Deposition of Plasma-Polymerized Polyacrylic Acid Coatings by a Non-Equilibrium Atmospheric Pressure Nanopulsed Plasma Jet

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Deposition of Plasma-Polymerized Polyacrylic Acid Coatings by a Non-Equilibrium Atmospheric Pressure Nanopulsed Plasma Jet

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Successful plasma-polymerization of acrylic acid (AA), aimed at depositing plasma-polymerized polyacrylic acid (pPAA) coatings stable upon water contact with a high amount of carboxyl groups, using a non-equilibrium atmospheric pressure nanopulsed plasma jet is reported. Special attention is devoted to the surface chemical characterization of the pPAA coatings deposited on pristine and plasma pretreated polymeric substrates. The investigation of the pPAA chemical structure is performed by means of attenuated total reflectance-Fourier transform infrared and X-ray photoelectron spectroscopies. Insights on the morphological characteristics of the coatings are also provided by optical microscopy.

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1. Introduction

Plasma-polymerization of acrylic acid (AA) has raised great interest for the production of adhesion-promoting interlayers, e.g., in carbon fiber/epoxy composites,[1] as well as for the development of biocompatible polymers[2] and for the immobilization of antimicrobial peptides on substrates.[3] In the frame of biomedical applications, plasma-polymerization of AA has been widely investigated to produce coatings containing carboxylic acid (—COOH) groups,[4] which are known to favor cell adhesion and can be also be exploited for biomolecule immobilization.[5]

Low pressure plasma enhanced chemical vapor deposition (PECVD) is nowadays one of the most widespread tools for the effective coatings deposition on substrates.[6] Several studies have been already performed with the aim to investigate the characteristics of plasma-

polymerized acrylic acid (pPAA) films deposited by means of PECVD technology. The obtained results show that the plasma operating conditions can strongly influence the chemical composition, the morphology, and the homogeneity of the pPAA coatings, as well as their water stability.[2,7,8]

In recent years, many efforts have been dedicated to develop coating processes relying on non-equilibrium plasma sources working at atmospheric pressure;[9–11] as an example, the possibility to employ atmospheric pressure dielectric barrier discharges (AP-DBD) to obtain functional surfaces with chemically reactive moieties such as amino[12] or carboxylic groups[13] was demonstrated. Solventless and environmentally friendly, like other PECVD methods, AP-DBD operates at room temperature (RT) and does not require vacuum pumps, compared to the low pressure plasma processes. Even if DBD reactors have been previously shown to possibly result in the deposition of scarcely homogeneous pPAA coatings,[14] it was recently demonstrated that this problem can be overcome by optimizing the design of the precursor inlet systems.[15] On the other hand, results of previous works on pPAA deposition[16–18] showed that in the AP-DBD system the effect of monomer fragmentation on the retention of —COOH groups turns out to be relevant: the higher the monomer fragmentation, the lower the amount of —COOH groups on the coated substrate,[16,19] as also experimentally evidenced by Palumbo et al.[19] through a correlation of optical emission spectroscopy and X-ray photoelectron spectroscopy results.

With the aim to contribute to overcome the problem of monomer fragmentation, recent studies were performed on the polymerization of an allyl monomer containing phosphorus[20] and the deposition of glycidyl methacrylate layer[21] with a nanosecond square-pulsed AP-DBD, in order to maximize the structural retention of monomers and preserve their functional groups. In fact, thanks to its very high slew rate, the ultra-short square pulses enable the generation of a short and homogeneous discharge with a large proportion of high energy electrons, which efficiently induce the creation of free radicals able, in turn, to initiate the free radical polymerization reactions, responsible of the high retention of the monomer functional groups.[21]

Differently from the AP-DBD systems, non-equilibrium atmospheric pressure plasma jet (APPJ) are well suited for localized treatment and coating of complex three-dimensional geometries, since the substrate does not have to be placed in the gap between electrodes. Furthermore, the possibility to scale down the dimension of the jet to the submillimeter range widens the field of the applications of the process. The studies performed with this kind of sources demonstrated the effectiveness of non-equilibrium APPJs in depositing polymeric films by means of monomer

polymerization. For example, Bhatt et al.[22] pointed out the possibility to employ a non-equilibrium Ar APPJ to deposit in open air PEG-like coatings for cell repellent applications, while Vogelsang et al.[23] reported the first successful deposition of hydrophobic C:F thin film on conductive substrates with a RF capillary atmospheric pressure microplasma jet. With regard to AA plasma-polymerization, Donegan and Dowling[24] investigated the water stability, the chemical/morphological characteristics, and the level of protein adhesion of pPAA coatings deposited onto silicon substrates by using two different plasma jet deposition systems. Chen et al.[3] highlighted the possibility to deposit pPAA coatings onto the surfaces of silk fibers (SF) using an atmospheric pressure glow discharge in order to immobilize antimicrobial peptide onto the SF surface. Carton et al.[25] employed a pulsed-arc atmospheric pressure plasma jet for the AA plasma polymerization and the deposition of organic coatings suitable for biomedical applications. The same plasma source was also used to perform the polymerization of AA and methylene-bis-acrylamide.[26] The latter compound was added as crosslinking agent to the precursor in order to improve the water stability of the deposited coatings. Ward et al.[27] performed the deposition, by introducing ultrasonic atomization of AA into an APGD, of pPAA layers characterized by good adhesive and gas barrier properties.

In the present work, results regarding the AA plasma polymerization process carried out on a polymeric substrate by using a non-equilibrium atmospheric pressure nano-pulsed plasma jet,[28,29] are presented.

The AA polymerization process herein reported was aimed at depositing on polymeric substrates pPAA coatings containing the functional groups required in the frame of biomedical applications to promote cell adhesion or biomolecules immobilization.[5,7] Films of polyethylene (PE) and polyvinylchloride (PVC) were selected as substrates since they are thermoplastic polymers widely employed in both industrial and biomedical field thanks to their exceptional easy processing characteristics and good mechanical properties. However, the modification of their surface chemical characteristics is often demanded in order to increase their biocompatibility.[30,31]

The process was performed in several operating conditions on PE and PVC films, both pristine and subjected to a plasma treatment immediately before the polymerization process.

The characterization of the coatings was performed by means of an attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and with the X-ray photoelectron spectroscopy (XPS), in order to get information on the chemical structure of the deposited pPAA coating, while some preliminary information about its thickness were garnered by means of optical microscopy.

2. Experimental Section

2.1. Materials

In order to obtain pPAA films, 99% anhydrous AA, containing 180–200 ppm MEHQ as inhibitor was used as monomer precursor for the plasma polymerization process. The deposition of the pPAA thin film was performed on PE and PVC substrates, both characterized by a thickness of 300 μm and a surface of $1 \times 1 \, cm^2$. The polymeric substrates were washed in ethanol before being subjected to the plasma polymerization process.

2.2. Non-Equilibrium Atmospheric Pressure Nanopulsed Plasma Jet

The plasma source adopted in this work is a single electrode plasma jet, suitable for the treatment of different substrates such as metals, polymers, glasses, and biological materials (**Figure 1**), developed in our laboratory and previously reported in Refs.[28,29,32–34]

The high-voltage single electrode is a 19.5 mm long stainless steel sharpened metallic needle with a diameter of 0.3 mm. The electrode protrudes from a quartz capillary (outer diameter of 1 mm) by 3 mm and for the case of plasma-polymerization process, described in this work, the plasma plume was ejected from the source tip through an orifice with a diameter of 4 mm. In this source, both a primary and a secondary gas can be introduced for specific applications. As can be observed in Figure 1c, the primary gas is injected through a diffuser with 12 channels (0.3 mm diameter) circularly disposed around the electrode and aimed at ensuring a uniform and laminar flow along the electrode tip. The secondary gas is instead introduced in the discharge region downstream the electrode tip through twelve 0.3 mm holes, tilted with respect to the plasma source axis.[28,29] The AA plasma polymerization herein reported was performed by introducing only one gas, carrying the monomer, through the primary channel of the plasma source.

The plasma source was driven by a commercial pulsed DC generator (FID GmbH-FPG 20-1NMK) producing high-voltage pulses with a slew rate of 3–5 kV ns^{-1}, a pulse duration around 30 ns, a peak voltage (PV) of 7–20 kV, and an energy per pulse of 50 mJ at maximum voltage amplitude into a 100–200 Ω load impedance, with a maximum pulse repetition rate (RR) of 1000 Hz.

2.3. Experimental Setup

The effectiveness of the AA plasma polymerization process performed by means of the non-equilibrium atmospheric pressure nanopulsed plasma jet was investigated for the deposition of pPAA coatings stable upon water contact with a high retention of functional groups on PE and PVC substrates. The process was performed on both pristine and plasma pretreated polymeric films, as described in the following.

For the AA plasma polymerization process, only the primary gas was used, whereas no secondary gas was employed. In particular, Ar with a flow rate of 3 slpm was introduced at first inside a bubbler, where the volume of the AA was kept constant at 35 ml, and then, carrying the monomer, to the plasma source. The mass flow rate of AA carried by the Ar flow was 0.05 ml min^{-1}. Two distinct operating conditions were selected, defined as "mild" and "strong:" the former was characterized by PV and RR of 10 kV and 330 Hz, respectively; the latter was characterized by PV and RR of 19.2 kV and 100 Hz, respectively. The treatment time varied from 3 to 20 min for the "mild" operating condition and from 5 to 20 min for the "strong" one.

The AA plasma polymerization process was also performed on plasma pretreated PE and PVC substrates. The pretreatment of polymeric substrates (PE and PVC) was carried out by introducing 3 slpm Ar in the secondary channel of the plasma source, while the primary channel was kept closed. The 10 min long pretreatment was performed with a PV and RR of 12.7 kV and 500 Hz, respectively. After the plasma pretreatment of the polymer substrate, the AA polymerization was carried out using the "strong" operating condition and a treatment time of 20 min.

For all the above reported operating conditions, the gap between the plasma source and the polymeric substrate was kept constant at 2 mm.
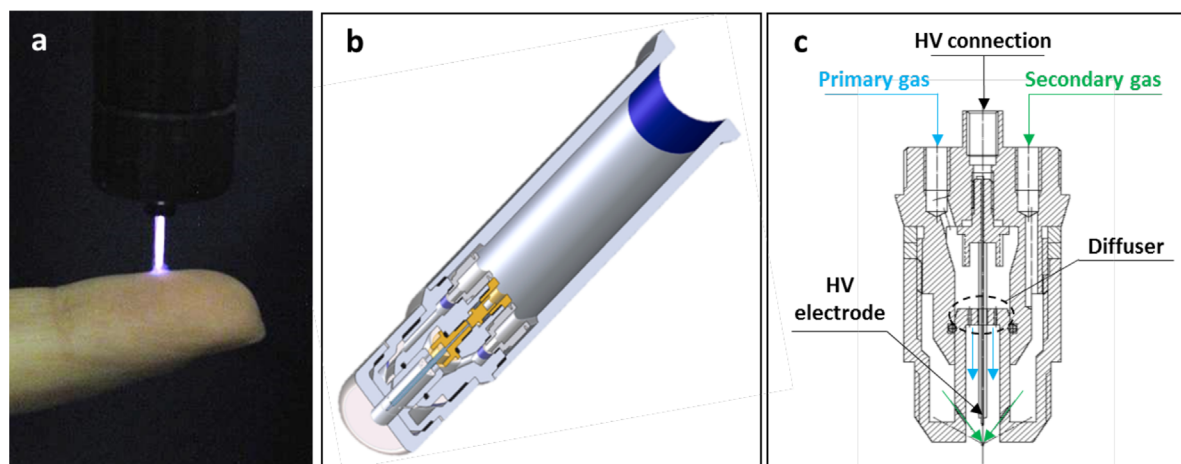

Figure 1. Non-equilibrium atmospheric pressure nanopulsed plasma jet: (a) picture while impinging on biological substrate; (b) assembly 3D rendering; (c) schematic of the head of the plasma jet with gas diffuser and gas pathways highlighted.

The schematic representation of the experimental setup with the gas connections required for both the plasma polymerization process and the plasma pretreatment of the polymeric substrates is reported in **Figure 2**.

2.4. Surface Characterization of the Deposited pPAA Coating

2.4.1. Water Contact Angle (WCA) Measurements

WCA measurements were performed to evaluate the wettability of pPAA deposited coatings and to compare it with that of the pristine substrate. WCA measurements were carried out at RT by means of a commercial Kruss Drop Shape Analysis System DSA 30. Using the software provided with the instrument, measurements of the static WCA was automated. A distilled water drop of $2.0\,\mu l$ was used as test liquid. Each measurement was run in triplicate and results are given as the average value $\pm$ standard deviation.

2.4.2. Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR was used to gather information on the chemical structure of the substrate before and after the deposition of the pPAA film by the plasma polymerization process. The Agilent Cary 660 FTIR spectrometer was used to collect infrared absorption spectra of the pPAA films deposited on PE and PVC substrates. The spectrometer was equipped with an ATR sampling accessory, using a diamond crystal as internal reflection element. Spectra were acquired at RT in absorbance mode, from 3900 to $400\,cm^{-1}$ with a resolution of $2\,cm^{-1}$; a total of 32 scans were recorded for each spectrum.

2.4.3. X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out by a VG Scientific ESCALAB, using a Mg $K_{\alpha,1,2}$ X-ray source (1253.6 eV). Under standard conditions, the X-ray source worked at 100 W, 10 kV, and 10 mA, and the pressure during the measurements was kept below 2×10^{-8} Torr. The pass energy was 100 eV for the widescans and 20 eV for the narrowscans. Measurements were carried out on electron taking-off (t.o.a.) from the sample surface with angle of $80°$. No charge neutralization was used. The binding energy scale was calibrated from the carbon contamination using the C_{1s} peak at 285.0 eV. All data analyses were accomplished using a VGX900x and PeakFit (version 4) software by SPSS Inc. Core peaks were analyzed using a linear background and peak positions and areas were obtained by a weighed least-square fitting of model curves (80% Gaussian, 20% Lorentzian) to the experimental data. Quantification was performed on the basis of VG's sensitivity factors.

2.4.4. Optical Microscope Analysis

In order to garner some preliminary information about the average thickness of the pPAA deposited coatings, a digital three-dimensional microscope Hirox Model KH-7700 characterized by high resolution optics 100–800X was employed. The instrument was equipped with a piezoelectric actuator on focus axis (z-axis), which enables a spatial resolution in the order of $0.5\,\mu m$. The analysis was performed on PE and PVC substrates partially masked during the AA plasma-polymerization process, in order to allow the deposition of the pPAA only in a well-localized area, easily identifiable by the instrument. Measurements were obtained by performing a multi-focus digital reconstruction of the specimen in the area subjected to the plasma-polymerization process and by
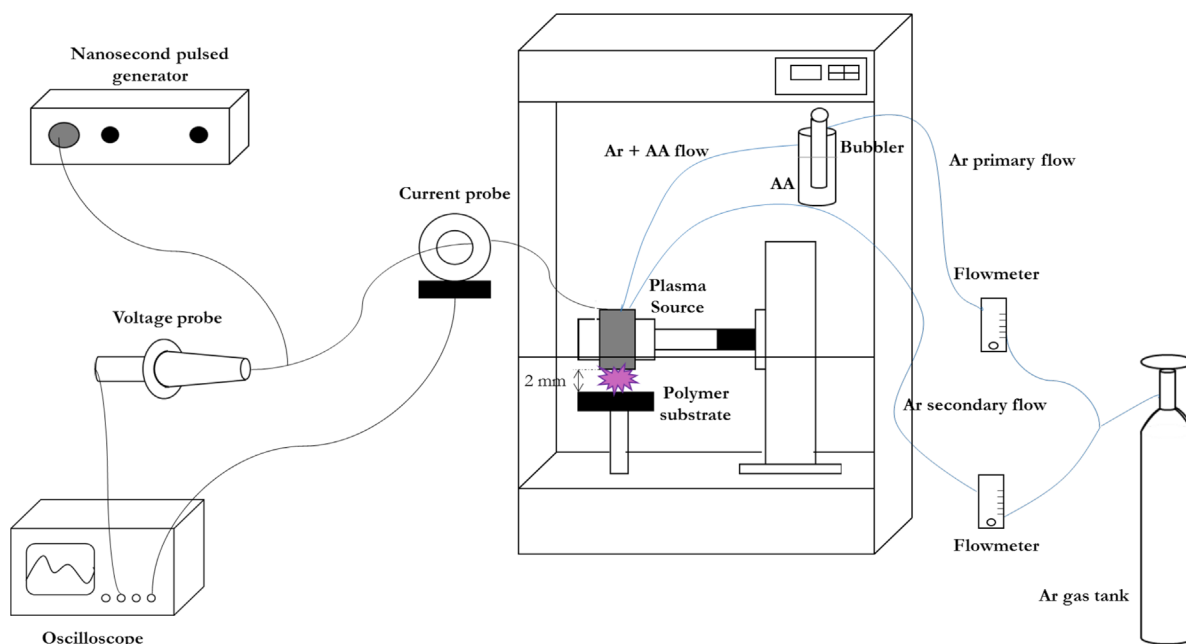

Figure 2. Experimental setup of the plasma polymerization processes with the gas connections required for both the plasma polymerization process and the plasma pretreatment of the polymeric substrates.

approximately evaluating the differences between each peak with respect to the level of the untreated area. The elaboration of the acquired data was performed using the proprietary instrument software. Each measurement was run in triplicate and results are given as the average value ± standard deviation.

3. Results and Discussion

Since this work was aimed at depositing onto a polymer substrate, a pPAA coating containing carboxyl groups, strongly required in the frame of biomedical applications to promote cell adhesion or biomolecules immobilization,[2,5,7,8,16,25] different operating conditions of the plasma polymerization process were evaluated.

As a first step, both PE and PVC substrates were subjected to the plasma polymerization process performed in "mild" operating condition, obtained by setting the PV and the RR at 10 kV and 330 Hz, for treatment times of 3, 5, and 20 min. The area of the polymeric substrate interested by the coating deposition was around 1 cm², significantly larger than the area of the plasma source orifice; this behavior is in agreement with the results presented by Onyshchenko et al.,[35] who thoroughly investigated the dimension of the area functionalized by an atmospheric pressure plasma jet treatment. The ATR-FTIR spectra, shown in **Figure 3**, highlighted that after 3 min of the plasma polymerization process the characteristic peaks of the PE substrate could still be easily identified, whereas after 5 min only the spectrum of the pPAA film turned out to be detectable.

Similar results, even though less self-evident due to the characteristic peaks of the underlying substrate, were obtained when PVC was taken as the substrate for pPAA deposition (data not shown). Taking into account the fact that with ATR-FTIR measurements the sampling depth is of the order of 600–700 nm,[36] since the spectrum of the underlying PE substrate could not be detected after 5 min of AA plasma polymerization, it is reasonable to hypothesize that the obtained pPAA film was characterized by a

thickness exceeding that dimension. The spectra collected for 5 and 20 min plasma polymerization processes exhibited a very strong absorption band at $1714\,cm^{-1}$ which can be assigned to C=O stretching vibrations of the carboxylic functional groups. The ATR-FTIR spectra shown in Figure 3 also contain a very broad band in the region $3600–2400\,cm^{-1}$, which can be attributed to OH stretching vibrations.[16,37] Superimposed on this broad peak, a band in the region $3000–2900\,cm^{-1}$ due to CH_x stretching vibrations is noticeable.[16,37] At lower wavenumber, an absorption peak due to coupled C—O stretching and OH deformation between 1400 and $1330\,cm^{-1}$, and a strong C—O stretching absorption peak between 1332 and $1135\,cm^{-1}$ with the maximum around $1200\,cm^{-1}$ can be found. Finally, the absorption band due to C(O)OH dimers appears between 999 and $875\,cm^{-1}$.[37,38]

Besides FTIR, the XPS technique can also provide useful information on the chemical composition of the pPAA deposited films and it is, differently from FTIR, a highly surface-sensitive technique. As known, the effective XPS sampling depth (d), which is the depth from which 95% of the electron signal arises, is calculated as $d = 3\lambda\sin\theta$, where θ is the electron take-off angle and λ is the electron mean free path. Thus, using λ of 1.4 nm, as determined by Clark and Thomas,[39] for C_{1s} photoelectrons, our results are representative of the composition of the approximately outermost 4 nm of the surface.

XPS analysis was performed on the PVC substrate subjected to 3 min AA plasma polymerization in "mild" operating condition. This sample was selected in order to verify if chlorine atoms of the underlying PVC were or not detected after 3 min pPAA deposition since for this sample the characteristic peaks of the PVC substrate were still detected by the ATR-FTIR, similarly to the case of PE substrate. Furthermore, in order to evaluate the role of the plasma polymerization time on the content of carboxylic acid (—COOH) and/or ester (—COOR) moieties, both characteristic of the pPAA chemical structure, the XPS investigation was also performed on 20 min plasma
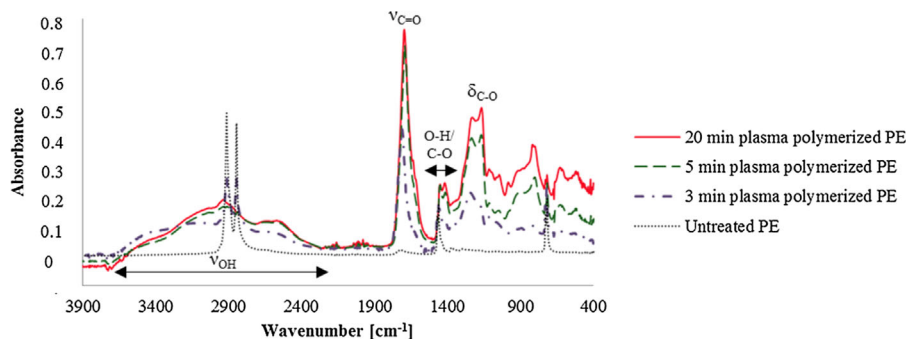

Figure 3. ATR-FTIR spectra of pristine PE and of PE substrates subjected to AA plasma polymerization process performed in "mild" operating conditions: 3, 5, and 20 min.

polymerized PVC samples. To obtain deeper insight into the chemical bonds on the surface of the samples, curve fitting of the high-resolution C_{1s} peak was performed. **Figure 4** shows the C_{1s} peaks of the PVC samples subjected to 3 min (Figure 4a) and 20 min (Figure 4b) plasma polymerization processes performed in "mild" operating condition.

The C_{1s} envelope of the deposited films can be deconvoluted into four distinct peaks: a peak at 285.0 ± 0.1 eV corresponding to $\underline{C}$—C and $\underline{C}$—H bonds, a peak at 285.5 ± 0.1 eV due to $\underline{C}$—COOH functional groups, a peak at 286.8 ± 0.1 eV due to $\underline{C}$—O bonds and finally, a peak at 289.1 ± 0.1 eV, attributed to carboxylic acid (—$\underline{C}$OOH) and/or ester (—$\underline{C}$OOR) groups. Furthermore, in the peak fitting of the C_{1s} envelope of the 20 min deposited pPAA

film, while the peak due to $\underline{C}$—O bonds almost disappears, a peak at 287.8 ± 0.1 eV, attributed to C=O groups, is present.

Interestingly, as shown in Figure 4a and b, no chlorine was detected in the C_{1s} envelopes of the deposited films. In light of this result, the thickness of the 3 min pPAA deposited film in "mild" operating condition can be supposed being in the region between the XPS and ATR-FTIR sampling depth. Moreover, the results, presented in Figure 4 and **Table 1**, bring out that the increase of the plasma polymerization time from 3 to 20 min leads to (i) the increase of the C—COOH, —COOH, and —COOR groups, (ii) the decrease of C—O and C—C functions, (iii) the appearance of C=O moieties in the chemical composition of the deposited film, (iv) the increase of O/C ratio from 0.44

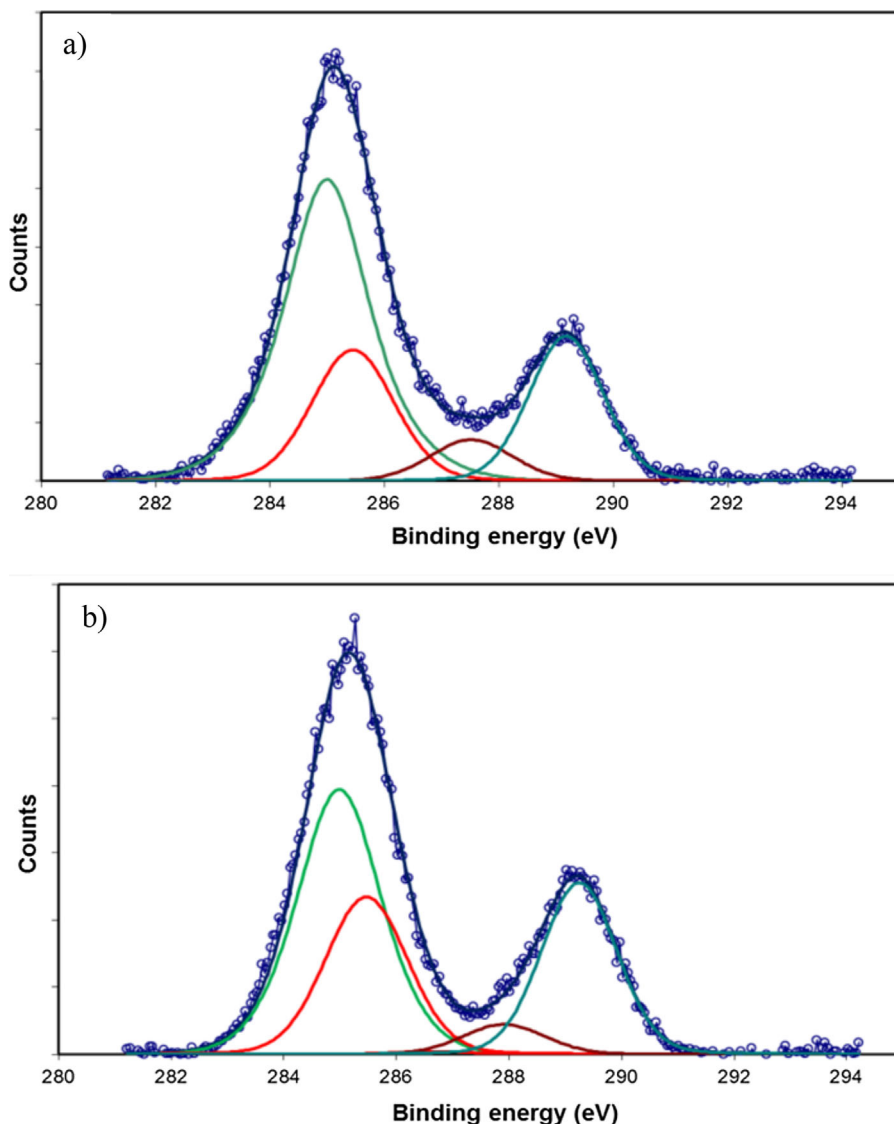**Figure 4.** XPS deconvoluted C_{1s} peak of pPAA deposited on PVC substrate by means of AA plasma polymerization process performed in "mild" operating condition: 3 min (a) and 20 min (b).

Substrate	Operating condition	C—C C—H 285.0 eV	C—COOH 285.5 eV	C—O 286.8 eV	C=O O—C—O 287.8 eV	—COOH —COOR 289.1 eV	O/C
PVC	3 min "mild" condition	48%	22%	8%	–	22%	.44
PVC	20 min "mild" condition	43%	26%	1%	5%	26%	.59
PE	20 min "mild" condition	44%	26%	0.5%	4.5%	26%	.54
PE	20 min "strong" condition	32%	27%	9%	5%	27%	.63

to 0.59. In particular, as reported in Table 1, the increase of the amount of carboxylic groups from 22 to 26%, jointly to the appearance of the carbonyl ones, suggests that a greater retention of functional groups on the substrate can be accomplished by increasing the plasma polymerization time.

With the aim of gathering some preliminary data on the average thickness of the deposited pPAA, optical microscopy was used to investigate the thickness of the film after a 20 min plasma polymerization process in "mild" operating condition carried out on both PE and PVC substrates. The obtained results showed that the pPAA coating deposited on the PE substrate had an average thickness of $42 \pm 15 \, \mu m$, while the one on the PVC substrate resulted to be $19 \pm 11 \, \mu m$ thick. Although the numerical values measured for the two analyzed samples turn out to be rather different, they are both in the order of few tens of micrometers, in agreement with observations of the collected ATR-FTIR spectra. In order to give a representation of the thickness and the morphological aspect of the deposited coating, an image, focused at the interface between the pristine PE (properly covered by the mask during the polymerization process, as reported in the Experimental Section) and the deposited pPAA, is reported in **Figure 5**.

As noticeable, the film turns out to have a quite relevant roughness and not a constant thickness on the whole deposition area, in agreement with the results of previous work.[23]

By applying "mild" operating conditions, the deposited film turned out to be highly water soluble and all peaks characteristic of pPAA were not detected in the ATR-FTIR spectra of the pPAA coated PE and PVC substrates dipped in distilled water for 30 s and air dried.

Therefore, "strong" operating condition (PV of 19.2 kV and a RR of 1000 Hz) was taken on to perform the AA plasma polymerization. The process in these conditions was carried out for both 5 and 20 min and, as reported in **Figure 6**, a comparison between the collected FTIR spectra of these samples and the one obtained after 20 min "mild" condition process was performed for both PE and PVC substrates.

As observed for the "mild" condition, after 5 min plasma polymerization in "strong" operating condition, the spectrum of the substrate cannot be detected anymore, while the pPAA spectrum results to be well defined. Interestingly, for the PE substrate, no relevant differences can be noted by comparing the spectra of the 20 min pPAA deposited in "mild" and "strong" conditions (Figure 6a). Conversely, in the case of PVC the pPAA spectra after 20 min "mild" condition process turned out to be very close to the one collected on the 5 min "strong" condition polymerized sample (Figure 6b).

After the polymerization processes performed for 20 min in "strong" operating condition, the stability upon water contact of the pPAA films was tested by dipping the samples in distilled water for 30 s. Although the drastic reduction of the absorbance of the pPAA characteristic peaks and the detectability of the spectrum of the underlying substrate, as shown in **Figure 7**, the pPAA film resulted not totally washed off after water dipping.
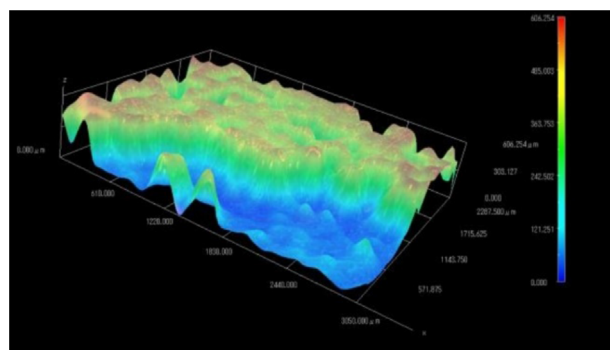

Figure 5. 3D Optical microscope image at the interface between the masked area of PE and the area where the pPAA was deposited on the PE substrate (20 min "mild" condition).
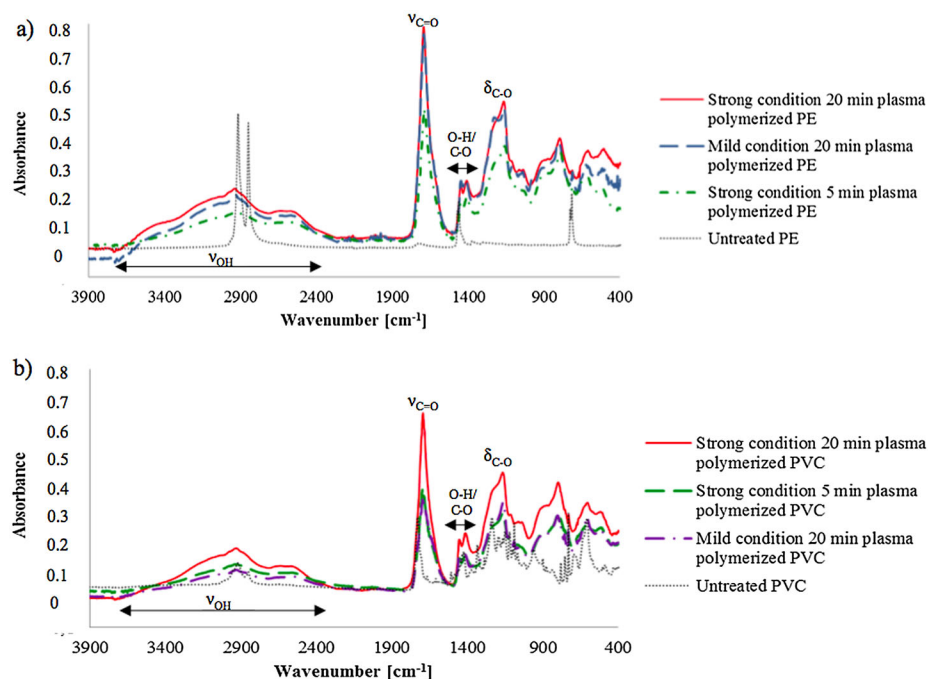
Figure 6. ATR-FTIR spectra of pristine PE and PE samples subjected to AA plasma polymerization process performed in ''strong'' operating condition: 5 and 20 min and in ''mild'' operating condition: 20 min (a); pristine PVC and PVC samples subjected to AA plasma polymerization process performed in ''strong'' operating condition: 5 and 20 min and in ''mild'' operating condition: 20 min (b).
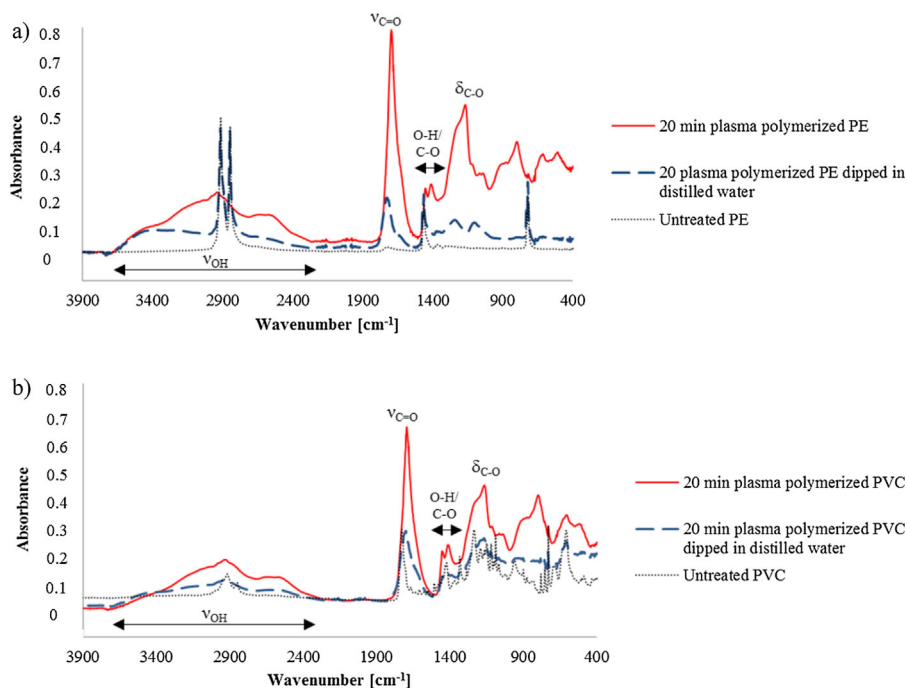

Figure 7. ATR-FTIR spectra of pristine PE and PE samples subjected to AA plasma polymerization process performed for 20 min in ''strong'' operating condition before and after being dipped in distilled water for 30 s (a); pristine PVC and PVC samples subjected to AA plasma polymerization process performed for 20 min in ''strong'' operating condition before and after being dipped in distilled water for 30 s (b).

Since the deposited pPAA resulted partially insoluble upon water contact, an indicative water contact angle (WCA) measurement was performed in the region of the substrate subjected to the AA polymerization process, immediately after the polymerization process itself. While the measured WCA values were $71° \pm 1°$ and $73° \pm 1°$ for the pristine PE and PVC, respectively, indicative WCA values of $8° \pm 1°$ and $8° \pm 3°$ were obtained on the pPAA coated substrates after a 20 min plasma polymerization process in "strong" operating condition. The increased water wettability of the plasma-polymerized surface provided further evidence for the presence of hydrophilic —COOH groups.

Since the pPAA deposited in "mild" condition was completely water soluble, the increase of the stability upon water contact after the "strong" condition process may be due to an increase of the degree crosslinking in the pPAA film, which is consistent with its higher water resistance properties, in agreement with results of previous works.[40–42]

With the aim to get some confirmation to this hypothesis in terms of the chemical composition of the pPAA deposited film, the XPS analysis was performed on 20 min plasma polymerized PE samples both in "mild" and in "strong" operating conditions; a comparison between the C_{1s} envelope obtained for the two kinds of sample is presented in **Figure 8**.

By switching from "mild" to "strong" operating plasma polymerization conditions, while the amount of carbonyl and carboxylic functions slightly increases, a significant decrease of not oxidized carbon species in addition to a relevantly higher content of alcoholic, ether, and peroxide functions, centered at $286.8 \pm 0.1\,eV$, and to an increase of O/C ratio, was detected in the PE samples (Table 1).

Due to the assembly of various molecular fragments produced in the plasma region,[43] the polyacrylic acid (PAA) films obtained from the AA plasma polymerization process have been found to be generally more crosslinked than the ones produced from chemical processes.[7,42,44,45] On this basis, the detected alcoholic, ether, peroxide, and carbonyl functions, which are generally not or barely identified in the PAA chemical composition, can be associated to the occurred crosslinking during the AA plasma polymerization. In this regard, some works[46] have already demonstrated that plasma polymers obtained from the plasma polymerization of acrylate monomers are characterized by the same chemical composition of the conventional polymer, with additional peaks at the binding energies corresponding to the C=O and O—C—O moieties, possibly due to the loss of an ester carbon.[46]

In order to better compare the effect of the operating conditions on the amount of the functional moieties of the deposited pPAA, the results of the XPS analysis are reported in Table 1. As demonstrated and already discussed, a great retention of —COOH and —COOR groups occurred independently on the employed operating conditions and on
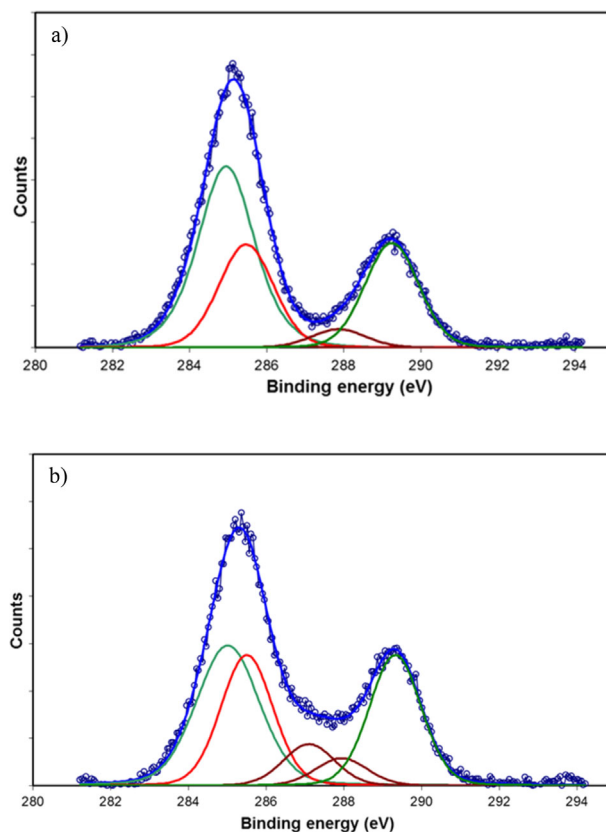

Figure 8. XPS deconvoluted C_{1s} peak of pPAA deposited on PE substrate by means of AA plasma polymerization process performed for 20 min in "mild" operating condition (a) and in "strong" operating condition (b).

the treatment time. As evident in Table 1, by comparing the amount of functional groups evaluated on 20 min pPAA deposited in "mild" operating condition on both PE and PVC substrates, no significant difference can be noticed, suggesting that, in the limit of the XPS sampling depth, the pPAA chemical composition is independent of the underlying substrate on which it is deposited. Furthermore, it is worth pointing out that with the increase of the plasma polymerization time, carbonyl moieties are detected and, operating at "strong" condition, a relevant overall amount of C=O, O—C—O, and C—O functional groups, jointly to an increase of O/C ratio, that could be attributed to a crosslinked chemical structure, is observed, conferring stability upon water contact to the film. As a last consideration on this aspect, since our studies on the plasma-induced mechanisms which lead to the crosslinking of the polymer chains are still ongoing, a resolving correlation between the plasma polymerization parameters and the amounts of both C=O, O—C—O, and C—O functions cannot be proposed yet.

The 20 min plasma polymerization process in "strong" operating condition was also performed on PE and PVC
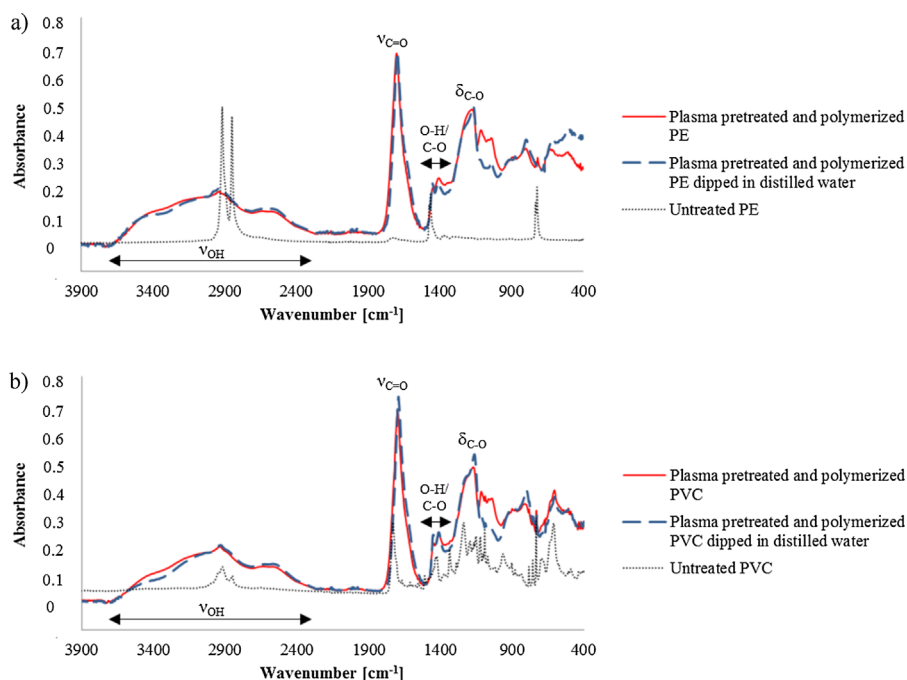
Figure 9. ATR-FTIR spectra of pristine PE and PE samples subjected to 10 min Ar plasma pretreatment and AA plasma polymerization process performed for 20 min in "strong" operating condition, before and after being dipped in distilled water for 30 s (a); pristine PVC and PVC samples subjected to 10 min Ar plasma pretreatment and AA plasma polymerization process performed for 20 min in "strong" operating condition before and after being dipped in distilled water for 30 s (b).

substrates previously subjected to a 10 min long Ar plasma pretreatment (PV of 12.7 kV, RR of 500 Hz, and dimension of the area affected by the pretreatment around 1 cm^2). As reported in **Figure 9**, for this process, the pPAA-deposited film turned out to be highly stable after 30 s water dipping for both the considered plasma pretreated substrates and no significant difference could be found by comparing the spectra collected before and after the samples water immersion.

Differently from the case in which the plasma pretreatment of the substrate was not performed, no great difference can be noticed by comparing the ATR-FTIR spectra collected before and after the water dipping. This result emphasizes that for the deposition of polymer coatings stable upon water contact, the adhesion of the polymer film to the substrate needs to be taken into account.

Finally, it is worth noticing that a very interesting work, reporting about the deposition of coatings from mixtures containing AA and ethylene by means of an atmospheric pressure DBD plasma jet, was recently presented by Bosso et al.[47] The paper highlighted that ethylene addition increased the deposition rate but also caused a slight reduction of the amount of the carboxylic groups retained in the deposited polymer with respect to the case in which only AA was plasma-polymerized. Interestingly, while thin films obtained without ethylene addition were unstable in water, coatings deposited from AA/ethylene mixtures were stable

and did not show significant modifications even after 72 h of water immersion. In fact, the obtained results reported that the amounts of —COOH/R detected by XPS before and after 72 h water immersion were almost unchanged, while the thickness loss after water dipping was around 7%.[47] Interestingly, the highest amount of —COOH/R detected by XPS in the deposited coatings was around 9%,[47] which is significantly lower than the amounts (22–27%) here reported, further highlighting the potential of nanosecond high voltage pulses for the deposition of coatings with a high retention of functional groups.

4. Conclusion

In the present work, the results regarding the AA plasma-polymerization by means of a non-equilibrium atmospheric pressure nanopulsed plasma jet, aimed at depositing pPAA coatings stable upon water contact with high retention of carboxylic acid groups on polymer substrates, have been presented. It has been observed that, in order to obtain the required characteristics, the operating conditions of the polymerization process need to be optimized. Results have shown that both the selected plasma-polymerization operating conditions ("mild" and "strong"), independently of the treatment time, enabled to obtain an amount of carboxylic acid

moieties always higher than 22%, highlighting that the AA plasma-polymerization was successfully performed. However, despite the great amount of —COOH functional groups verified by both ATR-FTIR and XPS, coatings deposited in "mild" operating condition were found to be highly water soluble, probably due to the low crosslinking of pPAA chains. Switching from "mild" to "strong" operating conditions, the overall amount of the detected C=O and C—O functional groups, that could be attributed to pPAA crosslinking, became noticeable, with a parallel enhancement of the pPAA stability upon water contact, even though the coating turned out to be still partially soluble. The plasma treatment of the polymer substrate before the plasma-polymerization process has been demonstrated to reduce pPAA coatings solubility upon water contact, since no great difference between the ATR-FTIR spectra collected before and after water dipping (30 s) can be observed.

The results obtained from the characterization of the chemical structure of the pPAA coatings allow pointing out that the plasma-polymerization process was successfully performed for all the investigated operating conditions and treatment times, since the high amount of typical pPAA functional groups detected on the substrates.

Furthermore, a preliminary but significant investigation of the morphology of the deposited coating, in terms of evaluation of its average thickness, was also performed by means of optical microscope and an average thickness of the coatings in the order of a few tens of micrometers after a 20 min plasma polymerization process was highlighted.

The thickness and morphology of the deposited pPAA coatings will be further investigated in the future, relying also on SEM and AFM analysis; moreover, future activities will be dedicated to investigate in detail the stability of the coating, evaluating its morphology and chemical composition after soaking in water and sonicating, in accordance with widely adopted experimental protocols.[26,47]

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