

Antibacterial nanocomposites based on Ag NPs and HMDSO deposited by atmospheric pressure plasma

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Abstract: The development of new multifunctional coatings with antimicrobial properties has a special interest in several applications for pharmaceutical and medical products. This work reports on the deposition of antimicrobial coatings based on silver nanoparticles (Ag NPs) embedded in an organosilicon film onto woven and nonwoven textiles. The Ag nanoparticles admixed with hexamethyldisiloxane (HMDSO) vapours are introduced by means of an atomizer system in the remote discharge of an atmospheric pressure plasma source operating in argon. The chemical properties and the surface morphology of the coatings with antimicrobial potential are discussed.

Keywords: atmospheric pressure discharge, Ag nanoparticles, HMDSO polymerization.

1. Introduction

Utilization of textiles in the medical applications requires special attention in order to diminish the intrahospital infections which usually conducts to prolonged healthcare and even increasing rate of mortality [1]. Among the strategies considered for obtaining material with antibacterial properties are those based on the surface processing by micropatterning [2], attachment of chemical groups or drug delivery systems [3]. Another approach consists of the introduction of metals with intrinsic antimicrobial properties, like Ag or Cu, for which the released ions interact with the bacterial cell wall and DNA conducting eventually to cell death [4]. In this case, the utilization of metal nanoparticles brings the advantage of a high surface - to - volume ratio leading to high release from small amount of metal and thus preventing the cytotoxicity and genotoxicity effects on human organisms.

In the present work, we present data regarding the synthesis of antimicrobial layers onto textile fabrics by atmospheric pressure plasma processing starting from an admixture of Ag nanoparticles with hexamethyldisiloxane (HMDSO) vapours introduced in the remote plasma.

2. Experimental part

The atmospheric pressure plasma source used for deposition of silver-polymer nanocomposites is based on the discharge with bare electrode (DBE) and consists in a co-axial plasma configuration in which the inner cylindrical electrode is RF active while the outer one is

grounded, as shown in Figure 1. Both electrodes are in contact with plasma. The precursor, consisting of an admixture of Ag NPs of 50 nm diameter with hexamethyldisiloxane (HMDSO) at a concentration of AgNPs /HMDSO of 1:50, is introduced through an atomizer in the interior isolated channel of the RF electrode and is forced to interact with the plasma jet in its remote region. Argon (99.999 % purity) is used as feeding gas at a flow of 2500 sccm; the discharge is generated with radiofrequency (13.56 MHz) power, at levels below 20 W. In order to ensure a uniform deposition, a translation stage was used for mounting the DBE plasma source. The argon flow passing through the atomizer was set to 900 sccm and the distance between the plasma source exit and the substrate was 1 mm. The scanning speed was 5 mm/sec and

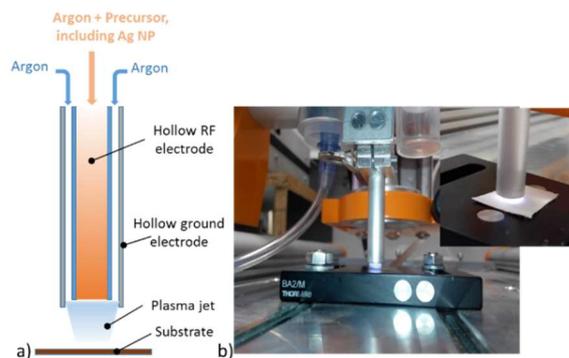


Figure 1: a) The discharge configuration and b) image during deposition experiments of the DBE plasma source

the number of scans was 100. The deposition experiments were carried out in open atmosphere, on Polyethylene Terephthalate - PET textile, with woven and non-woven texture.

Similar deposition experiments have been performed by using an atmospheric DBD plasma in air and respectively an atmospheric DC plasma jet in operated in N_2 .

The obtained coatings were analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDS) and Scanning electron microscopy (SEM).

3. Results and discussion

We performed current-voltage measurements in order to determine the effective power in the discharge as function of the forwarded power from the RF generator. In a first approximation, we considered an RX equivalent circuit of the discharge, with X the total equivalent reactance and R the plasma resistance. The average active power P_{AVR} can be determined as:

$$P_{AVR} = \sum_{n=1}^m [U_{RMS} I_{RMS} \cos \Delta\phi]_n \quad (1), \quad \text{where}$$

U_{RMS} and I_{RMS} are the quadratic average of the voltage and current, respectively, $\Delta\phi$ is the phase difference between the current and the voltage, n is the harmonic order and m is the maximum order for the considered harmonics ($m = 6$).

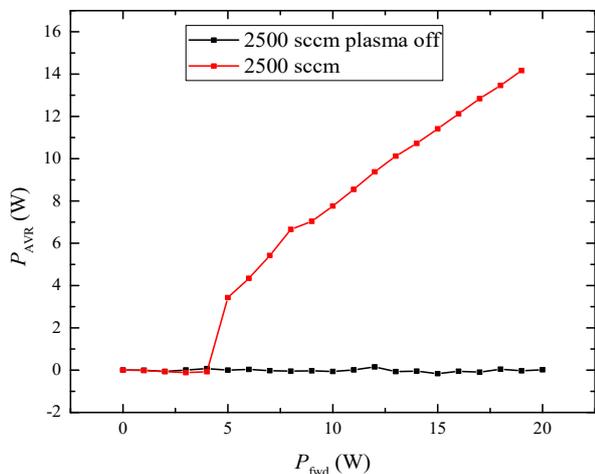


Figure 2. Dependence of the average active power upon the forwarded RF power (reflected power = 0 W)

The results pointed out that in the conditions used for the deposition, the actual power in the discharge is $\frac{3}{4}$ from the injected power.

In order to prove the successful deposition of the organosilicon layer and the inclusion of Ag in the deposits, we performed EDX analysis onto initial textile, HMDSO deposited textile, and AgNPs+HMDSO covered woven and nonwoven material. The results regarding the chemical

composition of the samples are presented in Table 1. We should mention here that the Ag presence could not be detected for the woven deposited material, being probably below the detection limit. On the other hand, for the non-woven material the ratio of Ag/Si was much higher than the expected values, considering the ratio between the HMDSO and AgNPs introduced in the process.

Table 1. Chemical composition of the samples.

| Sample type/atomic composition | PET ini | PET + HMDSO | PET + Ag NPs +HMDSO (nonwoven) |
|--------------------------------|---------|-------------|--------------------------------|
| C (At %) | 71.97 | 60.91 | 38.88 |
| O (At %) | 28.03 | 34.13 | 52.56 |
| Si (At %) | | 4.96 | 6.19 |
| Ag (At %) | | | 2.38 |

The investigation of the surface morphology as function of the deposition conditions was performed by means of Scanning Electron Microscopy. A rather homogeneous dispersion of the Ag nanoparticles was observed in the case of woven deposited material (Figure 3a and b). In the case of nonwoven textile, we could observe a tendency towards agglomeration of the Ag nanoparticles (Figure 3c and d) onto some fibers. These agglomerates can conduct to the overestimation of the Ag concentration by EDX in the nonwoven coated sample, while for the homogeneously covered woven coated textiles, the concentration can be below the detection sensitivity.

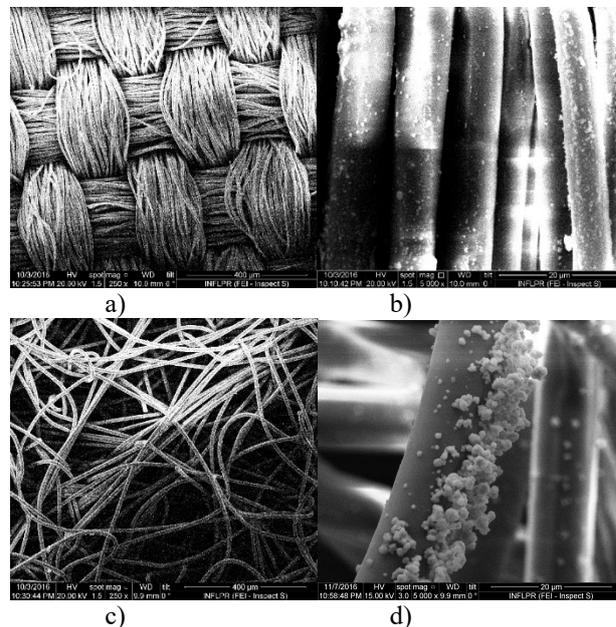


Figure 3. SEM images of the PET polymeric textile coated by nanocomposites consisting of Ag NPs and polymerized HMDSO. a) and b) show the case of woven material, while c) and d) that of non-woven material, for magnification of 250x and 5000x

However, considering the envisaged application as antimicrobial coating, one should underline that formation of agglomerates of NPs is undesirable since it may strongly affect the ion release.

The investigation of the chemical composition of the AgNPs+HMDSO layers was performed by Fourier transformed infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR). In Figure 4 are presented the FTIR spectra for nonwoven PET covered by AgNPs + HMDSO coatings with various Ag contents, and the main features of the IR spectra are indicated in Table 2.

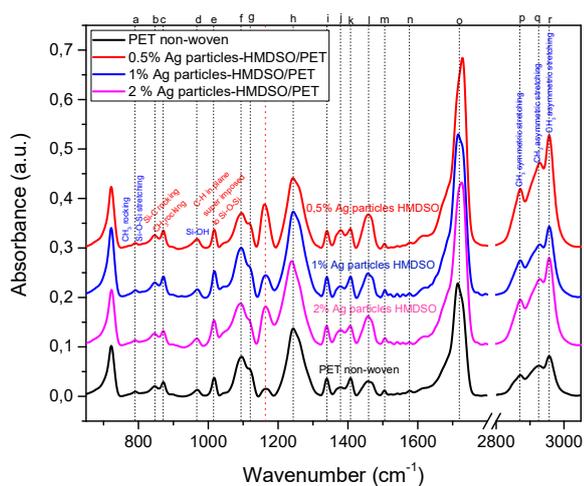


Figure 4. FTIR spectra of nanocomposite coatings of Ag NPs + HMDSO with various Ag loads onto PET nonwoven textile

The spectrum of untreated textile material is characterized by the presence of chemical bonds specific for PET [5]. Upon AgNPs + HMDSO layer deposition by atmospheric pressure plasma, the textile materials present several differences in the region 750 – 2690 cm⁻¹, which are associated to the deposition of an organosilicon film obtained upon HMDSO plasma polymerizations [6].

One should mention here that the presence and chemical state of Ag NPs cannot be assessed by FTIR technique. In order to overpass this problem, XPS measurements were performed on samples obtained in a similar configuration by using a DC plasma jet operating in nitrogen, which consists of a pin-to-mesh electrode in a quartz tube. The high resolution spectra in the binding region of Ag 3d shows the presence of Ag 3d_{5/2} and Ag 3d_{3/2} peaks at 368.1 eV and 374.2 eV, respectively. They point out towards the presence of Ag in metallic state, but also a partial oxidation evidenced by the small shift of 0.1 eV encountered for the Ag 3d_{5/2} peak in respect to that of bulk metal Ag (at 368.2 eV) [7].

Table 2. Identification of the chemical bonds in FTIR spectra

| Label | Wavenumber (cm ⁻¹) | Chemical bond |
|---------|--------------------------------|--|
| a | 790 | CH ₃ rocking vibration and Si – O – Si stretching vibration |
| b | 847 | Si – C rocking and CH ₃ rocking vibrations |
| c | 871 | C - H out of plane deformation |
| d | 971 | Si – OH bending vibration |
| e | 1020 | C - H in plane vibration imposed to Si – O – Si stretching vibration |
| f | 1096 | C – H in plane vibration |
| g | 1120 | C - O - C stretching vibration |
| h | 1244 | CH ₃ deformation vibration |
| i | 1340 | CH-wagging vibration, imposed to O-H in plane deformation |
| j, m, n | 1409, 1505, 1576 | Triple skeletal aromatic vibrations |
| k, l | 1455, 1470 | CH ₂ scissoring vibration |
| o | 1712 | C=O bending vibration |
| p/r | 2870/ 2958 | CH ₃ symmetric/ asymmetric stretching |
| q | 2907 | CH ₂ asymmetric stretching |

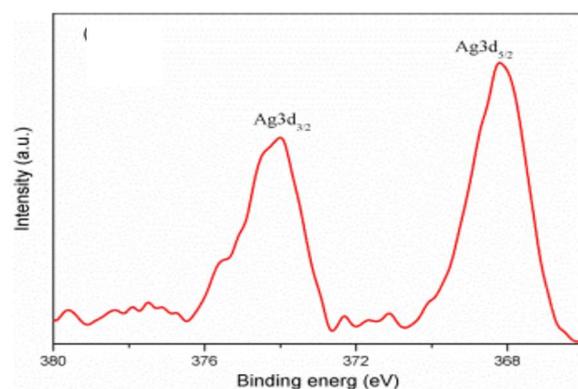


Figure 5. High resolution XPS spectrum in the Ag3d binding energy region for the nanocomposite films obtained with the DC plasma jet

4. Conclusions

An approach for deposition of nanocomposite coatings containing Ag nanoparticles on PET fabrics was presented. It is based on the utilization of an atmospheric pressure plasma source working in argon, in which the precursor admixture is introduced in the remote plasma region, conducting to the HMDSO polymerization and incorporation of Ag NPs. Preliminary tests regarding the antimicrobial activity (not shown) revealed that the silver containing surfaces are effective against *S. aureus* and *P.aeruginosa*.

5. Acknowledgement

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6. References

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