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3 **Ag:TiN-coated polyurethane for dry biopotential electrodes: from polymer**
4 **plasma interface activation to the first EEG measurements**

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7 Abstract. Several plasma treatments using argon, oxygen and nitrogen are studied in
8 order to increase the interfacial adhesion of the polyurethane/Ag:TiN system to be used as
9 biopotential electrodes. The optimized plasma treatments conditions (100 W, 15 min.,
10 regardless of the gas) promote a steep decrease of the water contact angle values. The
11 observed chemical and topographic alterations translate into excellent polyurethane/Ag:TiN
12 interfacial adhesion of the plasma treated samples. The in-service validation of the proposed
13 Ag:TiN-coated PU multipin electrodes is performed by acquiring EEG signals in parallel with
14 the standard wet Ag/AgCl electrodes. No considerable differences are found in terms of
15 shape, amplitude and spectral characteristics of the signals when comparing reference wet and
16 dry electrodes.

17

18 **Introduction**

19 The conventional wet silver/silver chloride (Ag/AgCl) electrodes are considered the most
20 suitable for biosignal acquisition^[1-3] and are widely used in routine clinical practices and
21 medical research, such as multichannel electroencephalography (EEG),^[4,5] or even brain-
22 computer interfaces.^[6-8] They exhibit an essentially non-polarizable, resistive behaviour, also
23 displaying an excellent reliability and low, almost frequency-independent skin-contact
24 impedance values, in the order of few tens of $\text{k}\Omega\cdot\text{cm}^2$.^[2,3] However, the wet Ag/AgCl
25 electrodes suffer from intrinsic technological drawbacks, including difficult, time-consuming,
26 and error-prone skin preparation,^[1] as well as limited long-term stability of the gel electrolytes

1 and constant risk of hair damage and skin irritation.^[2,3,8]

2 For the past few years, a new class of dry biopotential electrodes have been studied as
3 potential substitutes for the commercially used wet Ag/AgCl electrodes in applications where,
4 for instance, fast and easy montages are required. This new generation of electrodes does not
5 rely on the application of conductive gels and previous extensive skin preparation,^[3,9,10] which
6 translates into higher interfacial impedances. Moreover, incorrect and/or uncomfortable skin
7 contact may arise due to the stiff nature of some of the proposed base materials (aluminium,^[3]
8 steel,^[11,12] silicon,^[13,14] titanium^[15] and polycarbonate^[16]), and design-specific conceptual
9 problems (micro-needle electrodes^[13,14] and rigid planar plates/disks unable to interfuse the
10 hair layer^[15,16]). Hence, in order to reduce some of the referred drawbacks, several authors
11 focused not only on the development of new electrode designs, which allow an effective hair
12 interfusion,^[17-20] but also on the use of more compliant base materials, such as textiles^[21] and,
13 above all, flexible polymers.^[22-25]

14 Thermoplastic polyurethanes (TPU) have been extensively applied in several fields that
15 range from technical coatings to biomedical applications,^[26-28] due to their excellent balance
16 between mechanical properties (high flexibility, dependent on the composition), chemical
17 barrier behaviour, soft tact and biocompatibility,^[29,30] thus being appropriate to be used as
18 biopotential electrode base material. Nonetheless, since the present study aims at coating TPU
19 substrates with a previously optimized Ag:TiN thin film system,^[31-34] the TPU surface must
20 be suitably activated/functionalized,^[35-37] in order to take account of the low surface energy
21 and hydrophobicity (common to most polymers), which may result into poor TPU/Ag:TiN
22 interfacial adhesion. To improve this drawback, a set of low-pressure plasma treatments will
23 be studied, since they are able to tailor important surface characteristics, such as the
24 wettability and topography,^[38-40] without compromising the bulk properties of the polymer.
25 Moreover, the low environmental impact promoted by this technique, when compared to other
26 surface activation methods (chemical, thermal and electrical), has also been reported.^[29,41]

1 Depending on the plasma gases and parameters (gas flows, power, pressure and treatment
2 time), several individual physicochemical effects may be achieved,^[42-47] such as surface
3 cleaning (removal of contaminants), etching (roughness promotion), crosslinking, formation
4 of new functional groups and chain scission (formation of free radicals). The occurrence of
5 these individual effects, or even combination of them (namely increased roughness and
6 formation of new reactive groups), may promote beneficial effects on the adhesion, by acting
7 as interlock points for active polar groups,^[47] thus an increase of the surface wettability is
8 expected.^[44,47]

9 The present work, therefore, investigates, in a first stage, the effect of several argon,^[35]
10 oxygen^[30,35,39,48,49] and nitrogen^[29] plasma activation treatments, performed with different
11 times and powers on the surface characteristics of the TPU substrates, and subsequent
12 adhesion of the sputtered Ag:TiN film. Then, the plasma activated (using the best treatment
13 time and power for the different gases) novel dry Ag:TiN-coated polyurethane multipin
14 electrodes, which intends to combine the use of a flexible base material (polyurethane, PU)
15 with an optimized design (multipin, MP), were used in several EEG trials in comparison with
16 the wet Ag/AgCl ones. Finally, the quality of the monitored EEG signals was compared in
17 order to assess if the plasma-activated Ag:TiN-coated PU MP electrodes are suitable to be
18 used as biopotential electrodes.

19

20 **Experimental details**

21 **Activation and characterization of the polyurethane substrates**

22 The polyester-based thermoplastic polyurethane (TPU) substrates, ref. WHT-1495EC,
23 from Yantai Wanhua Polyurethanes Co., Ltd. were obtained by compression moulding in the
24 sheet form. Before all plasma activation treatments, the rectangular polyurethane substrates
25 (20×30×0.4 mm) were cleaned with ethanol (96% vol.). A Zepto laboratory-sized plasma
26 system from Diener Electronics ($\phi = 105$ mm, $L = 300$ mm, $V = 2.6$ L, excitation frequency =

1 40 kHz) was used for the plasma activation of the samples, which were placed in a substrate
 2 holder at the centre of the cylindrical chamber. Several plasma treatments were performed,
 3 taking into account the effect of three main parameters: (i) used gas, (ii) plasma treatment
 4 time and (iii) plasma treatment power. The plasma treatment experimental parameters are
 5 summarized in Table I.

7 *Table I.* Plasma treatment parameters.
 8

Parameter	Gas	Power (W)	Time (min.)	Pressure _{base} (Pa)	Pressure _{work} (Pa)
Δ Time	Ar	100	2, 5, 10, 15 and 20	3×10^{-3}	8×10^{-3}
	O ₂	100	2, 5, 10, 15 and 20	3×10^{-3}	8×10^{-3}
	N ₂	100	2, 5, 10, 15 and 20	3×10^{-3}	8×10^{-3}
Δ Power	Ar	100, 75 and 50	15	3×10^{-3}	8×10^{-3}
	O ₂	100, 75 and 50	15	3×10^{-3}	8×10^{-3}
	N ₂	100, 75 and 50	15	3×10^{-3}	8×10^{-3}

9
 10 Before and immediately after (maximum of 10 minutes) all activation experiments, the
 11 water contact angle (sessile drop method^[50,51]) was measured at room temperature, using a
 12 OCA 20 unit from Dataphysics, in air-facing polyurethane surfaces. A minimum of six
 13 contact angle measurements were performed for each condition. An optimized plasma
 14 treatment time (15 minutes) and power (100 W) were selected from the water contact angle
 15 measurements. The chemical bonding characteristics were analysed by Fourier Transform
 16 Infrared Spectroscopy (FTIR) in Attenuated Total Reflectance (ATR) mode, using a Jasco
 17 FT/IR 4100 system, equipped with a Specac MkII Golden Gate single reflection ZnSe ATR
 18 crystal. All ATR-FTIR measurements (64 scans, 4 cm^{-1} nominal resolution) were performed
 19 before and immediately after the activation of the samples. In addition, the surface chemistry

1 of the untreated and activated polyurethane samples was also assessed by X-ray Photoelectron
2 Spectroscopy (XPS), performed using a Kratos Axis Ultra spectrometer, equipped with the
3 VISION software for data acquisition and CASAXPS for data analysis. The experiments were
4 carried out with a monochromatic Al K_{α} x-ray source (1486.7 eV), operating at 15 kV (90 W)
5 in fixed analyser transmission (FAT) mode, with a pass energy of 40 eV for the regions of
6 interest and 80 eV for the overall surveys. Data acquisition was performed with a pressure
7 lower than 1×10^{-6} Pa, and a charge neutralization system was used. The effect of the electric
8 charge was corrected by the reference of the carbon peak (285 eV). The modelling of the
9 spectra was performed with the CASAXPS program, in which an adjustment of the peaks was
10 done using peak fitting with Gaussian-Lorentzian peak shape and Shirley-type background
11 subtraction.^[52]

12 The surface topography and average roughness (R_a) of the polyurethane substrates was
13 assessed before and after the plasma activation using a Multimode Atomic Force Microscope
14 (AFM) from Digital Instruments using the tapping mode (scan size 3 μm and scan rate 1 Hz).
15 A Nanoscope III controller and Tesp AFM tips from Bruker were also used.

16

17 **Thin film production and adhesion characterization**

18 The plasma activated polyurethane substrates were used to deposit Ag:TiN coatings with
19 a N/Ti atomic ratio of 0.7 and 6 at.% Ag by reactive DC magnetron sputtering, in a 60 L
20 custom-made laboratory-sized deposition system. This specific Ag:TiN composition was
21 optimized in previous works by the authors, in order to avoid Ag segregation through the
22 potential formation of Ti_xAg intermetallics.^[31-34] The thin films were prepared with the
23 grounded substrate holder positioned at 75 mm from the magnetron and with a 5 rpm
24 rotational speed. A DC current density of 75 A.m^{-2} was applied to the titanium target (99.96
25 at. % purity / $200 \times 100 \times 6$ mm), containing silver pellets (80×80 mm and 1 mm thick) on its
26 surface distributed symmetrically along the erosion area. The total surface area of the silver

1 pellets ($\sim 192 \text{ mm}^2$) was preserved throughout all depositions. A mixed gas atmosphere
 2 composed of Ar+N₂ was used to generate the plasma. The argon flow was kept constant at 25
 3 sccm in all depositions (partial pressure of $5.4 \times 10^{-1} \text{ Pa}$), while the flow rate of nitrogen fixed
 4 at 2 sccm (partial pressure of $4.6 \times 10^{-2} \text{ Pa}$). The working pressure was about $3.8 \times 10^{-1} \text{ Pa}$. A
 5 delay time of five minutes was used prior to positioning the sample surface in front of the
 6 Ti/Ag target, in order to avoid contamination of the coating resulting from previous
 7 depositions, which may have resulted in some target poisoning, as well as to ensure an almost
 8 constant deposition temperature during the growth of the films. All depositions were
 9 performed for 30 minutes at room temperature to avoid polymer degradation (together with
 10 the grounded condition of substrate holder). Operating conditions are summarized in Table II.

11

12 *Table II.* Ag:TiN thin film deposition parameters.
 13

Plasma treatments (performed before all depositions)	Ar 100 W 15 min. O ₂ 100 W 15 min. N ₂ 100 W 15 min.
Ar (Pa)	5.4×10^{-1}
N₂ (Pa)	4.6×10^{-2}
t (min.)	30
I (A.cm⁻²)	7.5×10^{-3}
T (°C)	Room temperature
Bias (V)	GND
Pressure_{work} (Pa)	$3.5\text{-}3.8 \times 10^{-1}$
Pressure_{base} (Pa)	$\sim 10^{-4}$
Area of Ag exposed (mm²)	192

14

15 The atomic composition of the as-deposited samples was measured by Rutherford
 16 Backscattering Spectrometry (RBS) using (1.4, 2.3) MeV and (1.4, 2) MeV for the proton and

1 ^4He beams, respectively. Three detectors were used. One located at a scattering angle of 140°
2 and two pin-diode detectors located symmetrically to each other, both at 165° . Measurements
3 were made for two sample tilt angles, 0° and 30° . Composition profiles for the as-deposited
4 samples were determined using the NDF software.^[53] For the ^{14}N , ^{16}O and ^{28}Si data, the cross-
5 sections given by Gurbich were used.^[54] The area analysed was about $0.5 \times 0.5 \text{ mm}^2$. The
6 uncertainty in the N concentrations is around 5 at. %.

7 The adhesion of the Ag:TiN films to the polyurethane substrates (untreated and plasma
8 treated) was assessed by performing the cross-cut tape test, according to the ASTM D3359-B
9 standard. This test covers procedures for assessing the adhesion of thin films by applying and
10 removing pressure-sensitive tape over cuts made in the coating. A lattice pattern was
11 manually made in the film (with the cuts reaching the substrate) with an x-cutter.
12 Subsequently, the pressure-sensitive tape was applied over the cuts and then removed. The
13 lattice pattern was observed in an electronic microscope before and after removal of the tape
14 and the delamination was classified according to the scale provided in the standard. The
15 SEM/EDS analysis was carried out in a FEI Quanta 400FEG ESEM/EDAX Genesis
16 microscope equipped with X-Ray Microanalysis operating at 15 keV.

17

18 **EEG monitoring**

19 In the EEG monitoring tests a conventional wet Ag/AgCl ring electrode (B10,
20 EASYCAP GmbH, Germany) was placed at frontal position Fp2, while a multipin (MP) test
21 electrode and another wet Ag/AgCl electrode were placed next to each other at occipital
22 position O2. Furthermore, a reference test using two Ag/AgCl electrodes at position O2 was
23 performed. Prior to electrode placement the skin at each electrode position was cleaned using
24 ethanol and a soft cloth. The Ag/AgCl electrodes were applied in combination with electrolyte
25 gel (Electrogel, EGI Inc., USA), while the MP electrodes (from each plasma activation
26 condition) were used in dry conditions only. Both occipital electrodes were connected to

1 independent bipolar channels of a commercial EEG amplifier (Refa Ext, Advanced Neuro
2 Technologies B.V., The Netherlands), while both channel references were connected to the
3 same frontal electrode at position Fp2. Electrode fixation and adduction was provided by a
4 custom-made silicone cap. The MP electrodes were contacted using custom brass mountings.
5 The measurement setup enables simultaneous recording of independent EEG signals. Hence,
6 a direct comparison of the acquired signals using conventional and MP electrodes is possible.
7 Resting-state EEG, alpha activity and eye-blinking artifacts were monitored during the in-
8 vivo tests. Also, a pattern reversal visual evoked potential (VEP) was recorded according to
9 ISCEV (International Society for Clinical Electrophysiology of Vision) standards consisting
10 of 300 trials. The three different MP electrodes (activated with argon, nitrogen and oxygen)
11 and the reference Ag/AgCl electrode were tested in three individual tests per material on three
12 volunteers (two male, one female), resulting in an overall number of 12 test sequences per
13 volunteer. Finally, the simultaneously recorded signals of the wet (w) and dry (d) electrodes
14 were compared by means of the Root Mean Square Deviation (RMSD), the Spearman's rank
15 correlation (CORR) as well as the Welch estimation of the Power Spectral Density (PSD).
16 Therefore, the signals were filtered using a bandpass with cut-off frequencies at 1-40 Hz and
17 automatically selected data sequences of 10 s were analyzed. Further details about the EEG
18 monitoring and analysis procedures can be found elsewhere.^[18]

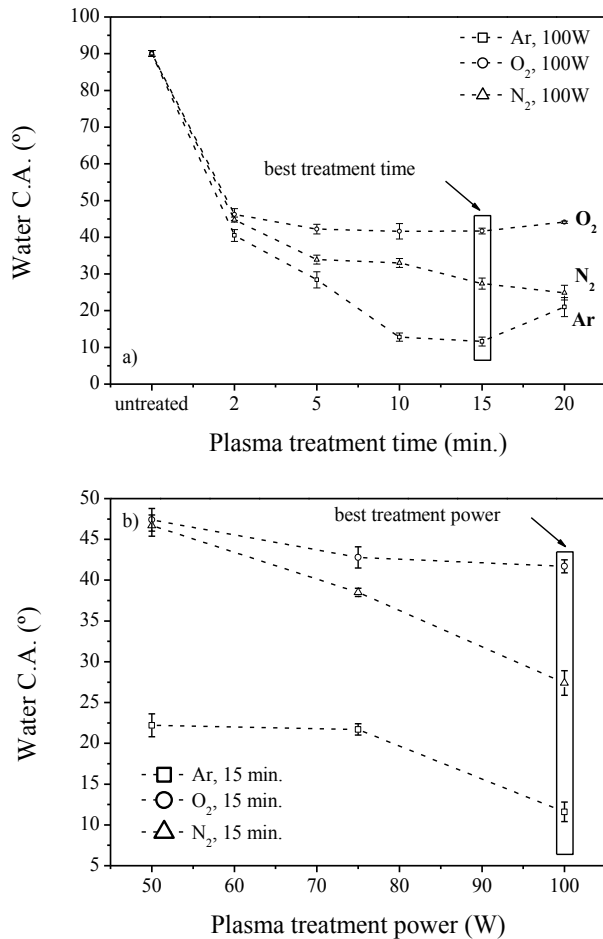
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20 **Results and Discussion**

21 **Wettability evaluation of the plasma treated PU surfaces**

22 The hydrophilicity of the untreated and Ar, O₂ and N₂ plasma treated polyurethane
23 samples was evaluated as a function of the treatment parameters that were used, since it is a
24 reliable indicator for the formation of reactive groups and surface roughness promotion,
25 which is expected to promote the desired thin film adhesion levels.^[55]

1 Figure 1 a) and b) represent the water contact angle (C.A.) evolution with increasing
 2 plasma treatment times and powers for the three used gases, respectively. Regarding the
 3 plasma treatment time parameter, Figure 1 a), all treatments were performed with a fixed
 4 power of 100 W (equipment maximum) and increasing exposure times from 2 to 20 minutes.



5
 6 *Figure 1.* Water contact angle evolution with (a) increasing plasma treatment times and with
 7 (b) decreasing plasma treatment power. Mean and standard error of the mean were calculated
 8 for all conditions (minimum of 6 measurements).
 9

10 Figure 1 shows that it is possible to reduce the water C.A. from 90° (untreated) to 40°-45°
 11 after only 2 minutes of activation (valid for all gases). Subsequently, with further increase of
 12 the plasma treatment time, a clear differentiation of the C.A. behaviour is patent, taking into
 13 account the different gases used. The most pronounced reduction of the C.A. is achieved
 14 using Ar, with a minimum of 12° after 15 minutes of exposure, corresponding to a
 15 hydrophilicity increase of 87%, comparing to the untreated value. When a 20 minutes

1 treatment is performed, the water C.A. values suffer a slight increase until 21°. Regarding the
2 nitrogen series, a constant decrease of the C.A. values can be seen up to 20 minutes of
3 treatment time (minimum of 25°, 72% hydrophilicity increase). As for the oxygen treatments,
4 a minimum C.A. of 42° is achieved after 5 minutes (53% hydrophilicity increase), with the
5 values remaining rather constant with increasing activation times.

6 Taking into account the results of the exposure time variation in the water C.A., the 15
7 minutes plasma activation treatment was selected as the best treatment time, since all surfaces
8 activated with the three used gases displayed the lowest C.A. value. In the case of the nitrogen
9 activation, the slight decrease of the C.A. observed from 15 to 20 minutes was not considered
10 as significant, taking into account that the error bars of both experimental data are overlaid.
11 Hence, after selecting the most appropriate treatment time (15 minutes), the effect of the
12 plasma power was also investigated by decreasing the values from 100 W (maximum power
13 output allowed by the equipment used) to 50 W, Figure 1 b). With the exception of the
14 oxygen treatments (which display roughly the same C.A. with 100 W and 75 W), the argon
15 and nitrogen plasma ones exhibit increasing C.A. values with decreasing plasma powers.
16 Consequently, regarding the water C.A. evolution, the plasma treatments that were found to
17 be more effective in increasing the wettability/hydrophilicity of the PU surface were the ones
18 performed with 100 W for 15 minutes, regardless of the used gas.

19 The water C.A. behaviour of the plasma activated PU surfaces, consistent with results
20 obtained by other authors,^[29,35,39,48] may be explained by considering the Wenzel's
21 equation.^[55,56]

$$22 \cos (\theta_w) = r \cos (\theta_Y) \quad (1)$$

23 Equation (1) describes the relation between the apparent C.A. on a rough surface (θ_w), the
24 surface average roughness ratio (r , ratio between the real and geometric area) and the C.A. on
25 a chemically similar smooth surface (θ_Y). Hence, taking into account this relation, it is
26 possible to claim that the wettability evolution is strongly related with the chemical and

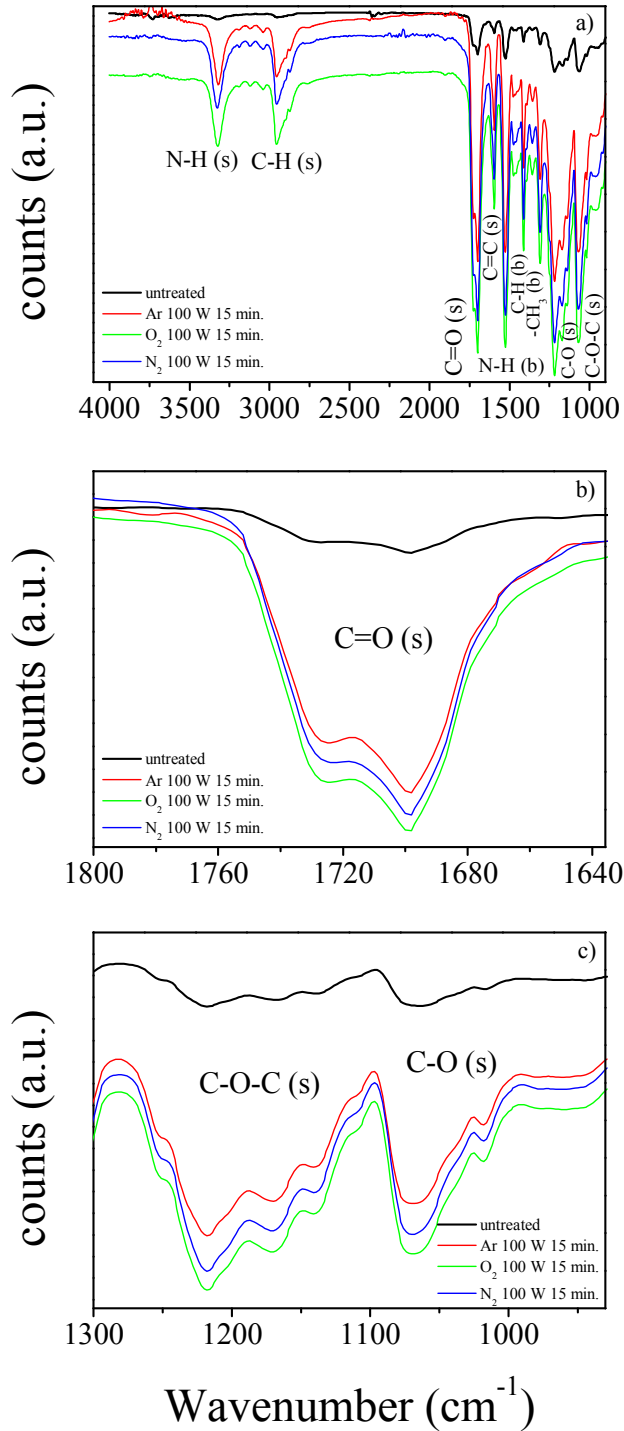
1 topographic changes promoted by the plasma activation treatments. Therefore, an extensive
2 surface chemical and topographical analysis will be performed in the subsequent sections of
3 this work, in order to draw correlations regarding the observed water C.A. behaviour.

4

5 **Chemical analysis of the plasma activated PU surfaces**

6 FTIR-ATR analysis

7 The FTIR-ATR analysis was again performed on PU surfaces activated with different
8 gases, exposure times and plasma powers (same conditions as in the previous section) in order
9 to validate the selection of the best plasma parameters (time and power) that were performed,
10 taking into account the water C.A. behaviour. However, unlike what was observed from the
11 C.A. measurements, no significant changes could be seen when focusing on the exposure time
12 and plasma power, with the respective spectra appearing overlaid. Hence, only the spectra that
13 refer to the plasma conditions that originated the lowest water C.A. values (100 W, 15 min.
14 for all gases) are shown in Figure 2. Note that the exhibited spectra were shifted in relation to
15 the baseline, in order to allow a better visualisation of the peaks.



1

2 *Figure 2.* FTIR spectra of the polyurethane samples (a) treated with the best treatment time
 3 and power for the three used gases. (b) and (c) represent magnifications of the reactive
 4 oxygen containing bonds. The signals were shifted in relation to the baseline in order to allow
 5 a better understanding of the promoted changes.

6

7 The bands at 3320 and 2956 cm⁻¹ refer to N-H and C-H stretching (s), respectively. As
 8 for the peaks detected between 2000 and 1500 cm⁻¹, that may be indexed to C=O (s) at 1700
 9 cm⁻¹, C=C (s) at 1600 cm⁻¹ and N-H bending (b) at 1528 cm⁻¹. From 1500 to 1000 cm⁻¹, the C-

1 H (b) at 1414 cm^{-1} , -CH₃ (b) at 1312 cm^{-1} , C-O (s) at 1216 cm^{-1} and C-O-C (s) at 1067 cm^{-1}
2 bonds were observed. All the FTIR spectra were indexed according to references.^[57,58]

3 Major changes regarding the intensity of the indexed bands can be seen on the FTIR
4 spectra of the activated surfaces when comparing to the untreated sample, meaning that the
5 performed plasma treatments effectively changed the chemical surface of the PU samples, by
6 increasing its reactivity (higher intensity of the reactive oxygen-containing groups can be
7 seen). However, no new species were detected, regardless of the used gas, exposure time and
8 plasma power, which was somewhat expected since FTIR is known for not being particularly
9 sensitive to small amounts of chemical species.^[55]

10 Since the inclusion of reactive species is an important indicator of good polymer/thin film
11 interfacial adhesion levels and may also explain the water C.A. evolution (bearing in mind the
12 Wenzel's equation), the effect of the performed surface activation on the promotion of C=O,
13 C-O and C-O-C bonds is depicted on Figure 2 b) and c). Despite the small intensity
14 differences that are, once more, perceivable, the same behaviour is patent when taking into
15 account the changes promoted by the three gases. As expected, the Ar 100 W 15 min.
16 treatment consistently gives rise to lower amounts of oxygen-containing reactive species, due
17 to the fact that argon is a non-reactive, ideal gas.

18 Hence, argon should mainly promote the formation of free radicals (dangling bonds) that
19 may later recombine with oxygen and other elements (including water) when exposed to
20 ambient air.^[35,55] It is important to note that the activated PU samples were analysed shortly
21 after the plasma treatments, thus only a very brief exposure to ambient air occurred. In
22 opposition, the treatments performed with nitrogen and, especially, oxygen are more effective
23 in creating further amounts of reactive groups. Nitrogen, despite not being a noble gas, acts in
24 a similar way to argon, by promoting the formation of free radicals due to the occurrence of
25 extensive polymer chain scission.^[29,30] The reactive groups are then formed by combination
26 with ambient oxygen. When using oxygen as working gas, the reactive oxygen-containing

1 functionalities are obtained during the plasma treatment itself.^[35] Furthermore, some free
2 radicals may also be formed and later recombine with the elements present in ambient air.

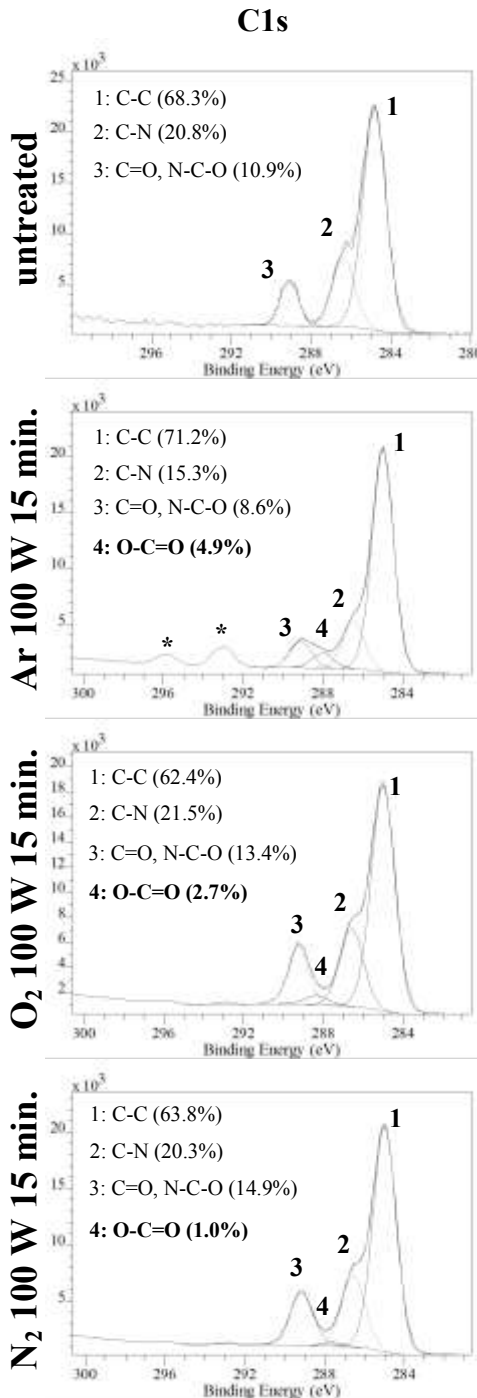
3 In conclusion, due to the lower water C.A. values already observed and beneficial
4 inclusion of reactive species, the Ar 100 W 15 min., O₂ 100 W 15 min. and N₂ 100 W 15 min.
5 plasma treatments were selected to be further investigated.

6

7 XPS analysis

8 Since the FTIR investigation was not sufficient to clearly differentiate the chemical
9 effects of the used working gases, an extensive XPS analysis was performed on the PU
10 surfaces activated with the previously optimized plasma conditions, Figure 3. The
11 identification of the peaks was performed using references.^[30,59]

12



1

2 *Figure 3.* XPS spectra (C1s signal only) of the untreated and plasma treated polyurethane
 3 substrates. * refers to impurities found in the bulk polymer.

4

5 From the XPS spectra analysis it is possible to see significant changes when comparing
 6 the untreated and plasma treated samples, namely regarding the C1s signal (N1s and O1s
 7 spectra are not shown since no significant changes were found). It is important to note that

1 some contaminations (F, Na, S, Cl, K and Ca) were detected (peaks identified as * in Figure
2 3). These contaminations were probably introduced in the manufacturing of the PU samples,
3 since the related peaks were not reduced after ionic etching. This should mean that the
4 impurities are part of the bulk polymer and not promoted by the plasma treatments.

5 All plasma treatments promoted the increase of the oxygen-containing functionalities
6 (13.5%, 16.1% and 15.9% for the Ar, O₂ and N₂ treatments, respectively), when comparing to
7 the untreated PU sample (10.9%) in the C1s spectra. These results are consistent with the
8 FTIR analysis performed in the previous section. Moreover, the insertion of a new chemical
9 functionality at around 288 eV is perceivable due to the formation of C=O or N-C-O bonds at
10 the surface of all activated PU samples. Note that in the FTIR analysis no new reactive groups
11 were detected after the performed plasma treatments. Despite not being reactive gases, the
12 XPS analysis proves that argon and nitrogen are effective (although not in the same extent as
13 oxygen) in promoting the desired chemical changes, including the creation of new
14 functionalities, which should be mainly due to the higher ability to induce the formation of
15 free radicals that later act as anchoring points for the oxygen species present in the ambient
16 air. Oxygen is then the most effective working gas regarding the production of reactive
17 groups. The grafting of such reactive oxygen-containing groups should, in fact, be responsible
18 for the increased hydrophilicity of the activated samples.

19 Nevertheless, this set of results seem to indicate that the chemical alterations studied by
20 FTIR and XPS do not provide a clear explanation for the wettability differences that were
21 promoted by the different working gases. As previously seen, the Ar 100W 15 min. plasma
22 treatment promoted lower water C.A. values (12°) than the N₂ 100 W 15 min. (25°) and
23 O₂ 100 W 15 min. (42°) ones, despite being less effective in the chemical functionalization of
24 the PU surfaces. It is also important to note that the argon treatment promoted the least
25 amount of oxygen-containing groups (13.5%), followed by nitrogen (15.9%) and finally
26 oxygen (16.1%). Hence, considering only the surface chemical changes, no definitive

1 explanations can be found regarding the observed water C.A. behaviour. Consequently, taking
2 into account equation (1), the wettability behaviour should be further explained by
3 investigating the topography changes induced on the activated PU surfaces.

4

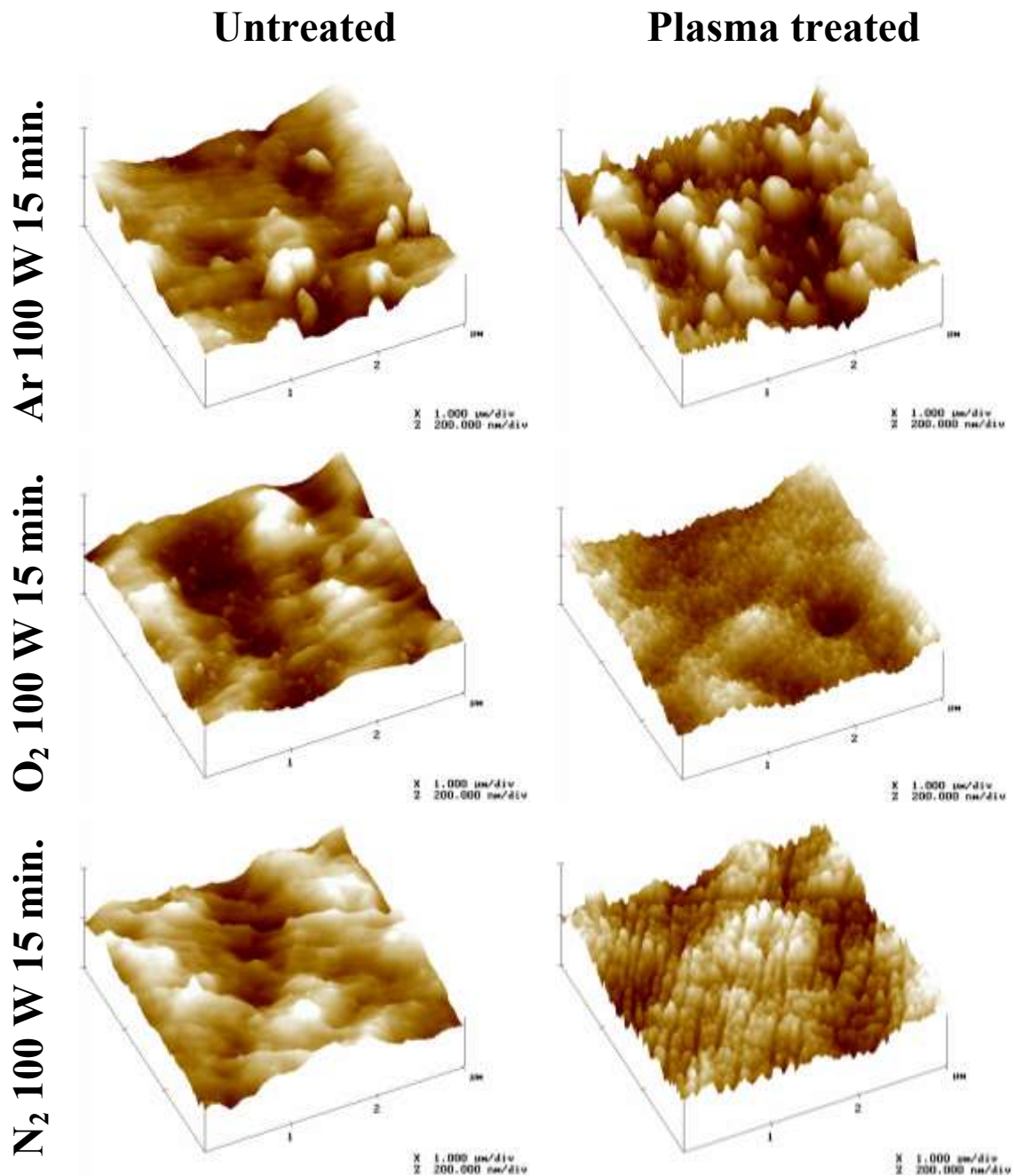
5 **Topographic features of the plasma treated PU samples**

6 Wenzel's equation shows that for a hydrophilic surface ($\theta_Y < 90^\circ$) the roughness should
7 turn the surface more hydrophilic and a hydrophobic surface ($\theta_Y > 90^\circ$) more hydrophobic.
8 However, for water C.A. close to 90° this parameter is insensitive to roughness variations. In
9 addition, the more hydrophilic the surface is, the higher the effect of the roughness on the
10 water C.A. It was seen that the water C.A. of the PU substrates decreased from 90° (untreated)
11 to a minimum of 42° , 25° and 12° for the O_2 100 W 15 min., N_2 100 W 15 min. and Ar 100 W
12 15 min. plasma treatments, respectively. These wettability variations from the untreated to the
13 plasma treated polymer can be explained, in part, by the significant grafting of oxygen-
14 containing species in the surface of the activated PU samples. However, as seen in the
15 previous section, the chemical changes are not able to explain the hydrophilicity changes
16 observed for the different working gases, since the sample treated with the gas that promoted
17 the formation of higher amounts of reactive oxygen-containing groups (oxygen, 16.1%)
18 displayed the higher water C.A. (42°). In opposition, the Ar treatment exhibited the lowest
19 water C.A. (12°) despite promoting the formation of less amounts of reactive species (13.5%).

20 Hence, the wettability behaviour should be further explained by the topographic changes
21 promoted by the different plasma treatments, Figure 4. In order to take account of potential
22 irreproducibility in the fabrication of the PU samples that may derive from the manufacturing
23 process (compression moulding), three untreated samples were selected, suitably identified
24 and then, activated with the selected conditions and working gases.

25

26



1

2 *Figure 4.* AFM micrographs of the untreated and plasma treated polyurethane samples.

3

4 Once more, clear topographic differences can be seen when comparing the plasma treated
5 PU surfaces to their untreated counterparts. Furthermore, the different topographic effects
6 promoted by each of the working gases are also clear. Finer topographic features seem to be
7 introduced by the nitrogen and oxygen treatments, while argon promotes the formation of a
8 coarser topography. Looking at Table III, it is possible to see that the Ar 100 W 15 min.

1 treatment gives rise to the highest increase of the average roughness of the PU surfaces,
 2 increasing from 19.3 nm (untreated) to 37.8 nm.

3

4 *Table III.* Roughness variation promoted by the performed plasma treatments. Mean and
 5 standard error of the mean were calculated for all conditions (3 repetitions).

6

Plasma treatment	untreated		plasma treated		ΔR_a
	R_a (nm)	RMS (nm)	R_a (nm)	RMS (nm)	
Ar 100 W 15 min.	19.3±1.1	24.5±1.4	37.8±1.1	46.6±2.3	+96%
O₂ 100 W 15 min.	16.4±1.3	20.9±0.8	21.6±1.4	27.2±1.7	+31%
N₂ 100 W 15 min.	19.5±1.6	24.6±1.7	28.9±2.7	35.2±3.3	+48%

7

8 The average roughness of the untreated sample was then almost doubled (96% increase)
 9 when using argon as working gas. In opposition, the oxygen treatment promotes the least
 10 amount of topographic changes, with the average roughness increasing from 16.4 nm
 11 (untreated sample) to 21.6 nm, meaning that only a 31% increase of the surface roughness
 12 was achieved. The N₂ 100 W 15 min. activation originates intermediate changes of the surface
 13 topography, with the roughness suffering a 48% increase, from 19.5 nm to 28.9 nm. It is
 14 interesting to note that all plasma treatments gave rise to increased surface roughness of the
 15 PU samples. These results are not consistent with the work of other authors,^[35] where a
 16 softening of the surface was observed, which must be due to the lower activation times that
 17 were used (3 min. vs. 15 min.). Hence, it is possible to say that higher plasma activation times
 18 are beneficial for the promotion of increased surface roughness on PU samples.

19 To summarize, regarding the influence of the chemical changes and surface roughness
 20 promotion on the wettability behaviour of the PU samples, a clear relation is perceivable. The
 21 samples treated with argon, which display the highest roughness increase (96%), are also
 22 more hydrophilic (lower water C.A., 12°), despite also exhibiting the lowest amount of

1 reactive oxygen-containing groups (13.5%). In turn, the PU samples activated using oxygen
2 as working gas, which present the most chemically active surface (grafting of 16.1% of
3 reactive species), display the least amount of topographic changes (31% roughness increase)
4 and the highest water C.A. value (42°). The samples activated with the N₂ 100 W 15 min.
5 plasma treatment exhibit intermediate water C.A. values (25°), which should be due to the
6 also intermediate roughness increase (48%) and grafting of oxygen reactive groups (15.9%).

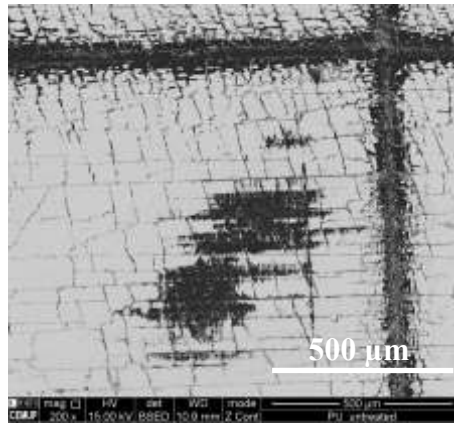
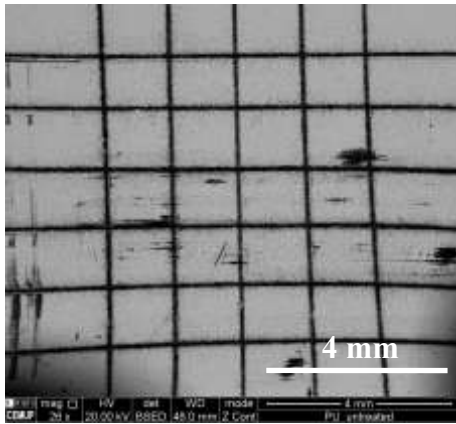
7 In conclusion, all plasma treatments performed with the optimized conditions (100 W, 15
8 min.) are effective in producing the desired wettability changes, through the grafting of
9 reactive oxygen-containing species and roughness promotion on the surface of the PU
10 samples. The extent of the aforementioned surface alterations is dependent on the used
11 working gas and the hydrophilicity behaviour is effectively explained by taking into
12 consideration the relation between chemical and topographic changes patent in the Wenzel's
13 equation (1).

14

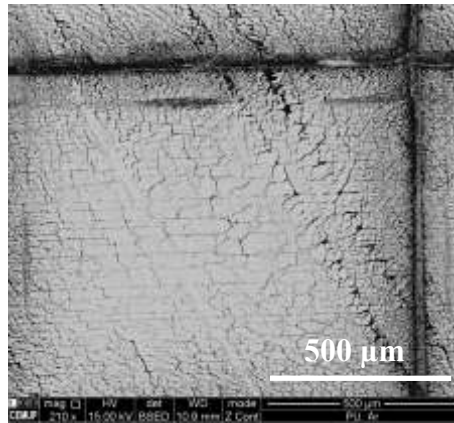
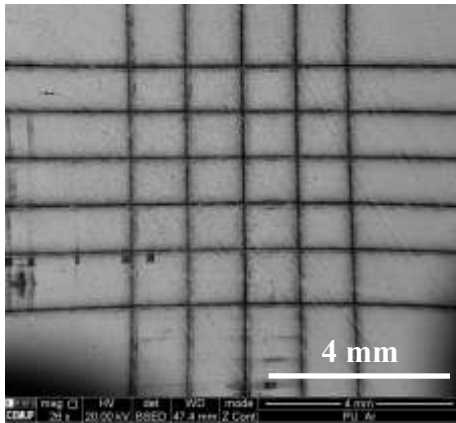
15 **PU/Ag:TiN adhesion assessment**

16 In order to investigate if the performed plasma treatments promote, in fact, an
17 enhancement of the PU/thin film interfacial adhesion, a Ag:TiN coating (with N/Ti atomic
18 ratio of 0.7 and 6 at.% Ag; thickness of ~600 nm) was deposited on the untreated and plasma
19 treated PU substrates. The adhesion was studied using the cross-cut tape test, according to the
20 ASTM D3359-B standard (which provides a decreasing adhesion classification between 5B
21 and 0B) and the results are patent in Figure 5.

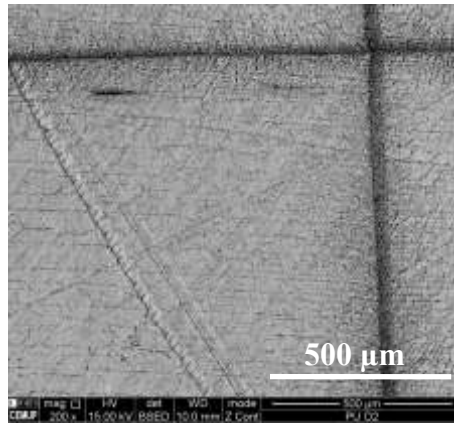
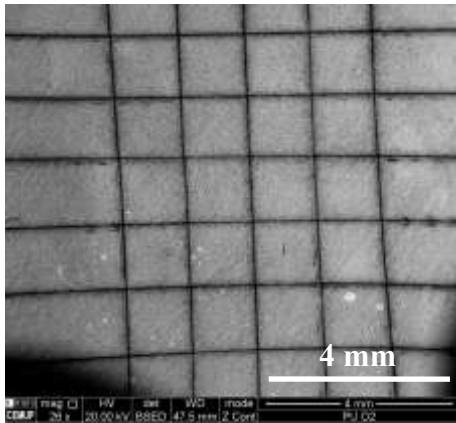
untreated



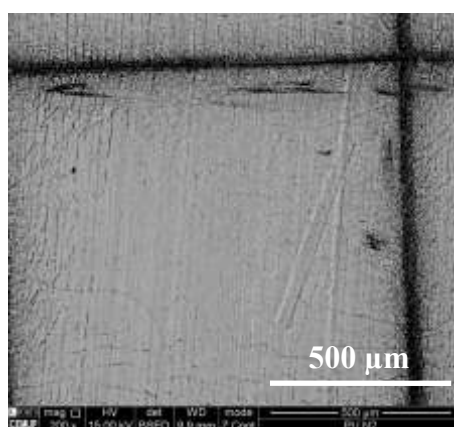
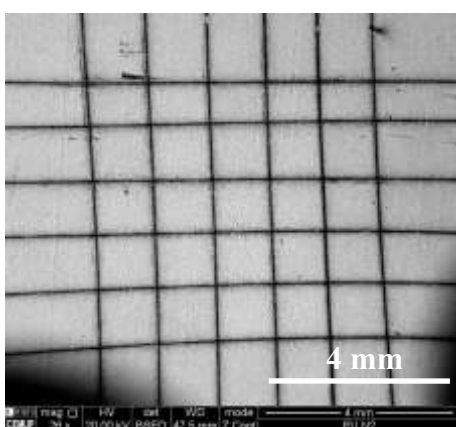
Ar 100 W 15 min.



O₂ 100 W 15 min.



N₂ 100 W 15 min.



1

2 *Figure 5.* SEM imaging of the cross-cut tape tests performed on the untreated and plasma
3 treated Ag:TiN-coated polyurethane substrates.

1 As expected, due to the significant chemical and topographic changes underwent by the
2 plasma treated PU surfaces (grafting of reactive oxygen-containing species and increase of the
3 surface roughness), the untreated sample exhibits the lowest adhesion to the Ag:TiN film. As
4 it can be seen from the backscattered images, extensive delamination can be seen not only
5 along the cuts, but also inside some of the squares (although in a smaller extent). According to
6 the aforementioned standard, the appropriate adhesion classification seems to be 3B: small
7 flakes of the coating are detached along the edges and at the intersections of the cuts; the area
8 affected is 5 to 15% of the lattice. In opposition, no definitive differences can be found among
9 the plasma treated samples. However, the argon treated sample seems to exhibit slightly
10 higher amounts of cracks, which may be an indication of the importance of the grafting of
11 reactive oxygen-containing groups. Note that the argon treatment promoted the formation of
12 smaller amounts of reactive species (13.5%). All plasma treatments, Ar 100 W 15 min.,
13 O₂ 100 W 15 min. and N₂ 100 W 15 min., translate into excellent levels of interfacial
14 adhesion (rated as 5B – the edges of the cuts are completely smooth; none of the squares of
15 the lattice is detached), since no delamination is perceivable. All chemical and topographic
16 combined results seem to indicate that the key parameter controlling the interfacial adhesion
17 should be the grafting of reactive chemical groups and not the observed roughness changes.

18 Hence, it is possible to conclude that the performed plasma treatments produced the
19 desired increase of the PU/Ag:TiN interfacial adhesion by effectively activating the PU
20 surface chemically and by increasing the surface roughness. Both parameters should lead to
21 an increase of anchoring and interlocking points to the sputtered Ag:TiN film.^[55]

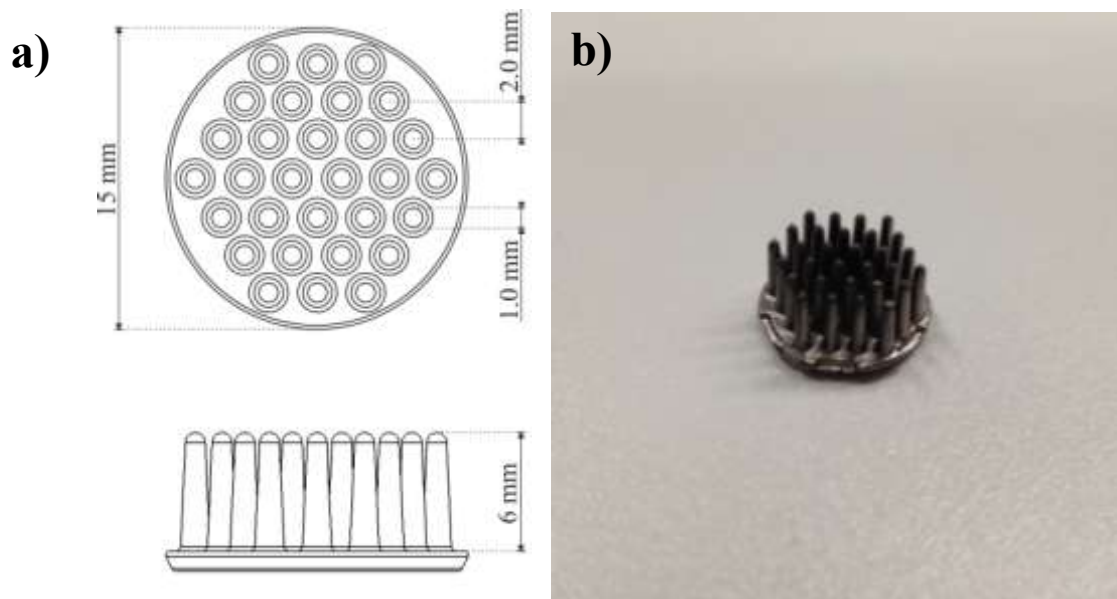
22

23 **EEG trials**

24 With the objective of investigating if the proposed technological approach was suitable to
25 be used as EEG electrodes, three sets of PU MP electrodes were activated using the
26 previously optimized plasma conditions and subsequently coated with the same Ag:TiN

1 coating used in the previous section. Since the non-treated PU flat samples did not display an
2 acceptable coating/substrate adhesion performance, – exhibiting strongly delaminated areas (a
3 phenomenon that would be even more relevant in the coating of complex substrate designs) –
4 only the plasma treated conditions were selected for the coating of the PU MP electrodes,
5 Figure 6.

6



7

8 *Figure 6.* PU multipin electrode used for the EEG tests. (a) electrode design and (b) plasma
9 activated Ag:TiN-coated electrode.
10

11 Subsequently, the dry MP electrodes were used in parallel with the commercial wet
12 Ag/AgCl electrodes in several EEG monitoring tests, in order to assess their characteristics in
13 a realistic EEG acquisition scenario and to evaluate if considerable signal differences could be
14 found among the electrodes.

15 After determination of the RMSD (root mean square deviation) and CORR (Spearman's
16 rank correlation) values for each plasma activated and reference electrodes (3 subjects, 3
17 repetitions) separately, the mean and the standard deviation over all subjects and test
18 repetitions was calculated. The resulting values are listed in Table IV. As it is possible to see,
19 the magnitude of the calculated RMSDs of the plasma activated and Ag:TiN-coated

1 polyurethane MP dry electrodes is only marginally lower (maximum difference of 2.4 μV)
 2 than the RMSD of the wet Ag/AgCl reference test.

3

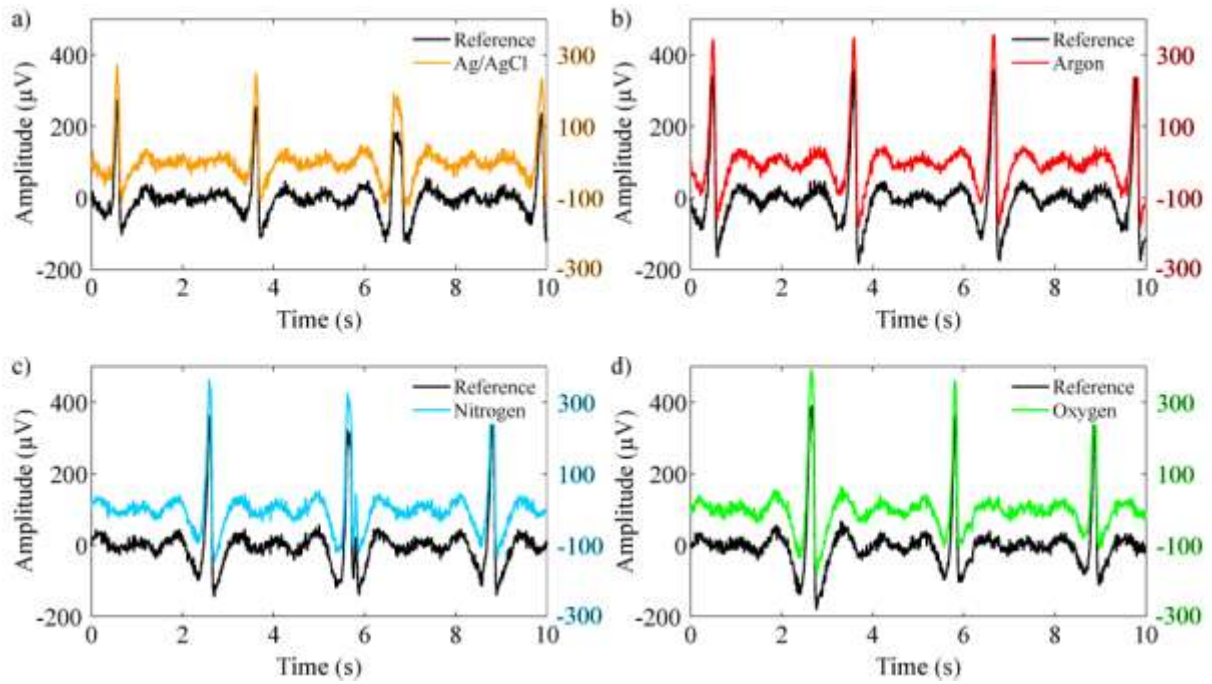
4 *Table IV.* Signal differences between the plasma treated Ag:TiN-coated polyurethane MP dry
 5 electrodes vs. Ag/AgCl reference wet electrodes calculated for the VEP, as well as for 10 s
 6 long sequences of resting state EEG, alpha activity, and EEG containing eye blink artefacts.
 7 Mean and standard deviation calculated over all subjects and repetitions.

8

Plasma treatment	RMSD (μV)				CORR			
	Resting	Alpha	Eye blink	VEP	Resting	Alpha	Eye blink	VEP
Ar 100 W	8.3	7.5	7.9	0.5	0.85	0.86	0.94	0.97
15 min.	± 2.9	± 2.6	± 1.9	± 0.08	± 0.15	± 0.18	± 0.06	± 0.01
O₂ 100 W	6.9	6.5	6.5	0.6	0.81	0.82	0.97	0.97
15 min.	± 3.7	± 2.5	± 1.6	± 0.06	± 0.20	± 0.17	± 0.07	± 0.01
N₂ 100 W	7.4	7.3	7.4	0.9	0.83	0.86	0.96	0.97
15 min.	± 2.6	± 2.0	± 1.3	± 0.09	± 0.12	± 0.13	± 0.08	± 0.01
Ag/AgC	5.9	6.0	6.2	0.5	0.88	0.89	0.98	0.97
reference	± 2.0	± 1.6	± 0.9	± 0.1	± 0.12	± 0.09	± 0.04	± 0.01

9

10 Similar trends are visible for the VEP results (maximum difference of 0.9 μV) and the
 11 Spearman's rank correlation. These negligible differences between the monitored EEG
 12 signals are likely caused by the spatial distance of the two occipital electrode positions, as
 13 well as environmental noise or even due to inevitable experimental differences that derive
 14 from the manual positioning and preparation of the electrodes.^[15,17,18] Moreover, taking into
 15 account the high correlation values (> 0.8) as well as the standard deviations (for both RMSD
 16 and CORR), no considerable differences in terms of signal quality can be identified: neither
 17 (i) between dry MP and wet electrodes, nor (ii) among the different dry MP electrodes.
 18 Furthermore, no considerable alterations of the shape and amplitude of the EEG signals can
 19 be seen, regardless of the used electrode, Figures 7 and 8.



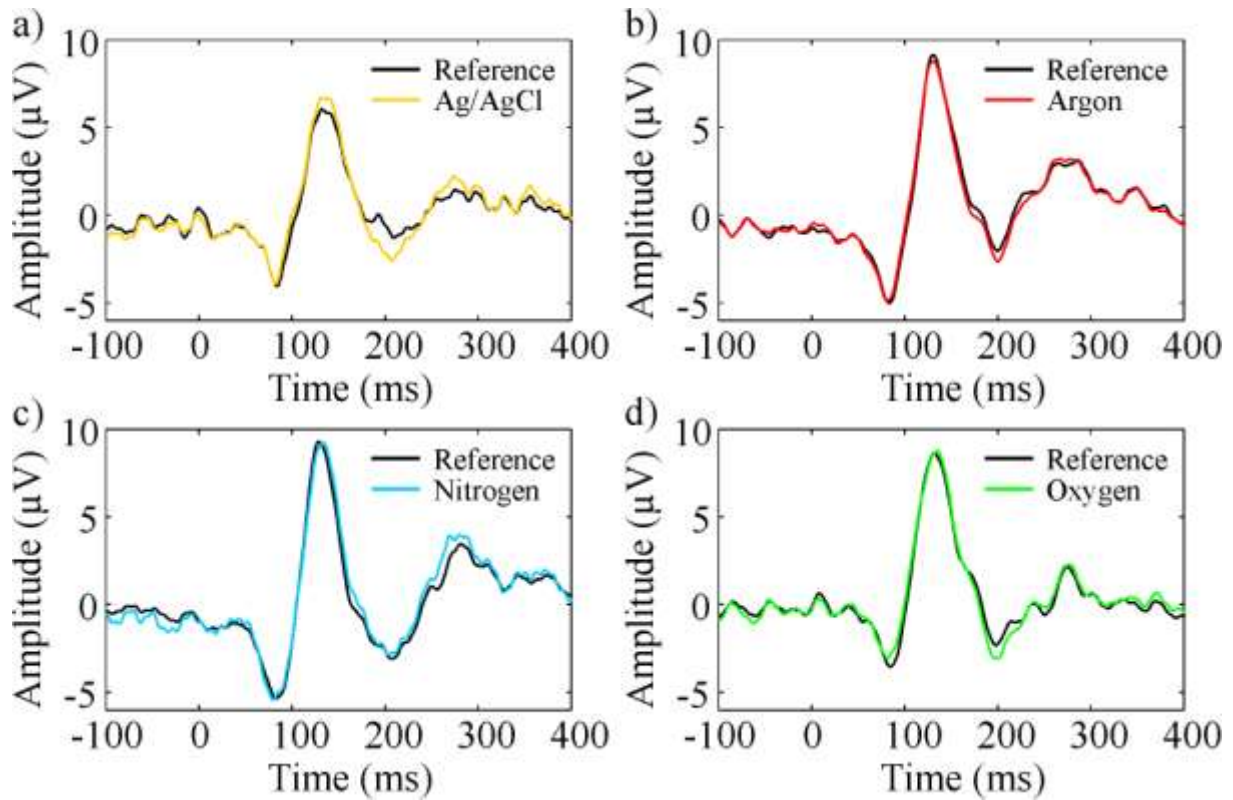
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2 *Figure 7.* Overlay plot of 10 seconds of EEG signal containing eye-blinking artefacts
 3 recorded with (a) two independent wet Ag/AgCl reference electrodes, (b) Ag/AgCl reference
 4 & Ar treated MP dry electrode, (c) Ag/AgCl reference & N₂ treated MP dry electrode, and (d)
 5 Ag/AgCl reference & O₂ treated MP dry electrode pairs.

6

7 Hence, data from Table IV, Figure 7 and Figure 8 indicate that the relevant EEG signal
 8 information can be recorded with both the proposed plasma activated and Ag:TiN-coated
 9 polyurethane MP dry electrodes and the reference conventional wet Ag/AgCl electrodes.

10



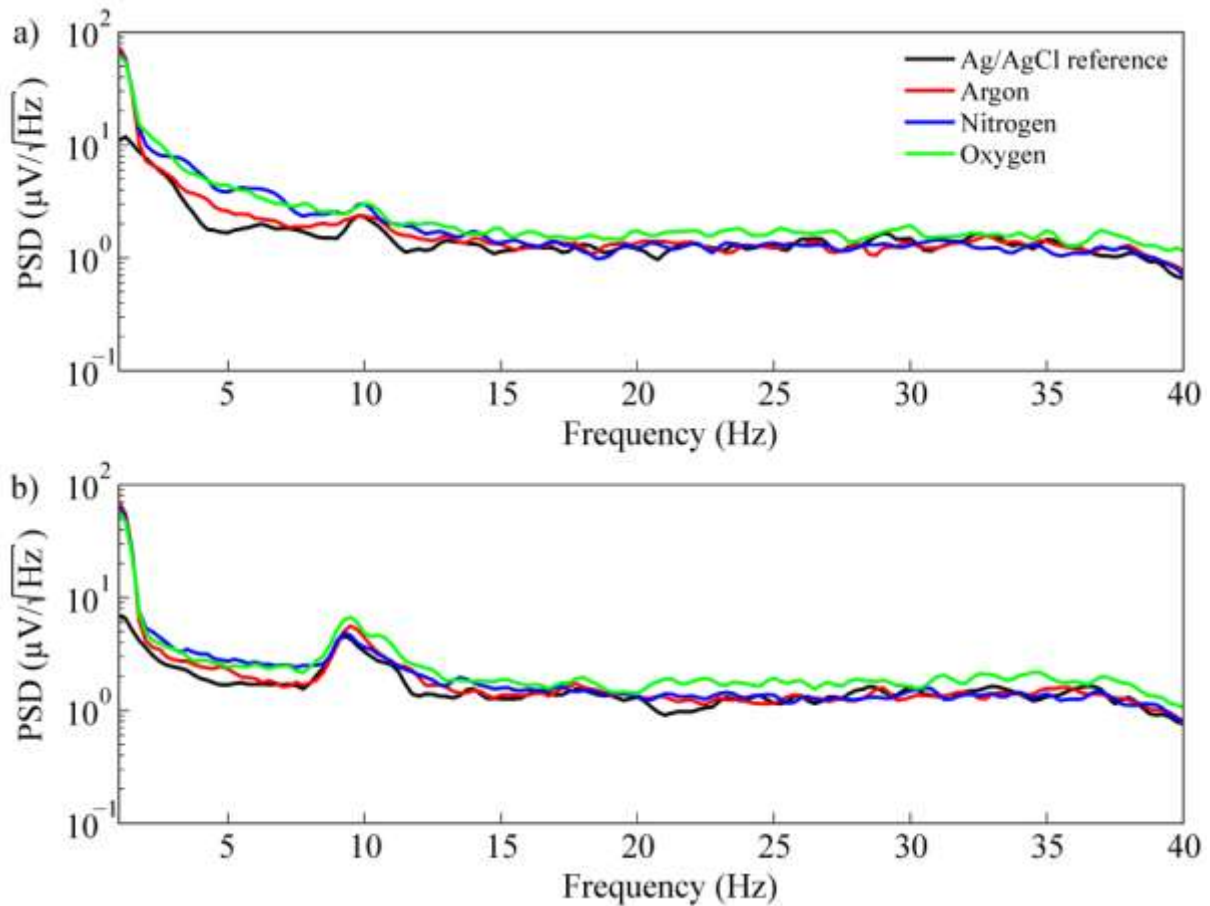
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2 *Figure 8.* Overlay plot of the VEP results 100 ms pre- and 400 ms post-stimulus acquired
 3 with (a) two independent wet Ag/AgCl reference electrodes, (b) Ag/AgCl reference & Ar
 4 treated MP dry electrode, (c) Ag/AgCl reference & N₂ treated MP dry electrode, and (d)
 5 Ag/AgCl reference & O₂ treated MP dry electrode pairs.

6

7 In order to analyse frequency-dependent signal differences, the mean power spectral
 8 density (PSD) of the EEG signals was calculated over all subjects and test repetitions and is
 9 shown in Figure 9 for the wet reference and the dry test signals. Resting state EEG and alpha
 10 activity (Figure 9 a) and b), respectively) show similar trends. The power increases for lower
 11 frequencies for all electrodes. For frequencies below 3 Hz, an increase towards higher values
 12 is perceivable in the plasma treated dry MP electrodes, which should be attributed to slightly
 13 increased drift behaviour, which was already observed in previous studies.^[17]

14



1
 2 *Figure 9.* Characteristic EEG signals acquired with the proposed plasma treated Ag:TiN-
 3 coated polyurethane MP dry electrodes and conventional Ag/AgCl electrodes: Welch
 4 estimation of the mean power spectral density of 10 seconds of (a) resting state EEG and (b)
 5 EEG exhibiting alpha activity calculated over all subjects and test repetitions.
 6

7 To summarize, the small differences found in terms of EEG signal characteristics, shape
 8 and amplitude indicate that the proposed dry MP electrodes are promising candidates to
 9 replace the standard wet Ag/AgCl ones, which should translate into faster and simple
 10 montages, beneficial for many clinical or ambulatory procedures.
 11

12 **Conclusion**

13 The present study focused on the optimization of the plasma treatment conditions with
 14 the objective of enhancing the PU/Ag:TiN system interfacial adhesion so that it may be later
 15 used as dry EEG electrodes. The optimal treatment conditions were selected taking into
 16 account the influence of the exposure time and plasma power on the wettability of the PU

1 surfaces. Minimum water C.A. values (42°, 25° and 12° for oxygen, nitrogen and argon,
2 respectively) were obtained using 100 W and 15 min., regardless of the used working gas.
3 The steep reduction from 90° (untreated PU) was attained due to significant chemical and
4 topographic changes of the PU surface. After FTIR and XPS analysis it was found that the
5 plasma activation promoted the grafting of reactive oxygen-containing groups at the PU
6 surface. Oxygen was the most effective gas, inducing the formation of higher amounts of the
7 referred species (16.1%), followed by nitrogen (15.9%) and argon (13.5%). Furthermore, the
8 Wenzel's equation predicted that also topography changes should play an important role on
9 the hydrophilicity evolution, thus from the AFM studies it was found that a 96%, 48% and
10 31% roughness increase was promoted by the argon, nitrogen and oxygen, respectively. As
11 expected, the promoted chemical and topographic changes translated into an excellent
12 PU/Ag:TiN interfacial adhesion, being rated with the maximum classification of 5B. The
13 untreated PU sample exhibited extensive delamination along the edges of the cuts and in some
14 areas inside the squares defined by the cross-cut tape test.

15 The results obtained from the EEG trials allowed to conclude that no considerable
16 differences in terms of shape, amplitude and spectral characteristics were found when
17 comparing signals acquired by conventional wet reference Ag/AgCl electrodes and the
18 proposed plasma activated and Ag:TiN-coated polyurethane dry MP electrode, regardless of
19 the used plasma working gas. No differences between the dry electrodes themselves could
20 also be found. Consequently, since most of the EEG signal information is maintained when
21 the dry electrode system proposed in the present work is used, it is possible to conclude that
22 the PU/Ag:TiN dry electrodes are promising candidates to substitute the standard Ag/AgCl
23 ones in specific clinical and ambulatory procedures.

24

25

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13

14 Keywords: Ag-doping; dry electrodes; EEG; interfacial adhesion; plasma activation

15

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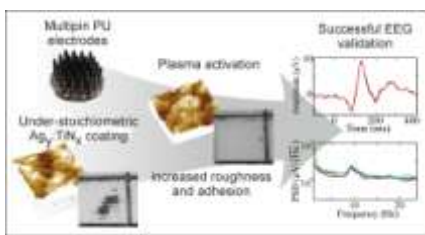
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1 **Table of Contents**

2 **The plasma activated and Ag:TiN-coated dry biopotential electrodes are promising**
3 **candidates to replace the standard wet Ag/AgCl electrodes.** The optimized plasma
4 treatments translate into excellent polyurethane/Ag:TiN interfacial adhesion of the samples.
5 The EEG validation of the proposed Ag:TiN-coated PU multipin electrodes showed no
6 considerable differences of the signals when comparing with the reference wet electrodes.

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