activations.

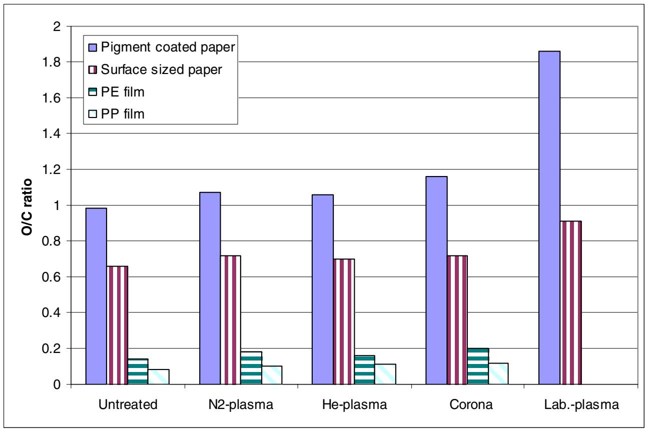

Figure 7. *O/C ratio for the substrates.*

High resolution C1s and FTIR-ATR spectra were measured from paper substrates. According to Table 4, the laboratory scale plasma treatment caused a change of surface chemical composition different from all the other treatments. The pilot scale treatments mainly decreased the C1 peak and increased particularly C3 peak. The laboratory scale plasma activation decreased clearly both C1 and C2 and increased particularly C4–C5 peaks. The C2 peak corresponds to ethers, alcohols and peroxides. The C3 peak is related to ketones and aldehydes, whereas the C4 peak includes carboxyl and ester groups. The C5 peak indicates carbonate groups from calcium carbonate pigment. Again, the difference between pilot and laboratory scale treatments can be explained by different treatment times. It seems that with longer treatment time also C2 peak, in addition to C1, starts to oxidize leading to more than two bonds with oxygen.

FTIR-ATR provides specific identification between the functional groups. The most significant differences between the spectra of treated and untreated samples were in the bands centered at 1730 cm^{-1} and 1640 cm^{-1}. The absorbance band in 1730 cm^{-1} is from ester groups, and the wide band near 1640 cm-1 is from carboxylate anions ($-COO^{-}$) [11]. According to the FTIR-ATR results, the plasma activation seems to break up the ester groups and forms carboxylate anions.

Table 4. Relatively portion of the molecular groups according to high resolution C1s spectrums.

Sample	C1 [%] C–C, C–H, C=C	C2 [%] C–O, C–OH, C–O–C	C3 [%] C=O, O–C–O	C4 [%] O–C=O	C5 [%] CO_3^{2-}
Untreated pigment coated paper	73.4	13.0	1.6	9.1	2.9
N_2-plasma treated	67.2	15.0	4.0	10.7	3.1
$\Delta_{N2\text{-plasma}}$	-6.20	2.00	2.39	1.65	0.16
He-plasma treated	65.4	16.4	4.7	10.3	3.3
$\Delta_{He\text{-plasma}}$	-7.96	3.33	3.07	1.16	0.41
Corona treated	63.0	16.5	5.7	11.3	3.5
Δ_{Corona}	-10.39	3.50	4.11	2.19	0.59
Lab.-plasma treated	62.9	9.1	3.0	16.6	8.5
$\Delta_{lab.\ plasma}$	-10.50	-3.94	1.39	7.46	5.60
Untreated surface sized paper	29.5	51.2	15.6	3.8	
N_2-plasma treated	27.3	49.2	18.7	4.9	
$\Delta_{N2\text{-plasma}}$	-2.22	-2.02	3.12	1.13	
He-plasma treated	27.0	51.7	16.7	4.7	
$\Delta_{He\text{-plasma}}$	-2.50	0.48	1.12	0.89	
Corona treated	27.8	49.8	17.0	5.5	
Δ_{Corona}	-1.69	-1.41	1.41	1.70	
Lab.-plasma treated	28.5	42.2	15.7	13.7	
$\Delta_{lab.\ plasma}$	-1.02	-9.01	0.15	9.88	

According to the AFM results, the pilot scale plasma activation increased slightly the root mean square (RMS) roughness, S_q, at micro scale for pigment coated paper (Fig. 8). Also here, the longest treatment time involving the laboratory scale treatment resulted in the largest roughness change. However, RMS roughness did not change for surface sized paper. It should be noted that the roughness of the surface sized paper was much higher than that of the pigment coated paper, which made it difficult to resolve the treatment induced changes.

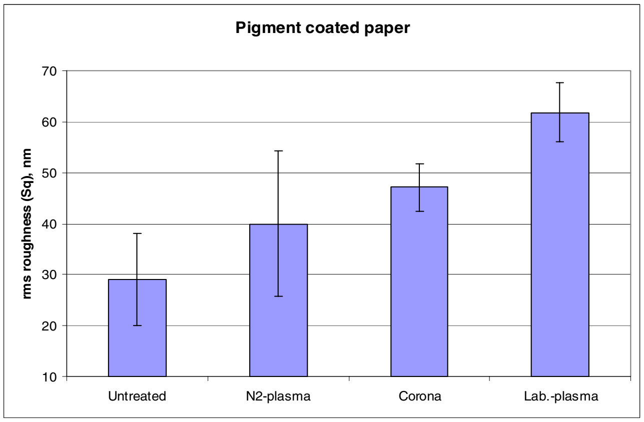

Figure 8. *Microscale roughness for the pigment coated paper.*

Printability

On PE film, pilot scale plasma and corona treatment improved inkjet print quality and on PP film degraded it. This was clearly seen by analyzing the printed lines (Fig. 9). The line width decreased for solvent based pigment ink on treated PE film, the differences being negligible on PP film.

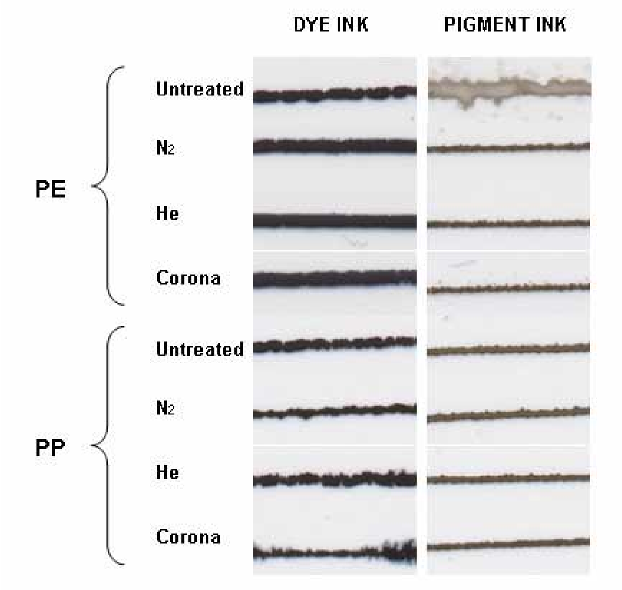

__Figure 9.__ Printed lines on untreated and pilot treated PE and PP films.

For both inks, edge raggedness decreased on PE film, whereas on PP film an increase in edge raggedness with pilot scale treatments was observed. With solvent based pigment ink, the effect of plasma and corona treatment on edge raggedness was greater than with solvent based dye ink (Fig. 10). The decrease in edge raggedness indicates an increase in surface uniformity.

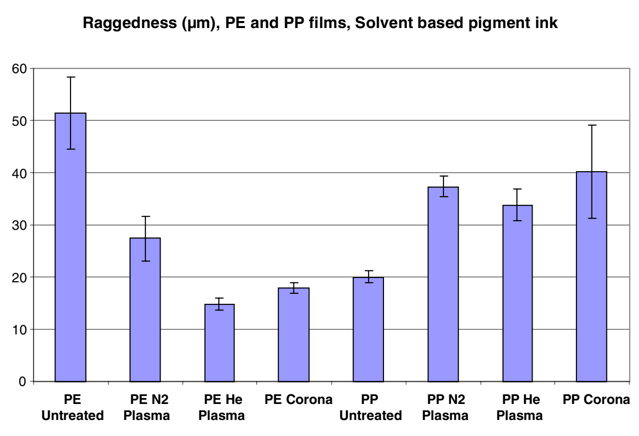

__Figure 10.__ Edge raggedness for printed lines on PE and PP film using solvent based pigment ink.

Although, pilot scale plasma and corona treatments had minimal effects on inkjet print quality on the paper substrates, some trends that seem to correlate with the results for surface energy and micro-roughness were found, especially for pigment coated paper. Even though the treatments had a greater impact on surface energy of the surface sized paper, no distinct correlation with print quality parameters was found. This difference between pigment coated and surface sized papers is thought to have been caused by the increase in microroughness for pigment coated papers after treatment as opposed to no change for surface sized papers, or the greater effect of the treatments on the O/C ratio on pigment coated paper. In the case of surface sized paper, the ink is assumed to have eventually penetrated deep into the paper surface structure after the initial drop impact. The increased surface energy may have an effect on the initial contact angle of the ink drop, but as drying of the ink proceeds, the effect of surface energy possibly decreases and is substituted by the capillary mechanisms of the fiber matrix that lead to lateral ink spreading.

For pigment coated paper, line width decreased with solvent based pigment ink (Fig. 11), with laboratory scale plasma activation having the most pronounced effect. Water based pigment ink exhibited a similar but weaker trend.

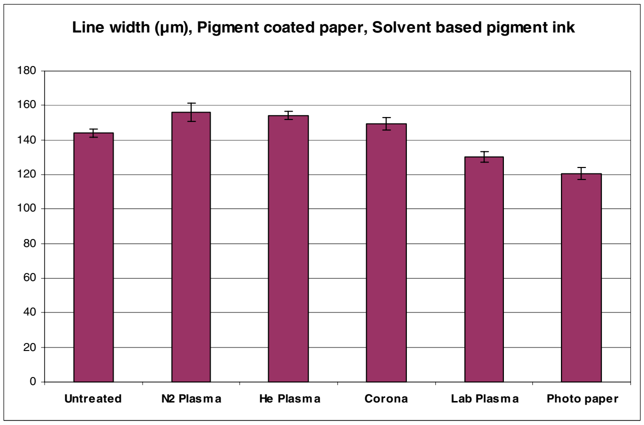

__Figure 11.__ Line width for printed lines on pigment coated paper using solvent based pigment ink.

The pronounced effect of laboratory scale plasma activation was also seen as a decrease in optical density with water based inks on pigment coated paper (Fig. 12). This can be explained through increased hydrophilicity due to an increase in polar molecular groups on the coated paper surface, which assists the penetration of the ink into the coating surface structure.

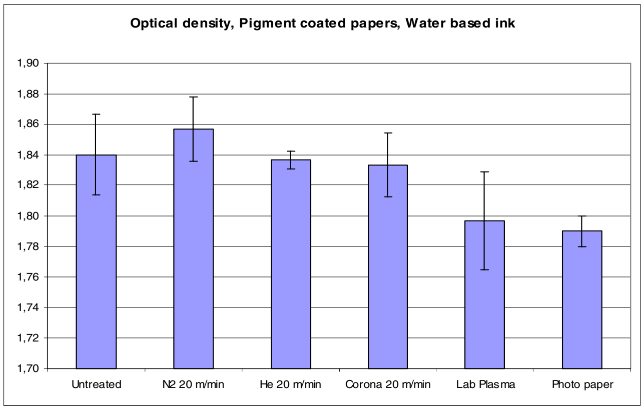

__Figure 12.__ Optical density on pigment coated paper using water based pigment ink.

Unevenness (mottling and graininess) decreased slightly for pigment coated paper and solvent-based dye ink with pilot scale corona and laboratory scale plasma treatment. For solvent based pigment ink the opposite trend was observed. Water based pigment ink gave no clear trend.

For rub-off resistance, the most significant effect of pilot scale plasma treatment was observed with water based pigment ink (Fig. 13). In figure 13, a low value indicates high rub-off resistance. Negative values indicate that the surface was polished due to the abrasion treatment. Water based pigment ink had by far the lowest rub-off resistance, but the degree varied interestingly depending on the treatment. For water based pigment ink, rub-off resistance increased slightly with nitrogen plasma treatment and decreased slightly with helium plasma treatment. The same behaviour for water based pigment ink was observed for both surface sized and pigment coated papers. The trend does not, however, correlate with surface energy results where corona treatment should have the greatest effect. This behaviour could not be explained. In general, the poor rub-off resistance of pigment inks can be explained by the three-dimensional pigment particles themselves providing a better contact for the abrading surface to remove them.

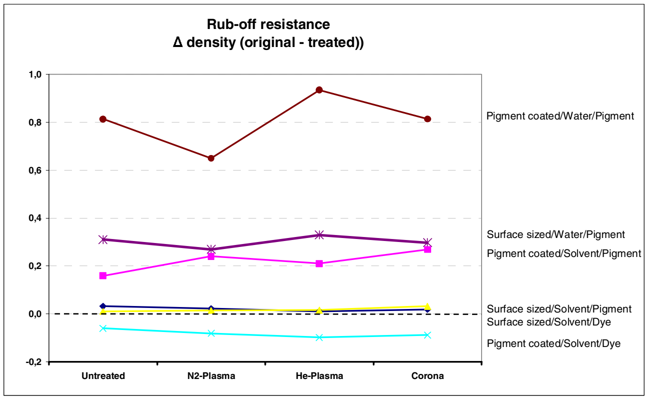

Figure 13. *Rub-off resistance for the studied samples.*

Concluding Remarks

All surface treatments oxidized polymer and paper surfaces and increased the total surface energy of the substrates. Particularly, the polar component of the surface energy increased due to increase of the base component. This provides a possibility to introduce polar interactions, especially with acidic inks. The corona treatment resulted in higher surface energy and oxidation levels than the pilot scale nitrogen and helium plasma activations. However, the impact on inkjet print quality was similar for both plasma activation and the conventional corona treatment. The laboratory scale plasma activation was the most efficient, because of the longest treatment time.

The treatments improved inkjet print quality on PE film; the line raggedness and widths were decreased considerably. On the contrary, treatments worsened print quality on PP film. Results showed that already small changes in surface chemistry and energy can change the print quality of polymer films. The effects of treatments on print quality with paper substrates were less obvious. On pigment coated paper, the laboratory scale plasma treatment decreased the line width for solvent based pigment ink. It is probable that ink absorption into the porous paper substrates complicates the picture, and further investigations are needed to clarify the role of the surface energy and chemistry changes on ink-setting and printability on these substrates.

Use of model inks in studying the effects of plasma treatment on inkjet printability could be interesting, because the inkjet ink studied here were adjusted in the right surface energy level in relation to the substrates. It could be also useful to estimate the acid and base characteristics of the inks in addition to the substrates, since treatments clearly increased the base component of the surface energy.

References

[1] L. Cernakova, P. Stahel, C. Kovacik and K. Johansson, Low-Cost High-Speed Plasma Treatment of Paper Surfaces. 9th TAPPI Advanced Coating Fundamentals Symposium, pp. 7–17. (2006).

[2] J.R. Roth, Industrial Plasma Engineering. Vol. 2: Applications to Nonthermal Plasma Processes. (IOP, Bristol and Philadelphia, 2001) pg 645.

[3] D. Ivutin, T. Enomae, and A. Isogai, Ink Dot Formation in Coating Layer of Ink-jet Paper with Modified Calcium Carbonate. 21st Int. Conf. on Digital Printing Technologies, pg. 448–452. (2005).

[4] J. Lahti, Dry Toner-Based Electrophotographic Printing on Extrusion Coated Paperboard. (Doctoral thesis, Tampere University of Technology, Institute of Paper Converting, Tampere, 2005) pg. 125.

[5] B. Mesic, M. Lestelius, G. Engström and B. Edholm, Pulp & Paper Canada 106, 11(2005). pg.36–41.

[6] T. Schuman, B.Adolfsson, M. Wikström and M. Rigdahl, Progress in Organic Coatings, 54 (2005). pg. 188–197.

[7] M. Rentzhog, Characterisation of Water-Based Flexographic Inks and their Interactions with Polymer-Coated Board. (Licentiate Thesis, Royal Institute of Technology. Sweden, 2004).

[8] E. Svanholm, An Experimental Study of Inkjet Receptive Coatings-Effects of Poly(vinyl alcohol) and Silica on Printability. (Licentiate Thesis, Karlstads University, Karlstad, Sweden, 2004).

[9] J. Heilmann, Measuring dynamic interactions between paper and microscale ink drops. IS&T/NIP17 Conference on Digital Printing, Fort Lauderdale, USA (2002).

[10] B. Zhmud, Dynamic Aspects of Ink-Paper Interaction in Relation to Inkjet Printing. Pira International conference: Ink on Paper,pg. 11. (2003).

[11] R.M. Silverstein, G.C. Bassier and T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th edition. (John Wiley & Sons 1991).

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Author Biography

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