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Abstract. Surface treatment of polymer films is usually necessary to improve surface wetting and adhesion characteristics. Traditional liquid chemical processes have several disadvantages in contrast to dry finishing processes, like plasma technology. Dielectric barrier discharges at atmospheric pressure are extensively studied for surface treatment, however, almost no research has been done on surface treatment with a dielectric barrier discharge at medium pressure. Therefore, in this paper, a polypropylene (PP) film is plasma-treated with a dielectric barrier discharge (DBD) in nitrogen at medium pressure (5.0 kPa). The surface properties of the plasma-treated samples are examined using contact angle measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Results show that the surface wettability is significantly enhanced after plasma treatment. The incorporation of nitrogen on the surface is significant (10 at%), demonstrating the ability of the used DBD set-up to generate nitrogen-containing functional groups on the PP surface. Nevertheless, a considerable amount of oxygen (10 at%) is incorporated onto the PP surface underlining the extreme reactivity of oxygen active species and the difficulty in overcoming the air contamination problem. Moreover, AFM analysis reveals that the nitrogen plasma creates large changes in the surface morphology of the PP film due to the selective etching of the amorphous regions of the polymer film.

PACS. 52.40.Hf Plasma-material interactions; boundary layer effects – 81.05.Lg Polymers and plastics; rubber; synthetic and natural fibers; organometallic and organic materials – 52.77.-j Plasma applications

1 Introduction

Plasma treatment is one of the most versatile techniques in surface modification. It has been widely used to improve the adhesion of coatings to metals and polymers [1], to increase the wettability and the printability of polymers [2,3], to enhance the biocompatibility of implants [4], . . . Plasmas, often considered as the fourth state of matter, are composed of an ionized gas containing a mixture of ions, electrons, radicals and photons. When these energetic active species collide with a surface, some of the chemical bonds will break making the surface more reactive. Depending on the type of gas in which the plasma is generated, certain new functional groups can be grafted on the surface [5]. Therefore, plasma surface modification can induce a specific surface chemistry without altering the bulk properties of the material [6].

Dielectric barrier discharges (DBDs) or “silent” discharges have been widely studied for the treatment of polymer films. A DBD is obtained between 2 electrodes, at least one of which is covered with a dielectric, when an AC high voltage is applied between the electrodes. The most interesting property of DBDs is that in most gases the breakdown starts at many points, followed by the development of independent current filaments (named microdischarges). These microdischarges are of nanosecond duration and are uniformly distributed over the dielectric surface [7,8].

Plasma reactors at atmospheric pressure are predominantly studied because the polymer industry requires a plasma technology which can be integrated in a continuous production or finishing line [9–13]. Therefore, low and medium pressure technologies are regarded as being non-competitive. However, plasma treatment at medium pressure has some advantages over atmospheric plasma systems. A large plasma volume, available for surface

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treatment, can be more easily obtained at medium pressure than at atmospheric pressure. This can result in a higher overall productivity at medium pressure. Furthermore, different (toxic) chemicals and gases can be used, since medium pressure technology works in a closed system. In addition, at medium pressure, the pumping equipment is relatively inexpensive. However, until now, only little research [3,14,15] is done on medium pressure plasma treatment of polymers. In a previous paper [16], De Geyter et al. have studied the effect of a helium/air discharge on a polyethylene terephthalate (PET) film at medium (6.6 kPa) and atmospheric pressure. They have stated that at low energy densities, plasma treatment at medium pressure is more energy-efficient than at atmospheric pressure. Recognizing the above, a DBD operating in nitrogen at medium pressure is used in this paper aiming to improve the surface properties of a polypropylene (PP) film. The nitrogen gas is selected due to the interest in the creation of nitrogen-related functional groups onto polymer surfaces aimed to be compatible with a biological environment. For example, it is recognized that amino groups provide an excellent basis for subsequent surface modification techniques as they allow to bond biomolecules with high selectivity [17]. In this paper, the effects of an N_2 DBD treatment on the surface of a PP film are examined, reported and discussed. The surface characterization is performed using contact angle measurements, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

2 Experimental set-up

2.1 DBD set-up

A schematic diagram of the plasma configuration is depicted in Figure 1. Two circular copper electrodes (diameter = 55 mm) are placed within a cylindrical enclosure. Both electrodes are covered with a glass plate (area = 72×78 mm; thickness = 2 mm) and the gas gap between the glass plates is 5 mm. The upper electrode is connected to an AC power source with a frequency of 50 kHz and the lower electrode to earth through a resistor of 10 Ω . Before starting the experiments, a PP film (Goodfellow Ltd., thickness = 0.075 mm) is placed on the lower glass plate. After introduction of the sample into the reactor, the discharge chamber is pumped down to 0.1 kPa and is afterwards filled with nitrogen (Air Liquide – Alphagaz 1) to atmospheric pressure. The discharge chamber is then pumped down to 5.0 kPa, while a gas flow of 750 sccm N_2 flows between the electrodes. Using this procedure, one can assume that a small fraction of oxygen remains in the discharge chamber with an order of magnitude of less than 0.1%. The gas exhaust is controlled by a pump and a needle valve is used in such a way that the pressure is maintained at 5.0 kPa during plasma treatment. The voltage applied to the electrodes is measured using a high voltage probe (Tektronix P6015A), whereas the discharge current is obtained by measuring the voltage over the resistor of 100 Ω , connected in series

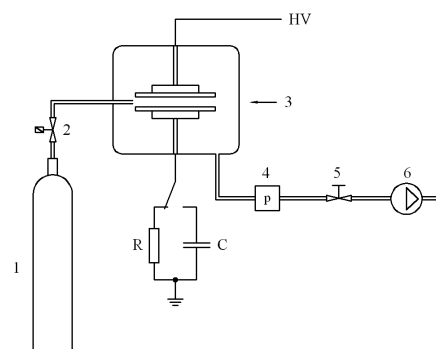


Fig. 1. Experimental set-up of the DBD (1. gas cylinder, 2. mass-flow controller, 3. plasma chamber, 4. pressure gauge, 5. needle valve, 6. pump).

to ground. This resistor can be replaced by a capacitor of 10 nF; the voltage across this capacitor is proportional to the charge stored on the electrodes. This latter measurement is widely used to obtain voltage-versus-charge plots, which form Lissajous figures [18]. From these figures, the electrical energy consumed per voltage cycle E_{el} can be estimated since this value is equal to the area enclosed by the Lissajous figure [8]. The electrical power P_{el} can be obtained by multiplying the electrical energy with the frequency of the feeding voltage, which is 50 kHz in this work [8]. All the above mentioned parameters are recorded using a digital oscilloscope (Tektronix TDS210–60 MHz) and the required calculations are then performed.

2.2 Contact angle measurements

The contact angles before and after plasma treatment are obtained using a commercial Krüss Easy Drop optical system (Krüss GmbH–Germany). This system is equipped with a software operated high-precision liquid dispenser to precisely control the drop size of the used liquid. 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, measurement of the static contact angles is fully automated. In this work, distilled water drops of 2 μl are used as test liquid. The values of the static contact angles, shown in this paper, are obtained using Laplace-Young curve fitting based on the imaged sessile water drop profile and are the average of 10 values measured over an extended area of the treated samples.

2.3 X-ray photoelectron spectroscopy (XPS)

XPS analysis is used to determine the chemical changes on the PP surfaces introduced by the plasma treatment. XPS measurements are carried out on a VG Escalab 220 XL system (Thermo Fisher Scientific–USA), using non-monochromatic Mg K_{α} -radiation ($h\nu = 1253.6$ eV) operated at 15 kV and 20 mA. The pressure in the analyzing chamber is maintained at 10^{-7} Pa or lower during

analysis and the size of the analyzed area is $8 \text{ mm} \times 8 \text{ mm}$. The high-resolution spectra are taken in the constant analyzer energy mode with a 40 eV pass energy and at a take-off angle of 90° relatively to the sample surface. The value of 285.0 eV of the hydrocarbon C1s core level is used as a calibration of the energy scale.

2.4 Atomic Force Microscopy (AFM)

AFM images are obtained in ambient conditions with a Multimode scanning probe microscope (Digital Instruments–USA) equipped with a Nanoscope IIIa controller. $3 \mu\text{m}$ scans are recorded in tapping mode with a silicon cantilever (OTESPA7–Veeco). Nanoscope software version 4.43r8 [19] is used for surface roughness analysis after the recorded images are modified with an X and Y Plane Fit Auto procedure.

3 Results

3.1 Electrical characterization of the discharge

As previously mentioned, the most common electrical diagnostic of a DBD consists of the measurement of the voltage applied to the electrodes and the resultant discharge current. Figure 2 shows the waveforms of the high voltage used to drive the discharge and of the discharge current, obtained with the PP film placed on the lower glass plate. As shown in Figure 2, numerous short peaks superimposed on the capacitive current can be seen. These peaks are an indication of the microdischarge activity and every peak corresponds to a series of microdischarges [7,8]. Therefore, one can conclude that the used nitrogen DBD operates in the filamentary mode. Figure 3 depicts the voltage-versus-charge plot or the so-called Lissajous figure. As stated before, this Lissajous figure can be used to calculate the electrical power [8], which in this case is equal to 8.6 W.

3.2 Contact angle measurements

A contact angle measurement represents the easiest and quickest method for examining the properties of surfaces and is a technique sensitive only to the topmost surface layer. Figure 4 presents the water contact angle on the treated PP film as a function of treatment time, measured within 1 min after plasma treatment.

As seen in Figure 4, the water contact angle of the plasma-treated PP film changes from 90.8° for the untreated sample to the lowest value 56.5° after 3 s of plasma treatment. However, when the treatment time is increased above 3 s, the water contact angle does not change anymore as a function of exposure time. This shows that there is a saturation of the plasma effect on the PP film after 3 s of plasma treatment.

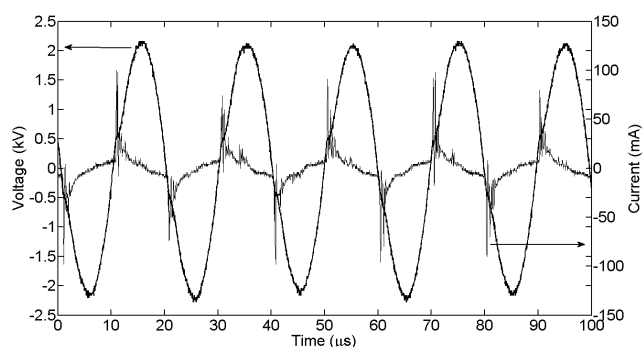


Fig. 2. Current-voltage waveform of the nitrogen discharge at 5.0 kPa.

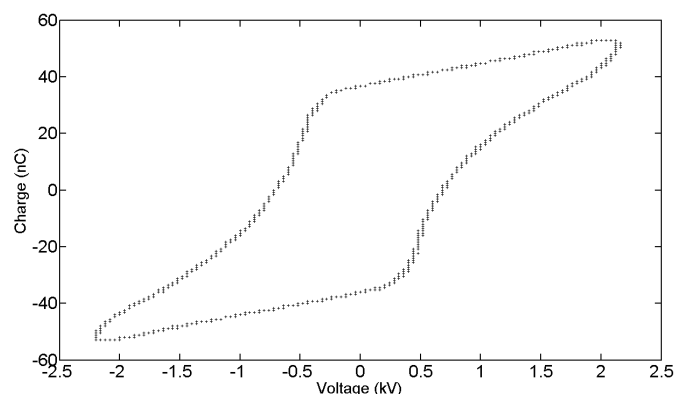


Fig. 3. Lissajous figure of the nitrogen discharge at 5.0 kPa.

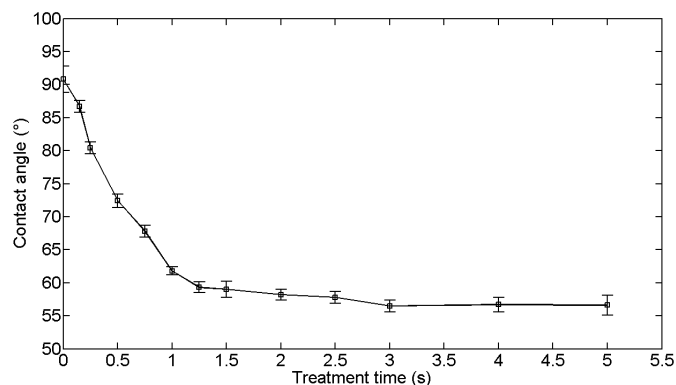


Fig. 4. Evolution of the water contact angle on the PP film as a function of plasma treatment time.

3.3 XPS analysis

XPS analysis is used to identify the chemical composition of the PP surface after DBD treatment and to quantify the respective contributions to the surface modification of reactive species present in the discharge. Besides nitrogen, which is the only reactive gas introduced between the electrodes, also a very small amount of molecular oxygen is present in the inter-electrode gap since it is very difficult, if not impossible, to ensure that DBD treatment occurs in a completely air-free environment. This molecular oxygen will be activated, ionized and dissociated in the discharge

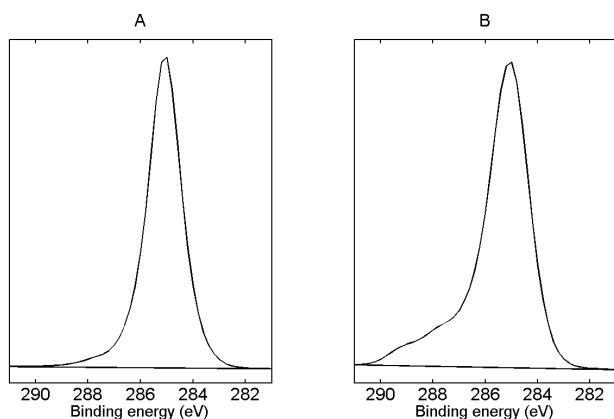


Fig. 5. C1s peak of the untreated PP film (A) and of the PP film after 4 s of plasma treatment (B).

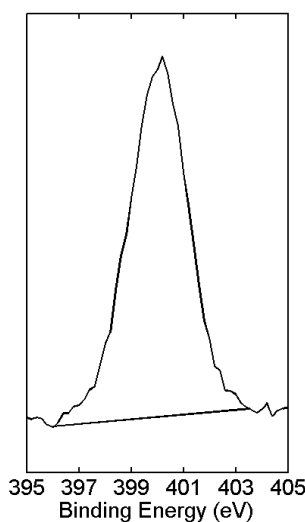


Fig. 6. N1s peak of the PP film after 4 s of plasma treatment.

to give extremely reactive oxygen species, which can readily react with the substrate surface [18,20].

Figure 5 shows the C1s peak of the PP sample before treatment (A) and the C1s peak of the sample after 4 s of plasma treatment in nitrogen (B). Figure 5 clearly shows that following plasma treatment, the C1s spectrum shows a long tail extending to 290.7 eV on the high energy side. The identification of the functional carbons based on the binding energies of the peaks is rather difficult when both nitrogen and oxygen species are present, since the energy difference between some nitrogen- and oxygen-related groups is too small to allow separation by mathematical reconstruction within error bars. The C1s binding energy of the different oxygen-containing carbon groups are well defined in literature [21], in contrast, for the carbon-nitrogen species, one can observe large discrepancies in binding energies. Moreover, also the N1s peak (see Fig. 6) cannot give a decisive answer about the nitrogen-containing functionalities on the PP surface, since the N1s peak of the samples lies between 397 and 403 eV. In this energy range, one can find several carbon-nitrogen

Table 1. Atomic content of oxygen and nitrogen species (in at%) on the plasma-treated PP films.

Treatment time (s)	O (at%)	N (at%)
0	3.9	0.0
0.25	5.8	1.3
0.75	7.4	3.6
2.00	9.4	8.6
4.00	9.6	10.1

species, such as amides, imides, nitriles, ... [23–25]. However, from the high resolution C1s and N1s XPS spectra, one can conclude that the treated PP surface contains carbon atoms that are singly- or doubly-bonded to oxygen, and carbon atoms that are mostly singly-bonded to nitrogen [21,22]. It is well-known from other research that it is rather difficult to incorporate nitrogen at polymer surfaces, even in the case of very well controlled N₂ environment vacuum plasmas run for extended treatment times. Therefore, it is reasonable to assume that only nitrogen singly-bonded to carbon groups exist on the surface [20]. Finally, amide groups (N–C=O) may also be present on the surface after plasma treatment. An appreciable presence of nitro (C–NO₂), oxime (C=NOH) and nitrate (C–ONO₂) groups on the surface after plasma treatment can be excluded, since the N1s peak does not extend to 406–408 eV [21,22]. A more precise identification of the chemical functional groups and further information concerning their relative concentrations will require the use of chemical derivatization schemes and of time of flight secondary ion mass spectrometry (TOF-SIMS).

However, a clear distinction between nitrogen and oxygen incorporation onto the surface can be made in terms of total atomic amount, as can be seen in Table 1. Table 1 presents the chemical composition (O and N species) of the PP films for varying treatment times. Important to notice is the fact that the untreated PP film appears to contain some oxygen species. According to the supplier of the PP film, this low-level surface oxidation is the result of a corona treatment applied to both sides of the PP film in order to promote adhesion. Table 1 also indicates that both oxygen and nitrogen species are incorporated onto the PP surfaces by the plasma exposure. Particularly, the incorporation of nitrogen is significant, up to around 10 at%, demonstrating that the implantation of nitrogen-related functional groups is possible by the DBD treatment performed at medium pressure. Nevertheless, besides the nitrogen incorporation, a considerable amount of oxygen species are implanted on the PP surfaces by the plasma, even when the oxygen is only present as a contaminant in the discharge. This underlies the extreme reactivity of the active species derived from oxygen and the difficulty in overcoming the air contamination problem.

3.4 AFM imaging

The physical modifications occurring on the PP surfaces during plasma treatment can be detected using AFM.

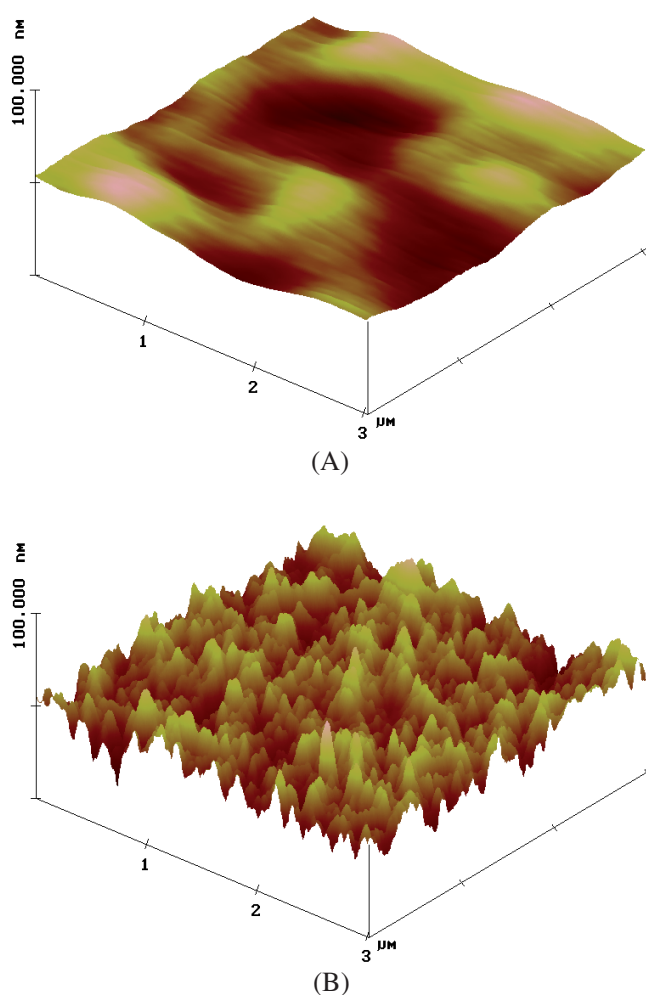


Fig. 7. (Color online) AFM images of the untreated PP film (A) and of the plasma-treated PP film after 3 s of plasma treatment (B).

Figure 7(A) shows the AFM image of an untreated PP film, while Figure 7(B) represents the AFM image of the PP film after 3 s of plasma treatment.

As seen in Figure 7, nitrogen plasma treatment significantly alters the morphology of the PP film: the pristine material has a smooth surface with no distinguishable features, while after plasma treatment, a large number of nanoscale depressions are created on the sample surface. Changes in morphology of the plasma-treated PP films are quantified by root mean square roughness values R_{rms} : the untreated PP surface has an R_{rms} value equal to 2.8 nm, while after 3 s of plasma treatment the R_{rms} value is equal to 6.5 nm.

This change in surface morphology is believed to result mainly from the bombardment of the surface by atomic oxygen present in the nitrogen discharge [26]. The chemical mechanisms associated with the incorporation of nitrogen and oxygen at the PP surface are different, whereby the former reactions induce much less chain scissions [27,28]. Therefore, it is believed that mainly atomic oxygen species are responsible for the etching process.

Inagaki et al. [29] have stated that nitrogen containing plasmas can create large changes in surface topography, since the discharge does not homogeneously etch the entire surface of polymer films but special parts of the polymer surfaces. Also Borgia et al. [30,31] state that the discharge preferentially physically etches the amorphous regions of the polymer surface. Therefore, it is believed that the creation of the large number of depressions is due to the selective etching of the amorphous regions of the PP film.

4 Conclusions

In this paper, the effects of a nitrogen DBD treatment on the surface of a PP film are examined, reported and discussed focusing on the chemical and physical modifications induced on the surface. Results clearly show that the nitrogen discharge can significantly increase the wettability of the PP film: the water contact angle can be decreased from 90.8° to 56.5° . Moreover, the results obtained underline the high efficiency of the present DBD set-up for the modification, since the surface is already saturated after a treatment time as short as 3 s.

XPS results indicate contributions from both nitrogen and oxygen to the attendant surface reactions. The incorporation of nitrogen onto the PP surface is significant, up to 10 at%, demonstrating that the implantation or generation of nitrogen-containing functional groups is possible by a DBD treatment at medium pressure. Nevertheless, besides this nitrogen incorporation, a significant amount of oxygen (up to 9.5 at%) can be found on the plasma-treated surfaces. This surface oxidation can be due to the presence of a low level of oxygen-containing impurities in the nitrogen flow or due to the contaminants initially present in the commercial PP. However, most likely, surface oxidation is due to the presence of residual air in the discharge chamber due to impossibility to operate in a completely air-free environment. Therefore, one can conclude that oxidation of the surface is significant even if oxygen is present only as a contaminant in the discharge. This conclusion underlines the extreme reactivity of the active species derived from oxygen in the discharge and the difficulty in overcoming the air contamination problem. Nevertheless, the obtained results are encouraging, since functional groups other than oxygen-related ones can be generated at the surface of interest.

AFM images indicate that saturation of the PP film is possible in a non-destructive way with the treated surfaces presenting an increased roughness compared with the pristine ones, an effect which is favorable for physical adsorption at the surface [30]. Therefore, one can conclude that the DBD system described in this paper provides an efficient and non-destructive means of altering the surface properties of polymer surfaces.

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