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Plasma polymerization of 2-isopropenyl-2-oxazoline: Improvement of the coating stability by co-polymerization with 1-octene

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ABSTRACT

Thin films were deposited by plasma co-polymerization of 2-isopropenyl-2-oxazoline and 1-octene, varying the total monomers flow rate and the 1-octene percentage in the mixture. The coatings wettability was evaluated by water contact angle measurements, while their stability was investigated by immersion in Phosphate Buffer Saline at 37 °C. The chemical characterization of the coatings, performed by means of Attenuated Total Reflectance Fourier Transform Infrared spectroscopy and by reaction with poly(acrylic acid), assessed a partial retention of the reactive oxazoline ring, as already observed for plasma polymerization of several oxazoline monomers alone. However, the addition of 1-octene had significant effects on the coating stability and on the surface availability of reactive oxazoline rings. Compared to those obtained by plasma polymerization of 2- isopropenyl-2-oxazoline alone, this coatings exhibited higher stability in aqueous environments but lower reactivity towards carboxylic acid groups.

1. Introduction

In the last decades, low-pressure plasma technologies have been gaining popularity as versatile tools for surface modification of different materials [1-3]. The use of plasma treatments and plasma polymerization for the introduction of different reactive functionalities onto inert surfaces has been extensively studied [3-7]. Literature abounds of works regarding plasma-produced surfaces containing COOH, OH, NH₂ and many others reactive chemical groups. Biomedical applications of these surfaces range between their direct exploitation to control biointerfacial interactions to their use as anchorage sites for the covalent immobilization of specific biomolecules [3]. However, regarding the creation of chemically reactive surfaces, plasma polymerization offers specific advantages over plasma treatments. In fact, the last ones suffer from surface adaptation, a phenomenon which involves reptation motions (some of the polymer chains move from the surface into the bulk) and chain rotation [8,9]. As a consequence, the density of inserted groups which are exposed and available for subsequent reactions decreases with the ageing time, thus complicating the exploitation of plasma treated surfaces. On the contrary, plasma polymers do not show surface adaptation since the high cross-linking degree decreases the mobility of the surface chains, and consequently can be better exploited over time [3].

Despite the stability during storage in air, another important requirement of surfaces designed to be used in biomedical applications is their stability in aqueous environments, in particular when they are employed for the outermost immobilization of specific molecules. Plasma polymers containing polar

functional groups in high concentration (such as hydroxyls, carboxyls, primary amimes) generally display hydrophilic character and poor stability in water, where they are easily dissolved [6]. In order to increase the stability in aqueous media of plasma coatings bearing reactive chemical groups, besides the optimization of the deposition parameters (power, monomer flow rate, pressure), the co-polymerization with non-polar monomers (such as octa-1,7-diene, hexane, styrene) has been successfully employed [7,10-12]. It is important to note that this approach allows also the fine tuning of the reactive groups density, which is hard to get by the simply variation of the deposition parameters [7].

Among the several plasma polymers which have been studied in the past, those obtained by plasma polymerization of oxazoline monomers (2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, 2-isopropenyl-2-oxazoline) displays interesting features which make them good candidate for use in biomedical applications [13,14]. Used as deposited, they were found to promote the adhesion and the growth of different kind of cells or to display anti-fouling properties, depending on the deposition conditions [13-16]. Moreover, they show a partial retention of the reactive ox- azoline ring, which has been certified by means of several characterization techniques [13,17]. This latter characteristic is particularly interesting, since the oxazoline ring can react with carboxylic acid in mild conditions, without activators or catalysts and at temperatures below 100 °C [17-20]. Intensive investigations of our and other groups have shown that reactive oxazoline plasma coatings display also good stability in aqueous environments, which can be achieved by operating in high-fragmentation conditions [13,17,20]. At the view of this, they have been successfully employed to immobilize antibodies for diagnostics purposes [21]. However, a further improvement of the coating stability could be useful for long-term biomedical applications.

Here, plasma coatings obtained by co-polymerization of 2-iso- propenyl-2-oxazoline and 1-octene (PP-2-IOX/OCT) were deposited onto different substrates and characterized in terms of their stability and their reactivity towards carboxylic acid groups. A correlation between the coating characteristics and the monomers mixture composition has been performed. Moreover, a comparison with previously studied coatings deposited from pure 2-ethyl-2-oxazoline (PP-2-EOX) and 2-isopropenyl-2-oxazoline (PP-2-IOX) is presented.

2. Experimental part

2.1. Materials

2-isopropenyl-2-oxazoline (>99%, Sigma-Aldrich) and 1-octene (98%, Aldrich) were used as received, without further purification. Commercial polypropylene (PP) films (Manucor SpA, Italy), aluminum foils, glass slides (Knittel Glaser, Germany) and silicon wafers were used as substrates for the investigation of the coating properties. These substrates were only rinsed in ethanol before use.

2.2. Plasma reactor and deposition protocol

The plasma co-polymerization was performed in a parallel-plates plasma reactor (Fig. 1 A), which has been previously described [6,22]. The two monomers (Fig. 1B) were co-polymerized in mixture with Ar, in order to sustain the discharge and to improve the formation of radicals on the surface of the growing layer. The 2-isopropenyl-2-oxazo- line and the 1-octene vapors were introduced in the chamber by means of two needle valves, with the monomer reservoirs which were maintained at room temperature. Both the monomers flow rate was measured through differential weighing. Instead, the Ar flow rate (fixed to 3.3 sccm) was measured directly with the aim of a flow meter EL-Flow series F—201C (Bronkhorst). The monomers vapors and the Ar gas carrier were mixed just before the introduction in the plasma reactor and was uniformly distributed by the upper showerhead

electrode. 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. Specimens were positioned on the lower grounded electrode.

Plasma depositions were performed in pulsed mode (peak power $W_p = 175$ W; duty cycle DC = 30%; $t_{ON} = 3$ ms; $t_{OFF} = 7$ ms; effective power $W_{eff} = 52.5$ W; deposition time = 20 min). The choice of these plasma parameters was made on the basis of previous experience on plasma polymerization of 2-isopropenyl-2-oxazoline [20]. The flow rates of the monomers (F_{IOX} and F_{OCT}), the total flow rate (F_{TOT}) and the octene percentage in the monomers mixture (%OCT) were varied in order to optimize the coating stability. During depositions, pressure was maintained between 12 and 14 Pa.

2.3. *Reactivity studies*

Reactivity towards carboxylic acid groups was investigated through reaction with poly(acrylic acid) (pAAc). Coated PP samples were immersed for 4 h in a 20 g/l aqueous solution of poly(acrylic acid), at 80 °C. Reactions conditions were chosen on the basis of previous experience with plasma-polymerized 2-isopropenyl-2-oxazoline [20]. At the end of the reaction, the PP films were gently rinsed in water, then washed in PBS for 4h at 37 °C and in HCl 0.01 M for 5 min. Before characterization, the samples were plenty rinsed in water and dried in air.

2.4. *Characterization techniques*

The coatings wettability was evaluated by means of contact angle measurements at room temperature, with a Dataphysics OCA 20 (Dataphysics) instrument. On each sample, 5 contact angle measurements with 3 μ l water droplets were performed and the mean value is reported.

The thickness of the deposits was measured with a Dektak-8 Stylus profilometer (Veeco), masking a portion of a silicon wafer during the deposition.

The chemical composition of the 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 cm^{-1} , were recorded. The amount of pAAc grafted onto plasma-coated PP films was also evaluated by means of ATF/FTIR spectroscopy [20]. ATR spectra of the PP samples after the reaction were acquired with the same instrument. Then, the region of these spectra between 1490 cm^{-1} and 1820 cm^{-1} was deconvoluted using Origin 8.0 software, following a procedure which has been previously described [20]. The amount of grafted pAAc was then evaluated from the area of the C=O peak around 1720 cm^{-1} , which was absent in the spectra of the coatings before the reaction.

The Z-potential of the sample surfaces was determined using a SurPASS electrokinetic analyzer with a clamping rectangular measuring cell, streaming current and streaming potential measurement methods for flat solid surfaces (Anton Paar).

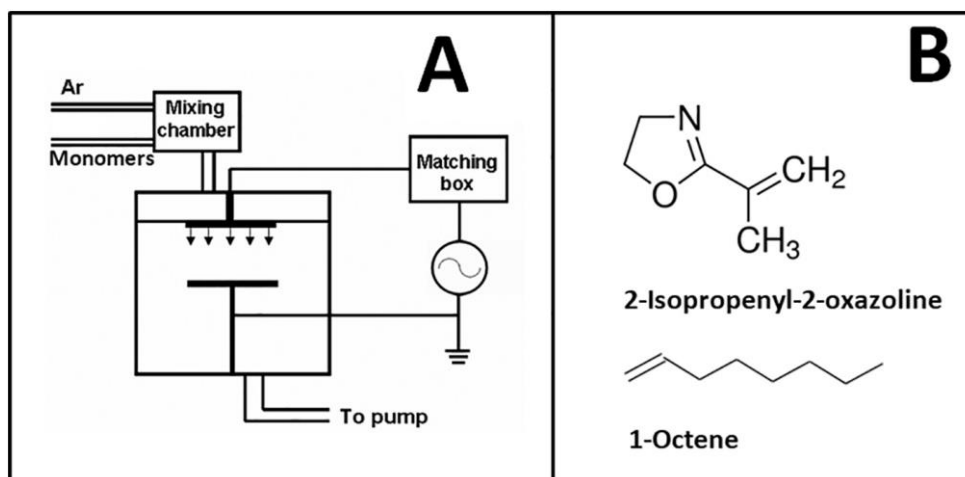


Fig. 1. Schematic of the employed plasma reactor (A) and chemical structure of the two monomers (B).

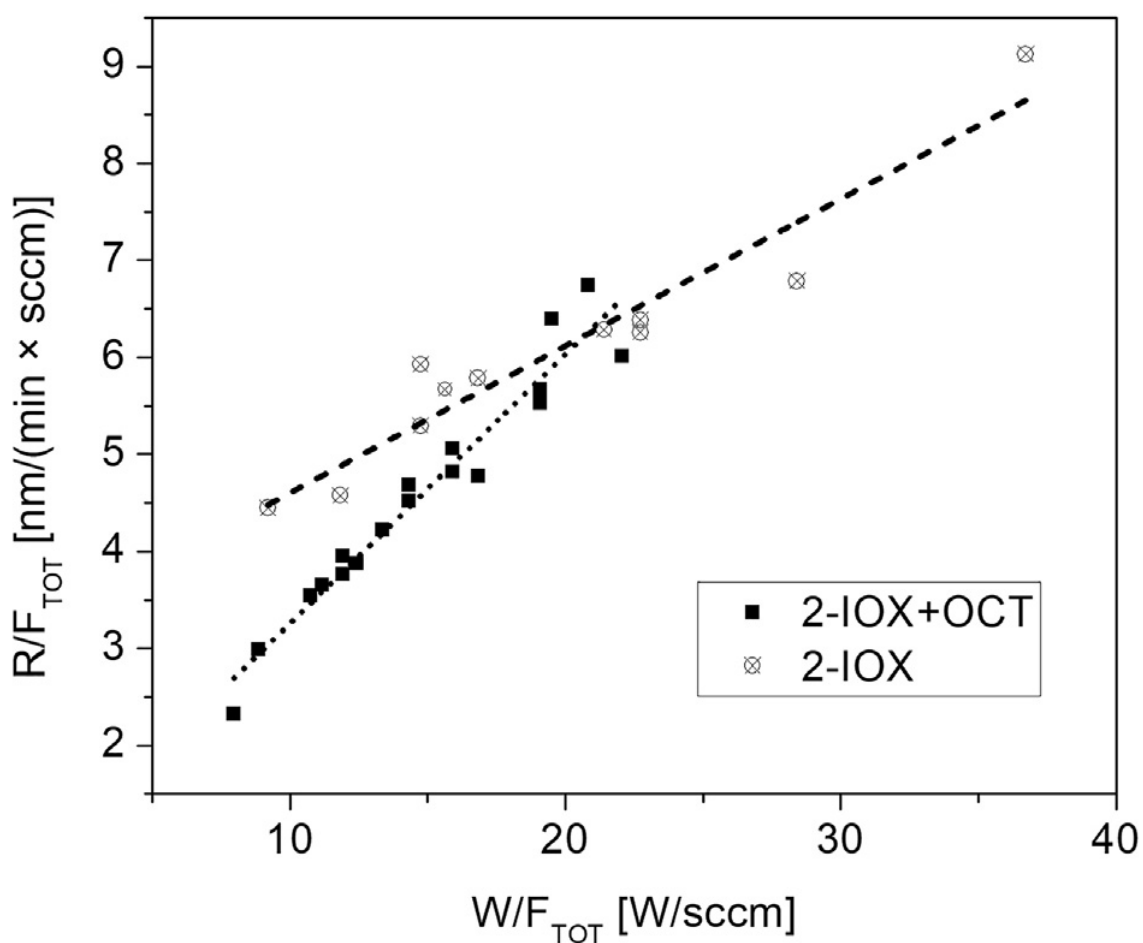


Fig. 2. Deposition rates of 2-isopropenyl-2-oxazoline/1-octene plasma copolymerization, measured for different W_{eff}/F_{TOT} ratio. For comparison, the influence of the W_{eff}/F parameter on the deposition rate of pure 2-isopropenyl- 2-oxazoline is also displayed. Lines were added only to guide the eye.

The measurements were performed with 0.001 M KCl as an electrolyte solution. The pH range was within 2-10 and adjusted by adding either NaOH 0.05 M or HCl 0.05 M. In the case of coatings deposited onto PP films, the gap in the clamping cell was formed with two coated specimens, while for the coatings deposited onto glass slides, the gap was formed between a coated sample and a standard polypropylene foil as a reference.

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3. Results and discussion

The trend of the normalized deposition rate (R/F_{TOT}) with the W_{eff}/F_{TOT} ratio is shown in Fig. 2. This ratio is an adaptation of the classic Yasuda factor that can be used for pulsed plasma co-polymerization [20,23]. It is calculated with the effective power (the product of the peak power times the duty cycle) and the total monomer flow rate ($f_{IOX} + f_{OCT}$).

The graph reports data obtained in this work from plasma copolymerization of 2-isopropenyl-2-oxazoline and 1-octene, keeping constant the DC (30%) and the peak power W_p (175 W) and varying the flow rates of the two monomers. For comparison, the influence of W_{eff}/F on the deposition rate of pure 2-isopropenyl-2-oxazoline is also displayed.

Both the normalized deposition rates increased with W_{eff}/F_{TOT} , and we can conclude that both plasma polymerization and co-polymerization happened in power-deficient conditions [23]. This is particularly important, since in these conditions the monomers are not totally fragmented in the plasma phase, and it is possible to maintain a partial retention of the reactive oxazoline ring in the deposited coatings. Addition of 1-octene to the oxazoline monomer globally resulted in a decrease of the deposition rate. It is important to remind that these data were obtained from mixtures which differed in composition and in the total flow rate (different $\%_{OCT}$ and F_{TOT}). We have not investigated independently the influence of these two parameters, since it was beyond the aim of our work. In particular, we have not studied the influence of the 1-octene percentage on the deposition rate at constant F_{TOT} , as already done in the past for plasma co-polymerization of other mixtures [7]. However, observing the linear trend in Fig. 2 it seems that, in the considered range of parameters (in particular for the fixed power we have chosen), during the deposition process the two monomers influenced each other and the mixtures behaved like a sole monomer independently on their composition (note that 2-isopropenyl-2-oxazoline and 1-octene display also almost identical molecular weights). In this respect, the trend of deposition rates measured for PP-2-IOX/OCT coatings seems to be nearly independent on the 1-octene percentage and to depend solely by the W_{eff}/F_{TOT} ratio. For example, we have observed that samples prepared with equal $\%_{OCT}$ (20%) but different W_{eff}/F_{TOT} showed different normalized deposition rates; instead, samples prepared with similar W_{eff}/F_{TOT} but different $\%_{OCT}$ showed similar deposition rates. This particular behaviour indicates that, for the tested mixtures and the fixed power we have investigated, the two monomers have similar reactivity (similar tendency to be converted into plasma polymers) but that this tendency is different from that of the oxazoline monomer alone. On the other hand, we cannot exclude this result to depend on the limited range of octene percentages we have investigated (15-50%), and further experiments should be necessary to confirm this behaviour also at lower/higher $\%_{OCT}$.

Fig. 3A shows the FTIR/ATR spectra of two coatings obtained from the plasma polymerization of 2-isopropenyl-2-oxazoline with and without 1-octene (PP-2-IOX/OCT and PP-2-IOX, respectively). Copolymerization was performed with $F_{2\text{-IOX}} = 3.46$ sccm, $F_{\text{OCT}} = 3.14$ sccm, $\%_{\text{OCT}} = 48\%$. Both spectra present peaks at 1137cm^{-1} and 1656cm^{-1} , associated respectively to the stretching vibrations of the C—O and C=N bonds of the oxazoline ring [17,20]. This indicates partial ring retention in both coatings, as later confirmed also by the reactivity studies.

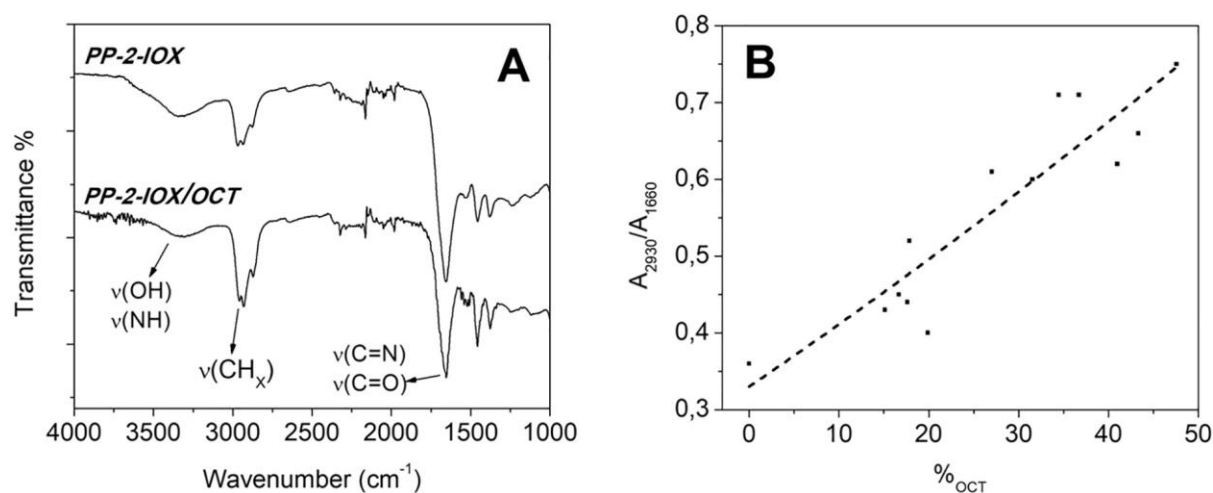


Fig. 3. (A) ATR/FTIR spectra of coatings obtained from plasma polymerization of 2-isopropenyl-2-oxazoline with and without 1-octene. (B) Influence of the 1-octene percentage on the CHX/C=N bands ratio. Line was added only to guide the eye.

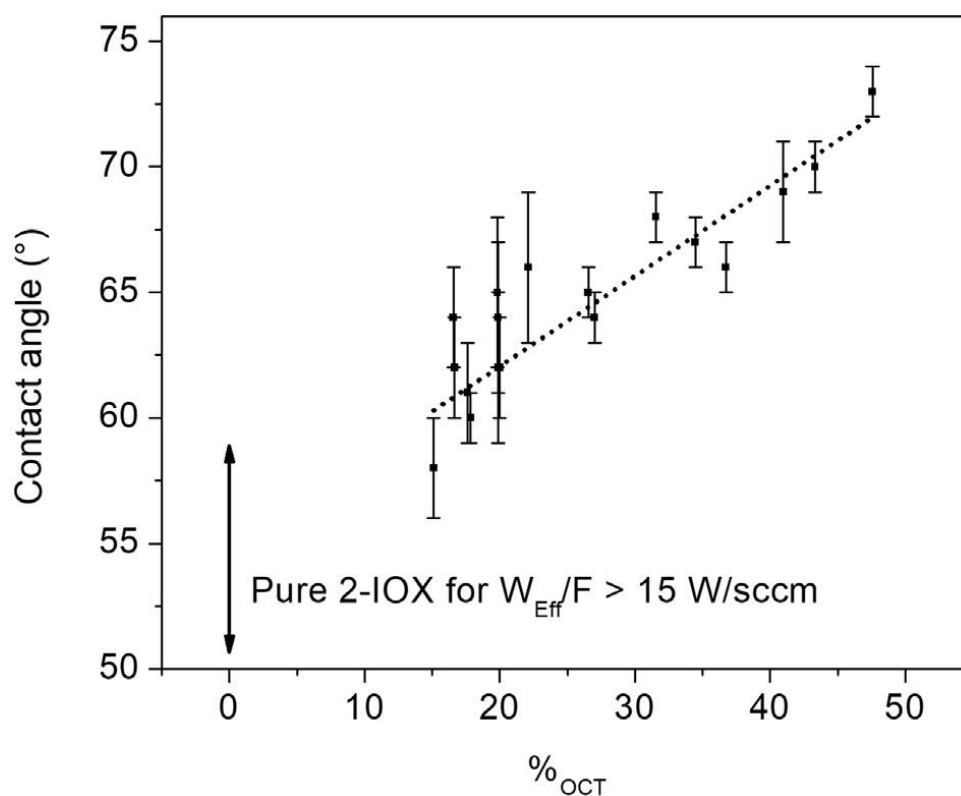


Fig. 4. Influence of the 1-octene percentage on the coatings wettability.

In Fig. 3A, the bands of the CH_x groups vibrations can be also detected: the CH_x stretching at $2900\text{--}3000\text{ cm}^{-1}$, the CH_2 bending at 1460 cm^{-1} and the CH_3 bending at 1380 cm^{-1} . Not surprisingly, these bands are more evident in the PP-2-IOX/OCT spectrum, while the peak at 1656 cm^{-1} is stronger in the PP-2-IOX one.

For all the acquired spectra, we calculated the ratio between the area of the bands relative to the CH_x and the $\text{C}=\text{N}$ groups ($2900\text{--}3000\text{ cm}^{-1}$ and 1656 cm^{-1} , respectively). This ratio increased with the 1-octene percentage in the monomers mixture (Fig. 3B) and we can conclude that the coating composition resembled that of the starting monomers and depended on their relative percentage. The almost linear trend in Fig. 3B is in agreement with similar reactivity of the two monomers in the range of mixtures we have investigated.

Finally, bands around 1540 cm^{-1} ($\text{C}=\text{N}$ stretching coupled with $\text{N}=\text{H}$ bending) and at $3100\text{--}3600\text{ cm}^{-1}$ ($\text{O}=\text{H}$ and $\text{N}=\text{H}$ stretching) hint the formation of new functionalities (hydroxyls, amides) from the fragmentation/recombination of the monomers during the plasma polymerization.

Influencing the chemical composition of the coatings, the 1-octene percentage in the monomers mixture determined also their wettability. Fig. 4 shows the water contact angles measured onto several PP-2-IOX/OCT coatings as a function of the 1-octene percentage. The range of contact angles measured onto relatively stable PP-2-IOX coatings deposited at $W_{\text{eff}}/F > 15$ is also displayed (see the double arrow at. $\%_{\text{OCT}} = 0$).

The contact angle of the PP-2-IOX coatings ranged between 51° and 58° . Instead, the abundance of non-polar CH_x groups from 1-octene made the PP-2-IOX/OCT more hydrophobic, with contact angles which increased almost linearly with the hydrocarbon percentage. This trend is in agreement with ATR results, which showed an increase of the CH_x groups with the octene percentage. Since ATR is a bulk analysis of the coatings (due to its high penetration depth), while contact angle is a surface one, this result was very interesting, since it allowed us to consider the surface composition of the coatings to be similar to the bulk one. This was also in agreement with the deposition protocol; in fact, the monomers input was stopped immediately after the plasma was switched off (in order to calculate the exact monomer flows by weight difference), so possible reactions of these double-bond possessing monomers with the radicals remained on the surface of the coating were minimized.

As specified in the Introduction section, the aim of this work was the deposition of reactive coatings bearing oxazoline rings with improved stability in water media. The coatings stability was hence investigated in detail by means of profilometer measurements, performed before and after immersion in PBS at 37°C for 72 h.

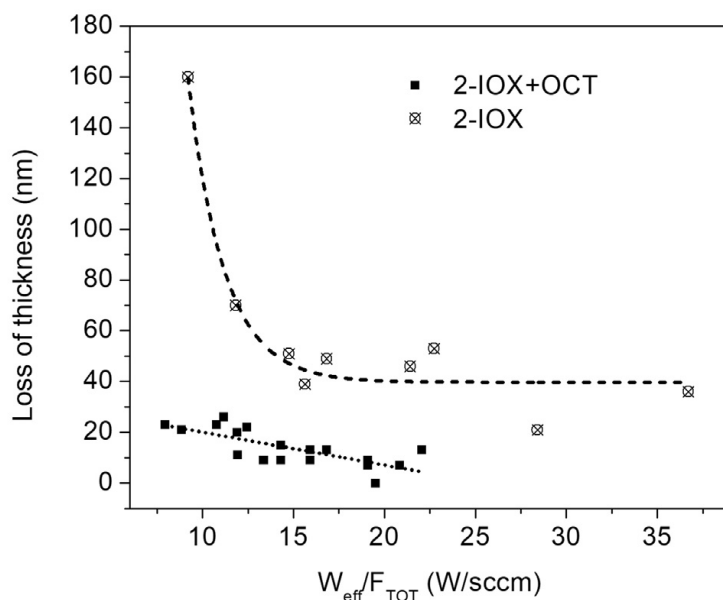


Fig. 5. Stability of PP-2-IOX and PP-2-IOX/OCT coatings deposited onto silicon wafers at different $W_{\text{eff}}/F_{\text{TOT}}$ ratios. Lines were added only to guide the eye.

Fig. 5 shows the absolute loss of thickness of PP-2-IOX and PP-2-IOX/OCT coatings deposited onto silicon wafers at different $W_{\text{eff}}/F_{\text{TOT}}$ ratios. All these coatings had an initial thickness around 350 nm. PP-2-IOX/OCT coatings displayed an interesting behaviour when subjected to prolonged immersion in PBS. They were considerably more stable than the PP-2-IOX coatings deposited in the same conditions, and initially we ascribed this characteristic to their lower wettability. However, the relative stability of several PP-2-IOX/OCT coatings deposited from different mixtures was poorly correlated with their wettability (data not shown) and slightly depended on the $W_{\text{eff}}/F_{\text{TOT}}$ ratio. This result was unexpected, since we hypothesized the coating stability to be dependent on their wettability (and hence on the 1-octene percentage). Again, the 2-isopropenyl-2-oxazoline/1-octene mixtures seemed to behave like a sole monomer whose coatings displayed higher stability than those obtained from 2-isopropenyl-2-oxazoline alone.

The dependence of the PP-2-IOX/OCT coating stability on the $W_{\text{eff}}/F_{\text{TOT}}$ ratio can be well appreciated in Fig. 5. We can follow the classical rules of plasma polymerization: by increasing this parameter, stronger monomers fragmentation in the plasma phase occurs, and the deposited coatings display higher cross-linking degree and are less prone to dissolution in water media. However, in this case the dependence was not marked as for the plasma polymerization of 2-isopropenyl-2-oxazoline alone. In fact, all the PP-2-IOX/OCT coatings displayed good stability in PBS, and only a slight improvement was detected by increasing the $W_{\text{eff}}/F_{\text{TOT}}$ ratio.

Fig. 6 shows the trend of Z-potential versus the pH for coatings deposited onto PP films (Fig. 6A) and glass slides (Fig. 6B). Co-polymerization was performed in high-stability conditions ($F_{2\text{-IOX}} = 2.20$ sccm, $F_{\text{OCT}} = 0.50$ sccm, $\%_{\text{OCT}} = 18\%$, $W_{\text{eff}}/F_{\text{TOT}} = 20$). The Z-potential is an indicator for charge formation at the solid/liquid interface and the surface charge is generated by the interaction of the solid surface with the electrolyte solution. Both PP-2-IOX and PP-2-IOX/OCT coating displayed negative charge at pH above 4-4.5, indicating the presence of chemical groups which can be deprotonated. Since the oxazoline ring itself cannot be deprotonated, it is reasonable to think these groups to be created by the strong monomer fragmentation which occurs in the plasma phase. It is interesting to note that, in physiological condition, both coatings displayed negative charge.

It may be also observed that, while PP-2-IOX and PP-2-IOX/OCT displayed similar trends, the curves obtained onto glass and PP are substantially different, where the measurements on polypropylene films hold higher zeta potential numbers. As a consequence, the IEPs of PP-2- IOX and PP-2-IOX/OCT coatings onto PP were within the range 4-4.5, while the IEPs of the same coatings onto glass were within the range

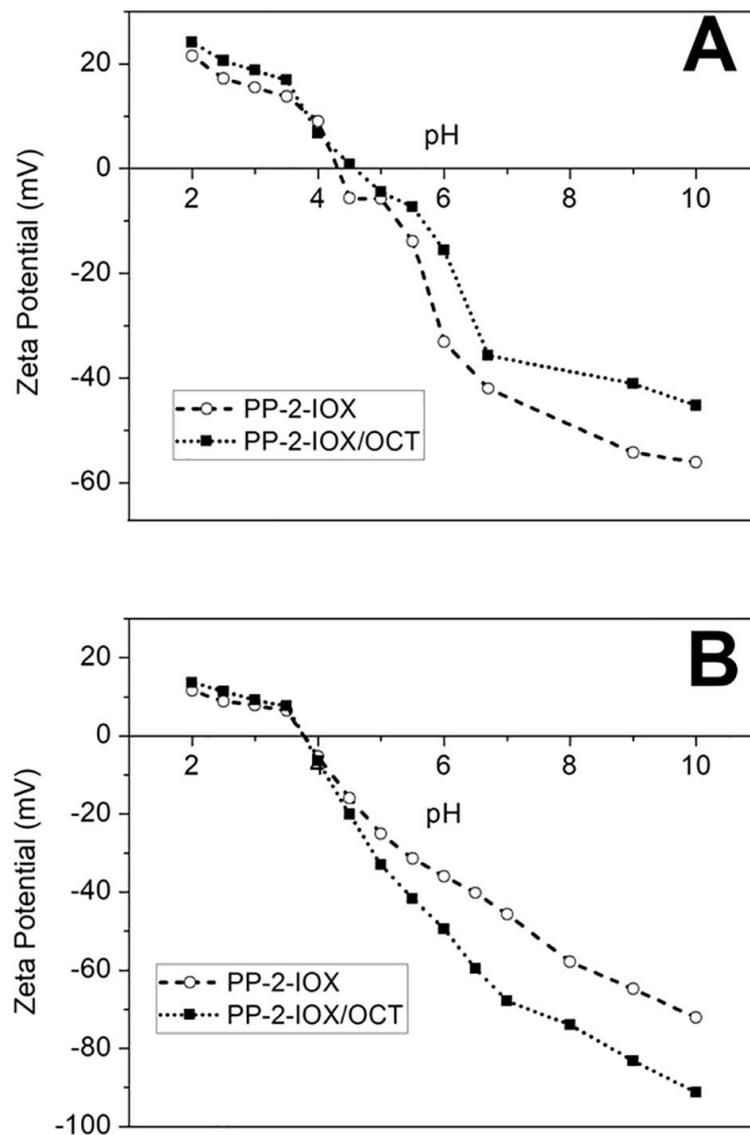


Fig. 6. Trend of zeta potential versus pH measured onto polypropylene films (A) and glass slides (B).

3.5-4. This difference between the obtained results may be attributed to partial detachment of the coating from the glass substrate (poor adhesion).

Positive Z-potential at pH below 4 indicates the presence of protonable groups (oxazoline rings, amino groups).

We have seen that ATR spectra suggest a partial retention of oxazoline rings in the coatings obtained by plasma *co*-polymerization. Since the oxazoline ring reacts with carboxylic acid to form a covalent

amide-ester bond, we have chosen to evaluate the ring retention (and hence the coating reactivity) by means of reactions with poly(acrylic acid). The questions we tried to answer were:

1. Are the retained oxazoline rings available for reactions with carboxylic acid groups?
2. How many oxazoline groups are available on the surface of PP-2- IOX/OCT coatings compared to the previously studied PP-2-IOX and PP-2-EOX ones?

The amount of grafted pAAc, expressed as C=O stretching ATR band area (see Experimental section) is displayed in Fig. 5 as a function of the composite *reactivity parameter* P_{react} :

$$P_{react} = \frac{W_{eff}}{F_{tot}} \times X_{oct}$$

where

$$X_{oct} = \frac{F_{oct}}{F_{iox} + F_{oct}}$$

is the molar fraction of 1-octene in the monomers mixture.

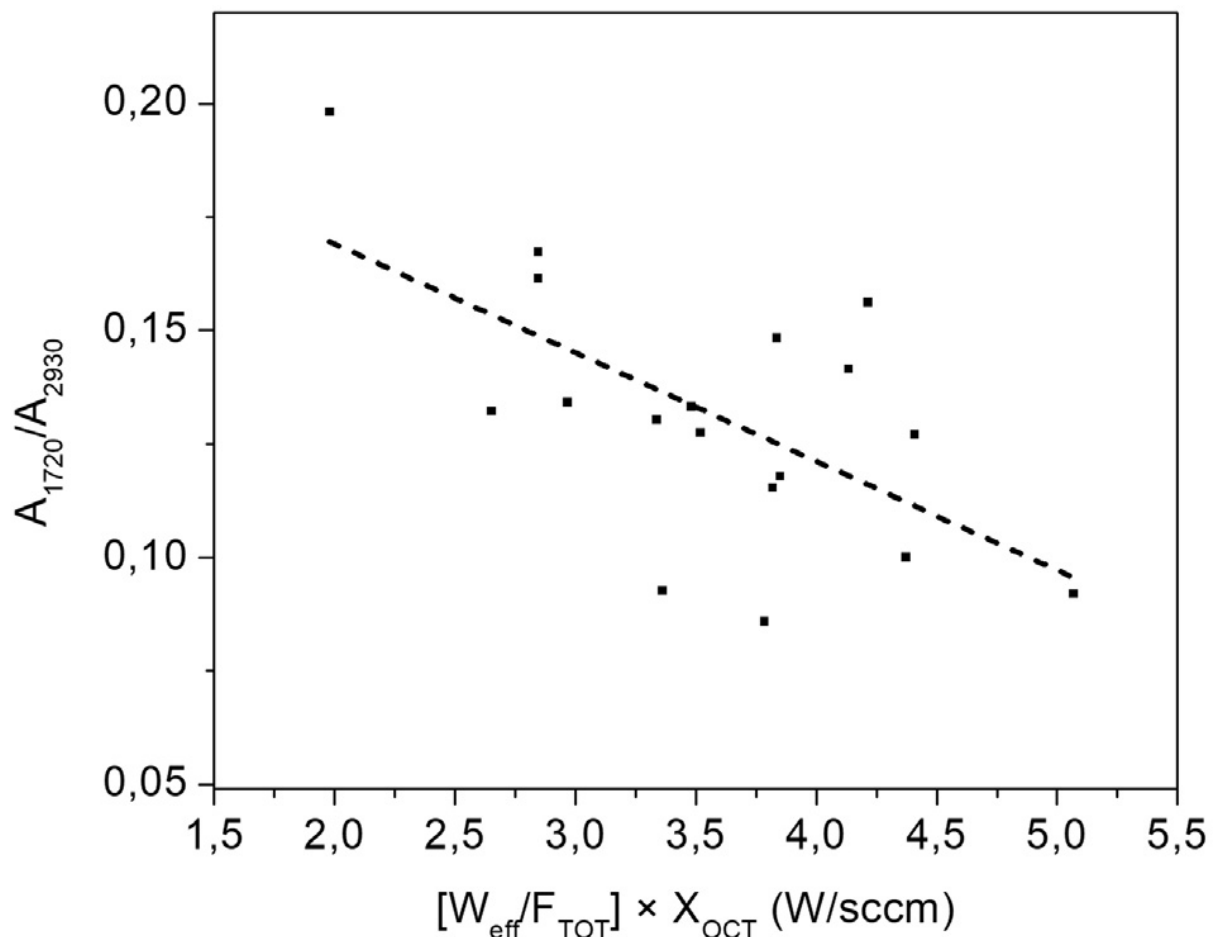


Fig. 7. Influence of the reactivity parameter on the amount of grafted pAAc. All reactions were conducted at 80 °C for 4 h. Line was added only to guide the eye.

In conceiving this parameter, we hypothesized that the retention of oxazoline rings in the PP-2-IOX/OCT coatings decreased by increasing the fragmentation of 2-isopropenyl-2-oxazoline in the plasma phase and the percentage of 1-octene in the monomers mixture. Since we have observed that during plasma co-polymerization the 2-isopropenyl-2-oxazoline/1-octene mixtures behaved like a

single monomer, the fragmentation of 2-isopropenyl-2-oxazoline is proportional to the $W_{\text{eff}}/F_{\text{TOT}}$ ratio. The trend in Fig. 7 confirms our hypothesis. The amount of grafted pAAc decreases by increasing P_{REACT} . It is worth mentioning that no correlation was found between the amount of grafted pAAc and the $W_{\text{eff}}/F_{\text{TOT}}$ ratio or X_{OCT} taken individually, to confirm that both these parameters influenced the density of oxazoline groups in the coatings. Moreover, we observed that other coating characteristics like the wettability and the CHX/C=N ratio depend only on the OCT percentage. This for two reasons:

1. As described in our previous publication [20], for $W/F > 15 \text{ W/ sccm}$ the contact angle is almost constant and do not depend on the W/F ratio (desappearance of oxazoline rings with formation of other hydrophilic groups due to plasma fragmentation);
2. the CHX/C = N ratio presented in Fig. 3B do not depends on the W/F ratio, since the increase of the monomer fragmentation in the plasma phase leads to destruction of oxazoline rings with formation of other C=O (or C=N) containing groups.

Given these results, the answer to our first question was that PP-2- IOX/OCT coatings displayed oxazoline groups which were available for reactions with carboxylic acid.

Fig. 8 gives an answer to our second question. The graph reports results obtained in our laboratory with different reactive coatings deposited by plasma polymerization of oxazoline monomers. The coatings reactivity is not a simple reflection of the surface density of oxazoline rings, but it also depends on their stability. In fact, after the reactions (which happened in water solution) a prolonged immersion in PBS was performed to wash-off all the unbounded moieties. It is clear that in both these steps, partial dissolution of not totally stable coatings leads to a decreased amount of grafted pAAc. This effect has been observed for PP-2-IOX coatings [20] and can be appreciated in Fig. 7 also for PP-2-EOX ones. In this case, two reactions with pAAc at different temperature were performed onto the same coating. It was prepared by continuous wave plasma polymerization of 2-ethyl-2-oxazoline with a power of 60 W, and displayed good stability in water environments at physiological conditions [17]. Despite the oxazoline/carboxylic acid reaction proceed faster at high temperatures [20,24], here we observed higher amount of grafted pAAc when the reaction was carried out at 40 °C. In fact, when we performed it at 80 °C, strong coating dissolution happens during the reaction and the subsequent washing in PBS. Instead, when the reaction was done at 40 °C, we observed only minor loss of coating, and higher amount of pAAc was grafted. This phenomenon was not observed with PP-2-IOX and PP-2-IOX/OCT, which displayed higher reactivity at 80 °C.

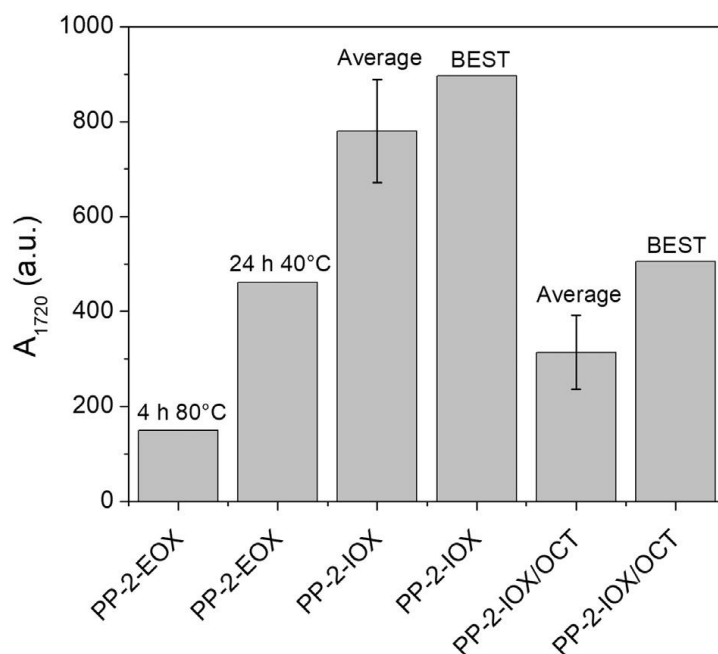


Fig. 8. Reactivity towards COOH groups of different coatings bearing oxazoline rings.

40 °C. In fact, when we performed it at 80 °C, strong coating dissolution happens during the reaction and the subsequent washing in PBS. Instead, when the reaction was done at 40 °C, we observed only minor loss of coating, and higher amount of pAAc was grafted. This phenomenon was not observed with PP-2-IOX and PP-2-IOX/OCT, which displayed higher reactivity at 80 °C.

Among the three coatings we have investigated, the PP-2-IOX one are the most reactive towards COOH groups. In this case, we have chosen to report in Fig. 6 the results for coatings deposited at W_{eff}/F between 12 and 16 W/sccm. PP-2-IOX coatings deposited in these conditions exhibited the highest reactivity [20]. Below 12 W/sccm, the amount of grafted pAAc was low due to PP-2-IOX dissolution (poor stability). Above 16 W/sccm, we observed a rapid decrease of the reactivity due to loss of oxazoline functionalities (excessive fragmentation). In Fig. 8, we report the average amount of pAAc grafted onto these coatings and the best result we obtained (for W_{eff}/F of 12 W/ sccm). It is worth noting that the pAAc grafted onto PP-2-IOX was roughly the double than that onto PP-2-EOX. Regarding the PP-2-IOX/OCT coatings, Fig. 8 shows the amount of pAAc grafted onto the most reactive one (the “best”). Interestingly, this coating was deposited at the same W_{eff}/F_{TOT} ratio employed for the most reactive PP-2-IOX one (12 W/sccm). Moreover, although it derived from the co-polymerization of an oxazoline-rich mixture (oxazoline percentage of 83%), it immobilized only 55% of the pAAc grafted onto PP-2-IOX. This was not an isolated result: the amount of pAAc grafted onto PP-2-IOX/OCT coatings was always significantly lower than that we expected from the W_{eff}/F_{TOT} ratio and from the oxazoline percentage in the mixture. This evidence is of difficult interpretation, since analyses previously discussed indicates that 1-octene homopolymerization do not prevail over co-polymerization with oxazoline. As a possible explanation, we can hypothesize a lower reactivity due to steric hindrance: oxazoline ring in the PP-2-IOX/OCT coatings could be partially masked by the alkyl chains of 1-octene, and hence harder to be reached by COOH groups. However, further investigations should be necessary in order to confirm this hypothesis.

Since all the PP-2-IOX/OCT coatings displayed good stability, we have chosen to include in Fig. 8 also the average amount of pAAc grafted on all of them. On average, PP-2-IOX/OCT coatings immobilized roughly 40% of the pAAc grafted onto the PP-2-IOX ones deposited between 12 and 16 W/sccm, confirming that the addition of 1-octene strongly decreased the coating reactivity.

4. **Conclusions**

Addition of 1-octene during plasma polymerization of 2-iso-propenyl-2-oxazoline has significant effects on the coating stability and on the surface availability of reactive oxazoline rings. In particular, compared to those obtained by plasma homo-polymerization of 2-iso-propenyl-2-oxazoline, PP-2-IOX/OCT coatings exhibit higher stability in aqueous environments but lower reactivity towards carboxylic acid groups. Only small amounts (around 15%) of 1-octene in the mixture strongly improves the coatings stability, but significantly decreases their reactivity. Finally, the PP-2-IOX/OCT coatings are significantly less reactive than the PP-2-IOX ones, also taking into account the percentage of 2-isopropenyl-2-oxazoline in every polymerization mixture. This latter result is not totally understood and needs further insights.

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