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Analysis of microscopic modifications and macroscopic surface properties of polystyrene thin films treated under DC pulsed discharge conditions.

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Abstract

Using a DC pulsed plasma for the polymer surface treatment allows the attainment of macroscopic modifications of the surface such as an important increase of the wettability. In the same time microscopic variations of the surface structure are mainly linked to low depth chemical modifications even if very weak roughness changes appear.

As a consequence this technique presents two major interests. The first one is an economical interest because of the low power consumption compared to other techniques like radiofrequency or microwaves plasmas. The second one is the very significant treatment (macroscopic) realized in soft conditions without degradation of the polymer.

These results composed of macroscopic and microscopic studies on polystyrene surfaces may allow to establish a macroscopic interpretation of the interaction between polymer and the DC pulsed plasma.

Keywords : Polystyrene, Surface Treatment, DC Pulsed Plasma, Glow Discharge, Wettability, XPS, AFM.

1. Introduction

Improving the surface properties of polymers using a DC pulsed glow discharge in reactive gases is of a great interest for industrial applications. This non polluting technique allows to contribute to some surface modifications such as the increase of wettability¹⁻¹⁷. Moreover, in numerous cases the adhesion mechanisms are improved even if the adhesion is not realized with water but more often with an epoxy adhesive¹⁰.

At last the very low energy cost of this recent treatment method is remarkable¹¹ : the duration of the discharge corresponding to one DC pulse is one hundred times lower than the

time period between two DC pulses. As a consequence polymer samples are mainly exposed to a “temporal afterglow” which underscores the important role of long-lived reactive species generated in the plasma ¹². In nitrogen and oxygen plasmas, metastable species like $N_2(A^3\Sigma_u^+, E = 6.17\text{eV})$, $N(^2P_{1/2,3/2}, E = 3.58\text{eV})$, $O_2(c^3\Delta_u, E = 4.2\text{eV})$, $O_2(A^3\Sigma_u^+, E = 4.43\text{eV})$, $O_2(c^1\Sigma_u^-, E = 4.5\text{eV})$ and $O(^1S_0, E = 4.17\text{eV})$ present enough energy to activate and functionalize the polystyrene chains which present bond energies in the range [2.6eV, 4.79eV] ¹³.

It is well-known that plasma treatments induce four important phenomena on polymers each one depending on the experimental conditions: *cleaning*, *etching*, *crosslinking* and *functionalization* ^{10, 14-17}.

The *cleaning* is of high importance to improve bonding. It consists in removing layers of organic contaminants present on the surface in the [10-100 Å] thick range ¹⁵. Typically for plasma treatments with an injected power of several mW/cm² the polymer has to be exposed numerous seconds to obtain sufficient cleaning and an increase of the adhesion ^{10, 15}.

The *etching* allows the removal of a bigger quantity of matter compared to the cleaning. This ablation process may end in the degradation of the polymer.

The *crosslinking* of the surface is realized by the formation of free radicals by the plasma phase. It is usually obtained in inert gases. As a consequence no new functionality appears on the surface ¹⁵.

At last the *functionalization* is widely studied and consists, without affecting the bulk properties, in the surface formation of new chemical functions in a depth typically of several hundreds Ångströms ¹⁶. By using reactive gases in the plasma like nitrogen or oxygen, the surface becomes more polar with the production of hydroxyl, alcohol, ether, carbonyl, carboxyl, amide and amine functions.

This paper is devoted to the analysis of macroscopic modifications and microscopic ones obtained on aPS (atactic polystyrene) thin films by using DC pulsed nitrogen and oxygen plasmas. The surface is analysed by several ways: study of the wettability by the measurement of water drop contact angles, XPS (X-ray Photoelectron Spectroscopy) and AFM (Atomic Force Microscopy).

In the first part of this paper the experimental set-up is described as well as the experimental conditions of polystyrene treatment.

In the second part the results are shown and a discussion is presented in order to obtain a better understanding of the interaction mechanisms between the polymer and the DC pulsed plasma.

2. Experimental set-up

2.1 Preparation of polymer thin films

Atactic PS (aPS) pellets were dissolved in toluene (*ca* 0.5 % v/w) during 1h respectively at room temperature. Some drops of this solution are deposited on glass slides (dimensions : $1,5 \times 3,75 \times 0,1$ cm ; area exposed to the plasma $S_{\text{aPS}} = 5.625 \text{ cm}^2$) cleaned beforehand with toluene and dried with acetone. These slides are stored in a dessicator, in which the evaporation of solvent is carried out under controlled atmosphere, in order to obtain homogeneous aPS films, with an approximate thickness of 10 μm .

2.2 Experimental set-up

Figure 1 presents the experimental set-up used for plasma treatment of aPS. The plasma reactor consists of two stainless-steel plane electrodes (10 cm in diameter) inside a stainless-steel chamber that can be pumped down to 5.10^{-3} mbar before each treatment. For the polymer treatment, the gap distance between the electrodes is set to 1 cm and the running pressure is 4 mbar in nitrogen or oxygen (purity > 99.99 %). One electrode is grounded and the other is negatively polarised using a high power DC pulsed generator. Two resistors are used in the electrical circuit: a load resistor R_L (200 Ω , value imposed by the HV supply manufacturer) and a measurement resistor R_m (50 Ω). The frequency of the pulsed voltage is set to 500 Hz with a pulse width t_g (glow duration time) of 20 μ s. So, the duty cycle C_T (defined as the ratio between the glow duration time (t_g) and the pulsed voltage period (T)) is 1 %. With these experimental conditions, a plasma corresponding to the abnormal glow discharge is generated between the two plane electrodes during each pulse. Discharge current and voltage waveforms are recorded via an oscilloscope (bandwidth and acquisition rate respectively equal to 300 MHz and 2.5 GS/s), the average power value $\langle p(t) \rangle$ is measured and fixed at approximately 6W during the period T. The total treatment duration time (t_t) is controlled by an oscillator counter fabricated in our laboratory.

From anode to cathode, this abnormal glow discharge consists of a positive column, a Faraday dark space and a negative glow. For each treatment, the aPS thin film is placed on the anode and on the cathode, namely, close to the positive column and the negative glow respectively.

2.3 Contact angle measurements

The treatment was characterised by measurement of the contact angle of a deionised water drop on the surface. Measurement is made immediately after the treatment (delay lower than 5 min.). Four drops are deposited at various places on a given polymer surface with a syringe (volume of 5 μ l) in order to obtain an average value of the contact angle. The error of measurement is estimated to be 5°. The results of wettability will be presented using the relative variation of the contact angle:

$$\Delta\theta/\theta_i = (\theta_i - \theta_f) / \theta_i \quad (1)$$

where θ_i and θ_f are respectively the initial and final contact angles (each one is an average value of four angles).

The initial contact angle is typically $\theta_i \approx 85^\circ$ (before treatment).

An image processing technique is used to measure precisely the contact angle. A grey-level image $I(x,y)$ of the drop deposited on the polymer is acquired with a video camera (ITM-M-SC Intertec components, miniature video camera: 260 lines). A typical image is shown in Figure 2a. From this image, the contours are extracted.

The contour detection processing consists in the following steps:

- First, the spatial (respectively vertical and horizontal) partial derivatives $\delta I/\delta x$ and $\delta I/\delta y$ are estimated using an exponential derivation filter¹⁸ applied respectively on lines and columns.
- Secondly, the modulus of the spatial gradient $\sqrt{(\partial I/\partial x)^2 + (\partial I/\partial y)^2}$ is computed (Figure 2b) and then thresholded by using an entropic approach as described in¹⁹. It yields a binary map showing the detected contours (points in black on Figure 2c).

- Then the binary contour tracker of Rosenfeld and Kak²⁰ is run to extract the set of connected pixels forming the exact frontier of the drop: we get a vector containing the indices of the contour points (chain-list), with their x- and y-coordinates.
- From this list, the triple points corresponding to x_{\max} and x_{\min} are easily extracted and the tangents to the drop at those two points are estimated by a least-squares algorithm taking into account N neighbouring points such that $y < y(x_{\max})$ and $y < y(x_{\min})$. Indeed, the origin of the image is classically taken in the upper-left corner. The base-line joining the two triple points is also automatically extracted and plotted.
- Finally, the angle is measured as the average value of the two angles on both sides of the drop (see Figures 2d and 2e).

Worth noticing is the fact that the measurement process is entirely automatic and the precision achieved by this image processing technique is better than 1.5 degrees. Moreover, this reliable method for measuring contact angles is very low cost.

2.4 X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were recorded using an SSI M-Probe spectrometer at room temperature. A monochromatic AlK_{α} X-ray (1486.6 eV) was used for the excitation. The analysis chamber pressure was of $5 \cdot 10^{-10}$ mbar. Survey spectra were recorded at constant pass energy of 150 eV and 50 eV for high-resolution analysis. A 5 eV flood gun was used in order to prevent charge effects. The take-off angle was set at 35° in order to have a constant depth analysis.

Experimental and theoretical bands were fitted (80% Gaussian and 20% Lorentzian) using a non-linear baseline with a least-square algorithm. Quantitative analyses were

calculated using Scofield factors ²¹ and binding energies were determined using the C1s binding energy of contamination carbon (284.6 eV) as the reference with an experimental error of ± 0.2 eV.

2.5 Atomic Force Microscopy (AFM)

We imaged the samples in ambient conditions using commercial (CP from Park Scientific Instrument) Atomic Force Microscopy (AFM) head, controlled by feedback electronics and software of conventional design. In this study, an AFM with a laser beam deflection sensor is applied. Cantilevers-type Si₃N₄ springs with integrated tips are used as force sensors. Typical tip radii of curvature are 20 nm and spring constant are 0.07 N/m. Images were recorded in the constant force mode, in the range 10-20 nN with a low scan frequency (1.0 Hz). One micron gridded and mica used as calibration samples, always gave the correct periodicity.

For a line containing N data points, the root-mean squared roughness (Rms) is given by the average deviation of the data, determined using the standard definition:

$$\text{Rms} = \sqrt{\frac{\sum_{n=1}^N (z_n - \bar{z})^2}{N-1}}, \text{ where } \bar{z} = \text{mean } z \text{ height} \quad (2)$$

The Rms is calculated on the total image sample (dimensions $5 \times 5 \mu\text{m}$); this variable will give us the signature of morphological changes occurring with plasma treatment. Images are recorded on different zones in order to be representative of the total sample surface state.

3. Results and discussions

3.1 Electrical discharge conditions

Experiments were realised under glow discharge conditions for the average power value $\langle p(t) \rangle$ injected into the plasma fixed at approximately 6W. The surface characteristic of the discharge can be estimated and is nearly of $S_{\text{electrode}} - (2 \cdot S_{\text{aPS}}) = 78.5 - (2 \cdot 5.625) \approx 67 \text{ cm}^2$. As a consequence the power level injected in the discharge is approximately of 90 mW/cm^2 which is highly sufficient to obtain cleaning of the surface and doubtless etching, crosslinking and functionalization ^{10, 15}.

Since the power remains constant during treatments, results are presented as a function of the treatment duration time t_t which is similar to the energy injected into the plasma :

$$E = \langle p(t) \rangle \cdot t_t \quad (3).$$

It should be mentioned that the effective time of plasma “ON” is one hundred times smaller than the treatment duration time because of the very low duty cycle (Figure 1) :

$$t_t = NT = N(t_g + t_{ag}) = t_{eg} + t_{eag} \quad (4),$$

N is the number of pulses injected into the plasma: $N=1000$ for $t_t = 2\text{s}$ and 30000 for $t_t = 60\text{s}$,

T the period of the signal: $T = 2\text{ms}$,

t_g and t_{ag} are respectively the glow and afterglow duration times: $t_g = 20\mu\text{s}$, $t_{ag} = T - t_g$,

t_{eg} and t_{eag} are respectively the effective glow and afterglow duration times (respectively Σt_g and Σt_{ag}).

3.2 Macroscopic analysis of the treatment : wettability modification of the surface

The effect of plasma treatment duration time has been studied in nitrogen when aPS films are deposited close to the negative glow or the positive column. Results are presented in Figure 3 where a well-known behaviour is observed: the wettability of the surface increases as a function of the treatment duration time to reach a plateau in several seconds^{9, 22}. The value of this plateau is obtained here for a contact angle relative variation close to 0.7.

In all cases a shoulder appears on the curves. When the polymer is placed close to the positive column the amplitude of this shoulder is weak and it is obtained for the treatment time of 6s. When the polymer is placed close to the negative glow the shoulder is obtained for the treatment time of 10s. It can be mentioned here that this shoulder on the contact angle relative variation has already been observed in plane to plane and point to plane electrode configurations^{11, 25}. Particularly remarkable, this phenomenon indicates a partial hydrophobic recovery of the surface during plasma processing. As it can be seen on Figure 3, this shoulder depends on the position of the polymer in the glow discharge: the recovery of hydrophobic state is obtained for different treatment times based on whether the polymer is placed close to the positive column or the negative glow.

According to previous results this shoulder seems also to depend on the gas used in the plasma (nitrogen or oxygen)¹¹. Figure 4 shows the contact angle relative variation as a function of the treatment duration time t_t in oxygen. It can be observed a weak shoulder in the curves whatever the polymer position is and for treatment times of 6s which confirms the role of the gas nature on this phenomenon. Moreover the amplitudes of the shoulders are very low compared to the treatments performed in nitrogen.

To summarize the conditions for which a shoulder is observed, it can be stated that the amplitude of this phenomenon is mainly depending on the gas nature (higher in nitrogen than in oxygen). Moreover the temporal position of this shoulder seems to be lower (≈ 6 s) in oxygen plasma and in nitrogen plasma when the polymer is placed close to the positive column of the glow discharge. The temporal position of this shoulder seems to be higher (≈ 10 s) in nitrogen plasma when the polymer is placed close to the negative glow.

Nevertheless and whatever the gas used, this shoulder appears for a treatment duration time in the 6 to 10s range. As a consequence this treatment duration time seems to be characteristic of the surface state. This characteristic treatment duration time will be denoted t_c .

3.3 Microscopic analyse of the treatment

3.3.1 Chemical modifications of the surface (XPS analyses)

Before treatment the aPS films were analyzed to know the chemical structure of the initial surface. The polymer surface is only composed of carbon as it has been described in ¹² : a peak at 284.6 eV corresponds to the aliphatic and aromatic carbon and a shake-up peak at 291.2 eV is characteristic of the aromaticity of the polystyrene. From this initial state the appearance of new main peaks of weak intensities can be observed whatever the gas is (nitrogen or oxygen plasma) : amine C-N (285.5 eV), C-O (286.1 eV), carbonyl C=O (287.5 eV), carboxyl O-C=O (288.9 eV) ¹¹⁻¹³.

Figure 5 presents the different spectra of untreated aPS film and treated aPS films by nitrogen and oxygen plasmas: the new surface functionalities due to plasma exposure are shown.

3.3.1.1 Quantitative analysis

As it can be seen in Figure 6, the nitrogen plasma introduces on the surface more oxygen bonds than nitrogen bonds. This well-known result ^{16, 26-28} already has been observed in a point to plane configuration ^{11, 13} and may be attributed to residual oxygen and water vapour contained in the reactor during the treatment or to reactions with oxygen during the sample exposure to the atmosphere.

As a consequence and whatever the position of the polymer is (close to the negative glow or to the positive column) the atomic N/C ratio increases very slowly to the 0.05 weak value and in the [0-60s] treatment duration time (see Figure 6). In the same time the evolution of the atomic O/C ratio is remarkable. When the polymer is deposited close to the negative glow it can be noticed that the atomic O/C ratio increases in the [0.1-0.15] range during the ten first seconds of treatment to reach finally the value 0.2. When the polymer is deposited close to the positive column the atomic O/C ratio is close to 0.2 in all the treatment duration time range. It should be mentioned that the wettability shoulder amplitude seems higher when the polymer is deposited close to the negative glow than to the positive column.

Results obtained in an oxygen plasma are presented in Figure 7. As it can be seen the atomic O/C ratio curves evolve similarly to the O/C ratio curve obtained when the polymer is deposited close to the positive column in a nitrogen plasma. Only here the values of O/C are higher: nearly 0.25 when the polymer is on the cathode and 0.33 when it is on the anode.

Finally and whatever the gas used and the position of the polymer, it can be observed in Figures 6 and 7 that in the wettability shoulder time range [6-10s], numerous weak shoulders appear in the O/C and N/C compositions.

3.3.1.2 Qualitative analysis

The percentage of the main chemical groups detected on the aPS surface (from relative intensities of C_{1s} components) is shown in Figure 8 as a function of the treatment duration time t_t in a nitrogen plasma and when the films are deposited close to the negative glow or to the positive column.

The behaviour of the amine bond (C-N) seems to indicate a slow increase of this chemical function in the weak range 2.6 to 5.2 % whatever the polymer position is. It can be noticed a peak at 5.6 % when the polymer is placed close to the positive column and for the treatment duration time of 8s.

The C-O bond is particularly interesting because it is the main component of the total oxygen grafted on the surface. When the polymer is placed close to the negative glow the percentage of this function increases to the value of 10.6 % until the end of the wettability shoulder time range. For longer treatment duration time (60s) a decrease of this function is observed (4.8 %). When the polymer is placed close to the positive column the C-O bond seems to remain constant during all the treatment duration time range [0,60s].

The carbonyl function (C=O) appears at the beginning of the treatment whatever the polymer position is but its percentage (≈ 5 %) is higher when the polymer is placed close to the positive column compared to the negative glow for the two first treatment duration times (≈ 2.5 %).

The carboxyl functions are present all the time when the polymer is placed close to the positive column. Its percentage is nearly of 3 % for the three first treatment duration times and attains the value of 5.7 %. Moreover it is remarkable that when the polymer is placed close to the negative glow the carboxyl function appears after the wettability shoulder time range and attains an important value of 7.4 % for longer treatment duration time (60s).

At last it can be observed that the shake-up peak decreases considerably for all the treatment duration times and the two positions of the polymer. This fact confirms the attack by the plasma of the phenyl rings which leads to a loss of the polymer aromaticity^{11-13, 22, 29}.

The percentage of the main chemical groups detected on the aPS surface (from relative intensities of C1s components) as a function of the treatment duration time t_t in a oxygen plasma when the films are deposited close to the negative glow or the positive column is presented in Figure 9. Similar results can be observed compared to the Figure 8 when the polymer is placed close to the positive column. Whatever the position of the polymer is, the C-O bond seems constant around the 10 % value and for all the treatment duration times (apart from the point at 8s for aPS films close to the positive column). Carbonyl function seems to stay also constant around the value of 6.5 % (apart from the point at 10s for aPS films close to the positive column). Carboxyl function increases slowly from 5.1 % to 6.5 % (apart from the point at 60s for aPS films close to the positive column) and the shake-up peak remains weak for all the treatment duration times (≈ 3 %, apart from the point at 60s for aPS films close to the positive column). At this time the four different results obtained when aPS films are placed close to the positive column (at 8s, 10s and 60s) are not clearly identify.

3.3.2 Morphological modifications of the surface (AFM analyses)

The untreated surface has been characterized by the Rms measurements. The initial state of the aPS polymer presents a very smooth surface with a Rms of 6 Å. In a previous paper¹² it was observed that the roughness increase obtained after the plasma treatment was mainly due to a preferential attack of the aPS amorphous zones. Moreover this roughness increase after plasma exposition in oxygen was obtained for a treatment duration time of 60 s.

Nevertheless the Rms never exceeds the value of 50 Å which corresponds always to a smooth surface. The morphological modifications due to the plasma are thus limited to the extreme surface in several 10 Å in depth. Consequently and as a first approximation it can be suggested that the mean plasma effect on the polymer is chemical and not physical. The important improvement of the wettability may thus be explained by the surface grafting of numerous oxygenated polar functions even if the gas used for the treatment is nitrogen.

In Figures 10 to 13 the Rms results and the atomic ratio O/C of oxygen grafted on the surface are presented as a function of the treatment duration time for different experimental conditions on the gas used (nitrogen or oxygen) and on the position of the polymer (close to the negative glow or the positive column).

At first it can be observed that in the wettability shoulder time range [6s-10s] and whatever the experimental conditions mentioned above are, a decrease of the Rms appears for the treatment duration time of 8s which corresponds to a more smooth surface. After this time of 8s the roughness increases slowly but never exceeds the 50 Å value.

Moreover the surface smoothness at 8s is more important for a nitrogen plasma and when the polymer is deposited close to the negative glow (see Figure 10) which may be correlated to the higher wettability shoulder in the same conditions.

At last and as it is shown in Figure 10, the surface smoothness at 8s is obtained for an atomic ratio O/C of nearly 0.1. In the other experimental conditions (Figures 11 to 13), it can be observed that this surface smoothness is obtained for atomic ratios O/C at least twice higher.

According to these results it can be suggested that the weak loss of roughness in the wettability shoulder time range obtained at 8s is due to the removing of matter on the extreme surface and not to an addition of matter.

3.4 Correlation between macroscopic and microscopic analyses : discussion

As it has been described in the above sections, the main aPS surface modification due to the plasma is macroscopic and corresponds to a significant improvement of the wettability. In the same time microscopic surface changes are weak and realized on the first macromolecular layers of the polymer. Indeed XPS shows that changes appear in a depth typically of several hundreds of Ångströms¹⁶ and AFM shows that the roughness of the surface evolves in a depth of several tens of Ångströms.

Keeping in mind the four important phenomena that realize a plasma on polymer (*cleaning, etching, crosslinking* and *functionalization*), it can be suggested that in our experimental conditions of DC pulsed plasma with a duty cycle of 1%, the surface *etching* may be negligible. Indeed the roughness measured stays always lower than 50 Ångströms whatever the experimental conditions of treatment are, which corresponds to a smooth surface. Nevertheless the etching effect may be carried out in a homogeneous way on the surface so that the low roughness does not quantify the possible real etching.

The gases used for the treatment are nitrogen or oxygen and not inert gases like argon or helium. The *crosslinking* (CASING: Crosslinking by Activated Species of INert Gases) may thus be neglected even if we have no information about the surface structure before and after any treatment.

Consequently and at this stage of analysis a macroscopic explanation may be given concerning the interaction between the aPS surface and the DC pulsed plasma. According to the curve of wettability presented in Figure 3 in which the aPS films are deposited close to the negative glow with a nitrogen gas the shoulder appears for the characteristic treatment duration time t_c of nearly 10s. At this characteristic time t_c and according to the quantitative XPS and AFM results, the atomic ratio O/C is about 0.1 (lower than in the other plasma conditions) and the Rms decreases to a low value (15 Ångströms).

In the $[0, t_c]$ time range, the plasma creates numerous reactive species which collide with the surface. These species have enough energies to break and react with the covalent bonds of the polystyrene. Thus they weaken the surface and realize rapidly the surface *cleaning*. Recall here that the effective glow discharge time t_{eg} is equal to :

$$t_{eg} = C_r \cdot t_c \quad (5),$$

where C_r is the duty cycle equal to 1%.

Thus during this first rapid treatment stage, the *cleaning* consists in leaving layers of organic contaminants which are in the same time oxidized. This is confirmed by the value of the atomic ratio O/C (nearly 0.1 lower than in the other plasma conditions) and by the decrease of the Rms which indicates a loss of matter as it has been suggested above (part 3.3.2). The hypothesis of a cleaning stage in the treatment seems coherent with the bibliography^{10, 15}. The [10-100 Å] thick range of known cleaning effect is in our conditions lower : the Rms never exceeds the value of 50 Å. Moreover the power level injected in the discharge is of 90mW/cm² widely sufficient to leave the organic contaminants: usually and for some plasma treatments with power injected of several mW/cm² the polymer has to be exposed numerous seconds to obtain sufficient cleaning. In our treatment conditions the power level is nearly a hundred times higher than in bibliography but the effective treatment duration times are nearly a hundred times lower.

At the characteristic treatment time t_c it can be supposed that the surface is in a new initial state and the treatment corresponding mainly in the surface *functionalization* begins. In the same time, we can suppose a slow *etching* of the surface because of the weak increase of the roughness. As a consequence the time range $[t_c, 60s]$ concerns the improvement of the macroscopic surface properties and is the second stage of treatment.

At last and as it has been said above this characteristic time seems to be weaker in an oxygen plasma and in a nitrogen plasma when the polymer is placed close to the positive column than in a nitrogen plasma when the polymer is placed close to the negative glow. This fact has also been verified in other experimental conditions ^{11, 25}. In a point-to plane configuration in DC pulsed discharges this characteristic time seems yet weaker. To sum up this characteristic treatment time t_c seems to be the necessary time to remove all the organic and oxidised contaminants of the surface. This time depends on the plasma conditions which correspond to the energy levels injected in the gas.

4. Conclusion

A macroscopic interpretation of the polystyrene treatment by a DC pulsed plasma has been described in this paper. The treatment is divided into two stages. The first consists in the *cleaning* of the surface and the second in its *functionalization*.

Using a DC pulsed plasma with very low duty factor for the polymer surface treatment presents a big interest. Economically the effective glow discharge duration time is one hundred times lower than in usual techniques. Moreover the industrial applications like the improvement of the adhesion may be obtained in soft conditions without degradation of the polymer.

Spectroscopic analyses of the plasma phase are necessary to identify the reactive species in the inter-electrode gap. Chemical analyses are also necessary to understand the surface reactions. These important stages of analysis are essential to obtain a microscopic interpretation of the interaction between surface polymer and DC pulsed plasma.

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Figure captions

Figure 1: experimental set-up.

Figure 2: contact angle measurement by image processing.

- (a) original image of the drop deposited on the polymer
- (b) modulus of the spatial gradient
- (c) binary map of detected contours
- (d) plot of the two tangents and the base-line
- (e) automatic computation of the contact angle

Figure 3: contact angle relative variation for two positions of aPS films as a function of the treatment duration time t_t in nitrogen ($\nu = 500$ Hz, $t_g = 20\mu\text{s}$, $p = 4$ mbar, $d = 1$ cm and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 4: contact angle relative variation for two positions of aPS films as a function of the treatment duration time t_t in oxygen ($\nu = 500$ Hz, $t_g = 20\mu\text{s}$, $p = 4$ mbar, $d = 1$ cm and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 5: example of C (1s) core level spectra obtained for (a) untreated aPS, (b) N_2 -plasma treated aPS and (c) O_2 -plasma treated aPS ($\nu = 500$ Hz, $t_g = 20\mu\text{s}$, $p = 4$ mbar, $d = 1$ cm and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 6: atomic ratios O/C and N/C as a function of the treatment duration time t_t in a nitrogen plasma and when the aPS films are deposited close to the negative glow (on the cathode) or close to the positive column (on the anode) ($\nu = 500$ Hz, $t_g = 20\mu\text{s}$, $p = 4$ mbar, $d = 1$ cm and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 7: atomic ratios O/C as a function of the treatment duration time t_t in an oxygen plasma and when the aPS films are deposited close to the negative glow (on the cathode) or close to

the positive column (on the anode) ($\nu = 500 \text{ Hz}$, $t_g = 20\mu\text{s}$, $p = 4 \text{ mbar}$, $d = 1 \text{ cm}$ and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 8: percentage of the main chemical groups detected on the aPS surface (from relative intensities of C_{1s} components) as a function of the treatment duration time t_t in a nitrogen plasma and when the films are deposited close to the negative glow (on the cathode) or close to the positive column (on the anode) ($\nu = 500 \text{ Hz}$, $t_g = 20\mu\text{s}$, $p = 4 \text{ mbar}$, $d = 1 \text{ cm}$ and $\langle p(t) \rangle \approx 6\text{W}$) : (a) amine bonds, (b) C-O bonds, (c) carbonyl bonds, (d) carboxyl bonds and (e) shake-up.

Figure 9: percentage of the main chemical groups detected on the aPS surface (from relative intensities of C_{1s} components) as a function of the treatment duration time t_t in an oxygen plasma and when the films are deposited close to the negative glow (on the cathode) or close to the positive column (on the anode) ($\nu = 500 \text{ Hz}$, $t_g = 20\mu\text{s}$, $p = 4 \text{ mbar}$, $d = 1 \text{ cm}$ and $\langle p(t) \rangle \approx 6\text{W}$) : (a) C-O bonds, (b) carbonyl bonds, (c) carboxyl bonds and (d) shake-up.

Figure 10: Rms and atomic ratio O/C as a function of the treatment duration time t_t in a nitrogen plasma and when the aPS films are deposited close to the negative glow ($\nu = 500 \text{ Hz}$, $t_g = 20\mu\text{s}$, $p = 4 \text{ mbar}$, $d = 1 \text{ cm}$ and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 11: Rms and atomic ratio O/C as a function of the treatment duration time t_t in a nitrogen plasma and when the aPS films are deposited close to the positive column ($\nu = 500\text{Hz}$, $t_g = 20\mu\text{s}$, $p = 4 \text{ mbar}$, $d = 1 \text{ cm}$ and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 12: Rms and atomic ratio O/C as a function of the treatment duration time t_t in an oxygen plasma and when the aPS films are deposited close to the negative glow ($\nu = 500 \text{ Hz}$, $t_g = 20\mu\text{s}$, $p = 4 \text{ mbar}$, $d = 1 \text{ cm}$ and $\langle p(t) \rangle \approx 6\text{W}$).

Figure 13: Rms and atomic ratio O/C as a function of the treatment duration time t_t in an oxygen plasma and when the aPS films are deposited close to the positive column ($\nu = 500\text{Hz}$, $t_g = 20\mu\text{s}$, $p = 4 \text{ mbar}$, $d = 1 \text{ cm}$ and $\langle p(t) \rangle \approx 6\text{W}$).

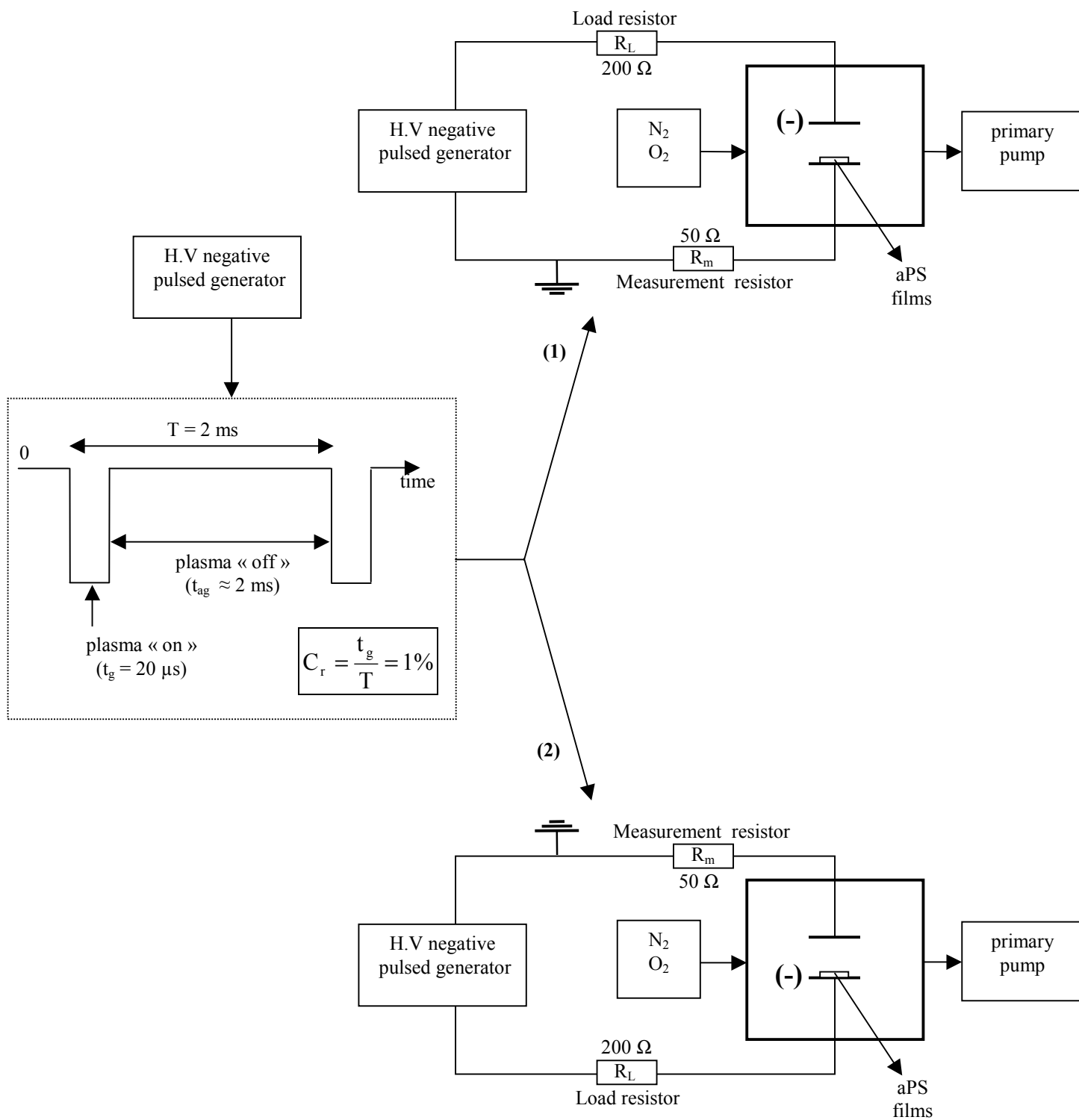


Figure 1

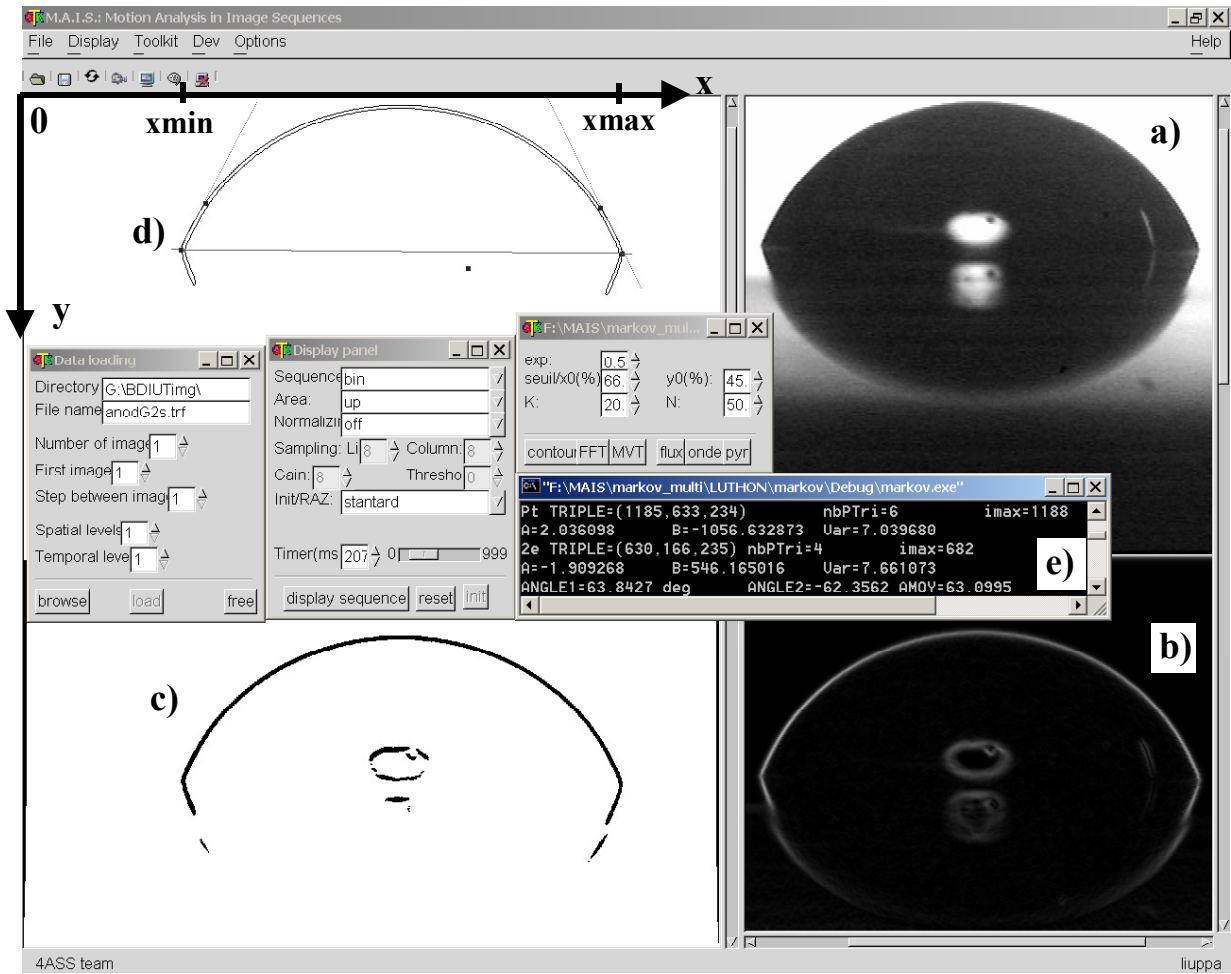


Figure 2

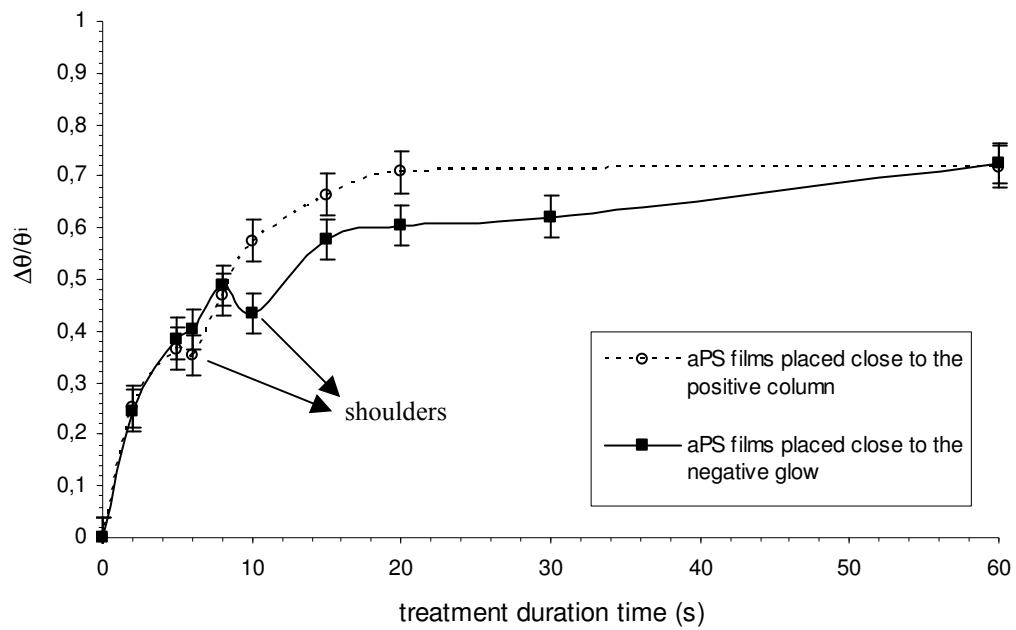


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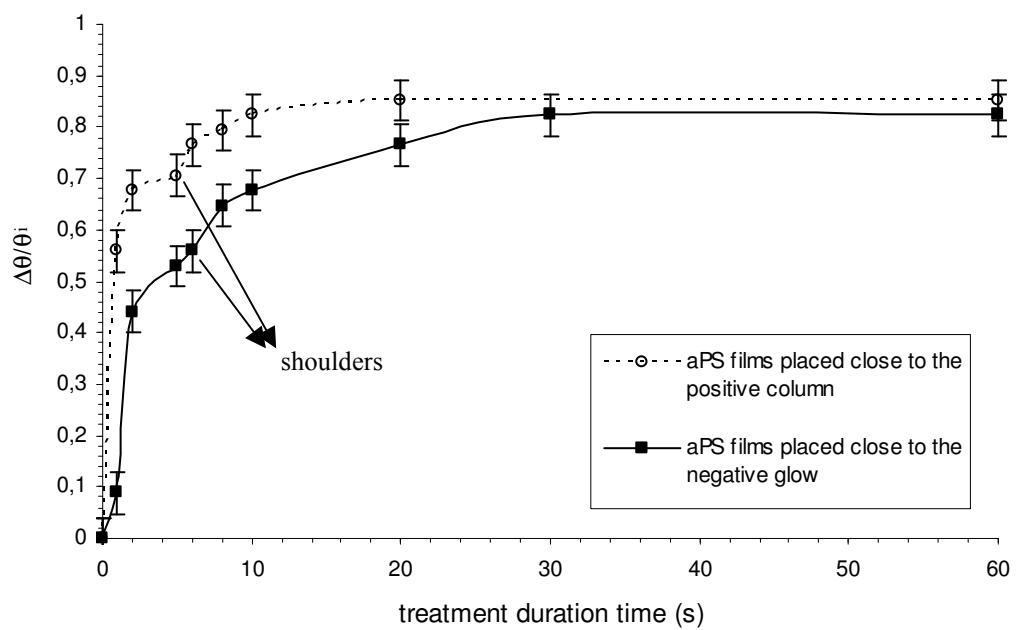
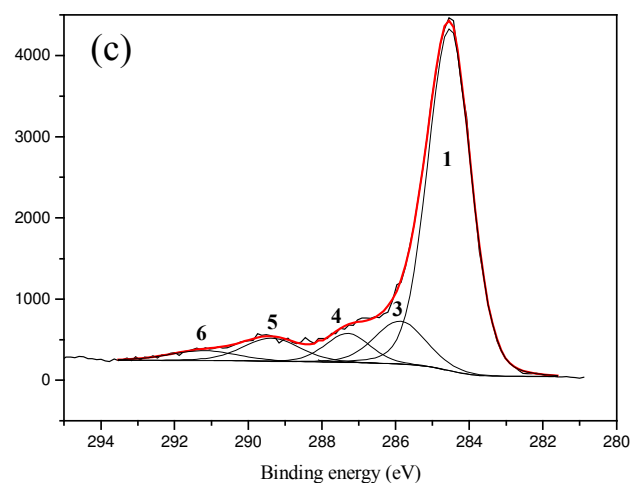
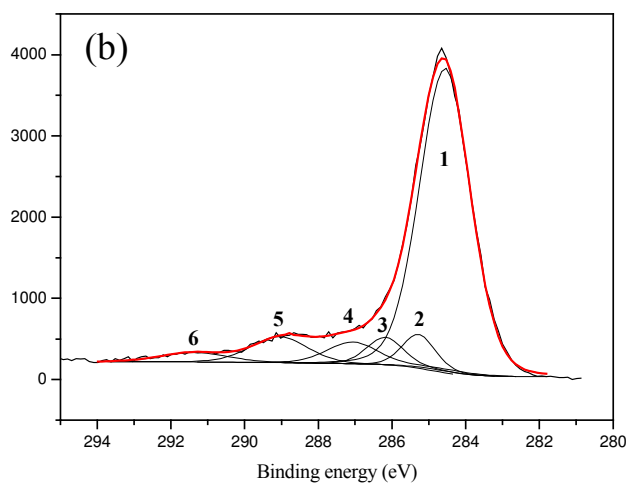
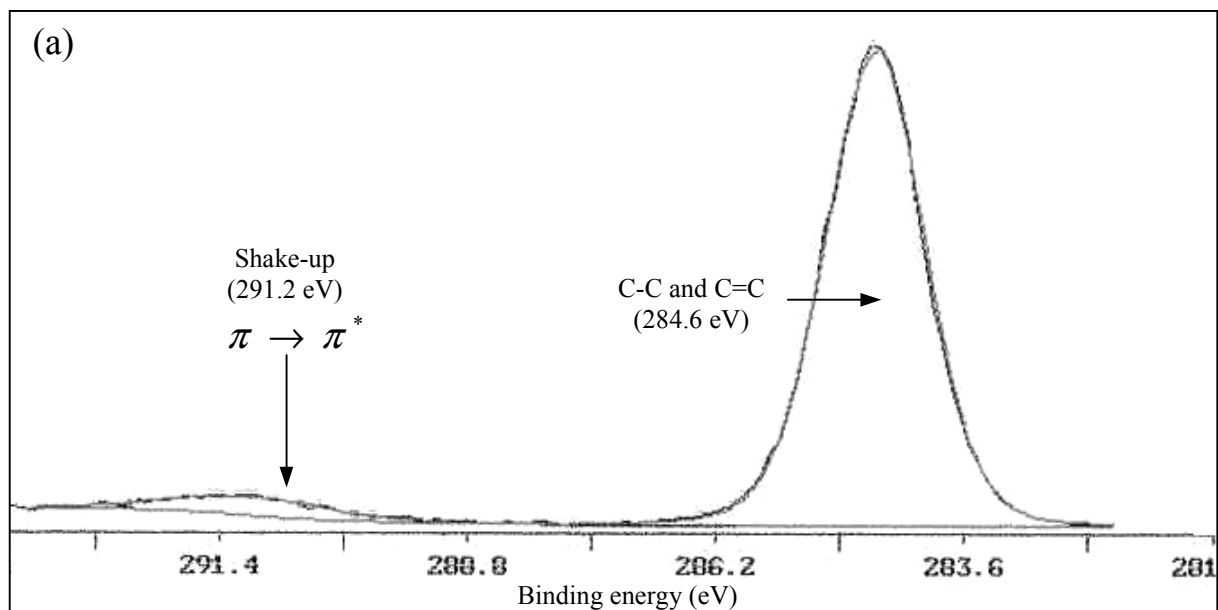


Figure 4



Chemical functions	Binding energy (eV)
1 : C-C and C=C	284.6
2 : C-N	285.5
3 : C-O	286.1
4 : C=O	287.5
5 : O-C=O	288.9
6 : shake-up	291.2

Figure 5

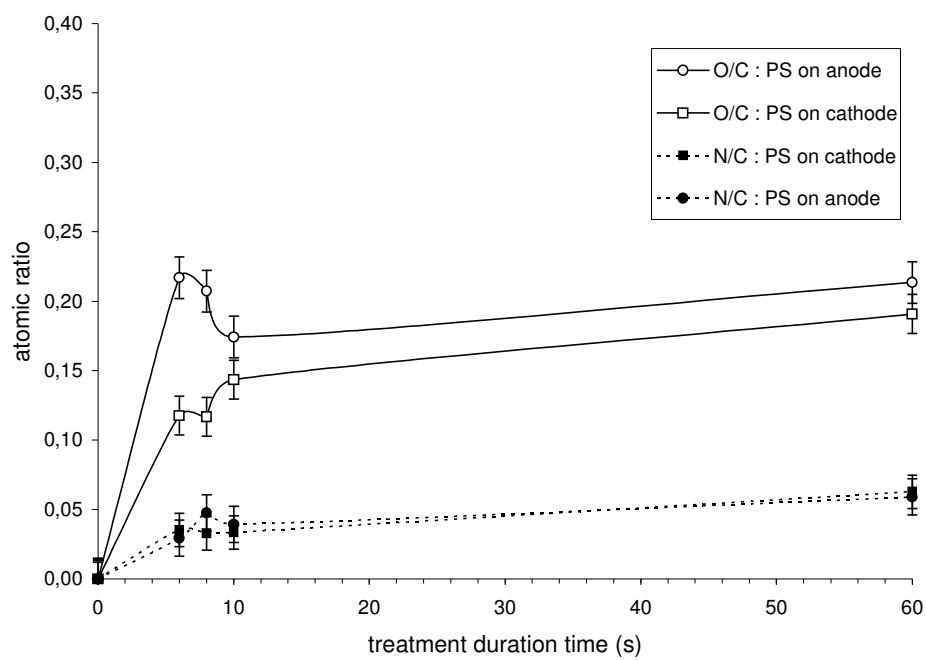


Figure 6

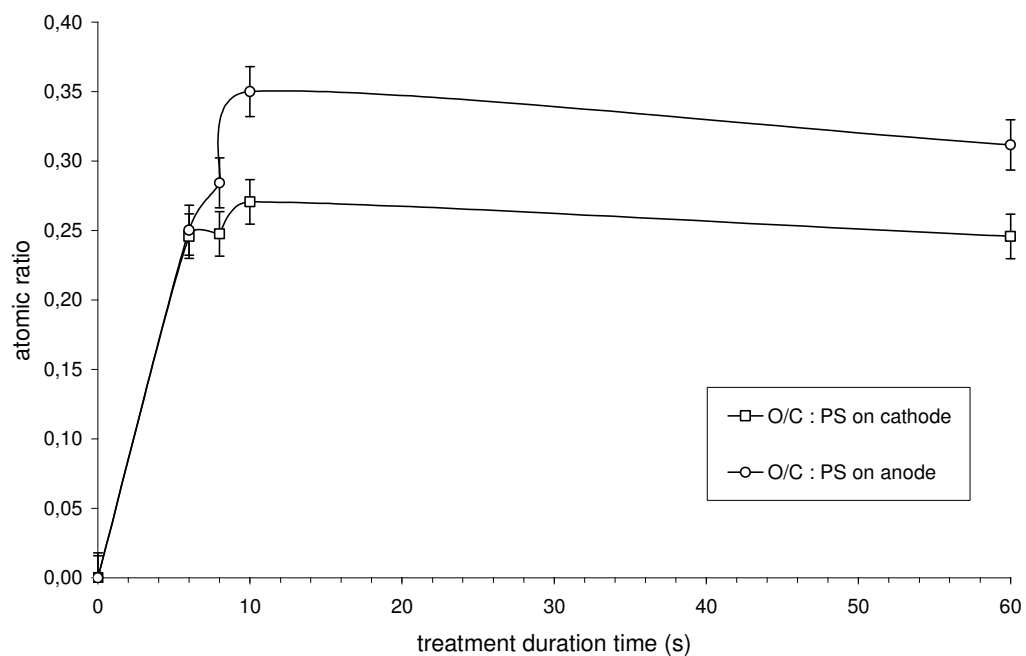


Figure 7

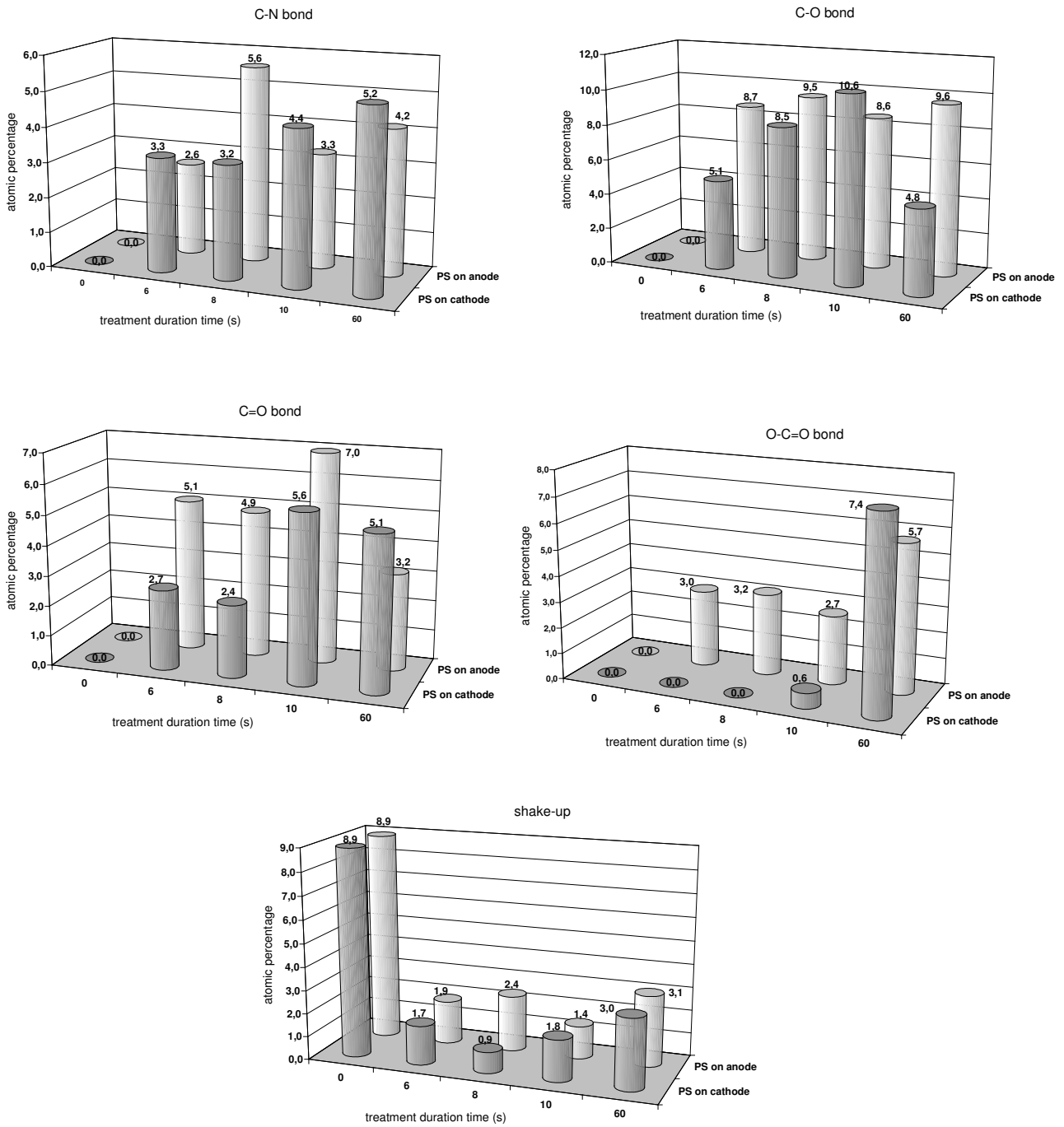


Figure 8

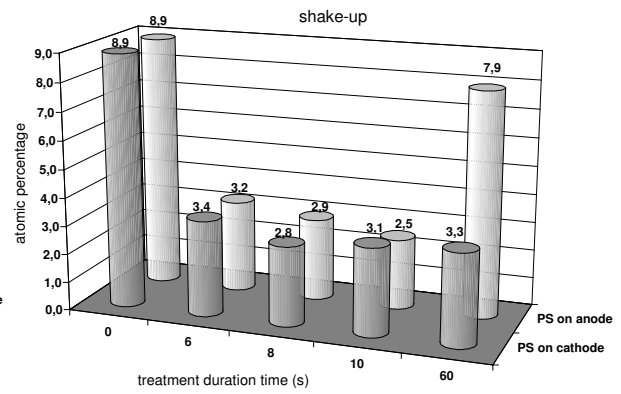
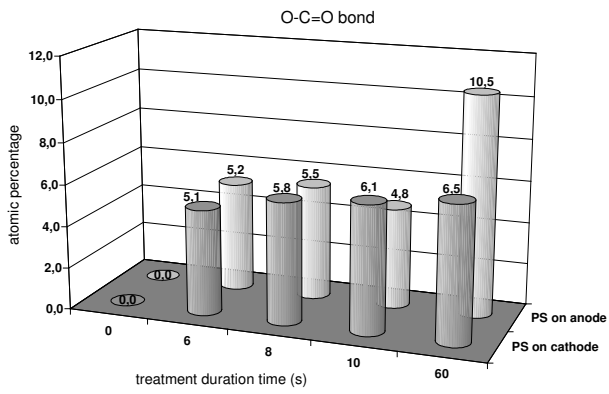
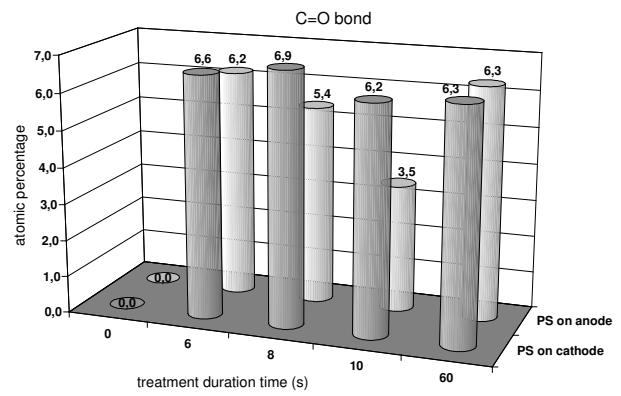
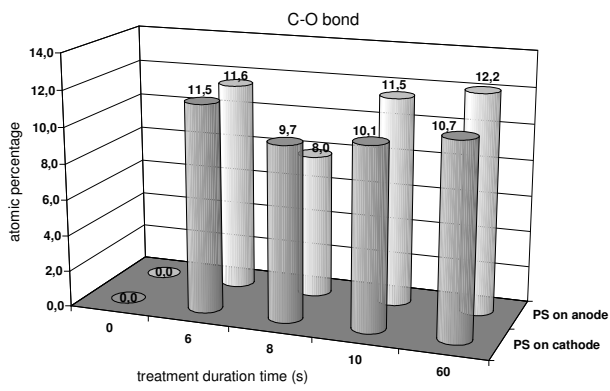


Figure 9

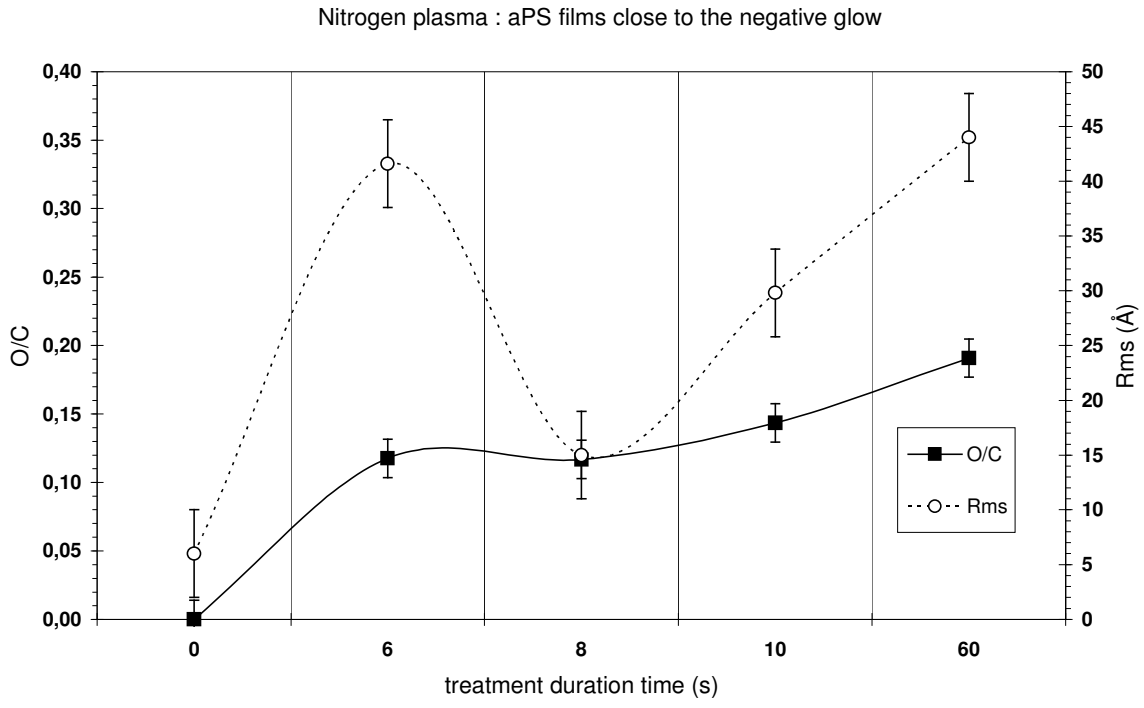


Figure 10

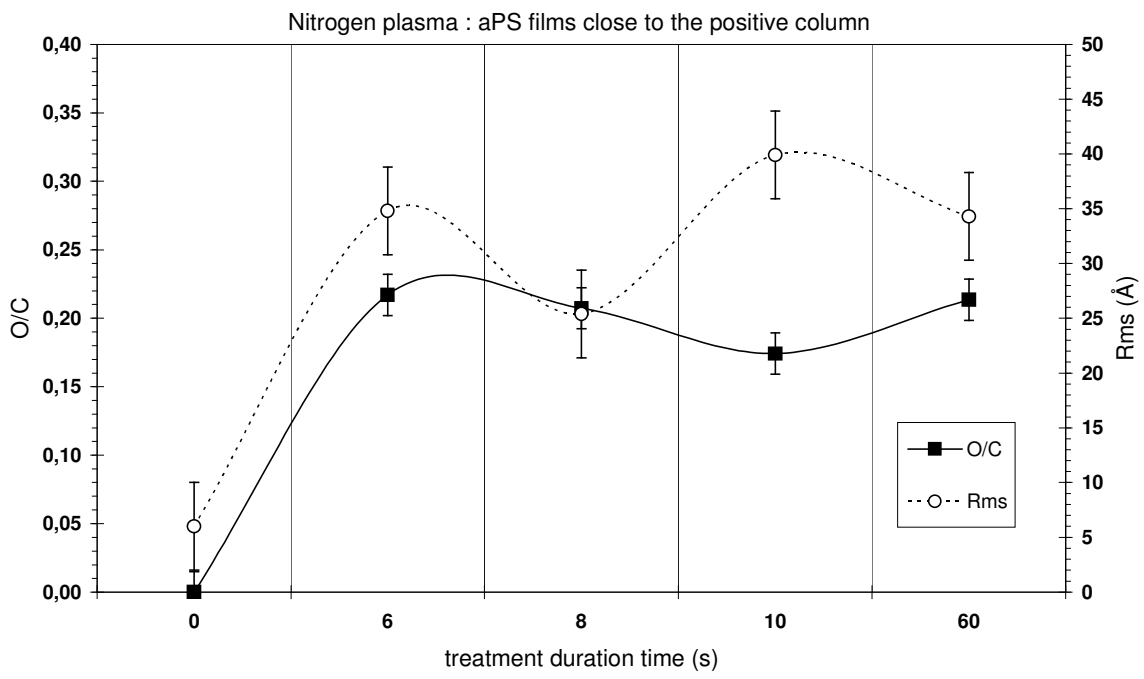


Figure 11

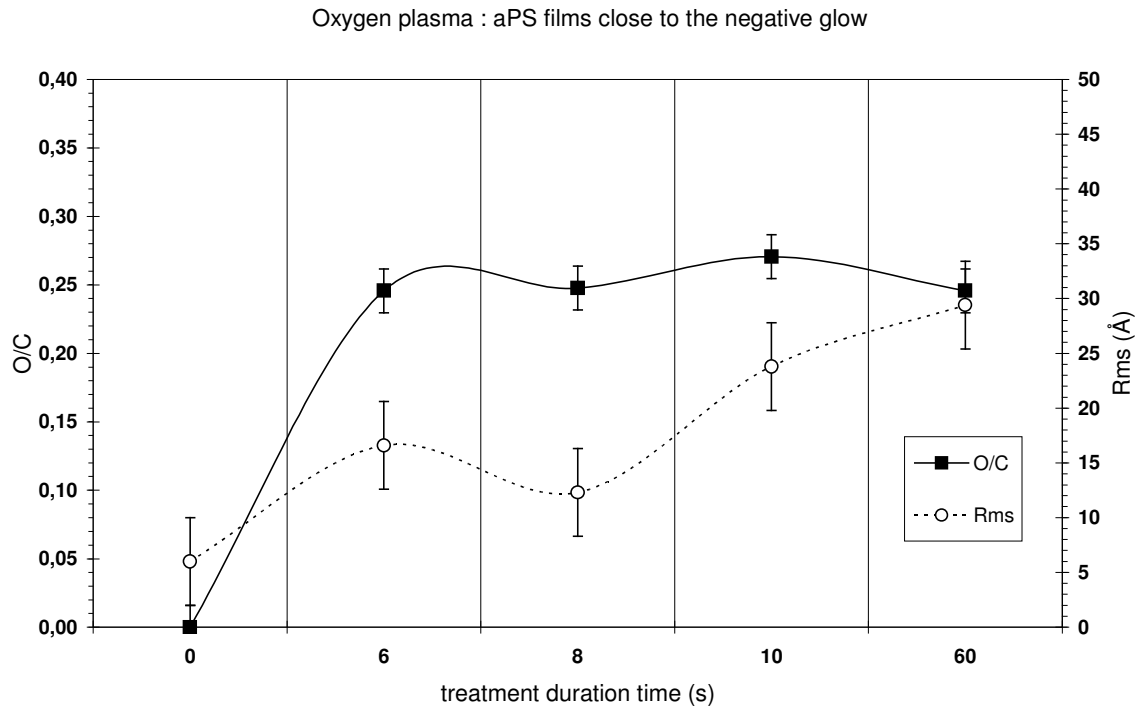


Figure 12

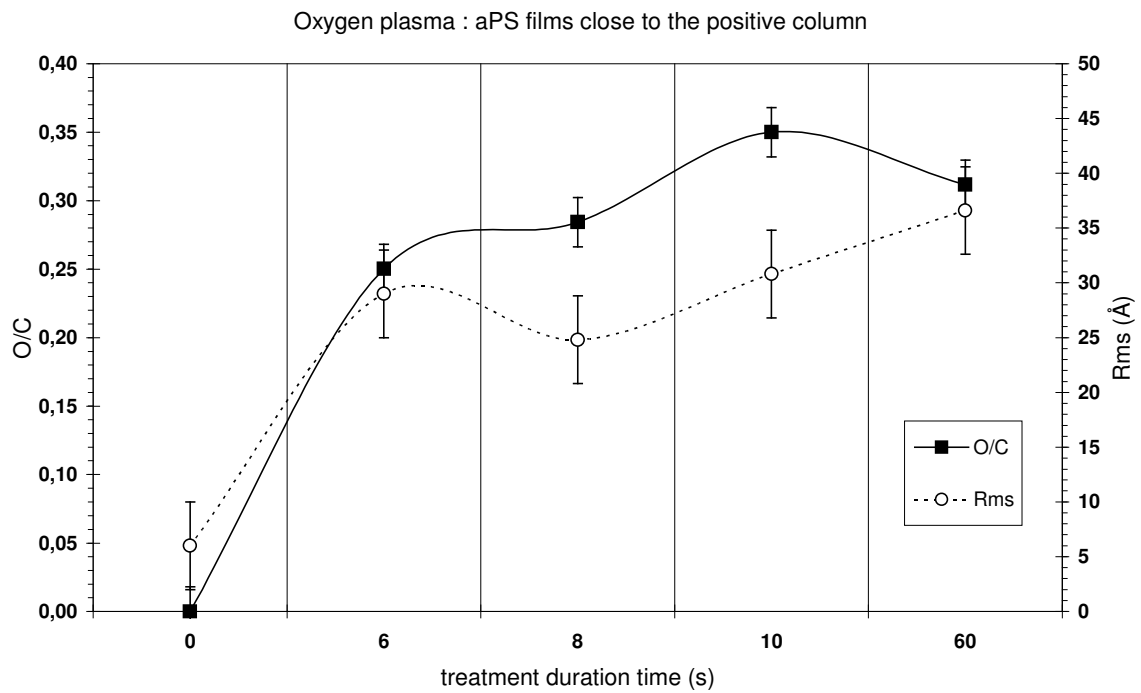


Figure 13