Surface morphology changes of poly(ethyleneterephthalate) fabrics induced by cold plasma treatments[*]

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Abstract. Some selective cold plasma processing modify specific surface properties of textile polymeric materials such as their dyeability, wettability and hydrorepellence. To correlate the sample surface changes with the acquired surface properties allows one to obtain information on the chemical and physical processing involved in plasma treatment. In this work, atomic force microscopy (AFM) has been applied to investigate the morphological and topographical surface modifications induced by RF cold plasma processing of poly(ethyleneterephthalate) (PET) fabrics. Rms surface roughness and surface area of the samples are measured before and after the treatments. The morphology changes have been analysed as a function of the treatment time and air gas pressure. Measurements have been performed also using plasmas produced by different gases such as He, Ar, SF_6 and CF_4. The PET shows different behaviour with different gas plasmas. In the case of air, He and Ar gases the sample surface modifications seem to be mainly due to etching effects, while the fluorine atoms grafting probably is responsible for surface rearrangement process using SF_6 and CF_4 gases. As a consequence different surface properties are produced in the plasma treated samples.

Keywords. Plasma processing of materials; poly(ethyleneterephthalate) fabrics morphology; atomic force microscopy.

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1. Introduction

Low-pressure cold plasma treatment can be employed to modify many surface properties of polymers, such as adhesion, friction, penetrability, wettability, dyeability and biocompatibility, to tailor their characteristics to specific applications [1]. This plasma processing can be performed by means of low pressure radiofrequency discharges of suitable gases. Such plasma species can give rise to several concurrent physical and chemical processes (etching, grafting, polymerization, cross-linking) that act only on the sample surface without modifying the original bulk properties [2]. It is important to stress that it is possible to produce a wide spectrum of surface chemistry with the wanted composition and that these changes are confined to a depth of a few nanometers due to the low level penetration of these processes. However, in spite of intense experimental work, plasma aided manufacturing is not yet fully considered as a viable finishing technology in industry. This is mainly due to the difficulties arising in obtaining stable and permanent surface modifications and in controlling the effective plasma–surface interactions and their role in the surface property modifications. In turn such drawbacks can be mainly ascribed to lack of suitable investigations of the physical and chemical actions of plasma on the polymeric surfaces and their influence on the surface dynamics. In the textile field, to obtain permanent modifications of surface properties through plasma processing is important for many purposes, for instance, to increase the dyeability or hydrophylicity of textiles. In this work, atomic force microscopy (AFM) has been applied to the study of low-pressure plasma processing of poly(ethyleneterephthalate) (PET) fabrics to obtain more clear quantitative information on morphological and topographical surface changes induced by plasma treatments.

2. Experimental

2.1 *RF Plasma reactor*

The plasma–surface interactions have been studied using a RF plasma reactor developed at the Laboratorio di Fisica dei Plasmi of the University of Milano-Bicocca [3,4]. A schematic view of the set-up is sketched in figure 1. The discharge is produced in a T-shaped cylindrical tube (diameter 10 cm, length 27 cm) and it is driven by a capacitive RF antenna, axially located within the chamber. At one cap the vacuum chamber is connected to a pumping system, which allows to evacuate the reactor up to a residual pressure lower than 10^{-6} mbar. A diffuse plasma region is usually produced in the chamber surrounding the RF antenna and extending longitudinally for about 10 cm. The reactor allows to expose the samples to be treated under different plasma and gas-phase conditions, depending on the location, the total pressure and RF input power.

2.2 *Atomic force microscopy*

An Autoprobe CP Research AFM by ThermoMicroscopes has been used to investigate the morphological and topographical changes of PET textile surface, resulting from air, He, Ar, SF_6 and CF_4 plasma treatments. Squares of 1 μm side were
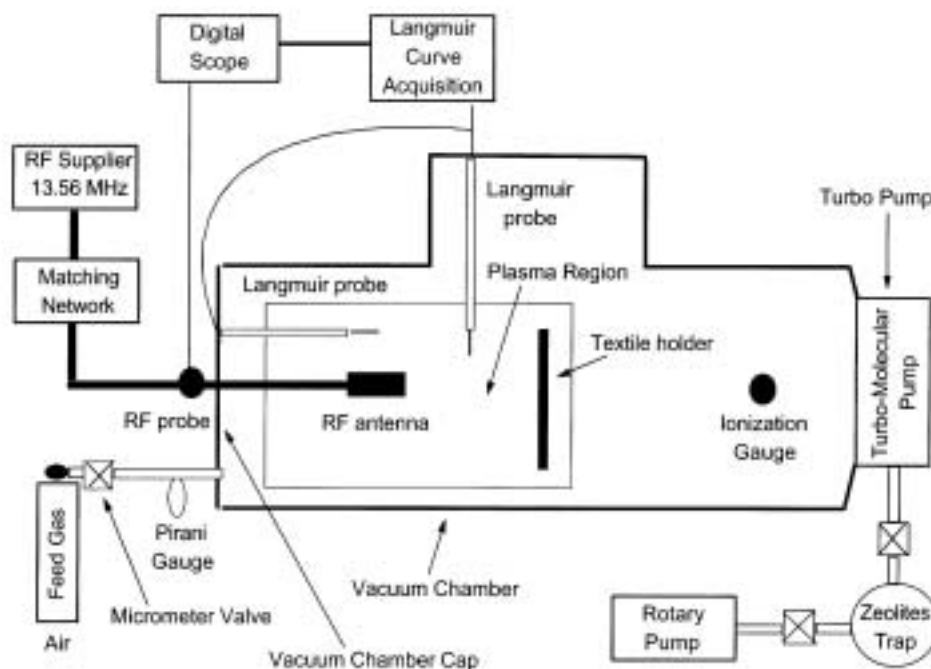
Figure 1. Schematic view of the RF plasma reactor set-up.

scanned in air in non-contact mode. For each sample, 15 images have been collected in different areas of the sample. The Image Processing and Data Analysis software of the quoted AFM was used for the rms surface roughness analysis and surface area measurements, as defined elsewhere [5]. Microfabricated V-shaped silicon cantilever with silicon conical tip (ThermoMicroscopes, Sunnyvale, CA, USA) of theoretical spring constant $k = 3.2$ N/m and resonant frequency of approximately 90 kHz has been used.

2.3 Experiments

Rms surface roughness analysis and surface area measurements have been performed to study surface modifications of PET fabrics as a function of the plasma treatment time using an air cold plasma at a pressure of 0.2 mbar with RF $f = 13.56$ MHz at a power of 150 W, 5 cm away from the antenna used to produce the plasma.

AFM images of an untreated PET textile sample (supplied from Test-fabrics Inc.) were first collected and then the same sample was air-plasma treated for four consecutive 30 s periods with AFM image collection after each treatment (to give respectively 30, 60, 90 and 120 s treated samples). To extend the investigation to longer treatment times, PET textile samples were treated for 180, 300 and 600 s in a continuous way.
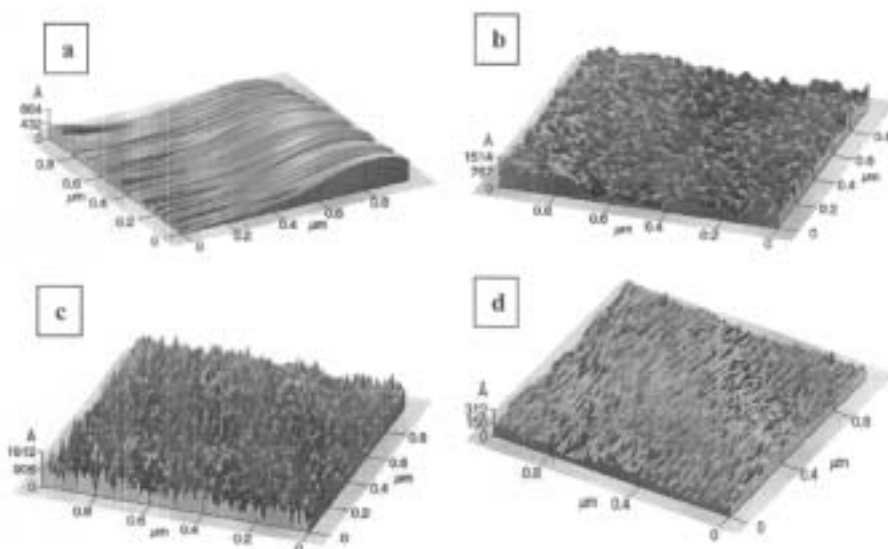
Figure 2. 3D views of non-contact mode AFM images of PET textile surfaces: (**a**) untreated surface, (**b**) 60 s air-plasma treated surface, (**c**) 120 s air-plasma treated surface, (**d**) 600 s air-plasma treated surface.

A second set of experiments was performed to study the morphology changes of the PET fabrics induced by different gas plasmas (i.e. air, He, Ar, SF_6 and CF_4) as a function of the gas pressure within the plasma. The above facility was operated at a power of 105 W for 60 s with the samples located at a distance of 7.5 cm away from the antenna.

3. Results

3.1 *Air-plasma treatment: Surface morphology changes as a function of plasma exposure time*

Air-plasma processing of PET fabrics produces a remarkable increase in hydrophilicity due to permanent surface chemical and physical modifications that have been correlated with both a modified chemical composition due to air-plasma oxidation of the surface and a physical change of the surface morphology [6,7]. Best and more durable wettability results are obtained under high RF power and negative polarization of treated samples, conditions in which the implantation of polar groups on PET surface, evidenced by XPS analysis, is accompanied by extensive surface etching and possibly cross-linking between activated species [6,7]. The analysis of the surface morphology performed using scanning electron microscopy (SEM) did not reveal any effect due to plasma processing [8,9]. Indeed SEM analysis is not the best way to investigate the involved phenomena, mainly because it does not allow any quantitative measurements or any comparison between surface roughness. More information on the morphology of the involved surfaces is provided by AFM. In fact, AFM analysis of the sample surface allows one to measure morphological

Table 1. PET textile rms surface roughness and surface area, as a mean value of 15 data, as a function of the exposure time to air-plasma treatment.

Exposure time (s)	Rms (nm)	Surface area (μm^2)
0	20.8 ± 4.8	1.39 ± 0.35
5	19.5 ± 4.2	1.28 ± 0.29
10	19.9 ± 3.3	1.76 ± 0.43
30	39.2 ± 8.8	2.56 ± 0.59
60	42.9 ± 8.4	6.04 ± 1.46
90	43.2 ± 7.4	5.78 ± 1.22
120	43.9 ± 6.9	4.43 ± 1.04
180	47.6 ± 6.2	4.91 ± 0.98
300	41.3 ± 5.5	3.77 ± 0.67
600	22.1 ± 3.6	1.58 ± 0.36

and mechanical characteristics of the surface such as the surface roughness and the surface area on nanometer scale and to obtain 3D images of the sample surface.

Four 3D topography AFM images of the untreated and air-plasma treated PET fabrics are shown in figure 2. The surface of the untreated PET textile shows a topography which resembles a series of slides located side by side in a well-ordered pattern. This order is lost after the air-plasma treatment which creates pits and micropores whose density, depth and size increase as a function of the exposure time as can be seen by examining the AFM images.

To characterise the surface of the untreated sample and the surface morphology changes induced by the air-plasma treatment, the rms surface roughness and the surface area have been measured from the AFM images. In particular, to minimise any effect related to the possible heterogeneity of the sample, the data have been determined on 1 micron square areas as the mean value of the measurements recorded in 15 different regions for each sample. Table 1 and figures 3 and 4 show the rms surface roughness and the surface area as a function of the exposure time to the air-plasma treatment respectively.

The rms surface roughness data show that plasma treatment times of the order of 5–10 s cause only a negligible change in morphology: this is probably related to the start-up characteristics of the plasma discharge. Figure 3a suggests the existence of a time threshold between 10 and 30 s above which the plasma-induced morphological modification occurs. For exposure times longer than 30 s the curve very rapidly reaches an apparently equilibrium value approximately twice that of the untreated sample (see figure 3a). The dependence of the surface area on the exposure time to the air-plasma treatment (see figure 4a) shows the same trend of the rms surface roughness curve, even if in this case the time threshold seems to be between 30 and 60 s. Nevertheless, in order to verify the curve trends of the rms surface roughness and of the surface area for longer exposure times the samples have been treated for 180, 300 and 600 s. The rms surface roughness and the surface area curves reach maximum values after approximately 180 s and decrease to the same values of the original untreated sample after approximately 600 s (see figure 3b and figure 4b). The data dispersion (error bars in figure 3 and figure 4) is not
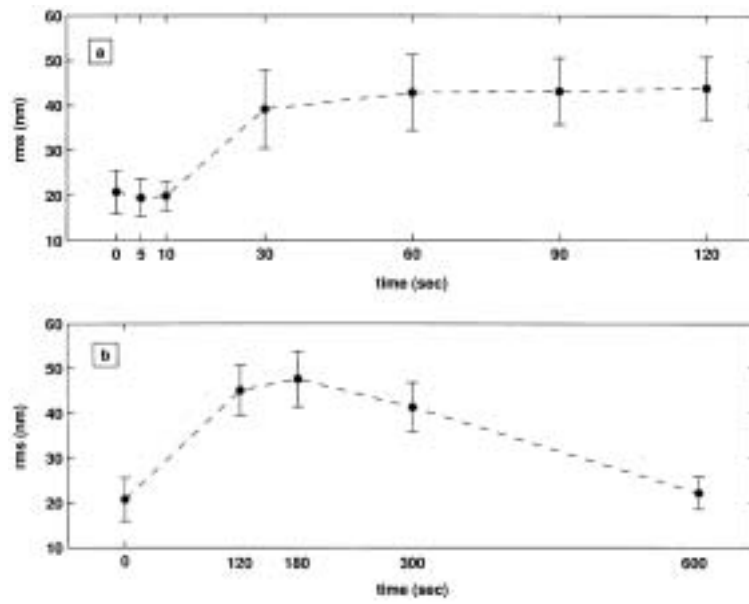
Figure 3. Rms surface roughness of PET fabrics as a function of the air-plasma treatment time: (**a**) exposure time up to 120 s, (**b**) exposure time up to 600 s.
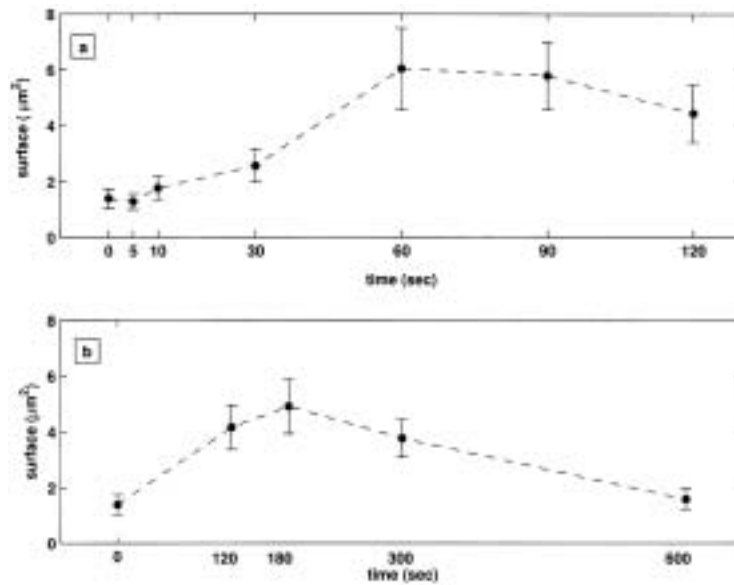

Figure 4. Surface area of PET fabrics as a function of the air-plasma treatment time: (**a**) exposure time up to 120 s, (**b**) exposure time up to 600 s.

surprising taking into account that the experiments have been performed on a PET textile and not on a PET film.

It is important to stress that data collected by plasma treatment time of 600 s are very similar to the untreated sample data. This fact is certainly surprising, most of all since the AFM images of the 600 s treated sample appear to be quite different from that of the original untreated surface (see figure 2). To explain this phenomenon a hypothesis has been put forward that a local electric field is formed during plasma processing on the surface of the sample. This field prevents the ions in the plasma from reaching the more internal part of the surface after the electric field has been established. Therefore, the etching process concerns only the more external part of the surface. To understand more on the situation, other parameters characterising the surface have been evaluated (peak-to-valley distance, bearing ratio, height distribution etc.). A difference between the data concerning the intermediate plasma exposure times (60–120 s) and the 600 s exposure time data is evident. In particular the peak-to-valley distance is much greater for the 60–120 s treated samples than for the 600 s air-plasma treated samples. Besides, the distribution of the height histogram in the 60–120 s treated samples looks like a Gaussian (see figure 5a) while in the 600 s treated sample it is quite different and resembles that in the untreated samples (see figure 5b). But again the conclusion is that after an air-plasma treatment of 600 s, all the parameters recover to the original values of the untreated sample. Further AFM experiments are needed in connection with XPS measurements performed on the same treated samples to verify the possibility of a reorganisation of the sample surface to decrease the value of surface energy. In conclusion a complete and fully satisfactory explanation of
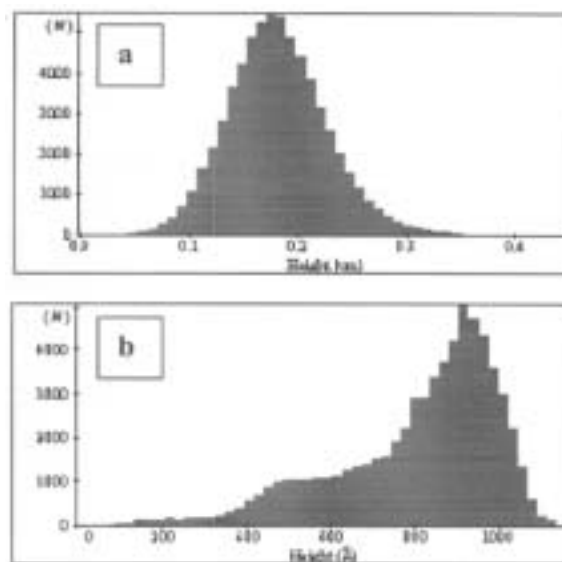

Figure 5. Height histogram of a 1×1 μm^2 PET fabrics surface: (**a**) 120 s air-plasma treated sample, (**b**) 600 s air-plasma treated sample.

Table 2. PET textile rms surface roughness and surface area, as a mean value of 15 data, as a function of the plasma gas pressure.

Gas	Pressure (mbar)	Rms (nm)	Surface area (μm^2)
Untreated		20.2 $\pm$ 4.7	1.34 $\pm$ 0.18
Air	0.1	39.7 $\pm$ 8.1	2.55 $\pm$ 0.39
	0.2	43.3 $\pm$ 8.2	3.41 $\pm$ 0.74
	0.4	48.2 $\pm$ 8.4	4.28 $\pm$ 1.01
He	0.4	37.9 $\pm$ 8.4	2.85 $\pm$ 0.43
	0.8	46.1 $\pm$ 10.2	3.32 $\pm$ 0.81
Ar	0.05	65.9 $\pm$ 9.6	5.85 $\pm$ 1.35
	0.2	77.7 $\pm$ 9.8	7.29 $\pm$ 1.63
	0.4	83.1 $\pm$ 10.3	7.98 $\pm$ 1.81
SF_6	0.05	32.2 $\pm$ 7.1	2.25 $\pm$ 0.72
	0.2	26.6 $\pm$ 6.7	2.08 $\pm$ 0.50
	0.4	24.9 $\pm$ 5.2	2.05 $\pm$ 0.41
CF_4	0.07	37.8 $\pm$ 7.1	2.47 $\pm$ 0.41
	0.2	35.7 $\pm$ 7.1	2.32 $\pm$ 0.52
	0.4	28.9 $\pm$ 6.0	2.13 $\pm$ 0.39

these facts is not available at present and probably it would require the support of chemical investigation too.

3.2 *Plasma treatment: Surface morphology changes as a function of plasma gas pressure*

To correlate the acquired properties by the plasma-treated samples with the characteristics of the plasma itself, measurements have been performed using different gases (air, He, Ar, SF_6 and CF_4) and changing their pressures in the usual range of operation for this kind of processes (0.05–0.4 mbar). The power of the RF source was maintained at 105 W and the plasma treatment time was 60 s at a distance of 7.5 cm from the antenna. The interest to characterise the fluorine-based gas behaviour is related to the fact that these plasma treatments impart water repellence to PET fabrics [8,10]. Four 3D topography AFM images of plasma-treated samples using different gases are shown in figure 6. The sample surfaces show pits and micropores, different in size and density depending on the plasma gas. To characterise the surface morphology changes induced by the plasma treatment, the rms surface roughness and the surface area have been measured from the AFM images. In particular, to minimise any effect related to the possible heterogeneity of the sample, the data have been determined on 1 micron square areas as the mean value of the measurements recorded in 15 different regions for each sample. Table 2 and figure 7 show the rms surface roughness and the surface area as a function of the gas pressure for all the studied gases.
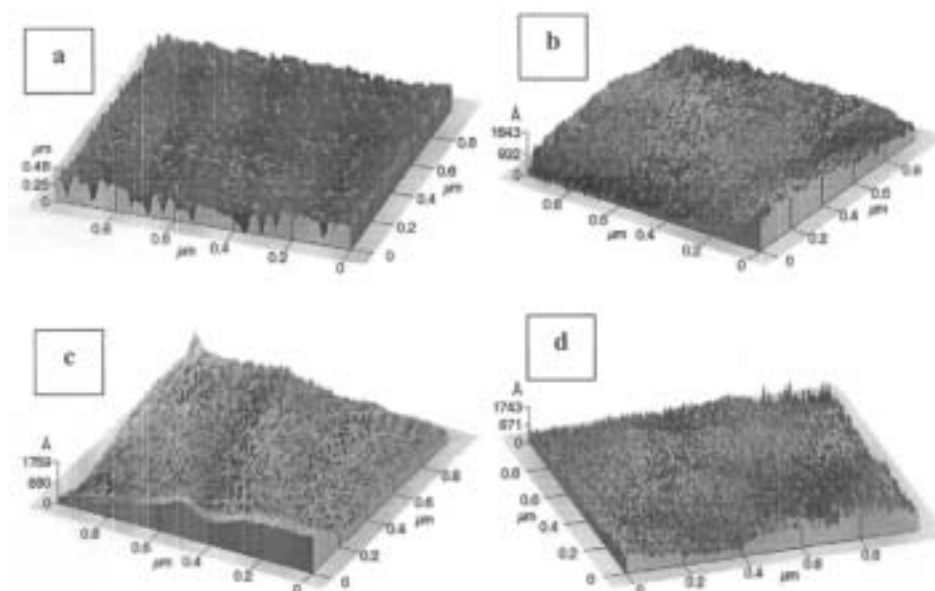
Figure 6. 3D views of non-contact mode AFM images of PET textile surfaces. The samples have been plasma treated for 60 s using different gases: (**a**) Ar plasma gas, (**b**) He plasma gas, (**c**) SF_6 plasma gas, (**d**) CF_4 plasma gas.

The data concerning He gas are made up by only 2 pressure values instead of 3 due to the difficulties in maintaining the discharge at very low pressure within the experimental chamber. The results point out that the studied gases show two different behaviours suggesting that the main effects of the plasma treatment are due to different processes. In fact, the curves in figure 7 show that the rms surface roughness and the surface area values increase as a function of the gas pressure using air, He and Ar gases while the same parameters decrease using SF_6 and CF_4 gases.

In the case of air, He and Ar plasma gases the curve trends strongly suggest the hypothesis that the etching process is mainly responsible for sample surface changes induced by plasma treatment. The increase of plasma gas pressure produces an increase in the number of bombarding ions on the sample surface and consequently an increase in the etching process and therefore of the rms surface roughness and of the surface area (see figures 7a and b). It may be pointed out that Ar plasma is more effective than air and He plasmas to promote an increase in the rms surface roughness and the surface area as a function of gas pressure. This is probably related to the dependence of the etching process on the mass and density of the bombarding ions and on their chemical activity.

In the case of SF_6 and CF_4 plasma gases the curve trends are quite different. In fact, the rms surface roughness and the surface area increase rapidly with an increase in gas pressure between 0 and 0.1 mbar approximately. At gas pressures greater than 0.1 mbar these parameters decrease slowly by increasing the gas pres-
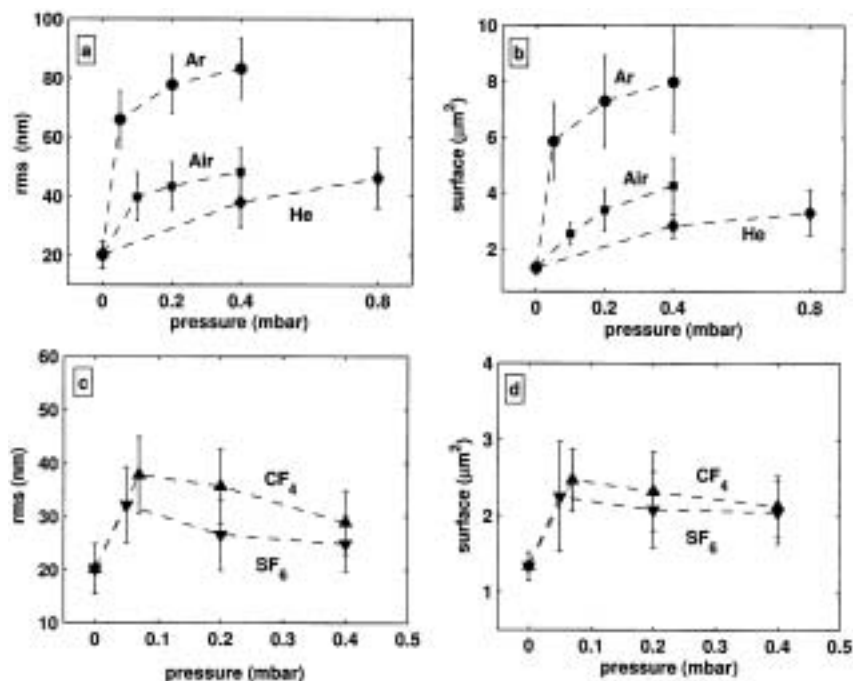
Figure 7. Rms surface roughness and surface area of plasma treated PET fabrics as a function of the plasma gas pressure using different gases: (**a**) arms surface roughness of air, He and Ar plasma gases, (**b**) surface area for air, He and Ar plasma gases, (**c**) rms surface roughness for SF_6 and CF_4 plasma gas, (**d**) surface area for SF_6 and CF_4 plasma gas.

sure (see figures 7c and d). A complete explanation of the experimental data is not available at present in the absence of XPS chemical data performed on the same samples. But the observed behaviour could be correlated with the grafting of fluorine atoms that modifies the surface properties as reported in [7,8,10].

4. Conclusions

Appropriate cold plasma treatments are widely employed to modify many surface properties of polymers such as dyeability, wettability and biocompatibility to adapt them to specific applications. Plasma processing are able to induce physical and chemical surface changes in polymeric materials through several concurrent processes without modifying their original bulk qualities. To better characterise plasma processing and to correlate surface properties induced by the plasma treatment, an AFM analysis on PET fabrics has been described. In particular, surface morphology changes as a function of air-plasma treatment time and as a function of plasma gas pressure for different gases have been quantified by means of rms surface roughness and surface area values.

A strict correlation between surface morphology and air-plasma exposure time has been put in evidence. The air-plasma treatment of PET fabrics for long exposure times (600 s) gives an unexpected result: all the parameters characterising the surface come back to the untreated sample values even if the AFM images of the sample surfaces are quite different.

The effects of the plasma gas pressure on the surface morphology of PET fabrics have been investigated using air, He, Ar, SF_6 and CF_4 gases. The air, He and Ar gases behave in a similar way but show different effects on the rms surface roughness and on the surface area probably due to the differences in mass and velocity of the produced ions and also due to the number of ions created in the plasma. The SF_6 and CF_4 gases behave in the same way that is quite different from air, He and Ar gases. The two different behaviours suggest that the main effects of the plasma treatment are due to different processes. In the case of air, He, and Ar gases probably the etching process is mainly responsible for surface morphology changes while the observed behaviour using SF_6 and CF_4 gases could be correlated with the grafting of fluorine atoms on sample surface that changes the surface properties.

AFM analysis allowed to clarify the effects on surface morphology modifications induced by cold plasma treatment of PET fabrics but left some points to be explained. To have a better insight on the discussed processes it is necessary to implement other chemical analyses, particularly the XPS analysis on the same samples.

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