JOURNAL OF Materials CHEMISTRY

# Characterisation of poly(ethylene terephthalate) and cotton fibres after cold $SF_6$ plasma treatment

**Elena Selli,*[a] Giovanni Mazzone,[a] Cesare Oliva,[a] Federica Martini,[a] Claudia Riccardi,[b] Ruggero Barni,[b] Bruno Marcandalli[c] and Maria Rosaria Massafra[c]**

*[a]Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano, via Golgi 19, I-20133 Milano, Italy. E-mail: elena.selli@unimi.it; Fax: +39 02 70638129*
*[b]Dipartimento di Fisica G. Occhialini, Università degli Studi di Milano-Bicocca and INFM, Piazza delle Scienze 3, I-20126 Milano, Italy*
*[c]Stazione Sperimentale per la Seta, Via G. Colombo 83, I-20133 Milano, Italy*

***Received 12th February 2001, Accepted 17th May 2001***
***First published as an Advance Article on the web 11th June 2001***

Poly(ethylene terephthalate) (PET) and cotton fibres, treated in an appositely set up RF $SF_6$ plasma reactor under different operating conditions, were characterised by XPS, EPR, DSC, XRD, ATR analyses, water contact angle and water droplet roll-off angle measurements. The ageing of plasma-treated samples was also investigated under different post-treatment conditions. Plasma treatment led to efficient implantation of fluorine atoms on the surface of both polymers; this resulted in water repellence without altering the bulk properties of the polymers. The radical species formed in the plasma-activated polymer surface were involved in its fluorination and in the subsequent uptake of atmospheric oxygen. Surface reorganisation of polymer segments, tending to reduce the interfacial energy between the polymer and the phase in contact with it, induced the surface modifications observed under ageing and in samples plasma-treated several times. An increase in the depth of the fluorinated layer, leading to outstanding stable hydrorepellence, was achieved by repeated $SF_6$ plasma treatments, followed by surface rearrangements favoured by swelling.

## 1 Introduction

The continuous development of finishes of textile fabrics demands innovative production techniques to impart specific surface properties.[1] This is particularly important in the case of natural fibres, as their surface properties can only be altered through changes of their surface chemical structure or morphology, while for synthetic fibres this can also be achieved through modifications of their synthesis.[2]

Many surface properties of polymers, such as wettability, adhesion or biocompatibility, can be tailored to specific applications by appropriate cold plasma treatments.[3–5] Such dry-processing methods have several advantages over more traditional treatments,[6] that is, they are rapid, clean, and, depending on the chosen gas, environmentally safe. Cold plasma treatments are known to induce physical and chemical surface changes in polymers through activation, etching, grafting, implantation, polymerisation and crosslinking processes,[3–5] usually without interfering with their bulk properties, although this is not necessarily true in the case of fibres,[7] due to their high surface to volume ratio.

Plasma treatments may be used to introduce a specific element or functional group onto a polymeric surface. In particular, in the present work we have investigated the possibility of imparting water repellence and soil-resistant properties to fabrics through surface fluorination. Poly(ethylene terephthalate) (PET) and cotton fibres were treated in an appositely set up $SF_6$ radiofrequency (RF) plasma reactor under different operating conditions. The nature of the plasma-induced surface processes was investigated by correlation of the properties of treated samples with the characteristics of the cold $SF_6$ plasma itself. These depend on the plasma intrinsic parameters such as gas pressure, gas-flow rate, forward radiofrequency power, and so on. A preliminary thorough study of the plasma properties[8,9] was thus essential for the interpretation of the results. Indeed, polymer surfaces undergoing plasma treatments are simultaneously bombarded with several energetic species (electrons, radicals, ions, photons). It is thus very important to identify which of them are chiefly responsible for the observed surface modifications and what is their prevailing action.[10] Also, a full elucidation of the overall process can only be achieved if surface modifications induced by the plasma itself can be distinguished from those arising from the subsequent exposure of plasma-treated samples to the atmosphere. The stability of the imparted surface properties obviously has great practical importance. Thus, surface modifications of differently $SF_6$ plasma-treated fabrics while they were undergoing different ageing treatments were also systematically investigated in the present work.

So far, surface fluorination by plasma treatments has been almost exclusively investigated on polymer films,[11–18] which have a much more regular surface microstructure than fibres, and organic fluorides were widely employed as a source of fluorine.[11–15,18,19] The use of the nontoxic $SF_6$ cold plasma is surely preferable in fluorination treatments of textiles,[20] mainly because any plasma polymerisation yielding undesired fluorinated surface films with poor durability should be avoided.[11,15,19]

## 2 Experimental

### 2.1 Materials

Prior to plasma treatments, cotton (118.7 g $m^{-2}$) and thermofixed PET (100.4 g $m^{-2}$) fabrics were washed for 10 min at 40 °C with a water solution containing 5 wt% of an anionic detergent. All samples (5.0 × 5.0 cm) were usually stored at $20 \pm 2$ °C and $65 \pm 2\%$ relative humidity (humid air). $SF_6$ was a Linde product (purity > 99.9%).

DOI: 10.1039/b101360m

### 2.2 Plasma reactor

The employed cold $SF_6$ plasma reactor has been fully described and characterised in detail elsewhere.[8,9,20] Briefly, it consists of three parts: *a*) a vacuum chamber connected to a pumping system; *b*) a plasma production system, composed of a radiofrequency (RF) power generator operating at 13.56 MHz, an RF matching network and a metallic antenna; *c*) plasma diagnostics (Langmuir probes) and sample holders. The system was specially devised to allow the evaluation of electron density both radially and longitudinally to the gas flow under different gas pressure and radiofrequency power conditions. A careful $SF_6$ plasma diagnosis[8,9] revealed that with RF powers up to 100 W a weakly ionised plasma rich in fluorine radicals was produced within the reactor, where several different regions were identified, characterised by different gas-phase compositions and plasma parameters.

### 2.3 Characterisation of treated samples

Water droplet advancing contact angles and rolling-off angles, as well as the absorption time of standard water droplets, were measured employing a home-made apparatus, by observing water droplets through a telescope equipped with a goniometer (Ramé-Hart 100 Goniometer System). Water droplet absorption time was obtained as the average absorption time of four 200 μl water droplets deposited through a standard procedure on different parts of each fabric specimen. Samples were classified as totally hydrorepellent, when, under the adopted standardised conditions, no water absorption occurred within the evaporation time of the droplets (*ca.* 150 min). Water droplet rolling-off angles (WDRA) could be measured only for sufficiently hydrorepellent substrates (the polymers should not absorb water droplets within the measurement time, *ca.* 15 s).

X-Ray photoelectron spectra (XPS) were recorded using an M-probe apparatus (Surface Science Instruments), using monochromatic Al-Kα radiation (1486.6 eV), an elliptical spot size of $0.4 \times 1.0$ mm and a pass energy of 25 eV, as already reported.[20,21] XPS analyses were carried out within 24 h after the plasma treatment. Electron paramagnetic resonance (EPR) spectra were recorded at 9.4 GHz by means of a Bruker ESP 300 spectrometer.[22] Attenuated total reflectance (ATR) spectra were recorded with a Perkin Elmer 1760 FTIR instrument, using a KRS-5 crystal as the reflecting element. A D-500 Siemens apparatus, equipped with a Cu FK 60-10 tube at 2000 W (Cu-Kα radiation at $\lambda = 1.54$ Å) was employed for X-ray diffraction (XRD) measurements in the range $2\theta = 6$–$30°$. Differential scanning calorimetry (DSC) tests were performed in a TA 3000 Mettler apparatus on 3.00 mg specimens with a heating rate of $10\ °C\ min^{-1}$. Tensile mechanical properties on single yarns were determined by means of an Instron 4501 fully electronically controlled apparatus. Scanning electron microscopy (SEM) tests were performed in a Leica Cambridge 440 StereoScan apparatus, equipped with EDXS X-ray analyser and a Link Analytical QX-2000 microanalysis system.

## 3 Surface modifications induced by RF $SF_6$ plasma

Diagnostics studies on the $SF_6$ RF plasma reactor[8,9] showed that, depending on the operating conditions and on their location inside the reactor, fabric samples could be exposed to different types of plasma, and this gave the possibility of controlling plasma–surface interactions. In any case drastic operating conditions were avoided to exclude fibre damage. Indeed, no weight loss was ever detected after the treatment.

Systematic variation of the following operation parameters were thus investigated in cold $SF_6$ plasma treatments of cotton and PET.

RF power, $W_{RF}$, which determined the electron density in the plasma and thus the rate of production of the active species. It was varied between 25 and 100 W.

**Table 1** Advancing contact angles of water on PET and cotton fabrics before and after $SF_6$ plasma treatment

| | Contact angle/degrees | |
|---|---|---|
| | Before treatment | After treatment |
| PET | 134 | 149 ± 5 |
| Cotton | 30 | 145 ± 2 |

Gas pressure, *P*. Although *P* does not affect the electron density directly, its variation has two effects: *i*) for a given plasma dissociation degree, the amount of active species was found to increase with increasing pressure, and *ii*) with increasing pressure (and thus gas density) the plasma region became progressively smaller and more concentrated around the antenna.[8,9] Gas pressure was varied between 0.1 and 0.5 mbar, within the limits of maximal RF efficiency.

Distance *d* of the sample downstream from the antenna. The amount of active species varied within the plasma region located around the emitting antenna and their fluxes also extended to the regions around the plasma itself. Different samples were treated at distances between 2.5 cm (full immersion in the plasma) and 12.5 cm from the antenna (out of the plasma itself, within the so-called "remote plasma" containing a substantial amount of reactive neutral radicals, in particular fluorine, escaping the discharge region).

Treatment time, $t_{tr}$, which determined the total amount of active species bombarding the sample. It was varied between 10 s (lower limit of plasma ignition and stabilisation) and 1 min.

### 3.1 Hydrorepellence

The effectiveness of the $SF_6$ plasma treatment in imparting hydrorepellence to PET and cotton fabrics was first of all verified by contact angle measurements. The data reported in Table 1 indicate an increase of hydrophobicity in PET after the treatment, while in the case of the intrinsically hydrophilic cotton a contact angle even greater than that of polytetrafluoroethylene (132°) was measured after the treatment.

Owing to the roughness and irregularity of textile surfaces, contact angles had a relatively high error and did not exhibit any clear trend as a function of the employed plasma parameters. Absorption time measurements (Figs. 1–4) proved to be a much better diagnostic tool for a systematic investigation of the hydrorepellence imparted to fibres by operating

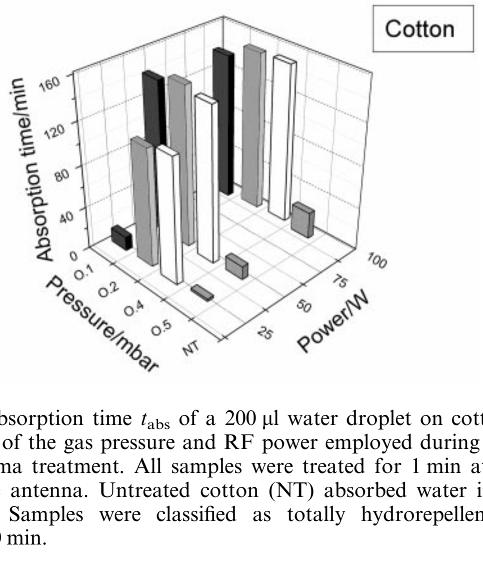

**Fig. 1** Absorption time $t_{abs}$ of a 200 μl water droplet on cotton as a function of the gas pressure and RF power employed during the $SF_6$ RF plasma treatment. All samples were treated for 1 min at 7.5 cm from the antenna. Untreated cotton (NT) absorbed water instantaneously. Samples were classified as totally hydrorepellent when $t_{abs} > 150$ min.

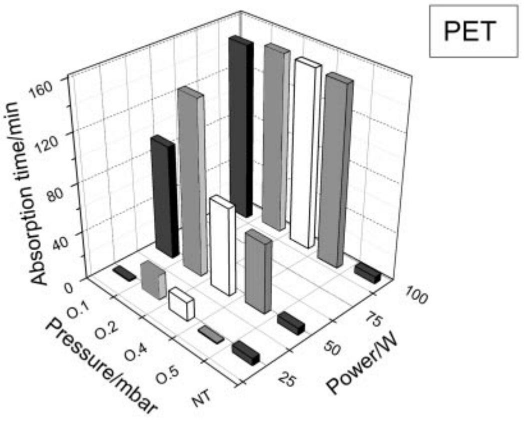

**Fig. 2** Absorption time $t_{abs}$ of a 200 µl water droplet on PET as a function of the gas pressure and RF power employed during the $SF_6$ RF plasma treatment. All samples were treated for 1 min at 8 cm from the antenna. Untreated PET (NT) absorbed water in about 5 min. Samples were classified as totally hydrorepellent when $t_{abs} > 150$ min.

under different plasma conditions. A net distinction could be drawn between totally hydrorepellent samples (absorption time $t_{abs} > 150$ min, see Experimental section) and partially hydrorepellent samples ($t_{abs} < 150$ min).

Fig. 1 shows that hydrophilic cotton fibres became totally hydrorepellent after $SF_6$ RF plasma treatments in the 0.4–0.2 mbar pressure range and with $W_{RF} \geqslant 50$ W. Very low hydrophobicity was attained at higher pressure (0.5 mbar) for any $W_{RF}$ value and at low pressure (0.1 mbar) and RF power (25 W). A similar trend was observed with PET (Fig. 2), although, surprisingly, to become totally hydrorepellent this partially hydrophobic fibre had to be plasma-treated with a higher RF power (*i.e.* $W_{RF} > 50$ W). Best results were obtained with PET by operating under a 0.2 mbar pressure.

The efficiency of the treatment decreased when the fabrics were located at distances *d* greater than 10 cm from the antenna (Fig. 3), in full agreement with the results of $SF_6$ plasma diagnostics,[8,9] which indicated a marked decrease in the fluorine radical concentration for $d \geqslant 10$ cm. Finally, the hydrophobicity of treated samples increased, as expected, with increasing treatment time (Fig. 4). Total hydrorepellence of cotton was achieved with $t_{tr} = 10$ s, while longer treatments were necessary in the case of PET, especially when operating at lower pressure.

Differences in effectiveness of treatment for totally hydrorepellent specimens could be appreciated through water droplet rolling-off angle (WDRA) measurements, which, however, could not be performed on insufficiently hydrorepellent substrates (*e.g.* untreated cotton). Of course lower WDRA values are indicative of more water-repellent surfaces.[19]

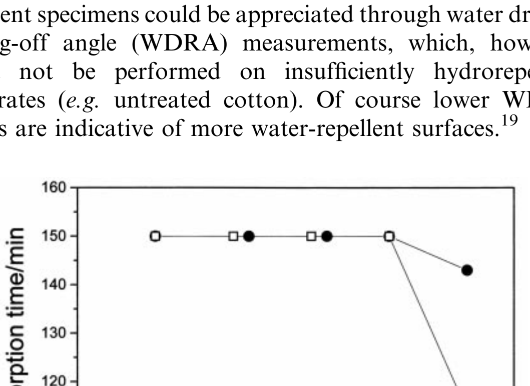

**Fig. 3** Absorption time of water droplets measured on cotton (squares) or PET (circles) fabrics after $SF_6$ RF plasma treatment at different distances from the antenna ($W_{RF} = 100$ W, $t_{tr} = 1$ min, $P = 0.2$ mbar).

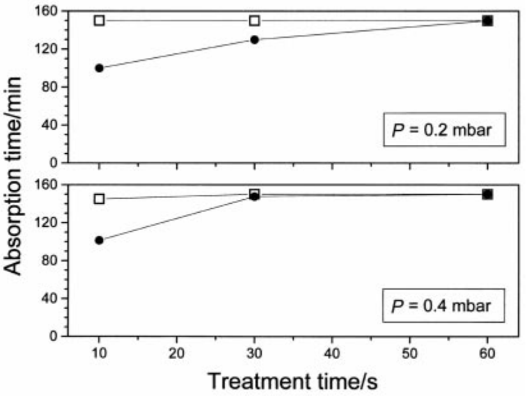

**Fig. 4** Absorption time of water droplets measured on cotton (squares) or PET (circles) fabrics after $SF_6$ RF plasma treatment for different times at two pressure values ($W_{RF} = 100$ W, $d = 7.5$ cm for cotton, $d = 8$ cm for PET).

Results obtained by this technique (Fig. 5) are in agreement with water contact angle and absorption time measurements. For both PET and cotton, optimal treatment efficiency was achieved by operating within the 0.2–0.4 mbar pressure range, at high $W_{RF}$ values and for $d \leqslant 10$ cm. Moreover, both PET and cotton samples treated at $d = 2.5$ cm were even more hydrorepellent than those treated under identical conditions at greater *d* values, suggesting that ions and UV radiation have a relevant role in surface activation.

### 3.2 Surface analysis by XPS

XPS analyses of freshly-treated samples (Tables 2 and 3) demonstrate that the hydrorepellence induced on PET and cotton by the $SF_6$ RF plasma treatment is strictly related to the presence of fluorine on the polymer surface. For instance, the

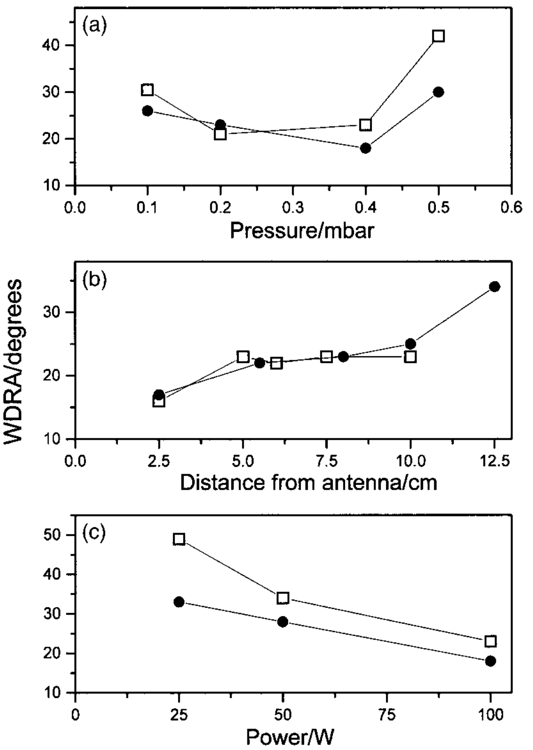

**Fig. 5** Water droplet roll-off angles (WDRA) measured on cotton (squares) or PET (circles) fabrics after $SF_6$ RF plasma treatment as a function (*a*) of gas pressure at $W_{RF} = 100$ W, $d = 7.5$ cm for cotton, $d = 8$ cm for PET, $t_{tr} = 1$ min; (*b*) of the distance from the antenna at $W_{RF} = 100$ W, $P = 0.2$ mbar, $t_{tr} = 1$ min; (*c*) of the RF power ($W_{RF}$) at $P = 0.2$ mbar, $d = 7.5$ cm for cotton, $d = 8$ cm for PET, $t_{tr} = 1$ min.

**Table 2** F : C and O : C atomic ratios of differently treated PET samples, determined by XPS analysis immediately after the plasma treatment ($P=0.2$ mbar, $d=8$ cm) and after conditioning in air for 30 days

| | | After treatment | | After 30 days | |
|---|---|---|---|---|---|
| $W_{RF}$/W | $t_{tr}$/s | O : C[a] | F : C | O : C | F : C |
| 25 | 60 | 0.31 | 0.32 | 0.30 | 0.14 |
| 100 | 60 | 0.24 | 0.40 | 0.26 | 0.34 |
| 100 | 10 | 0.24 | 0.31 | 0.26 | 0.28 |

[a]O : C ratio determined for untreated PET: 0.25.

$SF_6$ plasma treatment at 100 W for 1 min, imparting satisfactory hydrorepellence to both fibres, led to the highest fluorine surface concentration. For a better comparison of XPS results for the two fibres, the surface percent amount of each element was normalised to the percent carbon content, under the very reasonable assumption that the carbon content of polymer backbones was not affected by the plasma treatment.

The surface amount of fluorine on treated fibres increased with increasing RF power and treatment time (Tables 2 and 3). The O : C ratio increased in cotton after the treatment, while in the case of PET it did not exhibit any clear trend with treatment conditions. However, alterations in surface oxygen amount could only occur after the plasma treatment, by reaction of activated surface sites with atmospheric oxygen (*vide infra*). Only traces of sulfur were occasionally revealed on treated samples, suggesting that $^{\bullet}SF_x$ groups, though generated within the plasma in relatively high concentration,[8] were not competitive with the fluorine atoms for implantation on the surface, probably due to steric hindrance.[20]

Information on how fluorine binds to the polymer surface can be obtained from the deconvolution of XPS signals. For instance, as shown in Fig. 6(*a*), the C(1s) signal of untreated PET contains three well-separated peaks at 284.6, 286.3 and 288.7 eV, corresponding to carbon atoms bonded only to carbon or hydrogen in the benzene ring ($C_1$), to methylene carbons singly bonded to oxygen ($C_2$) and to ester carbon atoms ($C_3$), respectively.[15,23–26] After the $SF_6$ plasma treatment two new peaks appeared at 287.2 and 290.5 eV (Fig. 6(*b*)). The first one ($C_4$) can be assigned to –*C*–$CF_x$ and isolated C=O groups, while the second one ($C_5$) can unequivocally be attributed to $CF_2$ groups.[15,17,18,25,26] Moreover, the $C_1$ peak is markedly reduced, the $C_2$ peak is enhanced as it also includes signals from carbon atoms under the influence of long-distance F atoms, while the $C_3$ peak also includes the –CF– signals, besides the –COO– groups.[15] The marked decrease of the signal due to aromatic carbons bound to hydrogen atoms and the presence of the signal due to $CF_2$ groups in treated PET demonstrate that fluorine atoms attack both benzene ring carbon atoms (substitution of one hydrogen atom) and ethylenic carbon atoms (substitution of two hydrogen atoms). The presence of –*C*–$CF_x$ groups is also shown in the XPS spectrum of treated cotton, but no peaks appear in this case at binding energies greater than 290 eV, and this excludes the formation of $CF_2$ groups.

**Table 3** F : C and O : C atomic ratios of cotton determined by XPS analysis immediately after the treatment ($P=0.2$ mbar, $d=8$ cm, $t_{tr}=1$ min) and after having being stored in humid air or in helium for 20 days at 20 °C

| | After treatment | | Stored in air | | Stored in He | |
|---|---|---|---|---|---|---|
| $W_{RF}$/W | O : C[a] | F : C | O : C | F : C | O : C | F : C |
| 25 | 0.44 | 0.63 | — | — | — | — |
| 100 | 0.47 | 0.83 | 0.47 | 0.58 | 0.47 | 0.75 |

[a]O : C ratio determined for untreated cotton: 0.40.

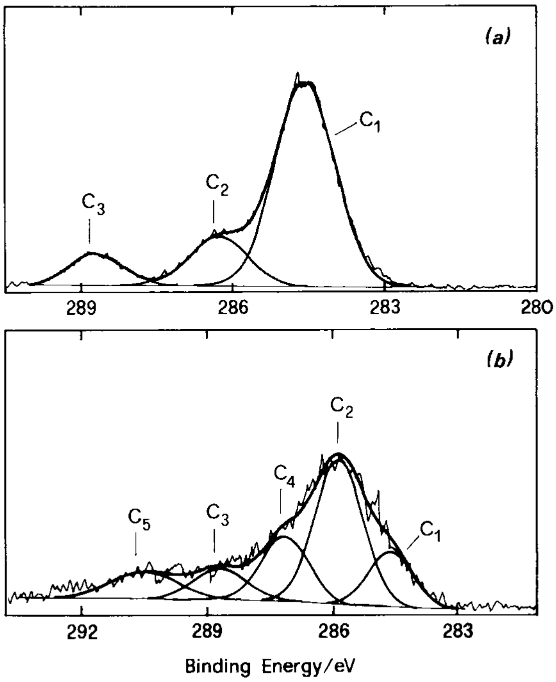

**Fig. 6** Deconvolution of the C(1s) XPS peak of (*a*) untreated PET and (*b*) plasma-treated PET ($W_{RF}=100$ W, $d=8$ cm, $P=0.2$ mbar, $t_{tr}=1$ min).

For both polymers, the deconvolution of the O(1s) signal exhibits two peaks, correlated to the presence of both C=O groups (531.8 eV) and –C–O– groups (533.8 eV).[26–28] The ratio between their integrated areas increase after treatment, confirming that surface oxidation occurs with atmospheric oxygen after the plasma treatment. The F(1s) signal in treated samples always consists of a single peak at *ca.* 687 eV. This excludes the formation of O–F groups, and thus the attack of fluorine atoms on oxygen atoms.[26]

It is worth noting that the amount of F implanted on cotton was always higher than that implanted on PET under identical operation conditions (Table 2), in agreement with the higher increase in hydrorepellence which could be achieved for cotton (Table 1 and Fig. 1 and 2). This is a consequence of the fact that, while in PET not all carbon atoms are bound to a hydrogen atom which can be substituted by a fluorine atom, in cotton (cellulose) every carbon atom carries at least one hydrogen atom.

### 3.3 EPR analysis

The EPR spectra obtained after PET treatment at RF power 25–200 W consisted of two bands. One of them, labelled with R, appears at *ca.* 3200 G ($g \cong 2$) and can be attributed to the formation of organic radicals on carbon atoms. The second band, labelled with SG, is more intense than the first one appears at zero magnetic field and presents an opposite phase with respect to the R band.

The R signal, which is not resolved for treatments at relatively low RF power, results from the sum of EPR bands from radicals on different carbon atoms. More information on this feature was obtained from the EPR spectrum of a PET specimen treated under more drastic conditions ($W_{RF}=200$ W). In this case the R band resolved into two lines (Fig. 7), 500 G from each other, and was attributed to two dipolarly interacting unpaired electrons in triplet state.[29]

Also the EPR spectrum of treated cotton exhibits two bands (also labelled SG and R in Fig. 8), with the same characteristics of those revealed for treated PET. In this case, the R band at $g \cong 2$, due to organic radicals, consists of a relatively narrow symmetric single line (bandwidth = 15 G). This band is similar

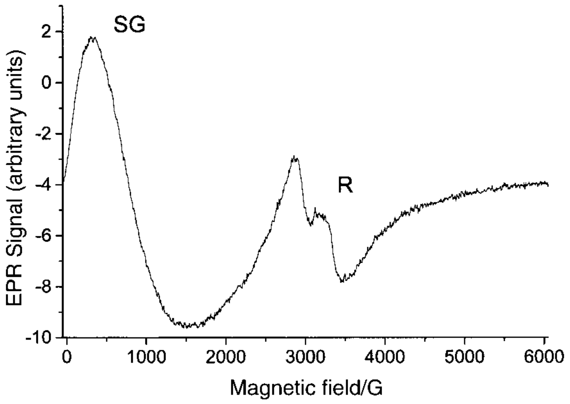

**Fig. 7** EPR spectrum of plasma-treated PET ($W_{RF}=200$ W, $d=8$ cm, $P=0.2$ mbar, $t_{tr}=1$ min).

to one reported in the literature[30] and attributed to the superposition of four EPR signals due to different radicals generated by the plasma treatment on different carbon atoms of the cellulose ring.

The total energy input on the sample during $SF_6$ plasma treatments seems to have a great influence on the formation of the SG-type bands. Indeed, the latter decrease in intensity with increasing energy input ($W_{RF} \times t_{tr}$), as shown in Table 4, an opposite trend to that observed for hydrophobicity and percent amount of implanted fluorine. Therefore the formation of the species responsible for the SG-type band is in competition with fluorine implantation on the polymer surface.

The SG band is typical of spin glass systems, characterised by competitive magnetic interactions between paramagnetic species of different chemical natures.[31–35] Such complex systems are able to absorb microwaves under very low or even zero external magnetic field (Low Field Microwave Absorption). In the present case, the spin glass phenomenon might tentatively be attributed to highly energetic species formed in the $SF_6$ plasma dissociation, such as $SF_5$,[36] $SF_4^+$,[37] $SF_4$,[36] $F_3$ or $F_3^{2-}$.[38] Although these species are hardly revealed by XPS analysis, they might remain on the polymer surface after the plasma treatment.

### 3.4 Other characterisation analyses

The morphological examination carried out by scanning electron microscopy (SEM) on both PET and cotton did not show any difference between treated and untreated samples. This excludes any relevant etching phenomenon on the micron scale.

Also tensile strength tests carried out on PET yarns after $SF_6$ plasma treatment under different conditions did not show any variation with respect to untreated PET, within the experimental uncertainty. In the case of cotton, an average 20% increase of the elongation at break and a parallel decrease of the Young modulus (*ca.* 15%) observed after the plasma treatment may be indicative of an increase of the elasticity of the fibres, probably as a consequence of a decrease in their crystallinity. This, however, was not confirmed by X-ray diffraction analysis, as identical XRD spectra were recorded for cotton before and after the plasma treatment.

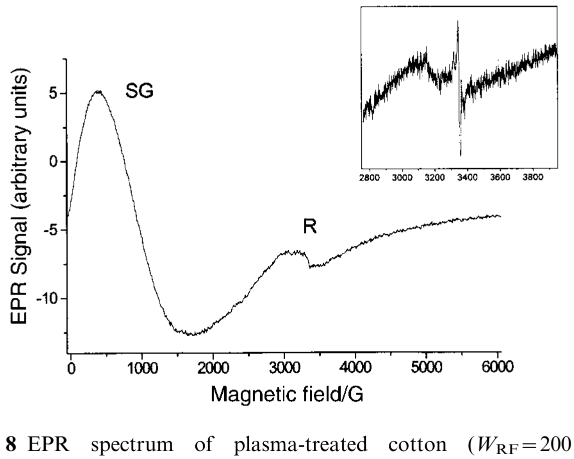

**Fig. 8** EPR spectrum of plasma-treated cotton ($W_{RF}=200$ W, $d=6$ cm, $P=0.2$ mbar, $t_{tr}=1$ min) and enlargement of the R line in the insert.

**Table 4** Relative intensity of the SG band (see Fig. 7) in the EPR spectra recorded after $SF_6$ plasma treatments of PET under different experimental conditions

| $W_{RF}$/W | $P$/mbar | $d$/cm | $t_{tr}$/s | Energy/kJ | Relative Intensity |
|---|---|---|---|---|---|
| 100 | 0.2 | 8 | 10 | 1 | 6 |
| 25 | 0.2 | 8 | 60 | 1.5 | 6 |
| 100 | 0.2 | 8 | 60 | 6 | 1 |
| 200 | 0.4 | 6 | 60 | 12 | 0.25 |

On the other hand, DSC and XRD analyses carried out on PET specimens before and after the treatment did not show any variation in the heat of fusion and crystallinity index, outside the experimental uncertainty. Thus, the results obtained by this kind of analysis confirm that plasma treatments do not interfere with bulk properties of fibres, at least under the adopted operating conditions.

### 3.5 Mechanism of fluorine implantation

XPS results indicate that $SF_6$ plasma treatment mainly provokes the substitution of hydrogen atoms for fluorine atoms on treated polymer surfaces, while neutral $SF_6$ molecules and $SF_x$ radicals or ions, though formed in large quantities within the plasma[8,9] and possibly responsible of the spin glass effect revealed by the EPR spectra of treated samples, are not grafted onto the polymer surface with high yield. We also expect F atoms to be the strongest hydrogen-abstracting agents in the plasma.[11]

The following reaction sequence may be proposed for F atoms implantation on the polymer surface.

$$SF_x \xrightarrow{\text{plasma}} {}^{\cdot}SF_{x-1} + F^{\cdot} \qquad x=6,....,1 \tag{1}$$

$$-C-H \xrightarrow[-H^{\cdot}]{h\nu,e^-,I,F^{\cdot}} -C^{\cdot} \xrightarrow{F^{\cdot}} -C-F \tag{2}$$

Of course, hydrogen abstraction can also be accomplished by the several different ions and radicals formed within the plasma, as well as by electrons or vacuum UV radiation (photons). Such highly reactive species contribute to surface activation, as confirmed by the presence of radical species on both polymers after the treatment, and can also induce etching or crosslinking of the polymer surface. Such processes are in competition with fluorine implantation, but should only involve the very outer layer of fibres, as their effects could hardly be detected by bulk characterisation techniques.

Surface oxidation, which is more relevant for cotton than for PET (Tables 2 and 3), should result from the after-treatment interaction of the long-lived free radicals, formed during plasma treatment, with atmospheric oxygen or water vapour. However, other types of plasma were reported to cause greater increases of surface oxygen content in treated polymers in contact with air.[10,24,25] Fluorination is by far the predominant process occurring under $SF_6$ plasma treatment.

## 4 Surface modifications in post-treatments and multiple treatments

Some of the above discussed analyses were repeated for stored plasma-treated samples under different conditions. The aim of these investigations was to shed light on surface modifications occurring after the plasma treatments, which notoriously limit practical applications of plasma-treatment finishing. Some specimens were also plasma-treated several times to enhance surface modification effects, as well as to investigate the reversibility of such effects.

### 4.1 XPS analysis

A lower surface content of fluorine was detected 30 days after the plasma treatment in all PET samples conditioned under humid air (Table 2). The observed percent decrease in F : C values was minimal in the case of samples treated under relatively high RF power (*i.e.* $W_{RF} = 100$ W), which maintained their hydrorepellence properties unaltered for a long time. The effect of the gas phase atmosphere on sample ageing was investigated in the case of cotton. As shown in Table 3, the treated cotton sample stored under an inert gas (helium) underwent a lower decrease of the F : C ratio, with respect to an identically plasma-treated sample, which had been stored in humid air.

It is worth noting that the O : C amount did not exhibit any marked variation with ageing, indicating that stable oxygen uptake by plasma-activated polymer surfaces occurred within the first few minutes following the plasma exposure.

### 4.2 Hydrorepellence stability

The hydrorepellence of cotton fabric plasma treated under optimal conditions (1 min, 100 W) and subsequently subjected to different treatments (conditioning in air, dry cleaning or washing in water and subsequent ironing) was checked by water droplet absorption time measurements. Total hydrorepellence ($t_{abs} > 150$ min) was maintained after conditioning in humid air for 30 days and after dry cleaning (in tetrachloroethylene). By contrast, wet washing caused a dramatic decrease of hydrorepellence ($t_{abs} = 10$ min). No increase of water droplet absorption time was observed if the sample was subsequently stored in dry air, while its hydrorepellence was partly restored ($t_{abs} = 110$ min) if it was ironed at *ca.* 250 °C.

### 4.3 Surface configuration changes

The fact that the hydrorepellence of treated cotton could be restored by ironing after washing in water demonstrates that the decrease of the surface fluorine content in aged samples is not due to fluorine removal from the polymer surface. The only explanation of the observed behaviour is that the C–F groups on the polymer surface are reversibly hidden within the fibres during ageing. Indeed, the molecular chains in the surface layer are supposed to have high mobility owing to the destruction of the three-dimensional network structure. The attractive or repulsive interaction force between the liquid or gas phase in contact with the ageing polymer surface determines the entity of this polymer chain rearrangement, which is driven by the difference in the surface energy of the polymer surface and the contact medium.[14,16,25,39] Such differential surface tension decreases by migration or folding of the hydrophobic polymer moieties toward the inside of the polymer.

Indeed, helium is more hydrophobic than humid air, and thus more fluorine groups remained on the treated fibre surface during ageing in helium (Table 3), while contact with water produced extended hindering of the hydrophobic C–F groups within the fibre. These dynamic processes are reversible and thermally activated, *i.e.* favoured by high temperature. Thus, the fluorinated hydrophobic groups, which had been hidden in the fibre in contact with water, in contact with air appeared on the surface again at a rate dependent on temperature, as evidenced by the increase in the hydrorepellence recovery rate observed by ironing (*vide supra*).

### 4.4 Repeated $SF_6$ plasma treatments

The fundamental role of dynamic phenomena involving the rearrangements of surface polymer chains in plasma-treated fibres was also confirmed by carrying out several cycles of plasma treatments of PET specimens followed by washing in water at 50 °C. Such a temperature should ensure enough swelling of the polymer surface layer, without strongly altering bulk properties ($T_g \cong 80$ °C). Progressively longer washing times were needed, as the polymer surface progressively became more and more hydrorepellent. Treated samples were characterised by ATR spectroscopy and DSC measurements after each step.

The results of the ATR analysis, reported in Fig. 9, show that a spectrum practically identical to that of untreated PET was recorded after only one plasma treatment. Although XPS analysis revealed that $SF_6$ plasma treatment induces fluorine substitution for hydrogen atoms bound to carbon atoms (Table 2 and Fig. 6(*b*)), this could not be revealed by ATR analysis. However, the ATR technique investigates a surface layer of some microns, while plasma treatment should involve a much thinner layer. An increase in the number of treatment and washing cycles showed a new absorption feature in the ATR spectrum around 1120 $\text{cm}^{-1}$, due to C–F stretching vibrations,[17] which progressively increased in intensity with an increase in the number of cycles.

It is worth noting that this stretching vibration was not observed in the ATR spectra of PET specimens plasma-treated several times but not washed after each treatment. Thus, the contact with water and the consequent swelling of the polymer surface is essential for ensuring enough mobility to surface polymer chains, to allow fluorine atoms migration inside the fibre within some hours. Consequently, polymer segments which do not contain fluorine atoms are exposed on the fibre surface. Such "fresh" surface undergoes fluorination in the next plasma treatment, followed by washing, *i.e.* swelling and fluorine migration inside the fibre, and so on. In this way fluorination extends to a much deeper surface layer (tenth of microns) and the presence of fluorine can be revealed by ATR analysis. Repeated plasma treatments not alternated with washing should produce instead the same results as prolonged treatments, with consequent concurrent etching effects, and finally lead to saturation with fluorine of a very thin polymer surface layer.

The involvement in fluorination of a progressively thicker layer of polymer surface with an increase in the number of treatment–washing cycles was confirmed also by DSC analyses, which showed a progressive decrease in polymer crystallinity. Indeed, as shown in Table 5, $\Delta H_{fus}$ values determined by DSC

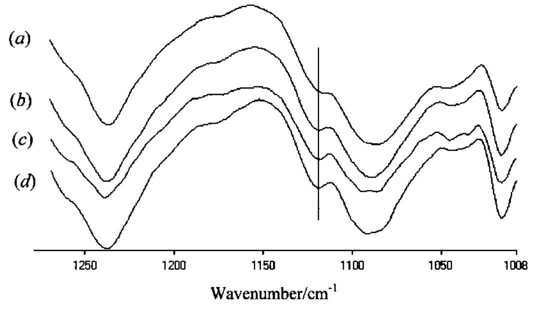

**Fig. 9** ATR transmittance spectra of PET specimens (*a*) before treatment and after (*b*) 1, (*c*) 3 and (*d*) 7 cycles of $SF_6$ plasma treatment ($W_{RF} = 100$ W, $d = 6$ cm, $P = 0.4$ mbar, $t_{tr} = 1$ min), followed by wet washing at 50 °C.

**Table 5** $\Delta H_{fus}$ values obtained from DSC analysis of PET specimens after several cycles of plasma treatment ($W_{RF} = 100$ W, $d = 6$ cm, $P = 0.4$ mbar, $t_{tr} = 1$ min) and wet washing at 50 °C

| Number of cycles | Washing | $\Delta H_{fus}$/J g$^{-1}$ |
|---|---|---|
| 0 | No | 61.7 |
| 1 | Yes | 62.6 |
| 3 | Yes | 58.7 |
| 5 | Yes | 53.1 |
| 7 | Yes | 50.2 |
| 7 | No | 59.3 |

analysis decreased with an increase in the number of cycles, indicating that a progressively greater portion of the polymer undergoes structural perturbation as a consequence of partial fluorine substitution for hydrogen atoms in the polymer chains. A smaller decrease in $\Delta H_{fus}$ was observed instead if washing did not follow each plasma treatment (Table 5).

## 5 Conclusions

$SF_6$ RF plasma treatment under optimal operating conditions imparts hydrorepellence to cotton and PET fibres through fluorine atoms implantation, without altering their bulk properties. Radical species formed in the plasma activation of the treated surface are involved in its fluorination and subsequent oxidation in contact with air. Surface dynamics play an important role in post-plasma treatments, tending to reduce the interfacial tension. Outstanding stable hydrorepellent fibres can be attained by increasing the depth of the fluorinated layer through repeated cycles of $SF_6$ plasma treatments, followed by wet washing-induced rearrangements of the polymer surface.

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