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Novel polyethylene oxide coatings implementing ultra-stable laser-ablated silver nanoparticles

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Abstract: Nanocomposites based on polyethylene oxide and silver nanoparticles (AgNPs) were developed as new active antimicrobial and antibiofilm coatings. Silver colloids were synthesized by nanosecond-pulsed laser ablation synthesis in solution using an organic solvent to ensure a long-term stability of nanocolloids and a good solubility in polymeric solution. AgNPs were incorporated in a biodegradable polymer matrix for the preparation of composite films. The coatings' surface chemical composition (assessed by X-ray photoelectron spectroscopy) was correlated with the ion release.

Keywords: silver; nanocomposite; nanoantimicrobials; laser-ablation; polyethylene oxide.

1. Introduction

Polymer nanocomposites have been developed to improve polymer's features [1]. The incorporation of metal or metal oxide nanoparticles into a polymeric matrix is generally used to confer additional properties to the organic medium [2]. Among available nanoparticles, AgNPs already find application in many real-life products [3–7], thanks to their broad-spectrum antimicrobial effect [8]. AgNPs can be prepared by a plethora of different methods; in this panorama, laser ablation synthesis in solution (LASiS) allows producing AgNPs which can be more suitable for medical and food-related applications, where it is important to use non-toxic chemicals [9,10]. One of the first examples reported in literature for LASiS of AgNPs is the work published by Tsuji et al. in 2000 [11,12], in which the different

experimental conditions were correlated to NP morphology and dimensions. LASiS-generated AgNPs are generally produced in water, which does not ensure good stability over time [13,14]. Therefore, increasing interest is paid to the use of NP stabilizers or different solvents. Nanomaterials and nanotechnologies are considered as an innovation and improvement in almost all technological and industrial fields, from the medical, biomedical and pharmaceutical sectors to the electronic and agri-food areas [15]. Nanoparticles can be dispersed into common polymeric matrices or can be distributed on their surface to develop composite nanomaterials [16]. The growing demand for microbially-safe products, along with the requirement to ensure increasing nosocomial safety, led to use of antimicrobial metal nanoparticles to confer biostatic and biocidal properties to common polymers [2]. The antimicrobial properties of metal-polymer materials are based on the migration of the antimicrobial substances from the composite surface [17]. This is an intentional and required process to exert the antimicrobial and antibiofilm action.

In this study, we propose a biodegradable nanocomposite for biomedical and active food packaging applications, based on LASiS-synthesized AgNPs, combined with PEO. We chose 2-propanol (IPA) as ablation medium, because it provided very stable colloids [18] and proved to be a very good solvent for PEO dissolution. PEO is a biocompatible synthetic polymer, approved by the Food and Drug Administration for the use in food and pharmaceutical products [19]. Both AgNPs and the corresponding AgNPs-PEO composites were here characterized by means of different analytical techniques. Kinetics of antimicrobial ionic release were also studied in physiological environment by means of electro-thermal atomic absorption spectroscopy (ETAAS).

2. Materials and methods

2.1 Materials

Unless otherwise stated, Milli-Q water (25°C, 18.2 MΩ) was used. Silver sheets (99.99% purity, diameter: 10 mm; nominal thickness: 1 mm) were purchased from GoodFellow Ltd. (Cambridge, UK). Isopropanol (IPA, >99.9%, HPLC grade), ethanol (EtOH, absolute, ACS reagent), HNO_3 (67%, Trace-SELECT® Ultra, for ultratrace analysis), NaCl (Trace-SELECT® Ultra, ≥ 99.999%, for ultratrace analysis), NaH_2PO_4 (Trace-SELECT®, ≥ 99.99%, for trace analysis), Na_2HPO_4 (Trace-SELECT®, ≥ 99.99%, for trace analysis), and PEO (MW~100000 g/mol) were purchased from Sigma Aldrich (Milan, Italy). Silver standard for AAS (1000 µg/mL in 2% HNO_3) was purchased from Perkin Elmer (Milan, Italy). Cu grids

(Agar Scientific, Stansted, UK), carbon-coated, 300-mesh, were used for the preparation of TEM samples.

2.2 LASiS synthesis of AgNPs and preparation of AgNPs-PEO composites

Synthesis of AgNPs was carried out by LASiS, similarly to what described in [18]. Briefly, a ns *Q-Switched* Nd:YAG Laser (Quantel-BRIO) was used. It operated at a fundamental wavelength of 1064 nm, with a pulse frequency of 20 Hz, a pulse energy of 46.5 mJ, and a nominal pulse duration of 4 ns. The Ag target was fixed to the wall of a 35 x 25 x 30 mm^3 vessel filled with 10 mL of IPA. Ablation duration was 60min. Fresh AgNPs were mixed at 1%$_{w/w}$. to a 5 g/L PEO solution, under stirring at 50°C. The resulting composite was deposited by spin-coating, with a rotation program of 500 rpm for 30 s, and 5000 rpm for 60 s. A volume of 500 µL was deposited on 25 x 25 mm^2 glass slides or Si wafers.

2.3 Morphological and spectroscopic characterization

Absorption spectra of the ablated colloids and AgNPs morphology were studied by UV-Vis and TEM, respectively, according to what reported in [18]. Dynamic light scattering (DLS) measurements were performed using a Zetasizer-Nano ZS from Malvern Instruments [18]. The surface chemical composition of AgNPs-PEO composites was assessed by XPS; experimental details can be found elsewhere [18].

2.4 Determination of silver release

The determination of the amount of silver released from the composites into aqueous contact solutions was carried out through ETAAS. The nanocomposite film was put in contact for 48 h with 500 µL of aqueous PBS solution (pH = 6.8, I = 0.1). At predefined times, 50 µL of contact solution were sampled from the PBS droplet, and subsequently diluted 1:100 with HNO_3 0.2%$_{v/v}$ to be analyzed by ETAAS. After each sampling step, the droplet volume was restored with the addition of 50 µL of fresh PBS. Measurements were performed with a Perkin Elmer PinAAcle AS900Z instrument. Release kinetic data were curve fitted by a pseudo-first order kinetic model. Further details are available as Supporting Info.

3. Results and discussion

3.1 LASiS of AgNPs and preparation of AgNPs-PEO composites

AgNPs were obtained by ns-pulsed laser ablation in pure IPA. The average colloidal concentration resulted equal to 0.11 ± 0.01 g/L. AgNPs showed a spherical morphology (Fig. 1a-b), and an average size diameter of 9 ± 3 nm (Fig. 1c). NPs were surrounded by a thin organic shell with lower contrast. As already reported in literature, IPA undergoes spontaneous oxidizing and radicalization processes under

LASiS pressure and temperature conditions [20,21], thus adsorbing on NP surfaces and stabilizing them. Hydrodynamic radius measured by DLS gave an average dimension of 260 ± 50 nm. The latter is in agreement with that of the NP agglomerates within the organic shell, as visible in Fig. 1a. UV–Vis absorption spectrum is shown in Fig. 1d, and shows typical Ag surface plasmon resonance (SPR) band, at 398.0 ± 0.5 nm [18]. This position is typical of spheroidal AgNPs [22]; the broad tail at higher wavelengths is relevant to the dark appearance of the colloid, and indicative of a certain aggregation, as confirmed by TEM images [23].

FIG 1 HERE

Figure 1: TEM micrographs (a, b) and corresponding size distribution histogram (c) of LASiS AgNPs. UV-Vis spectroscopic characterization of AgNPs (d).

As-prepared AgNPs were used for AgNPs-PEO composite preparation. Thin films were analyzed by XPS. Surface elemental composition of AgNPs-PEO is reported in Tab. 1; bare PEO was analyzed as reference. Presence of Ag on sample surface was demonstrated: Ag3d high-resolution region was centered at 368.1 ± 0.2 eV (Fig. S1). Due to its very low signal intensity, it was not possible to univocally assess Ag chemical speciation, in absence of corresponding Auger parameter, for low signal intensity, as well [24]. As shown in Fig. 2, polymer surface chemical composition was not significantly altered by the inclusion of AgNPs: from the comparison of C1s high-resolution regions of bare PEO (Fig. 2a) and AgNPs-PEO (Fig. 2b), main signal components remained unvaried (Tab S1). These components are in agreement with what expected for PEO in presence of adventitious contamination [25]. However, a slight increment in the relative atomic % of the C1s aliphatic component is observable for the composite; this could be due to the presence of the organic shell stabilizing AgNPs. The latter, as explained in [18], is made of variously branched ketones, carboxylic acids and is produced and produced during the ablation process. In fact, it is known that IPA decomposes above 700 K (a temperature easily reached within the cavitation bubble in LASiS with ns pulses), and undergoes a self-inhibited free radical chain mechanism, generating the organic stabilizing layer which covers NPs.

Elemental At. %	PEO	AgNPs/PEO
C	68.6 ± 0.5	41.4 ± 0.5
O	31.4 ± 0.5	58.6 ± 0.5
Ag	/	≤0.2

Table 1: Surface chemical composition of AgNPs-PEO composite. Data for bare PEO are reported for comparison. Errors are calculated as one standard deviation.

FIGURE 2 HERE

Figure 2: C1s XP high-resolution regions for bare PEO (a) and AgNPs-PEO composite (b).

3.2 Kinetics of silver release

Silver ions release kinetics followed a pseudo-first order kinetic [24,26]. Fig. 3 shows the trend of Ag^+ concentration in physiological solution, as a function of time: it grew in the first few hours, reaching a plateau (90 ± 7 ppb) in about 5 h. The measured silver concentration is expected to exert a biostatic activity, thus making such composite appealing for biomedical and food packaging applications [27]. Silver ion concentration at t = 0 was not negligible. This is known to be correlated to the presence of oxidized silver species on the nanoparticle surface, which readily solubilize when in contact with aqueous media. The composite materials appeared to be stable upon contact with physiological solution for two days: the same PBS solution used for release experiments was analyzed by TEM (data not shown). No traces of entire NPs were visible in the contact solution, thus excluding any nano-toxicological issue relate to the AgNPs-PEO material.

FIGURE 3 HERE

Figure 3: Silver ion release for an AgNPs-PEO composite film. Solid line shows data interpolation by means of a first order kinetics. R^2 value resulted equal to 0.9206.

4. Conclusions

Active PEO was prepared embedding LASiS-generated AgNPs in the polymer matrix. All the nanomaterials were characterized by means of UV–Vis and XPS spectroscopies, in order to study their optical properties and surface chemical composition. TEM microscopy was used to obtain NP morphology, showing that AgNPs are covered by a thin shell of organic matter stabilizing them and preventing flocculation. XPS demonstrated AgNP inclusion in the polymer matrix, and PEO surface composition was not significantly altered by the inclusion of inorganic nanophases. The silver release investigation was used to hypothesize a rationale for the antimicrobial actions of the novel nanomaterial. ISO antimicrobial tests are under way to prove the potential application of this composite in biomedical and active food packaging fields.

Author Contributions: M.C.S. and M.I. did most of the experiments and wrote the first draft of the paper. A.V. and M.C. optimized and performed laser ablation syntheses. R.A.P. performed XPS analysis. A.A. and N.C. coordinated the research and revised the paper.

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