TEKSTİL VE MÜHENDİS

(Journal of Textiles and Engineer)

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Poliamid Boyama İşleminde DBD Plazma Modifikasyonunun Etkisi

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António Pedro SOUTO, Fernando Ribeiro OLIVEIRA, Marta FERNANDES, Noémia CARNEIRO
University of Minho, Textile Engineering Department, Guimarães, Portugal

Online Erişime Açıldığı Tarih (Available online): 30 Mart 2012 (30 Mar 2012)

Bu makaleye atıf yapmak için (To cite this article):

António Pedro SOUTO, Fernando Ribeiro OLIVEIRA, Marta FERNANDES, Noémia CARNEIRO (2012): Poliamid Boyama İşleminde DBD Plazma Modifikasyonunun Etkisi, Tekstil ve Mühendis, 19: 85, 20-25

For online version of the article: http://dx.doi.org/10.7216/130075992012198505

Araştırma Makalesi / Research Article

INFLUENCE OF DBD PLASMA MODIFICATION IN THE DYEING PROCESS OF POLYAMIDE

António Pedro Souto*
Fernando Ribeiro Oliveira
Marta Fernandes
Noémia Carneiro
University of Minho, Textile Engineering Department, Guimarães, Portugal

ABSTRACT: In this work, a study of the dyeing of polyamide fabrics after surface modification by dielectric barrier discharge (DBD) plasma treatment was performed. Physical and chemical properties of the textile substrate were characterized before and after plasmatic modification, showing important changes in water contact angle, hydrophility, chemical surface composition and morphology. Dyeing properties with direct dyes were evaluated by means of dyebath exhaustion, color strength and washing fastness tests, demonstrating that plasma treated fabrics can achieve excellent dye uptake, high rate of dyeing and good uniformity, good fastness levels, meaning a great challenge and opportunity for industrial application.

Key words: DBD Plasma, Surface Modification, Polyamide, Dyeing

POLİAMİD BOYAMA İŞLEMİNDE DBD PLAZMA MODİFİKASYONUNUN ETKİSİ

ÖZET: Bu araştırmada, dielektrik bariyer deşarjı (DBD) plazma işlemi uygulanarak yüzey modifikasyonu yapılmış poliamid kumaşların boyanması üzerine bir çalışma gerçekleştirilmiştir. Tekstil yüzeyinin, plazma modifikasyonu öncesi ve sonrasındaki fiziksel ve kimyasal özelliklerinin karakterizasyonu su temas açısında, hidrofillikte, yüzey kimyasal kompozisyonunda ve morfolojisinde önemli değişimler olduğunu göstermiştir. Direk boyar maddeler ile boyama özellikleri boya tüketimi, renk verimi ve yıkama haslığı testleri dikkate alınarak değerlendirilmiştir. Sonuçlar, plazma işlemi görmüş kumaşların çok iyi bir boya alımına, yüksek oranda boyanabilirliğe, iyi uniformite ve haslık değerlerine sahip olabileceğini göstermiştir. Bu da yöntemin endüstriyel uygulamalar için büyük bir yenilik ve fırsat olacağı anlamındadır.

Anahtar kelimeler: DBD Plazma, Yüzey Modifikasyonu, Poliamid, Boyama

***Sorumlu Yazar/Corresponding Author:** souto@det.uminho.pt*
***DOI:** 10.7216/130075992012198505   www.tekstilvemuhendis.org.tr*

1. INTRODUCTION

The surface modification of different polymers using plasma technology has attracted quite high attention in the recent years [1]. The developments for newer and alternative technologies to find more quality and stringent ecological requirement have become essential to conserve limited resources like water and energy [2,3].

In plasma processing technology, it is well established that plasmas are able to generate reactive gases in an effective way to obtain cleaning effect, an increase of microroughness and wettability in textile materials without affecting bulk properties [3,4,5,6]. All fibres, from natural to synthetics, can be submitted to several irradiation methods with diverse and significant meaning in different areas of textile processing [3]. Despite the effectiveness of plasma treatments for textiles, almost all of the work done in this area uses low pressure discharge technologies, which require expensive vacuum system and are not readily amenable to continuous in line processing, which is a serious limitation of the commercial viability of this technique in textile industry [3,7]. However, recent research with DBD plasma generated at atmospheric pressure has revealed excellent results regarding uniformity, stability and applicability to processing and treatment of textiles [8]. This technology emerges with a tremendous potential for sustainable innovation and value creation in the area of textile processing operations [2,8]. In addition, the DBD plasma machine can be easily incorporated with continuous processes in the textile industry.

As a pre treatment to dyeing process, the plasmatic discharge is able to modify or remove the fibre's hydrophobic outer layer, improving dye-fibre interaction and increasing the flux of dye molecules through the fibre surface into the fibre bulk [9]. The dyeing rate, dyebath exhaustion and dyeing uniformity are highly improved by plasma treatment [10, 11].

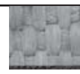
The purpose of this study is to investigate the tinctorial behavior (color strength, dyebath exhaustion) of three different polyamide fabrics after DBD plasma treatment. The experiments were conducted to determine the effects of the plasma treatments on surface wettability, morphology and chemical composition, by means of the static contact angle, wetting time, energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) techniques, the conductivity and pH of aqueous extract of the textile substrates and scanning electron microscopy (SEM) images.

2. MATERIAL AND METHODS

2.1. Fabrics and Dye

Three different polyamide plain weave fabrics were used (table 1) in order to study the surface modification after plasma treatment and its effect in the dyeing processes.

Table 1. Characteristics of polyamide fabrics

Fabric Properties	Polyamide 1 (PA1)	Polyamide 2 (PA2)	Polyamide 3 (PA3)
Specific weight (g/m^2)	61 	95 	135 
Yarn count (Tex)	Weft: 8, Warp: 8	Weft: 18, Warp: 8	Weft: 37, Warp:15
Warp density	42 thread/cm PA6.6	42 thread/cm PA6.6	40 thread/cm PA6.6
Weft density	32 thread/cm PA6	30 thread/cm PA6.6	18 thread/cm PA6.6

Dyeing of these polyamide fabrics has been performed with the direct dye Sirius Orange 3GDL, whose chemical structure is not disclosed yet, without chemical auxiliaries present in the dyebath.

2.2. Dielectric Barrier Discharge Plasma Treatment

Plasma treatment of fibers was carried out in a semi industrial machine (Softal/University of Minho patented prototype). The equipment has a system of ceramic electrode, a metallic counter electrode coated by silicone with 50 cm effective width, an electric generator and a high tension transformer. This machine works with air at normal conditions of temperature and pressure. The velocity (v) and power (P) are controlled and the fabric passes through the electrodes continuously. The plasma dosage is defined by the equation (1) [12]:

$$dosage = \frac{N\,P}{v\,w} \qquad (1)$$

Where: N (number of passages), P (power, Watt), v (velocity, $m.min^{-1}$), w (width of 0.5 m). For the treatment of polyamide fabrics, velocity and power were maintained constant at 4.0 $m.min^{-1}$ and 1000 Watt, respectively. The number of passages was varied from 1 until 9. Thus, the dosages applied to the samples were 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 $kW.min.m^{-2}$.

2.3. Characterization of DBD Treated Fabrics and Structural Analysis

2.3.1. Contact Angle Measurement and Water Drop Adsorption

Dataphysics equipment using OCA software was used for the measurement of contact angles of the water drops in all fabrics. In order to evaluate the wettability of the polyamide woven fabrics, a water-drop test was applied by measuring the time for its complete absorption into the material.

2.3.2. Energy Dispersive Spectroscopy and X-Ray Photoelectron Spectroscopy

Chemical analyses of samples were performed with EDS and XPS techniques. In EDS analysis an EDAX Si(Li) detector and an acceleration voltage of 5kV were used and for the XPS analysis the VG Scientific ESCALAB 200A equipment was selected.

2.3.3. Conductivity and pH of Aqueous Extract

The untreated and the discharged polyamide fabrics were immersed in distilled water with liquor ratio 1:10 during 1 hour and the pH and conductivity (mV) of aqueous extract were measured with a WTW pH meter 538 with a pH combined electrode with integrated temperature sensor Sentix 97T.

2.3.4. Scanning Electron Microscopy

Morphological analysis of polyamide fabrics was realized in an Ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company.

2.4. Dyeing Methods

The dyeing processes were carried out in a laboratorial "Ibelus" machine equipped with infra-red heating and the SIMCORT software was used for continuously assess dye exhaustion. The graphics of dyeing processes are shown in figure 1. Samples were sucessively taken during the dyeing time in order to study the kinetics of dyeing with a direct dye. Dyeing tests were performed for different temperatures (80ºC and 98ºC) and dye concentrations (1%, 2% and 3%). All the samples were dyed with a liquor ratio of 40:1. The pH of dye solution was fixed between 4.5 and 5.0.

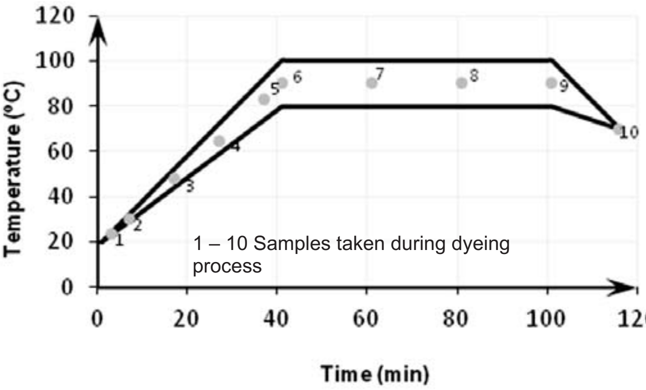


Figure 1. Programmes used for the dyeing processes

2.4.1. Color Strength

The color strength of the dyed fabrics was measured by using a Datacolor Spectraflash SF 600 Plus CT spectrophotometer. The average of five reflectance measurements (R), taken at different positions on the dyed fabric, was adopted. The relative color strength (K/S values) was then established according to the Kubelka-Munk equation.

2.4.2. Washing Fastnesses

The washing fastness was evaluated in accordance with stipulated in standard ISO 105 C06, method A1S.

3. RESULTS AND DISCUSSION

3.1. Contact Angle Measurement and Water Drop Adsorption

The surface properties of polyamide fabrics were analyzed by static and dynamic contact angle measurement to evaluate the effect of different plasma dosages (table 2). The static contact angle for the three untreated polyamide fabrics was 140.3º, 153.0º and 145.8º, being all of them considered as hydrophobic. After treating the fabrics with a plasma dosage of 0.5 kW.min.m^{-2}, the static contact angle decreased to 83.1º, 69.1º and 90.4º in the cases of polyamide 1, 2 and 3 respectively. This behavior is detected for the other plasma dosages. For polyamide 2, the treatment of 2.0 kW.min.m^{-2} was enough to obtain instantaneous water absorption. The same result was obtained for polyamides 3 and 1 with the dosages of 2.5 and 3.5 kW.min.m^{-2}, respectively.

These results suggest that the surface of the treated polyamide samples have been significantly changed due to chemical etching, which tends to create oxidized species on the surface of the polyamide fibers [13, 14]. With plasma activation of the textile substrate it is possible to considerably improve the water adsorption velocity, being this criterion used to choose the optimal plasma dosage of 2.5 kW.min.m^{-2} previous to dyeing process.

Table 2. Static contact angle of polyamide fabrics

Dosage kW.min.m^{-2}	140.3° 0	0.5	1.0	1.5	2.0	2.5	3.0
PA1	153.0°	83.1°	82.6°	52.0°	45.6°	41.4°	39.6°
PA2	145.8°	75.16°	55.3°	53.4°	instantaneous	instantaneous	instantaneous
PA3		90.4°	67.5°	44.4°	29.3°	instantaneous	instantaneous

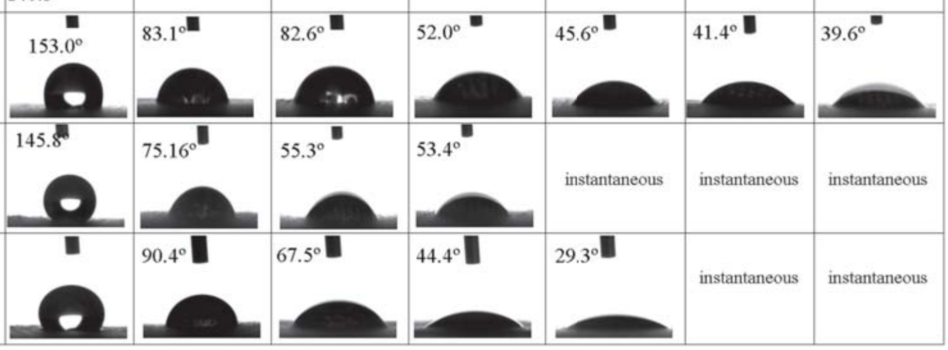


Figure 2 shows the wetting times of the untreated PA fabric compared with the substrate modified by plasma treatment (2.5 kW.min.m^{-2}). The times for the complete absorption of the water drop for the samples without treatment were 404, 63 and 77 seconds to PA1, PA2 and PA3, respectively, confirming high hydrophobicity. These values decrease very significantly to 70 (PA1), 1(PA2) and 1(PA3) seconds after application of optimal DBD plasma dosage. The polyamide synthetic fiber changes the nature from hydrophobic to hydrophilic which is key point for the adsorption of aqueous dye solutions.

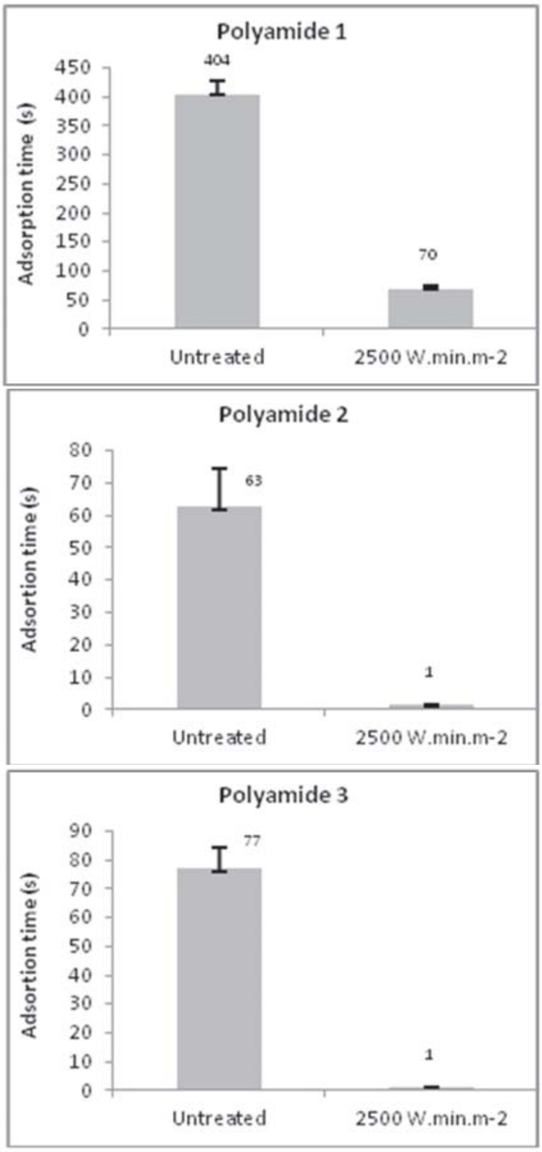


Figure 2. Absorption time of a water drop in the sample without treatment and treated with dosage of 2.5 kW.min.m^{-2}

The hydrophilicity of the polyamide fabric is highly improved by the plasmatic treatment in accordance with the results published by several authors for different synthetic and natural fibers, mentioning modifications in accessible polar groups at the surface and creation of microporosity [11,15].

3.2. Energy Dispersive Spectroscopy and X-Ray Photoelectron Spectroscopy

EDS analysis was used to obtain the degree of chemical modification of the fibres namely surface oxidation [16] and according to Joshi et al, the amount of nanoparticles near and at the surface can be estimated using this technique [17]. The EDS analysis of the polyamide fibers is shown in table 3. For the samples treated with DBD air plasma, when the dosage is increased the carbon content on the surface of the sample decreases. On the other hand, the oxygen and nitrogen elements increase when the DBD plasma treatments are applied. Etching may provoke chain scission in groups C-H, C-O, C-N, N-H and the formation of free radicals, causing the measured carbon content to decrease. Other surface reactions with air plasma can occur to produce reactive species such as O^-, N, N^+, O, OH^-, O_3 [18, 19] which would also result in carbon decrease and increase of nitrogen and oxygen atoms.

Table 3. Atomic percentage (At) by EDS analysis of samples untreated and treated with plasma 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

There are extensive studies using XPS technique in fabrics after plasma treatment [20, 21, 22, 23], in order to clarify chemical surface modifications. Table 4 shows that the oxygen and nitrogen content level in PA1 is increased after DBD treatment, which is in accordance to EDS analysis. This indicates a substantial incorporation of O and N atoms onto the fabric surface.

Table 4. XPS results in samples with and without DBD treatment in PA1 substrate

Sample	At (%)			Atomic Ratio	
	C	O	N	O/C	N/C
Untreated	74.67	17.75	7.58	0.23	0.10
DBD Treated	70.25	19.83	9.92	0.28	0.14

3.3. Conductivity and pH of Aqueous Extract

Conductivity and pH of the aqueous extract of the polyamide fabrics were measured before and after discharges as shown in figure 3. The pH of distilled water was 6.50 and the aqueous extracts of untreated polyamide fabrics were 5.79, 5.75, 6.06 concerning PA1, PA2 and PA3, respectively. These values decrease with increase of dosage, being obtained for the highest dosage of 4.5 kW.min.m^{-2} the pH values of 2.93 (PA1), 2.97 (PA2) and 2.87 (PA3). Consequently, conductivity increases from 54, 57 and 42 mV to 215, 220 and 230 mV, after DBD treatment in PA1, PA2 and PA3, respectively. These results indicate acidification, which is stronger for higher intensity of treatment, and due to chemical changes of surface groups. Similar result was obtained by [2], where the formation of carboxylic acid groups in the cuticle layer of cotton was detected.

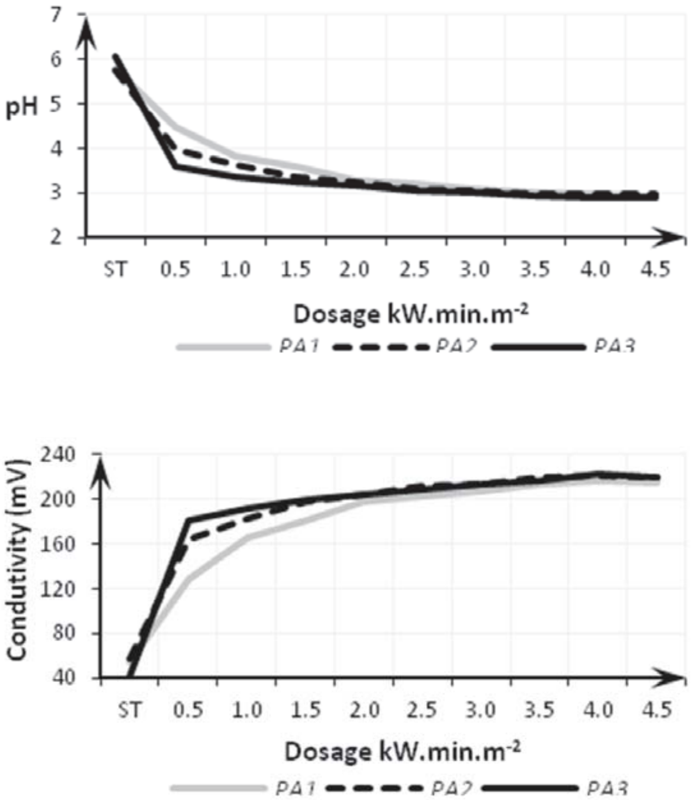


Figure 3. Conductivity and pH of aqueous extract of polyamide fabrics with and without DBD treatment

3.4. Scanning Electron Microscopy

SEM analysis of the polyamide fabrics before and after treatment gives information about the etching function of the double barrier discharge plasma. Borcia et al. [3] observed a localized strong melting of the polyester fibres where the bundles of fibres are crossing each other. In another study the micrographs obtained for the plasma exposed nylon films revealed the presence of micro-pits after 25 seconds of treatment [13].

Figure 4 shows the results of control and plasma treated PA1, PA2 and PA3 substrates with magnification of 10000 X. The surfaces of control samples were very smooth while a few small patches appear at the surface of plasma treated samples.

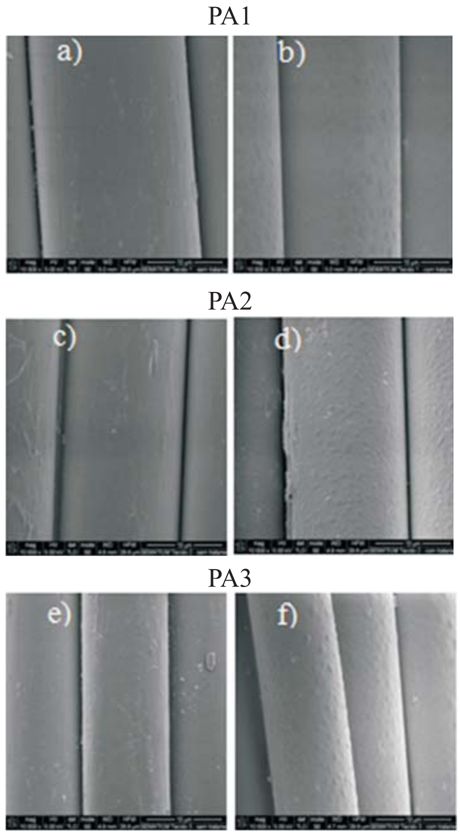


Figure 4. SEM image of polyamides untreated (a, c and e) and treated with dosage of 2.5 kW.min.m^{-2} (b, d and f) with magnification of 10000 X

3.5. Dyeing Results

Figure 5 shows the increase in color depth in dyeing of the polyamide fabrics using two concentrations of a direct dye (Sirius Orange 3GDL), increasing the dosage of discharge. The various particles formed in plasma induce the etching and oxidation of fibre surface and prolongation of treatment time may cause also partial removal of surface layer. Consequently, fibre becomes more accessible to water and dye molecules [24].

Table 5 shows the effect of dye concentration on dye uptake without and with DBD plasma treatment. Increasing dye concentration, more dye is transferred to the fabric and the depth of color is stronger, although more dye is lost in final bath. These results are very positively affected by plasma discharge, meaning deeper colors and less dye in the effluents.

Dyeing tests made with 1% of dye concentration at 98ºC and 80ºC demonstrate that huge differences in the intensity of color are due to previous plasma discharges being enormous advantage, since darker shades are obtainable using less concentration of dyestuffs at lower temperature and shorter dyeing times, independently of the textile structures of the fabric.

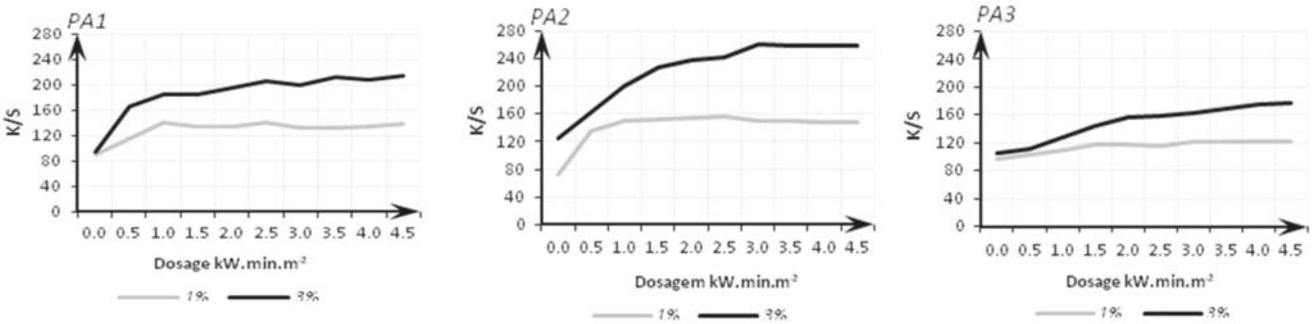


Figure 5. K/S values of dyed samples of polyamide pre-treated with different discharge dosages

Table 5. Dye exhaustion for PA2 and PA3 dyed with 1%, 2% and 3% of direct dye (UT-untreated, T-treated)

Temperature ºC	Time (min)	Dye Exhaustion (%)											
		PA2 1%		PA2 2%		PA2 3%		PA3 1%		PA3 2%		PA3 3%	
		UT	T	UT	T	UT	T	UT	T	UT	T	UT	T
44	**2**	4.0	4.2	1.7	2.8	0.1	1.7	0.0	2.3	0.3	2.4	1.9	3.0
60	**10**	9.1	15.6	2.4	8.4	4.2	5.0	1.9	5.5	2.1	6.2	2.6	4.5
92	**26**	38.4	98.6	7.7	65.4	12.2	47.4	29.9	58.3	12.4	24.7	11.4	21.0
98	**50**	61.0	99.3	18.6	92.6	24.6	63.7	74.3	97.8	40.2	68.1	22.0	43.6
98	**70**	66.0	99.3	21.2	94.9	24.8	69.7	83.9	97.9	47.3	78.2	23.5	48.5
98	**90**	70.2	99.4	22.9	95.4	27.7	70.7	88.6	98.2	49.9	82.7	25.3	51.9
82	**110**	73.6	99.6	27.6	96.4	27.5	73.4	90.3	98.5	54.1	87.0	35.8	56.8
70	**114**	75.6	99.7	36.7	96.9	29.8	75.9	90.5	98.8	54.9	88.5	36.2	59.0

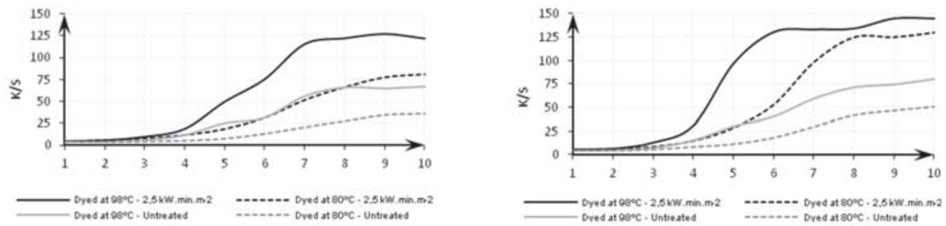


Figure 6. K/S values of dyed samples of polyamide 6.6 pre-treated with and without plasma treatment

3.6. Washing Fastness

Table 6 shows the results of washing fastness for direct dye Sirius Orange 3GDL in polyamide fabrics with three different concentrations. The results are very good, confirming the level of dye fixation. The surface modification of the polyamide fabrics after DBD plasma treatment permits to obtain darker colors, with the same level of staining comparing with the untreated sample.

Table 6. Washing fastness of polyamide samples with and without DBD treatment (Norm ISO 105C06/A1S)

Samples	Dye Concentration (%)	AC	CO	PA	PES	PAC	WO	Color Change
PA1 (Untreated - Treated)	1%	5 - 5	4/5 - 5	5 - 5	5 - 5	5 - 5	5 - 5	4/5 - 5
	2%	5 - 5	4/5 - 5	5 - 5	5 - 5	5 - 5	5 - 5	5 - 5
	3%	5 - 5	4 - 4	5 - 5	5 - 5	5 - 5	5 - 5	5 - 4/5
PA2 (Untreated - Treated)	1%	5 - 5	4/5 - 5	5 - 5	5 - 5	5 - 5	5 - 5	5 - 4/5
	2%	5 - 5	4/5 - 4	5 - 5	5 - 5	5 - 5	5 - 5	4/5 - 4/5
	3%	5 - 5	4/5 - 4	5 - 5	5 - 5	5 - 5	5 - 5	4/5 - 5
PA3 (Untreated - Treated)	1%	5 - 5	4/5 - 5	5 - 5	5 - 5	5 - 5	5 - 5	5 - 5
	2%	5 - 5	4/5 - 4	5 - 5	5 - 5	5 - 5	5 - 5	5 - 5
	3%	5 - 5	4/5 - 4	5 - 5	5 - 5	5 - 5	5 - 5	5 - 5

4. CONCLUSIONS

Atmospheric plasma treatment is able to modify polyamide fabrics, either chemically or physically, increasing the content of hydrophilic functional groups on the fiber surface as dosage applied is increased. The treated polyamide fabrics showed significant improvement in wettability, where the static contact angle and the wetting time values were found to depend on the dosage applied. For higher dosages, a lower contact angle and time of water absorption were obtained.

According to EDS and XPS measurements, plasma reactions changed the surface chemistry of the different polyamide fabrics. A decrease in carbon and an increase in oxygen and nitrogen atoms content at the surface after discharging polyamide are found. The polarity of the groups at the surface after DBD plasma is increased evaluated by means of pH and conductivity of the aqueous extract. Some roughness has been detected in plasma treated polyamide fabrics by SEM technique.

All these modifications of the fiber led to a remarkable increase in dyeing rate and the equilibrium exhaustion was established much faster and reaching almost maximum when compared to untreated samples. Moreover, when DBD treatment is applied to polyamide, lower temperatures, times and dye concentration can be used in the dyeing process, which is an excellent opportunity to reduce costs in energy, dyes and chemicals, achieving sustainable solutions highly convenient for industrial application as best available technique.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from FCT (Fundação do Ministério de Ciência e Tecnologia i.e., The Science and Technology Foundation of Portugal), for the doctoral grant SFRH / BD / 65254 / 2009.

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