SURFACE OXIDATION AND ENHANCED HYDROPHILIZATION OF POLYAMIDE FIBER SURFACE AFTER HE / AR ATMOSPHERIC PRESSURE PLASMA EXPOSURE

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Due to their bulk and surface properties the polymeric fibers are used for various applications as surgery, textile industry and many others. In the present paper the surface modification, wettability and chemical composition of polyamide 6 fibers, after direct atmospheric dielectric barrier discharge treatment, in helium and argon, are studied. The contact angle method, atomic force microscopy technique and X-ray photoelectrons spectroscopy were used to investigate plasma induced modifications of polyamide surface. Increased hydrophilic properties of plasma-treated surfaces were proofed by static water contact angle measurement, with values up to 70% lower than pristine polymer. It was found that the surface roughness increases up to 3 times after helium plasma treatment and 2 times after argon plasma treatment, for up to 7 days. Surface oxidation, after plasma exposure, was observed through X-ray photoelectrons spectroscopy. These experimental findings, proven by the good correlation of the obtained results from both plasma diagnosis and polymeric surface characterization, underline the usage of plasma sources for polymeric surface processing.

Key words: atmospheric pressure discharge, plasma-surface interactions, polymeric fibers, hydrophilization.

1. INTRODUCTION

Polymers are important in many fields such as: biology, medicine and various industries (machinery, textile, construction) and rather recently food industry. Nonetheless, in some situations, surface properties of polymers must be modified precedent to further specific processing due to the fact that their surface properties are often inadequate for some applications. They are used mainly as basic materials for various mechanical, electrical or bio components because of their bulk physico-chemical properties. However, in many applications the surface properties of the polymers are dominant and special attention is needed for both identification and
obtaining those properties. An extensively used method for customizing polymer surface properties is non-thermal plasma exposure. In a recent review study Vesel et al. [1] presented a large variety of methods and techniques used for plasma treatment and the exposure conditions are described. The reported results show various contradiction which, on one side might have various reasons and on the other side must be clarified. Thus, the reason for such variances might be either the specific processing methods used or even usage of polymers with various origin or geometrical forms of the sample. E.g. rather recently it was proven that polymeric fibers interact differently with gaseous plasmas compared to polymeric foils, as flat surfaces, due to the enormous surface-to-mass ratio [2]. Consequently, it is very important to know as many information as possible regarding polymers, especially polymeric fibers. Even though a multitude of experimental results have been published, the precise mechanisms are yet not fully established; therefore plasma-polymer surface interactions remain a hot topic [3–13].

Bearing this in mind, it is essential to know as many information as possible concerning polymeric fibers. Mostly, basic information’s about polymeric suture fibers are associated to their strength and diameter. A great deal of other polymer properties can be tuned up, such as: surface morphology or its energy, surface flexibility, and even its friction coefficient or interfacial tension coefficient. Consequently, the necessity of knowing all of these parameters leads to the development and optimization of new physico-chemical methods that can modify them. As mentioned above, atmospheric pressure non-thermal plasma exposure of polymers seems to be a promising way to modify the surface and to control the morphology either by physical or chemical reactions like cleaning, etching, crosslinking, functionalization or even polymerization [14–23]. Plasma operational parameters (e.g.: applied voltage, discharge current density, electrical mean power, total emitted light, excited and reactive species) will influence the main processes at the interface between plasma and polymer. Therefore, by adjusting these parameters we may monitor some plasma effects on the fiber surface. Commonly, due to atmospheric pressure working conditions, the surface is abundant in oxygen-containing chemical groups (e.g.: hydroxyl, carbonyl or carboxyl/ester) even though the plasma working gas was not oxygen, but rather air, carbon dioxide, helium or even argon [16, 24–35]. The opulence of oxygen-containing functional groups is usually assigned to the high affinity of oxygen towards plasma-exposed polymer surface.

This study is focused on the surface modification, wettability properties and chemical composition changes of polyamide 6 fibers after direct exposure to atmospheric pressure plasma produced by a dielectric barrier discharge (DBD) system working in He and/or Ar.

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2. MATERIALS AND METHODS

For present study samples of commercial polyamide 6 fibers (PA6, 150 µm diameter, 0.5 m long, carefully cleaned with deionized water and ethyl alcohol prior to all experiments) were exposed to the atmospheric pressure dielectric barrier discharge source. PA-6 was chosen due to the fact that it is a high surface polarity polymer, being thus expected to show significant surface modification after relatively short plasma treatment [36]. Moreover, PA6 is a common material used in many applications, including, among others, automotive (e.g. in airbag canisters), electrical and electronics (e.g.: low voltage switch gears, industrial connectors) railways pads, tubing and packaging [37–39], but also as 3D printing material (e.g. copolymer PA6 and PA6,6) [40, 41]. Although many of PA6 mechanical, electrical and thermal properties are well grounded, scarce information upon the surface properties of this material can be found in literature. However, new uses (eg in medicine) require new surface properties (involving the biocompatibility of the material). How environmental protection has become a priority, changing the surfaces of these materials in plasma seems a promising solution.

From the large amount of techniques used for surface characterization, in this paper we considered contact angle (CA), atomic force microscopy (AFM) and X-ray photoelectrons spectroscopy (XPS) for proving the functionalization of polyamide PA6 fibers after He and Ar plasma exposure.

The static contact angle method, the sessile drop technique, is a very convenient and direct method of revealing the surface properties (i.e. energy, hydrophilic / hydrophobic character). This technique involves that a liquid droplet is applied on a surface using a micro syringe. The contact angle is obtained using the droplet profile, at room temperature and ambient humidity immediately after equilibrium is established. In this way, taking the photo of the droplet and using the open-source ImageJ software [42], we can measure the static contact angle between a liquid droplet and the polymer sample surface.

Atomic force microscopy is a powerful technique for surface morphology characterization. The surface topography of PA6 samples was studied through atomic force microscopy. The NT-MDT Solver PRO-M scanning probe microscope was used for scanning imaging, which was operating in tapping mode. The samples were scanned using a standard NSG30 Si cantilever with tip curvature radius ≤ 10 nm, a force constant of 40 N/m and at a resonance frequency of 320 kHz. The scanning imaging was performed on 3 µm × 3 µm area of the samples.

After the treatment, the plasma effects upon PA6 fibers were studied by X-ray photoelectron spectroscopy (XPS). For the present study the Ulvac PHI 5000 VersaProbe high-resolution XPS spectrometer was used. This device employs monochromatic Al K$_\alpha$ radiation at 1486.7 eV for excitation of the surface, with a X-ray beam
diameter of $100 \, \mu m$, at $45^\circ$ electron take-off angle. The XPS survey-scan spectra were acquired at a pass-energy of 11.75 eV using an energy step of 0.4 eV; while the C1s high-resolution spectra were acquired at a pass-energy of 23.5 eV using an energy step of 0.1 eV. The main C1s peak was fixed to 285 eV for charge compensation. The XPS spectra were analyzed using MultiPak software. The information given by XPS is regarding the binding energy and chemical composition of the sample surface.

3. EXPERIMENTAL SET-UP

Plasma system

The dielectric barrier discharge (DBD) was produced in an open reactor with plane-parallel electrode configuration (FIG. 1).

![Fig. 1 – Sketch of the experimental arrangement: plane-parallel DBD plasma systems.](image)

The discharge is generated between two copper plates electrodes ($11 \, cm^2$ each), centered on the dielectric plates (glass $30 \, cm^2$ each), as in FIG. 1. The dielectric barriers were placed both on the ground and the high-voltage electrode. The gas gap was maintained constant at 3 mm. An amplification chain, using a Tabor WW5064 function generator and a Trek PD07016 amplifier, generates high voltage pulses that are applied on the power electrode. The high voltage power supply generates monopolar pulses of 1 to 10 kV amplitude, pulse duration between tens to hundreds of $\mu s$ and frequency in the range 10 Hz to 10 kHz. The experiments are performed at room temperature, in helium (purity 4.6) and argon (purity 4.8), with a constant flow rate of 3L/min (maintained by an MKS Type 247 flow controller). Experiments were performed without preliminary vacuum pumping, at atmospheric pressure. This mode of operation is motivated by the possible conditions used in industrial system for plasma surface treatment of the materials.

During all experiments the PA6 fiber sample was placed between the electrodes (middle of the electrodes gap, like in FIG. 1). The DBD plasma treatment time of...
polymer fibers was varied from 10 to 60 s.

4. RESULTS

4.1. ELECTRICAL CHARACTERIZATION

Using a 350 MHz digital oscilloscope the applied voltage waveforms $U_a$ on the electrodes and the total discharge current pulses, $I_d$, were stored (FIG. 2). Applied voltage was measured through a resistive and non inductive voltage divider (1:1000), the discharge current being measured via the voltage across a noninductive 100 $\Omega$ resistor, connected in series with the grounded electrode. The applied voltage on the electrodes was kept constant at 3.5 kV amplitude, the repetition frequency of the voltage pulses being of 2 kHz, and a pulse duration of 40 $\mu$s.

![Fig. 2 – The voltage - current waveforms for DBD plasma ignited in a) He and b) Ar.](http://www.infim.ro/rrp)

In these experimental conditions, for He plasma current amplitudes of 1.5 mA on the primary discharge (current pulse width of 0.6 $\mu$s) and 0.8 mA on the secondary discharge (current pulse width of 1.3 $\mu$s) was recorded. In the case of Ar plasma the current amplitude went up to 1.2 mA on the primary discharge (current pulse width of 2.7 $\mu$s) and 0.4 mA on the secondary discharge (current pulse width of 5.4 $\mu$s). The early ignition of the plasma in He (breakdown at 1.5 kV) was observed, rather than the case when Ar was used as working gas (breakdown at 3 kV). Furthermore, slightly smaller amplitude values of the discharge current for DBD plasma ignited in Ar were observed, but with wider current picks, in comparison to the e plasma current waveforms. Total electrical charge from the DBD source created during each applied voltage pulse (calculated as sum of electrical charge created during primary and secondary discharge) was found to be up to 0.7 nC for He DBD and up to 1.4 nC for Ar DBD. Moreover, the estimated discharge mean power was up to 7 W (or power...
density 0.2 W cm\(^{-2}\), which is in between the power densities of plasma sources used for polyamide treatment by Salem et al. up to 0.07 W cm\(^{-2}\) [16] or Gao et al. 6.3 W cm\(^{-2}\) [28]).

4.2. OPTICAL EMISSION SPECTROSCOPY

The total emitted light of the DBD plasma system was analyzed using an optical fiber (400 \(\mu\)m diameter, 200-1100 nm range) and a Triax 550 high-resolution scanning monochromator spectrometer equipped with a Peltier cooled CCD detector. The monochromator has two diffraction gratings (a 600 lines/mm grating blazed at 400 nm, and a 2400 line/mm grating brazed at 350 nm) and an adjustable entrance slit. Plasma emitted light was collected from the discharge volume (FIG. 3) in the 300 to 900 nm range, with and without polymer fiber between electrodes. No visible changes were observed when the polymer fibers were placed in the discharge.

![Emission spectra of the DBD plasma system (He / Ar flow rate 3 slm, \(U_a = 3.5\) kV, 3 mm gap).](attachment:fig3.png)

Emission spectra in the UV-visible range of the DBD plasma contains signatures of molecular and atomic excited species, in addition to the emission from the He-excited species and Ar-excited species (FIG. 3). The molecular bands are assigned to hydroxyl radicals, neutral nitrogen molecules and nitrogen molecular ion. The OH radical presents signatures between 306 - 310 nm. Bands of the molecular nitrogen (\(N_2\)) are observable in the spectral range of 315 - 380 nm and 399 - 405.9 nm. The nitrogen molecular ions (\(N_2^+\)) have bands at 391.4 nm, 427.8 nm and 470.0 nm. Atomic lines are assigned to helium atoms (lines at 588.8 nm, 668.5 nm, 706.6 nm and 727.5 nm) and argon atoms (lines at 696.5 nm, 706.7 nm, 727.3 nm, 738.3 nm, 750.3 nm, 763.5 nm, 772.3 nm, 794.8 nm, 801.4 nm, 811.5 nm, 842.4 nm) as working gas, and to oxygen atoms (lines at 777.8 nm and 845.5 nm) most likely as products of H\(_2\)O dissociation [43–45]. Furthermore, the presence of excited OH and
O species in the plasma, which act as strong oxidizing species, makes these plasma sources suitable for many applications, like functionalization, crosslinking, etching or polymerization. Nevertheless the differences in the light intensity of the $N_2$ and $N_2^+$ bands in Fig. 3 are based on the interaction processes between He atoms and nitrogen molecules (Penning effect) [45]. Nonetheless, the competition between reactive oxygen species / nitrogen species, on one side, and helium / argon species, on the other side, with their large amount of energy available for transfer to the polymer surface, can end both in crosslinking and functionalization on the polymeric fiber surface. Furthermore, Borcia et al. [46] suggest that, in such plasma treatment conditions, surface crosslinked layers can act like a barrier to the diffusion of molecules between the bulk and surface, thus, limiting the stochastic movement of polymer chain and restricting permeation.

4.3. EFFECTS OF PLASMA TREATMENT ON PA6 SURFACE MORPHOLOGY (AFM)

The AFM morphology images were recorded for each fiber on $3\mu m \times 3\mu m$ scanned areas, and were repeated on different sites of the fibers in order to ensure reproducibility. The results obtained are restricted mainly to 3D images of the pristine and treated polymer surfaces (FIG. 4).

Statistic AFM estimations permitted to characterize and compare the surface roughness by means of the root mean square roughness ($R_q$), before and after the treatment. The value of root mean square roughness ($R_q$) for pristine PA6 fibers is 2.96 nm, as previously measured by [12]. For shorter exposure time (10 s) plasma treatment moderately changes the topography of the polymer (as in FIG. 4 middle row), while relevant variation of the contact angle were observed (as in FIG. 5). This might show that plasma treatment related modifications are produced at atomic and molecular level.

For longer exposure time (60 s) the polymer surface is totally remodel. From last two 3D images of FIG. 4 it can be seen that the morphology and roughness of the PA6 fibers are obviously changed. This could be due to the reorganization processes of PA6 chains that occur at the polymer surface, in tandem with possible crosslinking or bond breaking reactions [47]. Experimentally it is observed that the value of the $R_q$ is increasing with the DBD plasma exposure time, up to 7.2 nm for He DBD treatment, and till 5.6 nm for Ar DBD plasma treatment (as in TABLE 1).

From the 3D images in FIG. 4 it can be seen the effect of the working gas upon the surface modifications. Combined with the exposure time, plasma treatments entirely remodel the polymer surface. Thus, numerous features rise on the surface, of course these effects can be seen also in the increasing of $R_q$ value, which is also dependent on the plasma exposure time (TABLE 1). Similar result, upon increased surface roughness after plasma exposure of polymer samples were reported
Fig. 4 – Typical topography of untreated PA6 surface (top figure), of 10 s and 60 s He / Ar DBD plasma treated PA6 surfaces.

Table 1.

<table>
<thead>
<tr>
<th>Treatment time (s)</th>
<th>He plasma $R_q$ (nm)</th>
<th>Ar plasma $R_q$ (nm)</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>6.0±0.1</td>
<td>4.8±0.1</td>
</tr>
<tr>
<td>60</td>
<td>7.2±0.1</td>
<td>5.6±0.1</td>
</tr>
</tbody>
</table>

also by [20, 24–28, 47, 49]. According to Wenzel et al. [48], the hydrophilic property of material increases with the surface roughness when WCA is smaller than 90°. We speculated that the increase in surface roughness is responsible for wettability improvement, as to be seen in the WCA measurements.
Instead of utilizing complicated plasma etching techniques (usually low pressure plasma devices or adding $O_2$ / CF etc to plasmas) that are often employed to increase the roughness of polymer surfaces, our results demonstrate control of material surface wettability and roughness simply by atmospheric pressure He/Ar DBD plasma treatment.

4.4. EFFECTS OF PLASMA TREATMENT ON PA6 SURFACE CA

In order to monitor the wettability properties of PA6 surface before and after the plasma treatment, contact angle measurements between distilled water and fiber surface were performed. This technique is a quick method for visualizing the surface modifications effects immediately after plasma treatment.

A home-made system, similar to [25], is used to measure and store the water droplets images. The polymeric fiber was fixed using two holders and placed between a microscope tube and a cold light source. Then distilled water droplets (1 $\mu$l volume) were placed on fiber surface using a 0.5-10 $\mu$l pipette. The photo of each water droplet is taken, through the microscope, after the equilibrium appears between the droplet and the fibers surface. Using sessile drop technique the value of water contact angle was determined. Unless stated otherwise, each measurement was made on a new spot. The data points represent the average from five independent measurements, with an standard deviation up to $\pm 2^\circ$.

![Graph showing water contact angle vs. treatment time and aging time for untreated and plasma treated fibers.](image)

Fig. 5 – Water contact angle $\theta$ of untreated and He / Ar plasma treated fibers and aging effect.

The contact angle value for untreated PA6 sample is $57.3^\circ$. After DBD plasma treatment the contact angle decreases down to $18^\circ$ (as in FIG. 5). This is a direct proof of surface functionalization [20,24–27,47,49].

For shorter treatment time (10 s), the DBD plasma treatment is very efficient. This is reflected in the water contact angle (WCA) measurements (as in FIG. 5).
Thereby for 10 s of PA6 surface treatment, the contact angle is 37° for He DBD (lower by 30% ) and 26° for Ar DBD (lower by 54%) plasma treatment. Increasing the treatment duration to 60 s, the contact angle value decreases to 30° for He (lower by 47%) and 18° for Ar DBD (lower by 68%) plasma treatment. These WCA values prove the usage of plasma sources for PA6 surface hydrofilization. Similar result, concerning lower WCA values after plasma exposure were reported also by [20, 24–28, 47, 49].

In order to monitor the stability of plasma treated surfaces, the PA6 treated fibers were stored in normal laboratory conditions for later WCA measurement. As it can be seen from FIG. 5 the surface recovery occurs after 24 hours for all studied samples. This process continues up to 7 days when the WCA values stabilize around the WCA of the pristine material. Nevertheless, those values are not reached.

4.5. EFFECTS OF PLASMA TREATMENT ON PA6 SURFACE CHEMISTRY (XPS)

For the chemical composition of the PA6 surface a PHI-Ulvac VersProbe 5000 X-ray spectrometer was used (Al Kα line). After various plasma treatments, in different conditions, the PA6 fibers were analyzed by XPS technique (as in FIG. 6).

Prior to XPS analysis all PA6 samples were outgassed overnight, under ultra-high vacuum conditions, to maintain an appropriate pressure in the analysis chamber. The inset presents SEM images indicating the X-ray beam center onto the PA6 fiber surface. Each peak envelope (for every studied element) is curve-fitted using combined Gauss-Lorentz profiles with linear-type background subtraction (as in FIG. 7) [46, 49]. For untreated PA6 fiber, the C1s core-level spectrum was deconvoluted with four individual carbon components (FIG. 7).
The main picks of the elements of PA6 are: C1s (285 eV), O1s (531 eV) and N1s (399 eV). The quantitative analysis, for the pristine surface, based on the peak areas gives for C 84\%, for O 10.8\% and for N 5\%, slightly different from the theoretical percentage (C 75\%, O 12.5\%, N 12.5\%) or previously reported by [6, 22, 24, 46, 50, 51]. The elemental composition of PA6 samples was calculated from wide-scan XPS survey spectra and revealed in TABLE 2. We observed that the atomic ratio changes upon plasma treatment.

**Table 2.**

<table>
<thead>
<tr>
<th>PA6 surface</th>
<th>Measured atomic ratio (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C (1s)</td>
</tr>
<tr>
<td>untreated</td>
<td>84.1</td>
</tr>
<tr>
<td>He plasma 60 s</td>
<td>80.4</td>
</tr>
<tr>
<td>Ar plasma 60 s</td>
<td>64.4</td>
</tr>
</tbody>
</table>

The peak C1 at 285 eV is attributed to CH$_2$ groups in the C – C chain (aliphatic carbon atoms). The peak C2 at 285.6 eV can be associated with the C – (C = O) –
groups (amino-carbonyls). The peak C3 at 286.4 eV represents the carbon atoms neighboring the amide nitrogen (\(-C\text{NH}-(C=O)\)), and the C4 at 287.8 eV is assigned to the \(-(C=O)-N\) group (amide carbonyl). The deconvolution of the XPS C1s spectrum for the He DBD and Ar DBD treated samples allows identifying the carbon groups. The carbon-single-bonded-to-oxygen species, i.e., \(C-OH\) or \(C-O-C\), at a 286.4-eV binding energy, are present in the highest amount. Lower amounts of higher oxidized carbon species, such as \(C=O\) and \(O-C=O\) at 287.8 eV, are also detected. These hydrophilic groups, in correlation to the WCA findings, are responsible for the increase in surface adhesion and polarity [24, 46, 52]. The deconvoluted O1s spectrum of the untreated polymer has one peak at 531 eV and for the plasma treated samples two peaks, at 531.7 and 533.3 eV. The oxygen peak at 531.7 eV is characteristic of the carboxyl acid group, whereas the second peak can be related to oxygen atoms absorbed from air or to the oxygen atom in the newly formed \(C-O\) or \(C-OH\) bond (for treated PA6 fiber) [24, 46, 52].

After the treatment of PA6 surfaces in He and Ar plasmas we measured an increased atomic fraction for oxygen and nitrogen content, while for carbon it can be clearly observed a decreasing of relative atomic fraction (TABLE 3). Simultaneously, the surface O/C and N/C ratios increase, with the treatment time. The N-content slight increase after 60 s of the PA 6 plasma treatment in He from 5 to 5.6 %, and up to 5.8 % after 60 s of Ar plasma treatment, is typically ascribed to the combination with oxygen at the surface [53]. The O-content increased from 10.8 to 13.9 % for He treated PA6, and up to 29.7 % in the case of Ar plasma treated polyamide. The above results suggest the elimination of the surface contamination layer. In addition, a definite incorporation of oxygen can be deduced, because the surface O-content determined after 60 s of the plasma treatment (13.9 % for He and 29.7 % for Ar DBD) significantly exceeds the O-content pertaining to untreated PA 6 (10.8 %). The observed increase of O-content can be due either to direct O-incorporation or to the hydrolysis of \(C=N\) bonds created upon previous N-incorporation. According to Novak et al. [54], such a hydrolytic reaction is fast and is known to lead to the creation of carbonyl groups.

It must be stressed here that the actual C content at the polymer surface after plasma exposure is not decreasing, but rather the O and N content is increased in the vicinity of the plasma-polymer interface due to water and N adsorption onto the polymer surface or / and their presence in the electrode gap (atmospheric pressure condition, proven with OES measurements FIG. 3), or / and their adsorption onto discharge vessel. These reactive oxygen and nitrogen species interacts with the surface and enhance the O and N content, at the expense of carbon bonds (as seen in the XPS results).

TABLE 3 presents the chemical content of the pristine and plasma treated polymeric fiber.
Table 3.

Chemical content of untreated and treated PA6 fiber surfaces.

<table>
<thead>
<tr>
<th>PA6 surface</th>
<th>Measured atomic content (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O/C</td>
<td>N/C</td>
<td>O + N/C</td>
</tr>
<tr>
<td>untreated</td>
<td>0.12</td>
<td>0.05</td>
<td>0.17</td>
</tr>
<tr>
<td>He plasma 60 s</td>
<td>0.17</td>
<td>0.07</td>
<td>0.24</td>
</tr>
<tr>
<td>Ar plasma 60 s</td>
<td>0.46</td>
<td>0.09</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The XPS analyses show that after plasma exposure, the oxygen-containing groups content rises together with the decrease of the primary \( C - C \) bonds in all. This is due to the plasma cracking the primary carbon-containing bonds, which leads to the formation of hydroxyl, carboxyl and double bonds of carbon to oxygen under atmospheric pressure conditions. This can be due to proportionality of hydrocarbon and amide functionalities [55]. This is also a proof that the surface, after the plasma treatment, is more wettable [24,25,28,47]. This is attributed to strong surface oxidation of PA6 fibers after plasma treatment, emphasized in the case of Ar plasma (up to 19% more O (1s), as seen in TABLE 2, respectively up to 4 times more O/C content as in TABLE 3).

In presence of an ROS and RNS, as is the case for atmospheric pressure plasmas, during the plasma treatment, chain-propagating radical reactions will occur, resulting in the formation of various oxidation products (such as: \( C - OH \) (alcohol), \( C = O \) (carbonyl, ketone, or aldehyde), \( COOH \) (carboxylic acid), \( C - O - C \) (ether), or even \( COOK \) (ester)) that will most probably interact with the polymer surface, modifying it.

5. CONCLUSIONS

In this paper, experimental results obtained concerning the electrical and optical diagnosis of an atmospheric pressure plasma source, running in He and Ar, and its effects on PA6 fibers surface after interaction are presented. We have shown that atmospheric pressure DBD can be used for treatment of PA6 fibers with successful promotion of wettability as well as overall increase in surface roughness depending on gas composition and exposure time.

It was found that the surface roughness increases up to 3 times after helium plasma treatment and 2 times after argon plasma treatment. Improved wettability of PA6 surface after the He/Ar DBD plasma treatment has been observed. After 10s of plasma exposure, the PA6 WCA decreases with up to 30% for He DBD and 50% for Ar DBD. Furthermore, after 60s of plasma exposure, the PA6 WCA value drops down to 50% for He DBD and 70% for Ar DBD, in comparison with the pristine
PA6 WCA. As a result of plasma exposure, the surface is more wettable. The surface roughness and wettability are augmented, all of which was found to be helpful to ameliorate the PA6 fiber’s hydrophilicity for up to 7 days.

The XPS analyses show that after plasma exposure of PA6 fibers, the oxygen-containing groups content rises, so we can conclude that, based on the combined WCA and XPS results, the surface energy of PA6 fibers had been modified after DBD plasma treatments.

These plasma-induced surface modifications combined with an enhanced hydrophilization, properties proofed by means of three surface characterization techniques mentioned above, makes plasma treated PA6 proper for applications in which the its surface must be both hydrophilic and adherent.

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