



Physical, Chemical and Morphological Characterization of Polyamide Fabrics Treated with Plasma Discharge

Fernando Ribeiro Oliveira^{a}, Fernanda Steffens^a, Poincyana Sonaly Bessa de Holanda^b, José Heriberto Oliveira do Nascimento^c, Katia Nicolau Matsui^d, António Pedro Souto^e*

^a Department of Engineering, Universidade Federal de Santa Catarina - UFSC, Campus Blumenau, Brazil

^b Postgraduate Programme in Mechanical Engineering, Universidade Federal do Rio Grande do Norte - UFRN, Natal, RN, Brazil

^c Postgraduate Programme in Textile Engineering, Universidade Federal do Rio Grande do Norte - UFRN, Natal, RN, Brazil

^d Department of Chemistry Engineering, Universidade Federal do Rio Grande do Norte - UFRN, Natal, RN, Brazil

^e Textile Engineering Department, Universidade do Minho, Campus Azurém, Guimarães, Portugal

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In this work, physical, chemical and morphological modifications of three different polyamide 6.6 (PA6.6) fabrics were investigated using double barrier dielectric (DBD) plasma treatment. Several techniques of characterization were used to study the effects caused by the interaction between plasma discharge and polyamide fabrics, such as: contact angle, water drop adsorption, Energy Dispersive Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), whiteness by Berger degree and tensile strength. All analyses performed in this study showed that DBD plasma discharge, when applied on PA6.6 fiber, produces significant modifications on the surface of this substrate, without altering its intrinsic properties, thus proving the effectiveness of this important technology to the textile industry.

Keywords: *Polyamide, Plasma, DBD, Surface Characterization*

1. Introduction

The surface modification of different polymers using plasma technology has received great attention during the last years¹⁻⁵. In fact, plasma treatment has assumed a great importance among all available surface alteration processes. It is a dry, environmental- and worker-friendly technique to achieve surface modification without modifying the bulk properties of the materials. In particular, non-thermal plasmas are especially appropriated because most textile materials are heat sensitive polymers^{6,7}. Among plasma technologies, atmospheric plasma is an alternative and cost-competitive method to wet chemical treatments, thus avoiding the need of expensive vacuum equipment and allowing continuous and uniform processing of fibers surfaces⁸. The dielectric barrier discharge in air is one of the most effective non-thermal atmospheric plasma sources and has been attracting increasing interest for industrial textile applications^{9,10}.

The DBD technology is a cold plasma consisting of the air ionization at atmospheric pressure, generated by an electrical high voltage and low frequency, and when applied to textile processing has revealed to be an efficient technique

to modify the surface properties of natural and synthetic fibers by several forms of interactions, such as electrons and ions, photons and ultraviolet among others^{11,12}.

These interactions between plasma and textile substrate may result in surface etching, chain scission, polymerization, creation of polar groups and surface roughness^{13,14}.

The application of DBD plasma discharge to the textile industry has a great potential to improve various operations, including preparation¹⁵, dyeing^{16,17}, printing^{18,19}, finishing^{20,21} and can be executed in a more efficient manner, reducing the pollutant load and optimizing energy costs.

Among the textile fibers, polyamide is widely employed in the textile industry. The polyamides properties, which include high strength, abrasion resistance, and resilience, make them very important in the manufacturing of clothing, carpets, airbags, ropes, among others products. However, due to the inherent hydrophobic nature of this material some surface treatment might be necessary before the application of processes such as: dyeing, printing, finishing with the aim to improve the interaction with dyes, pigments, and others reagents.

Therefore, in the present work, polyamide fabrics were treated with different dosages of an atmospheric double barrier discharge obtained in a semi industrial prototype, equivalent

* e-mail: oliveira.fernando@ufsc.br

to an industrial machine installed in a Portuguese textile plant [Pat. PCT/PT 2004/000008(2004)]²². The complete structural and chemical modifications of fabrics were further analyzed in terms of static and dynamic contact angle, water drop adsorption, energy dispersive spectroscopy, conductivity and pH of aqueous extraction, X-ray photoelectron spectroscopy, scanning electron microscopy, whiteness degree and tensile strength.

2. Materials and Methods

2.1. Materials

Three commercial polyamide fabrics with plain weave patterns were used in this study. In order to minimize contaminations, before dielectric barrier discharge plasma treatment was applied, the samples were pre-washed with a 1 g.L⁻¹ of non-ionic detergent solution at 30 °C for 30 min and then rinsed in water for another 15 min. Table 1 shows the main properties of the fabrics used in this study.

2.2. Plasma treatment

The DBD plasma treatment was conducted in a semi-industrial prototype machine (Softal Electronics GmbH/ University of Minho) working at room temperature and atmospheric pressure. The machine has a system of metal electrode coated with ceramic and counter electrodes coated

with silicon with 50 cm effective width. The gap distance was fixed at 3 mm, producing a discharge at high voltage (10 kV) and low frequency (40 kHz). The discharge power supplied by the electrodes and the velocity may vary, with maximum discharge of 1.5 kW and velocity of 60 m min⁻¹. For the plasma treatment of polyamides fabrics, the parameters velocity and power were kept constant with the values 4.0 m.min⁻¹ and 1000 Watt respectively, and the number of passages were changed from 1 to 9 times.

Table 2 shows the different dosages applied, which are calculated according to equation 1, where: N, number of passages; P, power (W); v, velocity (m min⁻¹); and l, width of treatment (0.5 m).

$$Dosage = \frac{N \cdot P}{v \cdot l} \quad (1)$$

2.3. Morphological and chemical characterization

2.3.1. Contact angle and water drop adsorption tests

Static contact angle of polyamide fabric before and after plasma treatment were characterized with Dataphysics equipment using OCA20 software with video system for the capturing of images in static and dynamic modes.

In order to evaluate the wettability of the fabrics, the water drop test was applied to measure the time of complete adsorption. For a better visualization of the adsorption mechanism, a drop with a dye solution (direct dye: 2 g.L⁻¹) was also used.

Table 1. Properties of polyamide fabrics.

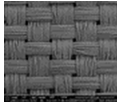
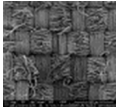
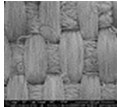
| Properties | Fabric 1 (PA1) | Fabric 2 (PA2) | Fabric 3 (PA3) |
|--|---|---|---|
| Grams per square meter (g.m ²) | 61 | 95 | 135 |
| Count Yarn (Tex) | Weft: 8, Warp: 8 | Weft: 18, Warp: 8 | Weft: 37, Warp: 15 |
| Warp density (yarn.cm ⁻¹) | 42 PA6.6 | 42 PA6.6 | 40 PA6.6 |
| Weft density (yarn.cm ⁻¹) | 32 PA6 | 30 PA6.6 | 18 PA6.6 |
| Polyamide Fabrics - Images (40 X) |  |  |  |

Table 2. Dosage applied on polyamide substrates.

| Samples | Speed (m.min ⁻¹) | Number of Passages | Power (W) | Dosage (W.min.m ⁻²) |
|---------|------------------------------|--------------------|-----------|---------------------------------|
| 01 | 4.0 | 1 | 1000 | 500 |
| 02 | 4.0 | 2 | 1000 | 1000 |
| 03 | 4.0 | 3 | 1000 | 1500 |
| 04 | 4.0 | 4 | 1000 | 2000 |
| 05 | 4.0 | 5 | 1000 | 2500 |
| 06 | 4.0 | 6 | 1000 | 3000 |
| 07 | 4.0 | 7 | 1000 | 3500 |
| 08 | 4.0 | 8 | 1000 | 4000 |
| 09 | 4.0 | 9 | 1000 | 4500 |

2.3.2. Energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS)

Chemical analyses were performed using the EDS technique with an EDAX Si(Li) detector with an acceleration voltage of 5 and 15 kV. The XPS measurements were performed on a VG Scientific ESCALAB 200A equipment with PISCES software for data acquisition and analysis. For the analysis, an achromatic Al(K α) X-ray source operating at 15 kV (300W) was used, and the spectrometer was calibrated with reference to Ag 3d5/2 (368.27 eV), operating in CAE mode with 20 eV pass energy.

2.3.3. Conductivity and pH of aqueous extract

Untreated and plasma treated polyamide fabric samples with different dosages were immersed in distilled water (liquor ratio 1:10) for 1 hour. The pH and conductivity (mV) were measured with a WTW pH Meter 538, Weinheim, Germany.

2.3.4. Scanning electron microscopy (SEM)

SEM analysis was used to study the morphology of the untreated and plasma treated polyamide samples. Images were obtained with an ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company. Samples were covered with a film of Au-Pd (80-20 wt %) in a high-resolution sputter coater, 208HR Cressington Company, coupled to a MTM-20 Cressington High Resolution Thickness Controller.

2.3.5. Whiteness degree

The effect of plasma treatment on whiteness degree of polyamide fabrics was studied. The whiteness index ($^{\circ}$ Berger) was spectrophotometrically obtained by Datacolor SF 600 Plus CT apparatus at standard illuminant D65 and observer 10 $^{\circ}$ combination.

2.3.6. Mechanical properties

Tensile strength and elongation of the samples before and after plasma treatment were measured on a Hounsfield Tensile Tester. The tests were performed according to the Norm ASTM D5034. At least 10 samples were measured for warp and weft direction and for each a stress-strain curve was achieved, showing the maximum tensile stress and strain that the fabric can handle, before breaking.






















3. Results and Discussion

3.1. Contact angle and water drop adsorption tests

The surface properties of the polyamide fabrics were analyzed by measuring of static contact angle. The influence of different dosages applied on the studied substrates was evaluated (Table 3). The initial values of the static contact angles of the three polyamide fabrics (PA1, PA2 and PA3) were 140.3 $^{\circ}$, 153.0 $^{\circ}$ and 145.8 $^{\circ}$, showing the hydrophobicity characteristic of this fiber. After applying a dosage of only 0.5 kW.min.m $^{-2}$, the contact angle decreases to 83.1 $^{\circ}$, 69.1 $^{\circ}$ and 90.4 $^{\circ}$ for polyamides 1, 2 and 3 respectively. This behavior of reduction of the contact angle was also detected for other dosages applied. For PA 2, plasma treatment with 2.0 kW.min.m $^{-2}$ was sufficient to obtain the instantaneous drop water adsorption. The same results were obtained for PA1 and PA3 with the dosages of 3.5 and 2.5 kW.min.m $^{-2}$, respectively. These results suggest that the surface of the polyamide samples was significantly altered due to the plasmatic discharge applied. With the plasma activation it was possible to improve considerably the water adsorption velocity, being this criteria used in the choice of the plasma discharge to be used in the fabrics.

In order to complement the wettability/hydrophilicity study of the polyamide fabrics, the complete adsorption of water and dye aqueous solution drops were also carried out in triplicate. Figure 1 shows the adsorption time of a

Table 3. Static Contact Angle for Polyamide Fabrics (Dosage: kW.min.m $^{-2}$)

| Dosage | 0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|--------|---|---|--|--|--|--|--|
| PA1 | 140.3 $^{\circ}$  | 83.1 $^{\circ}$  | 82.6 $^{\circ}$  | 52.0 $^{\circ}$  | 45.6 $^{\circ}$  | 31.4 $^{\circ}$  | 29.6 $^{\circ}$  |
| PA2 | 153.0 $^{\circ}$  | 75.16 $^{\circ}$  | 55.3 $^{\circ}$  | 53.4 $^{\circ}$  | instantaneous  | instantaneous  | instantaneous  |
| PA3 | 145.8 $^{\circ}$  | 90.4 $^{\circ}$  | 67.5 $^{\circ}$  | 44.4 $^{\circ}$  | 29.3 $^{\circ}$  | instantaneous  | instantaneous  |

water drop from untreated and modified polyamide fabrics treated with dosage of $2.5 \text{ kW}\cdot\text{min}\cdot\text{m}^{-2}$. The complete adsorption time to the untreated samples were $403,7s(\pm 25,3)$, $62,6s(\pm 11,7)$ and $77(\pm 7,1)$ seconds for PA1, PA2 and PA3 respectively, confirming the high hydrophobicity of the fabrics. These values decreased considerably for $70s(\pm 3,8)$ (PA1), $1,3s(\pm 0,20)$ (PA2) and $1,2s(\pm 0,11)$ (PA3) after plasma treatment, indicating surface changes for polyamide fiber from hydrophobic to hydrophilic, which is a key point for the adsorption/absorption of aqueous solutions.

A more accurate visualization of the studied fabrics' adsorption mechanism can be verified with the use of the Sirius Blue K-CFN dye solution as indicator. Figure 2 illustrates the results obtained at the initial time of contact between the dye solution drop and the untreated and plasma treated fabrics.

Significant differences can be observed when the initial contact of the dye solution drop with the fabrics occurs. The results revealed a higher hydrophilicity and capillarity of the fabrics previously treated with plasma, which proved once again that the wettability of the polyamide fabrics improves after DBD plasma treatment. Similar results can be observed in the literature for different synthetic and natural fibrous materials²³⁻²⁶.

DBD plasma discharge can be decisive for the superficial energy increase on textile materials, not only by chemical conversion but also by superficial cleaning process. This technology is capable of removing organic and natural contaminants, creating polar groups that improve the wettability of the substrate. However, a negative aspect of plasma treatment is the aging effect of the surface modification created. The hydrophilicity obtained is often lost with time, depending on the temperature and other environmental (storage) conditions^{27,28}.

The study of the aging effect of the polyamide fabric (PA3) after plasma treatment was also performed using static contact angle measurement. The samples were stored at standard temperature and pressure conditions, and their wettability was measured after plasma treatment (same day) and repeated after 1, 2, 4, 7, 10, 15, 21 and 30 days, in order to verify how stable are the effects produced.

The results presented in Figure 3 demonstrate the effect of plasma treatment ($2.5 \text{ kW}\cdot\text{min}\cdot\text{m}^{-2}$) on polyamide fabric

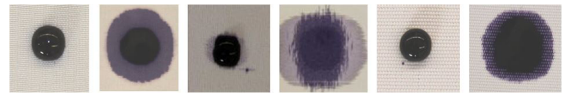


Figure 2. Dye solution drop adsorption on the polyamide fabrics before and after plasma treatment, initial time (t_0).

(PA3) and the temporal evolution, for the static contact angle performed with distilled water drops. Non treated samples obtained contact angle of 132.6° , after treatment, a considerable decrease occurs to 23.3° . In the first four days after plasma treatment there were no significant changes in static contact angle ($24.4^\circ \pm 3.7$, $28.8^\circ \pm 7.4$, $32.8^\circ \pm 8,2$). On the thirtieth day after plasma treatment, despite the fact that the sample presented a contact angle that is still much lower than the untreated sample, it is possible to observe a significant decrease in hydrophilicity (80.3°) when compared with treated samples measured in the same day of plasma treatment (23.3°).

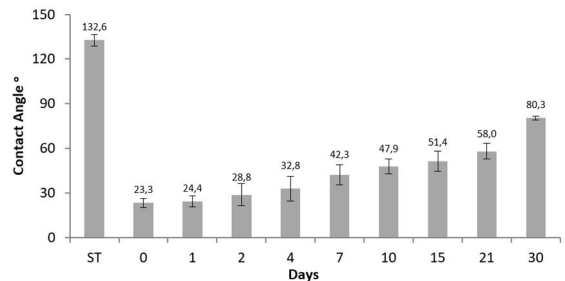


Figure 3. Results of static contact angle for PA3 - sample untreated (ST), treated with $2500 \text{ W}\cdot\text{min}\cdot\text{m}^{-2}$ (day 0) and the temporal evolution of the samples treated from first day until thirtieth day.

Hypotheses considered for this so-called hydrophobic recovery are based on subtle phenomena such as the dynamic behaviour of polymers at the surface or on mechanisms such as surface contamination and molecular dissociation^{29,30}.

3.2. Energy dispersive spectroscopy and X-ray photoelectron spectroscopy

The EDS analysis can be used on different materials to obtain in a specific point of the substrate the degree of the chemical modifications, including the possibility of surface

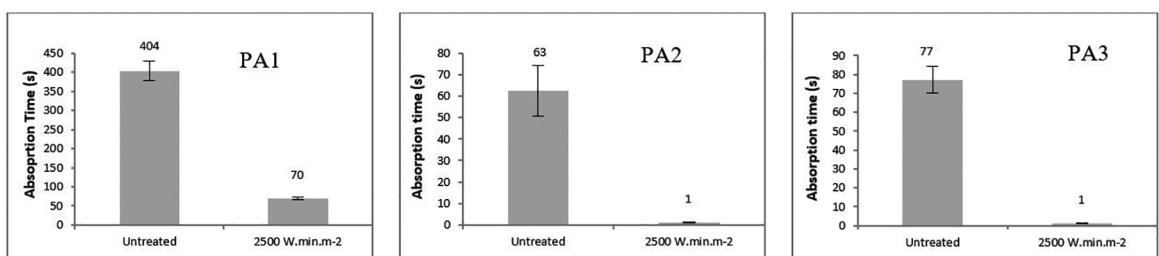


Figure 1. Water drop adsorption time for untreated and plasma treated samples ($2500 \text{ W}\cdot\text{min}\cdot\text{m}^{-2}$).

oxidation, defining the amount of nanoparticles close to the surface and the atomic percentage of fibrous substrates³¹⁻³³. Table 4 shows the results obtained by EDS technique using an acceleration voltage of 5 kV. For polyamide samples treated with dosage of 2.5 kW.min.m⁻² a reduction in the carbon atomic content and an increase in the atomic quantities of oxygen and nitrogen is observed.

Etching obtained by plasma/substrate interaction may have caused the polymer chains to cleave into C-H, C-O, C-N, N-H groups and the formation of functional groups with oxygen, resulting in the decrease of the carbon percentage. Other reactions caused by plasma discharge may occur, leading to the production of reactive species such as O⁻, N, N⁺, O, OH⁻, O₃^{34,35}. These species in contact with the polyamide fiber may also lead to a decrease in the atomic percentage of carbon and an increase in the percentage of nitrogen and oxygen atoms. An interesting point worth mentioning in this study is the fact that EDS analysis was carried out with a voltage acceleration of 5 kV, which can reach depths greater than 0.5 μm. This technique allows quantifying quickly the chemical composition obtained promptly after plasma discharge application. However, EDS is not the most adequate technique to evaluate carbon content after plasma treatment, thus for a more accurate study of the surface modifications provoked by plasma species interaction, the XPS technique is the most commonly mentioned in the literature³⁶⁻³⁸ and the results obtained with this important technique can be observed in table 5.

The data compiled in table 5 shows a substantial incorporation of the oxygen and nitrogen atoms on the fabrics surface. The increase of O/C and N/C ratios after a dosage of 2500 W.min.m⁻² is in accordance with the results obtained with the EDS analysis. It is noteworthy that, while EDS analysis occurs at a depth that may be greater than 500

nm, XPS analysis is performed at a depth of 5-10 nm, which explains the differences found when the two techniques are compared. All the chemical modifications presented by EDS and XPS corroborate with the results obtained by contact angle and water drop adsorption. The introduction of polar group is responsible for the increase in hydrophilicity of the plasma modified polyamide fabrics (PA1, PA2 and PA3).

3.3. Conductivity and pH of aqueous extract

Figure 4 shows significant difference in conductivity and pH of aqueous extracts of the polyamide before and after plasma treatment with different dosages. Conductivity values increase from 55 to 215 mV (PA1), 57 to 220 mV (PA2) and 42 to 230 mV (PA3) and pH decrease from 5.79, 5.75, 6.06 to 2.93, 2.97, 2.87 for the fabrics PA1, PA2 and PA3 treated with 4500 W.min.m⁻², respectively, confirming the presence of a significant concentration of acid species on the extracted solution.

Similar results were reported by Souto et al.² and Oliveira et al.³³, which verified the formation of carboxylic acids groups in the outer cuticle of the cotton fiber and an increase in acidification, in aqueous extraction of banana fiber after DBD plasma treatment.

3.4. Scanning electronic microscopy

Plasma treatment can provoke substantial morphological alterations onto fiber surface, especially enhancing its roughness and consequently increasing surface energy, wettability and adhesion³⁹. SEM images of untreated and DBD plasma treated polyamide fabrics (PA1, PA2 and PA3) with magnification of 10000 times show that the topography of the fiber was uniformly altered after plasma treatment in

Table 4. Atomic Percentage (At %) obtained by EDS analysis to untreated and plasma treated fabrics with dosage of 2.5 kW.min.m⁻².

| Atoms | PA 1 | At (%) | PA 2 | At (%) | PA3 | At (%) |
|-----------|-----------|---------|-----------|---------|-----------|---------|
| | Untreated | Treated | Untreated | Treated | Untreated | Treated |
| Carbon | 67.38 | 64.05 | 67.56 | 63.55 | 67.40 | 64.68 |
| Nitrogen | 9.95 | 10.82 | 10.40 | 11.39 | 9.70 | 10.95 |
| Oxygen | 22.67 | 25.13 | 22.04 | 25.06 | 22.90 | 24.37 |
| Ratio O/C | 0.33 | 0.39 | 0.33 | 0.39 | 0.34 | 0.38 |
| Ratio N/C | 0.15 | 0.17 | 0.15 | 0.18 | 0.14 | 0.17 |

Table 5. XPS Results of the polyamide samples with and without plasma treatment (2.5 kW.min.m⁻²).

| Atoms | PA 1 | At (%) | PA 2 | At (%) | PA3 | At (%) |
|-----------|-----------|---------|-----------|---------|-----------|---------|
| | Untreated | Treated | Untreated | Treated | Untreated | Treated |
| Carbon | 74.30 | 61.39 | 74.28 | 60.49 | 74.25 | 62.75 |
| Nitrogen | 8.33 | 10.46 | 9.41 | 10.96 | 9.38 | 10.28 |
| Oxygen | 17.37 | 28.16 | 16.26 | 28.55 | 16.37 | 26.97 |
| Ratio O/C | 0.23 | 0.46 | 0.22 | 0.47 | 0.22 | 0.43 |
| Ratio N/C | 0.11 | 0.17 | 0.13 | 0.18 | 0.13 | 0.16 |

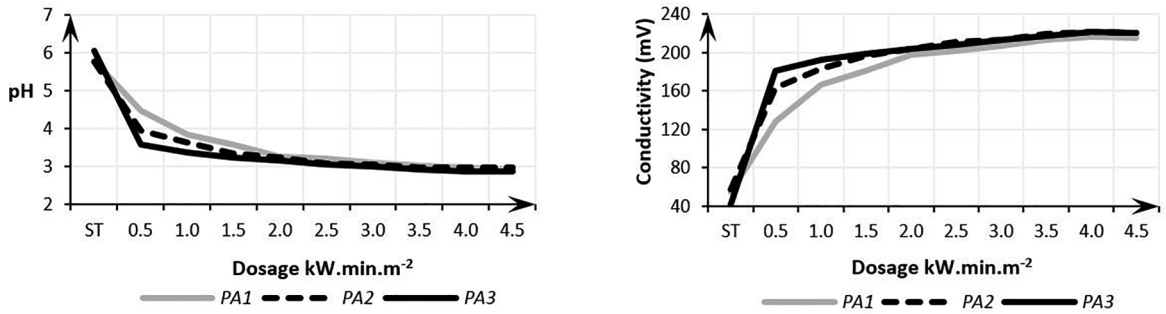


Figure 4. Conductivity and pH of aqueous extraction of the polyamide fabrics before and after plasma treatment.

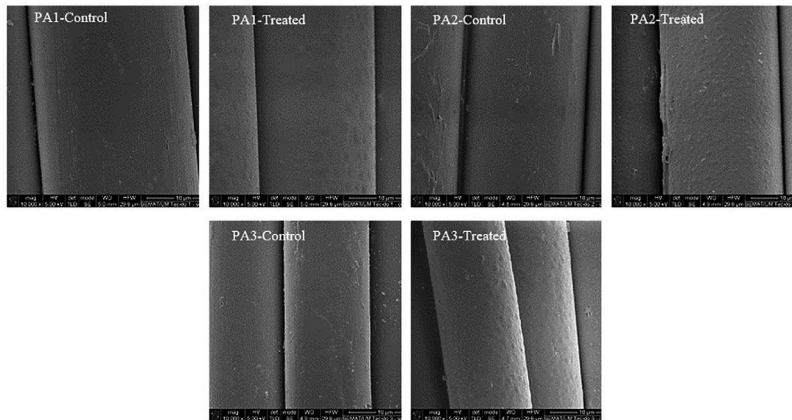


Figure 5. SEM images of PA1, PA2 and PA3 fabrics untreated and plasma treated with dosage of 2.5 kW.min.m⁻² with magnification of 10000 X.

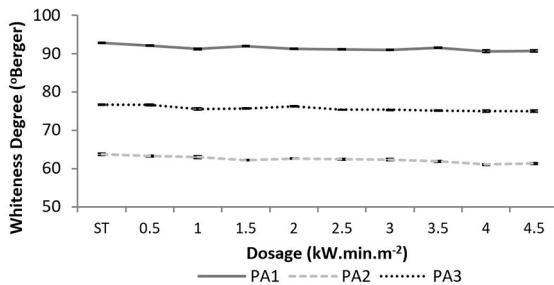


Figure 6. Whiteness Degree of the polyamide fabrics treated with different dosages.

the form of ripple-like structures of sub-micron size that were induced by plasma etching (Figure 5). The highly reactive and energetic plasma species, achieved by DBD atmospheric pressure plasma treatment promote synthetic fiber ablation and induce the increase of fiber surface roughness and hydrophilicity-dependent properties^{9,40}. Numerous mechanisms that illustrate the interaction between plasma and polymers via etching were suggested^{10,41}. Besides the etching process, the energetic electrons generated on the fabrics surfaces during plasmatic discharge can lead to scission of polymer molecular chains. This effect leads to the formation

of free radicals that interact with other plasma generated reactive species, mainly related with oxygen and nitrogen molecules (N_2^+ , N_4^+ , N^+ , O_2^+ , H_2O^+ , O_2^- , O^-), producing new functional groups on the polymers' surface^{10,42}. Due to the free radicals' actuation, the distinction between material removal and surface chemical modification becomes very difficult because these two processes occur simultaneously and synergistically, making the involved interaction mechanism (plasma/substrate) much more complex.

3.5. Whiteness degree

Figure 6 shows the graphic obtained for the whiteness degree before and after plasma treatment with different dosages. A slight decrease in this property can be observed when the dosage applied is increased. The difference between the untreated sample and the treated sample at a dosage of 4500 W.min.m⁻² is only 1.4, 2.4 and 1.7 values of whiteness by °Berger for PA1, PA2 and PA3, respectively. These results demonstrated that the applied plasmatic discharge did not cause significant influence on the whiteness degree of the samples under study, which means that plasma treatment modified the chemical and physical surface of the fabrics without changing the base color of the fabrics.

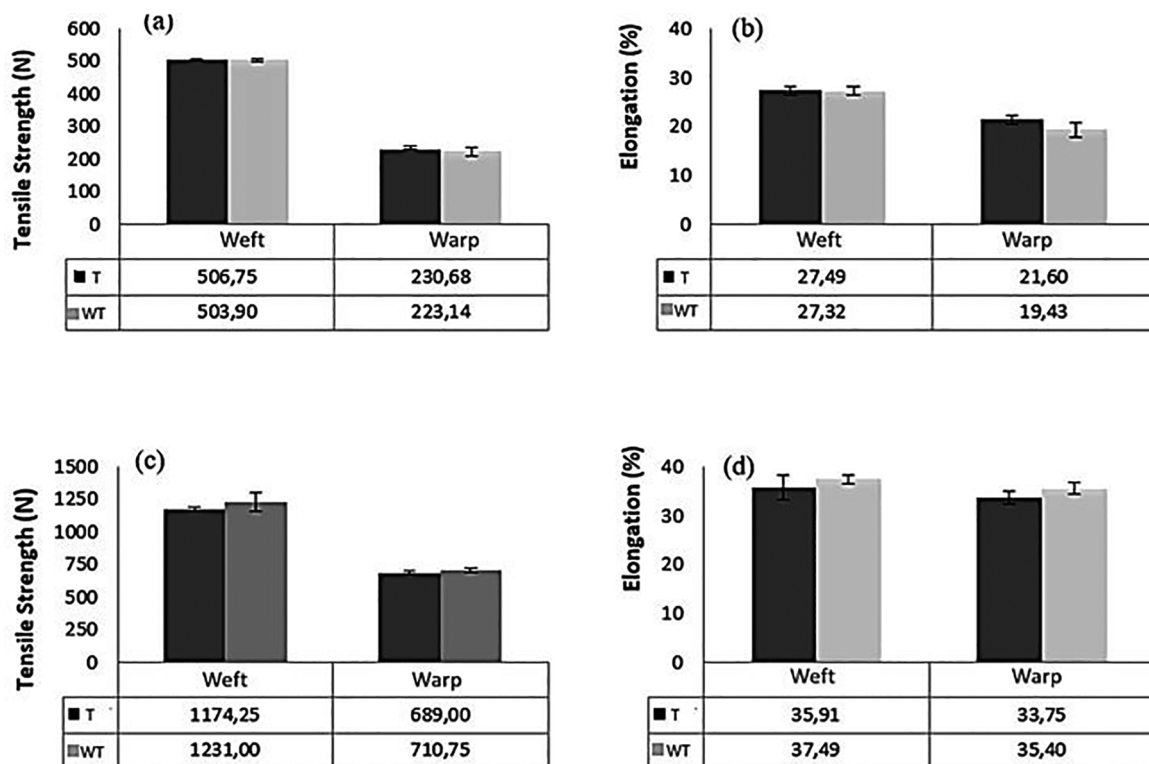


Figure 7. Graphics of tensile strength and elongation of the PA2 (a and b) and PA3 (c and d) untreated (WT) and treated (T) with 2500 W.min.m⁻².

3.6. Tensile strength

The results of tensile strength and elongation of the polyamide fabrics (PA2 and PA3) with (T) and without plasma treatment (WT), obtained in the weft and warp directions, are presented in Figure 7.

According to the results presented, it can be verified that there are no significant differences in the mechanical properties evaluated when comparing the fabrics previously treated with the samples without plasma treatment, which indicates that the bulk properties of the polyamide fabrics studied remained unchanged with the dosage of 2500 W.min.m⁻². These results confirm that the chemical, physical and morphological changes caused by the DBD plasma treatment did not modify the tensile strength and elongation at break of the studied materials. These results are according to what was reported by Abidi and Hequet⁴³, Kan and Yen⁴⁴ and Karahan et al.⁴⁵, who verified that plasma treatment does not affect negatively the mechanical properties of textile materials.

4. Conclusions

This research shows that a relatively low DBD plasma dosage, of around 2.5 kW.Min.m⁻², can effectively modify both physically and chemically the surface of polyamide fibers.

The static contact angle and water drop adsorption time values were found to depend on the dosage applied: higher

dosage lowers the contact angle and the time of water and dye solution adsorption. The introduction of polar groups, mainly oxygen and nitrogen from atmospheric air, is the main responsible for the improved wettability of the plasma modified polyamide fiber. This is clearly demonstrated by the significant increase in the ratios O/C and N/C obtained by EDS and XPS analyses. SEM images show that the topography of the polyamide fibers was uniformly altered after plasma treatment, increasing surface roughness. The whiteness degree results obtained showed that the surface modification performed did not alter significantly the colorimetric coordinate values of the substrates. Finally, no significant modifications were obtained in the mechanical properties of the fabrics studied, confirming that plasma treatment can modify the surface properties of polyamide fiber without changing its original bulk properties.

All the modification presented in this study may be important to expand the use of the polyamide fibers in the textile industry due the improvement that can be obtained in the dyeing, printing and finishing processes after plasma treatment.

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