Wettability and Aging of Polymer Substrates after Atmospheric Dielectrical Barrier Discharge Plasma on Demand Treatment

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Abstract. Plasma treatment is a commonly used technology to modify the wetting behavior of polymer films in the production process for, e.g., printed electronics. As the effect of the plasma treatment decreases in time, the so-called "aging effect", it is important to gain knowledge on how this effect impacts the wetting behavior of commonly used polymers in order to be able to optimize production processing times. In this article the authors study the wetting behavior of polyethylene naphthalate (PEN), polyethylene terephthalate (PET), polycarbonate (PC), fluorinated ethylene propylene (FEP) and polyimide (PI) polymer films after plasma treatment in time. The plasma treatment was performed using a novel maskless DBD plasma patterning technology, i.e., µPlasma Printing, at atmospheric pressure under nitrogen atmosphere. After treatment, the samples were stored at room temperature at 30%-40% relative humidity for up to one month. An increase in wettability is measured for all polymers directly after µPlasma Printing. The major increase in wettability occurs after a small number of treatments, e.g., low energy density. More treatments show no further beneficial gain in wettability. The increase in wettability is mainly due to an increase in the polar part of the surface energy, which can probably be attributed to chemical modification of the surface of the investigated polymers. With the exception of FEP, during storage of the plasma treated polymers, the wettability partially declines in the first five days, after which it stabilizes to approximately 50% of its original state. The wettability of FEP shows little decline during storage. As the storage time between production steps is mostly under two days, μ Plasma Printing shows good promise as a pre-treatment step in the production of printed electronics. © 2013 Society for Imaging Science and Technology. [DOI: 10.2352/J.ImagingSci.Technol.2013.57.3.030503]

INTRODUCTION

Polymer films are widely used in a broad range of industrial applications. In the area of printed electronics, polymer materials like polycarbonate (PC), polyimide (PI) and others are used as substrate material in the production of, among others, organic light emitting diodes, sensor applications and organic solar cells. Advantages of the polymer materials are, among others, flexibility, transparency, tensile strength and chemical resistance.¹⁻⁴ The fabrication of these printed electronic devices often requires patterned modification of the polymer substrates to promote or reduce adhesion or wetting. Atmospheric plasma treatment is a well-used, versatile and economic technology suitable for

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this task. Advances in dielectrical barrier discharge (DBD) plasma technology have made it possible to treat entire polymer surfaces rapidly, continuously and uniformly.^{4,5} However, for patterned plasma treatment most current plasma technologies require masking techniques to achieve satisfactory resolutions. Exceptions are plasma jet or plasma pen, which scan the surface of the substrate and are capable of patterned treatment with resolutions of approximately 1 cm in diameter. They are, however, relatively slow processes.

Recently, a new maskless plasma patterning solution, μ Plasma Printing, was developed, combining atmospheric dielectrical barrier discharge (DBD) plasma treatment with a digital printing platform (Figure 1). With the speed and accuracy of the printing platform, resolutions of 300 µm were reached without the use of masks.^{6–8} An example of the maskless μ Plasma Printing capabilities is shown in Figure 2.

DBD plasmas are characterized by the presence of a dielectrical insulating layer between two metal electrodes in addition to a discharge gap.^{8,9} The wealth of reactive particles in plasmas can be used to modify the chemical structure of the top surface layer of a substrate to promote or reduce adhesion or wetting, dependent on the plasma gas composition, without modifying the bulk layer. In time, the wetting properties of the treated polymer surface slowly revert to their original untreated state. This so-called "aging effect" depends on different parameters like temperature, humidity and polymer type. Nakamatsu et al. found that increasing storage temperature and humidity had an increased aging effect.¹⁰ It has also been shown that higher crystalline polymers show a reduced hydrophobic recovery. This is due to the more rigid crystalline polymer structure compared to an amorphous polymer, which has a higher chain mobility.^{11–13} Various other authors showed changes in wetting behavior over time due to this aging effect for polymers treated in DBD plasmas. De Geyter et al. showed that oxygen containing polar groups introduced by plasma treatment onto the surface of polyethylene terephthalate (PET) films improved the wetting properties of these films. After storage in air, the wetting decreased due to reorientation of these polar groups from the surface to the bulk of the material. The aging effect proceeds slower in air with relatively low humidity and low temperature.^{14–16} Similar results were found for PTFE in atmospheric pressure air DBD

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Figure 1. A Roth & Rau PixDro LP50 R&D Inkjet Printer. Innophysics μ Plasma Print technology is integrated on this platform (image courtesy Roth & Rau).



Figure 2. Illustration of the maskless patterned μ Plasma Printing technology. In this case, the Fontys logo was printed onto a silanized hydrophobic glass slide to create a hydrophilic surface using a nitrogen plasma. As the plasma treatment is not visible by eye, water was placed on the substrate to visualize the hydrophilic μ Plasma treated area.

plasma by Borcia.¹⁷ He also found that although the contact angle changes drastically, the amount of bound oxygen is very small in comparison to other polymers investigated, reflecting the C–F and C–H bond strengths.

For nitrogen plasmas on polypropylene (PP), polyimide (PI) and PET, it was found that the contact angle rapidly changes in five days after treatment, after which it stabilizes to a value roughly halfway between the initial treated and untreated values of the contact angle after one month. An increase in both N/C and O/C ratios was measured, indicating the formation of nitrogen and oxygen containing groups on the polymer surface.^{18–20} The oxygen containing groups are most likely formed due to impurities in the feed gas.

Investigation of the aging effect is important as the maskless localized plasma print technology used in this investigation is a pre-treatment step to improve localized wetting behavior in the production of organic electronics. The storage time between production steps is normally no longer than two days. In this article we will investigate the aging effect on the wetting behavior (surface energy) of selected polymer films using the maskless plasma print technology.

EXPERIMENT

For the plasma treatment, a Roth & Rau PixDro LP50 inkjet printer equipped with an Innophysics POD24 μ Plasma printhead is used (Fig. 1). The printhead consists of 24 needles (200 μ m in diameter) which can move up or down mechanically independently of each other. The needles are separated into two rows spaced 0.56 mm apart. In each row, the needles are separated by 0.28 mm horizontally and 0.14 mm vertically as shown in Figure 3.

An AC voltage is applied between the substrate table, holding the polymer films, and the needles. The resonance frequency is automatically tuned at approximately 61 kHz. As the needles move down on demand toward the substrate, at a critical distance, a plasma ignites and the substrate surface is modified. This critical distance is defined by the type of gas used, the gas pressure and the applied voltage and can be described by the Paschen curve model as shown in Figure 4.^{21,22} Precise needle control, i.e., height and voltage control, allow for accurate plasma treatment.

The combination of the digital printing capabilities of the Roth & Rau PixDro LP50 Inkjet printer and the Innophysics μ Plasma printhead offers the precise *xyz*-needle position control and voltage control needed for accurate patterned plasma treatment.

Polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide (PI), fluorinated ethylene propylene (FEP) and polycarbonate (PC) foils were purchased from Goodfellow (UK). All films had a thickness of 125 μ m with the exception of the FEP, which had a thickness of 100 μ m. All films were stored at room temperature (22–24°C) and at 30%–40% relative humidity for at least



Figure 3. Schematic drawing of the Innophysics POD24 plasma printhead. The needle moves mechanically up and down igniting a plasma as the Paschen curve is crossed. 24 needles (200 µm diameter) are placed in two rows, separated by 0.28 mm horizontally and 0.14 mm vertically in a single row. The two rows are separated by 0.56 mm at the closest point. Also shown is a multiple needle plasma discharge with streamers.

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Figure 4. The Paschen curve describes the breakdown voltage of a discharge between two electrodes as a function of pressure times distance between the electrodes. For μ Plasma Printing, the position of the needle electrode moves in time crossing the Paschen curve, creating a plasma discharge on demand.^{21,22}

24 h before being plasma treated. Just before plasma treatment, a protective film covering the PC film was removed. The other films were wiped with a clean dry cloth to remove dust particles before treatment. Although no measurements were made, it is expected that the surfaces of all used films are contaminated with adsorbed water.

For the aging experiments, an area of $30 \times 60 \text{ mm}^2$ of each film was treated with plasma at the following settings. At atmospheric pressure, 200 ml/min nitrogen (99.999% purity, Air Liquide) was flushed between the needles and the substrate to create a slight overpressure in the open chamber to expel surrounding air. The gap between the needles, in their lowest position, and the top of the polymer film was 300 µm. The peak-to-peak voltage applied was 5.0–5.2 kV with an automatically tuned resonance frequency of approximately 61 kHz. A single plasma treatment is defined as the printing of a bitmap, for example an area of $30 \times 60 \text{ mm}^2$, at 181 dots-per-inch (dpi) with a print head movement speed (print speed) of 40 mm/s at the above-mentioned voltage and gap settings. Each polymer film was subjected to from a single up to twenty identical treatments at the same position of the substrate, increasing the energy delivered to the affected area of the substrate.

The energy dissipated in the plasma, per needle per dot, is estimated in the range of $1-10 \ \mu J.^{6,23}$ As this value cannot be measured exactly within the current setup and is dependent on the printing parameters, the maximum value of 10 μJ of dissipated energy per needle per dot will be used to the determine the maximum energy density on the substrate. For a single treatment with the above-mentioned settings, this corresponds to an maximum energy density on the substrate of 40 mJ/cm².

The plasma treated samples were stored at room temperature $(22-24^{\circ}C)$ with a relative humidity of 30%–40% for up to 30 days, after which the surface energy was determined using a Data Physics OCA30 contact angle measuring instrument. Three 5 µl droplets of diiodomethane

 Table I. Total and dispersive and polar parts of the surface energy (SE) of the test

 liquids.²⁵

70.0		
/2.8	26	46.8
50.8	50.8	0
	50.8	50.8 50.8

Figure 5. Inkjet printed DEGDMA droplets on plasma treated PC film (N₂, 200 ml/min) with increased wetting at the treated areas (coalesced droplets) compared to the untreated areas (individual droplets). Three single pixel wide lines at intervals of 5 mm were identically plasma printed on the same location twice at intervals of 5 mm and are approximately 1.6 mm wide.^{7,26}

(Sigma Aldrich) and deionized water were placed within the plasma treated area, at least 5 mm from its edge. The contact angle was measured and the total, polar and dispersive parts of the surface energy of the substrate were determined by the Owens–Wendt–Rabel–Kaelble (OWRK) method.²⁴ In Table I the polar and dispersive parts of diiodomethane and deionized water used in the calculations are shown.

RESULTS AND DISCUSSION

To evaluate the effectiveness of the maskless μ Plasma Print technology a PC film was plasma treated. Three single pixel wide plasma lines were printed at a gap distance of 300 µm between the plasma needles and the PC film at 5.0-5.2 kV with 90 dpi and a table movement speed of 40 mm/s. The lines were separated by 5 mm and identically treated twice at the same location. After plasma treatment, the entire PC film was inkjet printed upon at 110 dpi with diethyleneglycol-dimethacrylate (DEGDMA, Sigma Aldrich) to visualize the change in wetting behavior between plasma treated and untreated areas. Figure 5 shows the result of this experiment. Clearly visible are the plasma treated lines in which the ink shows increased wetting behavior. The contact angle for DEGDMA changes from 32 degrees in the untreated areas to 20 degrees in the plasma treated areas. Using this experimental setup, the size of an individual plasma dot was determined as a function of the print height and number of plasma treatments. For a single plasma dot, printed at 5.0-5.2 kV and at a print height of 300 µm, the size of the affected area is approximately 1 mm in diameter. With 20 treatments this increases to 1.6 mm in diameter. The smallest affected area of approximately 300 µm in diameter was found at a print height of 50 µm and 4.2 kV with a single treatment.7,26

It was also found that the maximum change in surface energy was not always reached after a single plasma treatment. As shown in Figure 6, the surface energy increases as a function of the number of plasma treatments for the different films. The effect of the treatment saturates after



Figure 6. Change in surface energy as a function of number of treatments (gap distance 300 μ m, 5.0–5.2 kV, print speed 40 mm/s, 181 dpi, N₂-plasma 200 ml/min). A single treatment corresponds to an estimated maximum energy density of 40 mJ/cm².



Figure 7. Change in water contact angle (WCA) as a function of the storage time (gap distance 300 μ m, print speed 40 mm/s, 181 dpi, N₂-plasma 200 ml/min, five treatments). The lines without marker show the WCA of the untreated polymer film.

4–5 treatments or an estimated maximum energy density of 200 mJ/cm² for all films. This saturation is probably dependent on surface properties like affected sites, roughness and molecular structure of the polymer.^{14,16,27,28} Therefore, for consistent evaluation of the aging effect in the following experiments, all samples were treated five times to achieve the maximum change in surface energy.

The results of the aging experiments on the surface energy are shown in Figures 7 and 8. Fig. 7 shows the change in water contact angle (WCA) as a function of storage time. For all polymers the WCA decreases directly after treatment. In the following five days, the WCA for PEN, PET, PC and PI increases by 10 to 15 degrees, and stabilizes after approximately 10 to 15 days. A similar change is seen in Fig. 8, which shows the change in surface energy for the treated polymers. Directly after treatment PEN, PET, PC and PI show a strong increase in surface energy of approximately 11–24 mN/m compared to the untreated films. This is



Figure 8. Change in total surface energy as a function of storage time (gap distance 300 μ m, print speed 40 mm/s, 181 dpi, N₂-plasma 200 ml/min, five treatments). The lines without marker show the surface area of the untreated polymer film.

followed by a strong decrease in the following five days until the surface energy stabilizes after approximately 10-15 days. After one month, the WCA, on average, is still 27 mN/m smaller compared to the untreated PEN, PET, PC and PI. The surface energy, on average, remains 9 mN/m higher compared to the untreated films, thus showing a long-lasting improved wetting behavior after plasma treatment. Figures 9 and 10 show the polar and dispersive parts of the surface energy, respectively. Directly after treatment the polar part of the surface energy increases sharply while the dispersive part decreases to a lesser extent. The increase in the polar part is most likely due to changes in the chemical structure of the polymer surface due to the plasma treatment. Although the plasma chamber of the μ Plasma printer is continuously flushed with nitrogen, the plasma chamber is open to the atmosphere. In this case, oxygen and/or water vapor is expected to be present in the plasma as impurities. In time, the decrease in the polar part as well as the slight increase in the dispersive part of the surface energy point toward a restructuring of the functional groups on the surface to the bulk of the polymer, as described in the literature.^{14,18,19} XPS experiments on µPlasma printed samples treated with air plasma showed a decrease in O/C ratio with increased storage time.²⁹ FEP responds differently compared to the other films. Even though an initial decrease of 30 degrees in WCA and an increase of 16 mN/m in surface energy are measured directly after treatment, during storage the WCA and surface energy barely change. This is comparable to results found by Borcia with an atmospheric pressure air DBD plasma on PTFE.¹⁷

CONCLUSION

In this investigation we studied the aging effect on the wetting behavior of PEN, PET, PC, FEP and PI polymer films after plasma treatment. The plasma treatment was performed using a localized maskless plasma print technology at ambient pressure. Under the treatment conditions used, we found that the wetting behavior of all tested polymer films increased substantially after plasma treatment. The results



Figure 9. Change in the polar part of the surface energy as a function of aging time (gap distance 300 μ m, print speed 40 mm/s, 181 dpi, N₂-plasma 200 ml/min, five treatments). The lines without marker show the surface area of the untreated polymer film.



Figure 10. Change in the dispersive part of the surface energy as a function of aging time (gap distance 300 μ m, print speed 40 mm/s, 181 dpi, N₂-plasma 200 ml/min, five treatments). The lines without marker show the surface area of the untreated polymer film.

clearly show that the major changes in wettability occur after a small number of treatments. More treatments have little beneficial effect on the wettability. The changes in surface energy are mainly due to changes in the polar part of the surface energy, indicating chemical changes on the surfaces of the polymers. With the exception of FEP, during storage of the plasma treated polymers, the wettability partially declines in the first five days, after which it stabilizes to approximately 50% of its original change. FEP shows only little recovery after one month of storage.

As the storage time between production steps is mostly under two days, the localized plasma print technology shows good promise as a pre-treatment step in the production of printed electronics.

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