

# Studies on the Atmospheric Air–Plasma Treatment of PET (Polyethylene Terephthalate) Woven Fabrics: Effect of Process Parameters and of Aging

V. Takke,<sup>1</sup> N. Behary,<sup>2</sup> A. Perwuelz,<sup>2</sup> C. Campagne<sup>2</sup>

<sup>1</sup>Department of Textile Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

<sup>2</sup>Laboratoire de Génie et Matériaux Textiles (GEMTEX), Ecole Nationale Supérieure des Arts et Industrie Textiles (ENSAIT), BP 30329, 59056 Roubaix Cedex 01, France

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**ABSTRACT:** The effect of process parameters and of aging on the atmospheric air–plasma treatment of polyethylene terephthalate (PET) woven fabric were studied using surface analysis methods: wettability/capillarity method as well as tapping mode atomic force microscopy imaging. Treatment time and plasma power have significant effect on the variation in fabric capillary weight, surface water contact angle and surface topography. Plasma treatment of PET surface with plasma species not only degrades the surface but also causes surface restructuring as the speed is lowered and the power is increased. An optimal treatment of the PET fabric samples, in terms of increased hydrophilicity both inside and on the PET fabric, is achieved at 60 KJ/m<sup>2</sup> and at a lower speed of 1–2 m/min: water contact angle decreasing from

81° to 40° and capillary weight increasing from 55 to 380 mg. Aging experiments show that, the plasma-treated surface is degraded to a more disordered structure without light, whereas in presence of light a more eroded but organized structure is observed. Indeed wettability/capillarity test shows that light degrades the plasma treatment both at and inside the fabric structure. However, in absence of light, although aging is very slow at the fabric surface, a decrease in capillary uptake by the fabric is detected. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 348–357, 2009

**Key words:** atmospheric air–plasma treatment; polyester woven fabric; aging; capillarity; contact angle; atomic force microscopy

## INTRODUCTION

Plasma techniques have been used in materials science since 1960s, for the activation and modification of different materials. These last decades, plasma processes have been used to improve the surface properties of fibers for various textile applications: sterilization, desizing, wettability or hydrophobicity improvement, antishrinking finishing, dyeability enhancement, and adhesion promotion.<sup>1–4</sup>

The fibers that can be modified by plasma include almost all kinds of fibers, natural and man-made, metallic fibers, glass fibers, carbon fibers, and organic fibers.<sup>1–5</sup>

Using different plasma gases, not only the chemical structure of the surface is modified but also the topography of the surface of the fibers.<sup>1</sup>

Low-pressure plasma methods have been investigated, but they are difficult to apply in industry because they require vacuum and consume considerable amount of energy. Moreover, these treatments can be performed only in a batch process that

increases the treatment time. New methods based on atmospheric plasma treatments seem to be quite attractive for the textile industry. These treatments have the advantage of being applied on-line without vacuum and allow continuous plasma processing.<sup>3</sup>

Atmospheric plasma treatments are used to modify polymer surfaces using plasma gases made up of a mixture of charged particles (electrons and ions), excited atoms (free radicals, meta-stable molecules), and photons. To create a plasma field, the gases are brought through two electrodes that are charged a potential difference. During plasma treatment, the polymer to be treated is exposed to the plasma gases that interact with the polymer surface and modify it. Surface modifications vary with the nature of the substrate and the chemistry of plasma gases, as well as the treatment operating parameters.<sup>3,4</sup>

Among various atmospheric pressure nonthermal plasmas, the dielectric barrier discharge (DBDs) are studied mostly for the easy formation of stable plasmas and their scalability and numerous studies concerning surface modification of material using DBDs under atmospheric pressure have been undertaken mainly for treatment of polymers and metals. Dielectric barrier discharge (DBD) can be created between two metal electrodes covered with insulating layers

Correspondence to: N. Behary (nmassika.behary@ensait.fr).

(ceramic and polycarbonate). Under specific conditions, the DBD discharge can produce the so-called atmospheric pressure glow (APG) discharge, which can be also effectively used for the surface treatment.<sup>6,7</sup>

Studies on dielectric barrier discharge show that the highly reactive species in the discharge regime of DBDs can interact with the surfaces of materials and induce some physical and chemical changes (oxidation, polymerization, crosslinking, etching, etc) on them, and thus, surface properties such as wettability, printability, adhesion, and conductivity are improved.<sup>5,7</sup>

### Aging of plasma-treated surface

The ability of polymer surfaces to restructure their composition in response to the environment is of considerable interest both for fundamental surface science and for a number of technological applications.<sup>8,9</sup> As a result of aging, the surface properties, acquired after a plasma treatment, disappear and the polymer surface acts as if there was no treatment.<sup>8</sup>

Aging survey data<sup>10</sup> show that materials never fully return to their untreated surface state: the surfaces in fact stabilize a few days after the DBD treatment with most of the treated polymers then still presenting a reduction in the contact angle values of more than  $-30\%$  compared with that of the untreated films. Aging of surface-modified polymers can be detrimental to the performance of a device, and improved understanding of the aging of modified surfaces on storage is required to gain the ability to process polymer surfaces, under conditions that are optimized and lead to interfacial properties that are controlled and predictable at the time of use.<sup>9</sup>

The aging effects observed strongly depend on the nature of the polymeric materials, structure, crystallinity,<sup>11</sup> porosity,<sup>3</sup> etc.

Indeed, Novak et al.<sup>11</sup> showed that the degree of crystallinity of a polymer has an influence on the aging of atmospheric plasma-treated samples. They proved that restricted mobility (crystalline polymer) decreases the aging rate effect by reducing the surface polymer chains rearrangement.

In a previous article,<sup>3</sup> we showed that the fabric porosity influences the wash fastness of atmospheric air-plasma-treated polyethylene terephthalate (PET) fabrics. For a low-porosity-(high density) woven fabric, there would be more chain scissions created at the fiber surface, that is, smaller oxidized chemical species created which that be easily removed by simple washing. On the other hand, with a high-porosity textile structure, such as a nonwoven, fewer chain scissions would be created: the macromolecu-

lar chains remaining would be longer and would be thus, more efficiently linked to the polymer surface. These higher molecular weight species are indeed not removed by the washing water.

Our previous work<sup>3</sup> showed that air atmospheric-plasma treatment increases the surface energy of PET fabrics, and it highlighted the need of studying the atmospheric air-plasma treatment before use, so as to set up all the application parameters correctly, for each different type of textile material.

The work performed here aimed at studying the effect atmospheric plasma process parameters (speed treatment and electrical power) on the plasma treatment of woven PET fabrics, for optimal use. It also aimed at studying the effect of aging (in absence and presence of day light) on plasma-treated PET fabrics.

Various wettability measurements to characterize plasma-treated surfaces are described in the literature.<sup>3,12-15</sup> In our work, contact angle and capillarity test measurements as well as Tapping mode Atomic Force Microscopy (AFM) images have been used.

## EXPERIMENTAL WORK

### Sample preparation

#### Woven polyester fabric

A 100% polyester (PET) woven fabric of density 284 g/m<sup>2</sup> with a thickness of 0.56 mm and 63.5% porosity was used for the study. The PET-woven fabric was cleaned to be free from surface impurities and spinning oil. The cleanliness of the PET samples was checked by measuring the surface tension of final rinsing water (used to clean the PET samples), which remained constant and equal to 72.6 mN/m, that is indeed the surface tension of pure water.

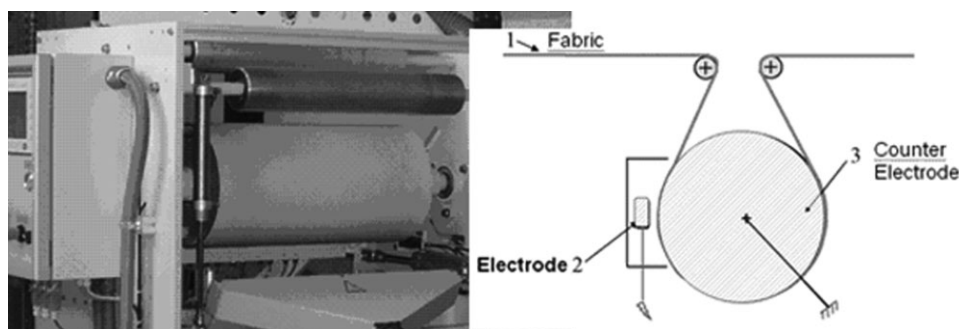
#### Sample preparation for plasma treatment

The PET-woven fabric was cut into squared pieces of 50 × 50 cm on the basis of the electrode length of the plasma machine  $-50$  cm. The speed of the fabric in the discharge zone could be varied using a given control panel.

#### Plasma treatment of woven PET samples

All plasma treatments were performed using an atmospheric plasma machine (Fig. 1) called "Coating Star" manufactured by Ahlbrandt System (Germany).

The following machine parameters were kept constant: electrical power of 1 kW, frequency of 26 kHz, electrode length of 0.5 m, and interelectrode distance of 1.5 mm.



**Figure 1** Plasma treatment under atmospheric pressure by means of dielectric barrier discharge using “Coating Star” plasma machine manufactured by the Ahlbrandt System Company.

The outer layer surfaces of both electrodes were of ceramic (a dielectric material), so that when these electrodes were subjected to a potential difference, a glow discharge called the “Dielectric Barrier Discharge” (DBD) was created.

Atmospheric air was chosen as the gas during the atmospheric plasma treatments. The textile samples were indeed subjected to varying plasma treatment power (TP) that is the plasma power applied per  $m^2$  of textile sample, expressed in  $kJ/m^2$ , and is related to the velocity of the treatment ( $V$ ) and the electrical power ( $P$ ) of the machine by the equation [eq. (1)]:

$$TP = \left( \frac{P}{V \times L} \right) \times 0.06 \quad (1)$$

Where  $P$  = electrical power (W);  $V$  = velocity of the sample (m/min);  $L$  = electrode length (m); TP = treatment power ( $kJ/m^2$ ).

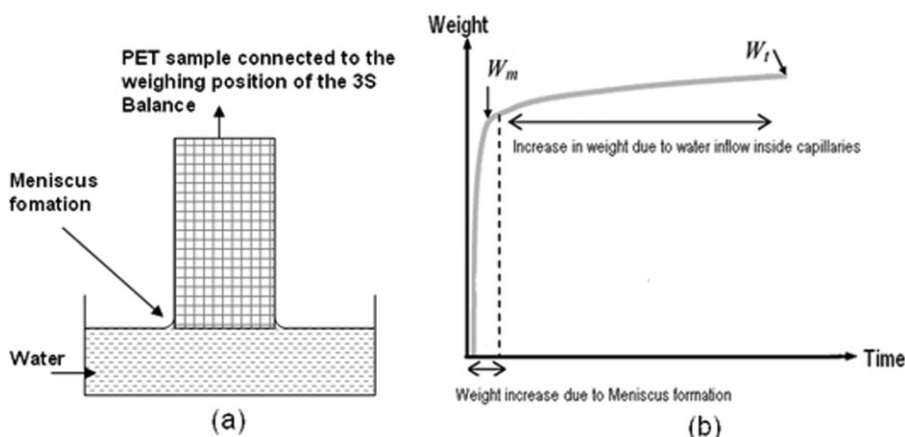
To vary the TP (treatment power) values, plasma treatment was performed at the following velocities “ $V$ ”: 1, 2, 5, and 10 m/min; and at each constant speed varying electrical powers “ $P$ ”: 400, 700, and 1000 W, respectively, were applied.

After plasma treatment, each plasma-treated sample was separated from waste fabric, then kept in aluminium foil away from light.

#### Contact angle and capillary measurements using wicking test

To quantify the surface treatment modifications, contact angle and capillarity measurements were carried out on a tensiometer, 3S Balance from GBX Instruments (France). The apparatus mainly consists of an electronic microbalance with an accuracy of 0.1 mg, a mobile stage which can move vertically, and a data acquisition computer.

During measurements, a rectangular-shaped fabric sample of size  $3 \times 5$  cm was connected to the “3S Balance” at the weighing position, and its weight zeroed, and then it was progressively brought into contact with the surface of a liquid placed in a container on the mobile stage [Fig. 2(a)]. The movement of the mobile stage was stopped when a sudden increase in weight was detected, which corresponded to a liquid meniscus formation on the



**Figure 2** (a) Wettability measurement with the tensiometer “3S Scale” from GBX INSTRUMENTS and (b) typical trace of wetting curve displayed on “3S Scale” tensiometer from GBX instrument, when the weight recorded is plotted against time.

fabric surface ( $W_m$ ). A continuous increase of weight with time was recorded owing to liquid flow inside the fabric structure by capillarity, and then this weight stabilized at a certain point and the total wetting force ( $W_t$ ) was recorded. The fabric sample was then separated from the liquid surface, and the weight of the liquid entrapped inside the fabric structure by capillarity ( $W_c$ ) read directly on the screen of the balance.

Figure 2(b) shows a typical wetting curve displayed on "3S Balance" tensiometer, when the weight recorded is plotted against time.

Capillary weight ( $W_c$ ) readings obtained are used for calculation of meniscus weight ( $W_m$ ) of the fabric sample by using eq. (2).<sup>16</sup>

$$W_m = W_t - W_c \quad (2)$$

where  $W_m$  = Calculated meniscus weight (g);  $W_t$  = Total weight at the end (g);  $W_c$  = Capillarity weight at the end(g).

### Water contact angle calculations

The water contact angle at the woven sample surface could be determined from the calculated "meniscus weight" ( $W_m$ ) using eq. (3),<sup>3</sup> because both the surface tension of liquid water and the perimeter of the contacting surfaces were known.

$$W_m \times g = \gamma_L \times \cos \theta \times p \quad (3)$$

where  $p$  = sample perimeter in contact with the liquid (mm);  $W_m$  = calculated meniscus weight (g);  $g = 9.81 \text{ g s}^{-2}$ ;  $\gamma_L$  = surface tension of the liquid (mN/m);  $\theta$  = contact angle ( $^\circ$ ).

Indeed the real perimeter of contact of each sample " $p$ ," was determined by making wetting measurements with a totally wetting liquid (decane), which yielded a contact angle " $\theta = 0^\circ$ ," i.e.,  $\cos \theta = 1$ . The parameters " $\gamma_L$ ," surface tension of decane, and the " $W_m$ ," meniscus weight, being known, " $p$ " of each sample was then calculated. Each sample was then dried in an oven to evaporate all the decane in the textile structure, before proceeding to wetting force measurements with the water.

On an average, five different samples were tested and their contact angle and capillary weight at 3 min measured, at varying speeds and electrical powers.

### AFM tapping mode images

Investigation using a "Nanoscope III" from DIGITAL INSTRUMENT was carried out for AFM imaging in the Tapping mode. Tapping mode tips "Budget sensor" from "Nanoandmore," of length 125  $\mu\text{m}$ , made of monolithic Silicon probe with Alumin-

ium reflex coating and with resonance frequency of 300 kHz were used.

Tapping mode AFM imaging technique was used to obtain topographic images of the plasma-treated PET fabric fiber surface samples. This mode was preferred to the AFM/LFM (contact mode AFM), because the Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces which may arise after a plasma treatment, and which would distort image data.

Tapping mode imaging was carried out in ambient air. The cantilever that scans the surface is oscillated at or near its resonant frequency using a piezoelectric crystal. The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface, reducing significantly the contact time.

The fiber surface roughness parameter  $R_a$ <sup>17</sup> was calculated directly from AFM signals using the computer software supplied Nanoscope III tool.

AFM imaging was carried out on five different fiber samples selected randomly from the PET fabric sample having been subjected to different treatment.

### Aging methods

Effect of aging on air-plasma-treated PET fabric sample was observed by monitoring changes in capillary weight and contact angle, as well as surface topography of the samples, 1, 4, 8, 12, 16, 22, and 30 days after plasma treatment, respectively. Aging of plasma-treated sample was carried out in two different ways:

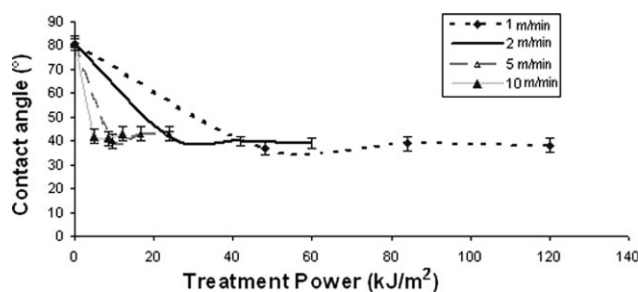
- Without light  
Plasma-treated samples were kept folded in aluminium foil and stored in cupboard, in a small dark chamber to avoid them from getting into contact with light.
- With light  
Plasma-treated samples were kept open in laboratory conditions allowing them to be in contact with light. Laboratory conditions with temperature of  $20 \pm 2^\circ\text{C}$  and relative humidity  $60 \pm 10\%$  were maintained during the experiment.

## RESULTS AND DISCUSSIONS

### Effect of varying speed and electrical powers on plasma treatment of PET-woven fabrics

The effect of varying speed and electrical powers on the plasma treatment of PET-woven fabrics was studied using the wicking test for contact angle and





**Figure 3** PET fabric water contact angle variations with plasma treatment power at various treatment speeds (1, 2, 5, and 10 m/min). At each speed, three different electrical powers: 400, 700, and 1000 W were applied.

capillarity measurements, and AFM tapping mode imaging.

The treatment speeds used were 1, 2, 5, and 10 m/min; and at each speed varying electrical powers “*P*”: 400, 700, and 1000 W, respectively, were applied. The treatment power “*TP*” was calculated using [eq. (1)].

#### Contact angle variation

Water contact angle values using meniscus weight ( $W_m$ ) from capillarity test are those measured at the PET-woven surface.

Figure 3 shows the contact angle variation of the plasma-treated fabrics with increasing treatment power at four different speeds. Whatever the treatment power and the speed used, the water contact angle after plasma treatment is always around  $45^\circ$ , whereas the untreated PET fabric water contact angle is  $80^\circ$ .

Figure 3 also shows that any decrease in speed or increase in treatment power has not a significant impact on this minimum contact angle value. For example, at same electrical power, lowering the speed of machine which allows PET fabric to spend more time in discharge zone, has small impact on the water contact angle of the plasma-treated sample. On the other hand, at the lowest speed of 1 m/min, a further increase in TP, even above  $60 \text{ kJ/m}^2$  does not affect the minimum water contact angle reached.

#### Capillary weight variation

Capillary weight was the weight of water held inside the capillaries of the PET-woven fabric, at the end of capillary weight measurement (Fig. 4). The end time of 3 min was chosen.

In general, capillary weight of plasma-treated PET samples increases with increasing treatment power at all speeds, compared with untreated samples ( $W_c$

= 50 mg), although the highest capillary weight values (around 350 mg) are obtained at lower speeds of 1 and 2 m/min.

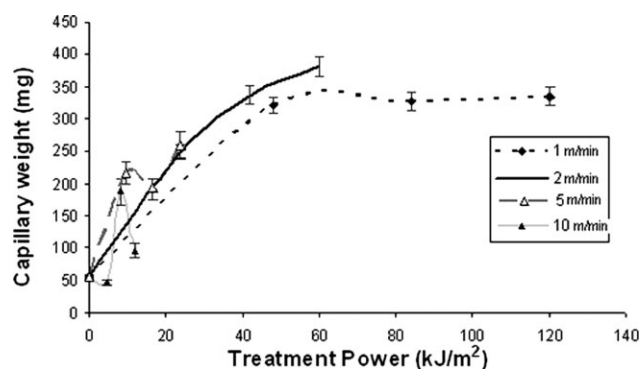
At higher speeds of 5 and 10 m/min, smaller capillarity weight and a nonuniform variation of capillary weight with treatment power are observed. Indeed, an increase of the electrical power from 400 to 1000 W, increases only slightly the treatment power [max  $24 \text{ kJ/m}^2$ : see eq. (1)] at these higher speeds. Thus, a maximum capillary weight of only  $\sim 240 \text{ mg}$  is obtained at an electrical power of 1000 W and speed of 5 m/min.

At lower speeds of 1 and 2 m/min, there is an increase in capillary weight from 55 to 380 mg when the TP is  $60 \text{ kJ/m}^2$ . Further increase in treatment power ( $TP > 60 \text{ kJ/m}^2$ ) by reducing the speed of machine to 1 m/min has nearly no effect on the water uptake by capillarity ( $W_c$ ) of the plasma-treated PET sample.

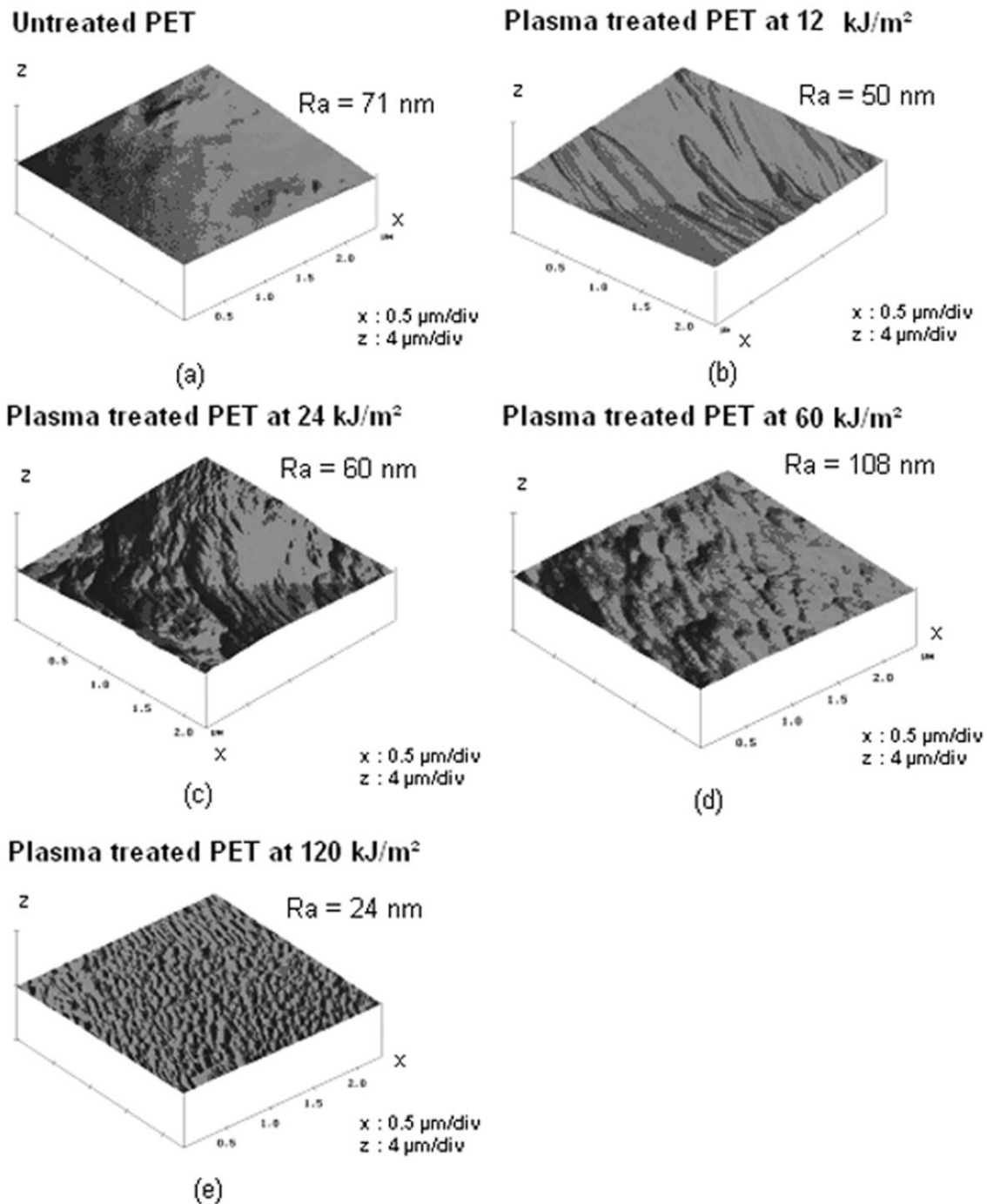
Heterogeneity in capillary weight at lower treatment power and higher speed (5 and 10 m/min) indicates that surface oxidation of fibers inside the textile structure has not yet been achieved.

By reducing machine speed, higher treatment power can be reached [see eq. (1)] because the PET fabric stays a longer time inside discharge zone, and this results in a more thorough plasma treatment of fibers inside the textile structure.

Wetting and capillarity results show that optimal hydrophilicity during plasma treatment of the fibers at the PET fabric surface can be readily achieved at any speed: at 1, 2, 5, or 10 m/min, and any electrical power ranging from 400 to 1000 W. However, a higher treatment power of minimum  $60 \text{ kJ/m}^2$ , reached at lower speeds (1 and 2 m/min) is necessary to treat fibers inside the textile structure.



**Figure 4** Capillary weight variations of air-plasma-treated PET fabric plotted against plasma treatment power (TP) at various treatment speeds (1, 2, 5, and 10 m/min). At each speed, three different electrical powers: 400, 700, and 1000 W were applied.



**Figure 5** Topographic image obtained by AFM in the tapping mode of an untreated PET fabric fiber surface (a), of a plasma-treated PET fabric fiber surface at treatment power "TP" of 12 kJ/m<sup>2</sup> (b), at 24 kJ/m<sup>2</sup> (c), at 60 kJ/m<sup>2</sup> (d), and at 120 kJ/m<sup>2</sup> (e).

#### Tapping mode AFM images

To investigate the impact of the air-plasma treatment on the fiber surface topography, tapping mode AFM images of fiber surfaces from both plasma treated and nontreated PET-woven sample were captured by scanning each time five different fiber samples from each fabric sample.

Typical tapping mode AFM images of samples subjected to an air-plasma treatment power (TP) of 0, 12, 24, 60, and 120 kJ/m<sup>2</sup> are shown in Figure 5.

These tapping mode AFM images show that with an increase in TP from 0 to 120 kJ/m<sup>2</sup>, intensity of surface restructuring goes on increasing.

At very low treatment power of 12 kJ/m<sup>2</sup> and at a speed 10 m/min, a smoother surface confirmed by

the decrease in mean surface roughness,  $R_a = 50$  nm, is obtained [Fig. 5(b)]. Most probably at this highest speed and low-plasma power used, etching of the very upper layer of the PET surface takes place. However, as the treatment power is further increased to  $24 \text{ kJ/m}^2$  at a lower speed of  $5 \text{ m/min}$ , further etching of the PET surface causes appearance of disordered bumps [Fig. 5(c)]. On increasing again the TP to  $60 \text{ kJ/m}^2$  at a lower speed of  $2 \text{ m/min}$ , more uniform scale-like structures [6 scales per  $\mu\text{m}$ , Fig. 5(d)] appear which increases further the mean surface roughness of the fiber surface:  $R_a = 108$  nm. Further increase in TP to  $120 \text{ kJ/m}^2$  (at  $1 \text{ m/min}$ ) causes further and uniform etching to yield tinier and more organized uniform flatter beads [12 beads/ $\mu\text{m}$ , Fig. 5(e)], which decrease mean the surface roughness ( $R_a = 24$  nm).

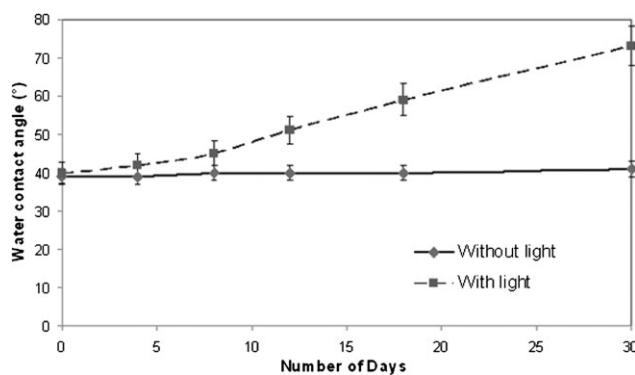
#### Discussions (on treatment parameters)

The increase in hydrophilicity of the PET fabric surface after the atmospheric air-plasma treatment is probably due to plasma oxidation, which destroys the surface chemical bonds, leading to an increase in polar groups.<sup>6</sup> Indeed, plasma treatments generate polymer chain scissions of the weakest bonds of the polyester, creating very reactive chain-end free radicals, which then react easily with the reactive species (e.g., oxygen radicals) present in the plasma generating polar species, such as carbonyl, carboxyl, and hydroxyl groups, which are polar species capable of increasing the surface energy.<sup>3</sup>

Already in a previous article, we showed using X-ray photoelectron spectroscopy (XPS) measurements<sup>18</sup> that there is an increase in concentration of oxygen at the fabric surface after air-plasma treatment of the PET fabric, and this would explain the increase in surface energy of the fabric surface.

Plasma treatment of a woven PET fabric depend on the plasma process parameters. The outer surface of a PET fabric is readily plasma treated to yield the same minimum water contact angle ( $45^\circ$ ), i.e., the same hydrophilicity at any speed varying from  $1$  to  $10 \text{ m/min}$ , and any treatment power from  $12$  to  $120 \text{ kJ/m}^2$ . However, the inner fabric fiber surface requires a greater treatment power of  $60 \text{ kJ/m}^2$  to reach a maximum polarity determined by the capillary weight; a lower speed is also needed to yield a more thorough treatment of the PET fibers inside the PET fabric structure.

The plasma treatment does not only cause chemical structuring of the PET surface by adding polar groups but also morphological surface changes are observed by tapping mode AFM imaging. Although the minimum contact angle ( $40^\circ$ ) is easily reached at even at low treatment power ( $12 \text{ kJ/m}^2$ ), further surface etching of the PET fiber surface takes place with increasing treat-



**Figure 6** Variation of water contact angle of plasma-treated PET samples with time, in the absence and presence of light.

ment power, increasing thus the surface roughness. At higher treatment powers ( $60$  and  $120 \text{ kJ/m}^2$ ), a more organized scale-like surface structure is observed.

#### Effect of aging on plasma-treated PET sample

Quantitative evaluation of aging of atmospheric plasma-treated PET-woven fabric in absence and presence of light was performed using contact angle and capillary weight measurements and compared with surface topography images obtained by Tapping Mode AFM imaging.

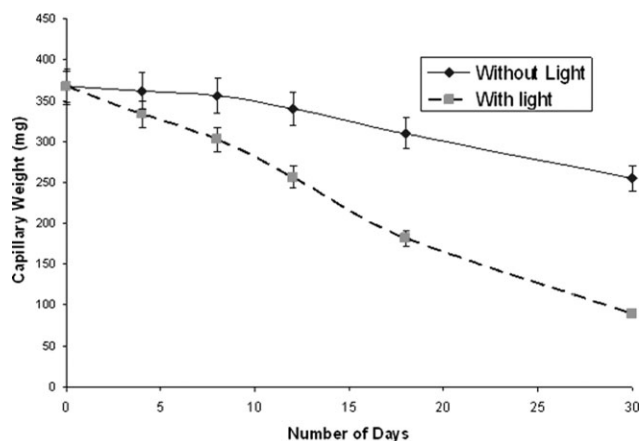
Aging of atmospheric plasma-treated PET samples kept in aluminum foils in dark chamber (absence of light) and in contact with day light at room temperature and pressure (RTP) were analyzed. Five different samples of plasma-treated PET-woven fabrics were tested in presence and absence of light, respectively, for a TP of  $60 \text{ kJ/m}^2$  treated sample.

#### Contact angle variation

Figure 6 shows the variation in water contact angle at the PET fabric surface, 1, 4, 8, 12, 16, 22, and 30 days in absence and presence of light. Five different samples were tested in each case.

In absence of light, very little change in contact angle was seen ( $\sim 37^\circ$  to  $43^\circ$ ). However, substantial increase in contact angle ( $39^\circ$ – $73^\circ$ ) was observed for plasma-treated PET samples kept open in laboratory conditions in contact with daylight.

Indeed, in absence of light (i.e., UV rays), samples kept in the dark chamber preserves plasma treatment giving very small change in contact angle over the 30 days period of experiment. The increase in contact angle with time, in presence of light, could be due to the loss of surface oxidation at plasma-treated PET fabric surface. Degradation of peroxide radicals because of UV rays of the daylight could be a major factor in increasing the water contact angle of the plasma-treated fabric.



**Figure 7** Variation in capillary weight of plasma-treated PET samples with time, in absence and presence of light.

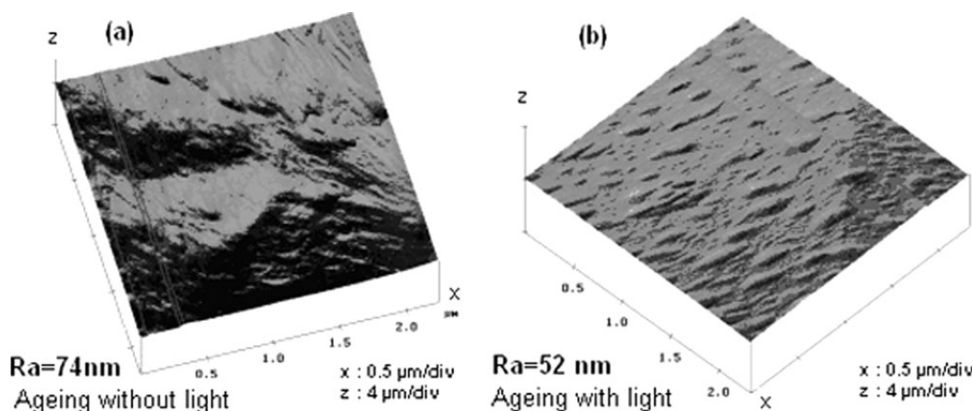
### Capillary weight variation

Figure 7 shows the variation of water capillary weight of plasma-treated PET fabric, measured using wicking test, 1, 4, 8, 12, 16, 22, and 30 days in absence and presence of light.

For both the samples kept in dark and in light, a decrease in capillary weight was observed, although in presence of light, a more drastic decrease was observed (360–100 mg) than in absence of light (360–250 mg) after 30 days.

### AFM analysis to study the influence of aging on plasma-treated PET fabric

Tapping mode AFM imaging of PET samples was carried out to observe the effect of aging with time in presence and absence of light, on the 20th day of aging. Figure 8(a,b) shows the topographic images of the plasma-treated sample ( $TP = 60 \text{ kJ/m}^2$ ) subjected to 20 day-aging conditions: (a), without light; b, with light, and these can be compared with that of a plasma-treated sample on Day 0 [Fig. 5(d)].



**Figure 8** Tapping mode topographic image of a PET plasma-treated sample (at  $60 \text{ kJ/m}^2$ ) subjected to a 20 day-aging without light (a) and with light (b).

Deformation of the scale-like structures [Fig. 5(d)] on the fiber surface formed as a result of plasma treatment, due to aging in absence of light is observed, giving a disordered surface structure [Fig. 8(a)], where big bumps still appear. There is a slight increase in the  $R_a$  roughness value.

In presence of light, smaller, flatter, and fewer blister-shaped structures, of different sizes, appear as if, the scales formed by plasma treatment had been nearly completely eroded, leaving a surface as seen in Figure 8(b), which has got a smaller roughness value ( $R_a = 52 \text{ nm}$ ).

### Discussions (on aging effect)

AFM imaging shows that aging degrades the plasma-treated scale-like PET fiber surfaces. Although in absence of light slow aging initiates a disordering of surface, aging in presence of light leads to an organized structure.

Wetting results show that this degradation may occur both at the fabric surface and inside the fabric structure because a higher contact angle and a lower capillary weight are measured, respectively, due to aging.

Without light, aging process may be very slow, because the outer plasma-treated oxidized fabric surface gives similar water contact angle after 20 days as the day 0. As only slight change in the surface topography is observed, the oxidized species should stay on the fiber surface and are not removed by aging without light.

With light, the aging process seems to be accelerated, both at the outer fabric surface and the inner fabric fiber surface.

Aging effect of plasma treatment has been observed by many researchers, and more particularly, Ferrero<sup>13</sup> observed a decrease in capillary uptake due to aging of plasma-treated PET fabrics.



However, very little literature is available to explain the difference between aging in absence and presence of light and their impact on the capillary uptake.

Krump et al.<sup>8</sup> give four different possible mechanisms for aging effects: (1) thermodynamic reorientation of the polar particles from the surface to the subsurface areas; (2) diffusion of the mobile additives or oligomers from the bulk to the surface; (3) formation of low molecular particles in the subsurface and consecutive migration to the surface; and (4) recombination of the free residual radicals giving rise to chemical change. The effects observed strongly depend on the nature of the polymeric materials, structure, crystallinity, etc.

To explain the different aging effect of light on the capillary uptake and the contact angle measurement the following hypothesis can be made: the oxidized species formed on the fiber surface at fabric surface and inside the fabric structure are not of the same nature. Those formed at the fabric surface are more resistant to aging in absence of light, whereas those formed at the capillary interface are rapidly subjected to aging with or without light. Already in a previous article,<sup>3</sup> we showed that the type of oxidized species formed depended on the porosity of fabrics (i.e., air permeability), so may be, as the contact surface area with air at the fabric surface and within the fabric structure, is not the same, different oxidized species are formed. Indeed, Leroux et al.<sup>3</sup> showed that a low air permeability in a textile structure (as in the case of inner fabric fiber surface) would yield more chain scissions during plasma treatment and the creation of smaller chemical species, which can be removed by simple washing as they are of smaller molecular weight. In a more highly porous structure with greater air permeability (the case of the outer fabric surface), fewer chain scissions are created yielding longer macromolecular chains, which are not easily removed by washing. Further chemical analysis of both inner and outer fabric fiber surface would allow us to better explain the differences observed. Although XPS analysis is a possible solution to analyze the outer fabric fiber surface by carrying XPS analysis on the fabric surface itself, an experimental setup should be built up to find a way to analyze inner fiber surface by XPS.

In presence of light, both a reduction in surface roughness and wettability are observed. To explain the mechanism behind the restructuring seen in Figure 8(b) in presence of light the following explanation may be given: aging in presence of light would surely lead to more chain scissions and the creation of lower weight oxidized species, which are more readily eliminated by water, wherein a bigger water contact angle, and lower capillary weight. Also, the recombination of oxidized (peroxide) species

because of a photoreaction, would lead to a decrease in oxidized species at the fiber surface. This recombination reaction may cause crosslinking with the possible elimination of species like CO<sub>2</sub> in presence of air and light, and this may also explain a reduction in wettability and surface roughness of the plasma-treated fiber in presence of light

## CONCLUSIONS

In light of the results obtained in this article, the following conclusions can be made as far as plasma treatment parameters, and the effect of light on aging of plasma-treated PET surfaces are concerned.

Our work demonstrated that plasma treatment depends on plasma process parameters used in plasma treatment. Air-plasma treatment increases the surface polarity of the PET (water contact angle 40° instead of 81°) even at low treatment power (12 kJ/m<sup>2</sup>), but a higher treatment power (60 kJ/m<sup>2</sup>) is required to treat fiber surfaces inside the fabric structure. Not only the surface polarity is increased but also the surface topography is also modified. As the power is increased the surface gets increasingly eroded but further power increase at a lower speed induces a more restructured, organized and uniform surface topography.

Aging experiments show that, the air-plasma-treated PET surface modifications depend on environmental conditions: In presence of light, surface polarity is decreased both at and inside the PET fabric structure. Surface topography modifications also occur in presence of light leading, however, to an organized structure, whereas in absence of light, slow aging initiates a disordering of surface structure.

Further studies should be carried out to better understand the effect of environmental conditions on the aging at and inside fabric structure. Further chemical analysis of the surfaces for example by XPS (X-ray photoelectron spectroscopy) would provide clearer information on the effect of light on plasma-treated samples.

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