



# Pulsed plasma-polymerized 2-isopropenyl-2-oxazoline coatings: Chemical characterization and reactivity studies

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## ABSTRACT

Thin coatings were deposited by means of low pressure plasma polymerization of 2-isopropenyl-2-oxazoline (2-IOX). Depositions were performed in the pulsed mode, exploiting the carbon-carbon double bond of the monomer, in order to maximize the retention of oxazoline rings in the coatings. The wettability of the thin films was assessed by water contact angle measurements, while their stability was investigated by immersion in different aqueous environments (Phosphate Buffer Saline (PBS) at 37 °C and aqueous solutions with different pH) and was found to be dependent on the deposition conditions. Chemical characterization of the coatings was performed by means of Attenuated Total Reflectance Fourier Transform Infrared (FTIR/ATR) spectroscopy, Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectroscopy and Gel Permeation Chromatography (GPC). All these techniques allowed to assess the retention of oxazoline ring, which can be exploited through reaction of the plasma deposited coatings with carboxylic acid groups. To this end, reactions with poly(acrylic acid) in different conditions (temperature, reaction time) were investigated.

## 1. Introduction

2-Oxazoline monomers are classically polymerized in solution by ring opening polymerization to give *N*-acyl polyethylenimine. The poly(2-oxazoline)s (POxs) obtained in this way, for example poly(2-methyl-2-oxazoline) (PMeOx) and poly(2-ethyl-2-oxazoline) (PEtOx), are water soluble, biocompatible, non-toxic and highly stable polymers displaying several possible applications. They can be employed in the conservation of cultural heritage, as pigment binder, to consolidate flaking painted layers, and as a barrier film for canvas and amber [1–3]. They can be also used in pharmaceutical and medical applications [4–8]. For example, they show antifouling properties similar to poly(ethylene glycol) (PEG), with higher stability and without any adverse effects in animal models [6–8].

For most biomedical applications, POxs are grafted on device surfaces or placed on it in the form of coatings. Since a weak binding would reduce the long term stability of the coating, it is necessary to immobilize the POx on the surface [9,10]. This is generally achieved by multistep processes, which often involve the use of expensive and non-compatible catalysts.

Recently, the use of plasma polymerization for the creation of 2-oxazoline-based coatings has been reported [11,12]. Plasma polymerization is a cost effective and environmentally friendly process,

which makes minimal use of monomers, does not require the use of solvents or initiators, does not create liquid organic wastes. These features make it a technique which is largely employed for the surface modification of materials for biomedical applications [16–19].

The characterization of both the coatings obtained by plasma polymerization of 2-methyl-2-oxazoline [12–14] and 2-ethyl-2-oxazoline [14,15] has shown partial oxazoline ring retention, certified by means of different characterization techniques (Nuclear Magnetic Resonance (NMR) spectroscopy, Attenuated Total Reflectance Fourier Transform Infrared (FTIR/ATR) spectroscopy, Time of Flight Secondary Ion Mass spectrometry (ToF SIMS)) and by reaction with carboxyl acid groups [20,21]. On one hand, this retention opens a wide range of potential applications, since the coatings can be exploited for the covalent immobilization of COOH-containing molecules (in particular biomolecules). On the other hand, it indicates that the mechanism of plasma polymerization of oxazoline monomers strongly differs from the ring opening polymerization which occurs in solution and that the coatings which can be obtained are not constituted by *N*-acyl polyethylenimine. This result is in agreement with previous studies on plasma polymerization of other organic compounds, which demonstrated that the film-forming species are the radicals deriving from the partial fragmentation of the monomer molecules [18,22]. Besides ring fragmentation which can occur in the plasma phase, radical formation

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on the pendant chain of oxazoline monomers without ring opening (for example on the ethyl group of 2-ethyl-2-oxazoline) is probably involved in the plasma polymerization of these monomers. At the light of these findings, we hypothesized that oxazoline monomers with an unsaturated group in the pendant chain (such as 2-isopropenyl-2-oxazoline, 2-IOX), which can be also polymerized by classical radical polymerization, could be useful for the plasma deposition of coatings with high oxazoline ring retention. In fact, by using such unsaturated monomers the plasma polymerization can be conducted in the pulsed mode, with high benefits regarding the retention of the oxazoline ring.

The disadvantage of classical continuous wave (cw) plasma polymerization lies in the strong monomer fragmentation, which has as main consequence the formation of irregular structures (from the chemical point of view) with major loss of the monomers functionalities [22,23]. In the pulsed plasma polymerization these limits are at least partially overcome. An important parameter for pulsed plasma polymerization is the duty cycle (DC), described by Eq. (1):

$$DC = \frac{t_{ON}}{t_{ON} + t_{OFF}} \quad (1)$$

For short duty cycles, during the plasma-on period the monomer molecules and the surface of the growing polymer layer are activated. During the plasma-off period, the monomer molecules strike the radical sites at the polymer surface, graft and thus form the growing macromolecular chain in a pure chemical process [22,23]. This allows the deposition of coatings with high monomer structure retention. By increasing the duty cycle, deposition during the plasma-on period cannot be neglected, and the coating grows through the alternation of the fragmentation/recombination mechanism typical of cw plasma polymerization and the pure chemical mechanism discussed above. However, in both cases the use of pulsed plasma polymerization allows the deposition of coatings with higher monomer structure retention compared to the cw mode. It is now evident that the radicals sites formed at the growing layer during the plasma-on period can be exploited in the plasma-off one only if the employed monomer possesses a polymerizable group, such as the carbon-carbon double bond of 2-isopropenyl-2-oxazoline. In other cases (e.g. in the plasma polymerization of 2-ethyl-2-oxazoline), the polymerization rate in the plasma-off period is negligible and the use of the pulsed mode does not bring appreciable benefits.

In this work, thin coatings were deposited by means of pulsed plasma polymerization of 2-isopropenyl-2-oxazoline. The plasma polymerized coatings (PP-2-IOX) were deposited onto different substrates (silicon wafers, aluminum foils, polypropylene films and glass slides). The influence of the deposition conditions (power input, monomer flow rate, duty cycle) on the thin film properties was investigated. The chemical characterization of coatings deposited with different process parameters was performed by means of Attenuated Total Reflectance Fourier Transform Infrared (FTIR/ATR) spectroscopy, Nuclear Magnetic Resonance ( $^1\text{H}$  NMR) spectroscopy and Gel Permeation Chromatography (GPC). The stability of the thin films was evaluated by immersion in Phosphate Buffer Saline (PBS) at 37 °C and in aqueous solutions at different pHs. Finally, the reactivity of the PP-2-IOX coatings towards carboxylic groups was investigated by reactions with poly (acrylic acid) (pAAc) in different conditions (temperature, reaction time).

## 2. Experimental part

### 2.1. Materials

2-Isopropenyl-2-oxazoline ( $\geq 99\%$ , Sigma-Aldrich) was used without any further purification. Poly(acrylic acid) ( $M_w$  100,000 uma) was supplied by Aldrich. Commercial oriented polypropylene (PP, 50 mm  $\times$  100 mm), aluminum foils (30 mm  $\times$  20 mm), glass slides (25 mm  $\times$  75 mm) and silicon wafers (10 mm  $\times$  10 mm) were used as

substrates. These substrates were only rinsed in ethanol before use.

### 2.2. Plasma reactor and deposition protocol

Plasma polymerization of 2-isopropenyl-2-oxazoline was performed in a parallel-plates plasma reactor, which has been previously described [24,25]. The 2-isopropenyl-2-oxazoline vapour was introduced in the chamber by means of a needle valve. The monomer reservoir was maintained at room temperature, without additional heating. The monomer flow rate was measured through differential weighing, just before and after the treatment. In order to sustain the discharge and to improve the formation of radicals on the surface of the growing layer during the plasma-on period, 2-isopropenyl-2-oxazoline was plasma polymerized in a mixture with argon. The Ar flow rate, fixed to 3.3 sccm, was measured directly with the aim of a flow meter (EL-Flow series F-201C by Bronkhorst). The 2-isopropenyl-2-oxazoline vapour, mixed with the Ar gas carrier, was uniformly distributed in the reactor by the upper showerhead electrode (with pinholes diameter of 2 mm). This electrode was connected to a 13.56 MHz RF power supplier (Advanced Energy RFX-600) which provided an RF voltage towards the grounded chamber. The lower grounded electrode was used as sample holder. Before the plasma deposition, the reactor was evacuated to  $10^{-3}$  Pa by means of a rotary pump combined with a turbo-molecular pump. Instead, during the plasma deposition (which was performed at a pressure of 10 Pa) the chamber was evacuated only by means of the rotary pump, protected with a liquid nitrogen trap. The pulsed plasma depositions were performed varying the main operative parameters (power input, monomer flow rate, duty cycle). Instead, the total duration of the deposition ( $t_{ON} + t_{OFF}$ ) was fixed to 20 min.

### 2.3. Characterization techniques

Chemical composition of the PP-2-IOX coatings was investigated by means of a Fourier Transform Infrared (FT-IR) spectrometer (Nicolet iS10, Thermo Scientific) equipped with an ATR sampling accessory with a diamond crystal (Smart iTR). For each spectrum 64 scans, with a spectral resolution of  $4\text{ cm}^{-1}$ , were recorded.

Contact angles (CAs) were measured on plasma coated glass slides, with a Dataphysics OCA 20 (Dataphysics) instrument at room temperature. Deposited water droplets had a volume of 3  $\mu\text{l}$ . Reported contact angles are the mean values of 5 measurements, taken on different points of each sample.

The thickness of each coating was measured with a Veeco dektak-8 stylus profilometer. An adhesive tape was used to mask a portion of a silicon wafer during the deposition. The adhesive mask was then removed and the coating thickness was measured. Mass deposition rates were evaluated from the coating thickness, after we were assured that their density did not vary with the deposition parameters.

$^1\text{H}$  NMR characterization was performed onto PP-2-IOX coatings deposited at 100 W and 175 W, with a duty cycle of 30%. For  $^1\text{H}$  NMR characterization, 10 mg of these coatings (deposited onto a 100  $\text{cm}^2$  glass substrate) were dissolved in 750  $\mu\text{l}$  of  $\text{CDCl}_3$  (Sigma-Aldrich, 99%) and placed in a 5 mm NMR tube.  $^1\text{H}$  NMR spectra were collected on a Bruker-500 spectrometer operating at 500.13 MHz with the following acquisition parameters: 90° pulse width 10 ms, spectral width 12 ppm and relaxation delay 2 s. The total number of scans for was 64 (four dummy scans) and the acquisition time 2.60 s. All  $^1\text{H}$  NMR chemical shifts reported in this work are relative to the residual peak of  $\text{CHCl}_3$ .

For GPC characterization, the PP-2-IOX coatings deposited at 100 W and 175 W onto glass substrate were dissolved in 5 ml of dried *N,N*-dimethylformamide (DMF, anhydrous, 99.8%) and heated for 10 h at 160 °C in presence of an excess of benzoic acid (ACS reagent, 99.5%), following a slightly modified procedure reported in Jerca et al. [26]. The polymer was then precipitated in diethyl ether after cooling and the resulting material was filtered and dried. By this reaction, aromatic rings could be introduced in the polymeric chain (by oxazoline ring-

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