DECORATIVE ANTIMICROBIAL COATING MATERIALS BASED ON SILVER NANOPARTICLES

Alexandra PICĂ[1], Cornelia GURAN[2], Denisa FICAI[3], Anton FICAI[4], Ovidiu OPREA[5]

Materialele peliculogene antimicrobiene au devenit destul de utilizate mai ales ca acoperiri decorative în spitale. În ultimii ani se observă o creştere a interesului în utilizarea argintului coloidal în acest tip de materiale peliculogene. Nanoparticulele de argint sunt materiale biocide ideale datorită eficacităţii ridicate asupra unui spectru larg de bacterii şi a toxicităţii reduse. În lucrarea de faţă se prezintă un studiu sistematic de încorporare a nanoparticulelor de argint în formulările de materiale peliculogene decorative, cu accent pe optimizarea dispersiei, rezistenţa la îmbătrânire a peliculei şi claritatea filmului. Obiectivul lucrării, îl constituie realizarea unui material peliculogen antimicrobian eficient, stabil 12 luni. Eficacitatea antifungică asupra unor ciuperci care sunt prezente în unităţile medicale este demonstrată pentru formulările de material peliculogen antimicrobian optimizate.

Film – forming antimicrobial materials have become quite used mainly as decorative coatings in hospitals. In the recent years it can be seen an increased interest in using this type of nanosilver coating materials. Silver nanoparticles are ideal biocide because of their high efficacy against a wide range of bacteria and their low toxicity. This paper presents a systematic study of incorporation of nanosilver in formulations of decorative coating materials, with emphasis on optimizing dispersion, resistance to aging of the coating film and film clarity. The objective of the paper is setting up an effective antimicrobial material, stable 12 months. Antifungal efficacy over some fungus, found in health facilities is demonstrated for optimized antimicrobial formulations of film-forming materials.

Keywords: antifungal efficacy, optimized formulations, silver nanoparticles

1. Introduction

[1] PhD student, Research Institute for Advanced Coating, Bucharest, Romania; e-mail: alexandra.pica@icaaro.com
[2] Prof., Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania
[3] Lecturer, Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania
[4] Lecturer, Department of Science and Engineering of Oxide Materials and Nanomaterials, University POLITEHNICA of Bucharest, Romania
[5] Reader, Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania

Due to the high traffic of people, hospitals are infectious risk environments, in spite of all measures of asepsis and antisepsis applied by medical personnel. An international study published in 2010 has assessed 1,400 intensive care units in 26 countries, including Romania and found that 31% of hospitalized patients had contracted infections inside the hospital. Protecting the furniture, floors and walls with antimicrobial coating materials removes the risk of developing microorganisms on their surface and consequently decrease the infections contracted in hospitals [1,2].

The control of microbial infections is a very important issue of the modern society. In general there are two ways to stop microbes from infecting humans or deteriorating materials-periodic disinfection and antimicrobial surfaces. The first is usually realized by disinfectants, which are a considerable environmental pollution problem. Antimicrobial surfaces are usually designed by impregnation of materials with biocides that are released into the surroundings, whereupon microbes are killed [3-5].

Ideally, antimicrobial materials show efficacy against a wide variety of microorganisms, being environmentally friendly. Also, it is an advantage to formulate antimicrobial materials, which are stable across a wide range of pH's and can be processed at very low temperatures [6].

2. Experimental part

2.1. Materials and Equipment

All the chemical substances were of analytical grade. Ethyl glycol acetate provided by Polydis, dispersion agents type Dispersogen PCE supplied by Clariant, film-forming material MPAS provided by ICAA (Research Institute for Advanced Coatings), dioctyl sodium sulphosuccinate surfactant supplied by Sigma-Aldrich and silver nanoparticles - AgNP presented in a previous paper [7].

MPAS was obtained starting from acrylic-styrene polymer dispersion with free carboxyl groups (the minimum film forming temperature being 20°C); calcium carbonate and magnesium silicate hydroxide used as extenders; titanium dioxide (rutile) used as white pigment; sodium polyacrylate used as dispersant and polyurethane dispersions used as rheological modifiers and were of reagent grade.

SEM analyses were performed on a Scanning Electron Microscope, NanoSEM 630.

Exposure of coatings to artificial aging was performed with ATLAS UV 2000 device.

Thermal analysis was performed with a TG-DSC STA Jupiter 449C, Netzsch at a speed of 10 K/min, up to 900^{o}C. Samples were placed in an Al_2O_3 open crucible, in a dynamic atmosphere of 20 ml/min dry air.

2.2 Obtaining antimicrobial film-forming materials based on nanosilver

Obtaining conventional coating film-forming material (MPAS)

The way to obtain the coatings, marked as MPAS, was as follows: in a pearl mill water, additives and NH_3 was added. After 5 min of mixing calcium carbonate, magnesium silicate hydroxide in the rain, and titanium dioxide were added and homogenized for other 20min. The last step consists in styrene acrylic polymer addition followed by an additional 10 min of mixing.

Incorporation of nanosilver in the film-forming material (MPAS)

Our synthesized nanosilver was presented in a previous paper [7] as dispersed in MPAS by ultrasonic dispersion. Before ultrasonication, silver nanoparticles were amended with ammonium hydroxide up to pH = 8 to settle the nanoparticles dispersion. It was also used a surfactant (sodium dioctyl sodium sulphosuccinate). The ultrasound occurred at constant frequency of 24 Hz and at constant temperature of 20^0C. In order to optimize the dispersion 5 MP formulations were made, in which varied amount of dispersion additive (Dispersogen PCE) were used. The results are presented in Table 1.

There have been 5 antimicrobial film-forming material formulations (denoted as MP5, MP6, MP7, MP8 and MP9). The amount of nanosilver in the film-forming material was of 550ppm.

Table 1

Formulating antimicrobial film forming materials with nanosilver

Sample	Dispersants Dispersogen PCE [%]	Surfactants %	Duration of exposure to ultrasound [hours]	Observations
MP 5	2	3	2	homogeneous dispersions; separated after 72 hours
MP 6	4	3	2	homogeneous dispersions; separated by 2 weeks
MP 7	6	3	2	homogeneous dispersions; separated by 8 weeks
MP 8	10	3	2	stable, homogeneous dispersions (12 months)
MP 9	8	3	2	stable, homogeneous dispersions (12 months.)

As shown in Table 1 the optimum amount of dispersant is of 8-10%. MP 9 was selected for economic reasons.

3. Results and discussions

3.1. Scanning electron microscopy - SEM

The morphology of nanosilver particles used in the formulation of antimicrobial film-forming materials was determined using scanning electron microscopy as follows: 0.01M nanosilver suspension in water was made and was mixed with ultrasound for 15 minutes. A drop of the obtained solution (nanosilver in water) was taken and placed on a silicon wafer, and then the solvent was evaporated in an oven at 150^{o}C. As shown in Fig. 1, silver nanoparticles have a spherical shape and the size of 20-60nm. It can be seen a slight agglomeration of particles and on their surface a dark layer, probably the styrene acrylic polymer in the presence of which were obtained nanosilver particles (7).

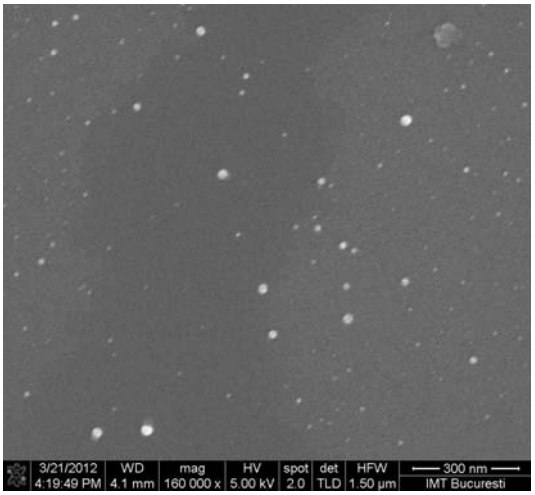


Fig. 1. SEM images of silver nanoparticles

3.2. Thermal analysis of antimicrobial film-forming coating material

The thermal analysis of MP 6, MP 7, MP 8, MP 9 show a similar thermal stability, all the samples beginning to degrade over 340^{o}C (Fig. 2). The residue from all samples is formed by MAPS elements that form solid oxides (especially CaO and TiO_2).

The principal data resulted from thermal analysis are presented in Table 2.

The onset decomposing temperature is situated in a narrow interval, but is increasing constantly from MP6 sample to MP 9. This increase can be attributed to the content of dispersant. The onset temperature is increasing up to 8% of dispersant and decreases for the MP 8 (which used 10% dispersant for the synthesis of the film-forming material) perhaps due to the decreasing degree of settling.

Table 2

The thermal analysis data for the MP 6-9 samples

Sample	Onset temperature [°C]	Mass loss up to 400°C [%]	Area of the first endothermic peak [J/g]	Residual mass [%]
MP 6	344.3	78.28	1206	4.64
MP 7	345.1	84.24	766	2.58
MP 8	348.2	76.24	133	4.99
MP 9	350.2	79.14	300	5.27

The magnitude of the first endothermic effect is decreasing sharply from MP6 to MP 8, increasing for MP9. This variation can be also related to the content of dispersogen PCE used to produce the samples. As the dispersogen PCE increases, the endothermic effects diminish in intensity. This aspect can prove useful when designed paints that will not aid the burning process by evolving heat.

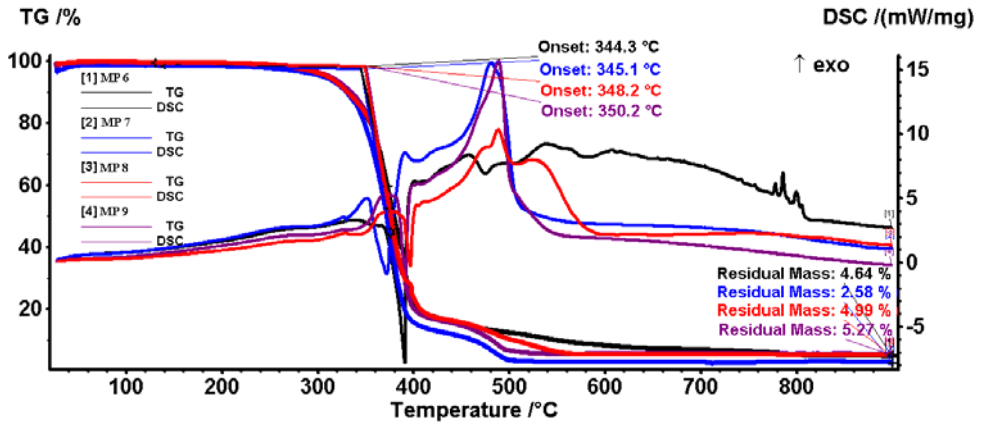


Fig. 2. The thermal analysis of the MP 6, MP 7, MP 8 and MP 9 samples

3.3. Resistance to aging of antimicrobial film-forming coating material

Silver has been used for centuries as an antiseptic, known not to be toxic to humans in low concentrations. In addition to its low toxicity, silver has several beneficial properties which make it an excellent candidate to be as used as an antimicrobial material. It is thermally stable, shows broad spectral activity against many target organisms, and is stable against UV/Visible radiation. These properties give an advantage for nano silver compared to organic antimicrobial

materials which can be toxic and degrade at high temperatures, and the presence of UV/VIS radiation

Exposure of antimicrobial coating material to artificial aging was made according to ISO 11507: 2007 with a 2000 UV ATLAS device. This allows exposure to UV fluorescent, spray and condensation. ATLAS 2000 UV produces photo degradation within days or weeks which in real conditions on the outside, occurs within months or even years. Light Source: Fluorescent UV lamps 340 with an intensity of 0,77 W/m^2/nm. The MP 9 and MPAS samples were applied on wooden plates and after 7 days from application were tested for stability in accelerated aging conditions at 55 °C to 30 repeated cycles of irradiation, spray and condensation. A cycle involves irradiation - 1 hour, spraying - 1 hour and an hour of condensation. The results are presented in Table 3.

Table 3

Antimicrobial film-forming materials testing to accelerated aging

Sample	Appearance of film after 5 cycles	Appearance of film after 10 cycles	Appearance of film after 15 cycles	Appearance of film after 20 cycles	Appearance of film after 25 cycles	Appearance of film after 30 cycles
MP9 antimicrobial film-forming material based on nano silver (550ppm)	No modifi-cations Clear Film	No modifi-cations Clear Film	No modifi-cations Clear Film	No modifi-cations Clear Film	No modifi-cations Clear Film	No modifi-cations Clear Film
MPAS film-forming material (without nanosilver)	No modifi-cations Clear Film	No modifi-cations Clear Film	No modifi-cations Clear Film	No modifi-cations Clear Film	slightly yellowed Clear Film	slightly yellowed Slightly opalescent

As seen from the data presented in Table 3 it appears that introducing nanosilver in the film-forming material influences the aging resistance of the film and its clarity. In the case of MPAS we can notice a slight yellowing of the film equipment probably due to the acrylic-styrene polymer degradation.

3.4. Antifungal efficacy of the film - forming antimicrobial materials based on nanosilver

Specimens with antimicrobial film-forming material MP 9 and MPAS (without nanosilver) were inoculated with the mixture of spores belonging to the 12 species of fungus (*Alternaria alternata, Aspergillus flavus, Aspergillus niger, Aspergillus ustus, Aureobasidium pullulans, Chaetomium globosum, Cladosporium herbarum, Paecilomyces varioti, Penicillium citrinum, Penicillium*

funiculosum, Stachybotris atra, Trichoderma viride). Microscopic observations were performed at 3, 14 and 28 days after inoculation, with a stereomicroscope with magnification of x 50. Evaluation of test results of antifungal effect, made in a laboratory is presented in Table 4 and in the attached photos.

Mold behaviour of samples, was expressed through the presence and size of mold growth inhibition zone around the samples and through the notes, from 0 to 5, reflecting the percentage of the surface coverage with mold.

Table 4

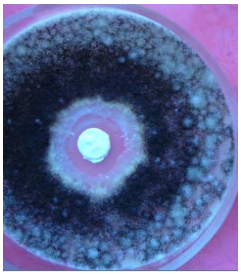
Antifungal synergism of the antimicrobial coating material - MP

Sample	Duration of exposure						**Micromycetes species**
	3 days		**14 days**		**28 days**		
	Zone of inhibition [mm]	Notes [0-5]	Zone of inhibition [mm]	Notes [0-5]	Zone of inhibition [mm]	Notes [0-5]	
MP9 antimicrobial film-forming material based on silver nanoparticles (550ppm)	15 mm	0	15 mm	0	15 mm	0	absence species It shows a slight opacity of the inhibition zone. Perhaps migration of a constituent of MP9
MPAS film-forming material (without silver nanoparticles)	7 mm	2.2	7mm	3.3	7 mm	4.8	covered with A. Flavus colonies

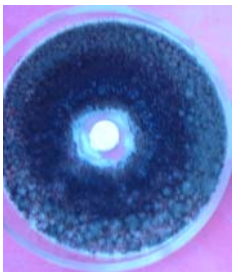
Notes: 0 - no mould; 5 - completely covered with mould

As shown in Fig. 3.A and table 3, the MPAS sample (without nanosilver) has no antifungal effect, even after 3 days fungus are present on the film surface. Instead, MP 9 has antifungal effect at 3, 14, and 28 days (Fig. 3.B-3.D.)

3.A



3.B




3.C 3.D

Fig. 3. The antifungal effect of antimicrobial coating materials: 3.A - antifungal effect of MPAS at 3 days; 3.B - antifungal effect of MP 9, at 3 days; 3.C - antifungal effect of MP 9, at 14 days; 3.D - antifungal effect of MP 9, at 28 days

4. Conclusions

Dispersion of silver nanoparticles in the film-forming material was performed using ultrasound and was selected the optimum film-forming material relative to quality/price. It was shown that the antimicrobial film-forming material selected has antifungal effect on fungus present in hospitals. The presence of nanosilver in this type of material beneficial influences the film clarity and resistance to aging of coverage. Nanosilver particle morphology used was determined by electronic scanning microscopy-SEM. Antimicrobial film-forming material is stable 12 months.

R E F E R E N C E S

[1] *Kwon, Hyuk-Min, Yun, Ho-Wook*, Antibacterial paint containing nanosilver particles and coating method using the same U S Patent 20050287112, 2005;

[2] *John Texter*, Bactericidal silver surfactant delivery into coating and polymer compositions US Patent AA01N5502FI, 2009;

[3] *Yan Lu, Yu Mei, Roland Walker, Matthias Ballauff, Markus Drechsler*, Nano-tree'-type spherical polymer brush particles as templatesfor metallic nanoparticles polymer*, Polymers* **47** (2006) 4985–4995;

[4] *Felix Siedenbiedel and Joerg C. Tiller,* Antimicrobial Polymers in Solution and on Surfaces: Overview and Functional Principles, *Polymers*, ***4*** *(*2012), 46-71;

[5] *Lichter, J.A.; Rubner, M.F*, Polyelectrolyte Multilayers with Intrinsic Antimicrobial Functionality: The Importance of Mobile Polycations. *Langmuir, **25** (*2009), 7686-7694;

[6] *Madkour, A.E.; Dabkowski, J.M.; Nusslein, K.; Tew, G.N*. Fast Disinfecting Antimicrobial Surfaces. *Langmuir **25***, (2009), 1060-1067;

[7] *Alexandra Pica, Denisa Ficai, Cornelia Guran*, In-situ synthesis of nanosilver particles used in obtaining of antimicrobial film-forming materials, Rev. Chim.*,* **63**(5), *(*2012), 459-462.