Development of super-hydrophobic PTFE and PET surfaces by means of plasma processes

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Abstract. In this work, Poly(tetrafluoroethylene) and Poly(ethylene terephtalate) substrates were modified by means of plasma techniques for the creation of super-hydrophobic surfaces. Both the materials were etched with an O₂ plasma, thus increasing their surface roughness which was investigated by means of Atomic Force Microscopy analysis. Plasma etching of PTFE surfaces under appropriate conditions results in the creation of super-hydrophobic surfaces, as assessed by measurements of dynamic contact angles and sliding angles. Chemical modifications of the PTFE surfaces was investigated with Attenuated Total Reflectance Fourier Transform Infrared spectroscopy and X-ray Photoelectron Spectroscopy analysis. The realization of super-hydrophobic PET surfaces needs the deposition of a hydrophobic top coating, which was realized through an hexamethyldisiloxane (HMDSO) plasma. The thickness of this top layer was varied by changing the plasma deposition time and the effects on the hydrophobic performances of the modified PET were investigated. Micro-nano structures created by plasma on PTFE and PET surfaces were characterized and correlated with the wettability.

1. Introduction

The wettability is usually determined by measuring the contact angle (CA) of a water droplet on a solid surface. When the CA of water is larger than 150° and the sliding angle of the drop is lower than 10°, the surface is called super-hydrophobic. Due to their ample variety of possible applications, super-hydrophobic surfaces have gained a lot of interest in the past few decades. Some practical applications of super-hydrophobic surfaces include biomedical devices, liquid separation, drag reduction, anti-icing, self-cleaning, anti-fouling [1]. In general, in order to create a super-hydrophobic surface, two factors are needed. First, the surface should have low surface energy (it should be initially hydrophobic). Second, the surface should exhibit micro- or nano-sized roughness, as well as hierarchical structure. Roughness combined with hydrophobicity often results in air pockets being trapped between the solid and liquid (composite solid–liquid–air interface), thus reducing the contact area between the surface and the water drop. This composite interface is needed for super-hydrophobicity.

In the past years, many approaches and techniques have been used to develop super-hydrophobic surfaces. For example, literature reports the creation of such surfaces by phase separation, electrochemical deposition, crystallization control, chemical vapor deposition, wet chemical reaction, layer-by-layer deposition, spin coating, sol–gel processing, lithography, electrospinning [1]. Plasma-based techniques are one of the most promising approach to the development of super-hydrophobic surfaces on polymeric substrates [2-4]. In particular, plasma technology is of great interest for the
creation of super-hydrophobic surfaces because plasma processing can be used for the modification of both the chemical and the morphological characteristics of a polymeric surface. For example, low surface energy coatings can be deposited by means of plasma polymerization [5]. On the other hand, plasma etching (which is the process of selective removal of materials from a surface by reactive plasma radicals) increases the surface roughness [3,6-8].

In general, etching can be used as pretreatment before coating the surface with a low surface energy layer, or it can be used to generate roughness on a low surface energy material. In this work, O$_2$ plasma etching was used to create super-hydrophobic Poly(tetrafluoroethylene) (PTFE) surfaces. Chemical modifications of the PTFE surfaces were investigated with Attenuated Total Reflectance Fourier Transform Infrared (ATR/FTIR) spectroscopy and X-ray Photoelectron Spectroscopy (XPS) analysis. Instead, super-hydrophobic Poly(ethylene terephthalate) (PET) surfaces were realized by means of an O$_2$ plasma etching followed by the deposition of an hydrophobic top coating, which was realized through a HMDSO plasma. The thickness of this top layer was varied by changing the plasma deposition time and the effects on the hydrophobic performances of the modified PET were investigated. Micro-nano structures created by plasma on PTFE and PET surfaces were characterized by means of Atomic Force Microscopy (AFM) analysis and correlated with the wettability.

2. Experimental

2.1 Plasma treatments

The O$_2$ plasma was produced inside a cylindrical stainless steel vacuum chamber (diameter 30 cm) with a symmetric parallel plate configuration (two parallel aluminum dishes, diameter 20 cm). The PTFE sheets (1 cm$^2$, thickness= 2 mm) and the PET films (thickness= 36 μm) were positioned on the centre of the lower grounded electrode. The upper electrode is externally connected, through a semi-automated matching network, to a 13.56 MHz RF power supplier (Cesar 133, Dressler) which provides a RF voltage with respect to the lower electrode and to the grounded chamber. O$_2$ was uniformly distributed in the reactor by the upper showerhead electrode (with pinholes diameter of 2 mm). Before operating the discharge the device is evacuated to 10$^{-3}$ Pa by means of a rotary pump, combined with a turbo-molecular pump. During the plasma treatment, the chamber is evacuated only by means of the rotary pump.

Plasma treatments were performed at a fixed pressure of 9 Pa. The RF power input was varied between 20 and 300 W, while the duration of the plasma treatment was varied between 2 minutes and 40 minutes. HMDSO plasma polymerization was performed in the same reactor, only on PET films. Only deposition time was varied (between 2 and 20 minutes), while the other relevant plasma parameters were kept constant (HMDSO flow rate= 0.6 sccm, HMDSO pressure= 3 Pa, power input = 30 W).

2.2 Samples characterization

Contact angles (CAs) were measured with 3 μl deionized water droplet on a Dataphysics OCA 20 (Dataphysics) instrument at room temperature. All the contact angles were determined by averaging the values obtained at 5–6 different points on each sample surface. Roll-off angles were determined with 10 μl and 50 μl water droplets, using a dedicated apparatus equipped with a goniometer.

Chemical modifications owing to the O$_2$ plasma treatment and HMDSO film structure were determined by means of a Fourier transform infrared (FT-IR) spectrometer (Nicolet iS10, Thermo Scientific) equipped with a ATR sampling accessory (Smart iTR). For each spectrum 32 scans, with a spectral resolution of 2 cm$^{-1}$, were recorded.

X-ray photoelectron spectra were recorded using a 5500-PHI (Physical Electronics) apparatus, with a monochromatic Al-anode K$_\alpha$ source and an electron take-off angle of 45°. The analyzed circular area had a diameter of 0.8 mm. The pressure in the chamber was around 10$^{-6}$ Pa. The spectrometer was calibrated by using the Ag 3d5/2 peak and the resulting energetic resolution was 0.46 eV.

AFM measurements were carried out using a Solver P47-PRO (NT-MDT, Moscow, Russia), in semi-contact (tapping) mode on dry samples using HA_NC (High Accuracy Non Contact) silicon tips.
(NT-MDT) of typical spring constant $5.8 \pm 20\% \, \text{N/m}$ and resonance frequency $200 \pm 10\% \, \text{kHz}$. Square images $(5 \times 5 \, \mu\text{m}^2)$ were collected at a typical frequency of 1.5 Hz and with 256 points per line.

3. Results and discussion

3.1 Creation of super-hydrophobic PTFE surfaces

Chemical characterization of O$_2$ plasma treated PTFE surfaces was performed by means of Attenuated Total Reflectance Fourier Transform Infrared (ATR/FTIR) spectroscopy and X-ray Photoelectron spectroscopy (XPS). Inset in Figure 1a shows the ATR/FTIR spectra of the untreated and of a plasma treated PTFE (power input= 200 W; O$_2$ pressure = 9 Pa; treatment time = 10 minutes). The spectrum of the untreated PTFE displays two main bands, at 1150 cm$^{-1}$ and 1204 cm$^{-1}$, which can be attributed respectively to the asymmetric and the symmetric stretching of the CF$_2$ groups. The spectrum of the plasma treated sample displays an additional band at 3000-3700 cm$^{-1}$, typical of the stretching of OH groups. A semi-quantitative evaluation of the extent of the plasma functionalization has been performed by integration of the OH and CF$_2$ bands, followed by the calculation of the OH/CF$_2$ band ratio. Results are shown in Figure 1a and Figure 1b.

By increasing the power input from 20 W to 200 W (Figure 1a), the OH/CF$_2$ band ratio increases, while a further increase to 300 W leads to a decrease in the insertion of OH groups. The influence of the treatment time on the OH functionalization is displayed in Figure 1b. It can be noticed that the plasma treatment at 200 W always leads to a higher insertion of OH groups on the PTFE surface and that, for both the power inputs, the OH/CF$_2$ ratio increases with the treatment time. These trends are in agreement with literature results: by increasing the power input plasma etching becomes prevailing over surface functionalization [3].

![Figure 1. (a) Variation of the OH/CF$_2$ ATR/FTIR band ratio with the power input. Inset - ATR/FTIR spectra of the untreated (dash line) and the plasma treated (full black line) PTFE (power input= 200W; O$_2$ pressure= 9 Pa; treatment time= 10 minutes). (b) Variation of the OH/CF$_2$ ATR/FTIR band ratio with the treatment time for samples prepared with power inputs of 200 W and 300 W.](image)

In order to better investigate the chemical changes owing to the plasma treatments at different power levels, we performed XPS analyses on sample treated between 20 W and 200 W. Results are displayed in Figure 2. The oxygen surface concentration (expressed as O/C ratio) is higher for samples prepared at power input $\leq$50 W. XPS analysis reveals also an increase in the oxygen content of the plasma treated samples with the ageing time. This post-plasma oxidation is a well documented phenomenon, which derives from the reaction between remaining radicals on the plasma treated polymeric material and atmospheric oxygen [9]. The trend in the oxygen surface concentration detected by XPS is not in agreement with that of the OH/CF$_2$ ratio obtained from the ATR/FTIR spectra. This result can be easily explained taking into account the different penetration depth of the two techniques. While XPS analysis probes polymeric material for a depth of few nanometers, the
penetration of ATR/FTIR analysis is of the order of few microns. Taken together, XPS and ATR/FTIR results indicate that for power levels \( \leq 50 \text{ W} \) there is a higher degree of OH functionalization of the outermost layers of polymeric chains, but a low penetration of the OH functionalization into the PTFE bulk. By increasing the power level, the penetration of the OH functionalization increases too, while the degree of OH functionalization of the polymeric chains near the surface decreases.

![Figure 2. O/C ratio, detected by XPS, on samples prepared at different power inputs.](image)

Morphological characterization of the plasma treated PTFE samples was performed by means of AFM analysis. Figure 3 displays the trend of the root mean square (rms) of the heights (for \( 5 \times 5 \mu \text{m}^2 \) AFM images) of the surfaces of PTFE samples treated at different power inputs. The values which are reported are the average of the r.m.s. of at least five images, acquired in different zones of the samples. Plasma treatments at low power inputs (20 W, 50 W) decrease the surface roughness of PTFE. Instead, treatments at higher power inputs (100 W, 200 W, 300 W) result in the formation of bigger globular structures on the PTFE surface, with a strong increase of the surface roughness. The formation of the globular structures observed for power levels \( \geq 100 \text{ W} \) is the consequence of a differential etching of the PTFE surface. This is a common phenomenon, which has been observed also for other polymeric materials. Some authors have hypothesized the deposition of etch inhibitors (unetchable material) to be the most important mechanism which can be related to the formation of the surface micro/nano structures [4,8]. In our case, XPS analysis gives important information with regard to the changes in the surface chemistry that could be connected with the roughness formation. For very low power input (20 W), no aluminum was detected on the surface of the plasma treated PTFE sample (Figure 3). Instead, all the samples prepared at power input \( \geq 50 \text{ W} \) are contaminated by aluminum. Since both the electrodes of our plasma reactor are made of aluminum, it can be hypothesized that the energetic and intense ion bombardment releases in the gas phase Al particles. In particular the upper RF electrode gets heated when high powers and long treatment times are used. Due to the RF sheath formation, ion bombardment happens causing some sputtering. Nonvolatile Al particles will redeposit on the nearby surface, including the PTFE surface. There, they can act as micromasks, causing local differential etching rates and promoting the development of micro/nano structures. The increasing amount of aluminum with the power input can be related to the increasing surface roughness. A more quantitative analysis, for instance by changing the electrode materials, although interesting, is beyond the scope of the paper.

Figure 4a shows the variation of the advancing and the receding contact angles with the RF power input, keeping constant the other relevant plasma parameters (\( \text{O}_2 \text{ pressure} = 9 \text{ Pa} \); treatment time = 10 minutes).
The contact angles were measured immediately after the oxygen plasma treatment, and the values for power input= 0 refer to the untreated PTFE. It can be noticed that the advancing contact angle remains substantially unchanged up to 50 W, then it increases with the power input. Instead, the receding contact angle strongly decreases (from 70° to a value around 20°) for power input ≤100 W, then it gradually increases. When the plasma treatment was performed at 300 W, a super-hydrophobic PTFE surface was obtained. This trend with the RF power input is in agreement with previous literature results [3]. ATR/FTIR data do not explain these results, since the measured OH/CF₂ ratio increases with the power input and the water contact angle should be expected to decrease. Instead, the trend of contact angle is better in agreement with the XPS analysis, which probes a lower depth into the surface and displays a decrease of the oxygen atomic concentration by increasing the power input. Moreover, the trend of the advancing and receding contact angle can be explained taking into account the increase in surface roughness which occurs by increasing the power input. In fact, surface roughness strongly influences the wettability, and contact angles measured on a rough surface can be interpreted by means of two main models. The Wenzel model predicts that the water penetrates the holes on the surface and therefore the contact area between water and solid surface increases with roughness. The contact angle on the rough surface can be calculated by means of the equation:

$$\cos \theta^W = \tau_s \cos \theta_e$$

where $\theta^W$ is the contact angle measured on the rough surface, $\theta_e$ is the equilibrium contact angle (measured on the flat solid surface) and $r_s$ is the surface roughness (the ratio of the actual surface area to the projected area of the surface). Since $r_s$ is always $>1$, for $\theta_e>90^\circ$ (as for our PTFE surfaces) the model predicts an increase of contact angle by increasing the surface roughness.

Instead, Cassie and Baxter proposed a model in which the liquid does not fill the grooves of a rough solid and sits on a composite surface made of solid and air [24]. They suggested that:

$$\cos \theta^{CB} = f_1 \cos \theta_e - f_2$$

where $\theta^{CB}$ is the contact angle measured on the composite rough surface, $\theta_e$ is the equilibrium contact angle (measured on the flat solid surface), $f_1$ is the surface area of the liquid in contact with the solid (in our case PTFE) divided by the projected area and $f_2$ is the surface area of the liquid in contact with air divided by the projected area ($f_1 + f_2 = 1$).
Figure 4. Variation of the advancing and receding contact angles with the power input: (a) angles measured immediately after the treatment; (b) angles measured after 30 days.

On the basis of the chemical and morphological characterization already discussed, the trend of contact angle displayed in Figure 4a can be interpreted in terms of a competition between surface functionalization (insertion of polar oxygenated groups) and chemical etching of the PTFE. At low RF power inputs the surface functionalization prevails, and the wettability increases. By increasing the power input, etching of PTFE surface becomes prevailing (Figure 3) and wettability decreases.

Figure 4b shows the contact angles measured 30 days after the plasma treatment, as a function of the power input. In contrast with XPS analysis results (which showed an increase of the surface oxygen content after 30 days), the advancing contact angles are greater than those measured immediately after treatment and, for power inputs ≥100 W, they are also greater than 150°, thus fulfilling the first condition for super-hydrophobic surfaces. The receding contact angles don't change with ageing time for power input ≤50 W, while they increase for power inputs ≥100 W. For power inputs of 200 W and 300 W the hysteresis angle significantly decreases with ageing time. This leads to super-hydrophobic surfaces, with very low roll-off angle (below 5°). Particularly interesting is the ageing behavior of the sample prepared at 100 W, with the receding contact angle that increases from 30° to over 130°. Noteworthy, receding contact angles measured after 30 days display a trend which strongly resemble that of the surface roughness of the samples, with a strong increase for power input higher than 50 W. The contact angle increase detected on aged samples can be easily explained in terms of surface adaptation. As a consequence of the reptation motion (that move some of the polymer chains from the surface to the bulk) and of chain rotation, the density of hydroxyl groups exposed to air decreases with the ageing time [9].

Figure 5 shows the variation of the advancing and the receding contact angles with the treatment time, for samples prepared at 200 W.

Full lines, which report contact angles measured immediately after the oxygen plasma treatment, display a maximum of hydrophobicity for 20 minutes of duration. Hysteresis angles are quite large, always greater than 20°, as a consequence of the introduction of some hydrophilic OH groups which was detected by ATR/FTIR spectroscopy (data not shown). The OH/CF₂ band ratio of these sample increases with the treatment time. Since it is known from literature that also surface roughness increases with treatment time [10], the trends displayed by full lines in Figure 5 (with a maximum in hydrophobicity at intermediate treatment time) can be interpreted in terms of competition between these two effects of the oxygen plasma treatment, with the highest contact angles which are obtained by reaching an optimal compromise.

Both advancing and receding contact angles increase with the ageing time, and hysteresis decreases. All the aged samples were super-hydrophobic, with roll-off angle lower than 5°.
3.2 Creation of super-hydrophobic PET surfaces

Plasma etched PET films were super-hydrophilic (contact angle <5°), and the realization of a super-hydrophobic PET surfaces needed the deposition of a hydrophobic top coating, which was realized through an HMDSO plasma [5]. The composition of this organosilicon coating, measured by XPS analysis and expressed as atomic percentage of the elements, was: C= 60%; O= 14%; Si= 26%. Figure 6 shows the variation of the advancing and the receding contact angles measured on PET films with the O₂ etching duration. The samples were etched at a power input of 200 W and then coated with a plasma-polymerized HMDSO layer, keeping constant the relevant operating parameters (HMDSO flow rate= 0.6 sccm, HMDSO pressure= 3 Pa, power input= 30 W, deposition time= 2 minutes, coating thickness= 50 nm). The sample at etching time= 0 refer to the PET film which was only coated with the plasma-polymerized HMDSO layer. Advancing contact angles increase with the etching time up to 10 minutes, then they remain almost constant. Instead, receding contact angles slightly decrease for short etching time (5 min), and display a big jump for longer etching times. Samples prepared with etching times of 10 minutes and 20 minutes were super-hydrophobic (dynamic contact angle >150°, hysteresis angle <5°). 5 × 5 μm² AFM images in Figure 6 refer to samples before HMDSO deposition (only etched samples). It can be noticed the difference in surface roughness of samples etched for 5 and 20 minutes, which results in different hydrophobic performances after the deposition of the HMDSO coating.
Figure 6. Variation of the advancing and receding contact angles of PET films with the etching time. Samples were etched at a power level of 200 W.

In the subsequent experiments, the thickness of the hydrophobic top layer was varied by changing the plasma deposition time. Before deposition, all the samples were etched with the oxygen plasma at 200 W for 20 minutes. The thickness of the coating (measured on Si wafers by means of a profilometer) was 50 nm for deposition time of 2 minutes, 220 nm for 10 minutes and 440 nm for 20 minutes. Results are displayed in Figure 7. It can be noticed that by increasing the deposition time, hydrophobic performances of PET samples decreases (decrease of dynamic contact angles, increase of roll-off angles). AFM analysis explains this result: by increasing the deposition time, surface structures seems to merge due to a partial filling of the voids between them, with a consequent decrease of the surface roughness.

Figure 7. Variation of the advancing and receding contact angles of PET films with the HMDSO deposition time.

Images in Figure 8a and 8b show the AFM Z-Height profiles of plasma etched PTFE and PET samples, measured on a line extracted from a 5×5 μm² image. Both the surfaces present columnar structures, although with different aspect ratio. Structures observed on PTFE sample are 500 to 600 nm high, and have a width at the base of about 1.5 μm. Moreover, a superimposed nano-roughness has
been detected. Instead, structures on PTFE sample are 700 to 800 nm high, and have a width at the base of about 700 nm. These differences can derive from the different etching rates of the two materials and/or from the different duration of the plasma etching. Images in Figure 8c and 8d show the AFM Z-Height profiles of two PET samples which were plasma etched and then coated with HMDSO layers of different thicknesses. It can be noticed that the HMDSO coating reduces the height of the structures (probably by filling the voids between them), which are only 400 nm high for the sample in Figure 4d. This "snowfall effect" has detrimental results on the hydrophobic performances (Figure 7).

Figure 8. AFM Z-Height profiles of: (A) Plasma etched PTFE (200 W, 20 min); (B) Plasma etched PET (200 W, 20 min); (C) Plasma etched PET with a HMDSO coating of 50 nm; (D) Plasma etched PET with a HMDSO coating of 440 nm.

4. Conclusions
PTFE sheets were modified with a pure oxygen plasma varying the RF power input and the treatment time. We found that both these operating parameters influence the chemical/morphological characteristics and the wettability of the plasma treated samples. PTFE samples treated at low power input (up to 50 W) are more hydrophilic than the untreated one, but dynamic contact angles gradually increase with the power input. XPS analysis suggests that for low power levels there is a higher degree of OH functionalization of the outermost layers of polymeric chains, which leads to an increased wettability. AFM analysis reveals that plasma treatments at high power inputs result in the formation of globular structures as a consequence of the differential etching of the PTFE surface, with a strong increase of the surface roughness. Although XPS analyses of the aged samples reveal a post-plasma oxidation, the dynamic contact angles measured after 30 days are greater than those measured immediately after treatment and, for power input ≥100 W, the plasma etched PTFE surfaces are super-hydrophobic. This result has been interpreted in terms of surface adaptation, which leads to a decreased density of the exposed hydroxyl groups.

Plasma etched PET films need to be coated with a HMDSO top layer in order to create super-hydrophobic surfaces. The thickness of this layer has been varied by changing the plasma deposition time. Increase of the HMDSO layer thickness result in a decrease of the hydrophobic performances of PET samples (decrease of dynamic contact angles, increase of roll-off angles). This has been interpreted in terms of a "snowfall effect": by increasing the layer thickness, AFM reveals that the surface structures merge together, with a consequent decrease of the surface roughness.
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