



Cold plasma-induced modification of the dyeing properties of poly(ethylene terephthalate) fibers

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Abstract

Surface modification of poly(ethylene terephthalate) (PET) fabrics induced by air radiofrequency (RF) plasma treatment has been investigated systematically as a function of plasma device parameters, to identify the plasma–polymer surface interactions prevailing under different operating conditions and leading to an increased color depth upon dyeing. Some tests have also been performed employing chemically inert argon as a feedstock gas. The dyeing properties of plasma-treated fibers were correlated to their topographical characteristics, determined by AFM analysis, and to their chemical surface composition, determined by XPS analysis, while the plasma-originated UV radiation was found to have no relevant effects in PET surface modification. The relative importance of plasma-induced surface processes, such as etching and grafting of polar species, is discussed in relation to their role in modifying PET dyeing properties.

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1. Introduction

When polymer surfaces are contacted with cold plasmas, several concurrent processes may occur at the plasma–polymer interface, depending on the

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chemical and physical characteristics of the plasma itself [1]. In fact, cold plasmas, produced by electrical discharges in low-pressure gases, consist of a mixture of highly reactive species, i.e. ions, radicals, electrons, photons and excited molecules. Their composition and characteristics strongly depend on device parameters, such as vacuum chamber geometry, gas pressure, gas flow rate and electrical power input and frequency [2]. In the case of chemically inert plasmas, the prevailing processes occurring at the polymer–plasma interface are hydrogen abstraction, etching and sputtering of low-molecular weight molecules [3]. Chemical functionalization may also occur consequent to the incorporation of polar groups either during the treatment in the case of chemically reactive plasmas and/or immediately after the plasma treatment on exposure to the atmosphere [4]. Crosslinking of radical or excited surface species may also contribute to the modification of the polymer surface structure.

Cold plasma treatment may be employed to tailor the surface properties of polymers for specific applications [5]. Indeed, high specificity in the chemical nature of the plasma and in its application conditions is required in many cases, such as in the modification of polymers for biological uses [6]. Thus, a deeper understanding of the different plasma–polymer surface interactions would allow a better control of the polymer surface modifications imparted by cold plasma treatment under different conditions.

In the present work, the surface chemical and topographical modifications induced on poly(ethylene terephthalate) (PET) fabrics by treatment with radio frequency (RF) plasmas of both a reactive and an inert gas have been investigated under different operating conditions, to correlate them to the plasma-induced variation of the dyeing properties of PET fibers. Polyester textiles are usually dyed with disperse dyes, a class of compounds possessing no specific chemical reactivity towards the fibers. Usually, the dyeing process is industrially performed above the glass transition temperature of the polymer to allow dye molecules to penetrate within the fibers and to remain there during the after-dyeing cooling process. Cold plasma treatment, employing either oxygenated or inert gases, have been reported to either improve or decrease the dyeability of polyester [7,8] and other fibers [9,10].

A better understanding of the plasma-induced surface modification may be useful for ascertaining if

and how the plasma-induced surface processes affect the dyeing properties of textiles. This can be achieved by correlating the modified dyeability of PET fibers to the different processes, such as etching, UV irradiation, ion bombardment or grafting, and prevailing under different plasma operating conditions. Indeed, cold plasma treatments have been shown to increase the wettability of PET films [11–15], as a consequence of surface chemical and topographical changes, which may have positive effects also on the dyeing properties.

2. Experimental

2.1. Materials and plasma reactor

Thermofixed PET fabrics (130 g m^{-2}) from Testfabrics (USA) were preliminarily washed as already described [16]. Treated and untreated textile specimens $5.0 \text{ cm} \times 5.0 \text{ cm}$ were usually stored under conditioned atmosphere at $20 \pm 2 \text{ }^\circ\text{C}$ and $65 \pm 2\%$ relative humidity. Air and argon were Linde products (purity $>99.999 \text{ vol.}\%$). PET fabrics were dyed with C.I. Disperse Blue Marine 94 (BASF).

The reactor employed for plasma treatment has been described in detail elsewhere [15–17]. The discharge was produced in a T-shaped cylindrical tube (10 cm diameter, 27 cm length) and it was driven by a capacitive RF antenna, axially located within the chamber. An Ocean Optics PS2000 spectrometer, equipped with optical fibers, was employed for the acquisition of the emission spectra from air plasma.

2.2. Dyeing procedure

Aqueous solutions, containing 1.0 wt.% of the dye and 0.1 vol.% of acetic acid for pH adjustment, were employed for dyeing PET fabrics in a Multicolor apparatus (Nosedà, Italy). The bath ratio was 1:300 (1 g of fiber in 300 ml of dye solution). The following dyeing conditions were adopted: initial temperature $40 \text{ }^\circ\text{C}$, followed by a temperature increase of $3 \text{ }^\circ\text{C min}^{-1}$ upto $100 \text{ }^\circ\text{C}$, holding for 1 h at $100 \text{ }^\circ\text{C}$ and overnight cooling at $40 \text{ }^\circ\text{C}$. Dyed fibers were repeatedly washed for 45 min at $45 \text{ }^\circ\text{C}$ with a water solution containing 5 g l^{-1} of a standard anionic detergent to eliminate any residual dye from their

surface, thoroughly rinsed with deionized water and dried.

2.3. Reflectance analysis and hydrophilicity measurements

The reflectance of dyed fibers at 570 nm, the wavelength corresponding to the maximum absorbance of the employed dye, was measured with a Lambda 19 Perkin-Elmer apparatus, equipped with an RSA-PE-19 Labsphere accessory for reflectance measurements. Each reflectance value was determined as the average of four measurements with an experimental error around 1–2%. Percent reflectance values (R) were converted into K/S values according to the Kubelka–Munk equation [18,19]:

$$\left(\frac{K}{S}\right) = \frac{(1-R)^2}{2R} \quad (1)$$

The percent increase in color depth, I , was obtained from the difference between the $(K/S)_{tr}$ value measured for each plasma-treated sample and the $(K/S)_0$ value of an untreated PET sample dyed in the same bath:

$$I = \frac{(K/S)_{tr} - (K/S)_0}{(K/S)_0} \times 100 \quad (2)$$

The surface hydrophilicity was evaluated through water droplet absorption time measurements, employing the already described home-made apparatus and procedure [15,20].

2.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded using a 5500-PHI (Physical Electronics) apparatus, with a monochromatic Al-anode $K\alpha$ source and an electron take-off angle of 68° . The analyzed circular area had a diameter of 0.8 mm. The pressure in the chamber was around 10^{-6} Pa. The impinging power was maintained at 200 W to avoid polymer degradation. An electron gun was used to neutralize the surface charging occurring on textile insulating samples. The spectrometer was calibrated by using the Ag 3d5/2 peak, and the resulting energetic resolution was 0.46 eV. The peak at 284.7 eV, due to aromatic carbon, was used for internal calibration of the energy scale.

2.5. Atomic force microscopy (AFM)

The morphological and topographical changes of PET fabrics were investigated by an Auto Probe CP Research Atomic Force Microscope (AFM) (Thermo-Microscopes, Sunvally, CA, USA), employing a microfabricated V-shaped silicon cantilever with silicon conical tip, as already described [21]. Changes in surface roughness of the plasma-treated fabrics were expressed as differences in the root-mean-square of the vertical Z -dimension values within the examined areas, which were calculated using the following equation:

$$RMS_{xy} = \sqrt{\sum_{x,y=1}^N \frac{(Z_{x,y} - Z_{average})^2}{N^2}} \quad (3)$$

$Z_{average}$ is the average Z value within the examined area, $Z_{x,y}$ is the local Z value, and N indicates the number of points within the area. Each surface roughness value was calculated as the mean of at least 15 measurements on $1 \mu\text{m}^2$ square areas in different regions of the textile. Errors were estimated as standard deviations.

2.6. Other characterization techniques

Scanning electron microscopy (SEM) tests were performed in a Leica Cambridge 440 StereoScan apparatus, equipped with EDXS X-ray analyzer and a Link Analytical QX-2000 microanalysis system. Attenuated total reflectance (ATR) spectra were recorded with a BIO-RAD FTS-40A apparatus, equipped with a diamond Golden-Gate accessory and a DTGS detector. Tensile mechanical properties on single yarns were determined by means of an Instron 4501 fully electronically controlled apparatus.

3. Results and discussion

3.1. Increase in color depth

All plasma-treated PET specimens exhibited a marked increase of hydrophilicity, especially on their side facing the RF antenna during the treatment. The water droplet absorption times t_{abs} measured imme-

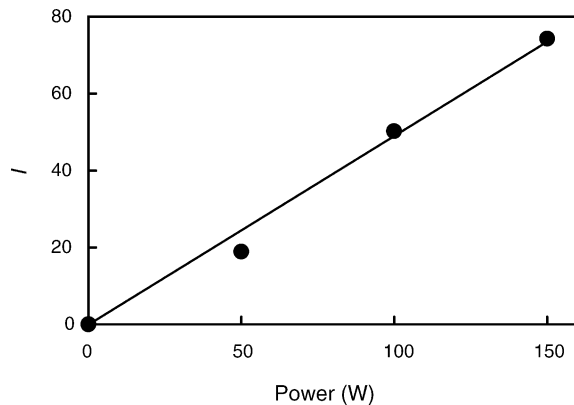


Fig. 1. Increased color depth I of PET fabrics after air plasma treatment as a function of the RF power, W_{RF} . Operating conditions: $P = 0.2$ mbar, distance = 7.5 cm, treatment time = 5 min.

diately after the plasma treatment were always below 10 s, to be compared with $t_{abs} \cong 350$ s of untreated PET. No correlation could thus be drawn between imparted hydrophilicity and air plasma treatment conditions.

Plasma-exposed PET fabrics generally also exhibited a higher increase in color depth upon dyeing respect to untreated PET, especially on their side facing the RF antenna during the treatment. The percent increase in color depth on such side I showed a marked dependency on the adopted plasma treatment conditions, as evidenced by the results reported in Figs. 1–4.

I values increased linearly with increasing the RF power W_{RF} employed in the plasma treatment, as

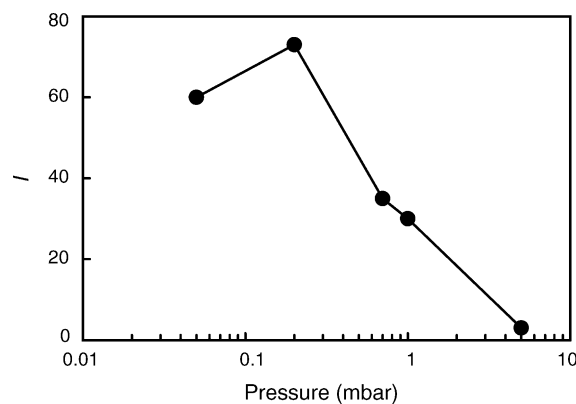


Fig. 2. Increased color depth I of PET fabrics after air plasma treatment as a function of gas pressure at $W_{RF} = 120$ W, distance = 12 cm, treatment time = 2 min.

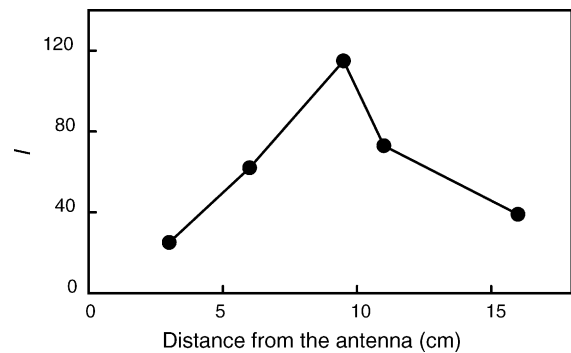


Fig. 3. Increased color depth I of PET fabrics after air plasma treatment at different distance from the antenna at $W_{RF} = 150$ W, $P = 0.1$ mbar, treatment time = 2 min.

shown in Fig. 1. This behavior confirms the central role played in polymer surface modification by the flux of electrons and charged species impacting on the polymer surface. According to plasma diagnostics analysis, in fact, the electron density within the plasma increased almost linearly with increasing W_{RF} and the ion density also increased as the square root of W_{RF} , while the electron temperature remained almost constant [22].

Fig. 2 illustrates the effects on increased color depth I of the gas pressure P inside the chamber during the treatment for samples placed at a fixed distance d from the RF antenna. The highest I value was attained employing a 0.2 mbar pressure. However, the optimal pressure during the treatment could be different if the

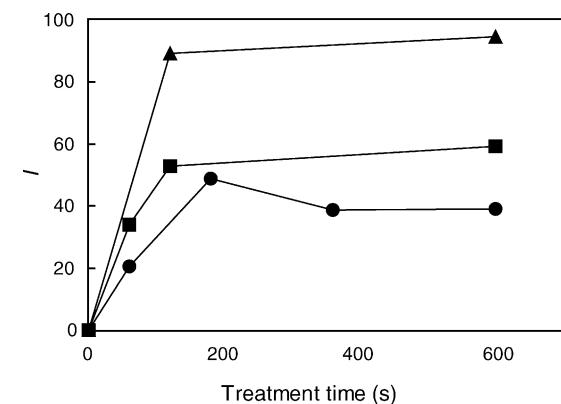


Fig. 4. Increased color depth I of PET fabrics air plasma-treated under different conditions, as a function of treatment time. (●) $W_{RF} = 100$ W, $P = 0.2$ mbar, $d = 7.5$ cm; (■) $W_{RF} = 120$ W, $P = 0.4$ mbar, $d = 5$ cm; (▲) $W_{RF} = 150$ W, $P = 0.4$ mbar, $d = 5$ cm.

samples were treated at a different distance from the emitting RF antenna. Indeed, by increasing the gas pressure, an increase in the amount of active species is expected with a simultaneous contraction of the plasma region around the antenna, and both factors modify the flux of reactive species impacting on the surface. This is reflected by the results shown in Fig. 3, reporting a typical trend of increased color depth of different PET specimens plasma-treated at a different distance from the antenna at a fixed RF power and gas pressure in the discharge. Depending on the gas pressure, they might be fully immersed in the plasma or out of the plasma itself, in the so-called remote plasma zone. Moreover, although the fluxes of reactive species within the plasma peak around the RF antenna, the highest I value was obtained in samples plasma-treated at a certain distance downstream from the antenna.

Finally, for fixed RF power and gas pressure values, the total amount of active species bombarding the samples at a fixed distance from the antenna was determined by the duration of the plasma treatment. Typical trends of color depth increase I , induced by exposing PET fabrics to air plasma treatment for different times, are shown in Fig. 4. Depending on the treatment conditions, more or less high I values were already obtained after a 2-min-long treatment, while a more prolonged treatment always only produced negligibly small further increments of I .

3.2. Kinetic effects

The kinetics of color increase on plasma-treated and on untreated PET specimens was investigated at 98 °C upto the establishment of equilibrium conditions. As shown in Fig. 5, the color increase followed a typical saturation behavior as a function of time. Experimental data were fitted to the Hill equation [7,23], suitable for describing the diffusion into an infinitely long cylinder or filament of radius r .

$$\frac{K/S}{(K/S)_{\infty}} = 1 - 0.692 \times \left[\left(\frac{-5.782Dt}{r^2} \right) + 0.190 \exp \left(\frac{-30.5Dt}{r^2} \right) + 0.0775 \exp \left(\frac{-74.9Dt}{r^2} \right) \right] \quad (4)$$

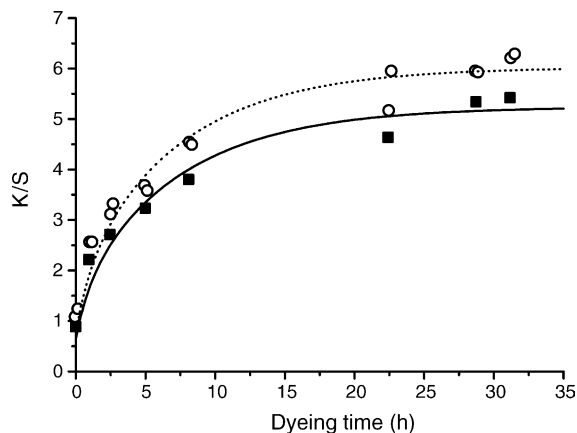


Fig. 5. Increase of color depth at 98 °C as a function of time on an untreated (■) and an air plasma-treated (○) PET fabric.

This empirical equation is derived from the series expansion of the solution of Fick's second equation and it is accurate for moderate and long time [24]. $(K/S)_{\infty}$, the Kubelka–Munk coefficient corresponding to saturation dye uptake, and D/r^2 , the ratio between the diffusion coefficient of the dye within the fiber and the square of the fiber radius, were obtained as optimized parameters from the regression analysis of the experimental data according to equation (4), truncated after the first exponential term. D/r^2 values for treated and untreated PET were 0.0232 ± 0.0042 and $0.0235 \pm 0.0031 \text{ h}^{-1}$, respectively, i.e. they practically coincided, indicating that the apparent diffusion coefficient of the dye within the fiber did not change after the plasma treatment. This is in agreement with ATR results (see below), indicating no appreciable changes in surface crystallinity. On the contrary, $(K/S)_{\infty}$ was higher in the case of treated PET (6.03 ± 0.18 against 5.22 ± 0.22 for untreated PET). Thus, the effect of plasma treatment on the dyeing process does not consist in an increase of the dyeing rate, i.e. it is not due to a kinetic effect. This was confirmed also by the trend of K/S values achieved at different temperatures after 1 h contact of PET specimens with the dyeing bath; under these conditions, the increase of K/S after the plasma treatment was almost independent of temperature.

The color increase observed on plasma-treated PET fabrics may be a consequence of either physical and/or chemical simultaneous modifications of the treated surface, which were investigated through AFM and XPS analysis.

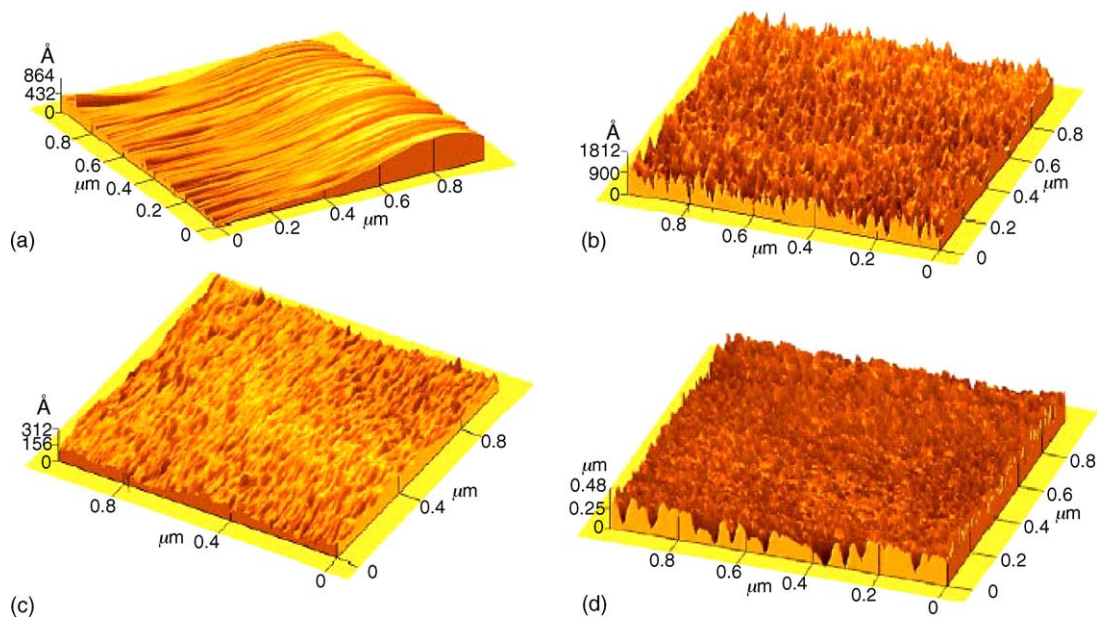


Fig. 6. The 3-D views of non-contact mode AFM images of PET fabrics: (a) untreated surface; surface air plasma-treated for (b) 60 s, and (c) 600 s; (d) surface Ar plasma-treated for 60 s. Operating treatment conditions: $P = 0.1$ mbar, $W_{RF} = 120$ W; $d = 5$ cm.

3.3. Surface characterization by AFM

Detailed information on surface topographical modifications induced by plasma treatment on PET fabrics was obtained by atomic force microscopy (AFM), while scanning electron microscopy (SEM) confirmed to be unable to give information at a nanometer level [15,16,20,25]. Fig. 6(a)–(c) reports some of the AFM images obtained in a systematic investigation on the topographical changes undergone by PET fabrics in successive air plasma treatments under fixed operating conditions. As shown in Fig. 6(a), the original surface of untreated PET fibers was characterized by the presence of elongated patterns, all oriented in the same direction. Fig. 6(b) points out that a 60-s-long plasma treatment gave rise to pits and craters, almost uniformly distributed on the surface. Prolonged plasma treatment (of the order of 10 min) finally led to a general smoothing of such features, producing a substantially isotropic surface (Fig. 6(c)).

By applying a statistical analysis to the AFM images, the topographical changes occurred on PET fabrics during the treatment could be quantified in terms of surface roughness data, expressed as root-

mean-square (RMS_{xy}) of the Z values (see Section 2). Such data, reported in Fig. 7, confirm that the surface roughness and surface area, exhibiting a parallel trend as a function of treatment time, initially increased during the treatment, followed by a slower decrease for treatment times above 3 min. After a 10-min-long treatment, both parameters were not far from those of untreated PET fabrics, though deriving from a completely different surface pattern (see Fig. 6(c) versus Fig. 6(a)).

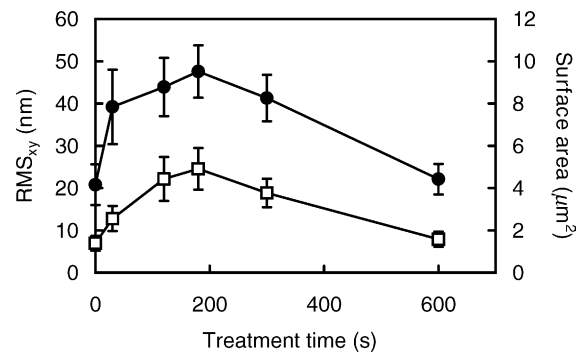


Fig. 7. Surface roughness RMS_{xy} (●) and surface area (□) of air plasma-treated PET fabrics. Operating treatment conditions: $W_{RF} = 120$ W; $P = 0.1$ mbar; $d = 5$ cm.

By comparing the effects of treatment time on the increased color depth (Fig. 4) and on the RMS_{xy} roughness and surface area of air plasma-treated specimens (Fig. 7), we find that these parameters follow similar trends, all of them initially increasing sharply. Thus, the observed increase in color depth upon dyeing may be correlated to the plasma-induced increase in roughness and surface area. This is in agreement with previous studies, attributing the observed increase in color depth upon dyeing of sputter-etched silk, aramid and polyamide fabrics only to the formation of microcraters, which severely restrict the reflection of incident light [26–28]. However, all PET specimens plasma-treated for more than 2 min exhibited an almost constant increase in color depth upon dyeing, while surface roughness increased further and then declined (Fig. 7), as already mentioned.

Changes in the topographical properties may occur during the contact between PET fibers and the dyeing bath [29], due to possible surface macromolecular rearrangements and possible removal of low-molecular weight material [8,30]. This would lead to a variation in the RMS_{xy} roughness value of plasma-treated specimens after the dyeing process. As shown in Fig. 8(b), however, air plasma-treated PET fabrics maintained after dyeing the same topographical aspect and RMS_{xy} value as before dyeing (see Fig. 6(b) for comparison), as confirmed by a careful statistical analysis excluding any change in both X and Y dimensions. Also, untreated samples maintained after dyeing almost the same RMS_{xy} roughness as before dyeing (see Fig. 8(a) versus Fig. 6(a)), confirming that the topography of both treated and untreated samples was not altered by the dyeing process. Therefore, the increased surface roughness of plasma-treated sam-

ples may contribute in increasing the K/S values measured after dyeing [26–29,31].

3.4. Surface characterization by XPS

Surface chemical modifications induced by air plasma treatment were determined by XPS analysis. Table 1 shows the results obtained for PET fabrics after air plasma treatment under different conditions, together with their increased color depth upon dyeing. All samples air plasma-treated at 120 W exhibit an O/C atom ratio around 0.30, which accounts for the oxidation occurred both during the plasma treatment and as a post-treatment effect in contact with the atmosphere, with no substantial difference for samples treated under different discharge conditions. Low amounts of nitrogen were detected on the PET surface after the treatment, confirming the surface grafting of reactive species during the treatment.

Information on how oxygen and nitrogen were implanted on the polymer surface as a consequence of air plasma treatment can be obtained from the deconvolution of XPS signals. As shown in Fig. 9(a), the C(1s) signal of untreated PET contained three well-separated peaks at 284.6, 286.3 and 288.7 eV, corresponding to carbon atoms in the aromatic ring (C_1), to methylene carbons singly bonded to oxygen (C_2), and to ester carbon atoms (C_3), respectively [13,14,20]. In the XPS signal recorded after air plasma treatment (Fig. 9(b)), a slight decrease of the peak at 284.6 eV (C_1) and a marked increase of the C_2 band peaking at 286.3 eV, attributed to $-C-O-$, can be observed. In this case, another band (C_4), overlapping to this latter and peaking at 287.0 eV, can be attributed to nitrogen-bound carbon atoms [13]. Moreover, an increase in the C_3 peak may also be

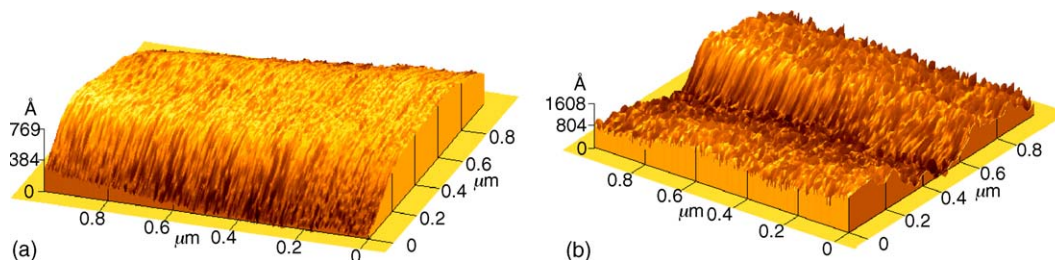


Fig. 8. The 3-D views of non-contact mode AFM images of PET fabrics after dyeing: (a) untreated surface; (b) surface air plasma-treated for 60 s. Operating treatment conditions: $P = 0.1$ mbar; $W_{RF} = 120$ W; $d = 10$ cm.

Table 1

Increased color depth I and surface atom ratios, determined by XPS analysis on PET fabrics after air^a or argon^b plasma treatment under different conditions

Gas	P (mbar)	W_{RF} (W)	d (cm)	I	O/C ^c	N/C	Fe/C
Air	0.2	120	10	104	0.30	0.025	0
Air	0.4	120	10	70	0.33	0.023	0
Air	0.4	120	5	63	0.33	0.031	≈0.02
Air	0.4	150	5	77	0.49	≈0	0.022
Air ^d	0.4	150	5	82	0.50	≈0	0.041
Air ^e	0.4	150	5	74	0.51	0.059	0.026
Air ^f	0.2	120	10	≈0	0.27	0	0
Air ^f	1.0	200	10	≈0	0.38	0	0
Argon	0.2	130	10	104	0.29	0.014	0.010
Argon	0.2	130	5	62	0.61	0	0.14

^a Treatment time: 2 min.

^b Treatment time: 4 min.

^c O/C ratio determined for untreated PET: 0.27.

^d Sample polarised at +30 V respect to the RF antenna.

^e Sample polarised at –63 V respect to the RF antenna.

^f Plasma-treated behind a quartz layer.

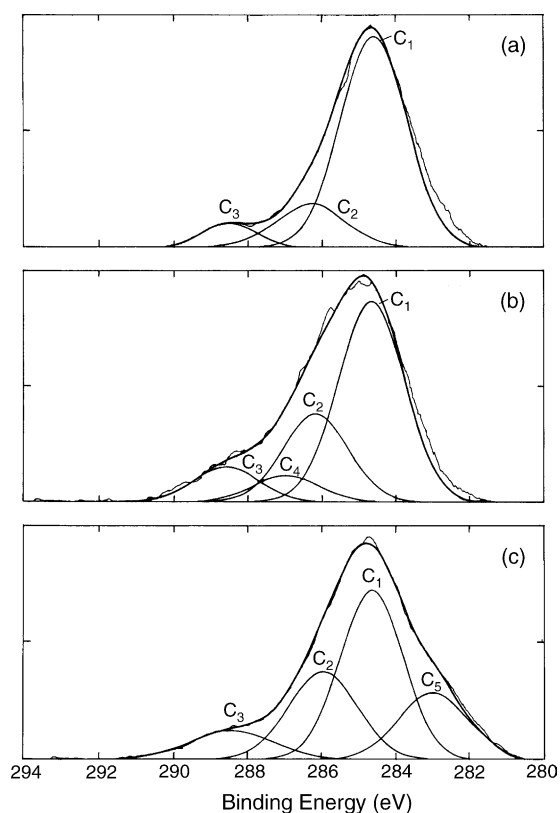


Fig. 9. Deconvolution of the C(1s) XPS peak of (a) untreated PET and (b) air plasma-treated PET ($W_{\text{RF}} = 120$ W, $P = 0.2$ mbar, $d = 10$ cm, $t_{\text{tr}} = 2$ min) or (c) argon plasma-treated PET ($W_{\text{RF}} = 130$ W, $P = 0.2$ mbar, $d = 5$ cm, $t_{\text{tr}} = 4$ min).

observed, being originated in this case by carbon atoms bearing to ester, amide and carboxylic groups [15].

An O/C atom ratio around 0.50, and thus a more extended surface oxidation, was attained when employing higher RF power (150 W), independent of the sample polarization respect to the RF antenna. Nitrogen was detected in this case only in negatively polarized samples, which is in agreement with the modeled composition of the plasma itself [22], identifying NO^+ and N_2^+ as the most abundant positively charged species. However, polarization at this W_{RF} value did not influence apparently the increased color depth of treated samples upon dyeing, their measured I values being all around 80%. Moreover, iron species appeared on the surface of PET samples plasma-treated at higher W_{RF} values and also at short distance from the antenna, clearly as a consequence of the discharge-induced sputtering from this latter.

As shown in Table 1, the highest increase in color depth was achieved in a sample plasma treated without polarization at a relatively long distance from the antenna, with $W_{\text{RF}} = 120$ W and $P = 0.2$ mbar. Neither an increase in the gas pressure within the reactor, nor a treatment closer to the antenna, both leading to higher O/C atom ratios from XPS analysis, was beneficial for increasing I . Therefore, the plasma-modified surface chemical composition may also affect the color depth achieved after dyeing, though not in a straightforward way.

Surface chemical composition certainly plays a relevant role in determining surface hydrophilicity, which was found to exhibit a trend very similar to that of increased color depth, for instance, upon aging. Indeed, the hydrophilicity of air plasma-treated PET fibers was shown to decrease with aging time [15] and progressively lower I values were attained in PET specimens dyed at increasing time after the air plasma treatment. Samples dyed 50 days after the plasma treatment exhibit a ca. 70% lower color depth increase respect to identical samples dyed immediately after the plasma treatment. XPS data confirmed a restoration of benzene carbon atoms bound to hydrogen on the aged PET surface and a corresponding decrease of $-C-O-$ and $-C-N-$ groups, due to the folding of surface chains, tending to decrease the interfacial tension in contact with air [15]. This confirms that a lower increase in color depth upon dyeing can be attained on less hydrophilic and less polar fiber surfaces.

3.5. Modification of PET fabrics by argon plasma

PET fabrics were also treated with cold argon plasma to ascertain whether the chemical nature of the employed plasma influences the observed increase of their color depth upon dyeing. Argon plasma is usually employed for cleaning and etching polymer surfaces by taking advantage of the absence of reactive neutral species and of the relatively high atomic mass of argon, resulting in a more efficient energy transfer from the ionic species produced in this type of plasma. In principle, grafting of polar groups onto the polymer surface is not expected to occur during the plasma treatment, which should produce only etching and activation, and any change in the surface chemical composition should occur as post-treatment effect in contact with the atmosphere [5,13,14].

Argon plasma treatment caused the increase of both hydrophilicity and color depth of PET fabrics upon dyeing. The I values obtained after treatment at W_{RF} in the range 120–150 W were similar to those determined after air plasma treatment under similar conditions. They varied from 60% for samples treated very close to the antenna (5 cm), to more than 100% for samples treated under an Ar pressure of 0.2 mbar at the optimal distance of 10 cm from the antenna, with a trend very similar to that shown in Fig. 3.

AFM analysis (see Fig. 6(d)) evidenced that a much higher surface roughness and surface area were achieved respect to those imparted by air plasma treatment under similar experimental conditions, as already reported in detail elsewhere [21]. For instance, the surface roughness of PET fabrics after air plasma or argon plasma treatment under identical conditions ($t_{tr} = 1$ min, $d = 7.5$ cm from the antenna, $W_{RF} = 105$ W, $P = 0.2$ mbar) were 43 ± 8 and 78 ± 10 nm, respectively. The corresponding surface areas were 3.4 ± 0.7 and $7.3 \pm 1.6 \mu\text{m}^2$, to be compared with the surface roughness (20 ± 5 nm) and surface area ($1.34 \pm 0.18 \mu\text{m}^2$) values of untreated PET fabrics. The remarkable topographical modification is due to the efficiency of the argon ionic bombardment with the possible contribution of neutral metastable excited atoms. However, the much higher RMS_{xy} surface roughness and surface area achieved by Ar plasma treatment did not correspond to an increase in color depth markedly different from that observed after air plasma treatment.

Information on the surface chemical composition of PET after the argon plasma treatment is also reported in Table 1. The observed grafting of nitrogen species on the treated surface most probably is not due to a post-treatment effect; it rather occurs during the plasma treatment due to residual air within the reactor [32] or the treated fabric. A moderate surface oxidation was confirmed by the small increase of the O/C atom ratio and by the decrease of the $\underline{C}H-C\dot{H}$ peak at 284.6 eV (C_1) in the deconvoluted high-resolution XPS spectrum of C(1s) (Fig. 9(c)), by the simultaneous increase of both $\underline{C}-O$ (C_2) and $\underline{C}OO$ peaks (C_3), which can be related to the observed high hydrophilicity and high I values of Ar plasma-treated PET fabrics. Optimal conditions were once more achieved by plasma treatment at a certain distance from the antenna. Also in this case, plasma treatment closer to the antenna lead to lower I values and to the implantation of Fe on the treated surface, as confirmed also by the appearance of a peak at 283 eV (C_5) due to carbide species in Fig. 9(c).

Thus, the results of Table 1 so far discussed point to the conclusion that besides the plasma-treatment induced increase of surface roughness, the grafting of polar groups on the polymer surface also contributes in increasing I values, possibly as a consequence of increased wettability. However, other effects depen-

dent on the characteristics of the plasma itself also plays a role. For instance, the presence of Fe species on the polymer surface treated close to the antenna apparently reduces the dyeing properties, or more probably, this effect is a consequence of the more crosslinked surface structure obtained under these conditions. Indeed, the electron density within the plasma, producing radical species on impact with the polymer surface, is maximal close to the antenna and increases with increasing the RF power [20,22]. A crosslinked structure may be originated from surface radical species, which was suggested to be also responsible for the reduced rate of surface reorganization observed when investigating the surface hydrophilicity decrease occurring during treated specimens aging [15].

3.6. Role of photons

Several energetic species simultaneously bombard the polymer surface during the plasma treatment and it is still a matter of debate which of them are chiefly responsible for surface modification. In particular, the respective roles of ions and photons are still unresolved, both species having been shown to produce polymer surface modification independently [32,33]. UV photons may be important agents in promoting surface modification, especially in the plasma treatment of polymers able to absorb incident radiation, as is the case of PET [34]. Indeed, PET fibers exposed to excimer laser radiation have been recently demonstrated to exhibit improved dyeability [35].

The actual role of photons was thus investigated under the plasma treatment conditions employed in the present work. We first verified spectrometrically that the cold air plasma produced in our device presented several emission lines in the 200–350 nm region, which can be absorbed by PET, the most intense one being the 337 nm emission line typical of N₂. Two PET fabric specimens were then air plasma-treated under identical conditions; one of them was placed behind a quartz layer, allowing the transmission of short-wavelength photons. No differences in wettability and color depth upon dyeing were ever observed between untreated PET fabrics and those treated behind the quartz protection (Table 1), while full hydrophilicity and *I* values around 100% were

attained in the samples treated outside the quartz protection. Moreover, as the photon flux from cold air plasma was shown to increase with increasing both the RF power and the pressure within the reactor [22], some PET samples were treated behind the quartz layer at $W_{\text{RF}} = 200$ W and $P = 1.0$ mbar. Negligible modification of the hydrophilicity and dyeing properties were also obtained under these conditions, while XPS analysis revealed a still lower surface oxidation than in specimens treated without the quartz protection (Table 1). We thus conclude that near-UV photons had a negligible role in PET surface modification under the adopted experimental conditions.

3.7. Other characterization tests

Possible changes in the surface crystallinity induced by plasma treatment, which may influence the adsorption of dye molecules on the PET fibers, could be evidenced by ATR spectroscopy. The intensity of the band at 1340 cm^{-1} assigned to the *trans* rotational isomer of the O–CH₂–CH₂ group, which is associated to the crystalline phase, is usually employed for this kind of analysis. Its intensity is normalized respect to the band at 1410 cm^{-1} , resulting from the phenylene ring vibration, which is assumed to be insensitive to conformational changes [36,37]. However, no changes in the intensity of the 1340 cm^{-1} band were noticed in the ATR analysis of PET specimens after treatment under different plasma discharge conditions. This does not totally exclude surface crystallinity variations, since the ATR accessory investigates a surface depth of about $1\text{ }\mu\text{m}$, which is much greater than that interested by plasma-induced processes.

Finally, tensile strength tests carried out on PET yarns after plasma treatment under different conditions did not evidence any variation respect to untreated PET, within the experimental uncertainty. This confirmed that bulk properties of PET fibers were not altered by the employed plasma treatment.

4. Conclusions

An increase in color depth upon dyeing was obtained after treating PET fabrics with the two types of plasma employed here. This may be easily related

to optical effects connected to the plasma-induced increase of surface roughness, which contributes to the increase of K/S values of dyed PET specimens by decreasing the fraction of light reflected from treated surfaces respect to more smooth surfaces. Other effects, such as the increased surface area and the modifications of the partition equilibrium of the dye between the dyeing bath and the macromolecular surface in contact with it, can also play a role. Indeed, the introduction of hydrophilic groups, induced by both reactive and chemically inert plasmas, may increase the water swelling capability and the affinity of PET fibers for dyes containing polar groups.

Polymer surface modification is essentially due to species bombarding the polymer surface during the plasma treatment, UV photons having been demonstrated to have almost no effect under the adopted treatment conditions.

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