Plasma Surface Activation and TiN Coating of a TPV Substrate for Biomedical Applications

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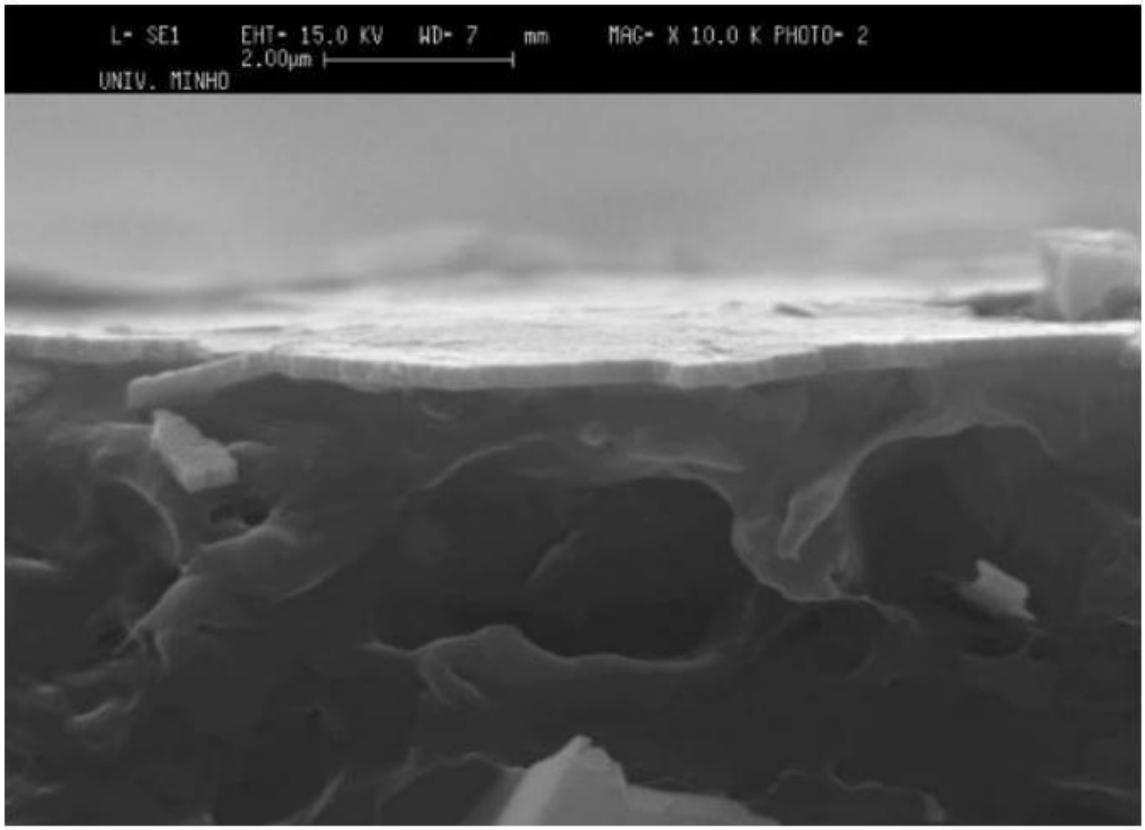
A thermoplastic vulcanizate (TPV) substrate was coated with a thin conductive film of titanium nitride (TiN), by dc reactive sputtering, aiming to develop polymer-based electrodes for bio-signal acquisition, namely for electroencephalographic (EEG) and electrocardiographic (ECG) applications. After the preparation process, TPVs were characterized in terms of their mechanical and surface properties. A detailed experimental protocol was followed in order to improve the adhesion of the film, consisting of a three-stage plasma treatment in an argon atmosphere. The electrochemical properties of the coated samples were studied in synthetic sweat solutions by open circuit potential (OCP) measurements and electrochemical impedance spectroscopy (EIS). The results showed that the surface plasma treated TPV with a 60% EPDM and 40% PP composition coated with a nanometric TiN film exhibited good mechanical properties and electrochemical behavior, according to the main requirements of an electrode to be used in common EEG and ECG exams.



Introduction

The rapid advancement of medical technologies over the last decades has contributed to significantly improve the

quality of medical care, but the financial charge over the health systems has also substantially increased. An important decrease of the health care cost could be achieved if part of the exams could be performed at the patient home. To that end, the contribution of engineers and physicians should focus on the development of reliable, portable, and easy-to-handle devices. Electroencephalographic (EEG) and electrocardiographic (ECG) are just two examples of exams that could be easily carried out by the own patient if plug-and-play electrode-systems were available.

The gold standard for electrophysiological signal recording is the silver/silver chloride (Ag/AgCl), due to its good signal stability and reproducibility. Nevertheless, to reduce the impedance at the electrode/skin interface the application of these electrodes require a previous skin preparation and the application of a gel between the electrode and skin. These operations are time consuming and require the participation of a trained technician, among other disadvantages.

A possible alternative would be the dry electrodes, which dispense with the use of gel paste or skin preparation,
relying exclusively on the skin/electrode mechanical contact. [1−3] Therefore, this kind of electrodes would be particularly suitable for the design of a plug-and-play system. The authors developed and tested titanium nitride (TiN) coated titanium (Ti) sensors whose

performance for EEG recording in human volunteers proved to be similar to that of the Ag/AgCl electrodes. [4]Ti and TiN were selected due to their biocompatibility, electrical conductivity, and electrochemical resistance in contact with synthetic sweat. [1,5–7] Furthermore, TiN has excellent mechanical properties, namely in what concerns wearing resistance. [8] However, the utilization of Ti substrates has some disadvantages, namely its weight (density), cost, and the rigidity, that does not let the electrode adapt to the skin, becoming uncomfortable to the patient.

Thus, it would be convenient to develop a low cost, flexible, easy-to-process, and functional sensor based on a polymeric material. Thermoplastic vulcanizates (TPVs) are potential candidates for this application due to their biocompatibility, low density, and tunable flexibility, easiness of processing, and low cost. Among TPVs, those based on polypropylene/ethylene-propylene-diene rubber (PP/EPDM) blends with high amounts of EPDM display the highest flexibilities. [9–11]

TiN films display excellent properties for the coating of the TPV. However, like most polymeric materials, TPVs have a very low surface energy, making TiN/polymer adhesion a challenging problem. Plasma treatments have been successfully used in these cases to activate polymeric surfaces. [12–15] Several studies showed that plasma treatments in argon atmosphere substantially increased polymer surface energy and roughness and enabled the formation of reactive radical species, [16–20] while the use of different gases (air, Ar/H_2O and Ar/C_2H_5OH) demonstrated that after treatment, the surface energy increased due to the formation of surface polar groups. [17]

There are also studies where EPDM samples were subjected to plasma treatments in various atmospheres (O_2/Ar, N_2/Ar, and $N_2/H_2/Ar$), which favored the increase of surface energy, as well as roughness. [18] On the other hand, recent studies on the application of TiN thin films on polymeric substrates using different parameters, both for plasma treatment and for film deposition, showed good adhesion of the film to the substrate. [19,20]

The present work aims to develop a new sensor based on a TiN film applied on a flexible TPV substrate. The plasma treated TPVs were characterized from the morphological and chemical points of view and compared with the original polymer. The TiN coating was assessed for adhesion to the TPV substrate and its electrochemical behavior was studied in contact with synthetic sweat. At the end, a well adherent and chemically stable TiN thin film was successfully obtained on the plasma treated TPV substrate.

Experimental Section

Materials

The EPDM rubber (K2340A: 53wt. −% ethylene and 6wt. −% ENB; Mooney viscosity (1 + 4) at 125°C: 25) used in this study was supplied by DSM Elastomers BV. The thermoplastic phase used, isotatic PP homopolymer, with melt flow index of 47 g/10 min at 230°C/2.16 kg was supplied by Sabic Europe. Octylphenolformaldehyde resin (SP1045, Schenectady International, USA) called resol in this work, stannous chloride and zinc oxide (Aldrich) were used as the crosslinking system. Irganox 1076 from Aldrich was used as a stabilizer.

A 60/40 w/w EPDM/PP TPV was prepared using a resol crosslinker (5 parts per hundred rubber, phr) and a combination of $SnCl_2 \cdot 2H_2O$(1.5phr) and ZnO(1.8phr) as activators. Irganox 1076 was used at 0.25wt.−%, relative to the total amount of polymers (EPDM and PP).

Thermoplastic Vulcanizate (TPV) Preparation

The TPV was prepared in a HAAKE POLYLAB OS RheoDrive 6 mixer of Thermo Electron Corporation. The rotor speed was 80 rpm and the set temperature was 200°C. The mixing sequence involved introducing the PP into the hot mixer. After melting the PP, the stabilizer (Irganox 1076) was added (0.25w/w relative to the total polymer mass), and finally the EPDM rubber was incorporated. The torque reached a constant value after about 4 min , indicating that a homogenous melt was formed. Samples were collected after an additional 5 min mixing. From the prepared material, rectangular samples of $20 \times 50 \times 1$ mm^3 were prepared by compression molding. These samples were further characterized and used as substrates.

Plasma Treatment/Thin Films Deposition

All the plasma treatments were performed in a laboratory size unbalanced (type II) direct current (dc) magnetron sputtering system, with a current density of 25 $A \cdot m^{-2}$, during 900 s . The argon (Ar) partial pressure was 0.48 Pa (80 sccm). The base pressure in the reactor was always in the order of 10^{-4} Pa and the target to substrate distance set at 70 mm . During plasma treatments, the discharge voltage on the substrates was around 400 V . During the film deposition, the target voltage was around 425 V . The titanium nitride (TiN) films were deposited on the plasma treated polymer substrates, according to previous optimization by the authors. [1] The thin film depositions were carried out immediately after the plasma treatments, without subjecting them to atmospheric contact. In order to check the consistency of the plasma treatments, the same TiN film was deposited on non-treated and treated PC polymer substrates, according to previous optimization by the authors. [1] The film, $TiN_\chi (x \approx 1)$, was prepared with the substrate holder positioned at 70 mm from the target, using a dc current density of 75 $A \cdot m^{-2}$ on the titanium target (99.6 at.-% purity). Agas atmosphere of $Ar + N_2$ was used. The Ar flow was set at 60 sccm (partial pressure of 0.4 Pa) and the N_2 flow was set at 5 sccm (partial pressure of 0.08 Pa). No substrate bias voltage or temperature was applied. During the plasma treatments and the film deposition, the
substrate temperature was monitored through a temperature sensor placed near to the substrate surface, to guarantee that the samples were maintained below melting point. The maximum temperature that the samples reached was about 60°C.

Characterization Techniques

The EPDM crosslinking degree was characterized by gel content determination by extraction in cyclohexane at room temperature. Approximately 200 mg of each TPV sample were weighed and then immersed in cyclohexane for 48 h ; the cyclohexane was refreshed after 24 h . After drying the sample in a vacuum oven at 100°C for 12 h , the weight was determined. The EPDM gel content was calculated assuming that the residue consists of insoluble PP, ZnO, resol, $SnCl_2$, and crosslinked EPDM.

Thermoplastic vulcanizate (TPV) mechanical properties were characterized by tensile, hardness, and adhesion tests. Tensile tests were carried out according to ASTM D638 and performed in Zwick/Roell Z005 equipment at room temperature with a speed of $50\ \text{mm} \cdot\ \text{min}^{-1}$ and a load cell of 5 kN . The hardness of the substrates was determined in a Bareeis hardness indenter (Hardness Shore A and D) using the procedure based on ASTM D2240.

In order to perform comparative analysis of the coatings adhesion an empirical adhesion test of the TiN coated samples with and without plasma treatment was carried out. It consisted in applying a pressure sensitive tape against the whole coated surface of the sample and then to quickly pull-out the tape, what leads to a certain degree of delamination at the thin film/polymer interface. The effect of the test was assessed by qualitative analysis of the samples against a bright light, as the weight measurements performed on the samples with a precision laboratory scale before and after the tape test did not allow detecting any mass differences.

Morphological analysis of the coated and non-coated substrates was carried out using several microscopic techniques. The analysis by optical microscopy (OM) was made on a CSM Instruments Ravetest microscope fitted with image acquisition. All samples were analyzed using different magnifications (50, 200, and 500 times) at room temperature. Scanning electron microscopy (SEM) was performed using a Leika Cambridge S360 equipment, where images were obtained at different magnifications. Atomic force microscopy (AFM) was performed in the tapping mode, using a Digital Instruments Multimode equipment controlled by Nanoscope III.

Structural characterization of the substrates and coated samples was made by X-ray diffraction (XRD) on a Phillips PW 1710 equipment, using a CuKα radiation in Bragg-Brentano configuration. Chemical analysis of the samples surface, before and immediately after plasma treatment, was carried out by Fourier transform infrared spectroscopy (FTIR) in the attenuated total reflectance (ATR) mode. In order to minimize the contact of the treated surfaces with the environment, namely aging phenomena or any severe oxidation or any other chemical contamination or radical formation, the analysis were carried out immediately after the removal of the samples from the PVD reactor. Sixty four scans were performed with a nominal resolution of $4\ \text{cm}^{-1}$. A ZnSe ATR crystal and a Perkin Elmer Spotlight 300 spectrometer were used.

The surface chemical composition of the samples (before and immediately after plasma treatment) was also evaluated by X-ray photoelectron spectroscopy (XPS), using a Thermo Scientific KAlpha ESCA instrument equipped with aluminum $K_\alpha 1.2$ monochromatized radiation at 1486.6 eV X-ray source. Due to the insulating nature of the samples it was necessary to use an electron flood gun in order to minimize surface charging. Neutralization of the surface charge was achieved using both a low energy flood gun, in the range of $0 - 14\text{eV}$, and a low energy Argon ions gun.

The XPS measurements were carried out using monochromatic Al- Kα radiation ($h\nu = 1486.6\text{eV}$). Photoelectrons were collected from a 90° take-off angle relative to the sample surface. The measurement was done in the constant analyzer energy mode (CAE) with 100 eV pass energy for survey spectra and 20 eV pass energy for high-resolution spectra. Charge referencing was done by setting the lower binding energy C1s peak at 285.0 eV for the C1s hydrocarbon peak. [21] The contact angles (CAs) measurements were performed before and after the plasma treatment with a Contact Angle System

equipment from OCA DataPhysics using the sessile drop method and water as the test liquid.

All characterization was performed within a day of the application of plasma treatments and the samples were protected from direct contact with the atmosphere after leaving the plasma treatment chamber.

The electrical resistivity of the films was measured using the four-point probe method (in linear geometry), [22] using 2×1 cm^2 samples.

Electrochemical Analysis

The electrochemical behavior of the coated samples was studied by open circuit potential (OCP) versus time measurements and by electrochemical impedance spectroscopy (EIS). The tests were carried out in an acrylic electrochemical cell containing a solution of synthetic sweat with the composition as proposed by J-O Randin: [23] 20 g $\cdot$ L^{-1} sodium chloride (NaCl), 17.5 g $\cdot$ L^{-1} of ammonium chloride (NH_4Cl), 5 g $\cdot$ L^{-1} urea, 2.5 g $\cdot$ L^{-1} acetic acid and 14.2 g $\cdot$ L^{-1} lactic acid, the pH being adjusted to 4.7 with sodium hydroxide.

An EG&G PAR 273A potentiostat, driven by the CorrWare/ CorrView software from Scribner was used for the OCP measurements. A platinum wire and the saturated calomel electrode (SCE) were used as counter-electrode and reference respectively. EIS spectra were acquired via a Solartron 1250 frequency response analyzer connected to a EG&G PAR 273 potentiostat driven by the Zplot/ZView software from Scribner. The amplitude of the AC signal was 7 mV (rms).

Results and Discussion

Basic Thermoplastic Vulcanizate (TPV) Substrates Properties

Figure 1 shows typical torque and temperature versus time curves during the dynamic vulcanization of the EPDM/PP TPV in the batch mixer. The first and second peaks in the torque curve correspond to the introduction of PP and EPDM

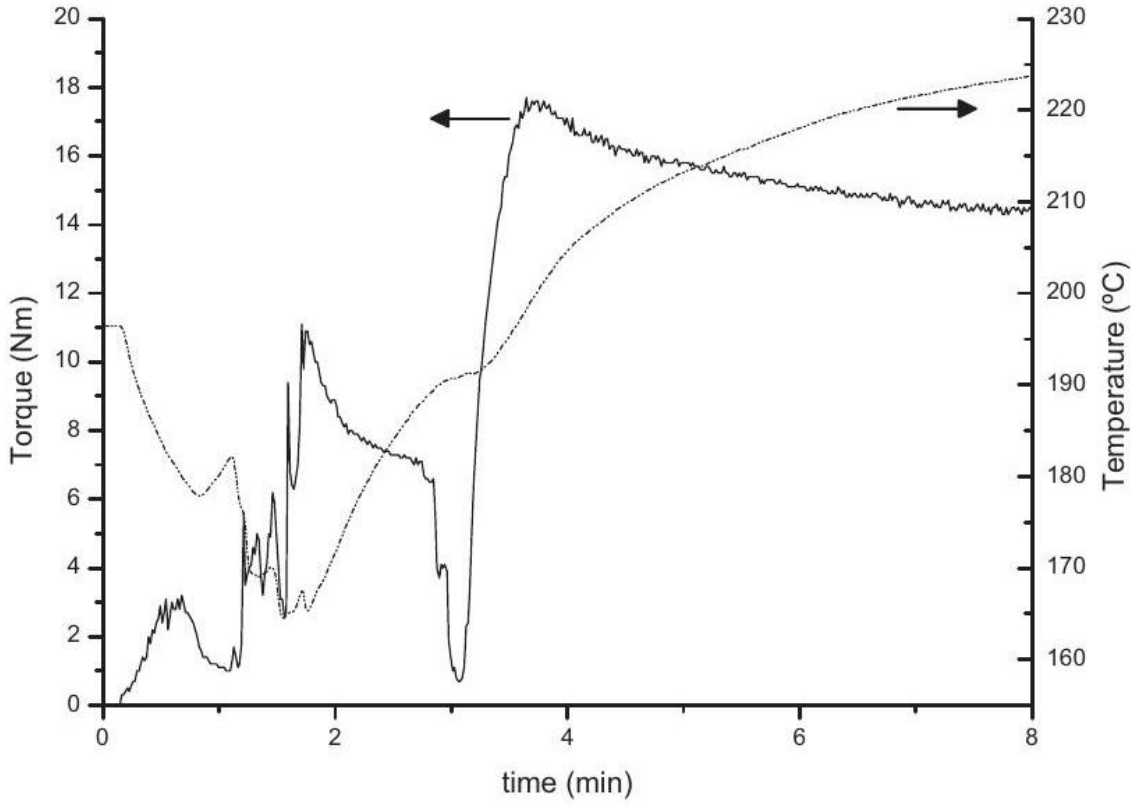


Figure 1. Torque and temperature evolution during TPV preparation.

into the mixer, respectively. The torque reaches an approximate constant value (7.5 Nm) at 2.5 min , indicating complete melting of PP and full homogenization of the EPDM/PP blend. The addition of the crosslinking system produces an immediate torque decrease, which is attributed to its lubrication effect. Then, at 3.6 min the torque increases steeply and reaches a maximum (17.7 Nm), which is related to drastic changes in the viscosity and elasticity of the EPDM phase due to crosslinking. After 8 min mixing the torque shows a moderate but continuous decrease being the final value 14.4 Nm .

The prepared TPV has an EPDM gel content of 100%, which means that all rubber is cross-linked. The stressstrain measurements showed that it has 300% elongation at break, a Young modulus of 72 MPa and a yield stress 5 MPa . Moreover, it has a hardness value of 91 shore A.

Plasma Treatment

Figure 2 shows SEM micrographs, before and after plasma treatment of the TPV substrate, showing a significant change on the surface morphology, which is a clear indication of the surface mechanical "damage" that was

introduced by the Ar activation/modification process in the polymeric surface due to ionic bombardment. Such morphological changes can also be seen in the AFM images, Figure 3. The AFM analysis allowed quantifying the magnitude of such changes, showing that the sample's surface roughness (Ra) increased from 18 to 61 nm with the Ar plasma treatment.

In order to have a more quantitative evaluation of the surface changes that resulted from the Ar treatment/ activation process, a detailed analysis of the CA values was carried out. The results obtained for the non-treated and plasma treated TPV were 97° and 117°, respectively. The increase in CA is quite unexpected, as activation treatments in polymers usually lead to a hydrophilicity increase. The atmospheric exposure effects of the samples were first considered as a possible explanation. According to Siow et al. [24] in their excellent review on plasma treatment of polymers, the surface modifications underwent by polymers after a plasma treatment may be ascribed to two main processes: (i) post-plasma oxidation of the formed radicals by atmospheric oxygen diffusion and (ii) surface restructuring, which involves movements of polymer chains from the surface into the bulk of the polymer.

The main effect of the treatment with Ar is the formation of radicals, that upon atmospheric exposure react with oxygen and water giving rise to polar oxygenated groups and therefore to hydrophilicity increase and corresponding water CA decrease. [24] However, in the present work this behavior was not observed. Conversely, surface restructuring (hydrophobic recovery), another well known ageing effect, would give rise to a CA increase. However these effects are less likely to occur in cross-linked polymers, as in the case of TPVs, due to the restricted chain movements. [24] Besides, these processes have usually high time constants.

A more probable explanation for the CA increase may be the increase of surface roughness during the plasma treatment, as described by Wenzel's equation. [25] Wenzel's equation correlates the CA of the rough surface (θ_0) with the CA of a similar smooth surface (θ) through the roughness factor (R_f) [Equation (1)]:

$$\cos\ \theta_0 = R_f \cos\ \theta \qquad (1)$$

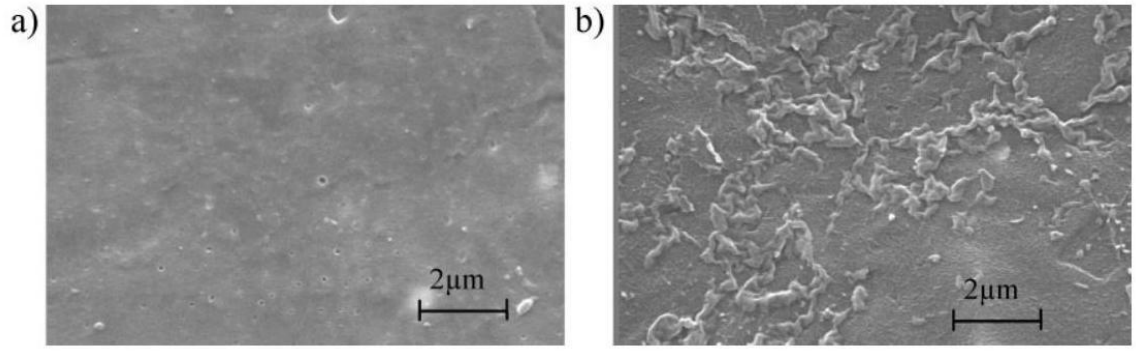


Figure 2. Scanning electron microscopy (SEM) micrographs of TPV sample (a) before and (b) after plasma treatment.

where, R_f is defined as the ratio between the areas of the actual (rough) surface and the geometric (smooth) surface [Equation (2)].

R_f = actual surface/geometric surface

According to Equation (1) it is possible to conclude that if the CA of the smooth

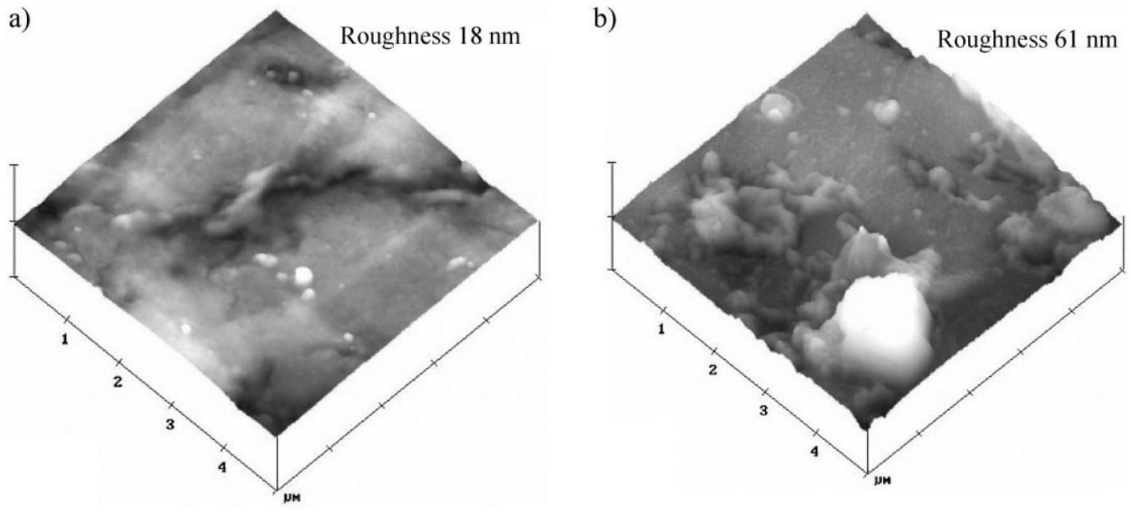


Figure 3. Atomic force microscopy (AFM) topographic representation of TPV sample (a) before and (b) after plasma treatment.

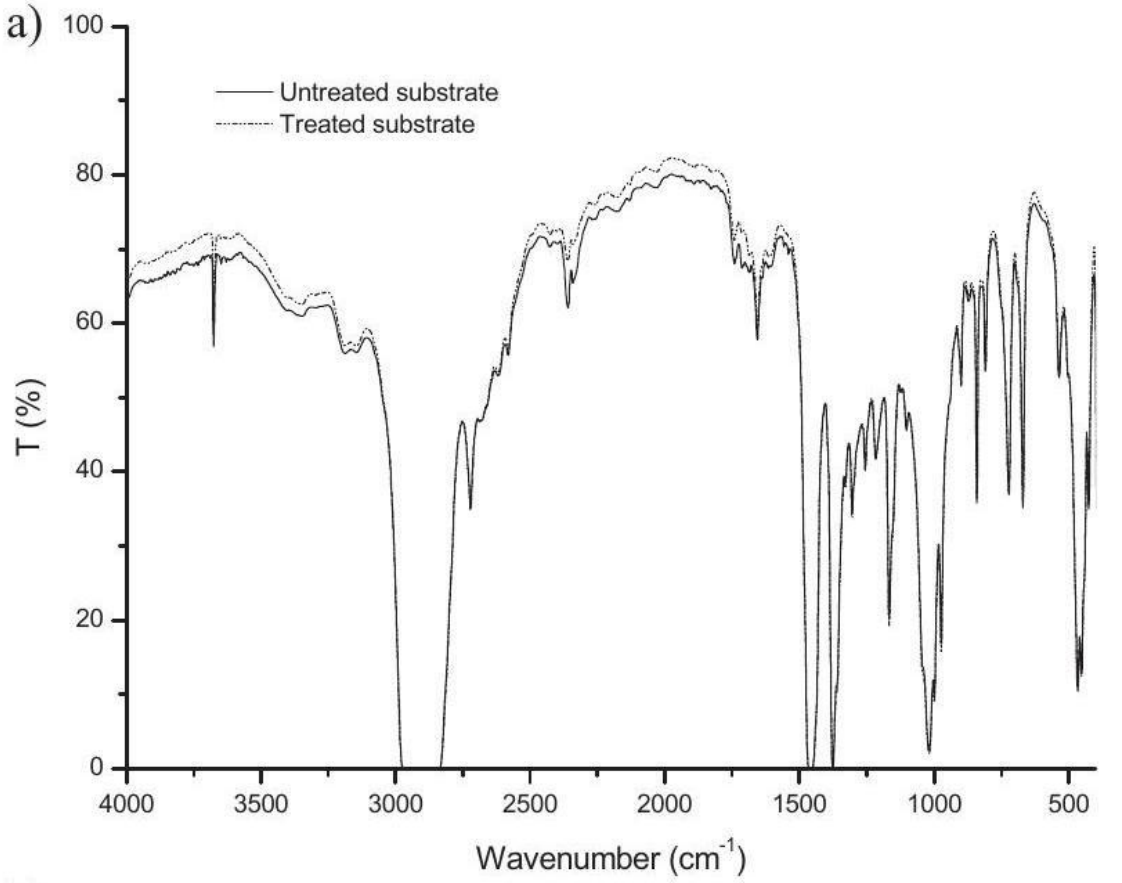
surface is above 90°, then the CA of the rough surface will increase with roughness. However, if the CA of the smooth surface is bellow 90°, the CA will decrease with surface roughness. It follows that for a hydrophilic surface ($\theta < 90°$) an increase in surface roughness leads to a more hydrophilic surface and for a hydrophobic surface ($\theta > 90°$) an increase in surface roughness leads to a more hydrophobic surface. As argon plasma treatments tend to increase surface hydrophilicity, it is possible that the plasma treatment was not enough to induce a CA drop below 90° and in this case the roughness increase led to an increase of the CA, as observed.

The X-ray diffractogram of the untreated and plasma treated TPV surfaces (not shown) revealed no changes in shape or position of the diffraction peaks, which means that the plasma treatment did not have a significant effect on the degree of crystallinity of the TPV samples surfaces, and thus it did not change the polymers structural integrity. A detailed analysis of the mechanisms of interaction of magnetron plasma with polymer surface was discussed by the authors in a previous work. [26]

Surface Chemistry Composition

In order to minimize chemical reactions of the radicals formed during the plasma treatment with water vapor and molecular oxygen, which would change the surface chemical composition, the samples were analyzed by FTIR and XPS shortly after their removal from the PVD reactor.

Figure 4 shows FTIR spectra obtained for the untreated and plasma treated substrate. A careful analysis of the spectra shows that plasma treatment did not induce significant chemical changes at the surface. Only a very small shift of the peaks to higher wavenumbers in the


a)
Untreated substrate
Treated substrate
T (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

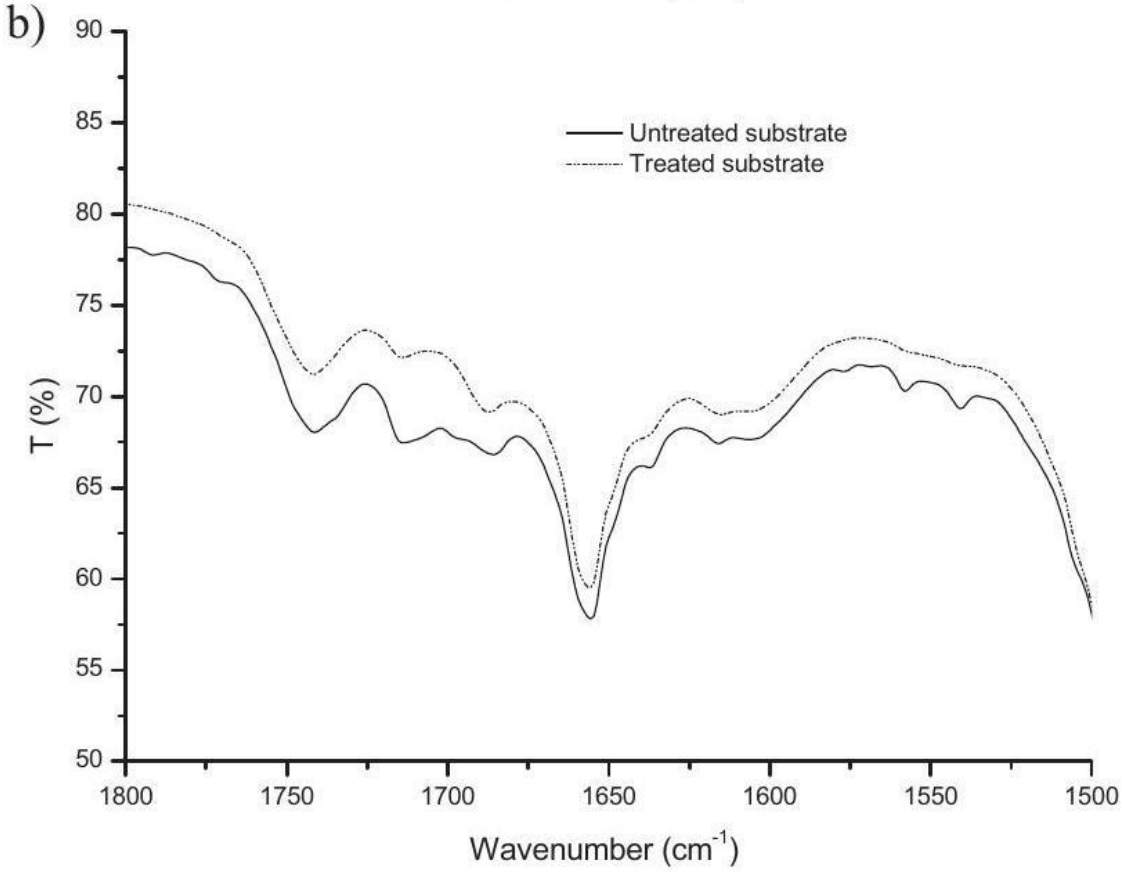

b)
Untreated substrate
Treated substrate
T (%)
90
85
80
75
70
65
60
55
50
1800
1750
1700
1650
1600
1550
1500
Wavenumber (cm-1)

Figure 4. Fourier transform infrared (FTIR) spectra of the untreated and plasma treated TPV substrate (a) full range and (b) between 1800 and 1500 cm^{-1}.

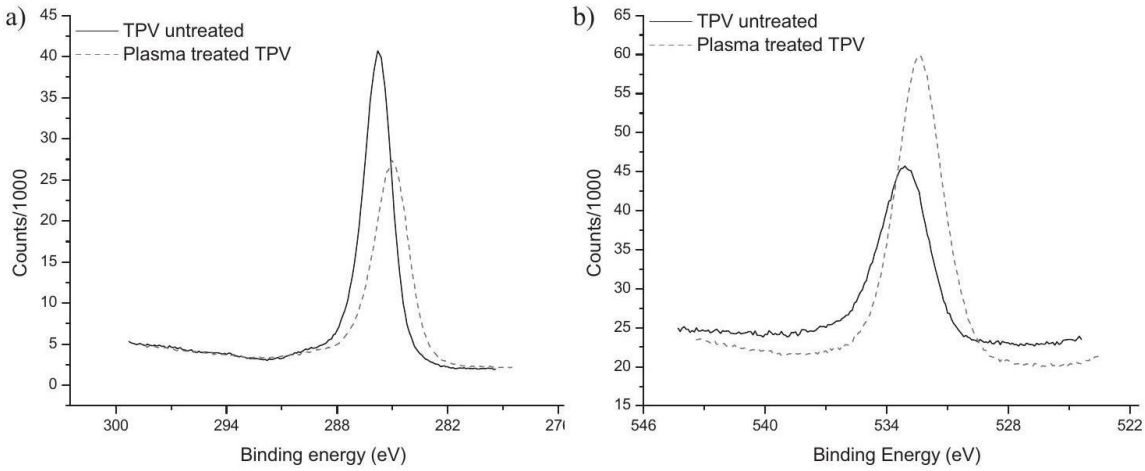


Figure 5. XPS spectra of TPV before and after plasma treatment: a) C1s and b) O1s.

1750-1 650 range (Figure 4b), corresponding to changes in $C = O$ bonds, can be noticed. This means that almost no chemical changes on the surface occurred due to the plasma treatment. Further investigation on surface composition of untreated and plasma treated samples was performed by XPS analysis.

Surface chemical modifications induced by plasma treatment were also assessed by XPS analysis. Figure 5a and *b* show the XPS spectra of carbon and oxygen of the untreated and plasma treated samples surfaces. Untreated and plasma treated samples exhibit binding energy and peak intensity differences. A small shift from 285.8 to 285.1 eV and from 533.1 to 532.4 eV can be observed for C and O, respectively. Furthermore, peak intensity decreases for C and increases for O . Changes in the binding energy show that the plasma treatment induced changes in the oxygen content at the surface and also changes in $C - O$ bonds. In the elemental composition (Table 1), the C1s decreases about 18% while the O1s content increases approximately 8% and the O1s/C1s ratio increases. These results indicate that a small amount of oxygen was incorporated into the polymer surface. Since the plasma treatment was performed with N_2, the increase of oxygen can be explained by the reaction of the radicals formed during plasma

Table 1. Elemental composition of the samples determined by XPS.

Exposure time [min]	Elemental composition [at.-%]		
	C1s	O1s	Ratio O/C
	85.4 ± 3.0	12.2 ± 3.0	0.14
15	66.8 ± 3.0	20.8 ± 3.0	0.31

treatment with environmental oxygen or water vapor during the time that the samples were exposure to air, between samples removal from the PVD reactor and XPS analysis.

Information on how oxygen was incorporated in the polymer surface as a consequence of the plasma treatment can be obtained from the deconvolution of XPS signals using the Gaussian-Lorentzian fit. The C1s deconvoluted spectrum of untreated TPV is shown in Figure 6a. Three peaks were identified, at 285 eV due to $-CH_2$ and $-CH-$ groups (C1 component), at 287.30 eV due to -C-O-groups (C2 component) and at 289.29 eV due to $O-C=O$-groups in ester linkages (C3 component). Also O1s level spectrum for the original TPV (Figure 6c) was decomposed into two components: one at 532.99 eV due to $C=O$ (O1 component) and the second at 534.78 eV , due to $O-C=O$-groups in ester linkage (O2 component).

The plasma treatment, as shown in Figure 6b and d, led to changes in the C1s and O1s spectra, respectively. In the C1s spectrum, the component C1 decreases (Table 1). This result can be associated to the scission of the $C-C$ or $C-H$ bonds at the polymer surface and the broken bonds recombine with oxygen atoms to produce surface oxygen containing groups. The O1s spectrum of the plasma treated sample indicates only the presence of the O1 component (Figure 6d), which increased significantly (Table 2). This change is in good agreement with the decrease of the C1s peak that may be ascribed to the formation of C -O-groups induced by the plasma species.

Even though new oxygen groups were observed by XPS analysis, these groups will not be presented in the plasma-activated surface seen by Ti, N, and N_2, once film deposition was performed after the plasma treatment without taking the samples out of the PVD reactor. However, from the XPS results it is possible to detect the efficiency of the plasma treatment to produce reactive species.

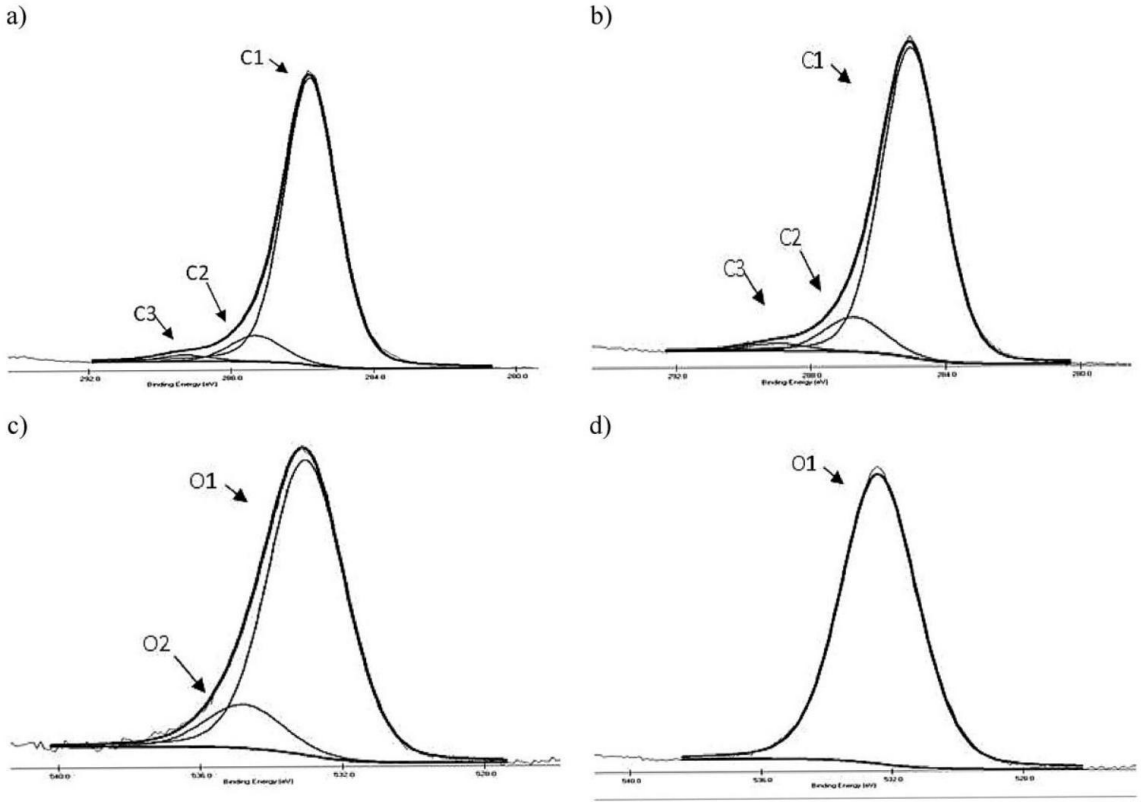


Figure 6. C1s spectra of (a) untreated and (b) plasma treated TPVs; O1s spectra of (c) untreated and (d) plasma treated TPVs [Intensity (a.u.) vs. Binding Energy (eV)].

Titanium Nitride (TiN) Thin Film

Cross-section analysis of the coated substrates revealed a good adhesion of the thin film, as well as a good surface uniformity and a sharp interface between the film and the TPV substrate, Figure 7. AFM analysis confirmed the different morphological features of TiN films deposited on

Table 2. X-ray photoelectron spectroscopy (XPS) of C1s and O1s peaks deconvolution and possible groups in untreated and plasma treated TPV.

	Peak	Position [eV]	Area	Group
Untreated TPV	C1	285.75	76117	C-H/C-C
	C2	287.30	6966	C-O
	C3	289.29	1694	O – C = O
	O1	532.99	62444	C = O
	O2	534.78	9252	O – C = O
Plasma treated TPV	C1	284.98	56501	C – H/C – C
	C2	286.71	6334	C-O
	C3	288.99	1369	O – C = O
	O1	532.37	121307	C = O

non-treated and plasma treated TPVs substrates. The film deposited on plasma treated substrate revealed an increase of roughness from 15 to 46 nm . In fact, and due to the roughness increase that was observed for the treated surfaces (see Figure 2 and 3) it is expectable that the grown film will also display a higher roughness.

X-ray diffraction (XRD) analysis on the TiN coated TPV substrates revealed the growth of a poorly crystallized cubic face-centered structure, Figure 8. The fact that no external heating was used, together with the grounded condition in

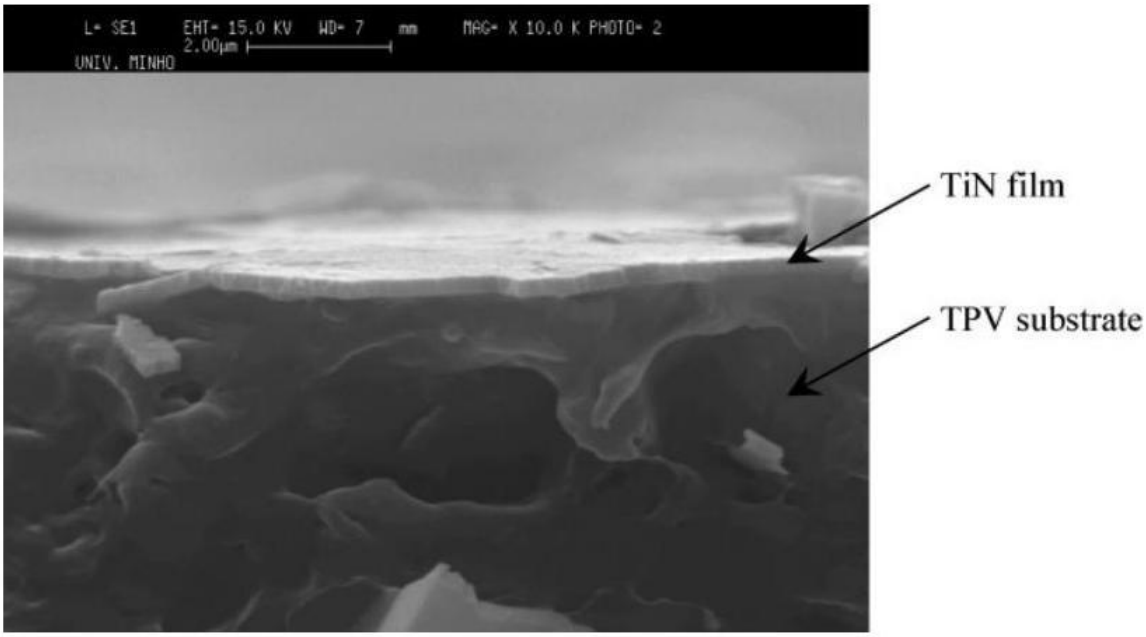


Figure 7. SEM cross-section micrographs of TiN deposited on the plasma treated TPV substrate.

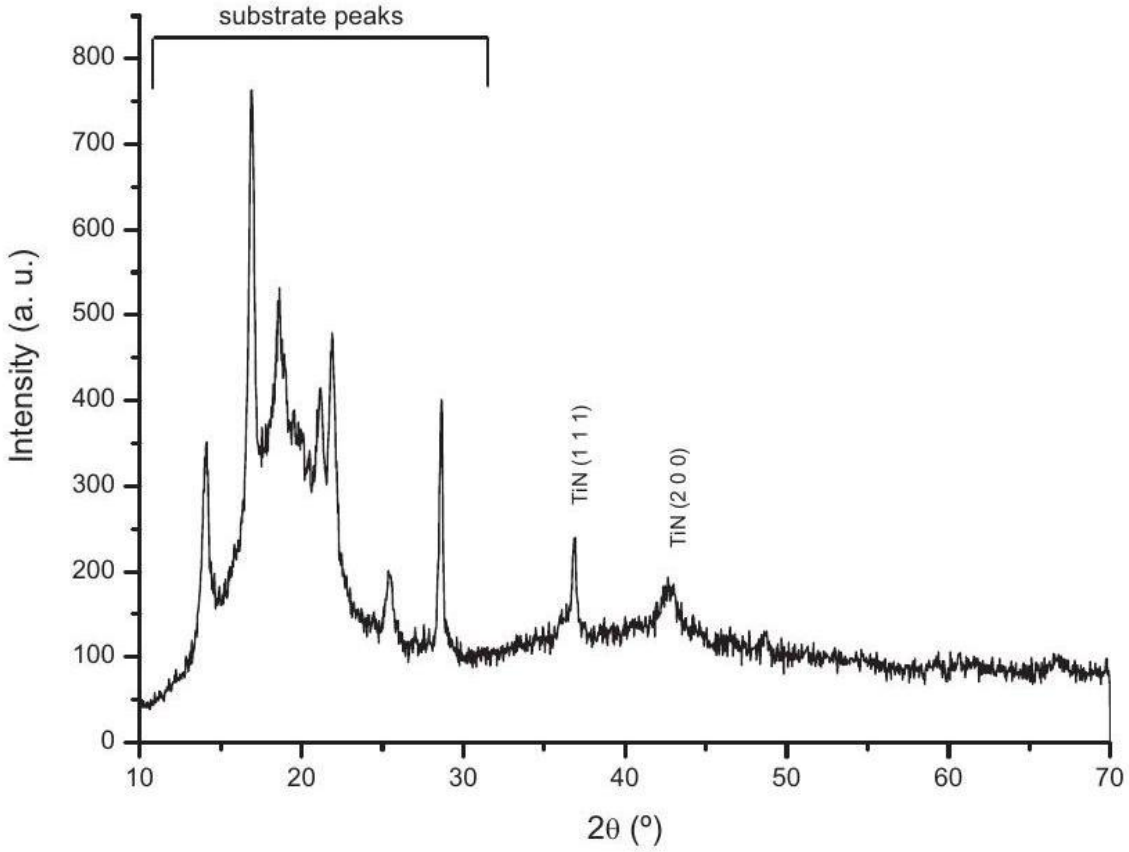


Figure 8. XRD difractogram of TiN deposited in the plasma treated TPV substrate.
which the films were grown, resulted in reduced atomic mobility and thus poorly crystallized structures are expected. Nevertheless, it is worth to notice that the substrates consistency is still retained, as no structural changes were observed, even after the film deposition and thus implying that the activation and functionalization of the TPV to act as EEG or ECG sensors is not compromised.

The adhesion test revealed that the plasma treatment allowed improving significantly the adhesion of the TiN film, as illustrated in Figure 9. This result and the aggressiveness of the tape test are good empirical indications of the excellent adhesion of the film promoted by the Ar plasma treatment. In the non-treated sample, Figure 9a, it is possible to observe that the percentage of light areas (corresponding to delaminated sections) is much higher than in Figure 9b. In fact, the several processes that take place during plasma treatment play an important role in adhesion enhancement. Figure 2 and 3 clearly show that "plasma etching" is occurring, as the roughness (AFM) and

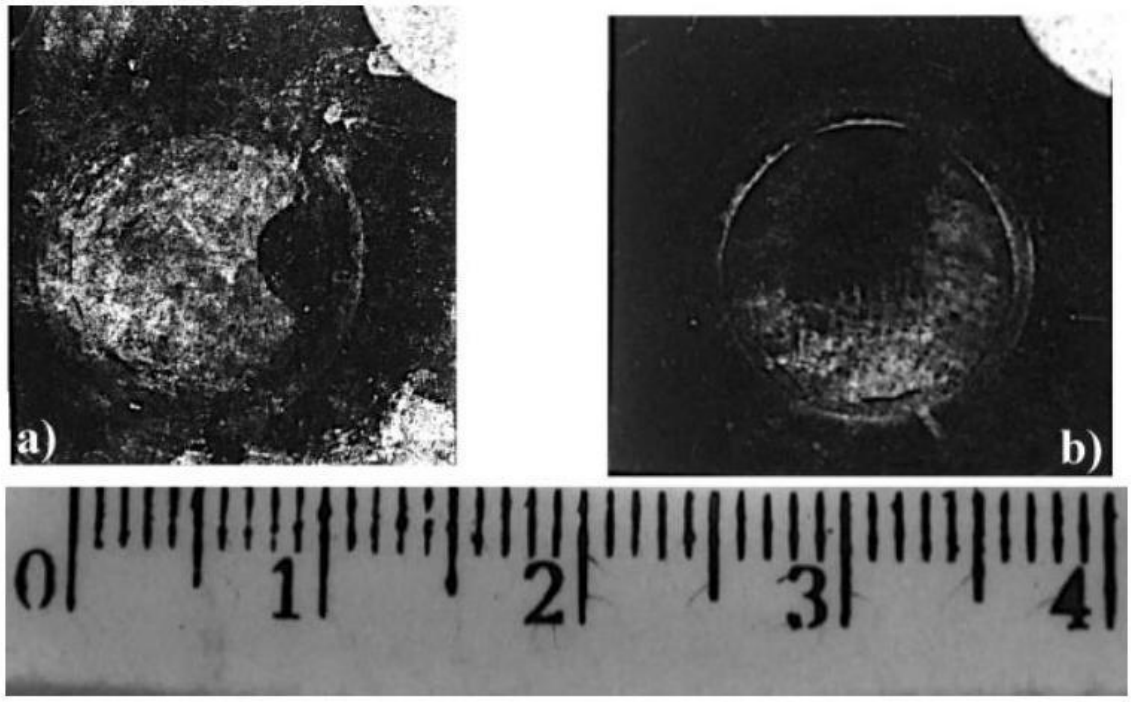


Figure 9. Adhesion assessment of TiN deposited on (a) untreated and (b) plasma treated TPV surfaces.
superficial aspect (SEM) of the sample before and after plasma treatment change significantly. Such roughness contributes to the enhancement of the thin film adhesion by an interlocking mechanism. On the other hand, the surface chemical composition of the sample also suffers important changes, namely the formation of active species, leading to the formation of new and reactive functional groups (oxygen incorporation at the surface), evidenced by FTIR (Figure 4) and XPS (Figure 5 and 6). The formation of such active species has a definitive role in the enhancement of the TiN adhesion.

These results provide a good indication about the possibility of using the Ar optimized plasma treatment for the functionalization of a TPV substrate with a TiN_x conductive film.

Electrochemical Behavior

The electrochemical assessment of the TiN coated TPV samples with and without plasma pre-treatment was studied in a synthetic sweat solution, in order to test the effects of perspiration on the chemical behavior and electric potential stability of the TiN films. The studies were carried out with four samples for each condition, the reported results representing the average response. To note that a stable electrochemical potential in the absence of a biological signal is of uppermost importance for bioelectrode application, as tiny ECG ($\sim$ 1mV) or EEG ($\sim 100\mu$ V) signals may be easily buried in a noisy background or in a base-line with a strong drift, such as those displayed by reactive interfaces. The OCP versus time curves reveal that TiN coatings on plasma treated samples exhibit lower drifts and more noble potentials than the TiN films formed on non-treated surfaces, Figure 10. The meaning of such differences is not clear, although it may be hypothesized that the plasma treatment gives rise to chemically more homogeneous and stable coatings, by thoroughly cleaning the TPV surface at the atomic level.

The interfacial impedance induced by the presence of a sweat layer was assessed by EIS, Figure 11. Such impedance represents the electric resistance against signal transfer and its dependence on frequency. Generally speaking, the impedance increases and the phase angle approaches 90° as frequency decreases, an indication that charge transfer is at least partially capacitive, unlike with the silver/silver chloride electrodes where the resistive charge transfer mechanism dominates the charge transduction process. [27] This conclusion stems from the fact that the TiN is essentially non-reactive, unlike the silver/silver chloride electrode system.

The impedance of the TiN/electrolyte system is higher than that of the silver/silver chloride electrodes, [27] but still lower than the values displayed by the skin barrier when no gel paste is applied. [3] To note that the impedance of the non

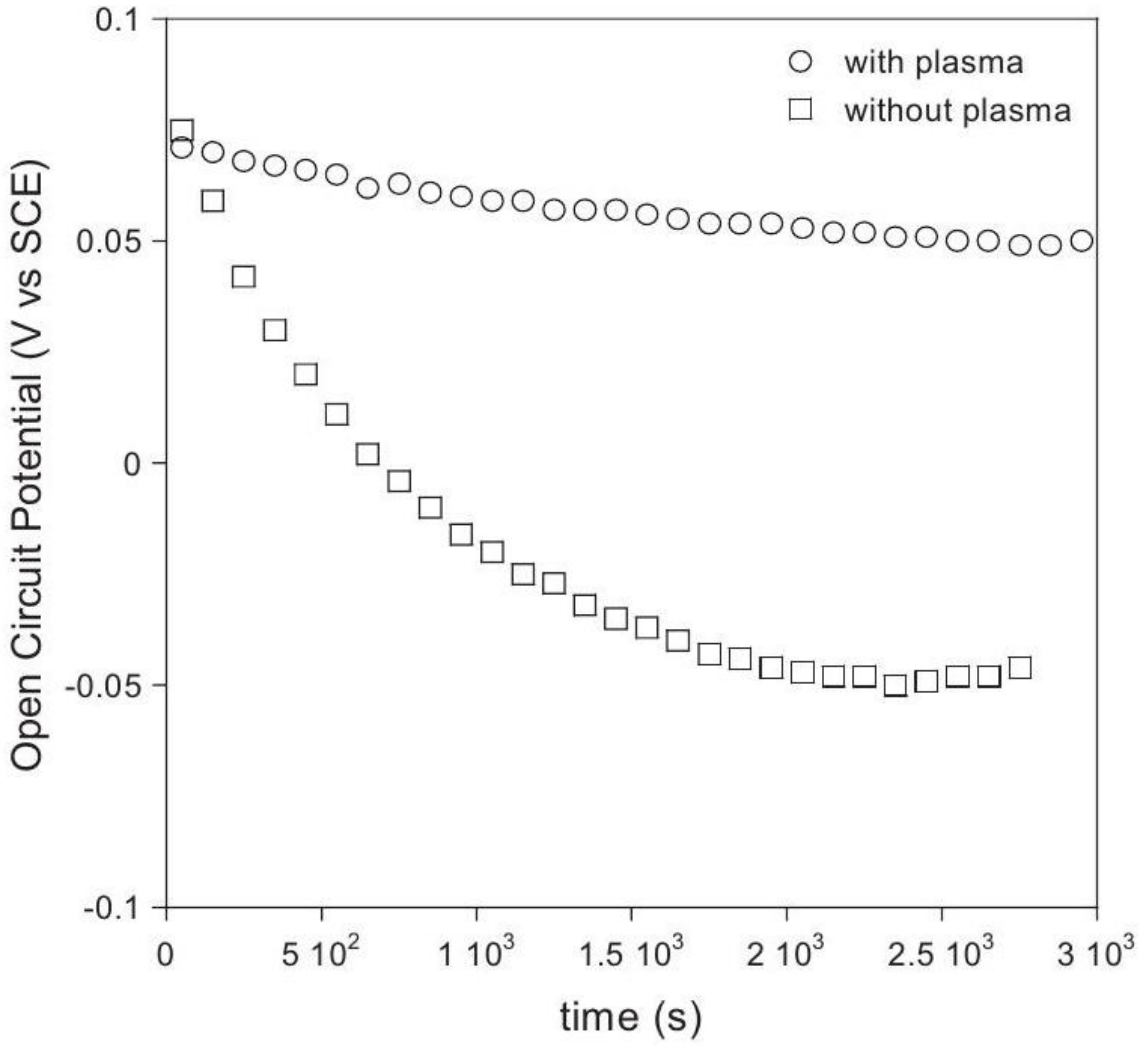


Figure 10. OCP versus time typical curves in synthetic sweat solution for TiN films deposited on non-treated and plasma treated TPV substrates.
plasma-treated sample is higher than that of the treated sample, what can be ascribed to two factors: (i) the higher roughness of the plasma-treated sample and (ii) the worse adhesion of the coating that and the flexible nature of the substrates may induce an easier micro-cracking. Anyway, these results highlight once more the importance of the surface plasma pre-treatment for achieving a conductive coating with superior properties.

The impedance plateau above ~ 10 Hz corresponds to a frequency region where all capacitors were short-circuited

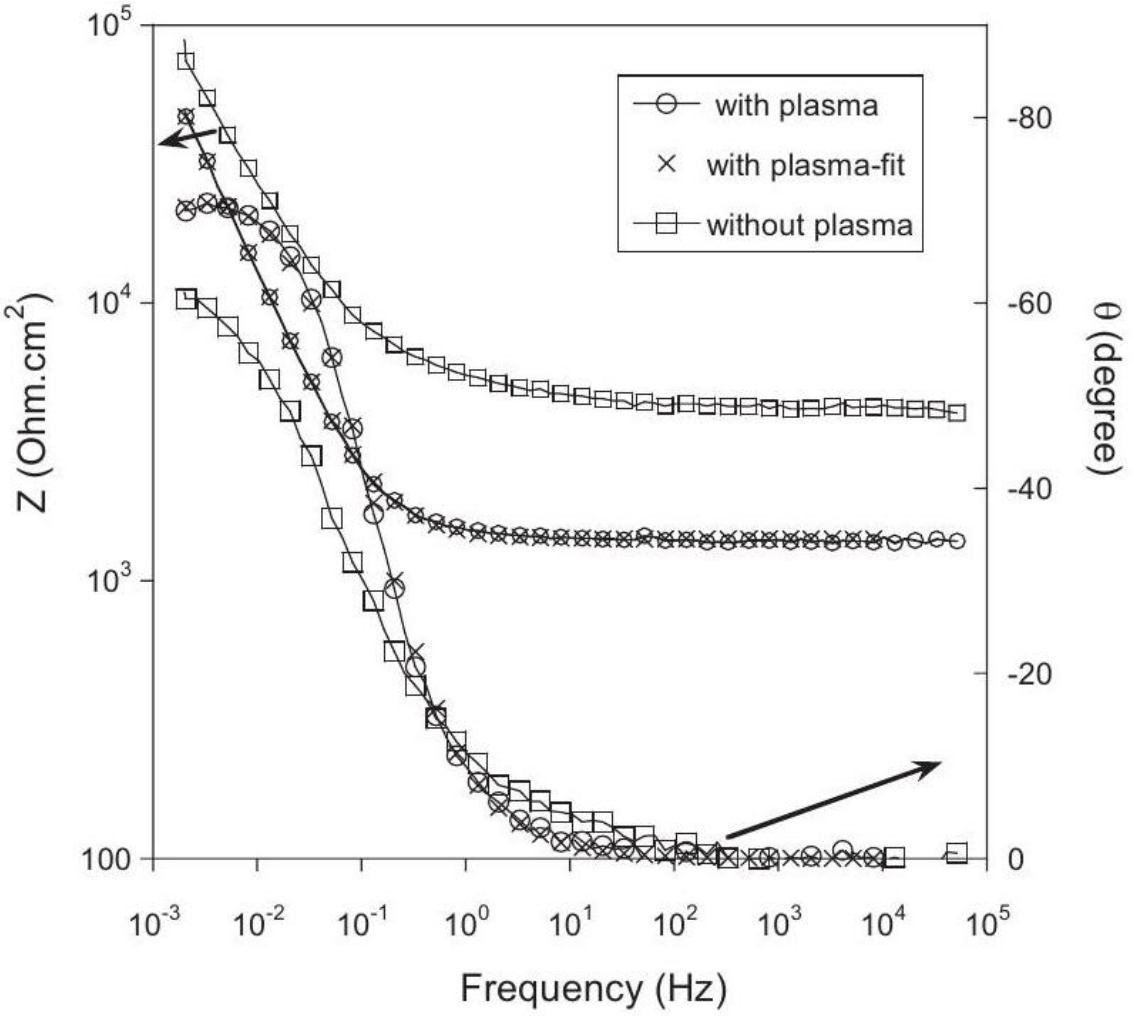


Figure 11. Impedance tests performed for TiN samples, obtained with and without plasma treatment. The crosses represent the simulated spectrum.
(the phase is nearly zero), the resistance value thus corresponding to the sum of the electrolyte and TiN thin film resistances. Since the resistance of the electrolyte is around a few Ohm, [1] the measured value should correspond mainly to the resistance of the TiN film. This is a quite high value since the resistance of the titanium/ electrolyte interface is of the order of $10 - 20\Omega \cdot \text{cm}^2$. [1] The surface resistivity of the films was found to be of $0.2\Omega \cdot$ cm, well above the $60\mu\Omega \cdot$ cm value displayed by TiN films deposited on glass substrates. [28]

The same EIS high resistance values were also found for TiN films grown on ABS substrates. [29] The reasons for such differences between morphologically and structurally similar TiN films may be (i) the very different growing temperatures of the films (200°C and $60 - 70^{\circ}\text{C}$ for the glass and polymer grown films), (ii) the high surface roughness of the polymer samples, and specially (iii) the important dimensional changes that polymers may undergo during the deposition process ($60 - 70^{\circ}\text{C}$), that may induce microcracking of the TiN films. However, it is important to note that such impedance values do not prevent the utilization of the films for bio-signal acquisition as the skin/dry electrode interfacial impedance may amount to $60100\text{KOhm} \cdot \text{cm}^2$ or even higher values in dry conditions.

The impedance spectrum of the TiN film obtained on the plasma treated substrate was simulated according to a simple Randles-like circuit, in agreement with our previous work, [1] Figure 10. A charge transfer resistance of $0.7 M\Omega \cdot cm^2$ was obtained, demonstrating the excellent chemical resistance of TiN deposited on TPV in contact with synthetic sweat.

Conclusion

Thermoplastic vulcanizate (TPV) flexible substrates were successfully coated with TiN films, aiming their application as biomedical electrodes. A low resistance TiN thin film and a satisfactory TPV/TiN adhesion were only achieved upon the application of an argon plasma treatment before TiN deposition. Such treatment allowed activating the TPV surface, as confirmed by XPS from the oxygen enrichment of the surface after a short atmospheric exposure. An empirical but aggressive adhesion test clearly showed the important TPV/TiN adhesion differences between the plasma treated and non-treated TPV samples. The study of the electrochemical properties of the TiN films in contact with synthetic sweat showed that the plasma pretreatment of the TPV surface is essential to achieve a low electrochemical potential drift and a lower resistance to signal transfer. Although the resistivity of the TPV deposited TiN films are clearly higher than their metal or glass deposited counterparts, it is still adequate for biomedical electrode application, due to the commonly
higher values of the electrode/skin impedance. The TiN films proved to display a suitable chemical stability in contact with synthetic sweat.

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