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Influence of atmospheric plasma polymerisation on the printability of polycarbonate and poly (methyl methacrylate)

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Short abstract

Polycarbonate and poly (methyl methacrylate) are very promising materials with generally extremely critical and challenging printability. Polycarbonate finds extensive utilization in the fields of food packaging, aircraft components and medical applications. Poly (methyl methacrylate) is a prevalent alternative for inorganic glass with its shatter-resistance and it is utilized in electronic instrument displays as well as in the medical sector. Despite their excellent characteristics, mentioned above, these polymers require surface modification prior to the printing process to improve wettability and therefore ink adhesion. Plasma polymerisation is a special possibility to enhance this adhesion by depositing an ultra-thin film of organic monomers on the surface of the substrate. An experiment was conducted with UV inkjet printing on the mentioned substrates by using a plasma system to improve printability. This plasma process includes one process gas, three process speeds and two power levels for plasma generation. The adhesion properties were compared with untreated samples by crosscutting tests (according to DIN EN ISO 2409) and surface characterisation by surface energy analysis combined with polymerisation film thickness measurements and FTIR analysis. All four analyses show coherent results and lead to a most promising set of parameters at the plasma process for long lasting inkjet prints on polycarbonate and poly (methyl methacrylate).

Keywords: plasma polymerisation, polycarbonate, PMMA, printability, print-adhesion, inkjet

1. Introduction and background

The printing industry often deals with a variety of substrates that possess unique physical and chemical features. To achieve first-class output, it is important to understand and consider substrate properties. Amongst the many properties, surface energy holds great significance for achieving desirable print quality by facilitating the adhesion of ink onto substrates (Lahti, et al., 2004).

In this context, it is important to achieve a best match in surface energy of substrate and ink as well as further, the printing process positively affecting, surface characteristics. Various surface treatment technologies are established since many years. There are techniques for improving surface properties like corona discharge, flame treatment and chemical primers (Lahti, et al., 2004). But conventional treatment methods have quite often drawbacks related to their impact on the environment and the ejection of harmful volatile organic compounds that affect human health and surroundings.

Recent advancements in nanotechnology have led to the development of plasma surface treatment technology that offers improved performance as well as sustainability (Friedrich and Hidde, 2015). This process can also ensure more uniform and longer-lasting results compared to traditional surface modification approaches (Pykönen, et al., 2007). As printing systems are frequently adopting new technologies for modified surfaces, this study aims to examine the effect of plasma polymerisation on the surface characteristics and printing performance of polycarbonate (from now on written PC) and poly (methyl methacrylate) (PMMA).

The main-focus of this study is to enhance the adhesion quality of inkjet printed UV-ink on PC and PMMA by identifying the optimal combination of parameters in the atmospheric plasma polymerisation. Finally, the durability of the treatment results is determined by measurements with samples printed immediately after plasma treatment, 24 and 48 hours after plasma treatment.

Related work has been conducted to obtain printability on different polymers by focusing on the process parameters of different surface modification methods:

- Izdebska-Podsiadly (2021) examined the effects of cold plasma surface modification on the print quality of two different types of biodegradable polylactide (PLA) films with flexographic water-based and solvent-based inks.
- Pykönen, et al. (2007) conducted an experiment for determining the effects of atmospheric dielectric barrier discharge (DBD) plasma activation at inkjet print quality with paperboard, polyethylene and polypropylene films. Three black inks (solvent-based pigmented, solvent-based dye ink and water-based pigment ink) were used with paperboard. With polyethylene and polypropylene films, solvent-based black ink was used.

In wider field of research in the context of plasma treatment further work has been conducted:

- Dimić-Mišić et al. investigated the influence of dielectric barrier discharge nitrogen plasma treatment on the transfer of solvent-based photovoltaic (PV) inkjet printing inks (IP) onto enzyme-pretreated fibre-derived micro/nanofibrillated cellulose (MNFC) films. The drop-on-demand inkjet printing process was utilized for the visual inception of the printability of plasma-treated and untreated films (Dimic-Misic, et al., 2019).
- In addition to the aforementioned research, Dimić-Mišić et al. conducted an extensive study examining the effect of oxygen, nitrogen and oxygen followed by nitrogen DBD plasma as well as different treatment exposure time (120 s and 240 s) on MNFC film surfaces. The surface characteristics were determined by surface energy calculations and assessing material composition, surface roughness. The investigation aimed to further evaluate printability and print uniformity by transferring a highly polar functional ink with yellow-orange tint on treated and untreated films (Dimić-Mišić, et al., 2021).

In this study, atmospheric pressure plasma processes will be considered to prepare two different polymer surfaces PC and PMMA prior printing . Moreover, the influence of plasma power and deposition speed will be studied in order to improve the adhesion to the UV-curable ink.

2. Materials and methods

To achieve the results, the surface of PC and PMMA plates with dimensions of 180 mm × 550 mm × 2 mm, density of 1.20 g/cm^3 to 1.22 g/cm^3 and toughness from 140 °C to −20 °C, were plasma-treated and printed.

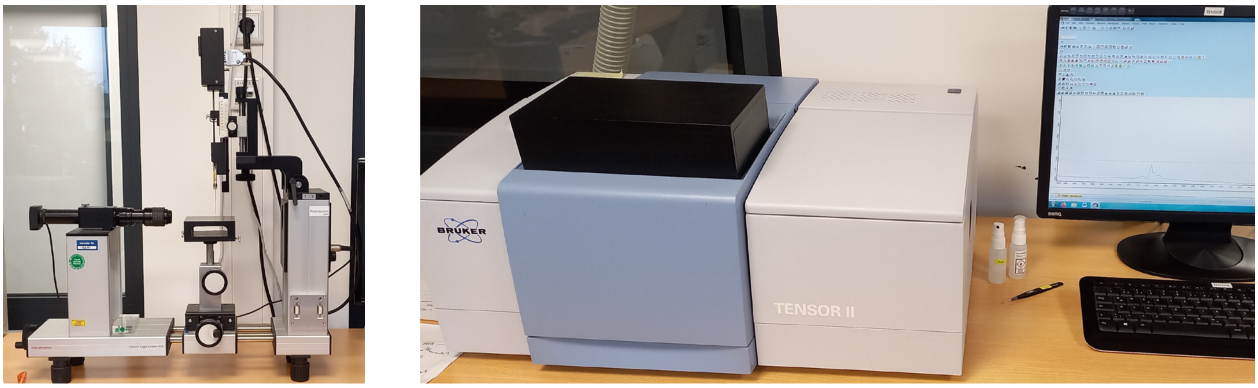
2.1 Equipment

The plasma activation and plasma coating of the polymer surfaces were realized with an atmospheric plasma treatment system provided by Plasmatreat GmbH (Plasma Scanner PS700; Figure 1a). The plasma scanner is equipped with two different rotational jets, one for activation and one for the coating, both suitable for large surface treatment. The reference plates, the plasma-activated plates, and the plasma-coated plates were printed with a flatbed UV-curable inkjet printer (Mimaki UJF 3042 MKII Ex; Figure 1b) using corresponding UV-inks (LUS-120 (C, M, Y, K, W, Cl)).

a) b)

Figure 1: Plasma treatment system (a) (Plasmatreat, 2023), and flatbed UV-curable inkjet printer (b) (Mimaki, 2023)

Further equipment consisted of a contact angle measurement device (OCA; Figure 2a) for surface energy analysis, a spectrophotometer (x-rite i-1 pro Rev) for colour analysis, an interference reflectometer (Ocean optics Nano calc 2000) for coating thickness measurements and a FTIR setup (Tensor II Bruker optics; Figure 2b) for chemical information concerning the plasma induced coating.



a) b)

Figure 2: Setup for contact angle measurements (a) and an ATR-FTIR setup (b)

2.2 Test chart designs

Three test chart designs were printed on the plates and used for large area analysis with CMYK solids (Figure 3a), ink superpositioning analysis with a CMYK image (Figure 3b) and colorimetric halftone analysis with various area coverages of CMYK (Figure 3c).

a) b) c)

Figure 3: CMYK solids (a), CMYK image (b) (Mimaki, 2023),
and halftone patches with various area coverages in CMYK (c)

2.3 Experiment

All the experimental trials were performed at constant room temperature (21 °C). All samples were cleaned with isopropyl alcohol before being exposed to the plasma surface treatment. The surface tension of all inks was 29 mN/m (min. 27.2 mN/m, max. 30.1 mN/m), calculated corresponding to the algorithm of Daerr and Mogne (2016).

2.3.1 Plasma polymerisation

The plasma polymerisation was carried out at two power levels (450 W and 550 W) and three process speeds (5, 10 and 15 m/min). All the other parameters, like ionisation gas (air), ionisation gas flow (72 L/min), heater- and evaporator-temperature (520 °C and 270 °C) as well as the distance between the plasma setup jethead and the substrate (2 mm), remain the same for all trials.

2.3.2 Printing and analysing PC and PMMA

Following the treatment, the plasma-modified plates were printed immediately with the mentioned UV inkjet printer and analysed concerning surface energy, print adhesion and colour values:

- Surface energy is estimated via contact angle readings (mean value out of five measurements) by using three test liquids (water, ethylene glycol and diiodomethane) on treated and untreated samples. Considered are the surface tensions and their relevant dispersive and polar component using the Owens, Wendt, Rabel, and Kaelble's (OWRK) method (Yu, et al., 2020).
- Print adhesion was analysed via cross cutting tests in accordance with DIN EN ISO 2409 (Deutsche Institut für Normung, 2020) for treated and untreated samples.
- Colour density values according to DIN 16536-1 (Deutsche Institut für Normung, 1997) of the solids as well as CIE $L^*a^*b^*$-colour-coordinates (CIE, 1971) of halftones were derived from the measured spectral data (mean value out of five measurements) concerning the treated and untreated samples.
- Colour deviation analysis was operated with the colour values of the print on untreated samples as reference in the ΔE_{00} formula (CIE, 2001) to identify potential colour changings due to treatment.

2.3.3 Further surface characterisation

To achieve additional chemical information concerning the plasma induced coating, an ATR-FTIR analysis was performed by using treated and untreated copper plates (because PC interferes the signal within the utilised infrared wavelength range) (Munshi, et al., 2018). The treatment was realised with the same plasma polymerisation parameters as with the PC and PMMA plates.

To get information concerning the thickness of the plasma induced ultra-thin film coating, spectroscopic reflectometry was used to measure the corresponding SiO_2 layer on a silicon wafer, which was also treated with the same plasma polymerisation parameters as the PC and PMMA plates.

2.3.4 Durability test

Finally, the durability of the treatment is determined by analysing the contact angle and the print adhesion additionally for samples printed 24 and 48 hours after the plasma treatment. The samples were heated up to 80 °C for three hours and kept the rest of the time in constant humidity- and temperature-conditions or kept in water for the complete time.

3. Results and discussion

First, the numbers for the surface energy analysis are presented in diagrams, followed by the adhesion results, that clearly show – using images of the crosscut results – the positive effect of the plasma polymerisation for both substrates at different process speeds and different power levels.

Colorimetric analysis shows the impact of the treatment on the colour reproduction up to 4.5 ΔE_{00} units and the ATR-FTIR combined with the layer thickness measurements confirm the speed and power level related trends, found in the surface energy analysis.

Finally, the durability results show the significant influence of power level and process speed on the print-adhesion (even if the samples were kept in water), which leads to a most promising parameter setting at the plasma system.

3.1 Surface energy effects due to plasma polymerisation

Figure 4 shows the strongest decreasing of surface energy due to plasma polymerisation with 550 W power level in the dispersion component at the slowest process speed (5 m/min) in the plasma setup. With higher speed, this effect is reduced again. The polar component is increased compared to the untreated sample but is decreasing again with higher process speed. The surface energy is only slightly modified due to plasma polymerisation and remains nearly unchanged.

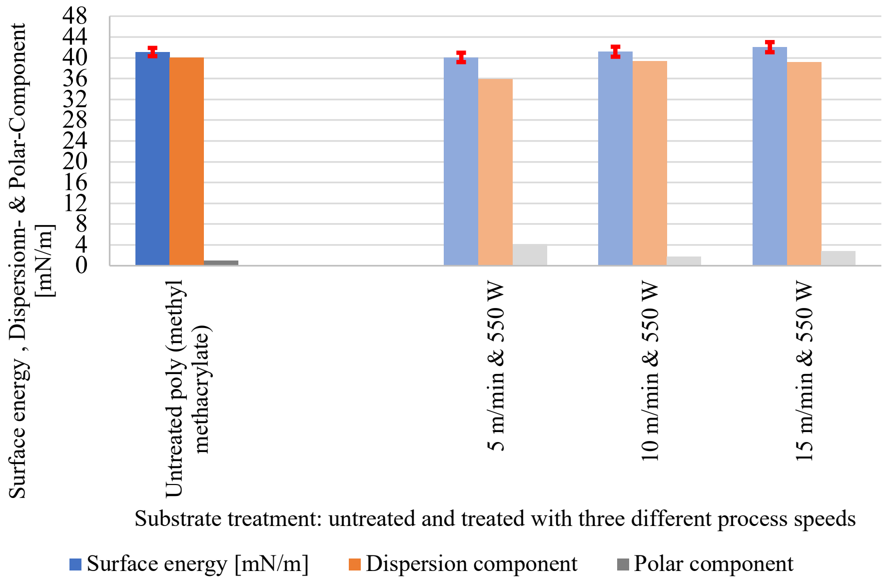


Figure 4: Surface energy at untreated and with 550 W plasma treated PMMA at different process speeds.

The same behavior was also observed with a lower plasma power of 450 W on PMMA and PC but is not presented in detail here.

This surface energy effects, caused by the plasma treatment, lead to significant improvements in print adhesion at the samples. Figure 5 shows the crosscutting test results for untreated samples (Figure 5, top) and samples that were treated with power levels 450 W (Figure 5, middle) and 550 W (Figure 5, bottom) at process speed 5 m/min printed immediately after the treatment.

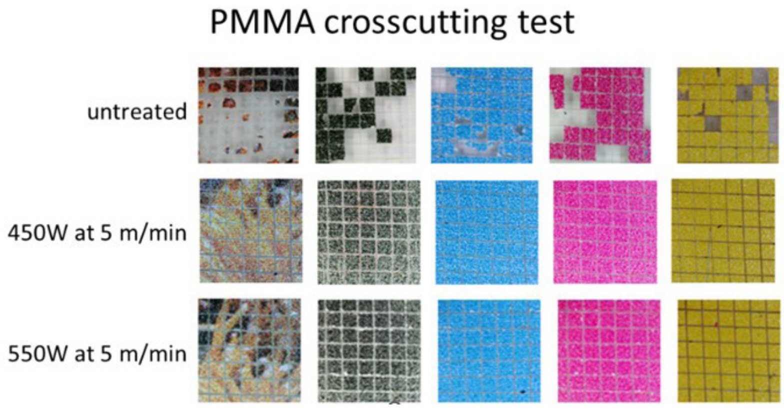


Figure 5: Crosscutting test at PMMA after plasma coating: untreated (top), 450 W (middle) and 550 W (bottom) power level at process speed 5 m/min

3.2 Colorimetric analysis

Concerning print density analysis, it can be seen that the surface modification of samples with plasma polymerisation showed mainly a 0.1 higher print density as compared to untreated surfaces.

Since the print-adhesion is perfectly given with these plasma parameter settings (when printed immediately after treatment), all halftones colour values are clearly affected by the treatment. Since the solids (100 % area coverage) show minor effects due to the treatment (< 2 ΔE_{00} at 100 % black & cyan, compared to the colour values determined at untreated samples), there are strong effects up to 4.5 ΔE_{00} at the halftones with lower tonal values (50 % black and cyan at 550 W power level with 10 m/min process speed (Condition 2)). Figure 6 shows the effects on trapping for the inks with the most uniform effects with 5 m/min (Figure 6, Condition 1) process speed for all area coverages. At process speed 15 m/min (Figure 6, Condition 3) the effect decreases with increasing tonal values. The treatment with 10 m/min (Figure 6, Condition 2) show inhomogeneous effects, which must be double checked.

For perfect colour reproduction results, it is obviously necessary to adapt the printer profile to the plasma induced changed situation including the inks that are not included in this figure.

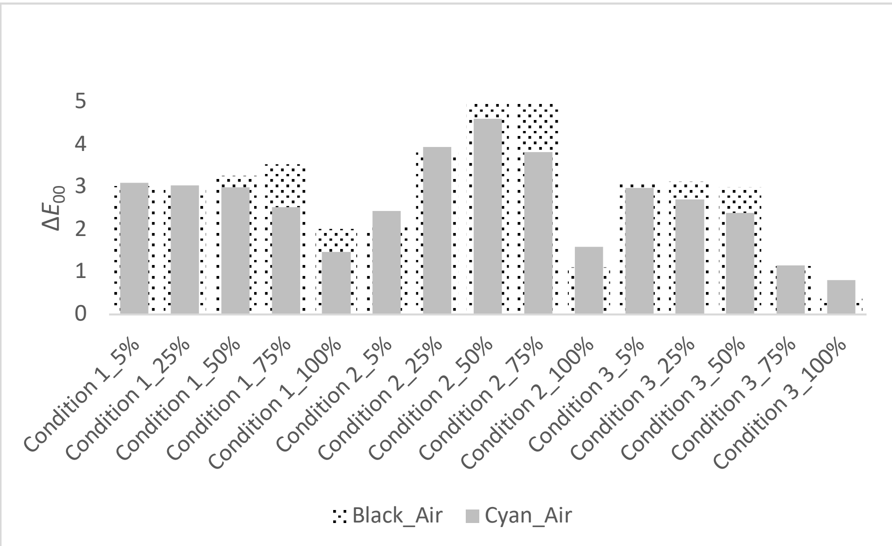


Figure 6: Colorimetric results for halftones of cyan and black printed on PMMA treated with 550 W, printed immediately after treatment; power level at 5, 10 and 15 m/min process speed (Condition 1, Condition 2, Condition 3)

3.2 Thickness measurements of the plasma induced ultra-thin coating

Referring to the reduced effects at the surface energy due to increasing speed at both power levels and to the reduced effect on the ink transfer (especially with black and cyan) it is predictable, that the coating thickness would be reduced in the same manner with both power levels, as it is shown in Figure 7. The ultra-thin thickness of the coating was representative measured on a silicon wafer, which is necessary due to the spectroscopic reflectometry technology with model Siox and refractive index 1.4571.

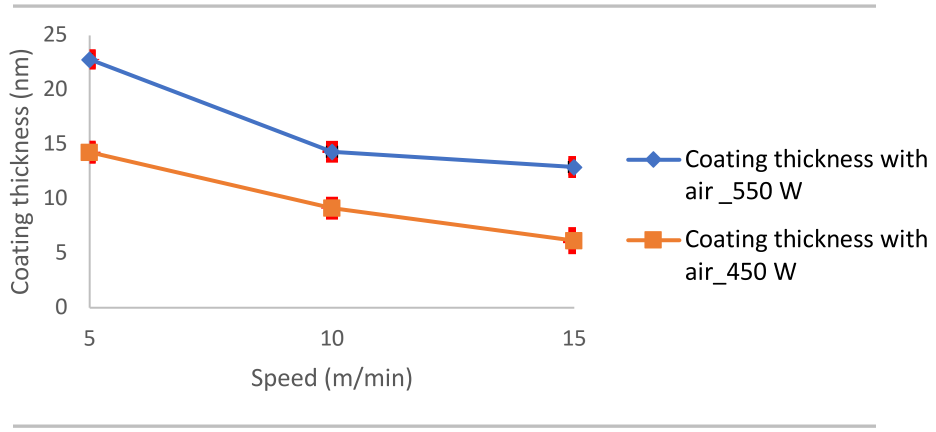
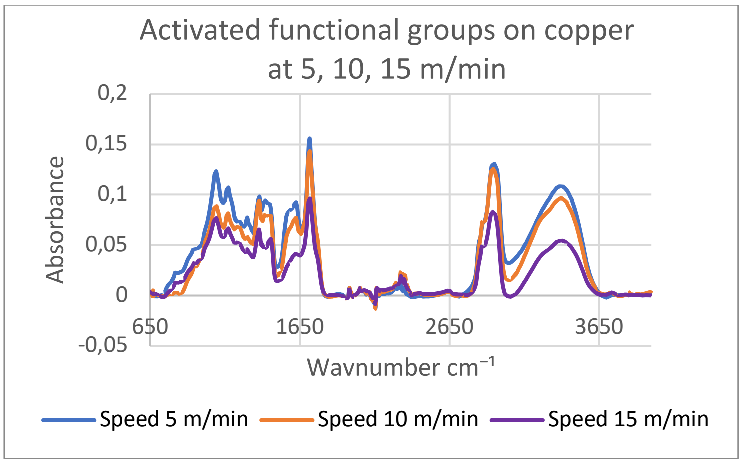


Figure 7: Plasma induced coating thickness at different speed, and two power levels 450 W and 550 W

3.3 ATR-FTIR analysis for more chemical information of the plasma induced coating

Referring to the effects identified at the surface energy and the coating thickness analysis, the same speed-depending characteristics should be obvious also with the functional groups within the coating. Figure 8 confirms this with higher absorbance values in all relevant areas at 5 m/min process speed compared to the values at 10 m/min or 15 m/min concerning a copper plate (Figure 8a). Relevant functional groups with corresponding wavenumbers are shown in Figure 8b. A Silane precursor was introduced in the plasma discharge, the FTIR confirmed the plasma polymerization mechanism with SiO bands clearly identified around 1200 cm^{-1}.



a)

Wavenumber	Functional group
951 cm^{-1}	Vinyl C-H out-of-plane bend
1123 cm^{-1} 1176 cm^{-1}	Alkyl substituted ether, C-O Stretch
1303 cm^{-1}	Vinylidene C-H in-plane bend
1721 cm^{-1}	C=O stretching vibration of ester groups
2868 cm^{-1}	Methyne C-H Stretch
2957 cm^{-1}	Methylene C-H asym./ sym. Stretch
3200-3570 cm^{-1}	Hydroxyl group, H bonded OH stretch

b)

Figure 8: ATR-FTIR chart for plasma coatings with 5, 10 and 15 m/min process speed (a), relevant functional groups with corresponding wavenumber (b)

3.4 Durability of surface energy effects due to plasma polymerisation

Especially in the crosscutting test results with higher process speed (and lower power level), the reduced print-adhesion becomes obvious. Figure 9 shows the strongly reduced positive impact due to waiting 24, or 48 hours after treatment before printing: large areas of the print are removed during the test.

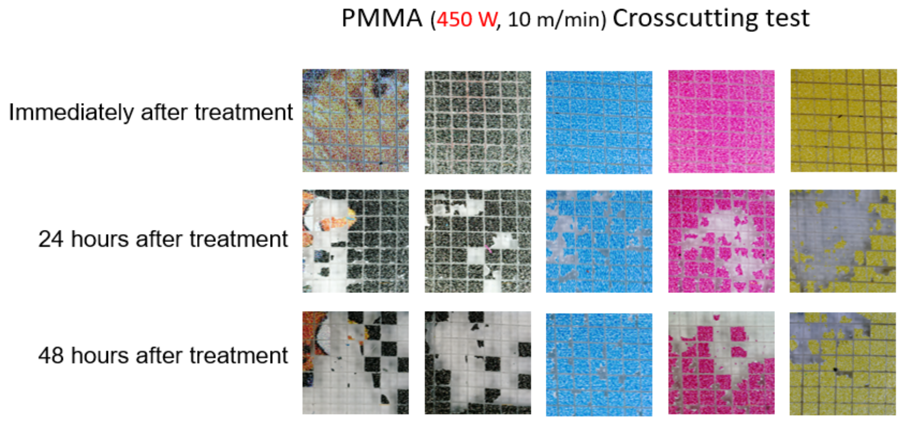


Figure 9: Crosscutting test at PMMA treated with 450 W power and 10 m/min and printed 24 / 48 hours after treatment

By reducing process speed and increasing the power level, the samples become more resistant, even if the samples are kept in extraordinary conditions like in water between treatment and printing. This can be seen in Figure 10 and 11.

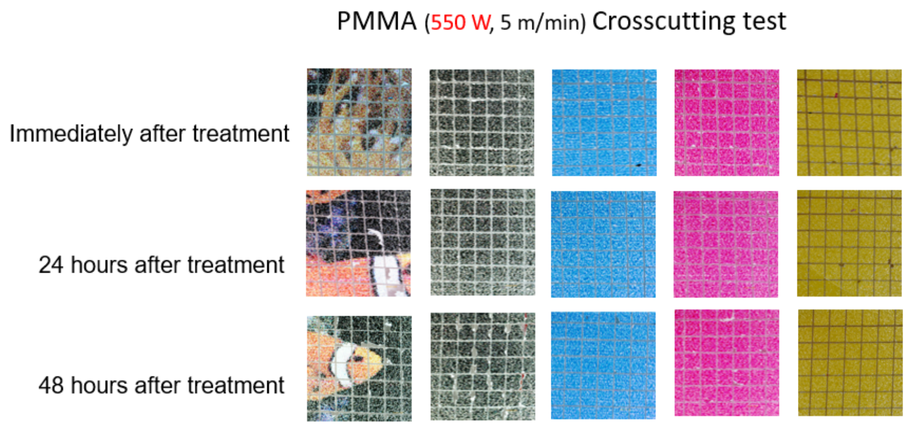


Figure 10: Crosscutting test at PMMA treated with 550 W power and 5 m/min, printed 24 / 48 hours after treatment

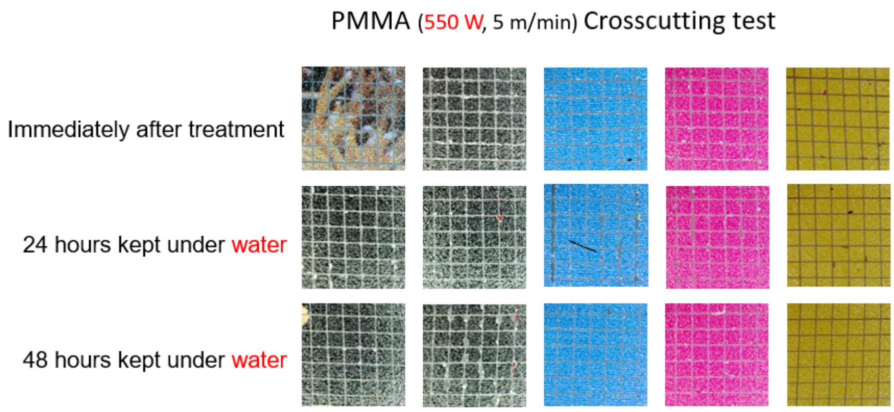


Figure 11: Crosscutting test at PMMA treated with 550 W power and 5 m/min, printed 24 / 48 hours after treatment and kept in water

Even if now, the print-adhesion is perfectly given for this plasma parameter setting, the colour perception of the printed halftones is affected by the treatment. Since the solids (100 % area coverage) show minor effects due to the treatment, there are increasing effects at the halftones with decreasing tonal value. Figure 12 shows this especially for black and cyan and indicates an effect on the trapping, which must be considered. For perfect colour reproduction results, it is necessary to adapt the printer profile to the plasma induced – and waiting-time depended – surface characteristics.

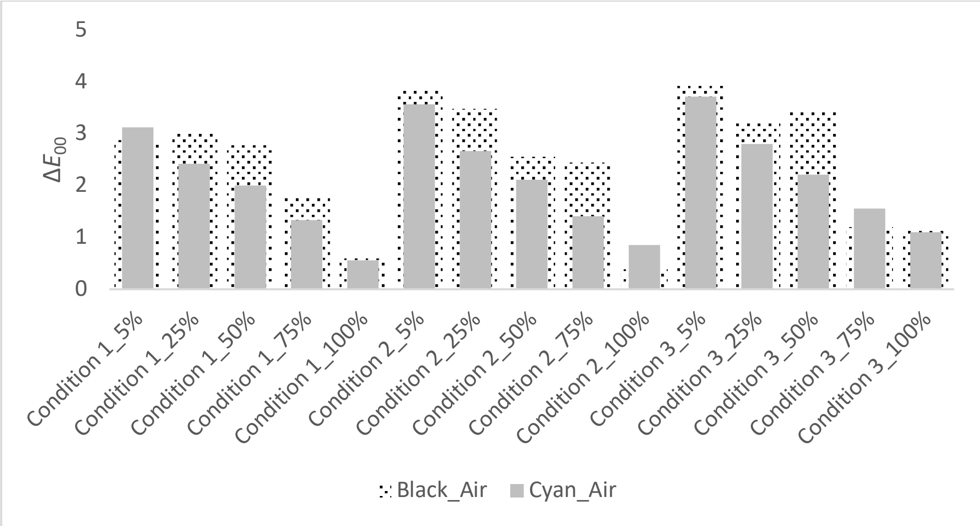


Figure 12: Colorimetric results for halftones of cyan and black printed on PMMA treated with 550 W power level at 5, 10 and 15 m/min process speed (Condition 1, Condition 2, Condition 3), 48 hours after treatment

4. Conclusions

Atmospheric plasma polymerisation ensures ink bonding on PC and PMMA by increasing the polar components and achieving optimum surface energy. Furthermore, the increased presence of functional groups supports covalent bonds between substrate surface and ink. This leads to stronger and more durable print-adhesion, which becomes obviously with the crosscutting test especially at PMMA samples that were treated with the identified process parameters and were kept 48 hours in harsh conditions before printing.

The plasma induced effects on the ink trapping can be easily considered in the printer-profile, to ensure first-class output with a high accuracy in the colour reproduction and high print-adhesion.

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