Effective deposition of plasma-polymerized polyacrylic acid thin film by means of a plasma jet driven by nanosecond high voltage pulses

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Abstract: The effectiveness of a nanopulsed non-equilibrium atmospheric pressure plasma jet for the deposition of plasma-polymerized polyacrylic acid thin films on polymeric substrates has been demonstrated. A relevant retention of carboxyl groups can be achieved after just 5 min of plasma polymerization. Furthermore, operating conditions can be properly optimized in order to deposit a coating with water resistant properties.

Keywords: non-equilibrium atmospheric pressure plasma, plasma polymerization, nanopulsed generation, plasma-polymerized polyacrylic acid, carboxyl groups

1. Introduction
Plasma-polymerized polyacrylic acid (ppAA) has raised great interest for the production of adhesion-promoting interlayers, e.g., in carbon fibre/epoxy composites [1], as well as for the development of bio-compatible polymers [2] and anti-fouling coatings [3]. In the frame of biomedical applications, plasma polymerization of acrylic acid (AA) has been investigated in order to produce coatings with a high density of carboxylic acid (-COOH) groups [4], which make the substrate highly bio-compatible to support cells adhesion and proliferation as well as immobilization of molecules.

Low pressure plasma enhanced chemical vapour deposition (PECVD) is nowadays one of the most widespread tools for effectively deposit coatings on substrates [5]. In recent years, many efforts have been dedicated to develop also coating processes relying on non-equilibrium plasma sources working at atmospheric pressure [6]; 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 [7] or carboxylic groups [8] was demonstrated. Solventless and environmentally friendly, like other PECVD methods, AP-DBD operates at room temperature and does not require vacuum devices compared to the low pressure plasma processes. However, despite the satisfactory results for carboxylic functionalization rate accomplished with both low pressure PECVD and AP-DBD technologies through AA polymerization, coatings presented a poor stability upon contact with water [2, 8]. Earlier studies suggested that the copolymerization of the selected monomer with an unsaturated silane, such as vinyltrimethoxysilane, could allow overcoming the reported drawback [8].

Aiming to get deeper insight on the process of depositing ppAA on polymeric substrates with atmospheric pressure non-equilibrium plasma, we employed a plasma jet, operating in open air at atmospheric pressure, for the AA plasma polymerization.

The plasma jet, developed in our laboratory and previously described in [9, 10], employed for the AA plasma polymerization process was driven by voltage pulses with nanosecond rise time and pulse duration in the order of few tens of nanoseconds. The ultra-short rise time and pulse duration were chosen to maximize the structural retention of monomers and preserve their functional groups, as suggested by previous works at low pressure [11,12], which investigated the effects of reducing the pulse duration from milli- to microsecond. Nevertheless, while a recent study was performed on the deposition of an allyl monomer containing phosphorus with a nanosecond square-pulsed AP-DBD [13], to the authors’ best knowledge a nanopulsed plasma jet has never been implemented for the deposition of organic and polymeric coatings.

The presented AA polymerization process was carried out using polyethylene (PE) and polyvinylchloride (PVC) as substrates; two different operating conditions were evaluated with the aim to investigate the role of electrical parameters and treatment time on the characteristics of the deposited coating and on its stability after water dipping. The characterization of the deposited coating was performed by means of an Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) spectrometer, with the aim to evaluate the intensity of the functional groups of the deposited ppAA coating. Furthermore, some insights on the next steps to deeper characterize the polymeric thin film are here presented.

2. Materials and Methods
Non-equilibrium atmospheric pressure plasma jet
The plasma source adopted in this work is a single electrode plasma jet developed by the authors and previously reported in [9, 10]. The high-voltage electrode
is a long stainless steel sharpened metallic needle and protrudes from a quartz capillary by 3 mm. In this source, a primary gas is introduced for sustaining the plasma, whereas a secondary gas can be introduced when required in specific applications. As already reported above, the plasma source is driven by a commercial pulse generator producing high-voltage pulses with a slew rate of few kV/ns, a pulse duration around 30 ns.

Experimental setup and operating conditions

As ppAA precursor, anhydrous acrylic acid (AA) purchased from Sigma Aldrich was used, while the ppAA was deposited onto both PE and PVC substrates having a thickness of almost 300 µm. In the polymerization process, the monomer is added to the primary gas (Ar 3 slpm), by means the passage of the gas through a bubbler in which the volume of the monomer was kept constant.

In order to evaluate the effects of electrical parameters on the deposited film chemical structure, two operating conditions were tested. The first one was characterized by a peak voltage (PV) of 20 kV and a pulse repetition frequency (RR) of 125 Hz. The second one was characterized by a PV and a RR of 28 kV and 1000 Hz (maximum PV and RR values allowed by the generator). For both the operating conditions, the gap between the plasma jet outlet and the substrate was fixed at 2 mm. The effect of treatment time was also evaluated, performing the experiments for 5 and 20 min. Furthermore, for the first operating condition, the chemical structure of the substrates was also evaluated after 3 min of plasma polymerization.

ATR-FTIR Spectrometry

FTIR was used to gather information on the chemical structure of the substrate before and after the deposition of the ppAA thin film by the plasma polymerization process. The Agilent Cary 660 FTIR spectrometer was used to collect infrared absorption spectra. The spectrometer was equipped with a single ATR accessory. The collected spectra are the result of 32 scans.

3. Results and Discussion

To evaluate the effectiveness of the non-equilibrium plasma jet for the deposition of ppAA thin film on the polymeric substrates, two different operating conditions were tested and for each of them at least two different treatment times were evaluated. Useful and interesting information regarding the chemical structure and the amount of functional groups in the deposited film were deduced from the analysis of the ATR-FTIR collected spectra, before and after the plasma polymerization process.

Results achieved for the first operating condition, characterized by a PV of 20 kV and a RR of 125 Hz, clearly highlight a relevant deposition of ppAA after only 5 min of plasma polymerization, as shown in Fig. 1.

**Fig. 1.** ATR-FTIR spectra of PE before plasma polymerization and after 5 min of plasma polymerization (PV = 20 kV, RR = 125 Hz).

Fig. 1 shows that the FTIR spectrum for the 5 min plasma polymerized PE is characterized by a very strong absorption band at 1710 cm⁻¹, which is assigned to C=O stretching vibration of carboxylic acids, and a broad absorption band in the region 3600-2400 cm⁻¹ attributed to OH stretching vibrations in carboxylic acids [14][15]. Superimposed on this broad peak, a smaller peak in the wavenumber region 3000-2900 cm⁻¹ due to C-H stretching vibration can be detected [14][15]. The FTIR spectrum of plasma-polymerized acrylic acid films also shows two small peaks at 1450 and 1410 cm⁻¹, which are likely due to the combination of C-O stretching and OH deformation vibrations [14]. Based on these considerations, it is possible to affirm that the deposited film after 5 min plasma polymerization contains a significant amount of carboxylic acid groups.

In order to evaluate the role of the treatment time on the amount of the deposited functional groups, the FTIR spectra after 3 min and 20 min of plasma polymerization were also collected, keeping constant the electrical parameters. As reported in Fig. 2, the chemical structure of the substrates turns out to be strongly linked to the exposure to the polymerization process. In fact, while only some slight differences in the absorbance can be evaluated by passing from 5 to 20 min of plasma polymerization, a noticeable change in the substrate chemical structure is detected when the treatment time is increased from 3 to 5 min. In fact, while for a 5 min treatment PE peaks can not be observed, after only 3 min the PE characteristics peaks can be still noted, even though the typical ppAA absorption bands turn out to be quite strong. Effectively, a strong correlation between the amount of the deposited groups and the treatment time can be underlined.
Fig. 2. ATR-FTIR spectra of PE before plasma polymerization and after 3 min, 5 min and 20 min of plasma polymerization (PV = 20 kV, RR = 125 Hz).

As a second operating condition, the one characterized by a PV of 28 kV and RR of 1000 Hz was selected. Fig. 3 reports the collected spectra for the untreated PE and for the PE subjected to the AA plasma polymerization for both 5 and 20 min. Also in this case, the ppAA spectra turn out to be well-defined after just 5 min of AA plasma polymerization and, as already noted, the longer the treatment time the higher the amount of functional groups detected on the substrate.

Fig. 3. ATR-FTIR spectra of PE before plasma polymerization and after 5 min and 20 min of plasma polymerization (PV = 28 kV, RR = 1000 Hz).

Besides the interest in evaluating the functional groups amount for the maximum PV and RR enabled by the generator, this operating condition was selected with the aim to evaluate the possibility to deposit a water resistant coating on the polymeric substrates. In fact, in their work on the polymerization of AA by means a medium pressure DBD [15], Morent et al. suggested that the increase of the discharge power lead to a higher input per molecule of the monomer and consequently to a higher monomer fragmentation and thus less carboxylic acid functions. However, the greater monomer fragmentation results in an increase in reaction pathways available, which manifests itself as a deposit containing a higher crosslinking degree [15, 16]. As a result of this crosslinking degree, the deposited thin film tends to be less soluble in water.

It is worth pointing out that our results turn out to meet the suggestion proposed by Morent et al. In fact, comparing the spectra reported in Fig. 2 with those of Fig. 3, for the 5 min plasma polymerization, the amount of carboxylic acids is higher for the first condition than for the second one. Furthermore, our experiments highlight that the coating deposited with a 20 min plasma polymerization in the first operating condition is rather water soluble (data not shown), while carrying out the treatment for the same time, but in the second condition, the water resistance of the coating results to be enhanced. In fact, as shown in Fig. 4, some characteristic peaks of the ppAA are still clearly observable after dipping in distilled water, even though their absorbance is quite lower than that of the undipped plasma polymerized sample.

Fig. 4. ATR-FTIR spectra of PE before plasma polymerization; after 20 min of plasma polymerization; after 20 min of plasma polymerization and distilled water dipping (PV = 28 kV, RR = 1000 Hz).

As expected, the results obtained on the PE substrate were confirmed by the same experiments performed on the PVC samples (not reported).

4. Conclusion

The effectiveness of the non-equilibrium atmospheric plasma jet driven by a nanopulsed generator for the deposition of ppAA thin films on polymeric substrates has been demonstrated. Two operating conditions were tested, both evaluated at least for two different plasma polymerization times. It is worth noting that a relevant deposition of ppAA can be obtained after just 5 min for both the conditions, as demonstrated by the collected ATR-FTIR spectra. Furthermore, it has been highlighted that, by optimizing the operating conditions, the deposition of a water resistant coating can be accomplished.

As next steps, X-ray photoelectron spectrometry analysis will be performed in order to better investigate the topmost surface layers of the deposited films, by collecting data on the ratios of the different chemical elements present at the surface and on the molecular environment of each element. Further characterizations will be carried out with the aim to garner some
information about the thickness of the deposited coating and to investigate the possible correlation between the measured value and the treatment time. Moreover, other experiments to enhance the coating stability after the immersion in water will be also performed.

5. References

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