Influence of successive plasma treatments on PP foils

T. Jacobs*, R. Morent, N. De Geyter, C. Leys

Research Unit Plasma Technology (RUPT), Department of Applied Physics, Faculty of Engineering, Ghent University, Jozef Plateaustraat 22, 9000 Gent, Belgium

* Corresponding author: Tinneke.Jacobs@UGent.be

Abstract. Polypropylene (PP) foil is treated with a dielectric barrier discharge (DBD) plasma operating in helium at medium pressure. The influence of exposure to the atmosphere between successive treatments is studied by varying the exposure time. Each PP sample is treated with subsequent treatment steps of 5 s. Between two treatment steps, different procedures are applied: 1) the sample remains in the discharge chamber at medium pressure (under helium atmosphere) for a certain time before it is treated again or 2) the pressure is increased to atmospheric pressure, so the sample remains exposed to atmospheric air for a certain time and afterwards the system is pumped down again to medium pressure before it undergoes a successive helium plasma treatment. The treated samples are analysed using contact angle measurements. The results show that exposure to the atmosphere between two treatment steps leads to a lower contact angle. The longer the exposure time, the lower the contact angle becomes.

Another experiment showed that the treatment effect could be gradually removed by applying several short plasma treatments of 1 s to saturated samples. With every short treatment step, the contact angle becomes higher. It is believed that this is due to etching of the surface. In the near future, both atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) analysis on some selected samples are planned to elucidate the chemical and/or physical nature of the observed phenomena.

1. Introduction

Polymers are frequently used in industry for packaging, protective coatings and sealing applications, because they have good bulk properties such as transparency, good thermal resistance, a high strength-to-weight ratio, ... [1]. However, they are often unsuitable to use due to their low surface energy leading to poor wettability, adhesion and printability [2]. Surface modification is often needed. In recent years, plasma treatment of polymers to modify their surface properties has been extensively studied as an environmentally friendly alternative to the classical wet-chemical techniques [3,4]. Different types of plasmas have been used for this purpose [5-9] and several treatment effects have been investigated [10-12]. Since industry requires a plasma technology which can be implemented in a continuous production line, vacuum and medium pressure technology is regarded as being non-competitive with atmospheric technologies. However, medium pressure plasma surface treatment has some advantages over atmospheric pressure. It is easier to create a large plasma volume at medium pressure than it is at atmospheric pressure which could lead to a higher productivity. Also, the pumping equipment for medium pressure is relatively inexpensive. [9-11, 13, 14]

In this study, a dielectric barrier discharge (DBD) operating at medium pressure is used to treat polypropylene (PP) foil. A DBD is typically generated between two metal electrodes, of which at least
one is covered by a dielectric material. By applying a sufficiently large alternating voltage to the electrodes, a plasma is generated in the gap between the two electrodes. Review papers on the properties and applications of DBDs can be found in [15-18].

In this paper, a DBD operating at medium pressure in helium will be used to modify the surface of a PP film. The samples are treated for successive short treatment steps of 5 s and between each plasma treatment step the samples are either kept in the plasma chamber under the helium atmosphere or exposed to atmospheric air. After each treatment step, the plasma treated samples will be examined using contact angle measurements. By using this treatment procedure, the influence of exposure to air between successive helium plasma steps can be studied, which has not been done before.

In a next set of experiments, the saturated plasma treated samples were exposed to several shorter helium plasma treatment steps of 1 s. It was found that the treatment effect could be gradually removed by these shorter treatment steps. This phenomenon has also not been studied before.

2. Experimental set-up

2.1. DBD set-up

A schematic diagram of the DBD configuration can be seen in figure 1. Two circular copper electrodes (diameter = 7 cm) are placed within a cylindrical enclosure. Both electrodes are covered with a glass plate (thickness = 2 mm) and the distance between the plates is 7 mm. The upper electrode is connected to an AC power source (frequency = 5 kHz), the lower electrode to the earth, through a resistor R (50 Ω). The AC power source is a low frequency generator, providing the reference waveform, which is then amplified by a linear amplifier (Crest Audio Model 8200, 4500 W) whose output is applied to the primary winding of a transformer (Tauscher, 2000 VA, 60V/15 kV) in series with a 4.7 Ω resistor. The upper electrode is connected to the secondary of the transformer thereby applying an AC high voltage to the upper electrode.

![Figure 1: Schematic diagram of the DBD-setup (1. gas cylinder, 2. mass flow controller, 3. plasma chamber, 4. pressure gauge, 5. needle valve, 6. pump).](image)

The discharge current is obtained by measuring the voltage over the resistor R, whereas the applied voltage is measured using a high voltage probe (Tektronix P6015A). The current and voltage waveforms are recorded using an oscilloscope (Tektronix TDS210-60MHz), connected to a computer. The resistor can be replaced by a capacitor (10 nF). The voltage across this capacitor is proportional to the charge stored on the electrodes. Together with the applied voltage, this results in a Lissajous figure. By measuring the area of the Lissajous figure, the electrical power can be calculated [17,18].

Before starting each plasma modification procedure, a PP film with a thickness of 75 μm is placed on the lower glass plate. These commercially available PP foils were purchased from Goodfellow Cambridge Limited (England) and are not subjected to any pre-treatment step before plasma
modification. Afterwards, the chamber is pumped down below 2.0 kPa using a rotary vane pump and then filled with helium at a rate of 5.2 slm (standard litres per minute). When atmospheric pressure (101 kPa) is reached, the plasma chamber is pumped down to 5.0 kPa while the gas flow is decreased to 200 sccm (standard cubic centimetres per minute). Subsequently, the AC power source is turned on while the gas flow maintains at 200 sccm and the pressure in the discharge chamber is kept constant at 5.0 kPa by slightly pumping during plasma treatment. In this work, most plasma treatments will be performed in helium purchased from Air Liquide (Belgium) with a 99.999% purity. After this first plasma treatment step, the PP samples will be subjected to different procedures, which will be further explained in detail. Also some treatments in dry air (Alphagas 1 – Air Liquide) will be performed.

2.2. Contact angle measurements

The wettability of the untreated and plasma-treated PP films is evaluated using water contact angle measurements. The contact angles of the foils are obtained at room temperature by using a commercial Krüss Easy Drop optical system (Krüss GmbH, Germany). This system is equipped with a high precision liquid dispenser to precisely control the drop size of the used liquid. A drop of distilled water of 2 µl is placed on the treated substrate. The drop image is then stored, via a monochrome interline CCD video camera, using PC-based acquisition and data processing. Using the computer software provided with the instrument, measurements of the static contact angle are fully automated. The values of the static contact angle are obtained using Laplace-Young curve fitting based on the imaged sessile water drop profile. For each sample, an average of at least 5 measurements was made and standard deviations vary from 0.3° to 1.5°.

3. Results and discussion

3.1. DBD characterization

The voltage and current waveform of the DBD helium discharge is given in figure 2. The amplitude of the applied voltage is approximately 3 kV. Superimposed on the capacitive current, there are several short peaks. These peaks are an indication of the microdischarge activity in the DBD plasma [19]. Every current pulse corresponds to a series of microdischarges.

![Figure 2: Voltage and current curves of the DBD discharge.](image)

The Lissajous figure, which gives the charge on the electrodes as a function of the voltage over the electrodes, is shown in figure 3. From this figure, an electrical power of 1.08 W can be calculated. This power is kept constant during all measurements.
3.2. Effect of exposure to the atmosphere in between treatments

To study the influence of exposure to the atmosphere between successive treatment steps of PP foil, three different treatment procedures are performed. A schematic diagram for the three procedures is given in figure 4 and the values for the different parameters are given in table 1. For each procedure, one treatment step consists of exposing the sample to the DBD discharge for 5 seconds \((t_1 = 5 \text{ s})\). For procedure A, the samples remain in the discharge chamber in helium at medium pressure between two treatment steps \((t_2 = 0.1 \text{ s})\). For procedure B, the samples were exposed for 10 seconds to the atmosphere by letting air into the discharge chamber \((t_2 = 10 \text{ s})\). Afterwards, the chamber is pumped down and filled again with helium. For procedure C, the samples were exposed for 5 minutes to the atmosphere between two subsequent treatment steps \((t_2 = 5 \text{ min})\). The contact angle is measured for each procedure after one, two, three, four and five treatment steps. The contact angle after one treatment step is of course the same for the three procedures. However, after more treatment steps, the contact angle decreases more rapidly for the samples which are being exposed to the atmosphere. This is shown in figure 5. The contact angle also decreases with longer exposure to the atmosphere between two plasma treatments.

It is clear that exposure to the atmosphere has an influence on the treatment, as indicated by the changes in contact angle. By exposing the samples between two treatment steps to atmospheric air, oxygen can be built in. This increase in oxygen content is believed to be due to the reaction of the surface radicals created by the plasma treatment with the oxygen species present in the air. This change in oxygen content at the surface will have an influence on the contact angle. The longer the exposure, the more oxygen can react with the surface radicals and the greater the change in contact angle.
To validate the phenomenon of surface radicals reacting with atmospheric oxygen, plasma treatments in dry air instead of helium were also performed. From the characterization of the discharge it was found that the discharge in dry air was filamentary and the power was 1.83 W. The same procedures A and C as before were used (see figure 4). In table 1, the values for the different parameters are given. Results of contact angle measurements are presented in figure 6. One can see that there is no significant influence of the exposure to the atmosphere in between two treatment steps. During treatment in a dry air plasma, all the created surface radicals immediately react with the oxygen species present in the plasma. No surface radicals are available to react with the oxygen species present in air during exposure to the atmosphere, which means that the surface composition and contact angle do not change.

Table 1: Parameters for the different treatment procedures

| Parameter       | Procedure A | Procedure B | Procedure C |
|-----------------|-------------|-------------|-------------|
| **Treatments in helium** |             |             |             |
| Pressure $p_1$  | 5 kPa       | 5 kPa       | 5 kPa       |
| Time $t_1$      | 5 s         | 5 s         | 5 s         |
| Gas 1           | helium      | helium      | helium      |
| Pressure $p_2$  | 5 kPa       | 100 kPa     | 100 kPa     |
| Time $t_2$      | 0.1 s       | 10 s        | 5 min       |
| Gas 2           | helium      | air         | air         |
| **Removal of plasma treatment effect** |             |             |             |
| Pressure $p_1$  | -           |             | 5 kPa       |
| Time $t_1$      | -           |             | 1 s         |
| Gas 1           | -           |             | helium      |
| Pressure $p_2$  | -           |             | 100 kPa     |
| Time $t_2$      | -           |             | 5 min       |
| Gas 2           | -           |             | air         |
| **Treatments in dry air** |             |             |             |
| Pressure $p_1$  | 5 kPa       | -           | 5 kPa       |
| Time $t_1$      | 1 s         | -           | 1 s         |
| Gas 1           | dry air     | -           | dry air     |
| Pressure $p_2$  | 5 kPa       | -           | 100 kPa     |
| Time $t_2$      | 0.1 s       | -           | 5 min       |
| Gas 2           | dry air     | -           | air         |
Figure 5: Variation of the contact angle as a function of the treatment time for the three procedures. Procedure A: no exposure to the atmosphere between two treatment steps; procedure B: several seconds of exposure; procedure C: several minutes of exposure.

Figure 6: Variation of the contact angle as a function of the treatment time for treatments in dry air.
3.3. Removal of treatment effect

The effect of applying several shorter treatments to a saturated helium plasma-treated sample is also investigated in detail. For the plasma treatments, procedure C is used. The treatment conditions (pressure, gas flow, power, …) for the short treatment steps are the same as those for the previous longer treatment steps. Only the treatment time ($t_1$) is changed: 1s instead of 5s (see figure 1 and table 1). Results of contact angle measurements are shown in figure 7. The contact angle gradually increases again, so some of the treatment effect is lost. This change in surface wettability is believed to be due to a decrease in oxygen content. By applying short treatment steps, the oxygen can be etched away from the surface, resulting in a more hydrophobic surface.

![Figure 7: Removal of plasma treatment effect. Procedure C was used to perform the plasma treatments.](image)

4. Conclusion

The results presented in the previous section show that the used DBD set-up is capable of reducing the hydrophobic character of the PP foil and decreasing the contact angle from 91.1° down to 68.4°, in less than 30 seconds of treatment time, at a power of 1.08 W. The exposure to the atmosphere between successive plasma treatment steps in helium at medium pressure has a significant influence on the surface modification. After 5 subsequent plasma steps, the contact angle can vary from 70.9° (no exposure between two successive treatment steps) to 68.4° (5 minutes of exposure). When the same experiments are performed for plasma treatment in air, no difference in contact angle was observed.

When using helium as discharge gas, surface radicals are created at the surface, which can react with oxygen present in air during atmospheric exposure. This increase in oxygen content at the surface will lead to a lower contact angle. When using air as plasma treatment gas, all the surface radicals will react with the oxygen species present in the discharge, leaving no radicals to react with atmospheric oxygen.

When shorter treatment times are performed to a saturated helium plasma-treated sample, the treatment effect can be etched away, and the contact angle increases from 68.4° to 77.1°.

It is believed that both the chemical composition and the surface roughness change during the plasma treatments in helium and air. X-ray photoelectron spectroscopy (XPS) measurements and atomic force microscopy (AFM) measurements on some selected samples are planned to determine the chemical and physical modifications that occur during plasma treatment. This information will make it possible to clarify the observed phenomena.
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