Functionalization of PET and PA6.6 woven fabrics

R. Bessada [a,b], G. Silva [b], M.C. Paiva [a], A.V. Machado [a,*]

[a] Institute for Polymers and Composites/I3N, Department of Polymer Engineering, Campus of Azurem, University of Minho, 4800-058 Guimarães, Portugal

[b] TRW - Vila Nova de Cerveira R&D, 4920-011 Vila Nova de Cerveira, Portugal

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Abstract

In the present work as received woven fabrics of polyethylene terephthalate (PET) and polyamide 6.6 (PA6.6) were exposed to a continuous dielectric barrier discharge (DBD), in air at atmospheric pressure, at selected discharge power values and conveyor speeds. The chemical modification of the fabric surface was studied by contact angle analysis, attenuated total reflection (ATR)-FTIR spectroscopy and X-ray photoelectron spectroscopy (XPS). The results confirmed that the treatment changed the fabric surface chemistry, increasing its wettability by polar liquids and its oxygen content. Contact angle results showed different behaviour of the two polymer fabrics toward ageing effects; while PET showed a contact angle increase along the subsequent days of treatment, the PA6.6 fabric maintained its hydrophilicity even 15 days after treatment. The surface morphology analysed by scanning electron microscopy (SEM), did not show any significant difference before and after treatment.

Introduction

Plasma treatments, under vacuum or atmospheric pressure, using reactive or non polymerizable gases, are intensively employed to modify polymer surfaces, resulting in desirable surface changes, including surface activation by etching, crosslinking, chain scission and oxidation [1]. The effects of plasma treatment on polymer surface chemistry are influenced by the gas chemistry associated with the plasma, as well as the chemical structure of the polymer surface. In general, the chemical modification process is quite complex, owing to the variety of possible surface reactions of the polymeric material placed in a plasma environment. In addition, the stability of the treated surface is an important issue, depending on the treatment and storage conditions, as well as on the practical application of the treated polymer surface [2].

Numerous gases have been used in plasma modifications of polymer surfaces depending on the required surface modification. A plasma treatment with gases does not produce a unique change on a polymer surface. Typically, a distribution of functional groups is produced, as well as morphological changes. The most common gases used in plasma treatments are O_2, N_2, NH_3, H_2O, CO_2, air, noble gases or mixtures of gases.

Plasma treatments in the presence of O_2 gas introduce oxygen groups on the polymer surface (polar functional groups), increas-

ing their hydrophilic character. Therefore improves some surface properties, like wettability [3-9] and printability [10].

Besides chemical changes, plasma treatment may also induced morphological changes on the surface due to etching, resulting in an increase in surface roughness, surface rippling and waviness [11,12]. When the roughness increases, the polymer surface becomes larger, which increases the contact area and enhances the adhesion towards other materials. The increase in effective surface area obtained with roughness, and in hydrophilic character, obtained by oxidising the surface, may enhance the contact with the coating material. Therefore, adhesion can be improved by both roughness increase and introduction of functional groups that have affinity or can form chemical bonds with the respective coating [10,13-20].

If adhesion is the main propose, the functional groups introduced by plasma treatment should be tailored according to the surface coating to be applied. The type of functional groups may be varied by changing the plasma gas and/or other plasma parameters [2].

To improve the hydrophobic character of a surface, it may be plasma treated to introduce certain functional groups via a coating or a graft co-polymer, removing hydrophilic functional groups or changing hydrophilic groups into non-hydrophilic ones [21-26].

This easy way of changing polymer surfaces has been used with enormous interest in the textile industry. Plasma treatments of textile fabrics and yarns have been investigated as an alternative to wet-chemistry fabric treatment and pre-treatment traditional processes, which are expensive and environmentally aggressive.

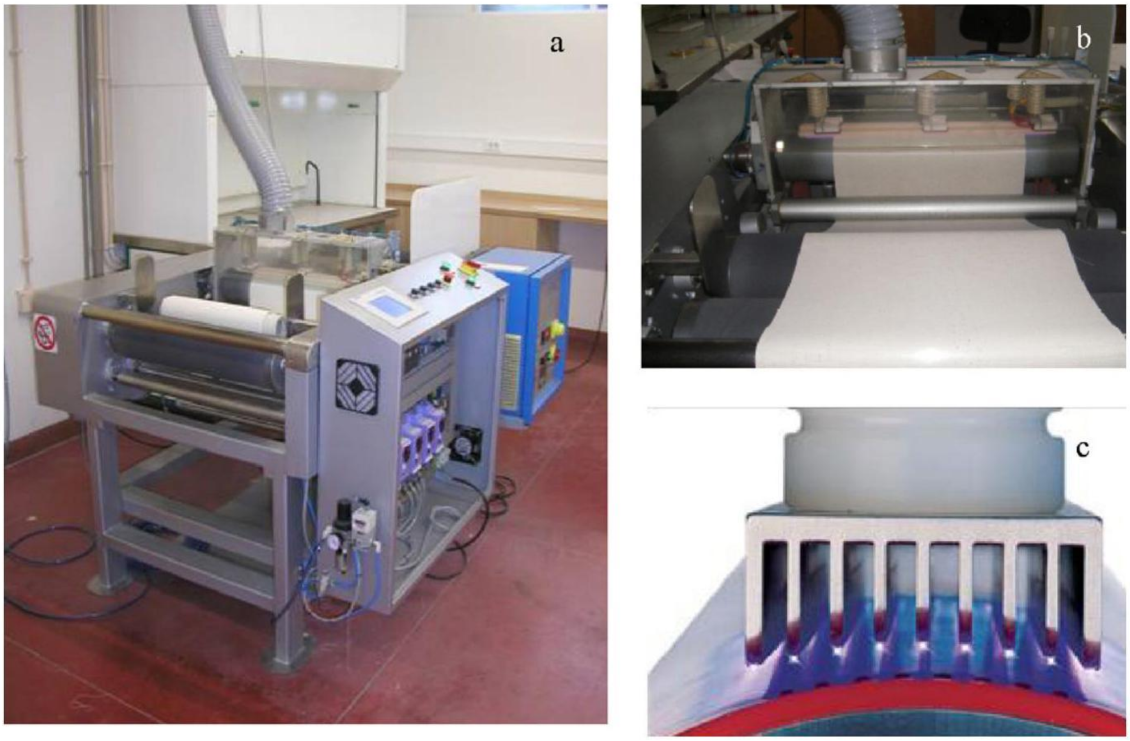


Fig. 1. DBD equipment: (a) Lisboa prototype; (b) detail of the electrode system and continuous sample passage; (c) discharge illustration.

Since plasma treatment is energy-efficient and does not produce any waste, it became a research topic in the application to textile materials [4,7,9,11,19,27-30].

Even though a large volume of research work has been published, in most cases it was carried out almost exclusively in laboratory conditions, with fabric washing processes before plasma treatment or using complicated plasma prototype machines, which do not represent the available conditions in industrial facilities. Thus, the aim of the present study is to investigate chemical and morphological changes of PET and PA6.6 commercial woven fabrics, exposed to a DBD discharge in air at atmospheric pressure. This treatment was performed without any cleaning pre- or post-treatment and in industrial conditions. The chemical and morphological changes were characterized by (ATR)-FTIR, XPS, contact angle analysis and SEM.

Experimental

Materials

A commercial PET woven fabric (470 dex, with 215 × 215, density of 214 g/m^2 and thickness of 0.26 mm -from BST Safety Textiles), and a commercial PA6.6 woven fabric (700 dtex, with 155 × 160, density of 240 g/m^2 and thickness of 0,37 mm-from UTT) were used. The samples were cut into 30 cm × 30 cm, treated and analysed as received, without any cleaning pre- or posttreatment.

Continuous dielectric barrier discharge (DBD) treatment

The atmospheric plasma treatments were carried out on a prototype equipment-Lisboa prototype-from SOFTAL Electronics GmbH, presented in Fig. 1. This treatment involves the application of a high voltage electrical discharge (around $10{,}000 \mathrm{~V}$) through the air, between two electrodes (a ceramic electrode and a counter-electrode with silicone coating), at a frequency of approximately 40 kHz , at room temperature and atmospheric pressure. The discharge power supplied by the electrodes and the velocity of the conveyor belt may be varied, with a maximum discharge of 1.5 kW and a maximum velocity of $60 \mathrm{~m/min}$. The samples, with a maximum width of 50 cm , moved between the electrodes in a continuous way.

Samples of woven fabrics of PET and PA6.6, with dimensions of $30 \mathrm{~cm} \times 30 \mathrm{~cm}$, were subject to the DBD discharge working in a filamentary mode, varying the discharge mean power ($0.5, 1.0$ and 1.5 kW), the speed of the sample (5,10 and $20 \mathrm{~m/min}$) and the number of times the sample was submitted to the discharge (1 and 3 times).

Surface characterization

Contact angle measurements

Contact angle measurements were performed to determine the wettability of the fabric surface, using the sessile drop technique. The wetting liquid was distilled water and the drop volume was $3.0 \mu \mathrm{~L}$. The contact angles were recorded using a Dynamic Contact Angle Analyzer OCA 20 from Dataphysics, equipped with a CCD camera and an image capture program. The measurements were performed at 0 seconds, as the drop is deposited on the fabric, in controlled temperature environment, at $25^{\circ} \mathrm{C}$.

The stability of the modified samples was monitored along the 20 days that followed the treatment, by repeating the measurements periodically within this interval.

Infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) analysis of the surfaces before and after DBD treatment was carried out in a Perkin Elmer 1600 spectrometer, using the attenuated total reflectance (ATR) technique. The ATR was equipped with a ZnSe Crystal prism, working at an incidence angle of 45°. The analysis was performed with a resolution of $4 \mathrm{~cm}^{-1}$ and 64 scans.

X-ray photoelectron spectroscopy

The surface chemical composition of the samples was evaluated by X-ray Photoelectron Spectroscopy (XPS) using a Thermo Scientific K-Alpha ESCA instrument equipped with aluminun K $\alpha 1.2$

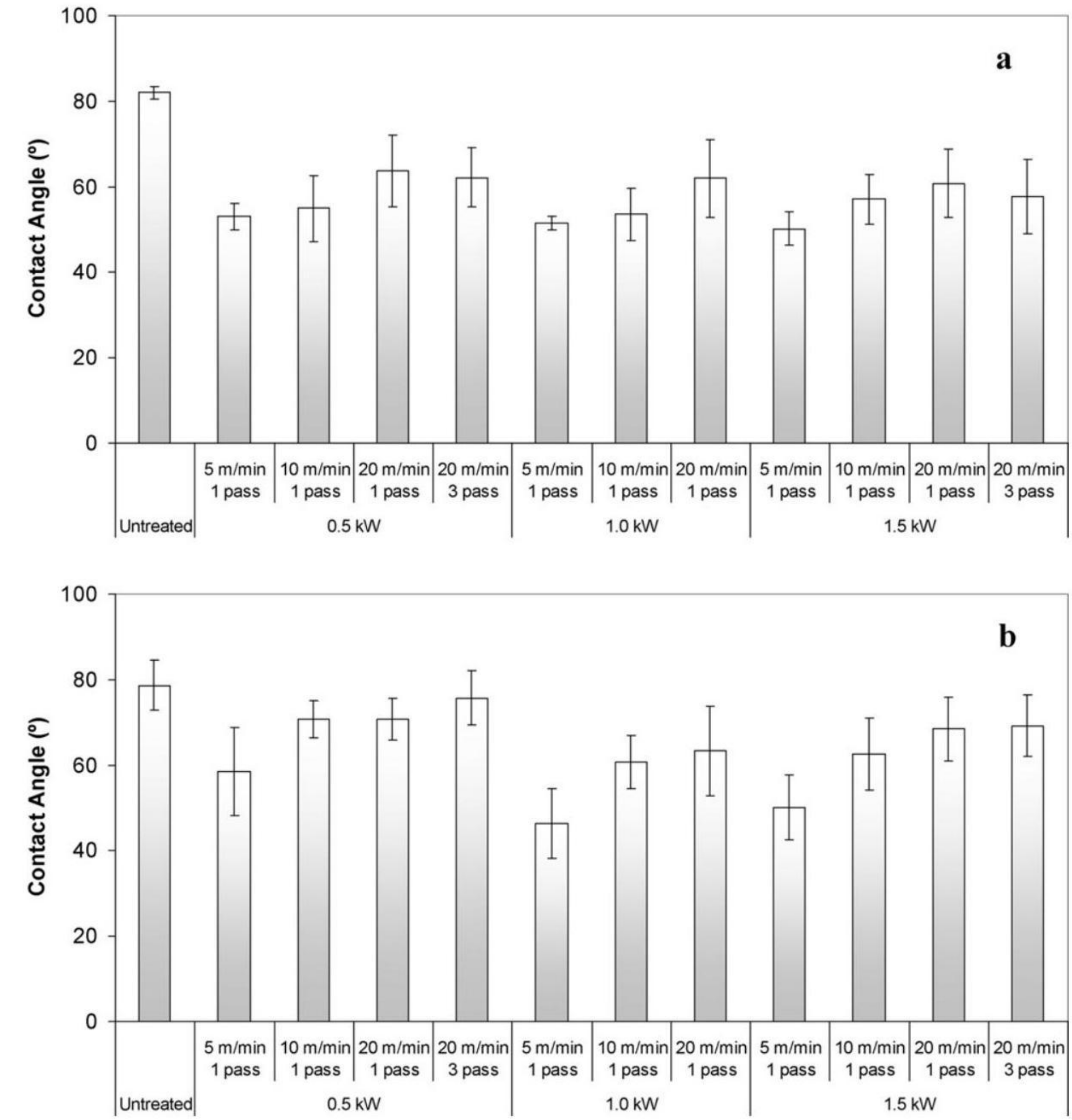


Fig. 2. Water contact angle of: (a) PET, (b) PA6.6 woven fabrics, treated under different conditions.

monochromatized radiation at 1486.6 eV X-ray source. Due to the insulating nature of the samples an electron flood gun was used in order to minimize surface charging. Neutralization of the surface charge was achieved using both a low energy flood gun, in the range of 0 – 14eV, and a low energy Argon ions gun. Photoelectrons were collected from a take-off angle of 90° relative to the sample surface. The measurement was done in a Constant Analyser Energy mode (CAE) with 100 eV pass energy for survey spectra and 20 eV pass energy for high resolution spectra.

Charge referencing was done by setting the lower binding energy C1s peak at 285.0 eV for the C1s hydrocarbon peak [31].

Surface elemental composition was determined using the standard Scofield photoemission cross sections.

Scanning electron microscopy

The surface morphology of the woven fabrics was investigated by scanning electron microscopy (SEM), on a NanoSEM-FEI Nova 200 (FEG/SEM). The samples were sputter-coated with a gold blend.

Results and discussion

Contact angle measurements

The contact angle results obtained, at 0 s , are illustrated in Fig. 2(a) for the PET samples and Fig. 2(b) for the PA6.6 samples. The contact angle variation is represented as a function of treatment conditions. Untreated samples depicted contact angle (θ), with water, near 80° (82° for PET and 79° for PA6.6), presenting, in general, a decrease after all DBD treatment under the different conditions. Similar trends were reported in the literature for different polymers after treatments under atmospheric pressure [6,19,32,33]. This increase in the wettability is generally attributed to the introduction of chemical polar groups on the polymer surface due to its oxidation.

The results presented in Fig. 2 show a maximum decrease in θ for treatments at the lower speed of $5\ \mathrm{m/min}$, showing a decrease from 80° to proximally 50° for both polymeric samples (PET and PA6.6). The decrease in θ indicates an increase in the concentration of polar groups at the surface. Thus, low speed results in a higher efficient treatment. The increase from 5 to $20\ \mathrm{m/min}$ in the sample speed, at constant power, lead to a less efficient treatment, as the contact angles obtained at $20\ \mathrm{m/min}$ are close to those obtained for the untreated sample, being more evident for PA6.6. The results demonstrate that there is a minimum contact time, between the applied discharge and the sample, required to improve the wettability of the fabric surface. It was also observed that treating the fabric several times at high speed did not increase their wettability, as similar contact angle values were obtained for samples that were treated at $20\ \mathrm{m/min}$ once or three times.

The results showed that the power applied (ranging $0.5-1.5\ \mathrm{kW}$) was not the critical parameter and that the contact angle decreased more significantly at low speed.

The shape profile variation of the water drop along the time as it wets the fabric and diffuses through it is highly dependent

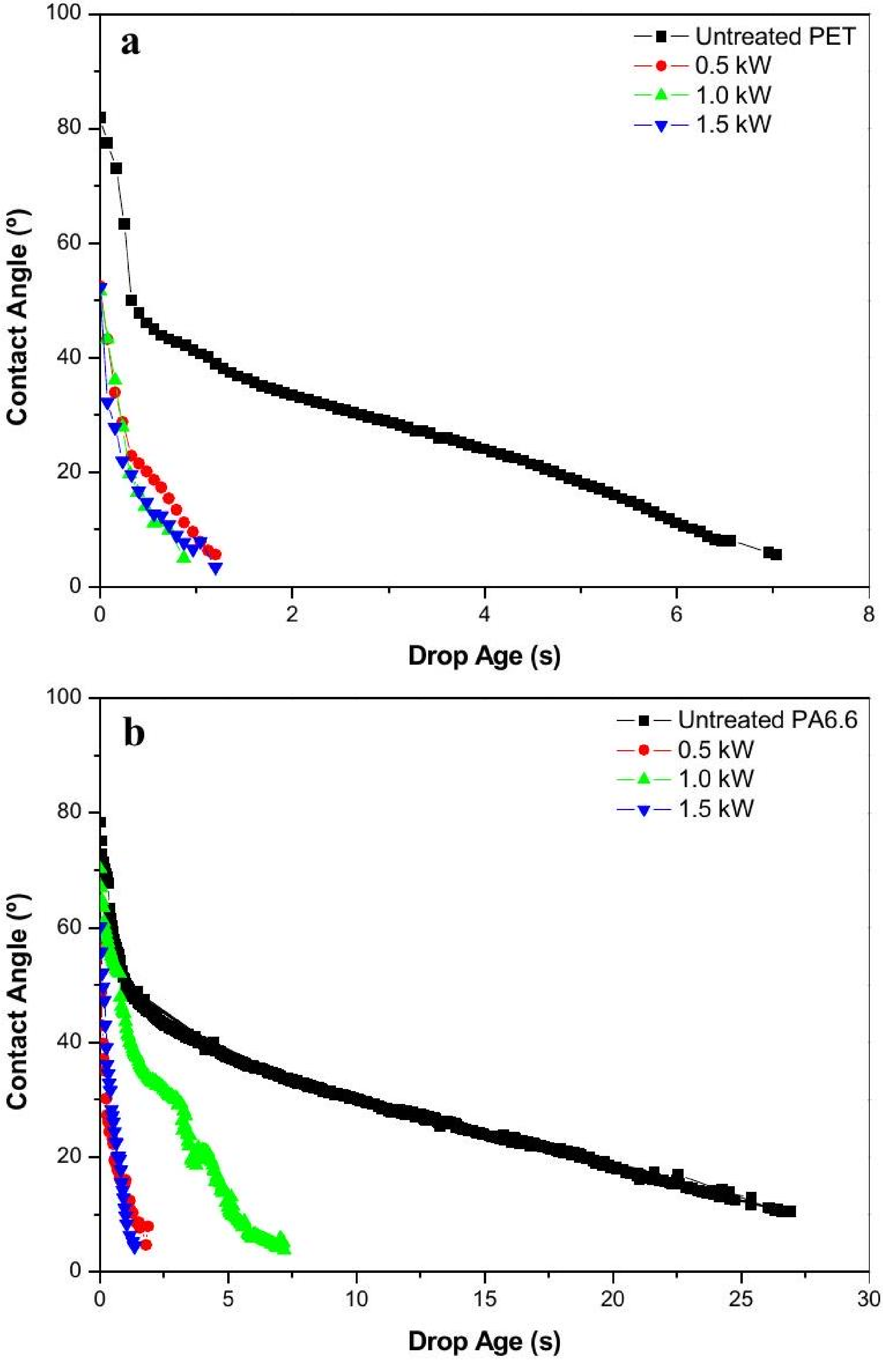
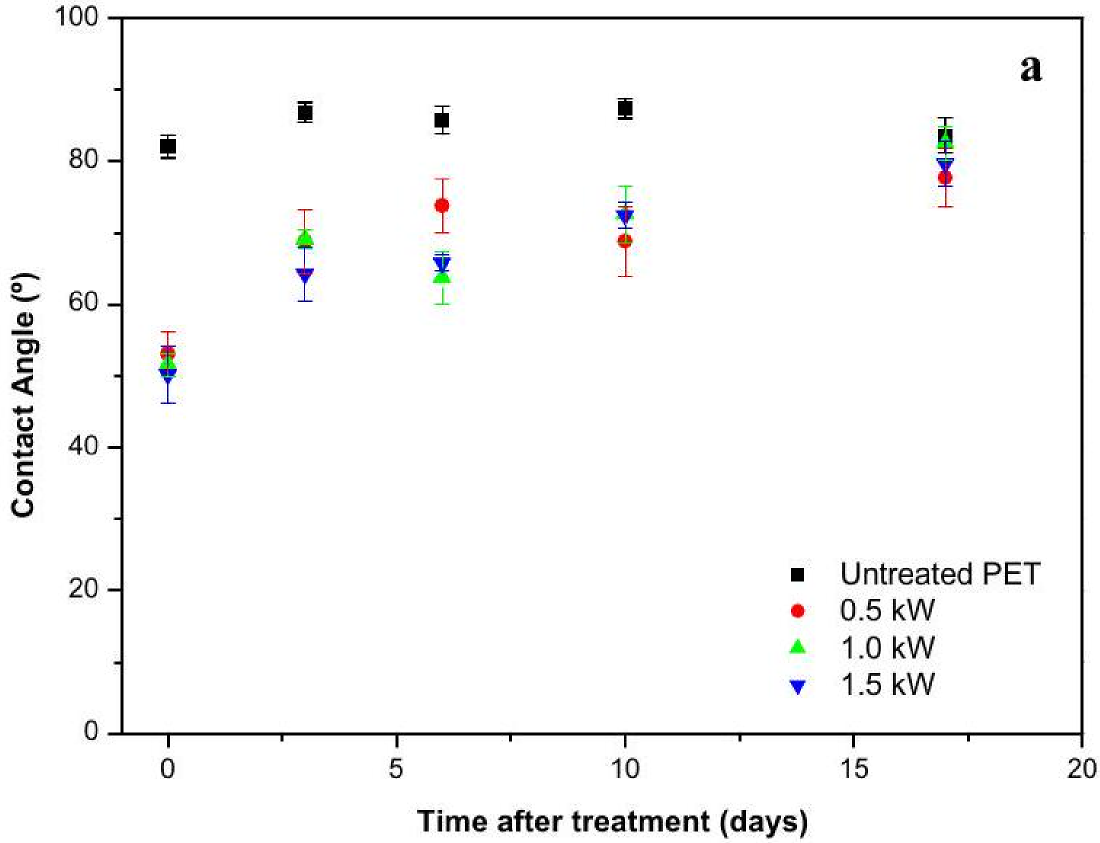
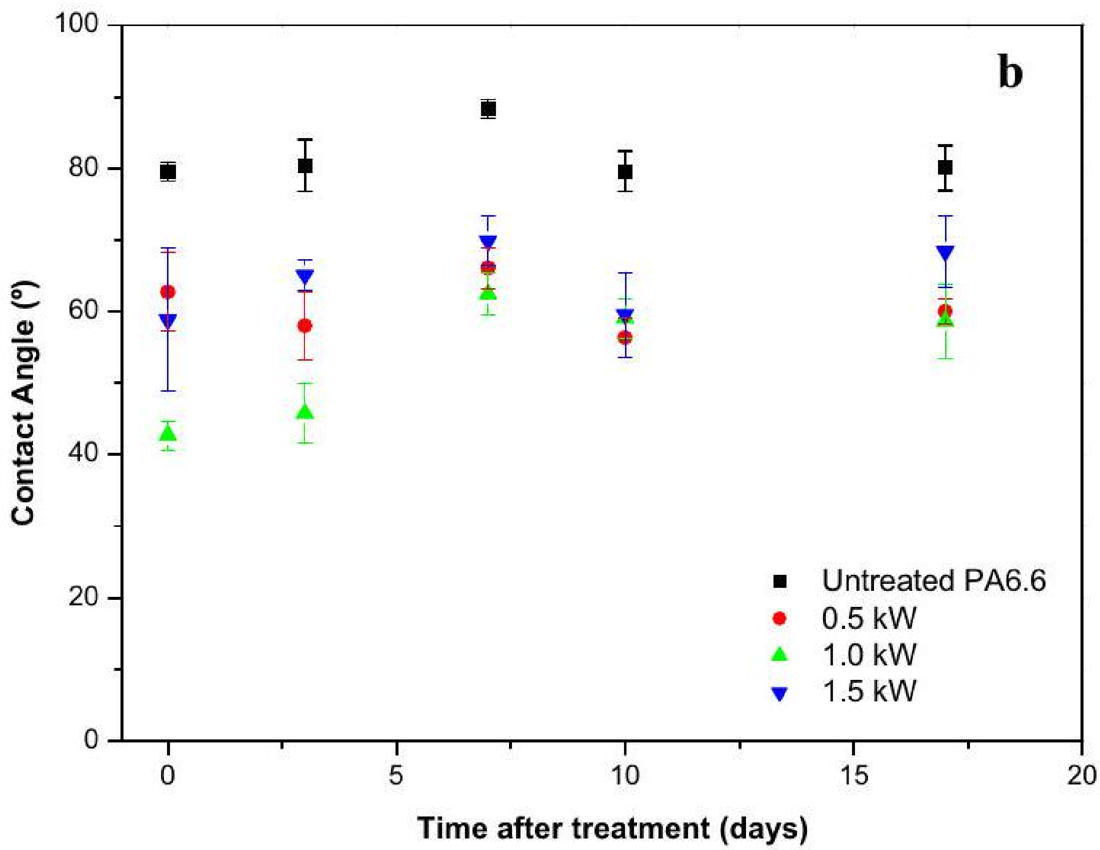

a
Untreated PET
0.5 kW
1.0 kW
1.5 kW
Contact Angle (º)
Drop Age (s)
b
Untreated PA6.6
0.5 kW
1.0 kW
1.5 kW
Contact Angle (º)
Drop Age (s)

Fig. 3. Diffusion of a distilled water drop ($4\mu L$) through untreated and treated woven fabrics ($5\ m/min$, 1 pass): (a) PET, (b) PA6.6.

on the polarity of the fabric surface. As the drop contacts the surface it spreads, reaching a given contact angle. Then it starts to penetrate the fabric decreasing the drop volume steadily, and thus decreasing the contact angle until total penetration. This process is faster for surfaces with higher polarity. The variation of the contact angle profile with time was recorded for the untreated fabrics and for the fabrics treated at the speed of $5\ m/min$ at different power levels. The results are presented in Fig. 3(a) and (b) for PET and PA6.6, respectively. As expected, a faster decrease was observed for



a
Contact Angle (º)
Time after treatment (days)
Untreated PET
0.5 kW
1.0 kW
1.5 kW



b
Contact Angle (º)
Time after treatment (days)
Untreated PA6.6
0.5 kW
1.0 kW
1.5 kW

Fig. 4. Contact angle of treated samples (5 m/min, 1 pass) as a function of ageing: (a) PET; (b) PA6.6.
the treated fabrics relative to the untreated ones, for both PET and PA6.6.

The effect of shelf life on the plasma treated surfaces of PET and PA6.6 fabrics was studied by measuring the contact angle variation with storage time, for fabrics stored under ambient conditions. Fig. 4(a) and (b) shows the variation of the contact angle of treated PET and PA6.6 fabrics, respectively, as a function of storage time. A noticeably different behaviour was observed for the two polymers. While the PET treated fabrics presented a strong ageing effect

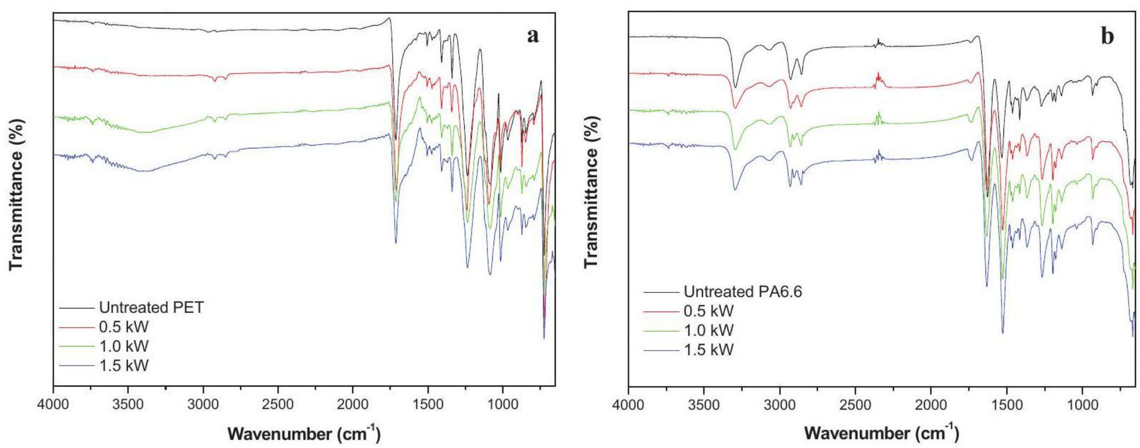


Fig. 5. FTIR/ATR spectra of (a) PET, (b) PA6.6 samples treated with 5 m/min, 1 pass.

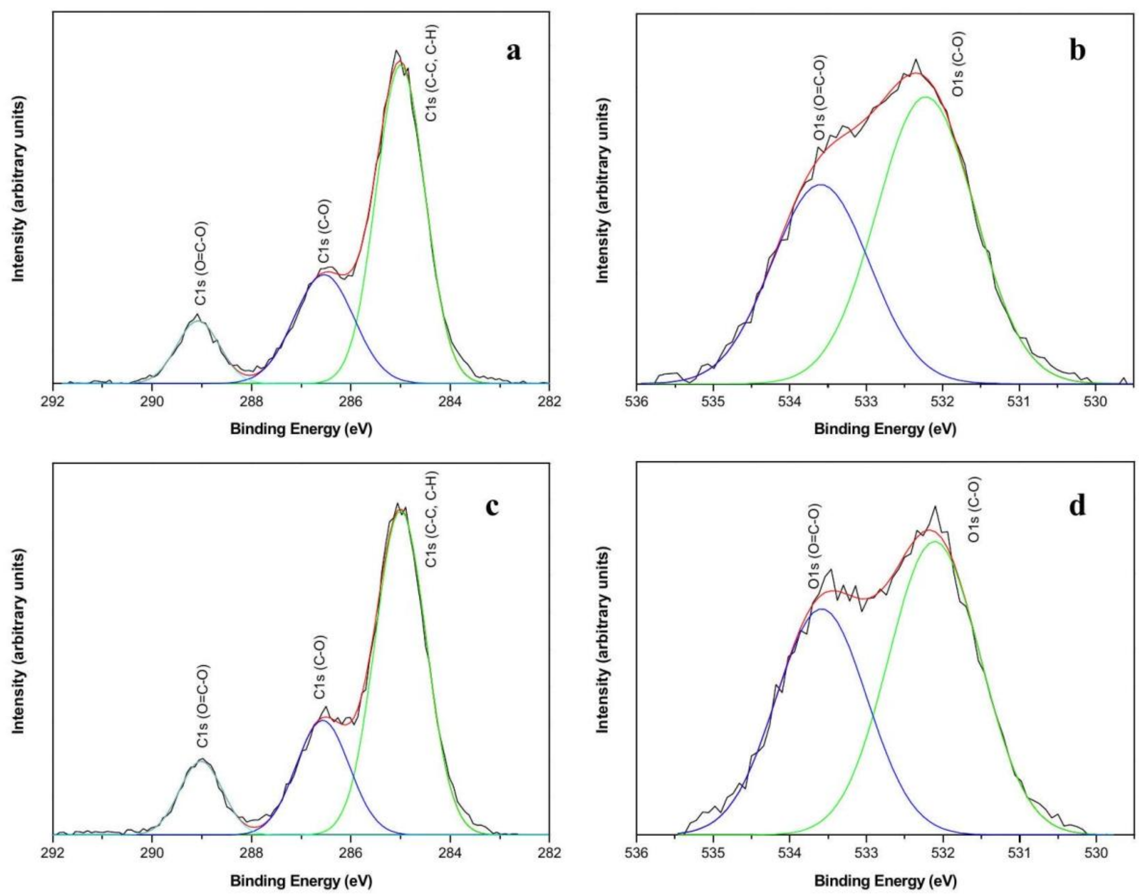


Fig. 6. High resolution XPS spectra for PET fabrics: (a) C1s spectra for untreated PET, (b) O1s spectra for untreated PET, (c) C1s spectra for treated PET and (d) O1s spectra for treated PET.

within the first four days after treatment reaching a plateau afterwards (Fig. 4(a)), the PA6.6 treated fabrics maintained the wetting characteristics almost unchanged even fifteen days after treatment (Fig. 4(b)).

Infrared spectroscopy analysis

(ATR)-FTIR spectra of the untreated and treated fabric samples are shown in Fig. 5. The spectra of samples treated at different power levels and speed of 5 m/min are compared in Fig. 5(a) and (b) for PET and for PA6.6 fabrics, respectively. The spectra were obtained immediately after the DBD treatment.

The formation of a broad band is observed in the $3200 - 3600\ cm^{-1}$ region of the spectrum for the treated PET fabric. This is indicative of the formation of hydrogen bonded -OH groups, as in carboxylic acid, on the fabric surface. A weak absorption peak near $3700\ cm^{-1}$ indicates the formation of a small amount of free -OH groups. The development of a shoulder on the lower wave number side of $1750\ cm^{-1}$ peak corroborates with the formation of carboxylic acid. This can be associated with chain scission of ester bonds to the aliphatic moieties [34]. The intensity of these peaks increases with the applied power discharge, demonstrating that the functional groups formed result from the DBD treatment effect on the fabric surface.

The spectra of PA6.6 treated fabrics, Fig. 5(b), show a clear breakdown of the bands at 2930 and $2850\ \mathrm{cm}^{-1}$, corresponding to symmetric and asymmetric C-H stretching vibrations, respectively, develop into multiple peaks. This behaviour suggests scission of the PA6.6 backbone, with DBD treatment, allowing the formation of new end groups at the fabric surface. At $3730\ \mathrm{cm}^{-1}$ a small band appears, visible only after DBD discharge, that may correspond to the formation of free -OH group. At $1745\ \mathrm{cm}^{-1}$ a slight increase is observed in the intensity of this band, indicating the formation of new carboxylic acid groups after DBD treatment. The concentration increase of this new carboxylic acid band with DBD power discharge, correlates with the decrease in the intensity of the amide I band ($C = 0$), at $1630\ \mathrm{cm}^{-1}$, and the increase in intensity of the amide II band ($\mathrm{C - N}$), at $1525\ \mathrm{cm}^{-1}$. The intensity of the bands at $1365\ \mathrm{cm}^{-1}$, corresponding to ($\mathrm{C - N}$), and at $1265\ \mathrm{cm}^{-1}$, corresponding to secondary amide (trans-form), increases with increasing power discharge DBD treatment. The opposite was observed for the intensity of the two peaks at 1195 and $1175\ \mathrm{cm}^{-1}$, characteristic of the $\mathrm{CH_2 - NH}$ group, showing that an increase in the DBD discharge decreases the peak at $1175\ \mathrm{cm}^{-1}$ and increases the peak at $1195\ \mathrm{cm}^{-1}$. These variations in the FTIR-ATR spectra of the treated PA6.6 fabrics are consistent with the carboxylic acid group concentration increase and with the amide group concentration change, possibly as a consequence of the -CONH- group reaction induced during DBD treatment.

The changes in the FTIR spectra of both PET and PA6.6 fabrics indicate that chemical changes occurred at the surface during DBD treatment, suggesting the chain scission of the polymer chain and the formation of new hydrophilic groups.

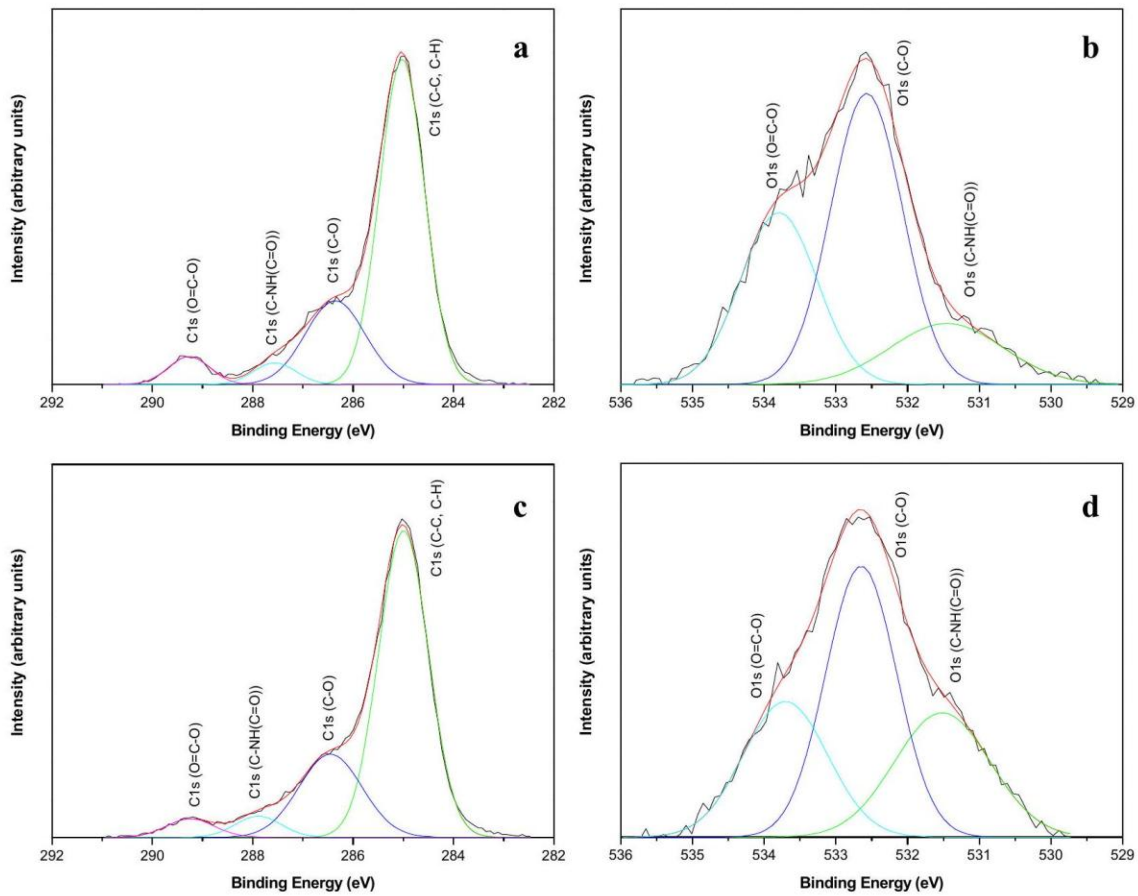


Fig. 7. High resolution XPS spectra for PA6.6 fabrics: (a) C1s spectra for untreated PA6.6, (b) O1s spectra for untreated PA6.6, (c) C1s spectra for treated PA6.6 and (d) O1s spectra for treated PA6.6.

X-ray photoelectron spectroscopy analysis

After treatment the modified fabrics were stored for a month, under ambient conditions, to confirm the stability of the DBD induced changes. The surface chemistry of the fabrics untreated and after treating (treated with 1.0 kW at 5 m/min and with one pass) and one month storage were investigated by XPS. Detailed high resolution spectra of carbon C1s and O1s peaks for untreated and after treating and storage fabrics are presented in Fig. 6 for PET and Fig. 7 for PA6.6. The atomic percentages of carbon, nitrogen and oxygen for untreated and treated and stored fabrics are presented in Table 1.

The C1s spectrum of the untreated PET fabric (Fig. 6(a)) was deconvoluted into three component peaks: one at 285.00 eV , attributed to the $\mathtt{C}-\mathtt{C}$ bonds in the polymer chain and to the $\mathtt{C}-\mathtt{H}$ bonds of the sp^2C of the phenyl ring, another at 286.57 eV that may be associated with the C-O bonds and the last one at 289.01 eV , typical of the binding energy of C in the ester group, $\mathtt{O}=\mathtt{C}-\mathtt{O}$. The O1s spectra (Fig. 6(b)) were composed by two component peaks at 532.11 eV and at 533.59 eV , corresponding to $\mathtt{C}-\mathtt{O}$ and $\mathtt{O}=\mathtt{C}-\mathtt{O}$, respectively. The C1s spectrum (Fig. 6(c)) and the O1s spectrum (Fig.

6(d)) for PET fabric one month stored after DBD treatment are similar to the untreated ones. The atomic percentages of carbon and oxygen and atomic ratios for untreated and treated and stored PET fabrics (Table 1) confirmed that after one month of storage the treated PET surface exhibits similar chemical composition to the untreated fabric. These results are in agreement with the data obtained from the contact angle measurements, which showed an increase of θ along the storage time.

The nitrogen content measured for PA6.6 untreated and surface treated fabric was 2.4 and 1.2%, respectively, as reported in Table 1. Even though this value is lower than the value of approximately 10% expected for this polymer, it may result from the excess of lubricant or spin agent typically used during the fibre spinning

Table 1
Atomic percentages of carbon and oxygen for untreated and stored treated PET and PA6.6 fabrics.

Samples	AT% (C)	AT% (O)	AT% (N)	O/C Ratio	N/C Ratio
Untreated PET	73.4	23.9	-	0.325	-
PET (stored after 1 kW; 5 m/min DBD treatment)	75.4	22.9	-	0.304	-
Untreated PA6.6	81.7	14.4	2.4	0.176	0.029
PA6.6 (stored after 1 kW; 5 m/min DBD treatment)	81.5	16.5	1.2	0.202	0.015

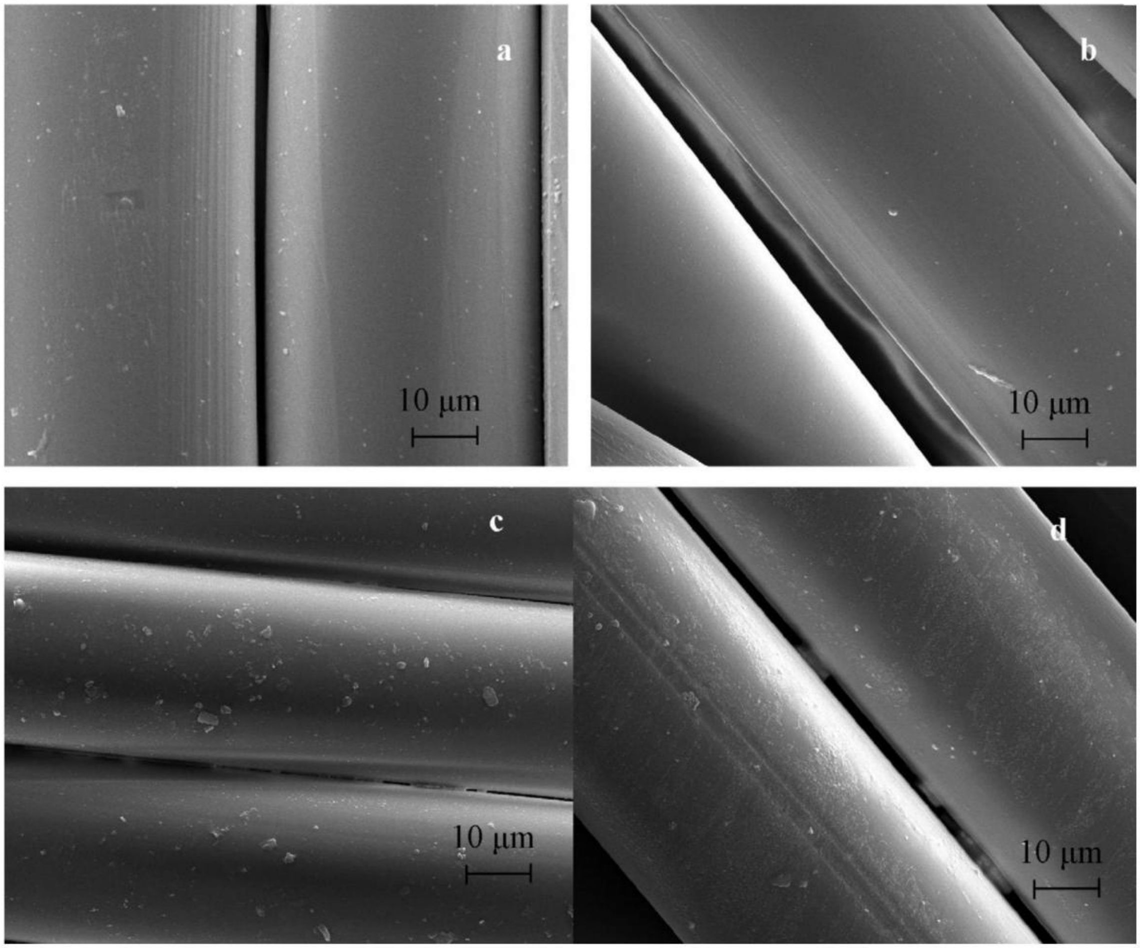


Fig. 8. SEM micrographs of: (a) untreated PET, (b) treated PET, (c) untreated PA6.6 and (d) treated PA6.6.

process, which remains at the fibres surface, or its surface oxidation as a consequence of post-treatment fabric. A similar result was reported before for PA6.6 [11]. The deconvolution of the C1s and O1s high resolution peaks for untreated PA6.6 fabric, Fig. 7(a) and (b), respectively, show the presence of a large concentration of $C-O$ and $O=C-O$ groups that may originate from such surface contamination. The C1s spectrum was deconvoluted into four component peaks at 285.00,286.45,287.89 and 289.24 eV . The first peak was attributed to the $C-C$ bonds along the polymer chain and to CH_2 groups, the second to the $C=O$ bond in the amide groups, the third was assigned to the C atoms neighbouring the amide N atom $-C-NH(C=O)$ and the last peak may be assigned to carbonyl carbons $O=C-O$ groups that might be originated from the mentioned surface contamination. The O1s peak was deconvoluted into three components, centred at 531.41 eV , assigned to the O atoms bonded to the amide C atoms ($C-NH(C=O)$), at 532.71 eV related to the $C=O$ bond, and at 533.90 eV corresponding to the $O=C-O$ ester type groups. The C1s and O1s spectra (Fig. 7(b) and (c)) for PA6.6 fabric one month stored after DBD treatment application are deconvoluted in the same peaks as the untreated ones but there is an evident increase in the oxygen concentration. While O 1 s component peak at 533.90 eV increased, the peak at 531.41 eV slightly decreased. Table 1 presents the quantitative data in terms of atomic percentage of carbon, oxygen and nitrogen. The atomic percentage of oxygen increases from 14.4% for untreated PA6.6-16.5% for treated and stored PA6.6 fabric and the O/C ratio from 0.176 to 0.202. These results show that the oxidation level of the stored PA6.6 fabrics surface is still higher even one month after treatment, in agreement with the data obtained by contact angle ageing.

Scanning electron microscopy analysis

Fig. 8 shows the SEM micrographs of untreated PET and PA6.6 fabrics (Fig. 8(a) and (c)), and after 1.0 kW and 5 m/min treatment (Fig. 8(b) and (d)). Untreated fabric filaments show a relatively smooth surface with some dispersed particles of unknown material deposited on the filaments surface (the presence of material on the surface of filaments may be attributed to the residual spin finishing [11]). After DBD treatment the SEM micrographs do not show any noticeable change in the roughness of these two polymeric materials.

Conclusions

PET and PA6.6 fabric samples were continuously treated in air, under atmospheric pressure DBD discharge, in industrial conditions.

The treated samples showed significant improvement in wettability and spreading of distilled water after treatment. The contact angle value was found to depend on the treatment mode, higher polarity changes were observed for samples treated at lower speed. Similar contact angle values were obtained for different power discharge suggesting saturation after 0.5 kW . Along storage time, a markedly different behaviour of the two polymer materials was observed. While PET sample presented a marked ageing effect in the first four days after treatment, the PA6.6 treated sample retained the surface polarity even fifteen days after treatment.

XPS results showed that treated PA6.6 surfaces presented new oxidation products even after one month stored. Conversely, treated PET samples presented similar oxidation levels as untreated PET, confirming ageing results obtained by contact angle measurements.

FTIR-ART spectra showed chemical changes after treatment, revealing the formation of new polar groups like carboxylic acids and amide groups (in PA6.6 case) and the break of covalent bonds present on PET and PA6.6 substrate surfaces. These changes were dependent on the power discharge; higher power induces more significant surface changes.

The application of this treatment did not change the roughness of the two polymeric materials, as observed by SEM.

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