Inkjet Printing of Functional Materials on Selectively Plasma Treated Surfaces

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Abstract

In manufacturing of organic electronics, inkjet printing as an alternative technique for depositing materials is becoming increasingly important. Aside to the ink formulations challenges, improving the resolution of the printed patterns is a major goal. In this study we will discuss a newly developed technique to selectively modify the substrate surface energy using plasma treatment as a means to achieve this goal. First, we look at the effects of the µPlasma treatment on the surface energy for a selection of plastic films. Second, we investigated the effects of the µPlasma treatment on the wetting behaviour of inkjet printed droplets to determine the resolution of the μ Plasma printing technique. We found that the surface energy for all tested films increased significantly reaching a maximum after 3-5 repetitions. Subsequently the surface energy decreased in the following 8-10 days after treatment, finally stabilizing at a surface energy roughly halfway between the surface energy of the untreated film and the maximum obtained surface energy. When µPlasma printing lines, an improved wetting abillity of inkjet printed materials on the plasma treated areas was found. The minimal achieved µPlasma printed line was found to be 1 mm wide. For future application it is important to increase the resolution of the plasma print process. This is crucial for combining plasma treatment with inkjet print technology as a means to obtain higher print resolutions.

Keywords: Plasma treatment, µPlasma printing, Inkjet printing, Surface energy

1. Introduction

In the past decade increasing attention is given to inkjet printing as an alternative technique for low cost manufacturing of organic electronics. This is due to its ability to reduce the number of manufacturing steps, high efficiency in regard to material usage and low cost production [1-4]. One of the challenges in inkjet printing for organic electronics is to improve the resolution of the printed patterns in order to produce smaller line widths and structures with higher complexity. Two routes are available to achieve this goal. In drop-on-demand inkjet printing small droplets are ejected from a nozzle and deposited onto a substrate. A smaller droplet volume will increase the print resolution but increases the demands on the ink specifications for it to be reliably ejected from the nozzle. Typical droplet volumes in commercially available production print heads from Xaar or Fujifilm Dimatix range from 10 to 85 pl [5, 6]. A different route is to control the droplet size on the substrate by changing the wettability of the substrate. On substrates with a high wettability (hydrophilic surface) the droplet has a larger diameter and a lower contact angle is obtained with respect to substrates with a low wettability (hydrophobic surface). Numerous techniques are available to control the surface wettability of a substrate, like cleaning, UV-ozone, plasma and adding or substituting surface groups. Most of these methods however homogeneously treat the total surface area of the substrate or use masks to selectively treat an area of the surface whilst protecting other areas from treatment [7-10].

A recently developed technique by InnoPhysics, called µPlasma Printing, is able to selectively and mask less treat the surface with an atmospheric plasma using digital patterning technology similar to drop-on-demand inkjet printing [11].

Plasma can be created by sufficiently heating or by applying an electric field over a gas, ionising a fraction of the gas atoms or molecules. Using an electric field, at a certain minimal voltage, gas pressure and distance between the electrodes enough electrons and ions are created to ignite a plasma. This effect is described for different gasses in the Paschen curve (Figure 9) [7, 11-13].



Figure 1. The Paschen curve describes the voltage required to ignite a plasma between two parallel plates as a function of the product of the plate distance d and the gas pressure p for different gases [12, 13].

At atmospheric conditions it can be seen that to ignite a plasma, a very small distance between the electrodes is needed.

InnoPhysics μ Plasma Printing uses this principle by moving needle shaped electrodes closer or further from a counter electrode plasma can be generated on demand (Figure 2).



Figure 2. Sideview of a plasma generated by multiple needles of a plasma printhead

Surface modifications due to plasma can be distinguished into three categories, activation, etching and deposition and depend largely on the type of gas or added precursor molecules. For instance oxygen or nitrogen can create radicals and ions like O_3 , OH or NH which can break or form new bonds, changing the surface energy of the substrate. Much research has been done to investigate the effects of gasses and additional precursors on surface wettability on larger surface areas [14-18]. However, by selectively changing the wetting behaviour using µPlasma Printing, large transitions in wettability between treated and untreated areas on a substrate surface can be created up to resolutions of 300 µm [11]. Combined with inkjet printing in which the same pattern can be printed with a functional ink it should be possible to increase the resolution and complexity needed for organic electronics.

In this paper we will present the effects of the μ Plasma Print technology on the surface energy for different plastics. Furthermore we will present initial results of the effect of μ Plasma treated substrates in combination with inkjet printing. Here, we focus on the minimal obtainable print resolutions produced with the μ Plasma visualized with inkjet printing.

2. Experimental details

For both inkjet printing and µPlasma printing an OTB PixDro LP50 R&D inkjet printer was used. For the inkjet printing a PixDro PL128-L printhead (range ~10-15 pl drop volume) was used (Figure 3, left). An InnoPhysics POD24 µPlasma printhead was used for the plasma treatment (Figure 3, right).



Figure 3. Inkjet (left) and plasma (right) printhead mounted in modular printhead holder of Pixdro LP50 R&D printer.

Diethylene glycol dimethacrylate (DEGDMA, Sigma Aldrich cas. 2358-84-1) with fluorescent marker (Fluorescenzrot 94720, Kremer Pigmente GmbH, Germany) and initiator (Irgacure 365, Sigma Aldrich, cas. 136797-29-0) was used as inkjet ink and polymerised under UV and nitrogen atmosphere for 2 min. after printing. The following plastics were investigated, polycarbonate (PC), polypropylene (PP), polyvinylchloride (PVC), polyethylene naphtalate (PEN) and polyethylene (PE). Table 1 shows an overview of the tested plastics and their surface energy before treatment.

2.1. Surface Energy

All plastics were pre-cleaned with isopropanol and air dried before being plasma treated. A $2x4 \text{ cm}^2$ bitmap was plasma treated at 282 dpi with 1, 3, 5 or 10 repetitions to increase treatment time at a voltage of 6.5 kV and gap distance of 500 µm under nitrogen atmosphere.

To investigate the long term effect of the plasma treatment the change in surface energy of plasma treated polycarbonate was measured after 0, 1, 2, 4, 8, 16 and 30 days after plasma treatment. Plasma treatment was performed on a $2x4 \text{ cm}^2$ polycarbonate film at 7 kV, a gap distance of 500 µm and printed at 181 dpi with 5 repetitions. Substrate surface energy was measured using the Owens, Wendt, Rabel en Kaelble (OWRK) method on a contact angle analyser (Dataphysics OCA 30, Germany). As reference fluids, deionised water, diiodomethane (Sigma Aldrich cas. 75-11-6) and ethylene glycol (Sigma Aldrich cas. 127-21-1) were used.

2.2. Plasma print resolution

Three methods were devised to determine the print resolution of the μ Plasma printhead.

The first method consists of plasma printing a bitmap of five, one pixel wide lines, spaced 2 mm apart, were plasma printed onto a Polyethylene Terephthalate (PET) film at 7 kV, a gap distance of 700 μ m and at 282 dpi in x-direction and 1128 dpi in y-direction without repetitions in an air atmosphere. Large drops (1 cm diameter) of blue coloured ethylene glycol were placed onto the treated area to optically visualize the treated areas.

For the second method the equal plasma treatment an film was used a in the first method. Instead of placing a single large drop, 10 pl droplets of DEGDMA ink were inkjet printed over the plasma treated area at 200 dpi covering the plasma printed pattern. At 200 dpi individual inkjet printed droplets coalesce at the plasma treated areas, but remain separate at untreated areas. Optical images of both methods were taken and analysed to determine line widths. For the third method a square bitmap of $2x2cm^2$ was plasma printed at 9 kV and a gap distance of 400 µm under an air atmosphere. The bitmap was printed at 9, 18 or 36 dpi, at 1, 3 or 5 repetitions to increase treatment times. After plasma treatment, 10 pl droplets DEGDMA ink was inkjet printed at 100 dpi covering the plasma treated areas. Detailed images were taken with a fluorescent microscope (Olympus) and analysed to determine drop diameters over the printed area.

3. Results & discussion

3.1. Surface Energy

In Figure 4, horizontally the number of print repetitions, i.e. to the duration of the plasma treatment is shown and vertically the surface energy of the plastic is given. The most left value represents the surface energy of the untreated film. At increasing plasma exposure the surface energy for all tested plastics increase reaching a maximum value after 3-5 repetitions. This represents, at 5 repetitions, a total treatment time of approx. one minute for a 10x10 cm^2 plasma treated area.



Figure 4. Change in surface energy for different films as a function of plasma print repetitions

In absolute values polycarbonate shows the largest surface energy after plasma treatment. Polycarbonate also shows the largest increase in surface energy, although the differences in between the films are small and in the range of 20 mN/m. An overview of the maximal change in surface energy is given in Table 1. Table 1 also shows that for polycarbonate, plasma treated under air atmosphere a lower maximum change in surface energy is found (12 vs. 20 mN/m for nitrogen plasma).

Figure 5 shows the long term effect of the plasma treatment on the surface energy of polycarbonate film in days after treatment. In the first 8 to 10 days a strong decrease in surface energy occurs. After 10 days the surface energy stabilises to a constant value significantly higher than the surface energy of the untreated film. This indicates a permanent change in the surface structure of the polymer. This could be either a change in morphology, roughness or chemistry of the surface or a combination of the latter. Similar results were obtained with PEN and PTFE films and are also in agreement with experimental results from literature [14, 15]. To determine the exact cause of this permanent change in surface energy further investigations with XPS spectroscopy or AFM is needed. Also the influence of µPlasma print settings like voltage, gap distance and process gas on the long term effects should be investigated further.

Table 1. Surface Energy for tested films before and after plasma treatment

Films ^[a]	$\sigma_{\text{before}} \\ (mN/m)$	Max. σ _{after} (mN/m)	Δσ (mN/m)
Polypropylene (PP)	19 ± 1	38 ± 1	19 ± 2
Polycarbonate (PC) ^[b]	28 ± 1	48 ± 1	20 ± 2
Polycarbonate (PC) ^[c]	39 ± 1	51 ± 1	12 ± 2
Polytetrafluoroethylene (PTFE)	15 ± 1	33 ± 1	18 ± 2
Polyvinylchoride (PVC)	28 ± 1	44 ± 1	16 ± 2
Polyethylene naphtalate (PEN)	28 ± 1	45 ± 1	17 ± 2
Polyethylene (PE)	23 ± 1	40 ± 1	17 ± 2

[a] films purchased from GoodFellow unless stated otherwise.

[b] polycarbonate (manufacturer unknown) used in Figure 4

[c] polycarbonate (GoodFellow) used in Figure 5 and inkjet experiments.



Figure 5. Change of surface energy for polycarbonate as a function of days after plasma treatment.

3.2. Plasma print resolution

Figure 6 shows an example of a blue coloured ethylene glycol drop on plasma treated PET film printed using previously described method 1. Clearly visible is the change in wettability between the plasma treated areas (T) and the untreated areas (U). As the plasma treated areas are in fact printed lines of 1 pixel wide and 2 mm apart, the minimal width of a plasma printed line is 1 ± 0.2 mm wide.

Figure 7 shows a detail of a similar 1 pixel wide plasma printed line covered with DEGDMA drops printed at 200 dpi on PET film using method 2. For this method a minimal line width of 1 ± 0.2 mm was determined..



Figure 6. Blue coloured ethylene glycol drop on plasma treated PET film showing multiple one pixel wide plasma printed lines. (T) is treated, (U) is untreated with plasma.



Figure 7. Detail of 1 pixel wide plasma printed line covered with DEGDMA droplets inkjet printed at 200 dpi on PET film. (T) is treated, (U) is untreated with plasma.

At 160 dpi inkjet printed DEGDMA droplets on PC film coalesce on the plasma treated area while at untreated areas the droplets remain separate (Figure 8). For this situation an equal line width of 1 ± 0.2 mm was measured.



Figure 8. Fluorescent microscope image of DEGDMA droplets inkjet printed at 160 dpi on plasma treated polycarbonate. The left and right side of the image are untreated, the middle area of the image equals a 1 pixel wide plasma treated line from top to bottom.

For the third method $2x2cm^2$ squares of individual plasma spots were printed at 9, 18, or 36 dpi, followed by inkjet printing DEGDMA droplets over the treated areas. For better comprehension of this method a simulation of this experiment was made. An example of this simulation is shown in Figure 9c. In the simulation an area of the substrate is µPlasma printed at 9 dpi and inkjet printed at 100 dpi, indicated by plasma spots (grey) and ink droplets (red). With a plasma spot size of 1 mm, plasma affected areas and non-plasma affected areas should be discernable by changes in wettability i.e. drop diameter of inkjet printed droplets.



Figure 9. a) Image of plasma printed PC at 9 dpi with lower half of image printed with 2 repetitions and top half at 5 repetitions. Visible are the individual local "plasma spots". b) Simulation of plasma spot experiment. Plasma spots (grey) printed at 9 dpi and 1000 μ m diameter, Inkjet droplets (red) printed at 100 dpi and 100 μ m diameter. c) Detail of fluorescent cross section image of inkjet printed DEGDMA (100 dpi) on top of plasma spots for five repetitions. The yellow line indicates the plasma treated areas.

In Figure 9a and c this effect is visualized experimentally. Figure 9a shows the plasma spots (photographed using a normal camera and special lighting) printed at 9 dpi and 3 (bottom) and 5 (top) repetitions. Figure 9c shows a detail of the horizontal cross section of the top half of Figure 9a after 5 print repetitions. Changes in wettability between DEGDMA droplets are visible between the treated plasma spots and untreated areas in between the spots. The difference in average drop diameter over the cross section for the plasma spots and untreated areas is shown in Figure 10.



Figure 10. Drop diameter of DEGDMA droplets over cross section of plasma treated surface as shown in Figure 9a and c.

Calculation of the plasma spot size in Figure 9 shows a spot size of 1.5 and 2 mm respectively for 3 and 5 print repetitions. At higher dpi (18 and 36 dpi) values for the µPlasma printing no changes in wettability for DEGDMA could be found indicating an overlap in plasma spots. Simulation of 1 mm diameter plasma spots at 18 dpi also shows an overlap in plasma spots confirming the experiments. The initial inkjet printing experiments show improved wetting behaviour of the DEGDMA ink on µPlasma printed areas. The transition between plasma treated and untreated areas is clearly visible in the changed wetting behaviour of the ink. The differences in measured spot size and line widths for the first two methods can be explained by different µPlasma print settings. However continuing research on finding the optimal µPlasma print settings has to be done to decrease the minimal line width further.

4. Conclusions

In this study we investigated the effects of µPlasma printing on the surface energy of polymer films and its potential benefit to increased inkjet print resolution. It was found that the surface energy in general for polymer films increases with treatment time until a saturation level is reached after 3-5 repetitions. After treatment the surface energy decreases rapidly until after 8-10 days it reaches a final value of 50% of its maximum change indicating a permanent change of the surface. Three methods were investigated to determine the plasma print resolution showing a minimal line width of 1 mm. Even though plasma treatment benefits the wetting behaviour of inks, µPlasma printing does not benefit improved inkjet print resolution at this moment. Further research is needed to understand the changes in surface energy and surface morphology. Plasma print settings like gap distance, voltage, print speed but also process gas and or the addition of precursor materials has to be investigated. For future application it is important to increase the resolution of the plasma print process. This is crucial for combining plasma treatment with inkjet print technology technology as a means to obtain higher print resolutions.

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