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Aerosol-assisted low pressure plasma deposition of antimicrobial hybrid organic-inorganic Cu-composite thin films for food packaging applications

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Highlights

• Development of an innovative aerosol-assisted low pressure plasma deposition process.

• Deposition of hybrid organic-inorganic copper containing thin polymeric films.

• Reduction up to three orders of magnitude of viability of Pseudomonas with active films.

Abstract

An innovative low pressure plasma process for deposition of copper-containing hybrid organic-inorganic thin films was developed. The discharge was fed with an aerosol of an aqueous solution of a copper complex, i.e. bis(ethylenediamine)copper(II) hydroxide and argon. Polymeric films, incorporating inorganic Cu(I) and Cu(II) compounds, were obtained. Morphological and chemical characterizations of the coatings were carried out.

Antimicrobial properties were assessed on two species of Pseudomonas spp. In vitro tests were carried out by contact of the optimized films, deposited on square polycarbonate samples (~ 4 cm^2), with cell suspensions of 1 × 10^4 CFU/mL for 18 h at 25 °C. It was demonstrated that, the hybrid organic-inorganic thin coatings have potential utilization as active packaging material, showing an antimicrobial effect of up to three orders of magnitude (final microbial concentration 10^5 CFU/mL), compared to control polycarbonate (final microbial concentration 10^8 CFU/mL).

Industrial relevance

An innovative low pressure plasma process for deposition of copper-based, hybrid organic-inorganic thin films was developed. The optimized thin coatings have potential industrial utilization as active packaging material, being very effective against pseudomonads. Viability of Pseudomonas was reduced by three orders of magnitude (from 10^8 CFU/mL to 10^5 CFU/mL) in the presence of developed films, thus suggesting further investigation of the technique under food packaging conditions.

Keywords

Low pressure plasma, Aerosol Antibacterial Cu-coatings, Active packaging

1. Introduction

Due to their antimicrobial activity, metals have been widely used for centuries as active agents in several fields, such as agriculture and healthcare (Furno et al., 2004, Gunawan et al., 2011, Hermans, 2006). However, the use of metals in industrial applications presents several challenges associated with the nature of the metal itself (Applerot et al., 2010, Rai et al., 2009). Consequently, one of their first applications was in the form of salt-based additives, as, for example, silver nitrate. While non-essential metals, as silver, can be toxic to bacteria, having biocidal activity even at exceptional low concentrations, essential metals, as copper, can be lethal above some threshold (Beeton et al., 2014, Lemire et al., 2013). Compared to silver, the potential biocidal activity of copper is lower (about 10 mg Cu2 +/kg in water are necessary to kill 106 cells of Saccharomyces cerevisiae) (Llorens et al., 2012a, Llorens et al., 2012b). Moreover, metallic copper is cheaper than silver, even though it presents corrosion problems at standard conditions. Copper is an essential element and it is present in most food in form of ions at levels generally below 2 mg Cu^{2+}/kg (meat, fish, pecans, green vegetables, etc.), but up to 39 mg Cu^{2+}/kg in cocoa and liver (Aaseth & Norseth, 1986). Living organisms require copper at low concentrations as cofactors for metal-proteins and enzymes. At high concentrations, Cu^{2+} induces inhibition of bacterial growth and has toxic effects on most microorganisms (Cioffi, Torsi, et al., 2005; Llorens, Lloret, Picouet, Trbojevich, et al., 2012).

In February 2008, the U.S. Environmental Protection Agency (EPA) approved the registration of copper alloys based on the claim that they reduce bacteria linked to potentially fatal microbial infections and confirmed the antimicrobial efficacy of copper against Escherichia coli O157:H7, Staphylococcus aureus, Enterobacter aerogenes and Pseudomonas aeruginosa (http:// www.epa.gov). Thanks to recent developments in material science, the use of metals as additives has been replaced by metal surfaces and coatings or by composite materials (polymeric matrixes embedding metal clusters) (Bodaghi et al., 2013). In particular, copper has been impregnated on the surface of cotton fibers, latex and other polymeric materials (Borkow and Gabbay, 2004, Chattopadhyay and Patel,

2010) and has been also incorporated in high-pressure polyethylene (Ushakov, Ul'zutuev, & Kosobudskii, 2008). In addition, various bio-based polymers have been used as carriers of antimicrobial copper. In this context it is worth considering the colloidal copper nanoparticles regularly distributed in chitosan films (Cardenas, Diaz, Melendrez, Cruzat, & Garcia Cancino, 2009). Nano-composite coatings can be also prepared by embedding Cu-nanoparticles with picosecond-pulsed laser ablation (Conte et al., 2013).

Copper can be further incorporated by plasma treatment, thus producing, for instance, Cu-grafted polymeric surfaces (Zhang et al., 2006) or antimicrobial polymer/metal composite films (Cioffi et al., 2005b, Cioffi et al., 2004, Cometa et al., 2013, De Giglio et al., 2013). In this last case, it was reported that a copper concentration of about 38% in the composite film is enough to achieve desired antibacterial properties (Daniel, Le Pen, Archambeau, & Reniers, 2009). Among the advantages of copper-containing polymeric coatings deposited employing the plasma technology, it is important to mention the excellent adhesion to substrates and the fact that coatings can be applied at such low thickness that the bulk properties of the treated material are not affected (Jeong, Lee, Ha, & Kim, 2009).

Plasma treatment has been historically performed with gases; however, aerosol-assisted processes have been recently reported, in particular at atmospheric pressure (Fanelli et al., 2014, Ogawa et al., 2009). This revolutionary technique allows exploiting the utilization of prohibited stabile precursors to obtain innovative surfaces and opens new areas of possible industrial use for plasmas: in a not too distant future, for example, also proteins, viruses, drugs and essential oils could be likely injected into low pressure plasma environments.

In this study, we performed an aerosol-assisted deposition process with a low pressure plasma in order to produce a hybrid composite organic-inorganic thin film with antibacterial properties. In particular, the discharges were fed with an aerosol generated by an aqueous solution of bis(ethylenediamine)copper(II) hydroxide (the “monomer”) in argon, in order to obtain polymeric coatings with inorganic particles containing active Cu2 + ions. The main advantage of this innovative

approach was the possibility of embedding in the polymer non-volatile Cu compounds with a simple single-step process.

The antimicrobial effectiveness of the deposited composite polymeric matrix depends on the release of cations (e.g. Ag^{2+}, Cu^{2+}) and this may affect the legal status of the polymer as a food contact material (Llorens, Lloret, Picouet, Trbojevich, et al., 2012). An intentional migration of the active element in the food matrix would fall under the Framework Regulation 1935/2004 (http://www.efsa.europa.eu) for active packaging materials.

The antimicrobial property of the films deposited on polycarbonate (PC) and the ability of copper ions to penetrate the bacterial cells were assessed on two species of Pseudomaonas spp. (P. fluorescens and P. putida) isolated from spoiled cheese. A significant antibacterial efficiency was detected with plasma-coated samples, while the control polycarbonate did not show any activity.

2. Materials and methods

2.1. Plasma deposition processes and surface characterization of the Cu-coatings

The low pressure plasma depositions of the hybrid organic-inorganic antimicrobial Cu based coatings were performed on square substrates (~ 4.0 cm^2) of polycarbonate (Goodfellow; Coraopolis, PA) and of c-Si(100) (Microchemicals; Ulm, Germany), preventively washed in pure ethanol (Sigma Aldrich; Saint Louis, US). The silicon substrates were utilized for thickness, morphological and chemical analyses, while those of polycarbonate were used for the other characterizations.

The schematic picture of the experimental apparatus employed for the depositions is reported in Fig. 1. It consisted of a cylindrical stainless steel reaction chamber (internal diameter: 280 mm, height: 330 mm) containing a circular stainless steel electrode (diameter: 270 mm), positioned on the bottom of the chamber, on which the samples were positioned during the deposition process. This electrode was connected to a 13.56 MHz radio frequency (RF)-power supply through an automatic L-type matching network unit. In the center of the upper flange of the vacuum chamber there was a 120 KHz

ultrasonic nozzle (Sono·tek Corporation) for the aerosol production. The reactor was pumped by a rotary pump and the pressure was measured and controlled with baratron gauge and manual throttle valve, respectively.

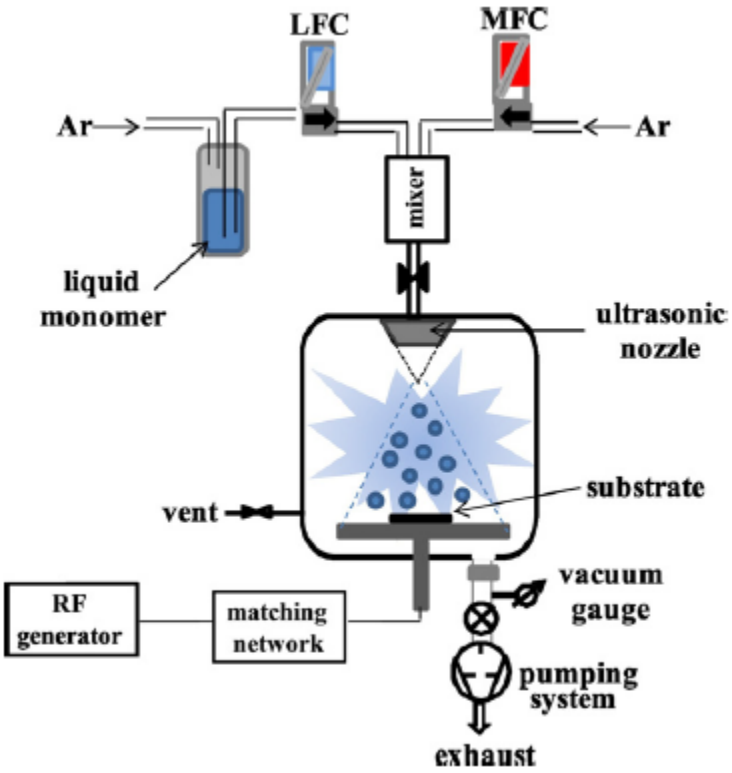

Fig. 1. Schematic representation of the experimental apparatus employed for the low pressure plasma deposition processes: LFC (liquid flow controller), MFC (mass flow controller).

The plasma was fed with an aerosol formed by 30 sccm of argon (purity 99.999%, Rivoira; Milano IT) mixed with 10 g/h of a solution 0.02 M of bis(ethylenediamine)copper(II) hydroxide in water (Sigma Aldrich; London, UK), stored in a cylindrical stainless container and kept under pressure with argon. The flow rates, expressed in standard cubic centimeters per minute (sccm), of the solution and argon were controlled by means of liquid (LFC) and mass (MFC) flow controller (MKS), respectively.

The plasma was ignited at 27 Pa with 30–150 W, since below 30 W the discharge was not stable and above 150 W a rapid degradation of the polycarbonate was observed. During the deposition process, the pressure increased up to 54 Pa.

The deposition mechanism in aerosol fed low pressure plasma is not well understood. An important role is surely played by the energetic species formed in the plasma phase (e.g. fast electrons and metastables) that react with the monomer molecules and form many fragments and film precursors. Several reactions are possible in the gas phase but, due to the low pressure (low collision frequency), the most important occur on the surfaces exposed to the plasma, resulting in film formation.

Thickness measurements were performed using a KLA-Tencor D120 profilometer, while the surface morphology of the coatings was investigated by means of a Zeiss SUPRA™ 40 field emission scanning electron microscope (FESEM). Images were acquired after gold sputter metallization, at a tilt angle of 0° and voltage of 3 kV. SEM investigations were performed on the coatings deposited on silicon substrates, in order to avoid the marked charging effects suffered by polycarbonate.

X-ray photoelectron spectroscopy (XPS) analyses were conducted with a Theta Probe spectrometer (Thermo Scientific) equipped with a monochromatic Al Kα X-ray source (1486.6 eV) operated at 15 kV, with a spot of 300 μm, (power of 70 W). Survey (0–1200 eV) and high resolution (C1s, O1s, N1s, Si2p and Cu2p) spectra were recorded in FAT (Fixed Analyzer Transmission) mode at pass energy of 200 and 100 eV, respectively. All spectra were acquired at a take-off angle of 37° with respect to the sample surface. Surface charging was neutralized with a flood gun and the C1s signal of the hydrocarbon component (285.0 eV) was used as internal standard for charging correction (Moulder, Stickle, Sobol, & Bomben, 1992). The best fitting of XPS detailed region was performed using XPS data processing software; the components are reported in Table 1.

Table 1. Data for X-ray photoelectron spectroscopy (XPS) coatings signals fitting. The full width at half maximum (FWHM) utilized and the binding energy (BE) characteristic of each signal component are reported.

Signal	FWHM (eV)	Signal component BE (eV)	Signal component BE (eV)	Signal component BE (eV)	Signal component BE (eV)
Cu2p$_{3/2}$	1.6 ± 0.3	Cu_2O 932.0 ± 0.3	CuO, NCu 933.7 ± 0.3	$Cu(OH)_2$ 935.5 ± 0.3	–
N1s	1.6 ± 0.3	NCu, NH 398.7 ± 0.3	NC 400.1 ± 0.3	NO 401.7 ± 0.3	–
C1s	1.5 ± 0.2	C-C, C-H 285.0	C-O 286.4 ± 0.3	N-C=O 288.0 ± 0.3	O-C=O 289.5 ± 0.3

The values are affected by variability due to the different experimental deposition conditions optimized in this study (i.e. different input power value applied to ignite the discharge).

The total copper amount of the coatings was determined by differential pulse anodic stripping voltammetry (DPASV) measurements, after dissolution of the films in nitric acid at 1% (Sigma Aldrich; Steinheim, Switzerland) at 100 °C, according to the procedure DIN38406/16.

Every datum was averaged on five measurements performed on five different samples and reported as mean value ± the relative standard deviation (RSD).

2.2. Evaluation of the antimicrobial activity

The antimicrobial activity of the plasma-deposited copper-containing coatings was evaluated with cell growth experiments. Two species of Pseudomonas spp. isolated from spoiled fiordilatte cheese, were used as test microorganisms. The two wild-type strains, identified as P. fluorescens and P. putida, were maintained in Plate Count broth (PC, Oxoid, Milan, IT) at − 20 °C with addition of 30% of glycerol as stock cultures. Prior to the antimicrobial tests, exponentially growing cultures were obtained by allowing each strain to grow in PC broth at 25 °C for 24 h. Then, the two strains of Pseudomonas spp. were mixed taking 1% of each culture (0.045 mL) and adjusted to approximately 104 bacterial cells/mL by dilution in PC broth. To ensure a high reproducibility of the inoculum preparation procedure, cell counts were standardized through the direct spread plate count technique. For testing the antimicrobial activity, the Japanese Industrial Standard (JIS) Z 2801:2000 method was used. To this aim, each plasma coated polycarbonate sample (~ 4 cm^2) was placed in a sterilized petri dish under aseptic conditions. All petri dishes were inoculated with 0.064 mL of microbial stock solution and incubated for 18 h at 25 °C. Afterwards, the samples were diluted to 1/100 with sterile NaCl solution (9.0 g/L) by stirring the sample for 180 s to obtain suitable plate counts. One mL of each dilution was inoculated on Pseudomonas agar base (PAB) medium modified by adding CFC (Pseudomonas cephaloridine-fucidin-cetrimide) selective supplement and incubated at 25 °C for 48

h. The colonies were counted, and the results were expressed as log10 of colony-forming units per mL of sample (log10 CFU/mL).

As control samples, virgin polycarbonate and petri dishes without any plasma coatings were also considered.

Data of antimicrobial tests are the average of five replicates. All data from antimicrobial tests were subjected to one-way analysis of variance (ANOVA). A Duncan's multiple range test with the option of homogeneous groups ($P < 0.05$) was carried out to estimate quantitative differences among samples. STATISTICA 7.1 for Windows (StatSoft Italia s.r.l.) was used.

3. Results and discussion

3.1. Morphological and chemical characterization of the Cu-coatings

In order to acquire information about the morphology of the thin films utilized in this study to evaluate the antimicrobial activity, SEM images were collected. Fig. 2 shows the typical surface of the optimized plasma-deposited coatings and shows that the deposit consists of a polymeric matrix incorporating copper-containing clusters of nanometric dimensions.

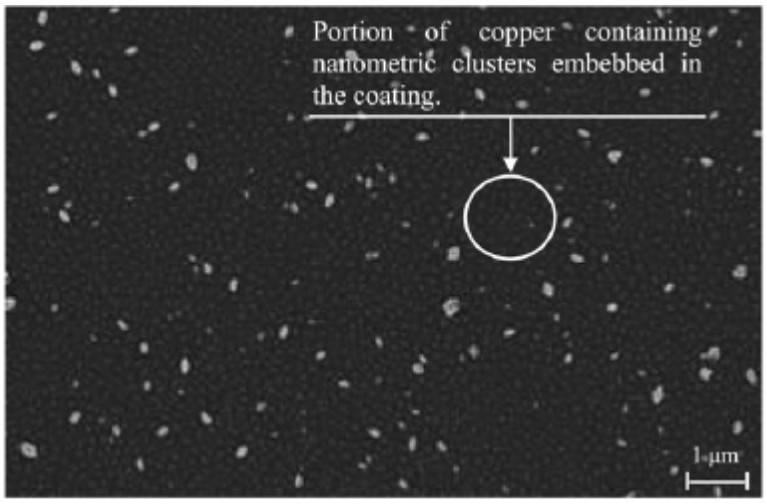

Fig. 2. Scanning electron microscopy (SEM) image of plasma coated Si-c(100) samples at 50 W. Magnification 15.000 ×.

Table 2 reports the XPS atomic surface concentration of the thin films plasma-deposited at different input power value. It can be appreciated that the copper concentration increases from 9 to 18% when the input power increases from 30 to 150 W. XPS allows also to identify the chemical state of the copper; in fact, from the fitting of the $Cu2p_{3/2}$ signal (Fig. 3), it results that copper is present as Cu(I) (i.e. Cu2O) and Cu(II) (i.e. CuO, $Cu(OH)_2$) (Beamson & Briggs, 1992). By the fitting of N1s and, in particular, by the presence of the peak centered at 398.7 eV, it is not possible to exclude that part of the copper is bound to nitrogen. The $[Cu^{2+}]/[Cu^{1+}]$ ratio (0.8 ± 0.1) was not influenced by the input power applied during the deposition which, therefore, only affects the overall Cu content and not its chemical nature. Also the fitting of the C1s signal is not affected by the input power value applied to ignite the discharges.

Table 2. X-ray photoelectron spectroscopy (XPS) surface atomic composition of the plasma deposited coatings, as a function of the input power value applied to ignite the discharges.

Input power (W)	Cu (%)	C (%)	O (%)	N (%)
30	9 ± 2	45 ± 3	29 ± 2	17 ± 2
50	13 ± 2	42 ± 2	26 ± 3	19 ± 3
150	18 ± 2	38 ± 3	28 ± 3	16 ± 2

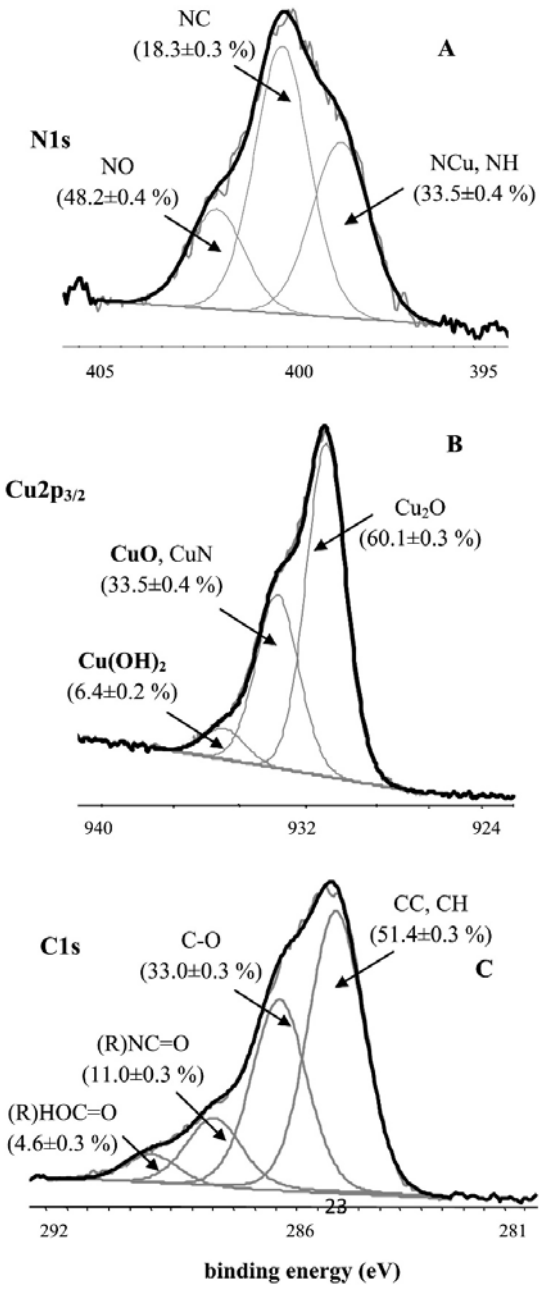

Fig. 3. Curve-fitting of the high resolution N1s (A), $Cu2p_{3/2}$ (B) and C1s (C) X-ray photoelectron spectroscopy (XPS) spectra of the Cu based coating, plasma-deposited at 150 W.

The total amount of copper contained in the deposits was evaluated with differential pulse anodic stripping voltammetry (DPASV) measurements. The results reported in Table 3 show that the copper content of the coatings, for the same volume of the thin film, increases with the input power in agreement to the surface analysis performed with XPS (Table 2).

Table 3. Total amount of copper, obtained with differential pulse anodic stripping voltammetry (DPASV) measurements, contained in the coatings plasma-deposited at different input power values.

Input power (W)	[Cu] (μg/cm^3)
30	$1.3 * 10^{-4} \pm 5 * 10^{-5}$
50	$3.2 * 10^{-4} \pm 7 * 10^{-5}$
150	$7.3 * 10^{-4} \pm 5 * 10^{-5}$

Film thickness: 160 ± 15 nm; substrate surface area: 4.0 ± 0.3 cm^2.

3.2. Antimicrobial properties of plasma-deposited Cu-coatings

The results reported in Table 4 show the initial microbial levels of Pseudomonas spp. and their level after contact with the different substrates. The initial Pseudomonas spp. concentration was 4.81 ± 0.18 $\log_{10}$CFU/mL in all the samples and a different microbial proliferation was observed, depending on the surface in contact with microbial cells. In the control samples (virgin polycarbonate and petri dishes without plasma-treated film) no inhibition occurred, thus reaching a final microbial population accounting for about 8 $\log_{10}$CFU/mL. On the contrary, if the polycarbonate surface was coated with the copper-containing plasma deposits, a clear inhibition was detected, since lower microbial concentrations than the controls were found. It is also worth noting that the inhibition improved as the copper content of the coating increased, i.e. for deposition performed at higher input power value (150 W). The microbial population, in fact, increased to less more than 6 $\log_{10}$CFU/mL with the coating deposited at 30 W ([Cu] = $1.3 * 10^{-4} \pm 5 * 10^{-5}$ μg/cm^3) and 50 W ([Cu] = $3.2 * 10^{-4} \pm 7 * 10^{-5}$ μg/cm^3), while for the film deposited at 150 W the Pseudomonas spp. concentration increased only up to less more than 5 $\log_{10}$CFU/mL ([Cu] = $7.3 * 10^{-4} \pm 5 * 10^{-5}$ μg/cm^3), 3 log less respect to the control samples.

Table 4. Antimicrobial effectiveness of plasma-deposited Cu based coatings against two species of Pseudomonas spp.

		Microbial cells load [log_{10}CFU/mL]
Initial cells load		4.81 ± 0.18
Cells load after 18 h contact at 25 °C	Control sample	8.24 ± 0.01[b]
	Control PC	7.98 ± 0.33[b]
	PC - 30 W	6.63 ± 0.80[a]
	PC - 50 W	6.21 ± 0.55[a]
	PC - 150 W	5.58 ± 0.16[a]

Control sample = petri dishes without any plasma coatings; Control PC = virgin polycarbonate; PC-30 W = plasma-treated polycarbonate at 30 W; PC- 50 W = plasma-treated polycarbonate at 50 W; PC- 150 W = plasma-treated polycarbonate at 150 W.
[a-b] Data in column with different letters are significantly different ($P < 0.05$).

To investigate the fate of copper after the contact of the active polymer with the inoculated medium, the total copper content was determined by DPASV measurements on polycarbonate samples coated with plasma deposit at 150 W, after immersion in the culture broth with and without microorganisms. While after immersion in the pure culture broth the copper amount of the plasma coating remained unchanged, a Cu reduction of about 36% was registered if the culture broth contained the microorganisms. These results allowed to conclude that the copper contained in the plasma deposits was not solubilized in the culture broth and, therefore, it is reasonable to assume that its antimicrobial activity was due to the direct penetration of Cu ions in the microbial cells. This effect is abundantly mentioned in the literature, in particular it has been reported that the efficacy of copper to prevent food spoilage is due to the closely interaction of copper ions with Gram-positive and Gram-negative bacterial membranes (Vreuls et al., 2010). Ren et al. (2009) specifically, studying active films with copper nanoparticles, supposed a release of Cu^{2+} ions by the coatings that disrupt bacterial cell membranes and provoke changes in the surrounding charge environment. Longano et al. (2012) also presumed irreparable damage in microbial cells as consequence of complex redox reactions provoked by copper nanoparticles. This effect may involve substitution of essential ions and block of functional

groups of proteins, inactivation of enzymes, production of hydroperoxide free radicals by membrane-bound copper and alterations of membrane integrity. Other studies suggested that DNA in bacteria exposed to copper surfaces might become degraded, since copper ions affect the sulfhydryl groups of proteins causing DNA damage (Nies, 1999, Warnes et al., 2010).

4. Conclusions

An innovative, fast and simple low pressure plasma process for deposition of organic Cu based coatings was developed. The plasma was directly feed with an aerosol of a solution containing a copper complex mixed with pure argon. The deposit uniformly covered the organic (flat polycarbonate) or inorganic (Si-c100 wafer) substrate. Film deposited at the highest input power showed the highest copper content which was generally present as mono- and, specially, as double-ionized cation (Cu^{2+}), whose antibacterial property is widely demonstrated in the literature. All plasma coated polymeric samples were effective against Pseudomonas spp. isolated from spoiled fiordilatte cheese. Direct contact of cell suspension with polycarbonate coated with the optimized films resulted in a reduction up to three orders of magnitude of the bacterial growth, if compared to the virgin polymeric case.

Due to the interesting results recorded, in the future, in vivo studies will be performed in order to suppose a real industrial employment of the Cu-coatings optimized in this work as active food packaging, for example, for fresh dairy products.

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