Treatment of PET and PU polymers by atmospheric pressure plasma generated in dielectric barrier discharge in air

K.G. Kostov [a,*], A.L.R. dos Santos [a], R.Y. Honda [a], P.A.P. Nascente [b], M.E. Kayama [a], M.A. Algatti [a], R.P. Mota [a]

[a] Faculty of Engineering in Guaratinguetá – FEG, State University of São Paulo – UNESP, Av. Dr. Ariberto Pereira da Cunha 333, Guaratinguetá, SP 12516-410, Brazil
[b] Department of Material Engineering, Federal University of São Carlos – UFSCar, Via Washington Luis km235, São Carlos, SP 13565-905, Brazil

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ABSTRACT

Plasma treatments are frequently employed to modify surface properties of materials such as adhesivity, hydrophobicity, oleophobicity etc. Present work deals with surface modification of common commercial polymers such as polyethylene terephthalate (PET) and polyurethane (PU) by an air dielectric barrier discharge (DBD) at atmospheric pressure. The DBD treatment was performed in a plain reactor in wire-duct geometry (non-uniform field reactor), which was driven by a 60 Hz power supply. Material characterization was carried out by water contact angle measurements, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The plasma-induced modifications are associated with incorporation of polar oxygen and nitrogen containing groups on the polymer surface. The AFM analysis reveals that the plasma treatment roughens the material surface. Due to these structural and morphological changes the surface of DBD-treated polymers becomes more hydrophilic resulting in enhanced adhesion properties.

1. Introduction

Polymeric materials are increasingly replacing the traditional engineering materials like steel and aluminum in fabrication of space and aircraft, automobiles, civil construction as well as in biomedical applications due to their superior properties like better corrosion resistance, high strength to weight ratio, relatively low cost and easy recycling. However, polymers are intrinsically hydrophobic, low surface energy materials, and thus do not adhere well to other materials. Therefore for some applications it is necessary to modify the polymer surface in order to increase its surface energy without changing the material bulk properties. Surface treatment of polymers by discharge plasmas is of great and increasing industrial application because it can uniformly modify the surface of treated samples and is environmentally friendly. The plasma acting mechanisms are very complex, but the main outcomes of plasma–surface interaction are surface cleaning, activation, cross-linking, and etching or in many cases combination of these effects [1]. The plasma processing generally promotes the formation of free radicals that interact with the polymer surface altering its adhesive properties. Among the many kinds of plasmas, the plasma processes that can be conducted under ambient pressure and temperature conditions have attracted special attention because of their easy implementation in industrial processing.

In the last few decades, gas discharges at atmospheric pressure have been extensively studied because of their potential applications in various industrial and technological processes. Dielectric barrier discharge (DBD) is a type of discharge in which at least one electrode is covered by a dielectric layer, i.e. it is not in direct contact with the gas [2]. The consequence of this arrangement is that, after the gas breakdown, the charge accumulation on the dielectric surface prevents the corona-to-spark transition and, eventually, stops the discharge if the voltage does not increase continuously. However, if an AC voltage is applied to the electrodes, the discharge starts again when the electric field is reversed. Usually, voltages of few kV and frequencies ranging from 50 Hz to several MHz are used. The mean electron energy in DBD plasmas is in the range of 1–10 eV, while the chemical binding energy of polymers is less than 10 eV. Therefore, energetic particles in DBD can easily break the chemical bonds of polymers and active radicals abundant in the plasma can react with the surface, modifying its adhesion properties [3,4]. DBD discharges at atmospheric pressure produce intense ultraviolet radiation, which can break molecular bonds and initiate physical and chemical processes that also take part of the polymer surface modification.

The present work reports the results of polyethylene terephthalate (PET) and polyurethane (PU) surface modification by air DBD at atmospheric pressure. The samples utilized in this study were cut from commercially available PET and PU polymers used for industrial applications. Material characterization was carried out by water contact angle measurements, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental setup

The experimental arrangement used to study DBD discharge at atmospheric pressure is sketched in Fig. 1. The DBD discharge is

* Corresponding author. Tel.: +55 12 31232844; fax: +55 12 31232840.
E-mail address: kostov@feg.unesp.br (K.G. Kostov).

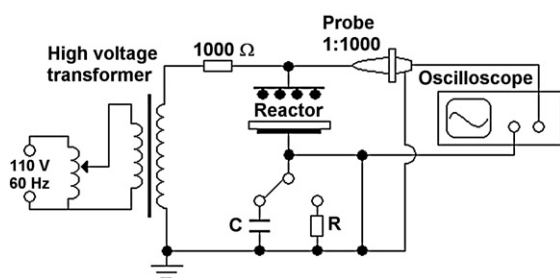**Fig. 1.** Schematic drawing of the experimental setup.

Fig. 2. Typical waveforms of the discharge current and voltage.

generated between two parallel electrodes. The top electrode, a flat 165×165 mm^2 array of 32 parallel Ni–Cr wires (0.3 mm diam), was employed as high-voltage electrode. The high-voltage power supply is consisted of a step-up high-voltage transformer (100/20000 V of V_{rms}, 60 Hz) driven by an autotransformer Variac. A load resistor of 1 kΩ, 25 kV protected the transformer in case of DBD to arc transition. The reactor bottom electrode was a 28 cm diam, 1.0 cm-thick aluminum disk which was grounded. The square high-voltage electrode was centered in the middle of the bottom circular electrode. As dielectric barrier served a 0.5 mm-thick, 30 cm diam Mylar sheet stuck on the grounded electrode. The enhancement of the electric field around the thin bare Ni–Cr wires helps to initiate AC corona discharge. Distance between the reactor electrodes was adjustable and during this experiment was held at 6 mm.

Treatments were performed on plates of commercial PET (cut from plastic bottles) with thickness of 0.5 mm and dimensions of 15×20 mm^2. PU samples with thickness of 1.5 mm, provided by the Perk Plast Industries, Brazil were sliced with the same size as the PET samples. Prior the DBD treatment, the samples were ultrasonically cleaned in distilled water and detergent for half an hour. To remove organic contaminants from the surface the samples were washed by rinsing in isopropyl alcohol for 10 min and after that dried at room temperature. The tests were performed with specimen placed on the dielectric barrier, which completely covered the grounded electrode. To ensure uniform treatment of the whole sample the axis of the circular bottom electrode was connected to a DC motor and could rotate with constant angular velocity during the tests. All plasma treatments were carried out in air at atmospheric pressure. The AC voltage applied to the reactor upper plate is measured by using a 1000:1 high-voltage probe (Tektronix P6015A, 75 MHz) and displayed on a digital oscilloscope (Tektronix TDS 2024B, 200 MHz).

For displaying the waveform of the discharge current on the oscilloscope the reactor down plate was grounded through a current measuring resistor of 1200 Ω. Fig. 2 depicts the typical waveforms of the discharge current and voltage. By applying an AC voltage across the wire-duct reactor (non-uniform field reactor) some differences were observed on the waveform of the discharge current in comparison with that of a parallel plate reactor [5]. The onset voltage of this wire-duct DBD reactor is about that of AC corona with the same geometry configuration. Beyond the onset voltage (about 7.0 kVp-p) the discharge starts inside the reactor in the form of filamentary streamers illustrated by many narrow current peaks. With further increase of the discharge voltage a stable corona, similar to common AC corona discharges, is established around the thin wires constituting the high-voltage electrode. Thus, the discharge current consists of large number of short micro-pulses typical for the DBD discharges that are superimposed to a wider current pulses associated with the corona formed around the thin Ni–Cr wires. The use of a higher frequency source (in the kHz range) can further reduce the discharge onset voltage, however a 60 Hz power supply is preferable in direct industrial applications. The advantage of this non-uniform field DBD reactor configuration is that due to the dielectric barrier the AC voltage across the reactor can be raised up to 20 kV peak voltage
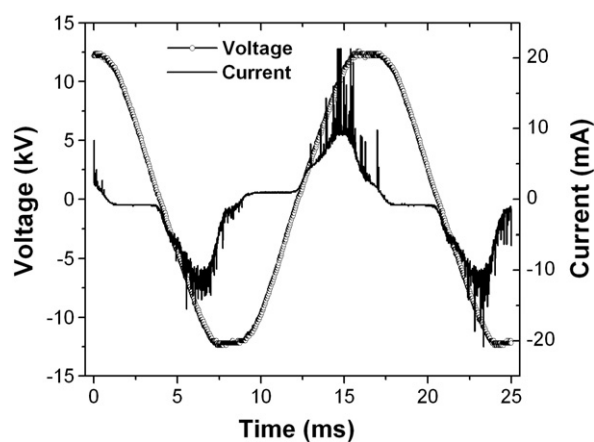
without arcing thus delivering more power to the plasma. Typically the discharge power of atmospheric pressure DBD reactors increases linearly with the applied voltage [5], however in this study the AC applied voltage was fixed at 25 kVp-p and the only variable treatment parameter was the plasma exposure time.

The contact angle was obtained by using the sessile drop method on a standard Rame–Hart goniometer, model 300. The volume of each drop was 2 µl and the average value of at least 5 drops was calculated.

Surface chemical characterization was carried out by X-ray photoelectron spectroscopy using a Kratos XSAM HS system. The base pressure in the analyzing chamber was kept below 10^{-7} mbar. As excitation source the Mg K$_\alpha$ line ($h\nu = 1253.6$ eV) was employed with the emission voltage and current of the source set to 6.0 kV and 5.0 mA, respectively. The obtained spectra were processed by the code provided by the apparatus manufacturer using the Shirley method for background subtraction. All peaks were fitted using Gaussian curves. The value of 284.8 eV of the hydrocarbon C1s core level was used for calibration of the energy scale.

DBD induced changes of the polymers' surface morphology were studied by atomic force microscopy — AFM. The AFM analysis was performed in air with a Nanoscope-V Multimode atomic force microscope. During the analysis, the microscope was operated in tapping mode with a scanning rate of 0.5 Hz for all scanning sizes using an etched silicon probe ($k = 50$ N/m).

3. Results and discussion

A simple and reliable method for obtaining the discharge power of DBD reactors is using the discharge Q–V Lissajous figures, when plotting transported electric charge Q through the discharge as a function of the applied periodical voltage [6]. Experimentally, the charge Q is obtained from the voltage drop across a measuring serial capacitor of 0.91 µF. A typical Lissajous figure of our DBD reactor is shown in Fig. 3. The average electric energy dissipated in one discharge cycle is simply the area of the characteristic Q–V diagram, which in most cases is nearly a parallelogram. Then the mean discharge power is calculated by multiplying the discharge energy to the frequency of the AC power supply.

All polymer treatments were performed in air at ambient pressure and temperature conditions for different DBD exposure time. The applied AC voltage was fixed at 25.0 kV$_{p-p}$, which corresponded to 30.0 W of discharge power. At fixed discharge power and voltage, (e.g. keeping the same density and energy of the plasma species), the degree of surface modification was controlled by varying the treatment time.

Contact angles between droplets of distilled water and polymer surfaces were measured in order to evaluate the degree of surface modification of the samples. The results from the water contact angle
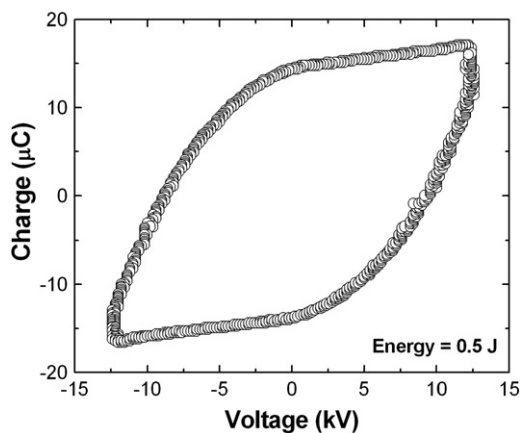
Fig. 3. Q–V Lissajous figure.

assessments are shown in Fig. 4. The value of the water contact angle of PET and PU polymers decreases gradually with the polymer treatment time. For plasma exposure time greater than 10 min the changes of the water contact angle become irrelevant and the contact angle values tend to saturate at about 60° for the PU and 40° for the PET. The considerable increase of the polymer wettability (contact angle reduction of about 50%) suggests that large number of hydrophilic groups was incorporated on the surface as a result of the DBD treatment.

It is well known that plasma treated polymers exhibit partial contact angle recovery after the plasma–surface modification [7]. This behavior can be explained by the fact that the plasma-treated polymers try to reduce their surface free energy [8]. This process is referred to as hydrophobic recovery or aging process. In order to study the evolution of surface wettability after the DBD treatment, the polymer samples were stored in air at room temperature and at relative humidity of 60%.

Fig. 5a and b shows the evolution of the water contact angle of plasma-treated PET and PU as a function of storage time. As can be seen in Fig. 5 for all time intervals of DBD treatment the aging process of both polymers is characterized by a rapid increase of the water contact angle during the first few days of storage followed by a slow recovery process during the next days. The hydrophobic recovery of PU is quick and the contact angle saturation value, attained after 1 day of storage, is quite close to that of pristine PU. On the other hand, the PET contact angle after the DBD treatment grows slowly eventually reaching a plateau after about 3 days of air storage. After 3 days of storage there are still small variations of the polymers contact angle, however no significant deviations were observed. It is important to
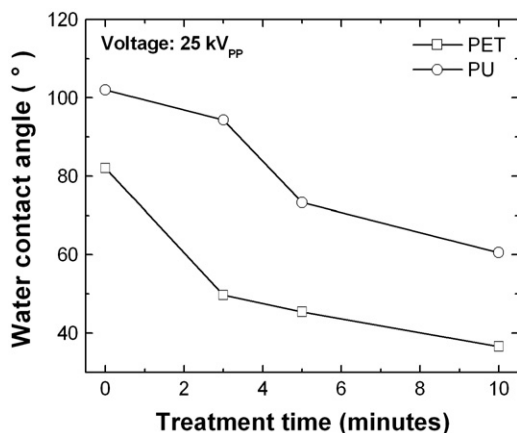

Fig. 4. Water contact angle of PET and PU measured half an hour after the DBD treatment as a function of plasma exposure time.
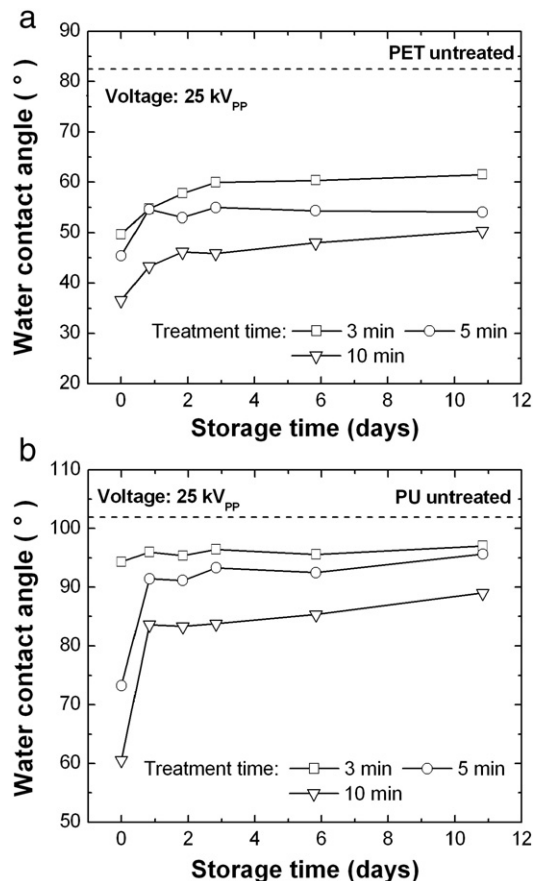

Fig. 5. (a). Hydrophobic recovery of PET samples treated for a different length of time. (b). Hydrophobic recovery of PU samples treated for a different length of time.

mention that nevertheless the partial hydrophobic recovery of both polymers the maximal water contact angle after more than 10 days of storage at ambient conditions is still lower than the water contact angle of the untreated samples. Similar aging behavior of plasma-treated polymer was observed in [8]. The authors in [9] followed the aging process of PET surfaces treated by air DBD for 24 days and no significant hydrophobic recovery after the tenth day of storage was noticed. Possible reasons for this polymer surface instability include the reorientation of polar groups at the surface layer and also the diffusion of unpolar groups from the bulk to the surface [9,10].

From Figs. 4 and 5 one can deduce that by increasing the time of plasma exposure, the effectiveness of the plasma treatment increases resulting in polymer surfaces with smaller water contact angle, which are also less susceptible to hydrophobic recovery. This finding means that as far as a certain amount of oxygen, introduced by the DBD treatment, remains on the polymer surface it will not completely recover its original wetting characteristics.

Two week after the DBD treatment, when the process of polymer hydrophobic recovery is practically saturated, the atomic composition of PET and PU samples was investigated using high-resolution XPS analysis. The elemental composition of the polymer surfaces before and after the plasma treatment is shown in Table 1. The Si content on the PU surface comes from the silicon oil, which is frequently used in the PU production reaction as surfactant to eliminate surface defects such as pin holes, orange peel, and sink marks. The O/C atomic ratio of the PET surface modified by DBD discharge increases to 0.56 in comparison with the untreated sample (0.41 O/C ratio). The PU O/C ratio increases from 0.52 for the pristine PU to approximately 0.78 O/C ratio after the plasma treatment. The increased O contents of the plasma-modified polymers suggest that new oxygen-containing groups are formed on the surface [11]. Furthermore, Table 1 shows

Table 1
Elemental composition of PET and PU surfaces (in atm.%).

Samples	Atomic concentration (%)			
	C	O	N	Si
Pristine PET	70.9	29.1	–	–
Treated PET	63.0	35.5	1.5	–
Pristine PU	54.2	28.4	1.0	16.4
Treated PU	47.4	37.2	1.4	14.0

that nitrogen content on the polymer surfaces also slightly increases as a result of the air plasma exposure. Therefore one can conclude that the reduction of water contact angle of DBD-treated polymers is mainly due to the formation of oxygen-containing polar groups and in lesser extend to the formation of nitrogen polar groups on the surface.

To evaluate which oxygen-containing functional groups are formed on the polymer surfaces after the plasma exposure the C1s peak of the XPS spectra is investigated in details.

Fig. 6 shows the C1s spectra of the untreated PET sample and the C1s peaks of the saturated PET surface after the air plasma treatment. The C1s spectrum of the pristine PET is deconvoluted into three components: a C1 at 284.8 eV due to the C–C and C–H bonds, a C2 component at 286.4 eV due to C–O bonds and a C3 component at 288.8 eV due to the O–C=O bonds [12]. As a result of the plasma treatment some changes in the C1s peak can be seen. Similarly, it can be decomposed into three components at 284.8 eV, 286.5 eV and 288.8 eV. However, the peak intensity at 284.8 eV decreases compared to the intensity of the peaks at 286.5 eV and 288.8 eV that increase. This finding is explained by the fact that atmospheric plasmas mainly attack the weak C–C and C–H bonds in the PET polymer chains to created C–O and O–C=O groups on the surface. The relative area of each peak is presented in the Fig. 6 showing that the concentration of the oxidized carbon species on the polymer surface increases after the plasma exposure. The DBD discharge in air creates many active species including atomic oxygen, ozone, nitrogen oxides, exited molecules etc. The oxygen is incorporated on the polymer surface introducing C–O and O–C=O polar groups which leads to increase of the PET surface energy and reduction of the water contact angle. These polar groups were also found on the surface by other authors [13] after air DBD treatment of PET films at atmospheric pressure. Similar to these authors our results show that no C=O groups at about BE = 287.3 eV [14] are formed on the polymer surface. However, formation of carbonyl groups was observed in cases when other polymers were treated with plasma [13,14]. This finding needs further investigations in order to determine the reaction pathway which leads to this oxidized PET structure. The N1s peak was

decomposed into two components at 400.0 eV and 401.9 eV related to the N=C and N–O bonds, respectively [15].

The C1s spectra of treated and untreated PU samples are presented in Fig. 7. Once again, the pristine PU spectrum is decomposed into three components C1 peak at 284.8 eV due to the C–C and C–H bonds, a component C2 at 286.5 eV due to C–O bonds and a C3 component at 289.2 eV due to the O–C=O bonds [12]. The urethane groups, NH–C (=O)–O are known to be situated at about BE = 289.6 eV, which suggests a slightly degraded pristine sample. The treated PU C1s peak spectrum consists of the same three peaks, however their intensities are different from those of pristine PU due to the polymer surface modifications induced by the DBD treatment. Plasma treatment of PET with DBD discharge in air introduces C–O and O–C=O groups on the polymer surface. Again no C=O groups were formed on the PU surface. The relative increase of the C2 and C3 peaks (in respect to the C1) after the DBD treatment of PU is more pronounce than that in the case of PET treatment. The XPS spectra of both PU samples, treated and pristine present a single N1s peak at 400.2 eV due to the N=C bonds [15].

According to the Wenzel equation [16] the surface roughness can enhance the mechanical interlocking thus influencing the surface wettability. Therefore the enhanced surface wettability of plasma-treated polymers can be correlated with two processes − the modified chemical composition due to air plasma oxidation of the surface as well as the physical changes in the surface morphology. From the AFM images of the sample's surface topography, average surface roughness (R_{av}), and root mean square roughness (R_{rms}) were determined. The results from the AFM analysis of pristine polymers and 10 min plasma-treated samples are summarized in Table 2. As can be seen from this table the surface roughness of both polymers increases as a result of plasma exposure. Bombardment of polymer surface by energetic particles such as electrons, ions, radials and excited species causes removal of surface contaminants, amorphous materials, oxide layers, and adsorbed species resulting in mild etching of the surface [17]. This plasma-induced morphological modification of the surface will also contribute for enhancing the wettability of PU and PET polymers.

4. Conclusions

The surface of PE and PU samples was modified by DBD in air. As evidenced by AFM and XPS analysis, the plasma exposure effectively changes both the surface morphology and the surface chemical composition. The surface became rougher and oxygen and nitrogen atoms were introduced onto the DBD-treated samples. The air plasma treatment produced more oxygen-containing functional groups (C–O
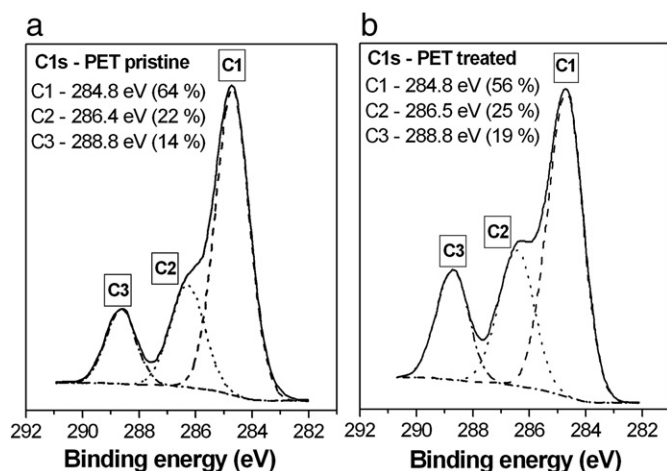

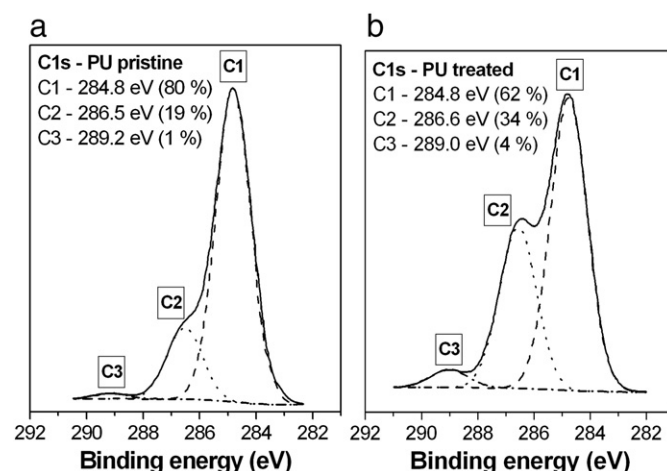**Fig. 6.** C1s spectra of (a) untreated and (b) DBD-treated PET.

Fig. 7. C1s spectra of (a) untreated and (b) DBD-treated PU.

Table 2
Comparison of the PET and PU roughness.

Material roughness	PET (nm)	PU (nm)
Pristine	$R_{av} = 1.14$	$R_{av} = 6.83$
	$R_{rms} = 2.38$	$R_{rms} = 12.65$
Treated	$R_{av} = 2.19$	$R_{av} = 9.14$
	$R_{rms} = 3.66$	$R_{rms} = 15.43$

and O–C=O) on the polymer surface. These surface modifications resulted in a decrease of the water contact angle and enhanced wettability of the DBD-treated polymers. However, the investigation of polymer aging behavior has shown partial hydrophobic recovery of the polymer surfaces (the aging effect is more pronounced for the PU samples). This process is probably due to the reorientation of induced polar chemical groups into the bulk of the material and the diffusion of unpolar groups from the sub-surface layer to the surface. The increase of DBD treatment time led to more intense surface modification effects (surface oxygenation and roughness enhancement) resulting in polymer surfaces with smaller water contact angle that were less susceptible to hydrophobic recovery. In the near future, an extended characterization (XPS and AFM analyses) of the exposed polymer samples will be carried out to determine which is the key factor for altering the polymer hydrophilicity: the plasma-induced chemical modifications or the surface etching produced by the plasma.

Acknowledgments

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