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# UNIVERSITÀ DEGLI STUDI DI TORINO

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# Effect of atmospheric oxidative plasma treatments on polypropylenic fibers surface: Characterization and reaction mechanisms

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## Abstract

Atmospheric pressure plasma-dielectric barrier discharge (APP-DBD, open chamber configuration) was used to functionalize polypropylene (PP) fibers surface in order to generate oxidized-reactive groups such as hydroperoxides, alcohols and carbonyl species (i.e. ketones and others). Such a species increased the surface polarity, without causing material degradation.

Three different types of plasma mixture (He, He/O<sub>2</sub>, He/O<sub>2</sub>/H<sub>2</sub>O) under three different values of applied power (750, 1050, 1400 W) were investigated. The formed plasma species (O<sub>2</sub><sup>+</sup>, O single atom and OH radical) and their distribution were monitored via optical emission spectrometry (OES) measurements, and the plasma effects on PP surface species formation were followed by X-ray photoemission spectroscopy (XPS). Results allowed to better understand the reaction pathways between plasma phase and PP fibers. In fact, two reaction mechanisms were proposed, the first one concerning the plasma phase reactions and the second one involving material surface modifications.

**Keywords:** Hernia-repair biomaterials; Plasma treatment; Polypropylene fibers; Surface modification; Oxidation mechanism.

## 1. Introduction

Surface chemistry finds many applications in polymer science. Plasma treatments [1–4] have recently gained much attention comparing with high energy radiations [5–7] for their ability to modify material surfaces without compromise their intrinsic chemico-physical and mechanical properties. E-beam [5] or  $\gamma$ -rays [6] (the most commonly used high energy radiation treatments), in fact, are especially utilized in sterilization processes, but both methods modify the chemico-physical structure of the original polymeric material, thus the mechanical properties are also altered. In particular, when the treatment is carried out in the presence of oxygen, the process starts with the formation of macroradicals (caused by C-H bonds breaking), leading to polymer oxidation [5,8]. Moreover, many authors [5–8] proposed that all the oxidized species begin to form at the same time, without preliminary hydroperoxides production (as in the Bolland cycle, which is valid for hydrocarbons in solution at high temperatures but not necessarily for solid polymers) [9].

Plasma treatments also present the advantage to be ecofriendly, together with the peculiarity to induce limited modification on the materials surface [2]. Plasma is a distinct state of matter consisting of electrically neutral gases and ionized species. Already present in nature (for example, in polar aurora and solar wind), an artificial plasma can be generated by ionizing a gas, which origins charged particles (positive and negative ions, electrons and/or radicals). Industrially, the gas ionization can be induced by a strong electromagnetic field, applied with a microwave generator, which causes bonds dissociation of reactive molecular species present in the gas mixture.

Plasma are characterized by different parameters, some of which are described in the following.

- The degree of ionization ( $\alpha$ ) is defined as:

$$\alpha = \frac{n_i}{n_i + n_a} \quad (1)$$

where  $n_i$  is the ions number and  $n_a$  is the neutral atoms number [4]: it corresponds to the fraction of atoms experiencing ionization phenomena. It is essentially controlled by the temperature.

- The plasma temperature provides information about the thermal kinetic energy per particle. Very high temperatures are usually needed to sustain ionization, whereas low temperatures allow ions and electrons to recombine into neutral species, reconvertng the plasma in a gas.

Moreover, plasmas can be classified in different categories, for instance thermal and non-thermal, hot and cold.

- Thermal plasmas contain both electrons and other particles at the same temperature, whereas non-thermal plasmas possess both ions and neutral species at a much lower temperature (normally room temperature, RT), whereas electrons are much hotter.
- Hot plasmas correspond to a fully ionized gas, whereas cold plasmas present only a small fraction of ionized gas species. It is noteworthy that both cold and hot plasmas contain electrons at very high temperature (thousands of degrees Celsius). Cold plasmas, and in general artificial plasmas, find applications in many technological fields, such as industrial metallurgy, surface treatments for coating, microelectronics, oxidation surface treatment allowing the adhesion of materials, sterilization [10-11].

Aim of this work is to propose a reaction mechanism between an oxidizing plasma and the surface of the polypropylene (PP) material, based on optical emission and X-ray photoemission spectroscopies. Three types of plasma mixtures were selected: the first one constituted by pure He (non-directly oxidative plasma) and should be totally inert, while the other two are originated by He/O<sub>2</sub> and He/O<sub>2</sub>/H<sub>2</sub>O gas mixtures, respectively, and are largely used for soft surface oxidation treatments. In order to verify the effects of the oxidizing mixtures, also three different values of powers were applied. Optical emission spectroscopy (OES) allowed to characterize plasma ionized species. X-ray photoemission spectroscopy (XPS) and also drop shape analysis (DSA) were the chemico-physical techniques selected for characterizing PP surface before and after plasma treatment. Radiation and plasma-induced polypropylene oxidation have been widely studied but many aspects are still unclear, thus the mechanism of plasma-induced reactions proposed in this paper should help in clarifying the effects of all the actors involved..

## 2. Experimental Section

### 2.1 Materials and plasma treatments

Monofilament sterilized polypropylene meshes for surgical applications were provided by Herniamesh<sup>®</sup> S.r.l. (Chivasso, Italy). Lightweight ( $\sim 30 \text{ g/m}^2$ ) meshes probes were  $6 \times 11 \text{ cm}$ , with  $0.32 \pm 10\% \text{ mm}$  of thickness, and fibers diameter of  $80 \pm 10\% \text{ }\mu\text{m}$ . Both sides of mesh probes were treated by Clean NT Lab (Torino, Italy) in an atmospheric plasma pressure glow dielectric barrier discharge (APP-GDBD), an open-air plasma apparatus following an already tested procedure [12]. **Table 1** summarizes all the experimental conditions used in this work. Helium was selected as gas-carrier for all the experiments. Each treatment was conducted for 15 s per mesh side at three different power values.

### 2.2 Plasma apparatus

The system consists of an open-air atmospheric plasma pressure glow dielectric barrier discharge (APP-GDBD): two stainless-steel parallel plates of  $80 \text{ cm} \times 23 \text{ cm} \times 3.5 \text{ cm}$  are available for sample treatment and five electrodes of  $80 \times 1 \text{ cm}$ , providing self plasma impedance adapting glow discharge, generate plasma phase. The type of discharge (filamentary or glow mode) is determined

from the space between electrodes and composition of dielectric. The maximum attainable process power is 2500 W (corresponding to 3.75 W/cm<sup>2</sup>). An energy loss of about 40% is expected. **Table 1** reports both the nominal and the effective power applied for each experimental conditions. For the sake of simplicity figures and discussions will report the nominal power values. A rotary pump and a heating box were used to produce water vapor for the treatment. The unit is a lab scale roll to roll version of an industrial production size system (it allows to work in continuous) and allows developing dedicated functionalization processes directly scalable up and transferable to industrial production. The picture of the apparatus is reported in **Scheme 1**.

## 2.3 Methods

X-ray photoemission spectroscopy (XPS) studies were carried out by a Versa Probe 5000 from PHI electronics, using Summit as software. Spectra were analyzed using Multipak 9.0. Al K $\alpha$  radiation (1486.6 eV), having a beam diameter of 100  $\mu$ m, was used as X-ray source.

C1s signals were analyzed. Each decomposed spectrum was obtained by normalizing each peak area to the experimental curve.

Optical emission spectroscopy (OES) was performed by using an Ocean Optic spectrometer LIBS2500 2plus-optic probe QP600-2-SR/BX, using integration times (Optical Scan) of 100 ms.

Drop shape analysis (DSA) was performed by using a Kruss DSA 100 with 25 $\times$  optical zoom available. The experiment was done with a drop of 3  $\mu$ l of double distilled water and with a released drop rate of 600  $\mu$ l/min. The instrument automatically calculates the contact angle, indicating the hydrophilicity/hydrophobicity ratio of the material surface. Each measure was repeated for three times.

## 3. Results and discussion

### 3.1 Plasma phase characterization: OES spectroscopic analysis and reactive species formation mechanism

Three different types of plasma, characterized by different oxidative capacities, were studied analyzing the OES spectra collected during each plasma generation experiment. Emission spectroscopy, in fact, allows to identify the exact composition of ionic and molecular species by their light emission. As a reference system, an atmospheric plasma made by the pure carrier, He, was considered. The choice of the gas-carrier is a key-point for an efficient material treatment, since carriers are responsible for the energy transfer to reactive species. Carriers need to be molecules (or, better, atomic elements) of small sizes which release kinetic energy by elastic collisions to the other molecules present in the environment and to materials surface in order to generate macroradicals [12]. Noble gases (monatomic) are the best carriers and, among those gases, helium is the most frequently used because of its small size and its high mobility.

Plasmas as those applied in this study are generated in air (consisting principally of N<sub>2</sub> and O<sub>2</sub>). This implies a variable composition of the plasma ionized species, and a consistent, not useful, energy dissipation given by molecular collisions [13].

**Figure 1** reports the spectrum of atmospheric plasmas obtained with 1050 W power. **Figure 1** and inset report the emission spectrum of He plasma. It shows the typical emission signals characterized by peaks at 501, 586, 667 and 706 nm [14-15]. The nitrogen peaks range (between 250 and 500 nm) is not reported for the sake of brevity [14]. Finally, signals at 728 and 777 nm are assignable to atmospheric oxygen ionized species (O<sub>2</sub><sup>+</sup>) [15].

Dashed line curve in the inset of **Figure 1** reports the spectrum of He/O<sub>2</sub> plasma. An increase of the oxygen signals, especially the peak at 777 nm, is visible, together with the formation of a new emission signal at 844 nm attributable to O single atom (<sup>•</sup>O<sup>•</sup>) [15-16]. This atomic species is generated by molecular oxygen breakage reactions caused by collisions with He.

The solid-line curve of **Figure 2** reports the spectrum of atmospheric He/O<sub>2</sub>/H<sub>2</sub>O plasma compared to He/O<sub>2</sub> plasma generated with the same power (dashed line). Water introduction decreases the

relative amount of carrier limiting helium reactivity in plasma phase. This provokes the He efficiency loss in activating oxygen breakage reactions (the O single atom signal at 844 nm disappears) and oxygen ionization (the  $O_2^+$  species signal at 777 nm decreases). However, water is more reactive than molecular oxygen, so new emission peaks due to water molecules homolysis appear: the former at 308 nm related to OH radicals, the latter at 656 nm related to H radicals (see **Figure 2** inset, solid line) [15].

A pattern of plasma phase reactions based on results of OES and on literature works [13,16] is proposed in **Scheme 2**.

The first reaction step involves the gas carrier ionization. Together with He, also the other two species present in the gas mixture ( $O_2$  and  $H_2O$ ) are ionized by elastic collisions with the excited He carrier, generating  $O_2^+$  (OES signal at 777 nm) and  $H_2O^+$ . Exciting with a power sufficiently high a mixture of He and  $O_2$ , we obtain He with enough kinetic energy to break the O=O double bonds forming O single atoms (OES signal at 844 nm). On the other hand, if we apply the same power to a mixture made of He,  $O_2$  and  $H_2O$ , the gas carrier concentration reduces together with its activating effect: thus, helium atoms have not enough kinetic energy to break oxygen molecules bonds, but they can easily cause homolysis of water molecules producing H radicals (OES signal at 656 nm) and OH radicals (OES signal at 308 nm).

Other plasma phase reactions are presented in the proposed mechanism, because they could occur, as confirmed in the literature [15]: for instance, hydroperoxy radicals  $HO_2$  and ozone  $O_3$  formation are possible [14,15], but we never detect them in the collected spectra.

### 3.2 Polypropylene fibers surface: XPS spectroscopic analysis and surface modification mechanism

Polypropylene surface was analyzed by X-ray photoelectron spectroscopy. XPS spectra of the reference fibers in C1s range (**Figure 3A**) shows the C-C signal at 284.5 eV and the C-H signal at 285.0 eV; no peaks related to oxidized C species are visible, as expected [11,17]. Fibers submitted to both oxidizing plasmas show the spectra reported in **Figure 3B** (meshes treated with plasma He/ $O_2$  at 1050 W) and **Figure 3C** (meshes treated with plasma He/ $O_2$ / $H_2O$  at 1050 W). C1s signal decomposition shows the presence of oxidized C species (the C-O signal at 286.0 eV and the C=O signal at 287.9 eV) [11]. The C-H signal (285 eV) is more intense for PP treated with He/ $O_2$ / $H_2O$  plasma than for He/ $O_2$  one, since water presence decreases the activity of reactive oxidizing species in plasma phase (according with OES results) limiting the oxidation state of the substrate. A quantitative comparison was carried out normalizing all the single contributions in respect to C1s signal total intensity, since this peak should be the most representative of PP matrix. The quantitative results indicated by XPS curves are confirmed by DSA measurements, which are reported in **Figure 4**. Untreated fibers present contact angle of  $132.0 \pm 0.4^\circ$ , confirming that the surface is essentially hydrophobic. After He plasma treatment, meshes present a reduction of the contact angle ( $113.2 \pm 0.7^\circ$ ). The contact angle decreases further to  $98.5 \pm 1.8^\circ$  for meshes treated with He/ $O_2$ / $H_2O$  plasma, whereas not-detectable contact angle is shown by He/ $O_2$  plasma treated meshes (water drop is not in equilibrium condition, but collapses into the material). These results allow to define an hydrophilicity scale of materials submitted to the different plasma treatments He/ $O_2$  > He/ $O_2$ / $H_2O$  > He > non treated PP.

XPS and OES considerations allows us to conclude that plasma oxidation on PP surface generates both C-O (hydroperoxides and alcohols) and C=O species (ketones and others) [5]. Moreover, we cannot exclude that a minimum amount of ketones can be originated by hydroperoxides decomposition, induced by high temperatures as theorized by the Bolland's cycle [9] following the reaction:



where the bimolecular thermal decomposition of hydroperoxides leads to the formation of water, alkoxy and peroxy macroradicals [5,11]. Nevertheless, we proposed that macroradicals can be directly involved in ketones formation [8,18], since alkoxy and peroxy macroradicals, formed in the

Bolland's cycle, can extract an H• from adjacent chains forming preferentially tertiary and secondary macroradicals (responsible for the propagation of the oxidation) [5].

**Scheme 3** shows the proposed reaction pattern involving He/O<sub>2</sub>/H<sub>2</sub>O plasma on PP surface [5,11].

The reaction pathway starts from polymer surface activation (in the square) induced by He\* (carrier) etching action [11] which is responsible of H• extraction and macroradicals formation. In general terms, considering the relative thermodynamic stability, a tertiary and a secondary macroradicals can be formed [5,7]. Tertiary macroradicals (pathway on the left) can react with the oxidizing species present in plasma phase: OH radicals (by direct formation of tertiary alcohols) and O<sub>2</sub> molecules (generating peroxy macroradicals). Subsequently, peroxy macroradicals can extract an H• from another PP chain originating a new macroradical, that carries on the oxidizing cycle, generating tertiary hydroperoxides [5,6].

A similar reaction pathway involving secondary macroradicals is reported on the right side of the scheme. Similarly to what described above, secondary macroradicals can form alcohols and hydroperoxides by reaction with OH radicals and O<sub>2</sub> species, respectively. Otherwise, the secondary macroradical can also react with O single atom giving an alkoxy macroradical [11] which can evolve towards a ketonic and/or other carbonylic species by H• extraction.

Some further details concerning the plasma effects derive from data reported in **Figures 5** and **6**. The first one shows C-H and C-C peaks intensity, normalized in respect to the total C1s signal, versus the nominal power applied (750 W, 1050 W and 1400 W) and versus the types of plasma (He, He/O<sub>2</sub> and He/O<sub>2</sub>/H<sub>2</sub>O). In **Figure 6** the dependence of C-O and C=O (and the total contribution Ox) on the plasma behaviors is represented. The former graph evidences the reactivity effects carried out by plasma treatments. For instance, the surface activation can be related to C-H depletion curves (**Figure 5A**). The data suggest that He/O<sub>2</sub> plasma causes the higher surface etching effect at 1050 W, whereas He/O<sub>2</sub>/H<sub>2</sub>O plasma at 1050 W possesses soft etching capacity leaving the C-H contribution almost at the same level of untreated meshes (~20%). On the other hand, it is possible to suppose that material degradation could be studied by the C C depletion graphs (**Figure 5C**). The values observed for C-C signal after He/O<sub>2</sub>/H<sub>2</sub>O plasma treatment, almost constant indicates that material degradation is negligible. The same situation is observed in the case of He/O<sub>2</sub> plasma at high powers (1050 and 1400 W).

The oxidation of the surface is monitored by two main contributions to C1s signal: the single bond C-O signal at 286.0 eV [11,17], generally due to hydroperoxides and alcohols, and the double bond C=O signal at 287.9 eV [11], mainly given by ketones but also by other carbonylic species. The absence of carboxylic groups is an indication of non degradative phenomena of PP material, since their presence should imply breaking of polypropylene backbone chains (C-C bonds) [5]. C-O and C=O contributions allow to follow the surface oxidation reaction (see **Figure 6A**). **Figure 6B** shows that He/O<sub>2</sub> plasma at 1050 W causes a slightly higher degree of oxidation (~25%) than that obtained for material submitted to He/O<sub>2</sub>/H<sub>2</sub>O plasma at the same power (~20%).

The comparison reported in **Figures 6** shows that the contribution of C-O species is O species is the most important (as well as in Ref. [2]) and fundamental in determining the oxidative species formation trend, since the C O signal is almost constant for all the plasmas [11,16,17].

### 3.3 Open-air vs. closed chamber plasmas: surface activation effects

An interesting comparison can be made considering the effects resulting from the experimental set-up described in this paper (open-air plasma chamber) and another common laboratory setup such as the one reported in Ref. [2] (closed plasma chamber): the following discussion should evidence advantages and disadvantages in the use of both configurations.

The open-air plasma chamber set-up implies an unknown gas mixture contamination, not avoidable, given by the molecular species present in the atmosphere (N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and so on). As a consequence, the efficiency of plasma is limited by undesired collisions which causes consistent energy losses. This means that open air plasma treatments need high powers applied, in order to

activate a sufficient number of carrier species. Vice versa, a closed reactor plasma device possesses a known gas flow composition, not affected by extra species, and needs lower powers because the reactive species are generated more effectively. The energy density applied in [2] (calculated by multiplying the plasma exposure time by the plasma power and dividing it by the plasma electrode area) is comprised between 45 mJ/cm<sup>2</sup> and 220 mJ/cm<sup>2</sup> for air or He plasma composition, respectively, whereas the effective energy density applied in our experimental set-up (see **Table 1**) is of about 17–31 J/cm<sup>2</sup>, i.e. two orders of magnitude higher. Therefore, in this case, power applied is very huge. Nevertheless, the surface species described in this study are essentially C-O and C=O, produced by C-H bonds break, whereas in [2], using an atmospheric plasma in a closed reactor, the formation of additional O-C=O species are evidenced, indicating C-C chain breakage and consequent undesired PP degradation. This indicates that an atmospheric open-air plasma allows to control and limit the effect of reactive species, but this implies the use of higher power applied (i.e., more expensive treatments) in order to overcome the dilution effect carried out by atmospheric contaminants. Additionally, open-air set-up is suitable to treat large amounts of samples and scale-up the process for industrial applications.

#### 4. Conclusions

The study of the interaction between the oxidizing species produced in APP-DBD atmospheric plasmas (He, He/O<sub>2</sub> and He/O<sub>2</sub>/H<sub>2</sub>O at different powers) and PP meshes surface allowed us to describe the process occurring during the treatments. By means of the combined use of XPS and OES techniques we were able to study the surface activation process considering simultaneously what happens in the plasma phase and onto the polymeric surface. This was useful to propose a reaction mechanism, involving macroradicals formation, to better understand the reaction pathways, to identify the plasma active species and to describe the polymer surface response.

The decomposition of XPS C1s peaks evidenced: (i) the formation of oxidized species in terms of C-O and C=O groups, both of them responsible for an increase of material surface hydrophilicity, and (ii) the PP surface activation by etching analyzed via C-H signal depletion.

Compared to close chamber set-up, open-air plasma apparatus needs higher power applied, i.e. expensive treatments, but does not evidence any polymeric material degradation, since carboxylic groups formation, caused by C-C chain breaking, was never revealed. Moreover, open-air set-up is suitable to treat in continuous large amounts of samples.

#### 5. Acknowledgements

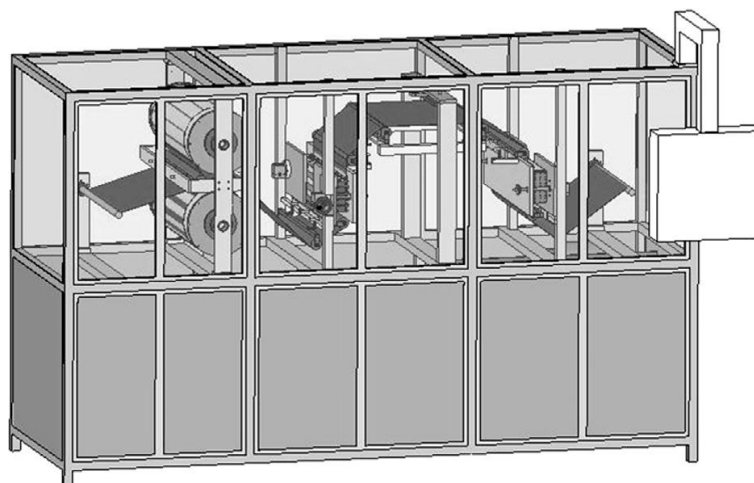
This work was realized with the contribution of the European funding program POR-FESR ASSE I (I.1.3 Innovation and SME, Regione Piemonte) within the framework of the research project PREVI.

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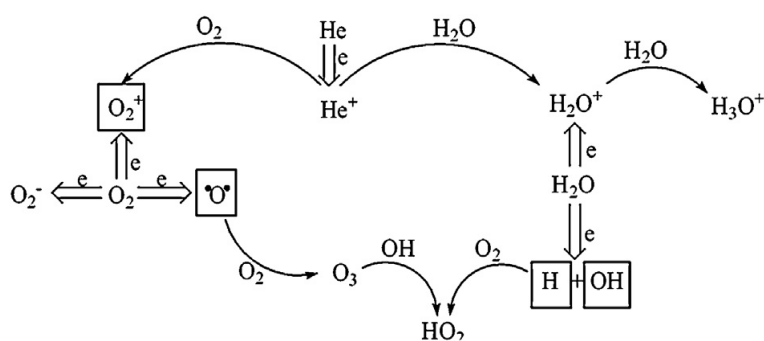
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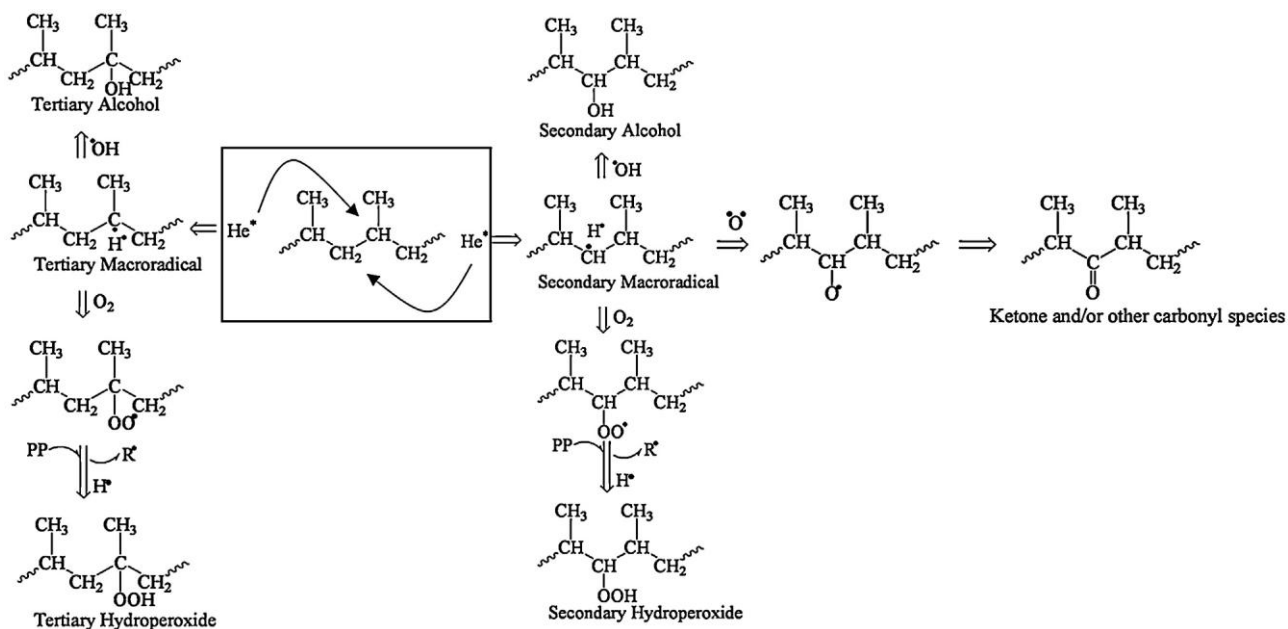
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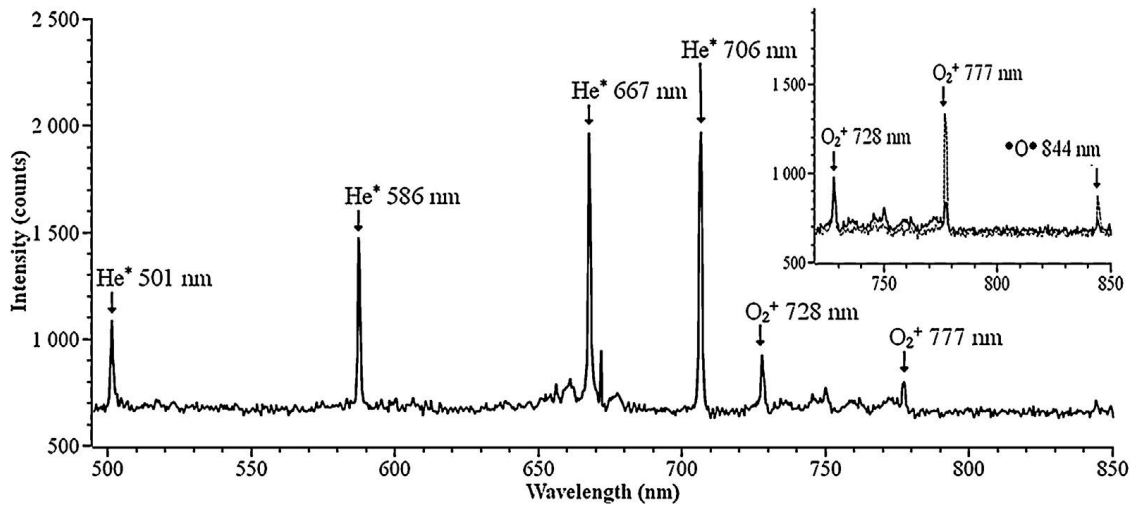
**Scheme 1.** Experimental set-up relative to the lab scale roll to roll plasma apparatus.



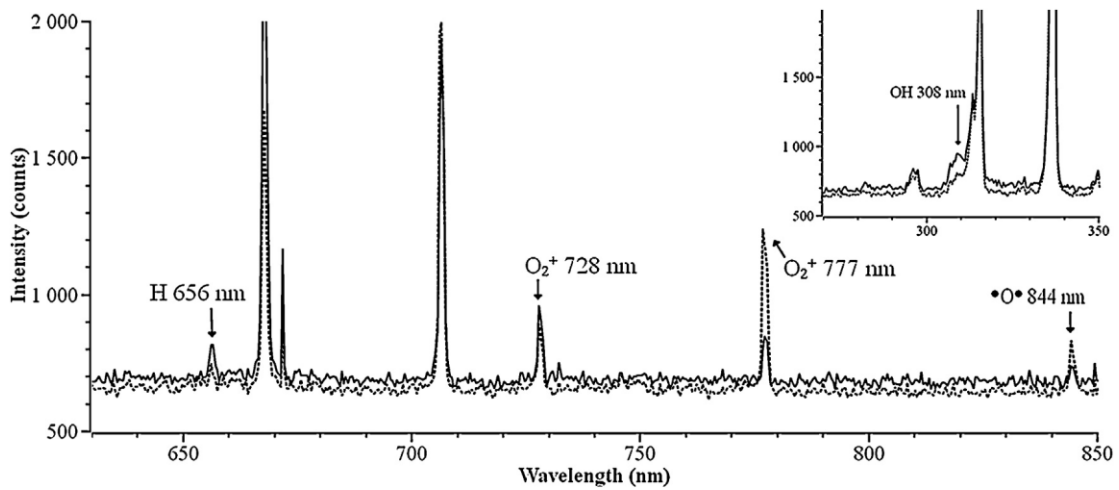
**Scheme 2.** He/O<sub>2</sub>/H<sub>2</sub>O plasma phase reaction pathway. The squares evidence chemical species detected by OES.



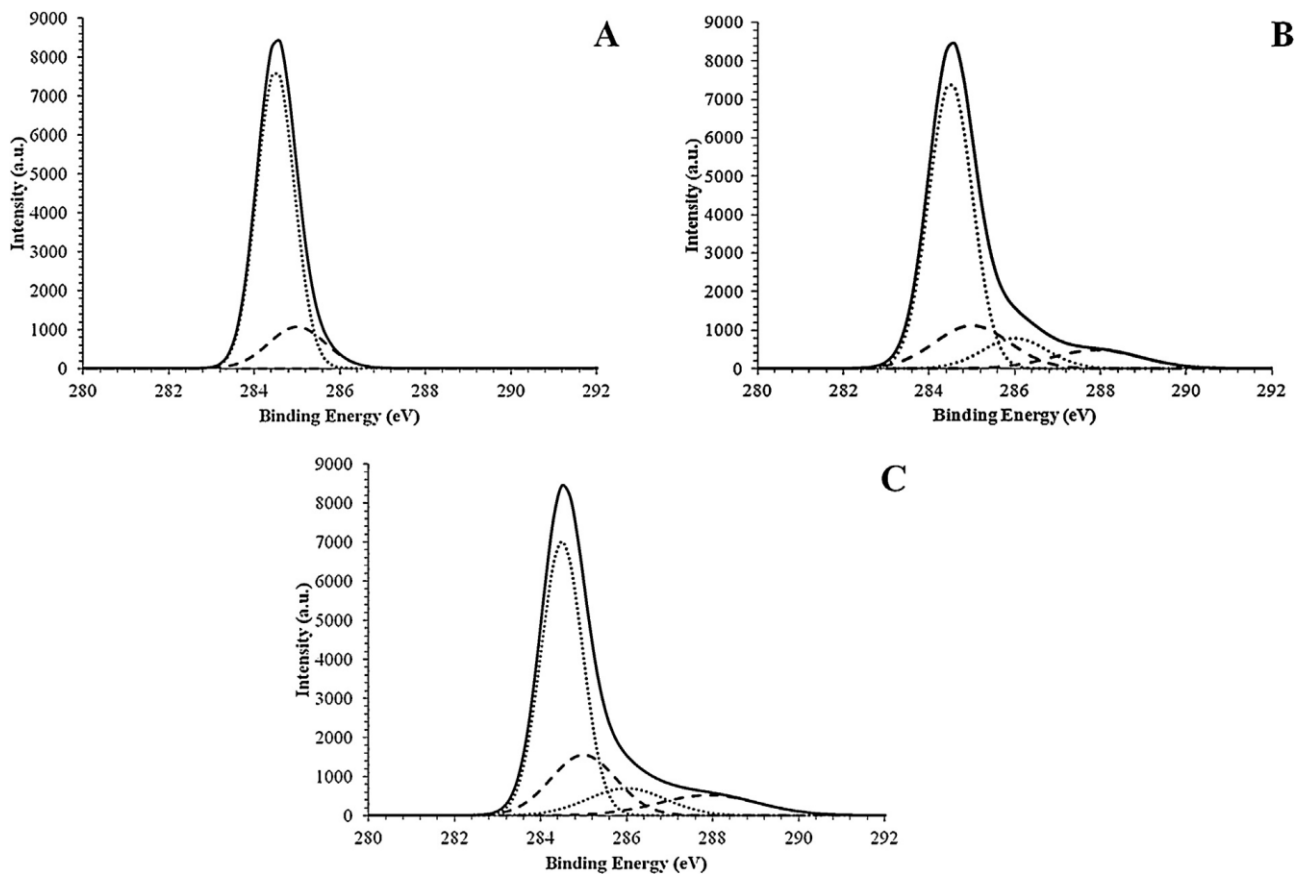
**Scheme 3.** He/O<sub>2</sub>/H<sub>2</sub>O plasma reaction mechanism on PP surface. The square indicates the first reaction step.



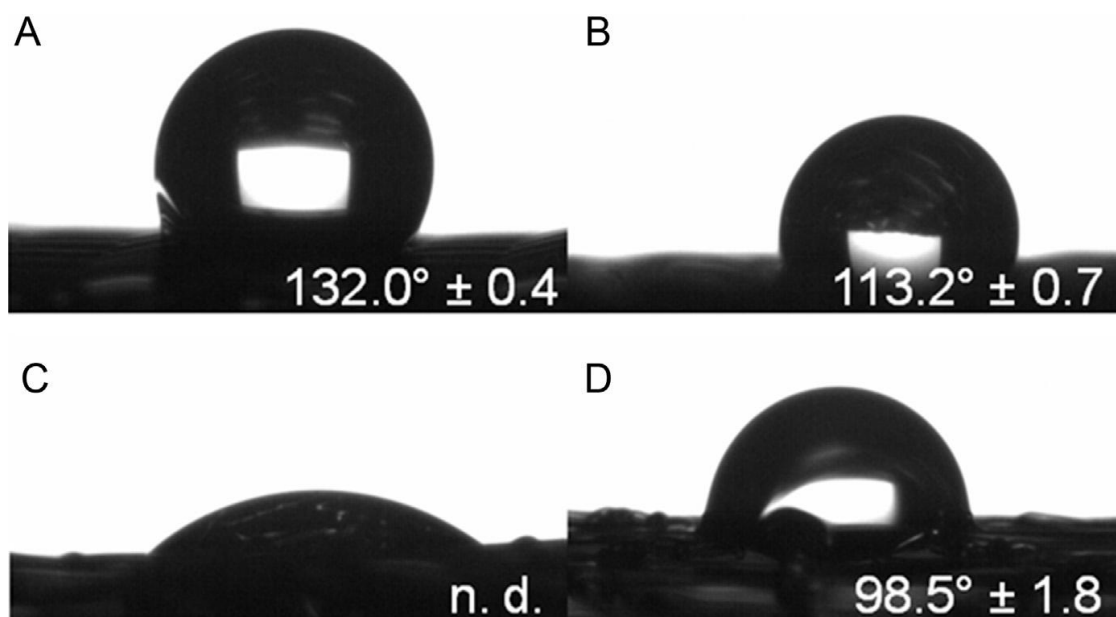
**Figure 1.** OES spectrum in the 495-850 nm range relative to He plasma. In the inset the same spectrum in the range 720-850 nm (solid line) is reported together with the He/O<sub>2</sub> plasma one (dotted line). The principal signals are labeled.



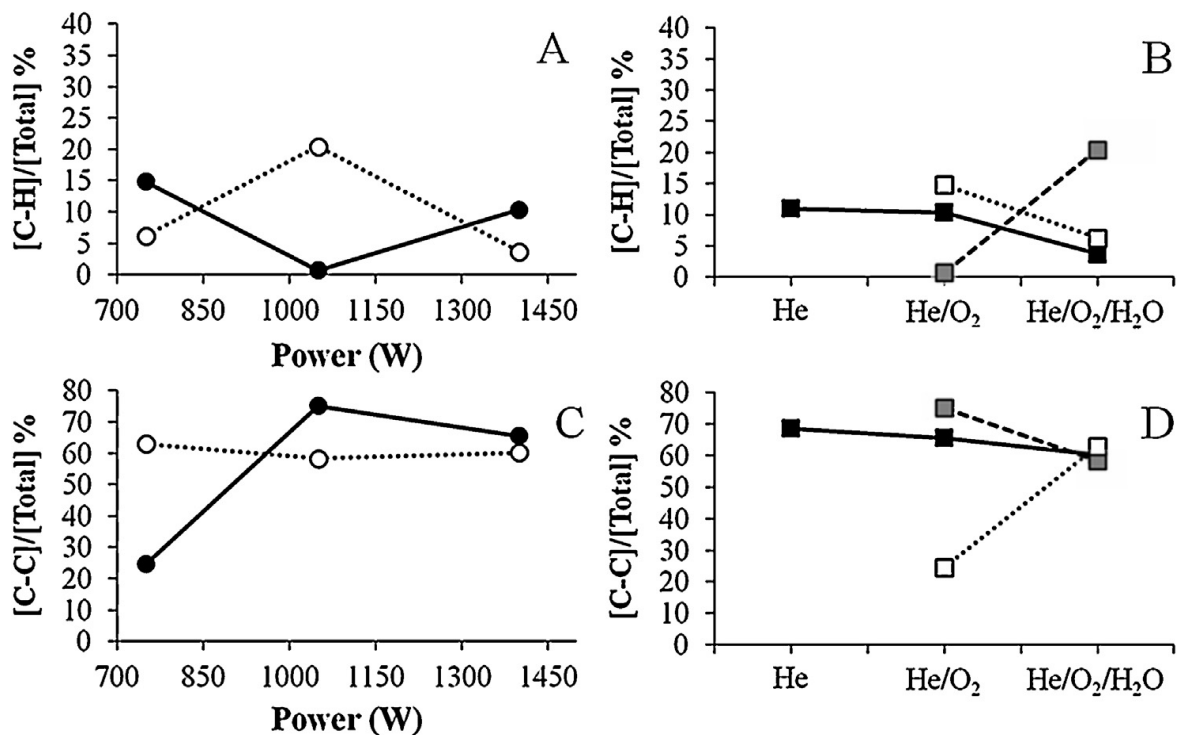
**Figure 2.** OES spectra in the 630-850 nm range: He/O<sub>2</sub>/H<sub>2</sub>O plasma (solid line) and He/O<sub>2</sub> plasma (dotted line). In the inset the same spectra in the range 270-350 nm. The principal signals are labeled.



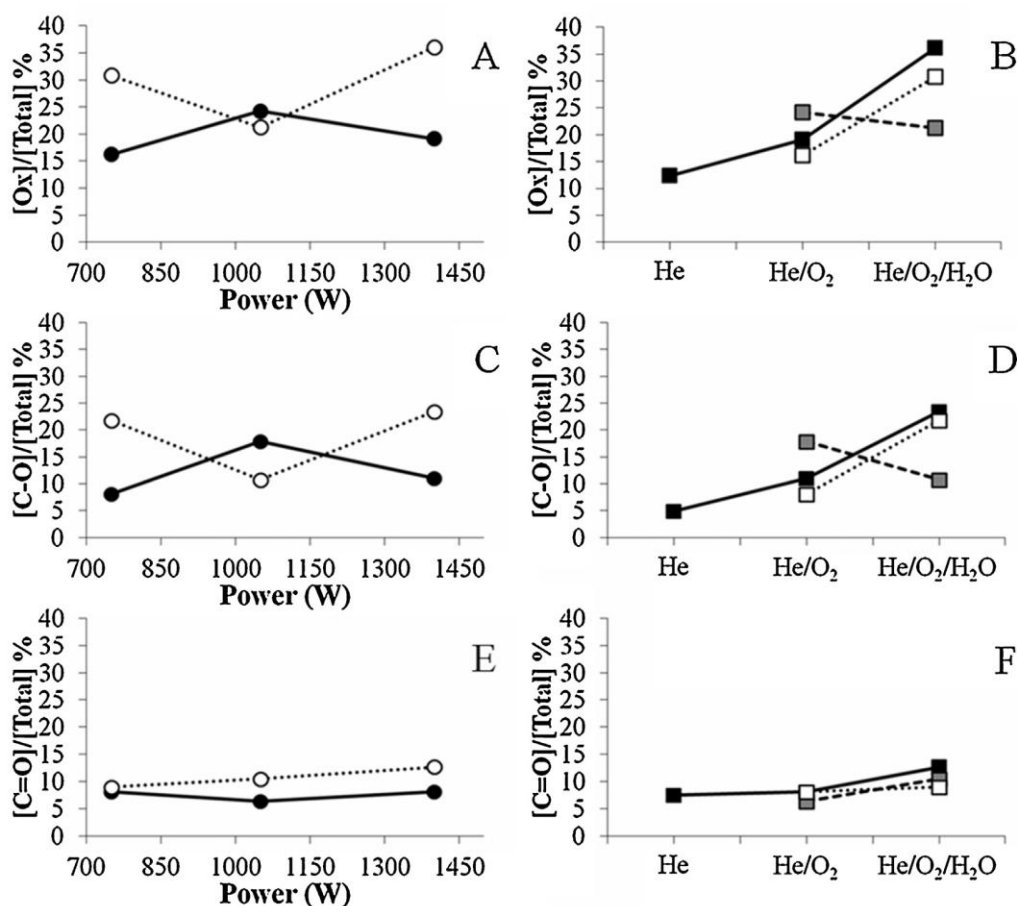
**Figure 3.** XPS spectra in the 280-292 eV range. Solid line curves: experimental curves; dotted lines: C-C signal at 284.5 eV and C-O signal at 286.0 eV; dashed lines: C-H signal at 285.0 eV and C=O signal at 287.9 eV. Spectra normalized at 284.5 eV. Section A: original not treated PP fibers; section B: He/O<sub>2</sub> plasma treated PP fibers (1050 W); section C: He/O<sub>2</sub>/H<sub>2</sub>O plasma treated PP fibers (1050 W).



**Figure 4.** DSA analyses of PP fibers: (A) before plasma treatments; (B) after He plasma treatment; (C) after He/O<sub>2</sub> plasma treatment; (D) after He/O<sub>2</sub>/H<sub>2</sub>O plasma treatment.



**Figure 5.** XPS intensities trends showing integral area of each contribution normalized in respect to the total C1s signal. (A) C-H normalized signals vs power applied (black circles: He/O<sub>2</sub> plasma; white circles: He/O<sub>2</sub>/H<sub>2</sub>O); (B) C-H normalized signals vs different types of plasmas (white squares: 750 W; grey squares: 1050 W; black squares: 1400 W); (C) C-C normalized signals vs power applied (black circles: He/O<sub>2</sub> plasma; white circles: He/O<sub>2</sub>/H<sub>2</sub>O); (D) C-C normalized signals vs different types of plasmas (white squares: 750 W; grey squares: 1050 W, black squares: 1400 W).



**Figure 6.** XPS intensities trends showing integral area of each contribution normalized in respect to the total C1s signal. (A) Oxidized species (C-O + C=O) normalized signals vs power applied (black circles: He/O<sub>2</sub> plasma; white circles: He/O<sub>2</sub>/H<sub>2</sub>O); (B) oxidized species (C-O + C=O) normalized signals vs different types of plasmas (white squares: 750 W; grey squares: 1050 W; black squares: 1400 W); (C) C-O normalized signals vs power applied (black circles: He/O<sub>2</sub> plasma; white circles: He/O<sub>2</sub>/H<sub>2</sub>O); (D) C-O normalized signals vs different types of plasmas (white squares: 750 W; grey squares: 1050 W; black squares: 1400 W); (E) C=O normalized signals vs power applied (black circles: He/O<sub>2</sub> plasma; white circles: He/O<sub>2</sub>/H<sub>2</sub>O); (F) C=O normalized signals vs different types of plasmas (white squares: 750 W; grey squares: 1050 W; black squares: 1400 W).

**Table 1.** Plasma treatment conditions applied on PP fibers.

Samples	Plasma components	Nominal power (W)	Effective power (W)	Time per side (secs)	Effective energy density ( $\text{J}/\text{cm}^2$ ) <sup>a)</sup>
PP01	He	1400	840	15	31
PP02	He/O <sub>2</sub>	750	450	15	17
PP03	He/O <sub>2</sub>	1050	630	15	24
PP04	He/O <sub>2</sub>	1400	840	15	31
PP05	He/O <sub>2</sub> /H <sub>2</sub> O	750	450	15	17
PP06	He/O <sub>2</sub> /H <sub>2</sub> O	1050	630	15	24
PP07	He/O <sub>2</sub> /H <sub>2</sub> O	1400	840	15	31
PP08 <sup>b)</sup>	----	----	----	----	----

a) Calculated considering: the effective power applied, an exposure time of 15 s and a total surface area relative to five electrodes of 400 cm<sup>2</sup> overall.

b) Original not treated sample.