Surface Modification of Polyester Fabric by Non-Thermal Plasma Treatment

R C Lima da Silva¹⁴, C Alves Jr², J H Nascimento³, J R O Neves⁴ and V Teixeira⁵

¹Mechanical and Materials Department, Federal Institute of Rio Grande do Norte, Mossorô/Brazil.
²Mechanical Engineering Department, Federal University of Rio Grande do Norte, Natal/Brazil.
³Textile Engineering Department, Federal University of Rio Grande do Norte, Natal/Brazil.
⁴Textile Engineering Department, Minho University, Guimarães/Portugal
⁵Physics Department, Minho University, Braga/Portugal

E-mail: 'ruthilima@yahoo.com.br

Abstract. In the present study it was carried out a surface modification of polyester fabric by plasma treatment with aim of providing hidrophilicity to fabric. In the process it were used three different gaseous atmosphere with mixtures of argon, nitrogen and/or oxygen [(1) Ar + N₂ (4:2), (2) Ar + N₂ +O₂ (4:2:2) and N₂ + O₂ (2:0.6)] and maintained others parameters such as pressure, current and time of treatment fixed at 1.35 mBar, 0.08 A and 30 minutes, respectively. The plasma treatment was monitored by optical emission spectroscopy (OES) to identify the species presents in the plasma reactor. Chemical changes in the fabric surface after plasma treatments were determined by Fourier Transform Infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). Wicking properties were used to evaluate hydrophilicity of the fabric. Wicking measurement showed that the hydrophilicity of polyester fabric was remarkably improved after treatment and was explained by XPS analysis indicating higher presence of functional groups containing nitrogen and oxygen.

1. Introduction
Non-thermal plasma treatment is a clean, dry and environmental friendly method of textile materials modification since it improves the surface characteristic of polymers without affecting their bulk properties and does not require water or chemical reagents dispensing effluents treatment (Fang and Zhang 2009[1]; Wang et al. 2008[2]; Barni et al. 2005[3]). Plasma is produced by an electric discharge combined with gas, by applying a voltage between two electrodes inserted in a chamber at low pressures. Due to this voltage, electrons are accelerated and collide with plasma, forming neutral particles, ions, excited particles and electrons. Thus, it can possibly break molecule chains, generate new functional groups and/or morphological alterations in the polymers surface, such as microporosity (Yaman et al. 2009[4]). The introduction of water compatible functional groups (–COOH, –OH, –NH₂, etc.) increases the hydrophilicity of polyester (Morent et al. 2008[5]). Therefore, oxygen and nitrogen are the type of gas chosen to be used in the study of this textile material modification.
The influence of the process parameter in the Plasma treatment of textile materials has been extensively studied. For instance, Sun et al. (2011) used an atmospheric pressure plasma jet (APPJ) to treat cotton yarns with helium/oxygen (He/O2) gas for the hydrophilicity and sizing property improvement. Kale and Desai (2009) studied the use of non-polymerizing gas in atmospheric pressure plasma to treat different textile materials. Navaneetha Pandiyaraj and Selvarajan (2007) investigated the effect of the exposure time, discharge potential and pressure level in the plasma treatment on cotton fabric, and they concluded that the dyeability of this fabric has been improved due to the increase of surface energy and roughness. Costa et al. (2006) analyzed the effect of the atmospheric composition in the plasma reactor on the surface of polyester fabric using mixture of oxygen, hydrogen, nitrogen and argon, and found an increase in the fabric wettability and roughness. However, they did not conclude that new functional groups (–OH and −NH₂) have been formed as it was expected.

In the present work was studied the surface modification of polyester fabric made from multifilament yarns using non-thermal plasma with different gaseous atmosphere. The study was based on hydrophilic and chemical changes of the polyester caused by mixtures of argon, nitrogen and oxygen in the plasma reactor.

2. Experimental

2.1. Materials and sample preparation

Multifilament yarns of polyester (1/318/95 or 1 cable with 318 Dtex and 95 filaments) commercially obtained were used to produce rectangular samples of fabric with 130 mm of length and 10 mm of width. Samples were washed with neutral soap for 30 min and kept in a bath of water for 8 hours.

2.2. Plasma Treatment

Non-thermal plasma was generated in a cylindrical chamber of 250 mm length and 180 mm internal diameter, made of borosilicate. The sample was fixed between two electrodes discs (anode and cathode). The scheme of the plasma system was shown in Figure 1. The ends of the chamber were closed using two stainless steel flanges. Thus, gases were introduced in by upper flange while the vacuum system, pressure sensor and thermocouples were held in the bottom flange.

Discharge plasma was produced at a vacuum pressure fixed in 1.35 mBar. The electric current and the time of tests were maintained in 0.08 A and 30 minutes, respectively.

The fabric was placed perpendicularly to the cylindrical axis, between the parallel disc electrodes at 7 cm of distance from cathode. This distance ensured that there was no alteration thermal in the fabric due to the high temperatures reached in the cathode (Figure 1).
Influence of the gaseous atmosphere on the surface modification of the polyester was analysed using nitrogen, oxygen and argon mixtures according to Table 1. Ocean Optics spectrometer was used to detect the species present in the reactor plasma during the treatment. Optical fibre cable had one end positioned to UV in the reactor and the other end linked to the optical emission spectrometer which was connected to the computer. During the plasma treatment a spectrum was recorded every 5 minutes.

Table 1. Gaseous atmosphere in the chamber of the plasma.

| Gaseous       | Proportion |
|---------------|------------|
| Ar, N₂        | 4 : 2      |
| N₂, O₂        | 2 : 0.6    |
| Ar, N₂, O₂    | 4 : 2 : 2  |

2.3. Surface characterization

2.3.1. FTIR analysis
Fourier Transform infrared spectral analyses of the treated and untreated fabrics were recorded in the range of 4000 – 400 cm⁻¹ using Nicolet-Avatar 360 with OMINIC 5.2 computerized software from Nicolet.

2.3.2. XPS analysis.
The chemical compositions of the sample surface were analyzed using an XPS model ESCALAB 200A (VG Scientific, UK) with data acquisition and analysis software PISCES. The X-ray source was Al Kα (1486.6 eV), operating at 300 W. The pressure within the XPS chamber was less than 10⁻⁶ Pa. The effect of the electric charge was corrected by the reference of the carbon peak (285 eV). The deconvolution of spectra was performed using the XPSPEAK41 program, in which an adjustment of the peaks was performed using peak fitting with Gaussian-Lorentzian peak shape and Shirley type background subtraction.

2.3.3. Wicking rate
A polyester fabric strip (130mm×10mm) was suspended vertically above the colored distilled water surface in a glass beaker in a way that the vertical bottom edge slightly touches the colored water. A spontaneous wicking occurs due to capillary force. The height of the liquid rise boundary is recorded every 20 s until 300 s.

3. Results and Discussion

3.1. Identification of species in the emission spectrum
The typical emission spectra obtained in UV region during the treatment are shown in the Figures 2, 3 and 4. Optical Emission Spectroscopy (OES) in UV is widely used for plasma diagnostics as non-invasive technique to identify the species present in the plasma. Thus, atomic and ionized species interacting with the samples can be identified.
3.2. Surface Chemistry
The FTIR spectrum of polyester fabric before plasma treatment is shown in Figure 5. Analyzing the results, it is possible to observe that the spectrum is similar to polyester spectrum present in the literature (Li et al. 2010[10]; Yaman et al. 2009[4]). Principal peaks are presented in the Table 2 together with its functional groups. It was also identified a peak at 2360 cm$^{-1}$ which is due to a different CO$_2$ concentration in the air in the IR cell.
Table 2. Functional groups associated with the peaks found in the FTIR spectrum of polyester untreated.

| Functional group                        | Wavenumber (cm⁻¹) |
|-----------------------------------------|------------------|
| Carboxylic acid (C=O)                   | 1709             |
| Aromatic ring                           | 1407             |
| Alkane (CH₃)                            | 1339             |
| Carboxylic acid (C=O)                   | 1238             |
| Ester (O=C–O–C) or amine (C–N)          | 1015             |
| Vinil (C–H)                             | 969              |
| Aromatic (C–H)                          | 870              |
| Aromatic (C–H)                          | 720              |

Regarding the analysis of FTIR spectra of untreated and treated polyester fabric, it was not identified significant variations in the spectra before and after plasma treatment. Since plasma treatment works in a nanometer scale, it is impossible to be detected by the FTIR analysis that works in a micrometric scale.

XPS overall scan of untreated and plasma treated polyester fabric are shown in Figure 6. According with the results, it was detected four atoms: carbon, oxygen, nitrogen and silicon. It was also observed that after the plasma treatment with the three gaseous atmospheres (Ar+N₂, N₂+O₂ and Ar+N₂+O₂), the oxygen and nitrogen peak intensified while the carbon and silicon peak decreased. Table 3 shows chemical composition of the samples before and after the plasma treatment. It was also noted an indication of nitrogen presence (0.32 at %) in the untreated sample, and that these amount of nitrogen increased with the treatment, as can be seen in Table 3. Furthermore, Yaman et al. (2009)[4] found a small amount of nitrogen (0.4%) in untreated polyester using the XPS analysis and observed that this amount increases after plasma treatment in air atmosphere. Haverkamp et al. (2002) when studying aging of polyester powder coating also detected slight presence of nitrogen (0.3%) in the new polyester.

O/C and N/C ratio presented in the Table 3 facilitates the visibility of the increase of C and N concentration after the plasma treatment. Higher ratio O/C was obtained with N₂+O₂ atmosphere. After treatment with Ar+N₂ it was observed that O/C ratio increased from 0.365 to 0.453, which was unexpected since there was no oxygen in the atmosphere of the plasma reactor during the treatment. Charpentier et al. 2006[12] studying surface modification of medical grade polyester using nitrogen-plasma also detected an increase in the O/C ratio. They suggested that this increase in the oxygen occurred due to the reactive species presents on surface treated sample reacting with oxygen from the air immediately after removal of the samples from reactor. These results suggest that nitrogen and oxygen-containing polar groups were created on the polyester surface after the plasma treatment.

Silicon presence in the fabric samples is not a characteristic of the polyester which suggests that the material was contaminated during its manufacture. After the plasma treatment with Ar+N₂ the silicon groups almost disappeared of the polyester surface and decreased more of 50% when treated with N₂+O₂ and Ar+N₂+O₂ (Table 3).
Figure 6. XPS overall scan of untreated (a) Ar and N₂ plasma treated (b) N₂ and O₂ plasma treated (c) and Ar, N₂ and O₂ plasma treated (d) polyester fabric.

Table 3. XPS data analysis.

| Sample            | Chemical composition (At%) | Ratio     |
|-------------------|----------------------------|-----------|
|                   | Carbon | Oxygen | Nitrogen | Silicon | O/C | N/C |
| Untreated         | 68.94  | 25.19  | 0.32     | 5.55    | 0.356 | 0.004 |
| Ar + N₂           | 66.99  | 30.36  | 1.77     | 0.88    | 0.453 | 0.026 |
| N₂ + O₂           | 63.86  | 32.21  | 1.71     | 2.23    | 0.504 | 0.027 |
| Ar + N₂ + O₂      | 64.92  | 31.59  | 1.12     | 2.36    | 0.486 | 0.017 |

Deconvolution analysis of C1s and N1s were realized to identify the chemical functional groups that were incorporated in the surface fabric after the plasma treatment (Figures 7 and 8). Figure 7 shows XPS spectra from the untreated and treated samples around the C1s energy region. The peak of the untreated polyester is composed of three main components: C–C or CH group which correspond at 285 eV and C–O and O–C═O groups referents at 286.5 eV and 289 eV, respectively. In the range of 286 and 286.5 eV can also be characterized the presence of the amine group (C–N) since it was detected nitrogen in the analysis.

After performing a treatment using three different gaseous atmospheres it is possible to observe that the peaks intensity regarding C–C and CH groups decreased while the peaks intensity referents to carboxyl and ester groups increased compared with those in the untreated sample. The variation of the relative area is presented in the Table 4 where can be noticed a reduction in the relative area of C–C and CH group after the treatment with Ar + N₂, N₂+O₂ and Ar+N₂+O₂, whilst the relative area of C–O and COO groups increased. These results evidence surface modification in some C–C and CH groups that have been oxidized forming C–O and O–C═O.
Figure 7. Deconvolution of XPS core level C 1s of fabric (a) untreated (b) Ar+N$_2$ (c) N$_2$+O$_2$ and (d) Ar+N$_2$+O$_2$.

Table 4. XPS data analysis of C 1s peak.

| Sample         | Relative area of different chemical bonds (%) |
|----------------|------------------------------------------------|
|                | C – C and/or CH (285eV) | C–O and/or C–OH (286.5eV)$^a$ | O–C═O and/or COOH (289eV) |
| Untreated      | 69                  | 12                  | 19                  |
| Ar + N$_2$     | 58                  | 19                  | 23                  |
| N$_2$ + O$_2$  | 58                  | 18                  | 24                  |
| Ar + N$_2$ + O$_2$ | 61              | 17                  | 22                  |

$^a$this value of energy also can refer to C–N.

Observing Table 5 which shows the relative area of different chemical compositions around the O1s energy region, it can be observed two peaks: 532 and 533 eV that refers to C=O and O–C═O, respectively. Furthermore, significant modification was found to the sample treated with N$_2$+O$_2$, where can be noticed an increase of relative area referent at 533 eV peak that is associated to COO and NO$_3^−$.

Figure 8 shows XPS spectra from the untreated and treated samples around the N1s energy region and it shows a peak at 399.9 eV in the untreated sample (Figure 8(a)) which can indicate the presence of amine (–NH–) group in the polyester fabric as also identified by Cascalheira and Abrantes (2008)[13].

Analyzing Figure 8 it is also possible to observe that different functional groups appeared after the treatment, according to the different atmosphere gaseous. Thus, in the treatment with Ar+N$_2$ and Ar+N$_2$+O$_2$ two peaks appeared: one at 399.9 eV and the other at 400.6 eV (Figure 8(b) and (d)). The first peak which is referent to –NH– (399.9 eV) increased in area when compared with the untreated sample. This increase was 75% when treated with Ar+N$_2$ and 46% when treated with Ar+N$_2$+O$_2$. As long as the 400.6 eV peak is concerned, it may indicate N-C bonds formation. Regarding the treatment using N$_2$+O$_2$, two nitrogen peaks were observed, one at 400.07 eV and the other at 407.6 eV (Figure 8(c)). As Figure 8(c) shows, the first peak (400.07 eV) which concerns to –NH– had an area increase of 153% when compared with the untreated sample. Thus, the second peak (407.6 eV) refers to Nitrate (NO$_3^−$) as noticed by the high relative area value of 533 eV (57%).
Figure 8. Deconvolution of XPS core level N 1s of fabric (a) untreated (b) Ar+N\textsubscript{2} (c) N\textsubscript{2}+O\textsubscript{2} and (d) Ar+N\textsubscript{2}+O\textsubscript{2}.

Table 5. XPS data analysis of O 1s peak.

| Sample            | Relative area of different chemical bonds (%) | Sample            | Relative area of different chemical bonds (%) |
|-------------------|---------------------------------------------|-------------------|---------------------------------------------|
|                   | C \equiv O (~532 eV)                         |                   | O – C\equiv O (~533 eV)                      |
| Untreated         | 49                                          | Ar + N\textsubscript{2} | 48                                          |
|                   |                                              | N\textsubscript{2} + O\textsubscript{2} | 43                                          |
|                   |                                              | Ar + N\textsubscript{2} + O\textsubscript{2} | 50                                          |
|                   |                                              |                   |                                              |
|                   |                                              |                   | *this value of energy can also refer to NO\textsubscript{3}\textsuperscript{−} |

3.3. Wicking rate – capillarity

As long as Figure 9 is concerned it shows the capillarity of untreated and treated samples. Thus, it is possible to observe that the untreated sample is totally hydrophobic since there was no vertical wicking during the test. However, after plasma treatment there was a significant increase in the samples capillarity. This behavior is due to the incorporation of polar functional groups as confirmed by XPS analysis.

During the first 25 seconds the wicking rate was the same to three treated samples. Although, after this time was noted a higher wicking rate to polyester fabric treated with Ar+N\textsubscript{2} which has reached the maximum length of the sample in 150s. This behavior can be associated to the higher concentration of nitrogen found in the fabric surface after this treatment, as shown in the Table 3. Furthermore, nitrogen can bind with hydrogen and carbon to form amines (NH and CN) that have high polarity which gives hydrophilicity to polyester. In this sample was also observed an almost complete reduction in silicon (Figure 6), which it may have contributed to higher capillarity.
4. Conclusions
Polyester fabric was treated in non-thermal plasma with three different gaseous atmospheres (Ar+N\textsubscript{2}, N\textsubscript{2}+O\textsubscript{2}, Ar+N\textsubscript{2}+O\textsubscript{2}). The samples were characterized by FTIR and XPS analysis and vertical wicking where was possible to conclude that:

1. The hydrophilicity of the polyester fabric was improved as found in the vertical wicking. This occurred due to the introduction of functional groups on the material surface as evidenced in the XPS analysis;
2. Combination of gaseous in the plasma atmosphere has influence on hydrophilicity results. Higher wicking rate was identified in the sample treated with Ar+N\textsubscript{2}. In this sample was observed an increase in the --CO-- and --COO-- groups and a decrease in the C–C and CH groups as well as higher count of nitrogen and also an almost complete reduction of silicon. All this factors together contribute to a higher polyester fabric hydrophilicity that was treated with Ar+N\textsubscript{2}.
3. Different compounds with nitrogen were found after the treatments. NH and N–C were identified in the samples treated with Ar+N\textsubscript{2} and Ar+N\textsubscript{2}+O\textsubscript{2}, while NO\textsubscript{3}– and NH were seen in the spectrum of the sample treated with N\textsubscript{2}+O\textsubscript{2}. These results underscore the importance of the gaseous atmosphere when pretending to carry out plasma treatment of polymers.

5. References
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