# Control strategies for polymerization processes assisted by atmospheric pressure plasma jets and aerosolized precursors

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**Abstract:** This work explores the possible control strategies for a polymerization process assisted by an AP single electrode plasma jet and an aerosolized precursor, aiming to advance the comprehension and the understanding of the process.

Keywords: aerosols, plasma polymerization, jets, process control, Yasuda parameter.

## **1.Introduction**

Nowadays, polymerization processes assisted by atmospheric pressure (AP) plasma jets are receiving interest in numerous industrially relevant sectors since they allow to coat complex 3D substrates without requiring expensive vacuum systems [1,2]. At the same time, as at AP the precursor can be injected into the discharge in liquid phase, aerosolized precursors are increasingly used because of the peculiar advantages respect to the vaporized ones, such as the lower complexity of the experimental setup and the less intense fragmentation of the precursor molecules in the discharge [3,4]. Therefore, finding proper strategies to control polymerization processes supported by AP plasma jets and aerosolized precursors has become a high priority research topic.

The Yasuda parameter W/FM (defined as the ratio between the discharge power, W, and the product of the precursor molar flow rate, F, and the precursor molecular weight, M) is a consolidated and extensively used controlling parameter for low pressure (LP) plasma polymerization processes [5,6]. Over the years, several research groups attempted to extend its application also to the AP case [7 - 9]. Nonetheless, the validity of W/FM as a controlling parameter at AP has been questioned because, differently from LP processes, 1) the precursor is usually highly diluted (typically in parts per thousand) in a ionization/carrier gas which takes part in the mechanisms of energy transfer to the precursor molecules and 2) it is not often possible to measure the discharge power with reasonable precision [10]. These criticisms become even more pronounced in case of plasma jets since their electrical characterization is typically not obvious and the related literature is less mature than, for example, the one associated to planar dielectric barrier discharges (DBDs) [11]. The presence of precursor droplets in the discharge, as well, induces peculiar mechanisms which complicate the exchanges of energies between the discharge and the precursor (respect to the case of vaporized or gaseous precursors) and in some cases have yet to be fully understood [12].

As a more accurate alternative to the Yasuda parameter, Nisol et al. developed a methodology for measuring the energy absorbed per precursor molecule in AP plasma polymerization processes [11]. Through the identification and the resolution of a proper equivalent electrical circuit, this methology allows to obtain values of energy per precursor molecule which can be used to gather information on plasma polymerization reactions. Nevertheless, despite being validated for different families of precursors, it is still limited to the context of planar DBDs and to gaseous and vaporized precursors.

This work explores the possible control strategies for a polymerization process assisted by an AP single electrode plasma jet and an aerosolized precursor, aiming to advance the comprehension and the understanding of the process. In the following, the study of the validity of the Yasuda parameter (W/FM) as controlling parameter is proposed as an example.

# 2. Materials and methods

The experimental setup used in this work is schematically reported in Fig. 1.

The employed plasma source is an atmospheric pressure single electrode plasma jet (AlmaJET, AlmaPlasma s.r.l.), which offers two separate channels for the introduction of the main gas and the precursor. An argon flow rate of 3 slpm was injected in the discharge region through the primary channel, while, simultaneously, an aerosolized precursor flow rate is introduced through the secondary channel. The liquid precursor used in this work is (3,3,3trifluoropropyl)trimethoxysilane (C<sub>6</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>Si, Sigma-Aldrich,  $\geq$  97.0%). A single-jet atomizer (BLAM, CH Technologies) fed with an argon flow was used to aerosolize the liquid precursor. To calculate the effective precursor feed rate, the quantity of liquid precursor consumed within a defined time interval (15 min) was measured. The argon flow rates were controlled by digital mass flow controllers (EL-FLOW, Bronkhorst).

The stainless-steel single electrode of the plasma source was connected to a micropulsed high voltage generator (AlmaPulse, AlmaPlasma s.r.l.), operated at a fixed frequency of 12 kHz and at a variable peak voltage; a ballast resistor of 70 k $\Omega$  was added along the high voltage cable between the generator and the plasma source. Bilayer films (area: 1 cm x 1 cm, thickness: 0.3 mm), composed of polyethylene (PE, approximately 0.15 mm thick) and polyvinyl chloride (PVC, approximately 0.15 mm thick) foils, were used as substrates. The deposition was performed onto the PE layer and the distance between the

plasma source and the surface of the substrate was kept constant to 10 mm. The substrate was placed on a polyvinyl chloride (PVC) plate (thickness = 8 mm) positioned on a metallic plate connected to the ground. The deposition time was fixed to 60 s.



Fig. 1. Experimental setup.

Nine different combinations of peak voltage and precursor feed rate were analyzed. Each combination, associated to a letter from A to I, is reported in Table 1 along with the corresponding discharge power and W/FM value. Conditions from J to M, reported as well in Table 1, were investigated to study the properties of coatings deposited under similar W/FM values but obtained with different combinations of power discharge and precursor feed rate. The performed comparisons are the following: D-J, E-K, F-L, and H-M.

Table 1.	Analyzed	deposition	conditions
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Deposition condition	Peak voltage [kV]	Precursor feed rate [g/h]	Discharge power [W]	W/FM [MJ/kg]
А	14	0.7	$11.7\pm0.6$	$60.2 \pm 3.1$
В	12	0.7	$7.5 \pm 0.4$	$38.6\pm2.1$
С	10	0.7	$5.1 \pm 0.3$	$26.2\pm1.5$
D	8	0.7	$2.8 \pm 0.4$	$14.4 \pm 2.1$
Е	6	0.7	$1.7 \pm 0.2$	$8.7 \pm 1.0$
F	6	1.2	$1.8\pm0.1$	$5.4 \pm 0.3$
G	6	2.1	$1.8\pm0.1$	$3.1 \pm 0.2$
Н	6	4.56	$1.9\pm0.2$	$1.5 \pm 0.2$
Ι	6	9.32	$2.2 \pm 0.1$	$0.8\pm0.0$
J	10	1.2	$5.3 \pm 0.4$	$15.9\pm1.2$
K	8	1.2	$2.9\pm0.1$	$8.7 \pm 0.3$
L	8	2.1	$3.0 \pm 0.2$	$5.1 \pm 0.3$
М	8	9.32	$3.8\pm0.2$	$1.5\pm0.1$

To calculate the discharge power, the voltage (V) and the current (i) were measured by means of a high voltage probe (Tektronix P6015A) and a current probe (Pearson 6585), both located on the high voltage cable between the resistor and the plasma source. The corresponding waveforms were recorded using a digital oscilloscope (Tektronix DPO4034, 350 MHz, 2.5 GSa/s).The average discharge power (P) dissipated over the applied voltage period (T) was calculated directly from measured voltage and current using the following formula (1):

$$P = \frac{1}{T} \int_0^T V(t) i(t) dt \tag{1}$$

The calculated discharge power was related to the precursor feed rate to calculate the corresponding W/FM values, which are presented as mean  $\pm$  standard deviation as well.

Fourier transform infrared (FTIR) measurements were performed to gather information on the chemical structure of the flat PE substrates before and after the deposition of the fluorinated silane coatings. The Agilent Cary 660 FTIR spectrometer was equipped with an attenuated total reflectance (ATR) sampling accessory, using a diamond crystal as internal reflection element and a beam set at 45°. Spectra were acquired in absorbance mode, from 4000 to 400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>; a total of 32 scans were recorded for each spectrum. X-ray Photoelectron Spectroscopy (XPS) was used to study the chemical composition of PE substrates and of the deposited fluorinated silane coatings. Spectra were recorded with a PHI 5000 Versa Probe Instrument equipped with a monochromatic Al Ka X-ray source excited with a microfocused electron beam. Analyses were carried out at 15 W on 150 µm area with a photo-electron take-off angle of 45°. The XPS binding energy (BE) scale was calibrated by centring the C 1s peak due to C-C, C-H hydrocarbon moieties of PE and "adventitious" carbon at 285.0 eV. Static water contact angle (WCA) measurements were carried out to evaluate the wettability of the deposited coatings and to compare it with that of the uncoated substrates. For the WCA measurements a drop shape analyzer (DSA30, KRUSS) was employed, depositing distilled water droplets (2  $\mu$ l) on the substrates, and using the Young-Laplace method. For each deposition condition, 3 replicates were analyzed, performing 5 measurements for each replicate. The results are presented as mean values  $\pm$  standard deviations. Scanning electron microscopy (SEM) was used to investigate the thickness of the deposited coatings. To facilitate the break in liquid nitrogen, polypropylene foils (thickness 0.5 mm and diameter 2 cm) were chosen as substrates (after verifying that the deposited coatings possess identical chemical characteristics to coatings deposited on PE/PVC foils) and a pre-cut was performed in the back of the samples prior to the deposition treatment. To carry out more accurate thickness measurements, the deposition time was set to 120 s. The observations were carried out using a SEM (Phenom ThermoFisher Scientific) by applying ProX. an accelerating voltage of 10 kV. A sputter coater (SC7620, Quorum Technologies) was used to cover the coating surface with gold before SEM analysis.

## 3. Results and discussion

The ATR-FTIR spectra of PE substrates before and after the deposition under different W/FM values are shown in Figure 2. The spectrum of uncoated PE exhibits two large absorption peaks at 2920 and 2852 cm<sup>-1</sup> due to C-H asymmetric and symmetric stretching vibrations in CH<sub>2</sub>, respectively. Furthermore, two smaller peaks can be observed at 1466 cm<sup>-1</sup> and 723 cm<sup>-1</sup>: the first corresponds to C-H deformation vibrations in  $-(CH_2)_n$ , while the second one to C-C rocking vibrations in  $-(CH_2)_n$ .



Fig. 2. ATR-FTIR spectra as a function of W/FM.

As W/FM decreases from condition A to condition E, no relevant differences in terms of peaks can be observed. All the spectra exhibit several peaks associated to silicon presence in the coating, such as the Si-O rocking at 450 cm<sup>-</sup> <sup>1</sup>, the Si-O-Si bending or stretching at 800 cm<sup>-1</sup>, the Si-O stretching at 900 cm<sup>-1</sup>, the Si-OH stretching at 930 cm<sup>-1</sup>, and the Si-O-Si asymmetric stretching at 1075 cm<sup>-1</sup> (transverse optical, TO). Furthermore, peaks corresponding to CF<sub>2</sub> deformation at 495 cm<sup>-1</sup> and to CF<sub>2</sub> asymmetric stretching at 1220 cm<sup>-1</sup> can be recognized in all the spectra. Additional peaks, like the CF2 asymmetric stretching at 1141 cm<sup>-1</sup> and the Si-O-Si asymmetric stretching (longitudinal optical, LO) at 1190 cm<sup>-1</sup>, can be clearly appreciated only by a proper deconvolution of the spectra.

A different behavior can be observed in spectra from condition E to condition I, since a progressively higher fluorine and carbon content in the coatings can be detected as W/FM decreases. Fluorine-related peaks observed also in conditions A-E, like the one at 1141 cm<sup>-1</sup>, become more pronounced, and the appearance of new peaks is registered at 553 cm<sup>-1</sup>, 1030 cm<sup>-1</sup>, 1270 cm<sup>-1</sup>, 1316 cm<sup>-1</sup> and 1370 cm<sup>-1</sup> mainly attributed to CF<sub>x</sub> (x=1,2,3), at 840 cm<sup>-1</sup> and 906 cm<sup>-1</sup> associated to CH<sub>x</sub> (x=1,2,3) vibrations, at 880 cm<sup>-1</sup> associated to Si-C stretching, and at 1040 cm<sup>-1</sup> related to C-O stretching. The described behavior occurs along with a reduction of the contribution of the Si-O-Si related peaks at 450, 1075 and 1190 cm<sup>-1</sup>.

The increasing presence of fluorinated groups by decreasing the W/FM ratio from condition E to conditio I is also confirmed by the atomic composition of the coatings

obtained from XPS elemental analysis (Table 2). Table 2 shows an evident increase in the fluorine content by decreasing the W/FM ratio.

Deposition condition	Ctot	(CF <sub>x</sub> )	0	F	Si
Uncoated PE	88.7	(0)	8.4	1.4	1.5
Е	19.9	(1.4)	54.2	4.8	21.1
G	16.4	(3.4)	51.1	11.6	20.9
I	27.2	(7.2)	32.8	24.9	15.1

Table 2. XPS atomic concentration of uncoated PE and coatings obtained under conditions E, G, and I

Water contact angles of thin films deposited under different W/FM values are reported in Figure 3. As W/FM decreases from condition A to condition E, the contact angle remains constant around 58° degrees. At lower W/FM values, the contact angle gradually increases, reaching a maximum value of about 83°. The uncoated PE substrate exhibits a contact angle of  $93.3^{\circ} \pm 4.8^{\circ}$ .



Fig. 3. WCA measurements as a function of W/FM.

The surface characterization results show the presence of two deposition regimes when varying W/FM: the regime associated to conditions from A to E and the one associated to conditions from E to I. Chemical and wettability characteristics of coatings deposited in the first regime do not change as a function of W/FM. The predominant presence of peaks related to vibrations of the bonding Si-O-Si in ATR-FTIR spectra and the low WCAs suggest that the W/FM values in the first regime lead to an intense fragmentation of the precursor in the discharge. In the second regime, as demonstrated by ATR-FTIR and XPS, a progressive increase in the content of fluorine and carbon in the coatings can be observed. This behavior can be explained considering the lower values of W/FM in the second regime respect to the ones in the first regime: as the energy per precursor unit is reduced, the fragmentation of the precursor in the discharge becomes less intense and an increased presence of the functional groups of the precursor can be observed in the coating. The progressive decrease observed in the wettability of the coating is in agreement with the progressively higher presence in the coating of carbon and fluorine in form of alkyl and fluoroalkyl groups (CH<sub>x</sub> and CF<sub>x</sub>, with x = 1, 2, 3), which are known to increase the hydrophobicity degree of a surface [13].

The presence of two deposition domains is supported also by the plot of the normalized deposition rate (obtained by dividing the deposition rate, DR, derived from SEM images for the precursor feed rate FM) as a function of W/FM (Figure 4).



Fig. 4. DR/FM as a function of W/FM.

Indeed, the behaviour shown in Fig 4. is similar to the one observed by Gilliam at al. [14], who investigated the plasma polymerization of fluorocarbon monomers in low pressure AF and RF discharges. Condition E can be recognized as the critical value of W/FM which marks the distinction in two deposition domains: the energy-deficient domain from I to E, where the slope of DR/FM as a function of W/FM is 880.85 [nm/kJ], and the monomer-deficient domain from E to A, with a slope of 119.97 [nm/kJ]. In the energy-deficient domain the system contains excess of precursor, and the formation of depositing species is dependent on the energy input. When the critical value of W/FM is reached, a further increase of energy does not create more depositing species and the normalized deposition rate remains almost constant.

According to the results presented and discussed so far, W/FM values from A to E lead to coatings with low retention of functional groups of the starting precursor and almost constant normalized deposition rate, while W/FM from E to I to coatings with higher retention of functional groups of the starting precursor and decreasing normalized deposition rate. Nonetheless, it must be pointed out that conditions from A to E have been obtained using the same precursor feed rate and decreasing the discharge power, while conditions from E to I using the same discharge power and varying the precursor flow rate. To prove the controlling role of the Yasuda Parameter itself in the process, coatings deposited under the same W/FM parameter but calculated with a different combination of discharge power and precursor feed rate were compared. Quantitative ATR-FTIR analysis and WCA analyses highlight almost identical chemical composition and wettability for coatings deposited under same W/FM values. The obtained results suggest that W/FM might be a proper parameter for the control of a polymerization process assisted by an atmospheric pressure single electrode plasma jet and a fluorinated silane precursor.

#### 4. Conclusions

In this work, the validity of the Yasuda Parameter (W/FM) as a controlling parameter for a polymerization process assisted by an atmospheric pressure plasma jet and an aerosolized precursor is investigated. The characteristics of coatings deposited under different W/FM values are assessed using ATR-FTIR spectroscopy, XPS analysis, WCA measurements, and SEM analysis. Surface characterization results reveal two deposition domains very well known in literature (the energy-deficient domain and the monomer-deficient domain), thus suggesting the validity of th th can be reached by varying W/FM. The key role of the Yasuda parameter in the process is further demonstrated since coatings deposited under the same W/FM exhibit similar properties, regardless of how W/FM is obtained.

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