Plasma Surface Modification of Polycarbonate and Poly(propylene) Substrates for Biomedical Electrodes

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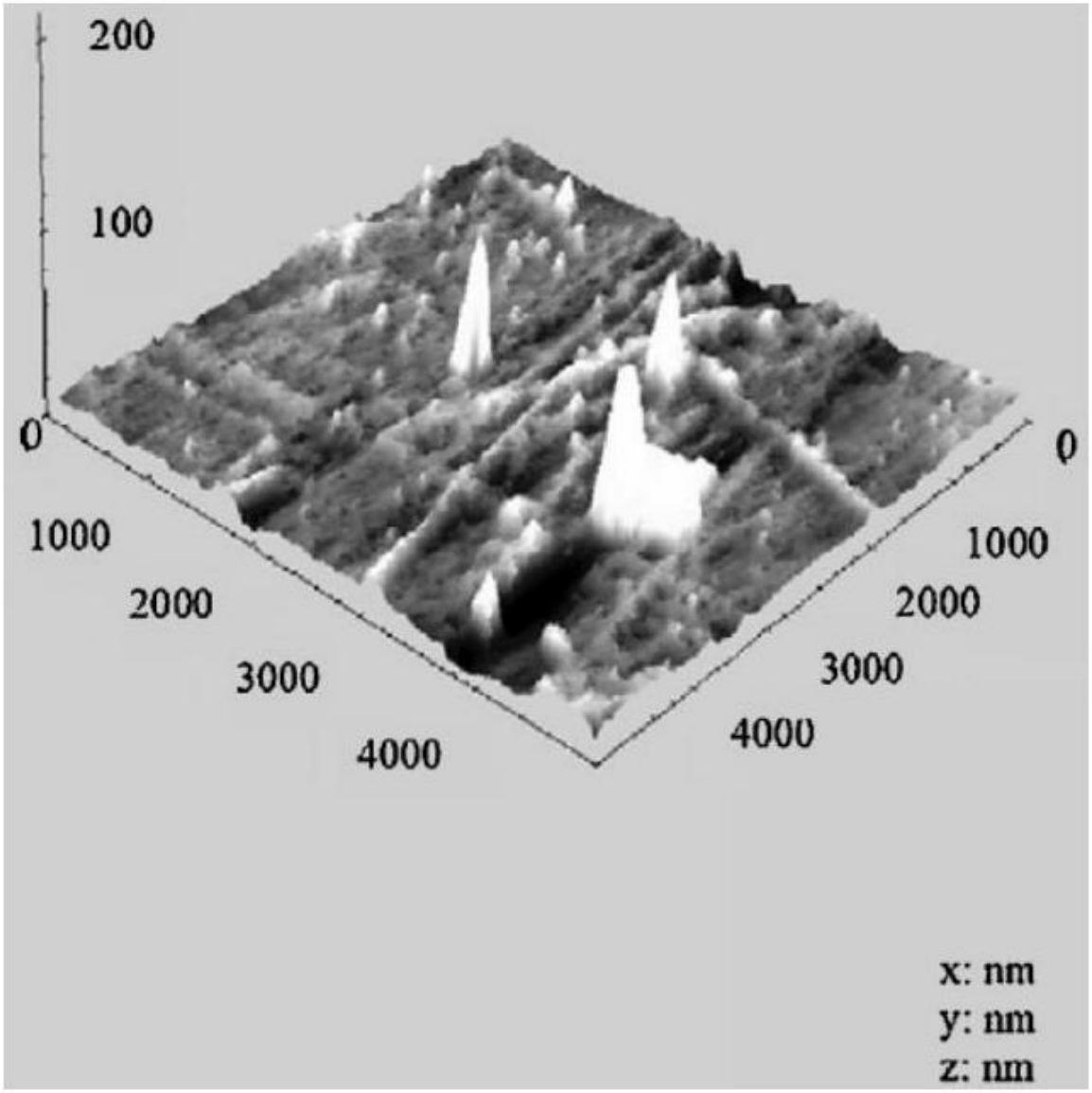
The effects of surface plasma treatments on the properties of PP and PC substrates were studied. Main results showed that the 0.48 Pa Ar treatment promoted the most favorable changes: roughness increased from 15 to 17 nm for PC and from 12 to 30 nm for PP, while the CA lowered from 95° to 59° and from 87° to 35° for PC and PP, respectively. The effects of the activation treatment on adhesion were checked by depositing a thin layer of TiN on both untreated and 0.48 Pa Ar plasma treated PC samples, and the adhesion to both substrates compared using the standard X-cut tape test. The Ar activated samples displayed better adhesion of the TiN film than the untreated ones, confirming the benefits of the surface changes induced by the plasma treatments.



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Introduction

Polymeric materials have a wide range of applications due to several advantages, such as flexibility, light weight, low cost and processability. Furthermore, a polymeric surface may be functionalized, for example by thin film deposition, [1–3] widening even more the application range for these materials in several areas of technological relevance, e.g. headlights, lenses or antibacterial packages. [4–6] Nonetheless, thin film coating of polymeric surfaces results very often in some critical problems, including the well-known lack of adhesion. [7] In fact, the optimization of the adhesion between thin metallic or ceramic films and common polymers represent some of the most relevant challenges in recent R&D projects, due to the very
important chemical and structural differences between those materials. Recent literature reveals an increasing number of scientific studies dealing with different treatments to improve adhesion of several kinds of polymeric substrates to thin films, according to their particular relevance for a certain application. [4,8–14] Among the several treatments that are known and accepted as resulting in an enhancement of the adhesion of functional coatings to polymeric substrates, those involving plasmas are often referred, not because of their outstanding results, in fact there are others equally important and with good results, [8–12] but basically because of their easy implementation. In fact, since most polymer coating procedures are based on plasma techniques, either PVD, [4,13,14] or CVD plasma-based ones, [15] a prior plasma treatment is normally quite easy to carry out and different parameters can be tested: powers, gas flows and gas mixtures or treatment times. [1–3,16–18] Despite the already significant number of possibilities, it is important to state that the plasma-based techniques are commonly used also due to the fact that they can improve the surface properties of the polymers, roughly without modifying their bulk properties. [19–22] Beyond several small effects that may occur during a plasma treatment, the surface of a polymer can be activated mainly by two basic mechanisms: i) the change in their surface topography (roughness), caused by the ionic bombardment with the gas species, thus influencing the adhesion of the film by an interlocking mechanism, [23] and ii) the occurrence of chain scissions of the existing chemical groups on the surface of the polymers creating, among others, radicals and new functional groups or dangling oxygen bonds, that will promote thin film/polymer chemical bonding. [5] In general, plasma treatments in O_2 and Ar gases result in the incorporation of oxygen-containing groups, whereas N_2 and NH_3 treatments incorporate both nitrogen and oxygencontaining groups. [24–28] These chemical changes occurring at the polymeric substrate surfaces lead to the formation of reactive species that will promptly bond to the thin film. [25–29]

The ultimate objective of this work is to optimize a plasma treatment that might be able to promote high adhesion levels between metallic-like thin films and different kinds of polymeric substrates, by increasing the substrate's surface roughness (interlocking mechanisms) and increasing of the surface energy, which is assessed by the wettability

increase, a reliable indicator for the formation of surface reactive groups. [30] To achieve this goal, the present study deals with different plasma treatments onto two polymeric materials: poly(propylene) (PP) and polycarbonate (PC), that were selected according to their wide use in our daily life. PP is a thermoplastic polymer used for packaging, textiles, laboratory equipment and automotive components. PC is also a thermoplastic polymer and, due to its interesting features (temperature resistance, impact resistance and optical properties), it is classified as an important engineering plastic. The application range for both polymers can be considerably widened upon functionalization with a metallic thin film. PP and PC were selected also due to their different physico-chemical properties, covering the properties of a wide range of polymeric materials: PP is a non-polar, semi-crystalline and flexible polymer, while PC is polar, amorphous and rigid. Beyond these applications and property-related features, the technological importance of these two materials in the present study is also related to their potential use in sensors for surface biomedical electrodes (electroencephalography - EEG, electrocardiography - ECG, electromyography - EMG), that could potentially replace the common silver electrodes. To this end, the polymer surface should be coated with a thin metallic-like thin film, thus allowing obtaining a lighter, less expensive, and eventually disposable electrodes. [31,32]

Experimental Part

The polymer substrates ($60 \times 60 \times 1$ mm^3 and $2 \times 2 \times 1$ mm^3) of poly(propylene) (PP) and polycarbonate (PC) were prepared by injection molding (ENGEL ES 200/45HL – V). The processing conditions were kept constant for all PP and PC samples produced. A polished mould was used in order to assure, as much as possible, a smooth surface. The samples were cleaned in an ultrasonic bath for 10 min in deionized water and fixed on a rotating substrate holder. All samples were placed at the same height in a vertical-like substrate holder configuration. [33] All the plasma treatments were performed in a laboratory size unbalanced (type II) direct current (DC) magnetron sputtering system, with a current intensity of 0.5 A, during 1200 s. The plasma treatments were carried out both in argon (Ar) and argon + oxygen (Ar +O_2) atmospheres. For treatments in pure Ar atmosphere, experiments were conducted using three partial pressures: i) 0.27 Pa(40sccm), ii) 0.39 Pa(60sccm) and iii) 0.48 Pa(80sccm). Regarding the mixed atmosphere (Ar + O_2), the two polymeric materials were treated using again three different combinations. In order to allow some possible correlations, the Ar pressure was kept constant, varying only the oxygen partial pressure. The Ar pressure that provided the best results, 0.48 Pa (80 sccm), was used with: i) 0.026 Pa (corresponding to a flux of 3.0 sccm), ii) 0.059 Pa (corresponding to a flux of 7.5 sccm), and iii) 0.12 Pa (corresponding to a flux of 15 sccm). Both types of substrates were plasma treated (see Table 1). The base pressure before the plasma treatments was below 4.4×10^{-4} Pa and the working pressure ranged between $\approx$ 0.27 and $\approx$ 0.62 Pa (plasma on), depending on the treatment applied to the samples. The deposition temperature was monitored trough a thermocouple that was placed close to the surface of the substrate holder on the plasma side (not in direct contact, since plasma treatments were done in rotation mode), and the temperature was measured during the discharge. There was no external heating of the samples, and the maximum temperature reached was 63°C, below PC and PP melting points.

Table 1. Plasma treatment parameters. Treatment time was 1200 s in all cases.

	Treatment	Ar flow rate	O_2 flow rate	Total pressure	O_2 partial pressure	Current	Temperature reached
		sccm	sccm	Pa	Pa	A	°C
Argon Treatment	1	40	-	0.27	-	0.5	50
	2	60	-	0.39	-	0.5	63
	3	80	-	0.48	-	0.5	59
Argon + Oxygen Treatment	1	80	3	0.44	0.026	0.5	67
	2	80	7.5	0.56	0.059	0.5	66
	3	80	15	0.62	0.12	0.5	67

In this study, the surface morphology of the polymer substrates before and after the treatments was investigated by atomic force microscopy (AFM), with a Pico Scan controller atomic force microscope, using the tapping mode. Structural changes were studied by X-ray diffraction (XRD) in a Phillips PW1710 device (Cu Kα radiation), in the Bragg-Brentano configuration. The contact angle (CA) measurements (sessile drop in dynamic mode) were performed in a DataPhysics OCA 20 device using water as a test liquid. Finally, infrared spectra of the non-treated and plasma treated samples were obtained in reflectance mode, on a Fourier Transform Infrared Perkin-Elmer Spectrum 100 spectrometer from 650 to 4000 cm^{-1}, using non-polarized light, with a resolution of 1 cm^{-1}.

In order to insure the consistency of the materials analysis and to acquire relevant activation/modification behavior of the polymers surface resulting from the experimental condition used, a maximum of two days was found to be the characterization time window to keep the polymers surface effects after the plasma treatments. [34] In order to achieve the highest accuracy possible, and to allow direct comparison between the different treatments effects, a special attention was given to keep constant as much as possible the time after each treatment, during which any of the characterization techniques was used.

In order to check the consistency of the plasma treatments, the same TiN_x film was deposited on non-treated and treated PC polymer substrates, according to previous optimization by the authors. [35] The film, $TiN_x (x \approx 1.2)$, was prepared with the substrate holder positioned at 70 mm from the target, using a dc current density of $100\ A \cdot\ m^{-2}$ on the titanium target (99.6at. $-$% purity). A gas atmosphere of $Ar + N_2$ was used. No substrate bias voltage, or temperature was applied. The X-cut tape adhesion test was performed following the ASTM standard D 3359-08. It consists on performing two cuts on the surface of the deposited metallic-like film with a 45° angle between them, forming an X . Then, a pressure sensitive tape is applied on top of the X -cut and pulled-out, leading to a certain degree of delamination at the thin film/polymer interface. The effect of the test is assessed by optical microscopy, by comparing the images before and after the application of the tape. The adhesion is rated according to an empirical scale

described in the above-referred standard, which goes from 0A - removal beyond the area of the X - to 5A - no peeling or removal.

Results and Discussion

Characterization of Plasma-Treated Polymers

The surface topography of plasma treated PC and PP were investigated by AFM. Figure 1 a-d shows the evolution of the PC surface morphology in the non-treated sample (Figure 1a) and after the plasma treatments with increasing Ar pressure (Figure 1 b through d . Only the PC results are shown due to the similarities that were observed in both polymers. As shown in Figure 1a, and since the samples were not polished, the surface of the non-treated PC sample presents some scratches which result from the manufacturing process; several sharp peaks (also called needle shaped spikes or protrudes), [2,36] most of them rather small in height, as it can be seen. The scratches are recursive in Figure 1 a-c, but completely disappear in Figure 1d, which is a clear sign of the surface mechanical "damage" that is introduced by the Ar activation/modification process in the polymeric surface with this Ar pressure. The number of protrudes is significantly reduced by the treatment undergone with 0.27 Pa (40 sccm), Figure 1b. In fact, this treatment seems to promote the lowest roughness value, even lower than that of the non-treated sample, which may be a result of some smoothening of the surface caused by the ionic bombarding process itself (let us recall that the polymeric substrates were attached in a metallic substrateholder and thus even if the substrates are non-conductive, there is always bombarding of its surface). On the other hand, Figure 1c shows that the surface treatment with an Ar pressure of 0.39 Pa (60 sccm) results in a significant increase in the number of protrudes, which appear to promote the desired increase in roughness, comparing with the nontreated sample. In fact, the treatment illustrated in this AFM image seems to be the one that leads to the highest change in surface morphology, which is a sign of the bombarding "damage" that may go deep inside the first monolayers of the polymeric surface. The 0.48 Pa (80 sccm) Ar treatment, Figure 1d, promotes an increase in the protrudes density

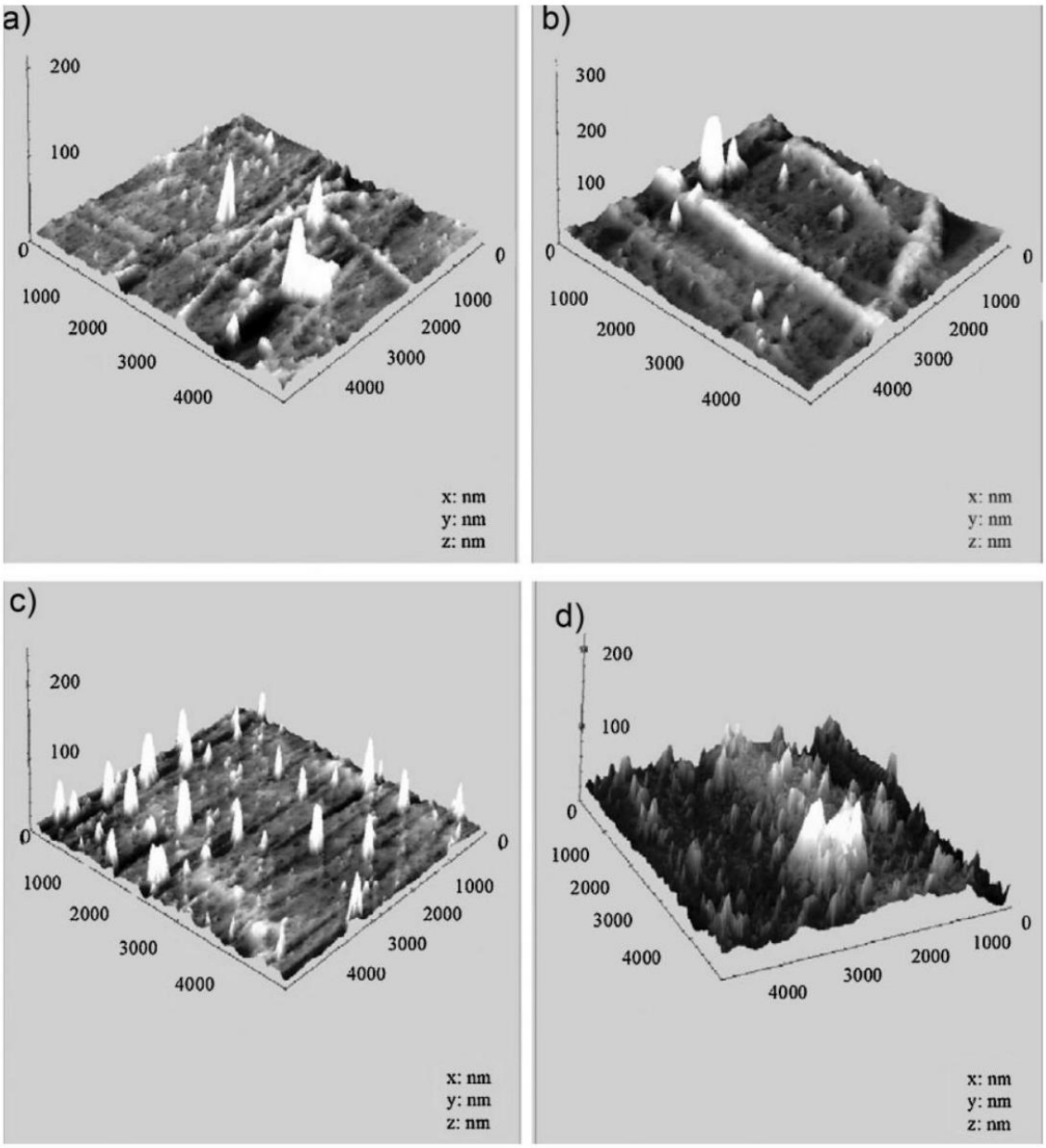

Figure 1. AFM surface images of the PC substrates: a) without treatment, and with treatments of b) 0.27 Pa(40sccm)Ar, c)0.39 Pa(60sccm)Ar and d) 0.48 Pa(80sccm)Ar.

the surface roughness is similar to that observed in the PC substrates, except that the tendency appears magnified. Since PC is relatively harder than PP, see Table 2, it results in an increasing difficulty to promote any morphological changes on the material surface by the well known "plasma etching" effect. [17] In fact, and since the ion bombardment is known to cause some micro-defects on the materials surface, the harder the surface is, the more difficult it will be to modify its morphology. The "odd" behavior (decrease of surface roughness when comparing with the non-treated one) that was observed for the PC sample treated with an Ar pressure of 0.27 Pa (40 sccm), may be explained by the fact that the used Ar flow rate/pressure was probably not enough to make chemical changes on the surface, but sufficient to "clean" any attached residue present, [3] resulting in a smoothening effect. Focusing on the CA measurements, knowing that the

drop size is much larger than the roughness scale in this case, and admitting that both surfaces are completely wet by the water, Wenzel Equation applies. [37] This Equation (1), describes the relation between the apparent CA on a rough surface (θ_w), the surface average roughness ratio (r, ratio between the real area and the geometric area) and the contact angle on a chemically similar smooth surface (θ_y) :

$$\cos(\theta_w) = r\cos(\theta_y) \quad (1)$$

Wenzel's Equation shows that for a hydrophilic surface $(\theta_y < 90°)$ the roughness turns the surface more hydrophilic, and a hydrophobic surface $(\theta_y > 90°)$ more hydrophobic. However, for CA values close to 90° this parameter is insensitive to roughness variations. On the other hand, the more hydrophilic the surface is, the higher the effect of the roughness on the CA. Bearing in mind these implications of Wenzel's equation, one can now analyze the evolution of the CA for PC with the plasma treatment conditions, Figure 2a. There is a slight but continuous decrease of CA, up to the 0.39 Pa (60 sccm) Ar treatment, followed by a steep decrease of the CA for the 0.48 Pa (80 sccm) Ar treatment. Given the initial CA close to 90° and the small roughness increase, one can state that, unless the chemical nature of the surface changed towards a more hydrophilic character, no significant changes of the CA were expected (roughness is proportional to " r " in the
but, in opposition to the previous treatment, the roughness is apparently lower. However, it is to note that although the number of protrudes is larger in Figure 1d, their height is considerably lower, as it is possible to observe by the scale (darker color → lower height).

In order to have a more quantitative evaluation of the surface "damages" that result from the Ar treatment/ activation process, the roughness values, obtained from the AFM results, as well as the water CA values obtained from CA measurements with water, are presented in Figure 2. Regarding the surface roughness evolution, the first interesting result that arises from this figure is that the evolution of the PC surface roughness is somehow consistent with the evolution of its morphology (compare Figure 1 and 2a). The treatments that promoted the highest values of the surface roughness in both polymers were those carried out with Ar pressures of 0.39 Pa (60 sccm) and 0.48 Pa (80 sccm), which were in fact those that produced the largest changes in surface morphology, when compared with the non-treated surfaces. In what concerns the PP samples (see Figure 2b), it can be stated that the evolution of
a)

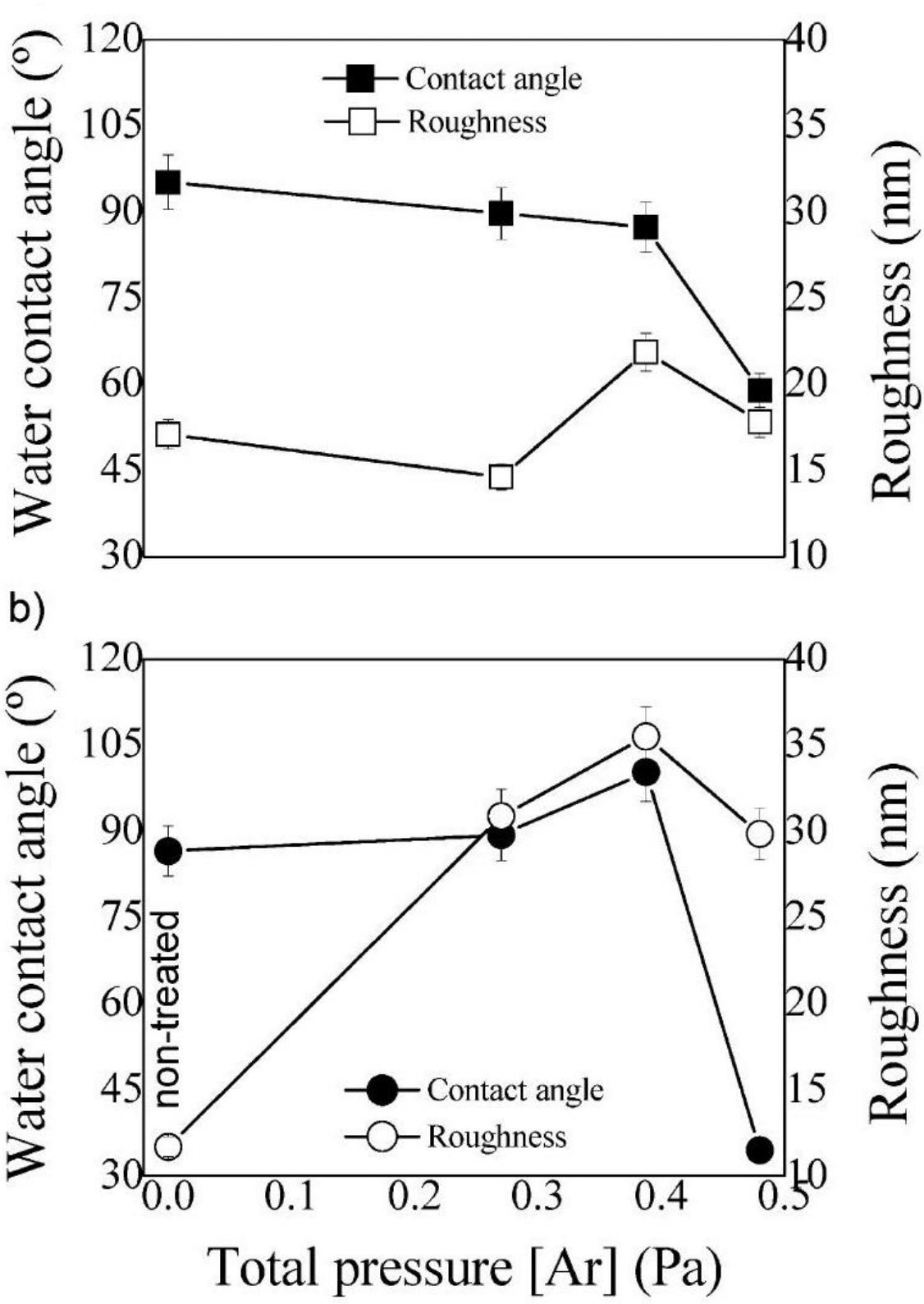

Figure 2. Evolution of a) PC and b) PP surface roughness and water contact angle with increasing the Ar pressure.

Wenzel's equation). The Equation suggests that, in fact, when the CA is close to 90°, the variations in roughness affect only slightly this parameter. Beyond the 0.39 Pa (60 sccm) treatment, the CA significantly decreased, in spite of the small roughness decrease, meaning that this treatment was effective in changing the hydrophilicity of the surface. Concerning the PP samples, again the CA of the non-treated surfaces are close to 90°, meaning that the roughness by itself shouldn't influence significantly the CA, as suggested by Equation (1). Therefore, the fact that the CA shows almost no variation up to the 0.39 Pa (60 sccm) Ar treatment leads to the conclusion that no hydrophilicity changes were induced by the Ar treatments up to this Ar pressure. However, the steep CA drop for the 0.48 Pa (80 sccm) Ar treatment, accompanied by a negligible roughness change, shows that, also in the case of PP, the 0.48 Pa (80 sccm) Ar treatment was effective in producing the desired hydrophilicity change. In order to further characterize the effects of the plasma treatments and their contribution to the evolution of the CA values, chemical analysis by Fourier transform infrared spectroscopy experiments (FTIR) and structural analysis by X-ray diffraction (XRD) were carried out. FTIR results of both polymers, obtained after each treatment, are shown in Figure 3a (PC) and Figure 3c (PP). The first notorious observation that can be drawn from this figure is that there are no significant differences between untreated and treated samples. In fact, by a closer look to both Figure 3a and c, as well as some detailed zones on Figure 3b and *d*, it can be easily observed that only a change in the intensity of the existing bands took place, and mostly in the PP substrate, since the PC seems to give rise to no change at all. Anyway, this may not be surprising, since it is known that FTIR technique is not sensitive to small amounts of chemical species. As the gas used was Ar, new chemical bonds (oxygen or others) should form after exposure of the plasma treated samples to atmospheric air. In this case, the radicals that were produced during plasma treatment would react with atmospheric air (oxygen) to produce polar groups that would change surface properties. It is reasonable to admit that the small amount of new bonds formed could not be detected by FTIR, although producing a change of the CA value, since this parameter is highly sensible to monolayer-level chemical changes. Pandiyaraj et al. [3] exhaustively studied by XPS the formation mechanism of new hydrophilic groups as a result of plasma treated/activated polymeric surfaces, and concluded that the new reactive functional groups are induced on the polymer surface by plasma action due to polymer chain scission or hydrogen abstraction by bombardment of plasma species. The created active sites can then bind to other reactive elements, namely oxygen. [18] In the present case, FTIR results are certainly not conclusive about this, but the reduction of the PP contact angle from about 86° towards roughly 35° (about 60% reduction from the original values) can only be

Table 2. Overview of some properties of the used polymers.

	Polarity	Hardness (Rockwell M - R)	Crystallinity	Melting temperature	Glass transition temperature	Young's modulus
				°C	°C	GPa
Polycarbonate	polar	70-121	amorphous	267	150	2-2.4

Poly(propylene)	non-polar	64-106	crystalline	160	-10	0.008-8.25

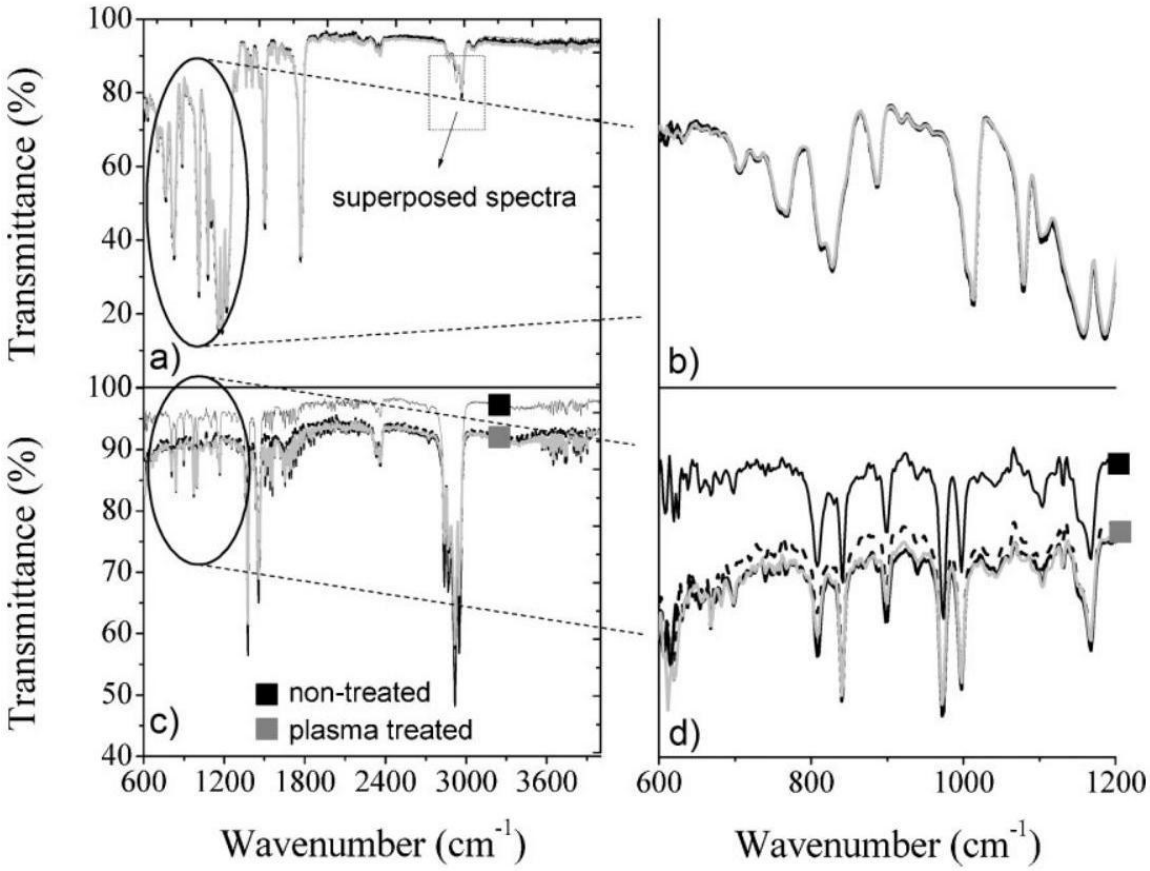

Figure 3. FTIR spectra of a) PC with b) detail and c) PP with d) detail before and after Ar plasma treatments.

explained by the formation of a small amount of hydrophilic groups (probably the same found by Pandiyaraj et al.) at the surface. The reduction of CA values is higher for PP than for PC (from about 90° to ≈ 60°, approximately 30% reduction), which can be explained by the chemical and structural differences between the materials. In fact, the PP chains have a higher mobility than PC chains for the plasma treatment temperature (see Table 2 for the differences in the T_g temperatures) and PP has a much lower softening point than PC (see Table 2). Pandiyaraj and co-authors stated that PP exhibits higher CA (more hydrophobic) when comparing with PET due to its non-polar nature. [3] However, Lai et al., which investigated PC and PP (similar to the present study), showed that PC (polar) exhibits higher CA values than PP (non-polar). [19] These results are in accordance with our own data (see Figure 2), and thus, it is also possible to claim that although important, the CA and wettability behavior may depend more on the kind of polymer and the experimental conditions used for its activation (thus affecting it according to its particular surface properties), and probably less on a particular feature such as its polarity.

In order to keep checking the effects of the plasma treatments on the behavior of the polymeric surfaces, a detailed analysis of the structural changes that occurred were also

followed by XRD. Figure 4 illustrates the X-ray diffractograms of both treated and non-treated PC (Figure 4a) and PP (Figure 4b) polymeric substrates. From the figures, the main conclusion that can be drawn is that
the shape of the peaks is consistent with the characteristics of both polymers (see Table 2). PC exhibits broad peaks, characteristic of amorphous materials, while PP exhibits sharp peaks which confirm its high degree of crystallinity. Regarding these different crystallinity features, Figure 4 also shows that there are no significant changes in the shape and position of the diffraction peaks, except that the diffraction patterns corresponding to the Ar treated samples are more intense and slightly wider than the nontreated ones. It is fair to say that there is probably a slight increase in the crystallinity degree on both polymers, not directly related to the plasma condition itself, but related to the temperature increase that was obtained with the increase of the Ar flow rate/partial pressure inside the deposition chamber (see Table 1), depending on the Ar flow rate and, consequently, on the total pressure. Moreover, it is important to bear in mind that the temperature was measured by a thermocouple placed 3 cm away from the substrate holder. Consequently, because of the low thermal conductivity

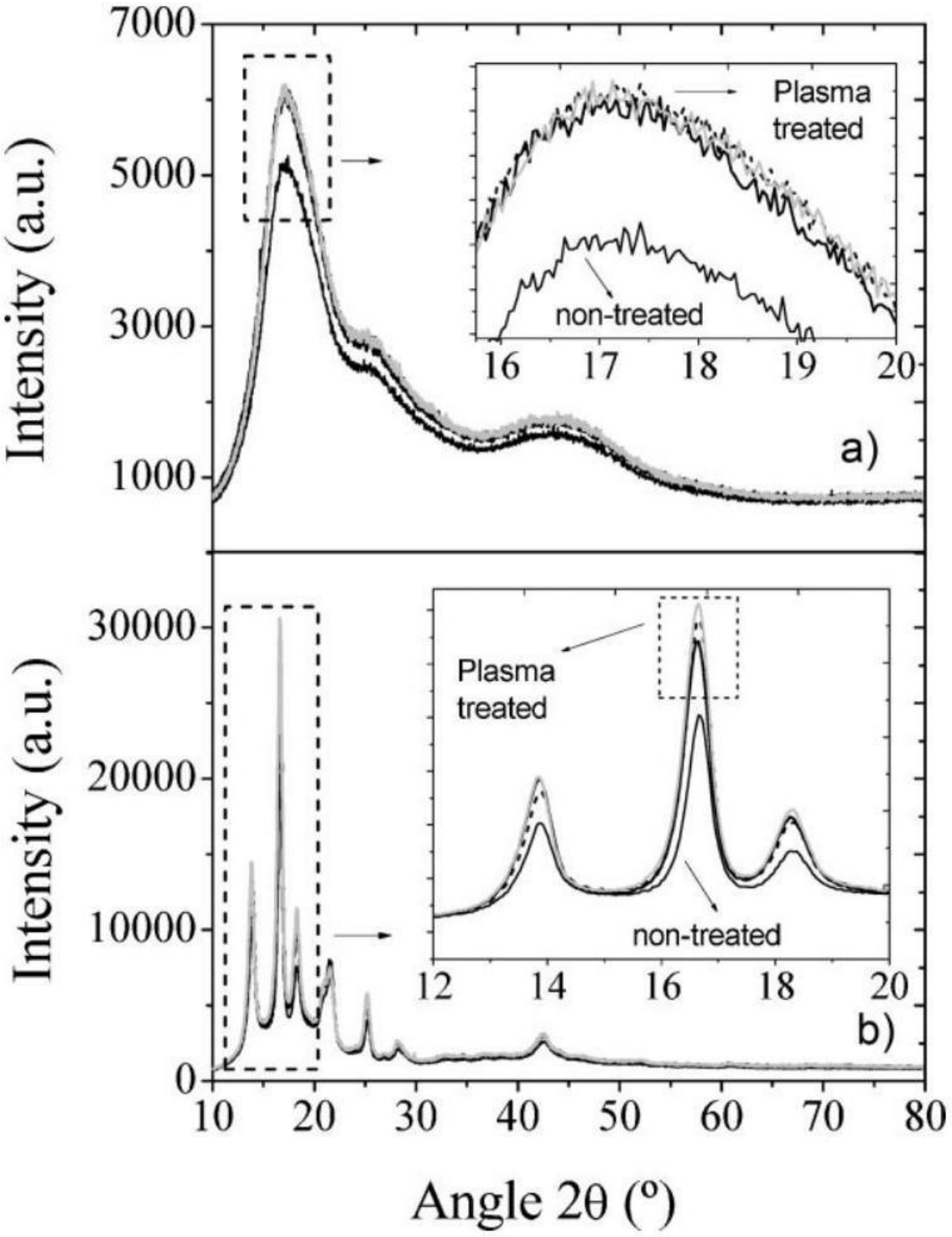

Figure 4. XRD patterns of a) PC and b) PP before and after different Ar treatments. under high vacuum, the temperature on the substrate holder will be different from the one measured by the thermocouple. However, despite this difference, the glass transition temperature of PC (150˚C) and the melting temperature of PP (160˚C) were certainly not achieved. Hence, the two polymers were perfectly able to withstand the plasma treatments imposed. To note that, longer and more aggressive plasma treatments or

even a future thin metallic film deposition will be potentially more dangerous to the PP substrates due to its low melting temperature.

At this point, it is possible to say that the 0.48 Pa (80 sccm) Ar treatment is the one that promotes the best balance between high roughness and low CA. In order to clarify if it is possible to further enhance the surface changes promoted by the Ar plasma treatment a new 0.79 Pa (90 sccm) Ar treatment was applied both to PC and PP (unpublished results by the authors). The obtained results revealed that an increase of the Ar pressure/flow rate beyond 0.48 Pa (80 sccm) is ineffective, since an inversion of the previous plasma treatment effects was detected: the surface became smoother and the CA were not affected. This indicates that saturation was reached due to the excess of gas ions in the system, promoting an excess of collisions among them, meaning that the Ar ions do not reach the surface with enough energy to promote any significant chemical change, only reducing the number of protrudes and consequently the surface roughness. In order to try to uncover the possibilities to enhance the surface modifications in the polymers by changing the chemical environment and explore the changes that might be induced in the CA values, PP and PC samples were submitted to a new series of plasma treatments. For this, oxygen was selected due to its high reactivity and ability to induce new functional groups and dangling oxygen bonds, such as the ones referred above. As our equipment requires argon to produce plasma, the new series of plasma treatments were conducted in an $Ar + 0_2$ atmosphere. Taking into account the results and the previous discussion, the Ar pressure of 0.48 Pa (80 sccm) was selected, since it was the one that promoted the best balance between surface roughness and CA values for both PC and PP. Three oxygen partial pressures were selected: i) 0.026 Pa (3.0 sccm), ii) 0.059 Pa (7.5 sccm) and iii) 0.12 Pa (15 sccm).

Figure 5 shows the evolution of the roughness and CA values for both series of plasma treatments. The overall results of this mixed $Ar + 0_2$ plasma treatment reveal some major differences when compared to those obtained with the Ar treatments alone, both in terms of CA and roughness evolutions. Regarding the PC substrates, the $Ar + 0_2$ treatments have only a small effect in promoting any important variations in the roughness values (Figure 5a). In fact, there seems to be a general tendency to a decrease in the roughness value with the increase of the 0_2 partial pressure which corresponded to an increase of the CA, in

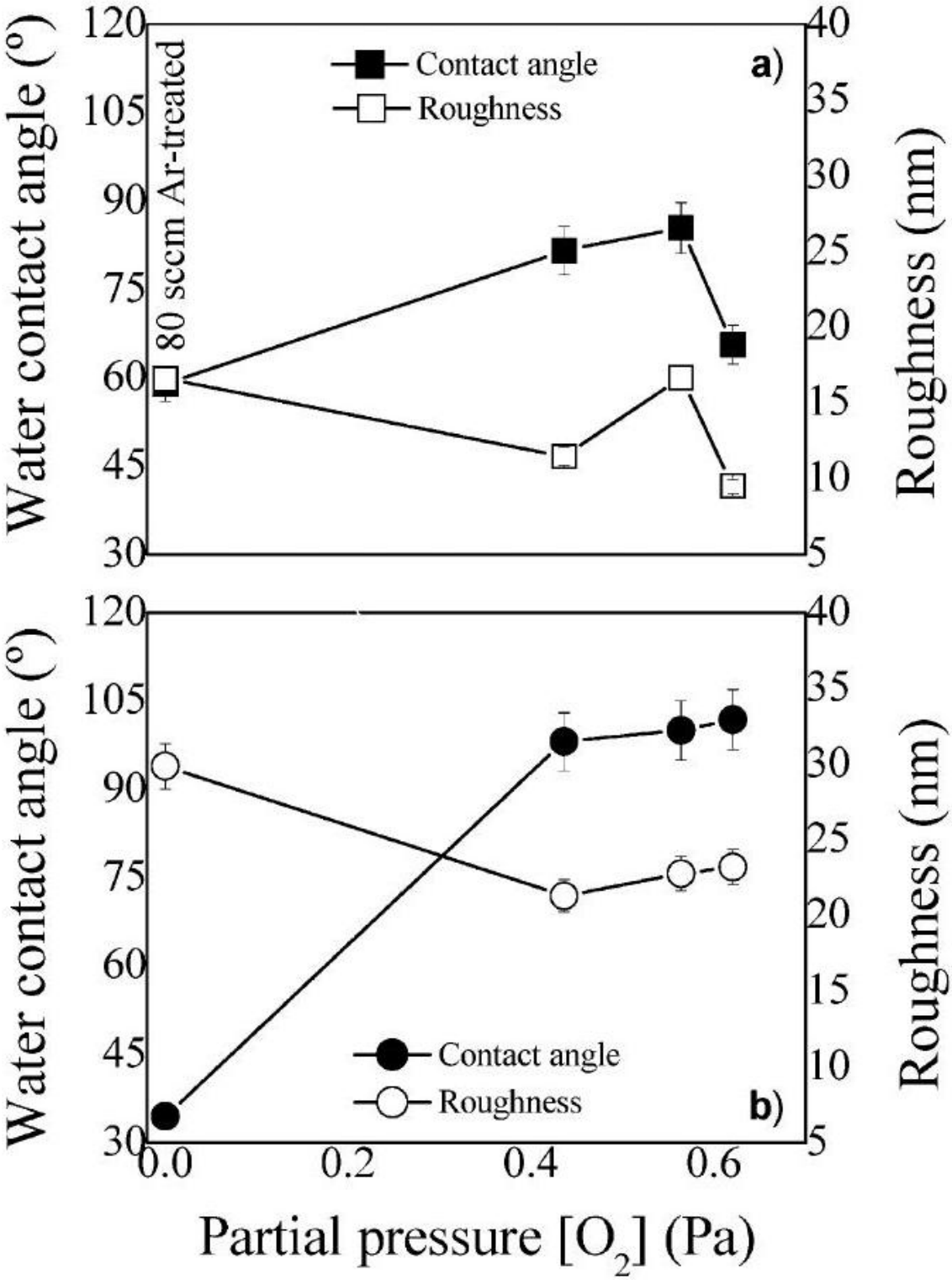

Figure 5. Evolution of a) PC surface roughness and water contact angle in comparison with b) PP surface roughness and water contact angle with increasing Ar + O_2 pressure. agreement with the Wenzel's equation for hydrophilic materials displaying CA significantly lower than 90°. If there was an increase of hydrophilicity, it was small enough to be counteracted by the roughness factor on the CA final value. It can be

concluded that, most probably, this treatment wouldn't contribute to an adhesion improvement neither by an interlocking mechanism (roughness increase) or by the creation of bonding sites (CA decrease). This apparent contradiction - the use of oxygen was carried out with the expectation that it would be more efficient than Ar in the formation of new hydrophilic functional groups due to its higher reactivity - suggests that Ar somewhat cancels this effect. [38] This might be understandable due to the significant number of collisions that may occur in the system before the ions hit the polymeric surface (with lower energy), and thus leaving few possibilities to oxygen to create/modify the chemical environment at the surface. The fact that a smoothening of the polymers surface was observed (lowering of the surface roughness values) may be consistent with this assumption. In order to check if significant chemical changes had occurred, FTIR measurements were carried out in both treated and non-treated samples. The first important note is that, again, these results (Figure 6a) do not show significant differences between non-treated and treated samples. The spectra are similar (almost over-

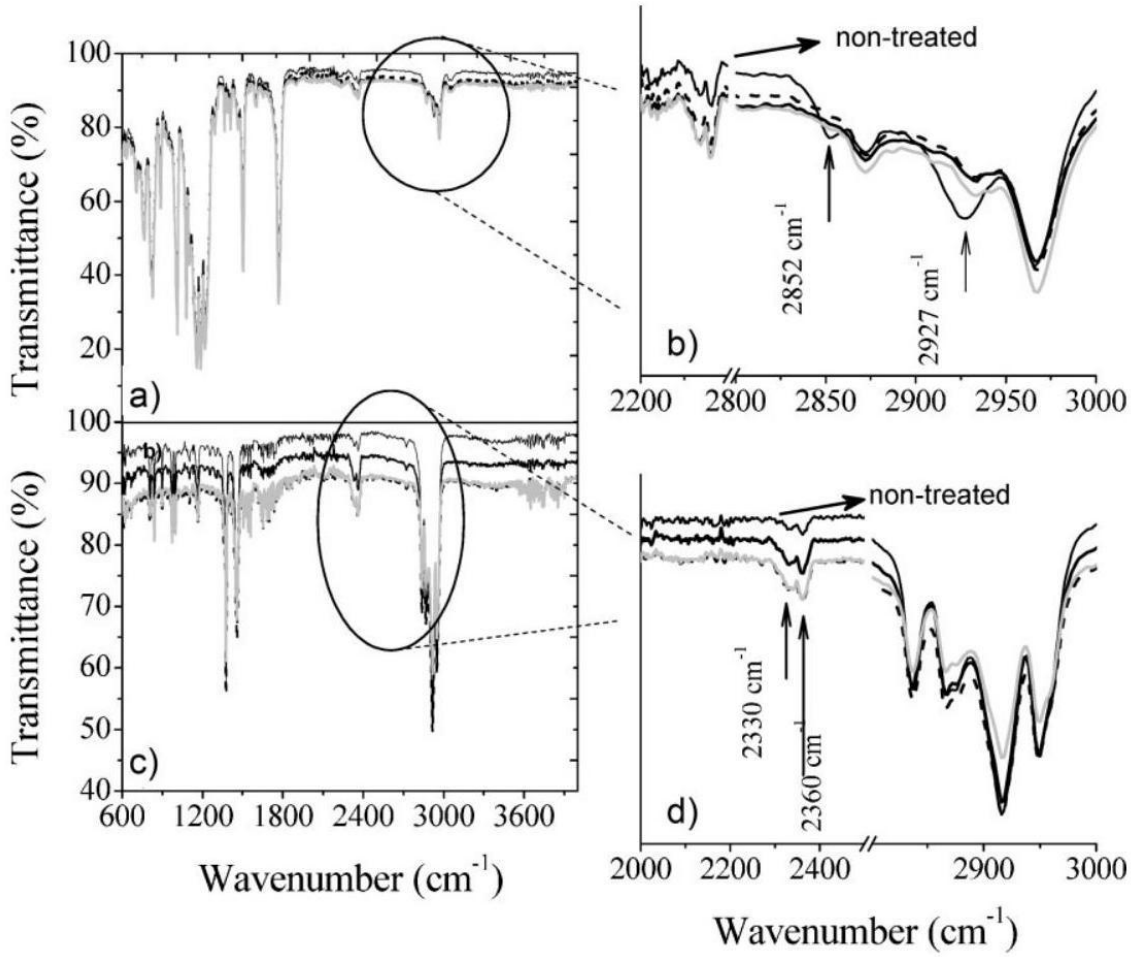

Figure 6. FTIR spectra of a) PC with b) detail, and c) PP with d) detail before and after $Ar + O_2$ plasma treatments.

lapped) to those obtained when the plasma treatments were done using only Ar, as seen on Figure 3. Even with a different treatment ($Ar + O_2$ plasma atmosphere), no significant changes were noticed. The spectra of both polymers (Figure 6a and Figure 6c)

do not show the presence of new peaks related to the formation of new chemical bonds with oxygen. The difference that can be observed on the magnified part ($2500 - 3000\ cm^{-1}$) of the spectra, correspondent to $C - H$ bonds, is a decrease of the peaks intensity. In the case of PC, the peak at $2852\ cm^{-1}$ present in the non-treated sample disappears after plasma treatment. In both cases, the decrease can be associated with scission of $C - H$ bonds under the conditions used. Since scission of $C - H$ bonds seems to occur, it would be expected to observe new bonds resulting from the reaction between the formed radical and the oxygen that was used in the plasma treatment. However, if new bonds were formed, the amount was very small because they could not be detected by FTIR. Results of roughness and CA of treated PP samples are plotted in Figure 5b. A noticeable increase of the CA values accompanied by a roughness decrease can be observed for samples treated both with Ar and O_2, a result very similar to the one displayed by PC.

To conclude, the effects of the $Ar + O_2$ treatment seem to be similar on PC and PP, except that they appear more visible in the case of PP, probably because of a lower initial CA, as Equation (1) implies, or because of the softer nature of
the PP structure. Concerning possible hydrophilicity changes, if they exist, they are small enough to be hidden by the roughness variation effects.

Simple Model of Surface Interaction of Plasma Treatments

Finally, and after the analysis of all previous results, it is possible to build a simple model capable of explaining the transformations suffered by the polymeric surfaces when submitted to several plasma treatment conditions. Figure 7 shows a schematics of what may occur when the plasma species collide with the surface of the studied polymers, illustrating the activation mechanisms referred above. At first, the surface morphology is modified due to the ionic bombardment that leads to the removal of any contaminants ("plasma cleaning") present at the surface, as well as to the modification/removal of the first layers of material ("plasma etching"). As seen before, hardness determines the magnitude of these changes. On the other hand, PP exhibits higher surface roughness variations due to the fact of being less hard (easier removal of material by ion bombardment) and more sensible to structural changes due to the temperature than PC. Anyway, it is important to emphasize that other important parameters worth particular attention for the change in a polymer surface characteristics. Among these, the contaminants (such as surface oxide layers) would play a fundamental role since the differences in bonding conditions would give rise to different roughness changes, or even sputtering yields of the surface elements of the polymer. In order to exclude these effects from the overall results, a careful control of the substrates quality was adopted during production. All PP and PC samples were produced under the same processing conditions, the same mould was used for both substrates and no mould release agent was used. The evolution of the CA with the roughness may be explained by the Wenzel's equation. The initial lack of sensitivity of the CA to the roughness variation may be ascribed to the CA values close to 90°. The 0.48 Pa (80 sccm) Ar treatment shows to be clearly effective in producing a significant contact angle decrease, what can only be ascribed to a chemical effect. This is observed in both samples. It is also important to correlate the gas flows/pressures with the changes that occurred on both polymers. As

seen in Figure 7, with increasing Ar flow rate/pressure, the amount of available

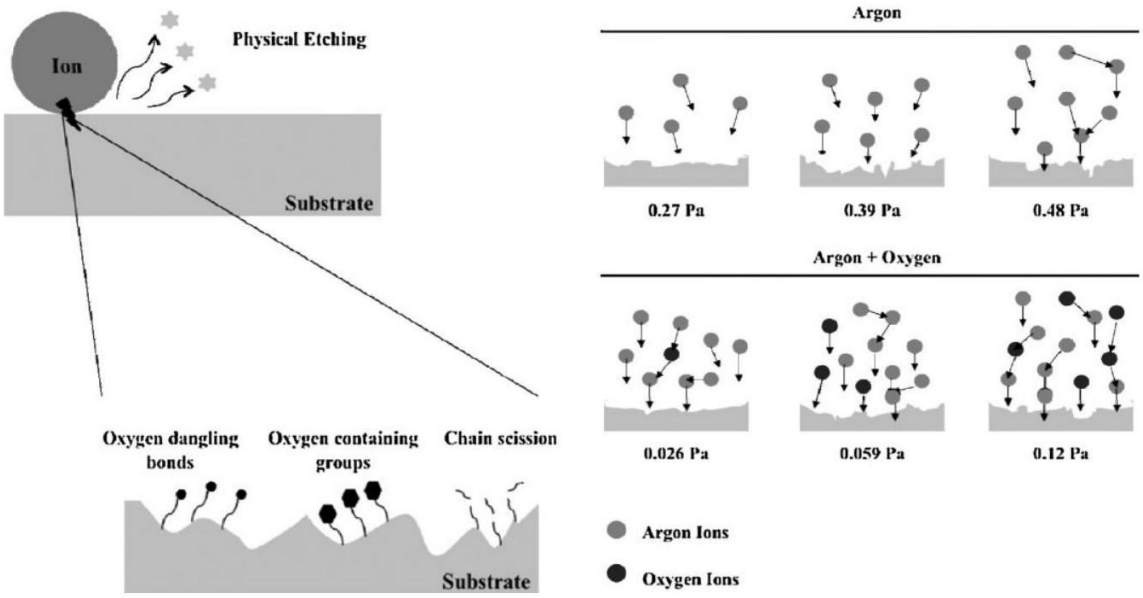

Figure 7. Model explaining several surface activation mechanisms and the influence of the reactive gas flow rate/pressure on roughness promotion.

ions to bombard the surface also increases until it reaches a saturation level (0.48 Pa – 80sccm, confirmed by the fact that using a 0.79 Pa – 90sccm Ar treatment, the changes are almost the same or even softer than at 0.48 Pa – 80sccm), beyond which there is a decrease of the surface roughness. This saturation has as a consequence the lowering of the mean free path of Ar ions, increasing the number of collisions and therefore decreasing the energy of the argon species that will hit the polymer surface. The CA, however, presents a global decreasing behavior. This fact indicates that the formation of new hydrophilic polar groups is somewhat promoted by the plasma treatments used, despite not being detected by FTIR (probably due to the small amount that may exist). One may conclude that lower CA are obtained with higher reactive gas flow rate/pressure, thus having a more pronounced activation of the polymer surface by mean of the several mechanisms explained above, mainly roughness evolution. Knowing that the combination of high roughness and low CA promotes good adhesion, [39] the PC and PP samples treated with 0.48 Pa (80 sccm) Ar, despite the small decrease of roughness comparing to 0.39 Pa (60 sccm) Ar treatment, are the most interesting ones so far. Referring to the Ar + O_2 treatments, it is possible to speculate that the saturation level reached at 0.48 Pa (80 sccm) will be also the key factor when oxygen is added. In this case, once again, fewer and fewer Ar and O_2 ions will be able to hit the surface with enough energy to remove material (and increase roughness) from a hard polymer such as PC (see Table 2). Again, CA evolution is regulated by the roughness changes. In opposition to the Ar atmosphere plasma treatments, oxygen additions lead to a decrease of this property, giving rise to a decrease of the CA values, as Wenzel predicts.

Thin Film Adhesion Behavior to the Treated Surfaces - Preliminary Results

As already mentioned, the main goal of the present work is related to polymeric surface modification/activation in order to allow their future functionalization with a metallic layer, towards the development of biomedical electrodes (EEG, ECG, etc.). To that end, a TiN_x coating was deposited on PC, as it was already shown by the authors to be a good solution from the chemical and mechanical points of view when deposited on titanium. [35] To test the adhesion degree of such thin film, the X-cut tape test (ASTM standard D 335908) was performed on each sample. Figure 8 presents the TiN_x coated PC sample: a) as deposited - treated with 0.48 Pa (80 sccm) Ar; b) after the X-cut - treated with 0.48 Pa (80 sccm) Ar (some cracks appear due to stress inflicted by the cut); c) after removal of the tape - treated with 0.48 Pa (80 sccm) Ar and d) after removal of the tape on the nonplasma treated sample. From these figures, it is possible to observe that there is a significant difference in the adhesion of the TiN_x samples from the treated to the non-treated sample, Figure 8c and d. This, and the aggressiveness of the tape test, are good empirical indications of the excellent adhesion of the film promoted by the Ar plasma treatment. By analyzing the interface of the X-cut, it is possible to claim that the adhesion level is quite good, being rated as 4 A (trace peeling or removal along incisions or at their intersection). Furthermore, the figure allows also detecting some cracking of the film (in both cases) on the borders of the X-cut (promoted by the stress induced by the cut itself). This result provides us a good indication about the possibility of using the Ar optimized plasma treatment for the functionalization of PC with a TiN_x conductive film.

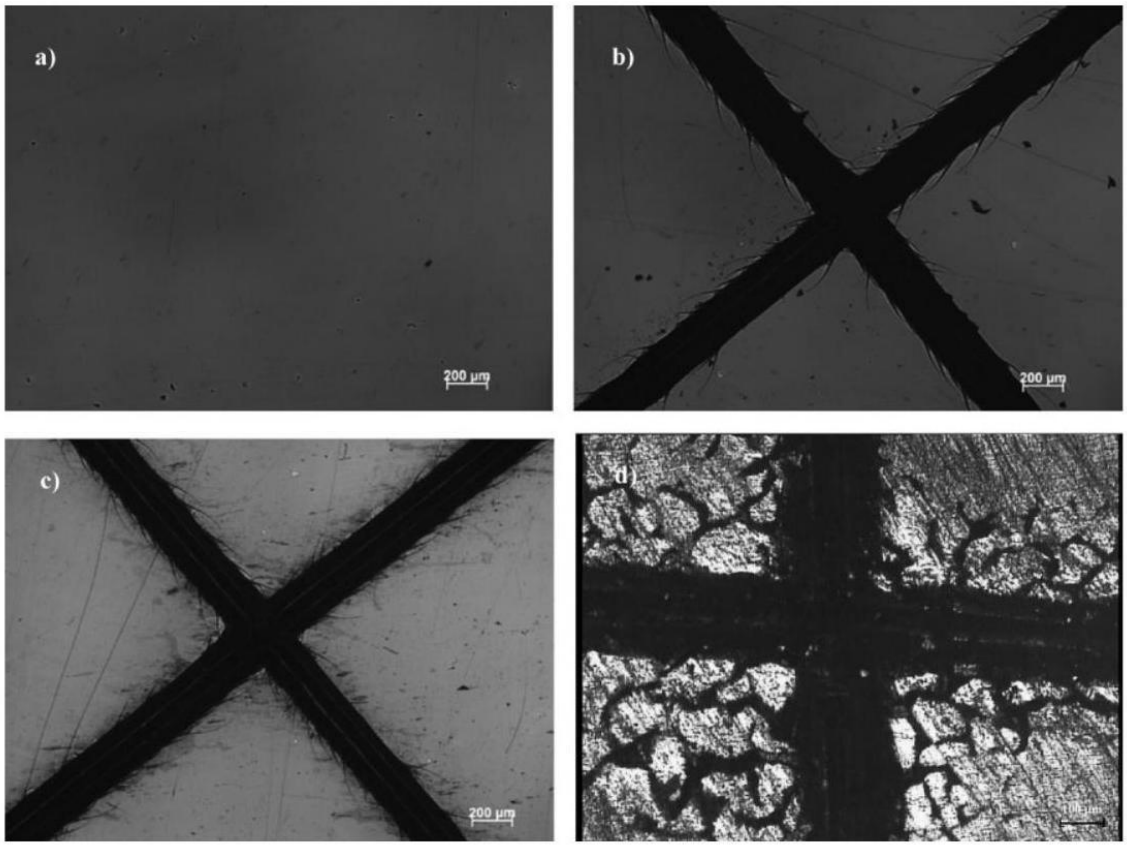

Figure 8. Surface aspect of the coated PC sample a) treated with 0.48 Pa(80sccm) Ar before the X-cut, b) after the X-cut, c) after removal of the tape, and d) without plasma treatment.

Conclusion

The effects of plasma treatments with argon and argon + oxygen mixtures on the surface properties of PC and PP were assessed by CA measurements, FTIR, X-ray analysis and AFM, aiming at activating the polymer surfaces for post-treatment functionalization with thin films. The lower argon pressures produce roughness changes, higher for PP than for PC, but only marginal CA changes for both polymers. A significant CA decrease is only achieved for an argon pressure of 0.48 Pa (80 sccm) for both PC and PP, for which the best activation results were achieved. For higher pressures (0.79 Pa – 90sccm), the morphologic and chemical effects on the surface seem to be reversed, probably due to excessive gas pressure that decreases the mean free path of the species and prevents them from reaching the surface with the energy necessary to produce measurable surface modifications. The addition of oxygen to argon didn't improve the surface activation results beyond those obtained with the 0.48 Pa (80 sccm) argon pressure for any of the polymers, probably due to the same reason. Both PC and PP display similar trends for the evolution of roughness and CA with the plasma treatment conditions, except that they appear magnified for PP probably due to the less hard and more temperature sensitive structure of PP. In order to confirm the benefits of the plasma activation treatment, 0.48 Pa (80 sccm) Ar treated and non-treated PC samples were used for the deposition of a TiN_x film. The adhesion tests performed on
both samples showed a much better adhesion of the TiN_x on the plasma-treated sample.

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