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Activation of polyethylene terephthalate using different plasma treatments

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In this work, several types of plasma treatments were performed on the surface of polyethylene terephthalate (PET) substrates. Experimental results show that an increase in contact angle is related to an increase in the average roughness. Contact angle values vary from 71 to 84º, with average roughness values ranging between 3.3 and 7.2 nm for different surface treatments. FTIR in mode of attenuated total reflection show that there were no significant chemical changes in the material, while XRD reveals that there are no detectable changes in the structure of the polymers. The stress-strain curves are similar to the material without treatment: linear up to about 8 % of strain, followed by a plastic deformation. The Young modulus, yielding stress and strain of the materials stay, regarding the experimental error, within the values obtained for the untreated polymer: 2.1 GPa, 109.4 MPa and 153.3 MPa, respectively. The adhesion of the titanium nitride (TiN) to the polymer is very strong, without any traces of film removal, despite the test method: ASTM-D3359-97 or peeling test at 90°. The set of results shows that the plasma treatments are effective in promoting adhesion of functional thin films, without any degradation of the polymer's base properties (chemical, structural or even mechanical ones).

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Keywords: Polymers, Plasma treatments, Surface modification

1. Introduction

Polymeric materials like polycarbonate (PC), polypropylene (PP) and polyethylene terephthalate (PET), among others, are increasingly replacing traditional engineering materials like steel and aluminium in the fabrication of secondary structures of aircraft, automobiles, railway coaches, and civil construction as well as in several biomedical applications. This is due to their superior properties like better corrosion resistance, high strength-to-weight ratio, relatively low cost and easy recycling [1–4]. However, polymers are innately hydrophobic, low surface energy materials, and thus giving rise to poor adhesion with other materials. A particularly noticeable example is the adhesion to thin films [1], which are becoming extremely attractive since it becomes possible to tailor the polymers surface to a set of desired properties. To overcome this undesirable drawback, recent developments in surface science have yielded robust techniques to control surface modifications of several types of polymers and to create structural features on the polymeric surfaces at micron and submicron levels [5-10]. A major class of these techniques is based on the creation of a stiff skin on the surface of the polymer and induces a strain mismatch between the created skin and a more compliant polymeric substrate. Examples of such techniques are oxidation, metal deposition and laser and plasma treatments [5–10]. Other approach is the formation of a nano-/micro-texture on the polymeric surfaces. In this sense, plasma etching processes have been reported to be effective to induce a texture on the micro/nano-scale of several polymers, among others, polydimethydisiloxane (PDMS) [11,12] and polyethylene (PE) [13] These methods are fast and easy when compared to lithographic approaches or deposition of structured coatings.

A particularly interesting polymer in modern technological applications is the polypropylene (PP). PP shows excellent mechanical properties, light weight and a high adaptability to complicated structures, thus being qualified for a broad range of applications, such as in the fields of coating, bonding, printing and metallization. For these applications, good adhesion between the polymer and a surface layer such as a lacquer or a metal film is required [1-3]. Another particularly interesting polymer in modern technological applications is polyethylene terephthalate (PET). PET is used in many technological fields for a wide variety of applications (packaging, decorative coatings, capacitors, magnetic tape, etc.) since it exhibits excellent bulk properties, such as crease resistance, solvent resistance, high melting point, resistance to fatigue and high tenacity either as a film or as a fibber [18]. However, bonding and finishing of many polymers, such as the deposition of a thin film to functionalize their surfaces, presents a problem due to the low hydrophilicity of their surfaces. It affects the wettability, printability, biocompatibility and adhesion. For this reason, polymer films require some additional treatment to raise the surface activity, for better wettability and adhesion properties. Acceptable adhesion between the final composite (polymer and the thin films) is essential to prepare high-strength laminates. PP has poor adhesion properties due to its non-polar nature and low surface energy [4,15]. For this reason and for many commercial applications it is necessary to modify their surfaces to increase the surface energy without changing the bulk properties.

Recently, research on the use of plasma treatments has grown in interest, since these processes are environmentally friendly and may give rise to a wide variety of modifications, thus opening a wide range of possible applications [13,15,16]. The glow discharge plasma treatment is a popular technique since it is a dry process and allows better uniformity in surface modification, and hence it can be widely used for industrial applications. The plasma acting mechanisms are very complex, but the main results obtained are surface cleaning, activation, cross linking, etching or, in most cases, a combination of the aforementioned effects [13]. Plasma promotes free radicals formation that can act as interlocking points for active species (polar groups) [17]. Furthermore, depending on the plasma forming gas and general conditions of the plasma treatment, it is possible to promote some surface etching/abrasion which can induce changes in surface topography, thus having a positive effect on wettability [17].

Taking all this into account, the main purpose of the present work consists on the modification/activation of PET surface, by using several different gas atmospheres, processing powers and treatment times in a PVD plasma reactor. After surface modification/activation, the polymeric substrates will be coated with different kinds of thin films aiming to obtain composites to be used in keypads and keyboards, wind electrical generators, position sensors, telephone dials, light deflectors, impact detectors, vibrating membranes, tactile sensors, respiratory sensors, etc.

2. Experimental details

Commercial polymer substrates of polyethylene terephthalate (PET) (Goodfellow LS305276) were used (dimensions $10\times30\times0.11$ mm^3). All plasma treatments were performed in a laboratory size unbalanced (type II) direct current (DC) magnetron sputtering system, where the samples are fixed on a rotating substrate holder placed in the centre of the reactor (vertical-like).

Four different sets of plasma treatment/activation experiments were carried out in the frame of this work. A first set of plasma treatments was carried out in a "pure" argon atmosphere, using four different gas flows: i) 45 sccm (corresponding to a total pressure of 2.7×10^{-1} Pa), ii) 60 sccm (3.9×10^{-1} Pa), iii) 75 sccm (4.8×10^{-1} Pa) and iv) 90 sccm (7.9×10^{-1} Pa). The treatment current (direct current, DC) was fixed at 0.5 A and the treatment time was also fixed at 300 s.

A second set of experiments was carried out aiming to extend the surface changes/activation procedures and thus to allow further and deeper analysis of the possibilities to enhance the adhesion of a particular coating material, which will be the final goal of the studied polymer material (PET). In this second set of experimental conditions, the polymeric surfaces were plasma treated using a fixed argon flow (75 sccm), but using three different approaches. In the first one, the treatment was carried out using three different direct current (DC) values applied to the substrates (fixed in a rotating – 7 rpm - metallic sample holder): i) 0.25 A, ii) 0.5 A and iii) 1 A. A second approach comprised the use of the same Ar flow (75 sccm) and a fixed DC current of 0.5 A, but using three different treatment times: i) 300s, ii) 600 s, and iii) 900 s.

Finally, in order to further explore the possibilities to change the polymers surface chemical activity and thus correlating these changes with the adhesion behaviour, a last set of experimental conditions were selected, where a reactive element was added to the plasma atmosphere: oxygen. For this last set of conditions, the plasma atmospheres were composed of the same argon flow as in the previous two sets (75 sccm), the same time and DC current (300 s and 0.5 A, respectively), but using three different oxygen flows: i) 4 sccm (corresponding to a partial pressure of 3.2×10^{-2} Pa), ii) 8 sccm (6.3×10^{-2} Pa), and iii) 12 sccm (9.4×10^{-2} Pa).

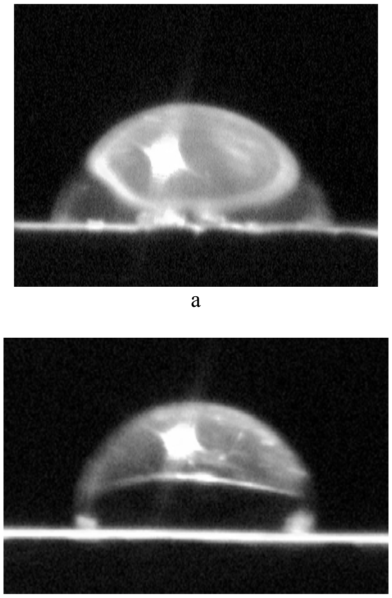
As it will be shown latter in this manuscript, the flow of 75 sccm Ar treatment promoted the most favourable changes, namely in what concerns high surface roughness and water contact angles, thus being selected for these two last sets of experiments. The base pressure before the plasma treatments was always below 2×10^{-4} Pa and the working pressure was included between 3×10^{-2} and 8×10^{-1} Pa (plasma on), depending on the treatment applied to the samples. There was no external heating of the samples, and the maximum temperature reached in the substrates holder was 55 ºC. A thermocouple was placed close to the surface of the substrate holder on plasma side (not in direct contact, since plasma treatments were done in rotation mode) and the temperature was measured immediately after stopping the discharge.

Measurements of the contact angle (CA) (sessile drop in dynamic mode) were performed in a Data Physics OCA 20 device using water as test liquid, and the measurements were set to a density of energy flow of ~250 W/m^2. All the micrographs were taken with the same focal distance (20 cm), and the volume of the drops was 20 μl. The surface roughness was assessed by AFM, carried out with a Pico Scan controller atomic force microscope, using the tapping mode. SEM images of the coatings were obtained by a NanoSEM FEI Nova 200 scanning microscopy. From the analysis of the images, the root mean roughness (Ra) and different topographic profiles measured on 50×50 μm^2 images were evaluated. To verify if the crystalline structure of the polymer changed during the plasma treatments/activation process, X-ray diffraction (XRD) experiments were conducted in a Philipps PW 1710 diffractometer, using Cu Kα radiation in Bragg-Brentano configuration. The chemical bonding features of the polymeric substrates were accessed by Fourier Transform Infrared (FTIR), working in ATR mode. For that, a Fourier Transform Infrared Perkin-Elmer Spectrum 100 spectrometer was used (500 to 4000 cm^{-1}), using non-polarized light, with a resolution of 4 cm^{-1}. In terms of mechanical properties, the PET samples were tested in uniaxial tension with a Shimadzu universal testing machine AG-IS -500N. Gauge length of 30 mm and widths of 10 mm were used with an operating crosshead speed of 1 mm/min.

3. Results and discussion

3. 1. Contact angle and morphology

The extent of hydrophilic modification of the plasma modified PET substrates was investigated by contact angle measurements. Contact angles can be measured by producing a drop of pure liquid on a solid, and represent a quantitative measure of the wetting of a solid by a liquid. The angle formed between the solid/liquid interface and the liquid/vapour interface, and which has a vertex where the three interfaces meet, is referred to as the contact angle. As an example, Fig 1 shows a drop of pure water used in the evaluation of the CA on one of the treated samples. The figure shows the good spreading of the liquid (wets well) in untreated PET, Fig. 1a), which will result in low values for the CA of the sample, while Fig. 1b) shows that after oxygen treatment, the sample exhibits poor wetting conditions, which is expected to result in higher values of the CA.


a

b

Fig. 1. Evaluation of the CA on PET: a) untreated substrates and b) oxygen plasma treated substrates.

Fig. 2 shows the variation of the contact angle of the PET substrates for the different treatments performed in this work. The first general observation is that the contact angle value, which was about 74.6º for non-treated samples, tends to increase for all of the applied treatments. Though this tendency is particularly noticeable in the treatments where oxygen was added to the plasma atmosphere, as evidenced before by Fig. 1. In fact, for all other treatments the values of the CA remain relatively stable, and a slight increase is only observed for the highest values of the varying parameter (argon flow, DC current and treatment time).

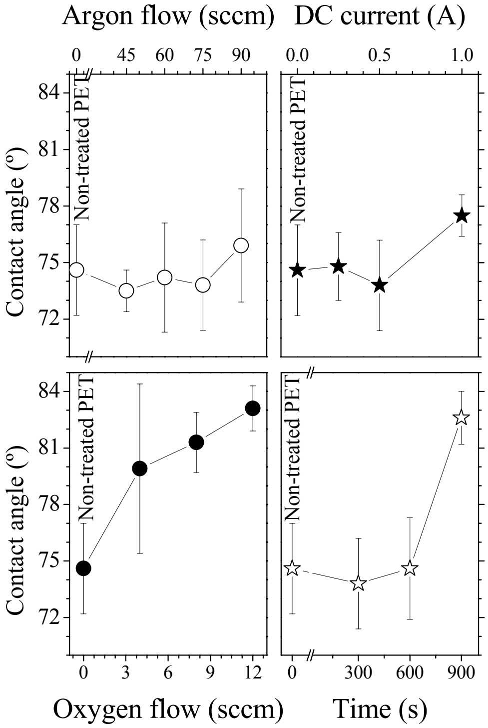


Fig. 2. Evolution of the PET CA concerning several plasma treatments.

The highest increase of the CA value was observed for treatments that involved the use of oxygen in the plasma atmosphere and also in those involving different treatment times. Under these two types of conditions, the CA increased from the initial value of 74.6º towards 84º. For treatments with argon and with variation of the applied DC current, the CA do not change significantly, varying only for the last treatments (using 90 sccm of argon and a DC current of 1 A).

According to Yang et al. [18], properties such as wettability, adhesion, printability, etc., strongly depend upon the surface free energy. A decrease of contact angle indicates that the plasma treatments are promoting some decrease of the polymers surface hidrophobicity and consequently an increase in their hydrophilic nature. This change in the CA values may result from the formation of new hydrophilic polar groups and/or surface topological modifications on the polymer surface, which changes their physical/chemical properties [17,19-21]. Pandiyaraj et al. [17] explained exhaustively the treatment/activation mechanism, claiming that it was resulting from the creation of new reactive functional groups that were induced on the polymer surface by plasma action. This was obtained due to polymer chain scission or hydrogen abstraction by bombardment of plasma species [17]. The active sites that are created can then bind to other reactive elements, namely oxygen [20]. Wenzels and co-workers [22], explained that, in many cases, the wettability also depends on the surface roughness [22], according to:

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

Wenzels introduced the roughness factor *r* into the Young's equation, $\gamma_{lv}\cos\theta = \gamma_{sv} - \gamma_{sl}$, arguing that in case of solid surfaces, the interfacial tension γ_{SV} and γ_{SL} should not be referred to the geometric area, but to the actual surface area. Based on the Wenzels equation it can be predicted that roughness should have a major effect on CA and hence on surface wettability [22]. In fact, in the present study one cannot un-doubtfully conclude that the increase of CA is the result of changes in the chemical environment at the polymer's surface that may be induced by the interaction of energetic species that bombard it (incorporation of different chemical groups – polar/non-polar, among others - on the PET surface), or if this increase is due solely to the change in the polymers surface morphology, namely in what concerns the changes in its roughness, promoted by the same energetic bombardment. In fact, it is known that PET is polar and bombardment of its surface with oxygen, for instance, may increase the polar groups that would decrease the CA value. The effect of the surface roughness bombarded with gas, oxygen or argon, causes an increase of cavities and this perhaps causes an augment in the CA values, making the surface of PET more hydrophobic.

Fig. 3a) shows the surface topography of untreated PET, while Fig. 3b-d) shows the evolution of the PET surface morphology with increasing time. Fig. 4a-d) shows the evolution of topography with increasing oxygen flow. As shown in Fig. 3a), the surface of the non-treated PET sample presents some scratches, which result from the manufacturing process. The scratches are recursive in Fig. 3b) and Fig. 4a), but disappear completely in Fig. 3c-d) and Fig 4b-d). Several sharp peaks (also called protrudes), most of them rather small in height, appear when the scratches disappear. The number of protrudes is reduced in the first treatments and increased significantly with the treatment of 8 sccm oxygen. This treatment seems to promote the highest roughness value and exhibits a significant increase in the number of protrudes, which appear to promote the desired increase in roughness, comparing with the non-treated sample. In fact, the treatment illustrated in this AFM image (8 sccm oxygen) seems to be the one that leads to the highest change in surface morphology.

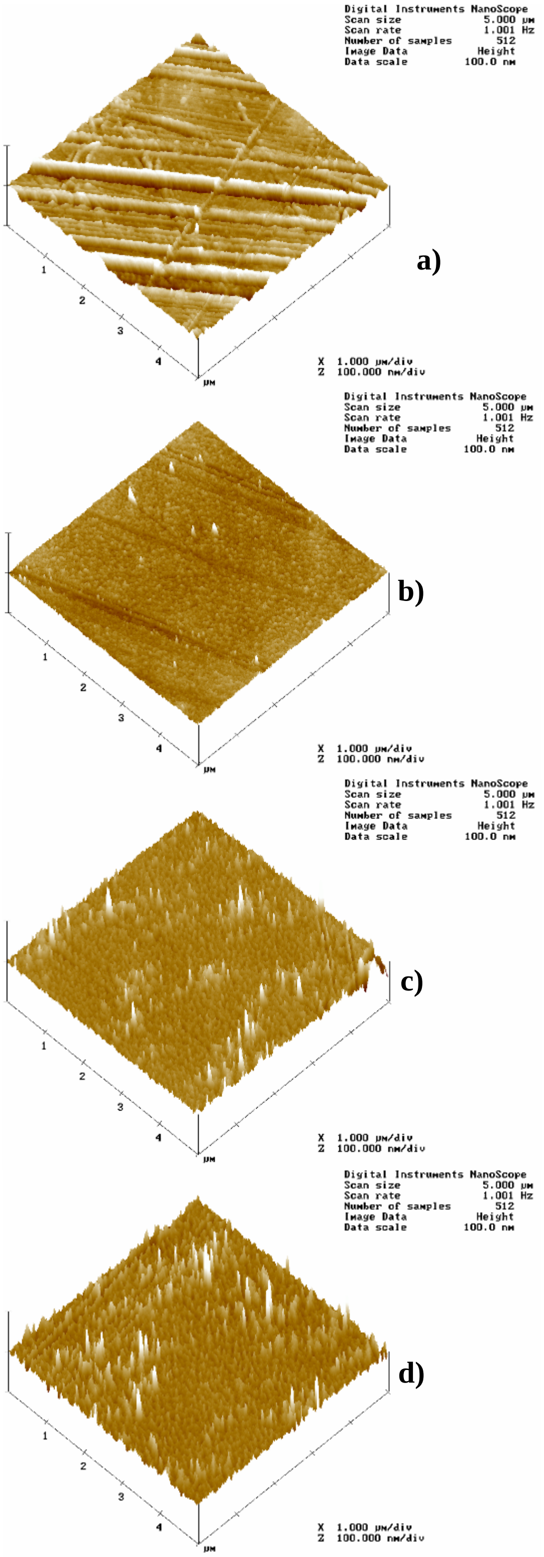


Fig. 3. AFM topographic images of plasma treated PET film surface with different exposure times: a) untreated; b) 5 min.; c) 10 min and d) 15 min.

Contrary to what was expected, the treatment with the higher oxygen flow rate does not exhibit the highest roughness values, presenting areas with major protrudes but also showing more smooth areas.

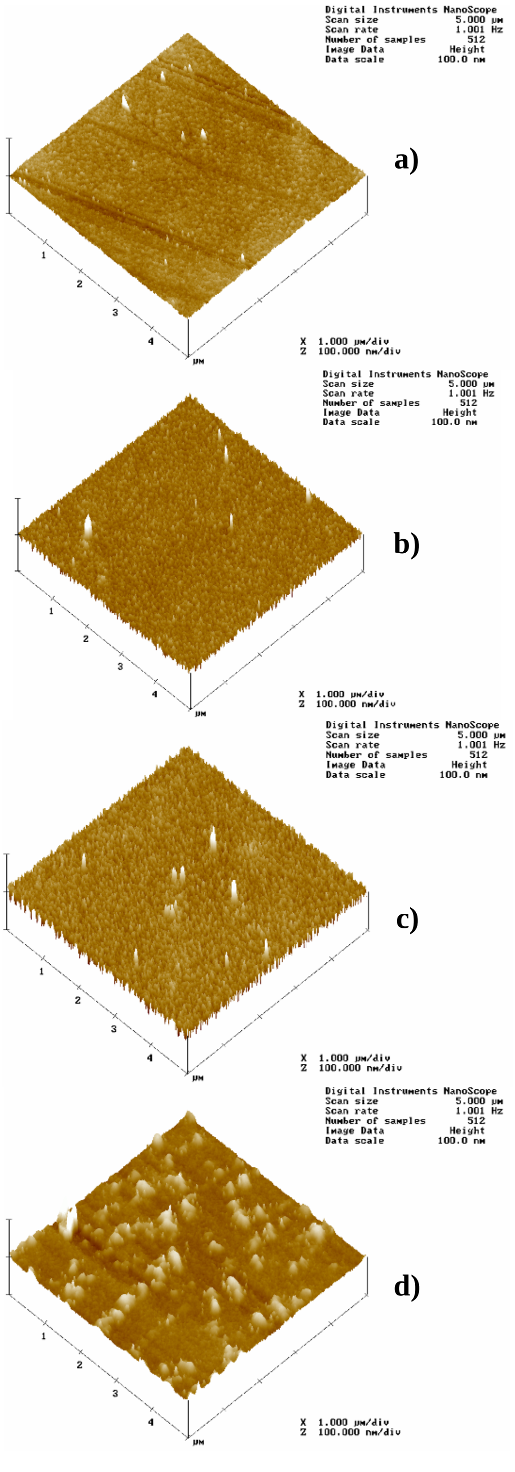


Fig. 4. AFM topographic images of plasma treated PET film surface with different flows of O_2: a) 0 sccm; b) 4 sccm; c) 8 sccm and d) 12 sccm.

The absolute surface roughness values (Ra), obtained from the AFM analysis are presented in Fig. 5.

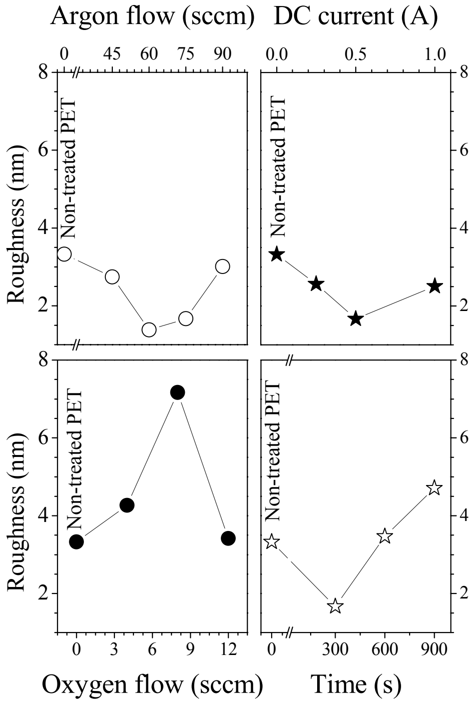


Fig. 5. Evolution of roughness with different, argon and oxygen flows, DC currents and exposure times.

The roughness was about 3.3 nm for the non-treated samples and it decreases with the treatments using argon and DC current and increases to the maximum the 7.2 nm for the treatment with oxygen, before recovering to the same values of the untreated PET. For treatments using different times, the roughness decreases to the minimum of 1.7 nm and then increases to a maximum of 4.7 nm. Comparing the surface roughness evolution (Fig. 5) and that of the CA (Fig. 2), it is possible to observe that for a global increase of the CA values there is an associated global increase of the surface roughness.

On the other hand, the relation between PET surface roughness and CA values is simpler: regarding the evolution of the CA, it can considered that the CA is not severely affected by the first two Ar and DC current plasma treatments like the surface roughness. On the other hand, the CA rapid increase for treatments using and different exposure times is correlated to the highest rugged for the same treatments.

It is clear that when the reactive gas ions collide with the polymer surface, the latter is modified due to the ionic bombardment (Fig. 3-4). This ionic bombardment lead to the removal of the first layers of material ("plasma etching") and contaminants ("plasma cleaning") present at the surface. This and other phenomena that may occur will be determinant for the subsequent polymer surface processes, including the adhesion of a certain type of coating. It is also important to correlate the reactive gas flows/pressures with the changes that occurred. With increasing Ar flow rate/pressure the amount of available ions to bombard the surface also increases until it reaches a saturation level leading to a decrease of the surface roughness, Fig. 5.

Surface chemical modifications were studied by FTIR in reflectance mode. Non-treated PET films were exhaustively studied by Nasef and co-workers [21], which associated the appearance of strong bands at 1740 and 730 cm^{-1}, representing the stretching vibration of the $C{=}O{-}O^{-}$ (ester group), and the absorption bands at 2872 and 2951 cm^{-1}, representing the symmetric and the asymmetric stretching vibration of the CH_2 group of ethylene, respectively, as depicted from the spectrum [21]. The presence of the benzene ring in the PET films is established by the =C–H stretching vibration at 3049 cm^{-1} and the skeletal C=C in-plane stretching vibrations at 1503 and 1598 cm^{-1}, respectively [21]. Figure 6 shows the FITR spectra of PET films having various flows of the oxygen. Comparing all spectra, one can say that after the oxygen treatment it not possible to detect the presence of new bands or the absence of the existing ones, which means that, if any chemical changes occurred at the polymer surface, its amount was not enough to be detected by this technique.

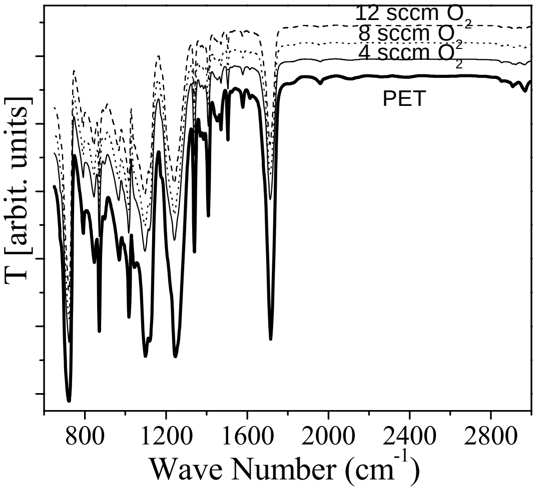


Fig. 6. FITR spectra of PET substrates treated with different oxygen flow rates in the gas atmosphere.

The apparent contact angle of a sessile droplet varies not only with physical texture or the roughness, as previous seen, but also with the chemical texture determined by the composition of the solid surface. The CA, however, presented a global increasing behaviour. This fact indicates that the formation of new hydrophobic groups is actively promoted by the plasma treatments used. One can conclude that higher CA are obtained with higher reactive gas flow rate or higher treatment times, and this change is maybe promoted by a more pronounced activation of the polymer surface by mean of the several mechanisms explained above.

To note that, during the treatment/activation phase, there was a slight temperature increase in the polymeric substrates (an increase from RT to about 55 ºC was commonly observed). This increase in temperature, together whit the bombardment itself might also have influence on the polymers structure. To clarify if the changes are due to chemical factors and not variations of crystallinity, a series of XRD experiments were carried out. Fig. 7 illustrates the X-ray diffractograms of the untreated and plasma treated (for the different oxygen flows used) PET film surfaces. It is clearly seen that there is no significant changes in shape and position of the diffraction peaks, except that the peak around 26º is more intense for the treated samples, indicating that a relatively higher degree of crystallinity of the PET film surface may have been developed after the plasma treatment.

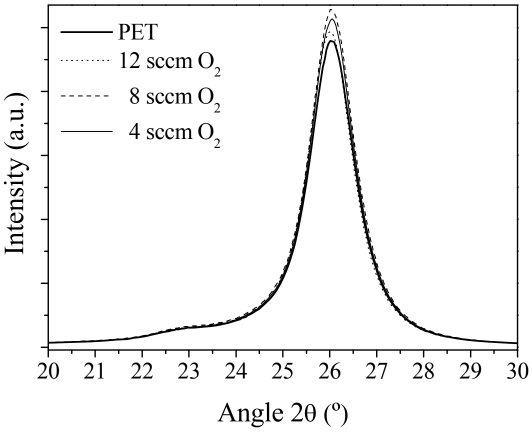


Fig. 7. Diffractograms of non-treated and Ar + O_2 plasma treated PET surfaces.

3. 2. Mechanical properties

Quasi-static mechanical measurements were performed in all samples in order to check if the plasma treatments resulted in any significant changes in the mechanical performance of the polymers. Independently of the surface treatment, all curves show a behaviour similar to the one of the pure material: a stress-strain linear region corresponding to the elastic behaviour of the material up to deformations of 8 %, followed by yielding and the plastic region of the polymer. The Young modulus, yielding stress and strain of the materials stay, regarding experimental error, within the values obtained for the untreated polymer: 2.1, 109.4 and 153.3 MPa respectively (Fig. 8).

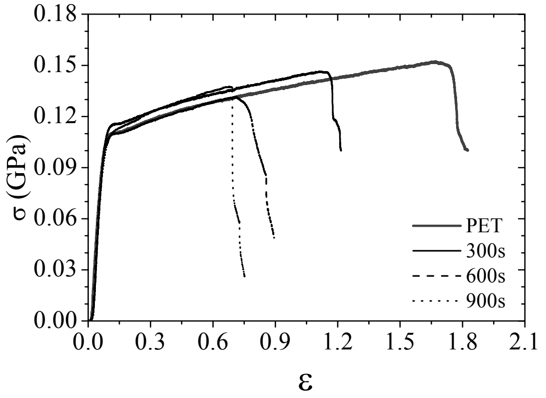


Fig. 8. Mechanical responses of non-treated and plasma treated PET substrates.

On the other hand, the maximum stress and strain progressively decrease by increasing the different surface treatments (Fig. 8). The fact that the samples break close to the clamps and not at the middle of the stretched samples indicate that increasing surface treatment produce increasing surface defects and earlier breakdown strains: during the stretching process and for large deformations and stresses, propagate along the sample thickness due to the conjugation of the compression and stretching forces existing in the clamps region. It can be concluded from the measured quasi-static mechanical response that the different treatments effectively affect just the surface of the samples with no relevant effect on the bulk mechanical properties of the polymer.

3. 3. Coated samples

In order to extend the range of possible applications, the optimal treatments in the early stages of this work were also applied to PVDF and PC. By using the upper discussed plasma treatments in these two polymers, a set of potential applications may arise, especially in what concerns to sensors on flexible platforms. The preparation of coated samples was performed in two distinct steps. The first step consisted in the treatment/modification of the polymers surface, selecting the plasma treatment that resulted in the most significant changes, i.e., the argon flow was fixed at 75 sccm, the exposure time was 900 s the current was 1 A. The second step consisted in the deposition of a TiN film, using a nitrogen flow of 5 sccm and a dc current of 1.5 A (75 A/m^2) in the Ti target. The used argon flow rate was 60 sccm [23]. The film was approximately 300 nm thick. This set of conditions is related with an optimization process that was carried out in a previous work [23]. The selected film conditions were intended to give rise to a stoichiometric TiN thin film, with a relatively low resistivity (in the order of tens or few hundred μΩ.cm) and high density.

To quantify the adhesion of TiN film on the polymeric substrates, two methods were used: i) the peeling test, Fig. 9a); and ii) the ASTM - D3359 – 97 test, Fig. 9b). The results of both test methods showed that the adhesion of the film to the polymeric substrates is very strong, in comparison to the untreated surfaces, where a clear removal of the film was observed.

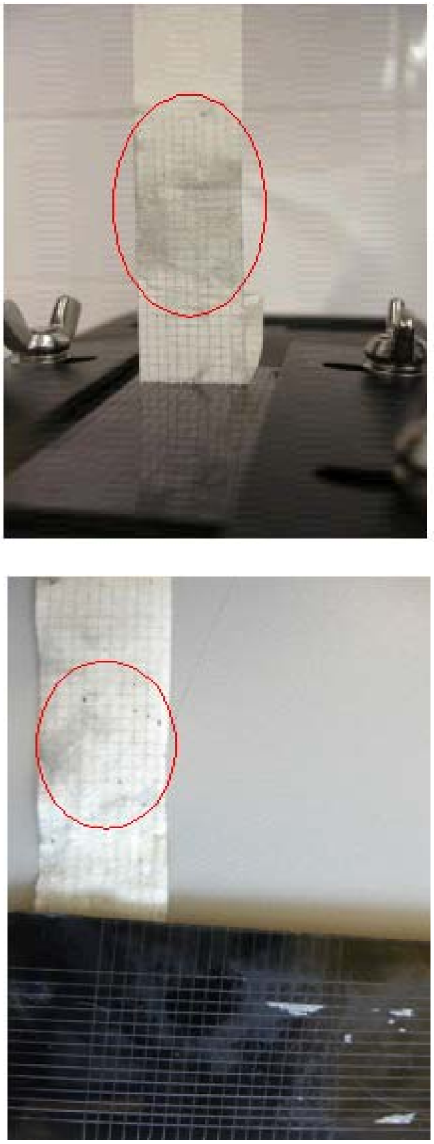


Fig. 9. TiN/PET adhesion test by the: a) the peeling test (θ = 90 º) and b) the ASTM - D3359–97 test.

Although the adhesion of the TiN film to the polymer is qualitatively high by using the surface plasma treatments, there is also another point that is worth mention: the different morphologies observed in the thin films surface, deposited in the treated and non-treated polymers (both depositions in the same batch). The obtained results show the development of mirror-like aspect (clean and undamaged) on plasma treated polymers, Fig. 10a), while a surface with a significant amount of defects is obtained when coating untreated polymers, Fig. 10 b).

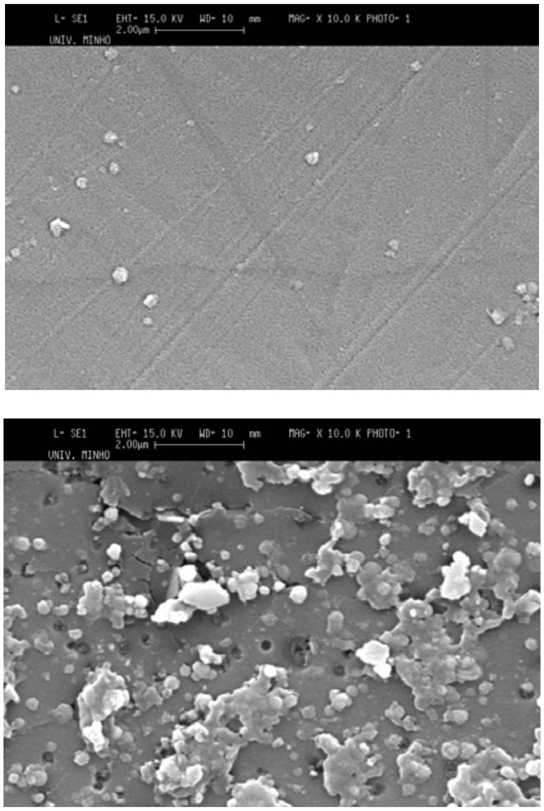


Fig. 10. SEM micrographs of TiN films deposited on: a) plasma treated PC and; b) non-treated PC substrates.

This result shows that beyond the much better adhesion that is obtained when coating plasma-treated polymers, there is also a significant effect on the quality of the deposited films. This improved quality is, as in the case of adhesion, the direct result of the plasma treatments, which led to a clear homogenization and cleaning of the polymers surface by removal of the majority of the surface defects.

4. Conclusions

It is clear that when the reactive gas ions collide with the surface of the studied polymers the surface morphology is modified due to the ionic bombardment. Moreover, the highest increases of the CAs were observed for treatments that involved the use of oxygen in the plasma atmosphere, but also in those involving different treatment times. Using these two types of conditions, the CA increased from the initial value of 74.6º towards 84º. For treatments with argon and with variation of the applied DC current, the CA does not change significantly. In fact, the CA increased only for the last treatment, using 90 sccm argon and a DC current of 1 A.

Comparing the surface roughness evolution and that of the CA, it is possible to claim that for a global increase of the CA values there is an associated global increase of the surface roughness. The changes are due to chemical factors and not variations of crystallinity. It is clearly seen that there are no significant changes in shape and position of the diffraction peaks, except that the peak around 26º is more intense for the treated samples, indicating that a relatively higher degree of crystallinity of the PET film surface may have been developed after the plasma treatment.

Independently of the surface treatment, it can be concluded from the measured quasi-static mechanical response that the different treatments effectively affect just the surface of the samples with no relevant effect on the bulk mechanical properties of the polymer.

The adhesion of the polymers to the thin films improves significantly when using surface plasma-based treatments. Another important point is related with the different morphologies observed in the deposited thin films surface. Results show that beyond better adhesion behaviour, plasma treatments of polymers surfaces result in an improved quality of the deposited films. The good adhesion is thus explained by the almost defect-free surfaces obtained after the plasma treatments, which, after coating, exhibit smoother surfaces.

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References

[1] G. Akovali, Z. M. O. Rzaev, D.H. .Mamedov, J. Appl. Polym. Sci., **58**, 645 (1995).
[2] D. S. Bag, V. P. Kumar, S. Maiti J. Appl. Polym. Sci., **71**, 1041 (1999).
[3] M. R. Sanchis, V. Blanes, M. Blanes, D. Garcia, R. Balart, Eur. Polym. J. **42**, 1558 (2006).
[4] M. Firedman, G. Walsh, Polym. Eng. Sci. **42**, 1756 (2002).
[5] C. M. Stafford, C. Harrison, K.L. Beers, A. Karim, E. J. Amis, M. R. Vanlandingham, H. Kim, W. Volksen, R. D. Miller, E.E. Simonyi, Nat. Mater., **3**, 545 (2004).
[6] M. M. Stevens, J. H. George, Science, **310**, 1135 (2005).
[7] Z. Ma, Z. Mao, C. Gao, Colloids Surf. B Biointerfaces, **60**, 137 (2007).
[8] M.-W. Moon, S.H. Lee, J.-Y. Sun, K.H. Oh, A. Vaziri, J.W. Hutchinson, Proc. Natl. Acad. Sci. USA, **104**, 1130 (2007).
[9] M.-W. Moon, S.H. Lee, J.-Y. Sun, K.H. Oh, A. Vaziri, J.W. Hutchinson, Scripta Mater., **57**, 747 (2007).
[10] J. Genzer, J. Groenewold, Soft Matter, **2**(4), 310 (2006).
[11] A.D. Tserepi, M.-E. Vlachopoulou, E. Gogolides, Nanotechnology, **17**, 3977 (2006).

[12] K. Tsougeni, A. Tserepi, G. Boulousis, V. Constantoudis, E. Gogolides, Plasma Process. Polym. **4**, 398 (2007).
[13] I. Gancarz, G. Pozniak, M. Bryjak, Eur. Polym. J. **36**, 1563 (2000).
[14] J. Behnisch, A. Hollander, H. Zimmermann, J. Appl. Polym. Sci. **49**, 117 (1993).
[15] Y. Zhao, S. Tang, S.W. Myung, N. Lu, H.S. Choi, Polym. Test. **25**, 327 (2006).
[16] J. Lai, B. Sunderland, J. Xue, S. Yan, W. Zhao, M. Folkard, B.D. Michael, Y. Wang, Appl. Surf. Sci. **252**, 3375 (2006).
[17] R. Molina, P. Erra, L. Julia, E. Bertran, Text. Res. J. **73**, 955 (2003).
[18] L. Yang, J. Chen, Y. Guo, Z. Zhang, Appl. Surf. Sci. **255**, 4446 (2009).
[19] K. N. Pandiyaraj, V. Selvarajan, R.R. Deshmukh, M. Bousmina Surf. Coat. Technol. **202**, 4218 (2008).
[20] K. Pandiyaraj, V. Selvarajan, R.R. Deshmukh, C. Gao, Vacuum, **83**, 332 (2009).
[21] M. M. NASEF, J. Appl. Polym. Sci. **84**, 1949 (2002).
[22] R. N. Wenzel, Ind. Eng. Chem. **28**, 988 (1936).
[23] L.T. Cunha, P. Pedrosa, C.J. Tavares, E. Alves, F. Vaz, C. Fonseca, Electrochimica Acta **55**, 59 (2009).

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