Copper-polysiloxane composites obtained by combined PVD/PECVD techniques working in sequential and simultaneous modes

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Abstract: This work reports on the plasma synthesis of Cu-polysiloxane nanocomposites with controllable copper content by a hybrid PVD/PECVD process, working either in sequential or in simultaneous modes, and on their topographical, optical and compositional properties in correlation to the antimicrobial activity. A growth inhibition effect correlated to the Cu content was encountered for *S. aureus* and *E.coli* strains.

Keywords: Cu-polysiloxane nanocomposites, hybrid plasma techniques, antimicrobial activity

1. Introduction

In the recent years, composite materials based on metal nanoparticles inclusions in an organic matrix were frequently studied due to their interesting properties like those electrical and optical, enhanced antibacterial activity, associated with a low cost [1, 2]. Among the widely used synthesis methods for nanocomposite materials are those based on plasma techniques [3].

The control of metallic fraction in metal-polymer composites can be obtained by varying the deposition conditions, such as, RF power, gas flow rate, deposition time and working pressure, making them suitable materials for a large number of applications [4]. Recently, copper is one of the largely used metals for synthesis of nanocomposite materials due to its catalytic potential, when combined with appropriate matrix, as well as for the antimicrobial activity [5, 2].

The present contribution is reporting on the synthesis of the Cu-polysiloxane nanocomposites using a combined PVD/PECVD techniques working either in sequential or in simultaneous modes. A comparison of the material characteristics upon the working mode of the hybrid PVD/PECVD set-up and the antimicrobial activity of these materials are presented here.

2. Experimental

Cu-polysiloxane synthesis was conducted in a stainless steel vacuum chamber provided with a magnetron sputtering source and a PECVD plasma source. The sources were mounted perpendicular one to each other, and respectively at 45 degrees in respect to the substrate, as seen in Figure 1. The setup allows the sequential or simultaneous substrate exposure to the PVD plasma source and to the PECVD plasma source.

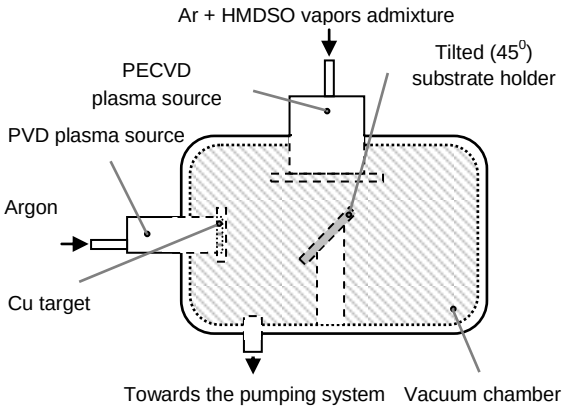


Figure 1. Schematic of the experimental set-up for the synthesis of Cu-polysiloxane composites

The copper target mounted on the magnetron sputtering gun is sputtered by igniting an argon discharge (5 sccm) at 100 W RF power, working pressure 0.07 mbar, in both functioning modes. The time frame for the metal deposition in the sequential approach was set between 10-60 seconds.

A controlled HMDSO flow (2 sccm) is carried in vapour phase by an Ar flow (20 sccm) through the shower-like RF powered electrode of the PECVD plasma source, setting up a working pressure 0.14 mbar. In sequential

working mode Ar/HMDSO RF plasma was set at 20 W, using a constant time frame of 60 s. In simultaneous working mode Ar/HMDSO plasma was set at RF powers in the range of 0-20 W.

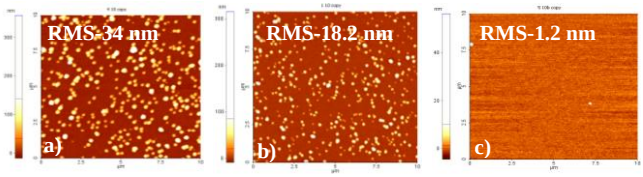
The distance between the substrate and the plasma sources can be varied from 8 cm to 14 cm from the magnetron sputtering source and from 3 to 9 cm from the PECVD plasma source, due to the tilted orientation of the substrate. The central position of the substrate, determined by the symmetry axes intersection of the PVD/PECVD sources, corresponds to 6 cm from the PECVD plasma source, and respectively 11 cm from the PVD plasma source.

Morphological properties of the Cu-polysiloxane composite synthesized both in sequentially and simultaneously modes were studied by AFM. Optical properties of the Cu-HMDSO materials were investigated by Spectroscopic Ellipsometry (SE). Chemical bondings and the elemental atomic concentration of the as-prepared samples were determined by FTIR and XPS techniques. The antimicrobial activity was tested using cellular cultures of *Candida albicans* as eukaryotic model and, respectively *Escherichia coli* (gram positive) and *Staphylococcus aureus* (gram negative) as prokaryote model. The growth inhibition and bacteria proliferation have been determined.

3. Results and discussion

Topographical characterization (AFM)

AFM technique allowed the investigation of the surface topography in respect to the synthesis conditions which influence the Cu incorporation ratio in the composite (e.g., distance from the PVD plasma source, RF power). The AFM images for the Cu-HMDSO nanocomposite synthesized by sequentially substrate exposure to the plasma sources (Figure 2) reveal the presence of spherical structures, which can be associated to the presence of Cu nanoparticles on the surface, probably covered by the polysiloxane-like material. The density and dimensions of



a) d_{PECVD} = 9.0 cm; d_{MS} = 8.0 cm

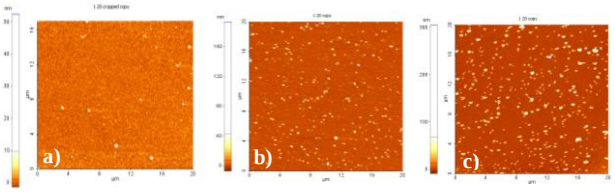
b) d_{PECVD} = 6.0 cm; d_{MS} = 11.0 cm

c) d_{PECVD} = 3.0 cm; d_{MS} = 14.0 cm

Figure 2. AFM images of the Cu-HMDSO composites synthesized in sequential mode as a function of distance from the PECVD (20 W) and PVD (100 W) plasma source

these particles are decreasing upon distance increase in respect to the PVD plasma source.

The AFM images for the Cu-polysiloxane nanocomposite synthesized in simultaneous regime (Figure 3) indicates Cu particles on the surface at intermediate levels of RF power on the PECVD plasma source, in the range 5-15 W, their density and sizes depending on the applied RF power. One may conclude that copper sputtering rate is diminished at higher deposition rate of HMDSO (higher level power) due to poisoning target process.



a) RMS = 1.5 nm RF_{PECVD} = 20 W

b) RMS = 7.5 nm RF_{PECVD} = 15 W

c) RMS = 15.8 nm RF_{PECVD} = 5 W

Figure 3. AFM images of the Cu-HMDSO composites synthesized in simultaneous mode as a function applied RF power on the PECVD plasma source (RF on PVD =100 W).

The hystograms of particles distribution upon dimension, presented in Figure 4, indicate a higher number of metallic inclusions in the polymeric matrix forming particles with a total average size around 200 nm for the synthesis by sequentially exposure of the substrate to the plasma sources. Nevertheless, due to inherently different deposition mode, we cannot exclude the presence of nanometric size Cu particles in the simultaneous deposition regime, leading however to a much smoother surface.

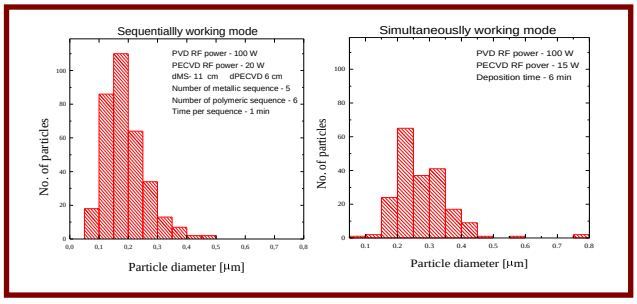


Figure 4. Hystogram of particles distribution for the Cu-polysiloxane composite obtained in sequential and simultaneous working modes

Optical characterization (SE)

Spectroscopic ellipsometry was used in order to determine the thickness and optical constants of the Cu-HMDSO nanocomposite obtained by sequential PVD/PECVD plasma.

The optical constants of the Cu-polysiloxane nanocomposites with various exposure times to the PVD plasma source are comparatively presented in Figure 5. The Cu-HMDSO composites with lower metallic inclusion ratio presented a clear absorption peak around 380 nm, associated with the surface plasmon resonance effect due to the presence of Cu nanoparticles in the

polysiloxane matrix [6]. At higher copper inclusions ratio we can observe a slight absorption peak which is shifted to higher wavelength, which is assimilated to an increased dimension of the Cu nanoparticles, while no absorption peak is present for the 60 s/60 s Cu-HMDSO ratios. This indicates that under such conditions, the Cu content is high, and particles already reach important dimensions, which do not allow the SPR to be noticed anymore.

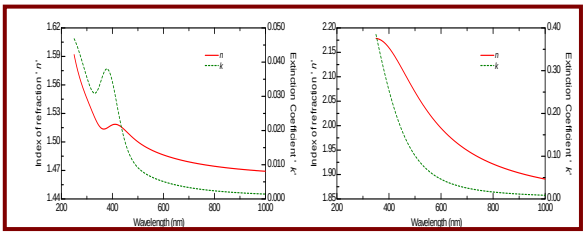


Figure 5. Comparison of the optical constants (n, k) of the Cu-polysiloxane with different metallic exposure time: 10 s (left); 60 s (right); exposure time for HMDSO was 60 s in all cases.

Chemical characterizations (FTIR & XPS)

FTIR technique allowed the investigation of the chemical bonds of the polymeric matrix obtained by hybrid PVD/PECVD plasma system working both in sequential and simultaneous modes. Typical FTIR spectra of Cu-polysiloxane materials reveal the presence of Si-C stretching mode at 797 cm^{-1}, absorbtion peaks at 1029 cm^{-1} and 1260 cm^{-1} associated to Si – CH_2 wagging and $Si(CH_3)$ symmetric stretching deformations, and the Si-O-Si bond specific originating from the HMDSO precursor at 1105 cm^{-1}. Additionally, a narrow peak of low intensity present at 2027 cm^{-1} indicates the formation of Si-H bonds. In the range 2800 – 3000 cm^{-1} the symmetric and asymmetric stretching modes of CH_x (x = 2, 3) can be noticed [7]. In Figure 5 are comparatively presented the FTIR spectra of Cu-polysiloxane composites obtained in simultaneous and respectively sequential mode of the hybrid PVD/PECVD system.

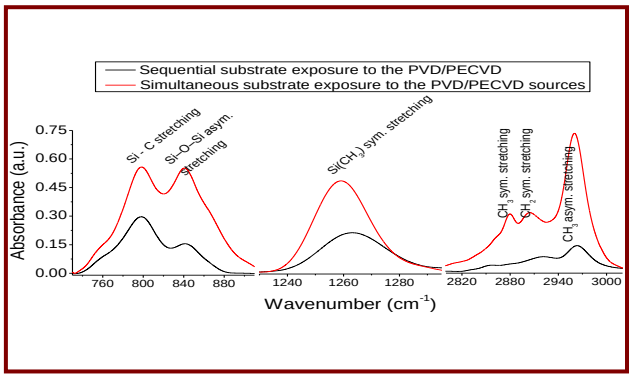


Figure 6. Comparison of the FTIR spectra of Cu-polysiloxane composites obtained in sequential (black) and simultaneous (red) working modes.

Although the general aspect of the spectra is quite similar, one can notice the overall intensity is decreasing for Cu-polysiloxane composite synthesized by sequentially working mode, although the total thickness was similar, most probably due to higher copper ratio in the nanocomposite volume which diminishes the signal associated to polysiloxane matrix.

Therefore, FTIR results correlates with AFM investigations, suggesting that the simultaneous working mode lead to nanocomposite materials with lower copper values. This is due to a lower number of Ar^+ ions available for copper sputtering, as they are also involved in the plasma chemistry of HMDSO fragmentation, and also to the poisoning of the copper target.

XPS measurements prove the incorporation of Cu in the polymeric matrix under all investigated conditions. In Table 1 are presented the elemental concentrations of Cu, as well as those of C, O and Si originating from the polysiloxane matrix, both for sequential and simultaneous working regimes, for applied RF powers of 20 W for PECVD and 100 W for PVD, respectively.

Table 1. Atomic concentrations of Cu-polysiloxane composites obtained using hybrid PVD/PECVD system

Working mode/ sputtering time/ atomic concentration	C (at%)	O (at%)	Si (at%)	Cu (at%)
Sequential 0.75 min sputtering	38.0	27.7	13.5	20.8
Sequential 2 min sputtering	13.5	27.0	17.0	42.5
Simultaneous for all sputtering times	10.7	56.2	28.2	4.9

variations along their depth, reaching more than 40% atomic concentration in the center of the region associated to the PVD exposure.

Another feature is the limited amount of C obtained in the simultaneous regime, explained by the additional energy provided from the PVD plasma source to the PECVD system which induces a higher fragmentation of HMDSO and the formation of silica-like material under these conditions, as evidenced by FTIR measurements as well.

Evaluation of Cu-polysiloxane composites antimicrobial activity

S. aureus ATCC 6538 (gram positive) and *E. coli* ATCC 10536 (gram negative) bacterial strains were grown in BHI broth (Brain Heart Infusion; pH 7.4) and *C. albicans* ATCC 10231 yeast strain was grown in YPG broth (Yeast Peptone Glucose; pH 5.0), for 24h at 37^0C, and centrifuged in order to obtain a number of 10^6 cell/ml for yeast strain and 10^7 cell/ml for bacterial strains. Afterwards, the microbial strains were incubated with

Cu-polysiloxane samples at 37^0C for 24h, then washed gently 4 times with PBS (phosphate buffer saline, pH 7.2) in order to remove non-adherent cells and fixed with methanol 96% for 15 min. Cell culture growth was estimated by determining optical density at 600nm for bacterial strains and 660nm for yeast strain. Assays were

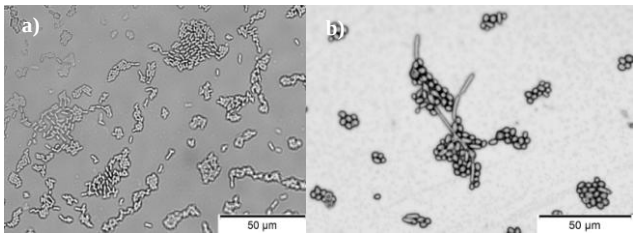


Figure 7. Optical images of pathogenic microorganism on the Cu-polysiloxane

carried out in triplicate. The distribution of the pathogenically microorganisms on the Cu-polysiloxane samples was evaluated by optical microscopy, and is presented in Figure 7 for *E.coli (a))* and *C. albicans (b)).*

The optical density measurements, presented in Figure 8, evidenced no significant antimicrobial effect against *C. albicans* ATCC 10231 yeast strain. Nevertheless, upon comparison with polysiloxane and Cu thin films obtained upon identical synthesis conditions to those implied in the nanocomposites, one can see that the Cu- based composites present an intermediate growth inhibition behavior between that of Cu, which clearly inhibit strain growth (OD 10%), and that of polysiloxane, which allows the proliferation of *C. albicans* up to 3 times in respect to the control..

On the other hand, the nanocomposites samples exerted

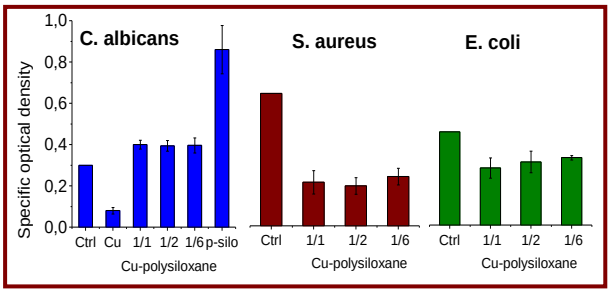


Figure 8. Specific optical density for the *C. albicans, S. aureus and E. coli* microorganisms

an inhibition growth effect compared with control samples against bacterial strains *S. aureus* ATCC 6538 and *E. coli* ATCC 10536, evidencing a reduction in cell growth up to 60% and up to 30%, respectively, as shown in Figure 8 as well. The optical density measurements indicate that the inhibition growth rate for the *E. coli* microorganisms is enhanced upon increasing the Cu content in the material.

4. Conclusions

Copper-polysiloxane nanocomposites with controllable content of metallic inclusions were obtained using hybrid PVD/PECVD techniques, working both sequentially and simultaneously modes. The polymeric matrix is characterized by FTIR absorption peaks typical for polysiloxane material. The SE and XPS data shown that the copper content can be tuned by varying the following experimental conditions: substrate position in respect to the plasma sources for both working regimes, exposure time during the PVD functioning in the sequential mode, RF power of the PECVD plasma source in case of simultaneous mode. XPS measurements indicated the Cu presence all along the material depth profile, with constant concentration for simultaneous mode and alternating concentration for sequential mode. On the surface, the composite material presents spherical structures with number and dimensions varying in accordance to Cu content in the sample.

Antimicrobial assays (OD) evidenced an inhibition effect especially for both gram positive and gram negative tested strains, and this effect is more pronounced upon increasing the Cu content in the material.

Acknowledgements

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References

[1] L. Bedel, C. Cayron, M. Jouve, F. Maury, Nanotechnol., **23**, 2012, 015603(1)-015603(8).

[2] N. Cioffi, L. Torsi, N. Ditaranto, G. Tantillo, L. Ghibelli, Luigia Sabbatini, Teresa Bleve-Zacheo, M. D'Alessio, P. G. Zambonin, E. Traversa, Chem. Mater. **17** (2005) 5255

[3] A. Daniel, C. Le Pen, C. Archambeau, F. Reniers, Applied Surface Science **256S** (2009) 82

[4] M. Hirasawa, H. Shirakawa, H. Hamamura, Y. Egashira, H. KomiyamaJ. Appl. Phys., **82**, 3 (1997)

[5] C. Walter, V. Bruser, A. Quade, K.D. Weltmann, *Plasma Process. Polym.* **6** (2009) 803

[6] D. Salz, B. Mahltig, A. Baalmann, M. Wark, N. Jaeger, Phys. Chem. Chem. Phys., 2000, **2**, 3105

[7] P. Raynaud, B. Despax, Y. Segui, H. Caquineau, Plasma Process. Polym., 2 (2005), 45