# A New Generation of Antibacterial Film Forming Materials

**ALEXANDRA PICA*, ANTON FICAI**
Politehnica University of Bucharest, 1-7 Polizu Str., 011061, Bucharest, Romania

*In this paper we present the antibacterial performance of some modified film forming materials used for a long lifetime protection of wood, concrete, gypsum boards and other building materials. The film forming material have antibacterial properties due to the presence of AgNPs in their composition. The structure and morphology of the antibacterial coatings were determined by scanning electron microscopy (SEM) and XRF. The introduction of 100-200ppm AgNPs in AMFF produces an optimum improvement in the antibacterial resistance. It has been shown that the new film forming material (AMFF) does not deteriorate even if subjected to 200 cycles of wet rubbing. AMFF shows antibacterial efficacy on the bacteria (gram-negative and gram-positive) after 200 washing cycles.*

*Keywords: nanoparticles, antibacterial film forming, multifunctional coatings*

Currently, hospitals face serious problems because of the nosocomial infections. Microbial infections and development of drug resistance to various pathogenic bacteria (gram positive and Gram-negative) represent a major cause of mortality [1]. The emergence in hospitals of multidrug-resistant bacterial strains at antibiotics is increasingly common [2]. Before the widespread use of antibiotics, silver and copper have been used since ancient times to treat microbial infections [3]. Increasing the number of infections caused by multiresistant bacteria contributed to the search for effective methods for dismantling drug-resistant microorganisms [4,5,6]. Advances in nanotechnology have led to the obtaining of a variety of materials for biomedical applications, including the antimicrobial [7], medicine [8, 9], biofouling [10], etc. The key to optimizing the use of silver nanoparticles as antimicrobial agent is to maximize the release of silver ions targeting the elimination of microbes [11,12]. It was found that the presence of microorganisms on the surface of organic material under conditions of high humidity and temperature can be harmful to the film coatings due to adhesion of the bacteria and their multiplication [13 - 15]. Organic materials must contain a biocide that confers them antibacterial properties. The nanosilver can be successfully used as a biocide in the film-forming materials due to its efficiency on 650 microorganisms [16]. However the introduction of nanoparticles in the organic / inorganic hybrid materials is difficult and because of this antimicrobial efficacy is low. Recent studies have shown that the antibacterial activity of Ag nanoparticles is closely related to the dispersion of particles [17]. To achieve an antimicrobial film-forming material is important that the Ag nanoparticles to be effectively dispersed in the polymer matrix . This dispersion must be stable and it is very difficult to achieve [18]. Nanoparticles, having high specific surfaces tend to agglomerate to form clusters or larger particles, which can cause decreasing of the biological properties [17].

In this work, the interest has been focused on the development of an antibacterial film forming, containing a small amount of AgNPs (100-200ppm), for use in indoor applications, such as hospitals. AgNPs used have an average diameter of 20nm.

## Experimental part

*Materials, equipment and methods*

In order to obtain AMFF has been used a water-reducible acrylic polymer Plextol D 498 from Synthomer. Calcite and titanium dioxide were purchased from Kronos Inc. Silane coupling agent (KBM-503) were purchased from Shin-Etsu Silicone.

SEM analysis for AMFF sample was performed on a HITACHI S2600N electron microscope, at 25 and 15 keV, in primary electrons fascicle, on samples covered with a thin silver layer.

X-Ray Fluorescence (XRF) is a common analytical technique which can be used for qualitative and quantitative determination of the elements. The elemental composition of AMFF7-AMFF9 was determined using X-MET handheld device TXR 3000 using an X-ray source of Rhodium.The instrument measures elemental composition of elements on the surface of the sample and very little depending on the power of penetration depth of X-rays in the material which depends on Z-average material.

Wet scrub resistance is a coating film's ability to withstand wet abrasive cleaning without removing the material from the surface. The Washability and Scrub resistance tester – Model 494, produces a repeatable, controlled condition to simulate every day use or wear patterns. The abrasion tester can examine washability and related properties that affect the stain resistance of coatings.

Preparation of antimicrobial film-forming materials AMFF

During manufacture, the colloidal stability of the coatings has an important effect on the final distribution of the particles in the coating and, consequently, has a great effect on the properties of the coating. If the particles lose their colloidal stability at some point during the manufacturing process, this leads to aggregation. The literature presents only a few structures of film-forming materials doped with NPs with antimicrobial properties. The polymers used are of alkyd (19), polyurethane]20], and vinyl type[21]. Various methods are known for the preparation of hybrid organic-inorganic materials. The mule techniques incorporating metals in special polymer matrix involves chemical reactions as reducing, mixing

* *email: alexpica02@yahoo.com*

nanoparticles with polymers or more complex physical processes such as: layer by layer deposition (22) spray [sputtering] (23) or plasma deposition (*24*). All these techniques take time, costs, multistage synthesis which determines the complexity of the manufacturing process of materials with embedded nanoparticles.

To avoid these difficulties it was tried to finding the supramolecular organic materials as “hosts” for stabilizing the AgNPs as methacryloxypropyl trimethoxysilane. We tried a more simple approach but that ensure the effective dispersion of the nanoparticles. First I swollen silver nanoparticles in propylene glycol and then, we have introduced AgNPs swollen , in AMFF.

Swollen of AgNPs: into a flask equipped with magnetic stirrer, were added 20g propylene glycol, 0.5g silane coupling agent over which was gradually added 10g AgNPs (2 g /10 min). The solution was left for 5 h into an ultrasonic bath, in the dark and at a temperature of 10°C. There were then added 5g acrylic polymer and 5g distilled water. The mixture was stirred magnetically for 20 min. It was obtained a colloidal solution, stable, dark brown.

Getting antimicrobial coatings materials - AMFF

In a vessel equipped with stirring, type Cowless, were added 150 mL of distilled water, 8 mL sodium polyacrylate, 0.2% silane coupling agent and different amounts of AgNPs swollen. Mixing for 10 min. 250g acrylic polymer, 250g fillers, 240g titanium dioxide and 100 mL of distilled water is added. The stirring was continued for 2 h. Finally add the additives and mix for 20min. The AMFF, thus obtained, were applied to the plasterboard and polyethylene film, and were allowed to dry for h at room temperature. The application was performed using an applicator (a rustproof blade provided with bumps of 120 microns).

Formulation of antimicrobial film-forming material achieved are presented in table 1.

## Results and discussions

Development of antimicrobial coatings materials was made possible due of an efficient dispersion of AgNPs in the polymeric material. In order to increase the colloidal stability, we used organic groups that reduce surface energy and provide the steric stability. Organic groups were provided by a silane coupling agent KBM-503. These antibacterial coatings act on microorganisms through silver ions which are released from the matrix material. Besides the aesthetic and protective function, these materials, also possess biological properties. AMFF were applied on a plasterboard or polyethylene substrate The application was performed using an applicator (a rustproof blade provided with bumps of 120 microns).

*Morphological characterization of film forming materials*

Three film forming materials AMFF7-AMFF9, and were analyzed by electronic scanning microscopy. It is an extensively used method for topography, material homogeneity, roughness and porosity examination. It can be seen that the roughness of AMFF is higher in the section than the surface. The surfaces of the composites were rough, and AgNPs crystals were homogeneously dispersed in the polymer matrix. SEM micrographs are similar. For this reason we have presented here, only the SEM micrographs of AFFM9 (fig.1).

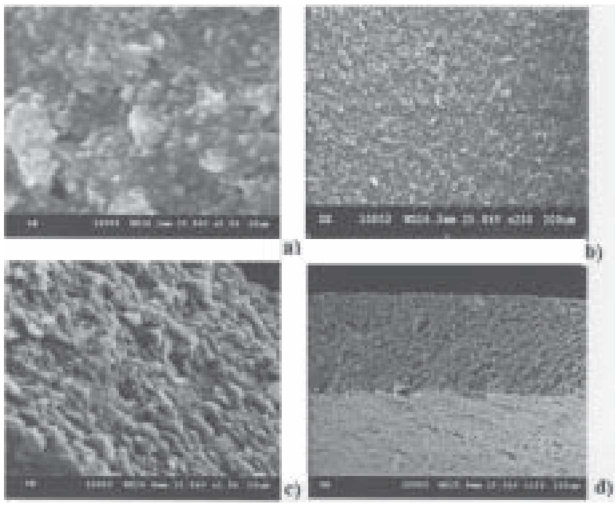

Fig. 1- SEM image for AMFF9: a, b - overview; c, d -in section

From the morphological point of view there are important similarities between the three synthesized materials (AMFF7-AMFF9). Mineral particles (fillers, $TiO_2$) can be clearly identified in all cases. SEM images attached to the surface and in section highlights a good uniformity of film-forming material. Explanation homogeneity of the three samples is based on the fact that silver nanoparticles are well dispersed in the film forming material and are no sedimentation or agglomeration.

*Elemental analysis of AMFF sample using X-ray fluorescence*

The elemental composition of AMFF7-AMFF9 was determined using X-MET handheld device TXR 3000 using an X-ray source of Rhodium. Each sample of AMFF was measured for 60s. The results are shown in table 2. The results confirm the main constituents of the material, respectively, Ti, Ca, Ag.

*Film stability*

The Washability and Scrub resistance tester – Model 494, produces a repeatable, controlled condition to simulate every day use or wear patterns. Wet-scrub resistance can be used to determine the ability of coatings to resist damage caused by repeated washing operations. If the AMFF does not resist to the wet scrub, silver nanoparticles could be released from such material and the antimicrobial properties could dramatically decrease. Samples AMFF7-AMFF9 and CM (without AgNPs - was conducted under the same conditions as AMFF ) were applied on PVC foil and dried under normal atmospheric conditions. His abrasive sponge moistened with approximately 4g anionic detergent solution in water. The samples were subjected to 200 cycles of wet rubbing.

**Table 1**
CONDITIONS OF PREPARATION OF AMFF

| Film forming materials | Rheological modifiers Content [%] | Wetting additive Content [%] | Light stabilizers Content [%] | Silane coupling agent Content [%] | AgNPs content [ppm] |
|---|---|---|---|---|---|
| AMFF 7 | 1.5 | 1 | 3 | 0.2 | 100 |
| AMFF 8 | 1.5 | 1 | 3 | 0.2 | 150 |
| AMFF 9 | 1.5 | 1 | 3 | 0.2 | 200 |

**Table 2**
ELEMENT MASS PERCENTAGE OF AMFF SAMPLE FROM XRF SPECTRA

| Sample | Ti wt% | Ca wt% | Ag wt% |
|---|---|---|---|
| AMFF7 | 25 | 25.4 | traces |
| AMFF8 | 24.9 | 25.2 | traces |
| AMFF9 | 25.2 | 25.1 | traces |

| Sample | mass loss [g/m²] | thickness loss [µm] | silver loss (calculated [g/m²] | Class(SREN ISO 11998-2007) |
|---|---|---|---|---|
| AMFF7 | 1.8520 | 1.988 | 0.0001 | 1 |
| AMFF8 | 1.8520 | 1.988 | 0.0001 | 1 |
| AMFF9 | 1.8520 | 1.988 | 0.0001 | 1 |
| CM (without AgNPs) | 1.8519 | 1.987 | - | 1 |

**Table 3**
MASS LOSS AFTER 200 WASH CYCLES

*Expression of results*

Mass loss of the coating per unit area L, in g/m² is calculated using the equation 1. Losing in dry film thickness. L ρfu, in millimeters, is calculated using the equation 2.

$$L = \frac{m_1 - m_2}{A} \quad (1)$$

$$L_{\rho_{fu}} = \frac{L}{\rho_{fu}} \quad (2)$$

where:

A - is the area crossed by abrasive sponge, in m², $m_1$ - is the initial mass, in grams, of the test film and dry film; $m_2$ - is the mass, in grams, of the test film and dry film after 200 cycles of friction; ρfu -is dry film density in g / cm³.

Depending on the coating film thickness loss the coating fits as follows: Class 1< 5µm ; Class 2 ≥ 5 µm and < 20 µm ; Class 3 ≥ 20 µm and < 70 µm; Class 4 < 70 µm; Class 5 ≥ 70 µm at 40 cycles of wet rubbing.

Note that the calculated mass loss in the case of the silver, is very small (0.0001 g /m²), and is not influenced by the amount of the silver in AMFF, probably due to relatively low silver content (table 3). The results allow us to affirm that the silver is well embedded in the AMFF.

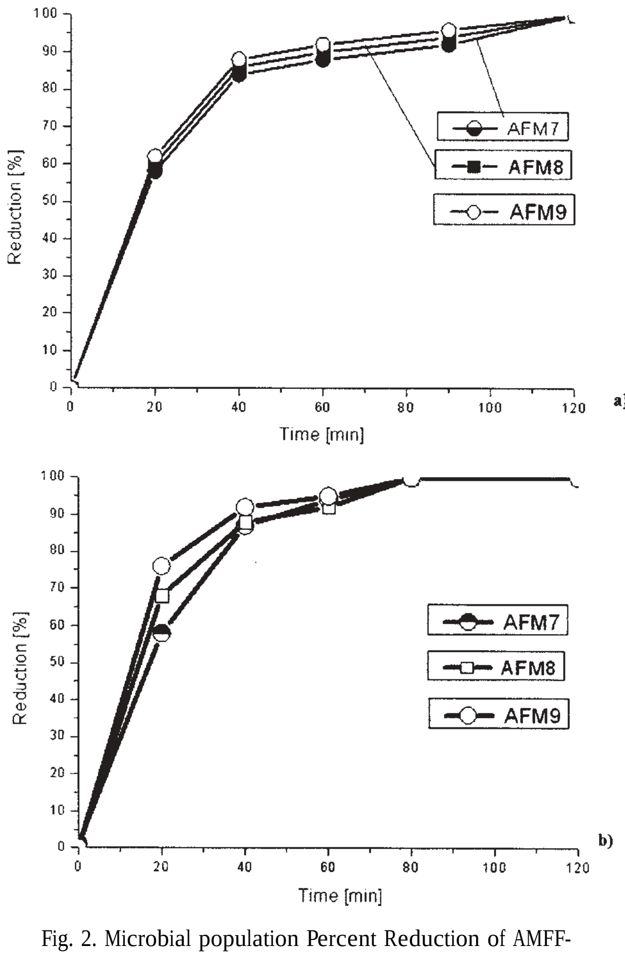


Fig. 2. Microbial population Percent Reduction of AMFF- a) on *Klebsiella pneumoniae* (Gram-negative); b) on *Bacillus cereus* (Gram positive)

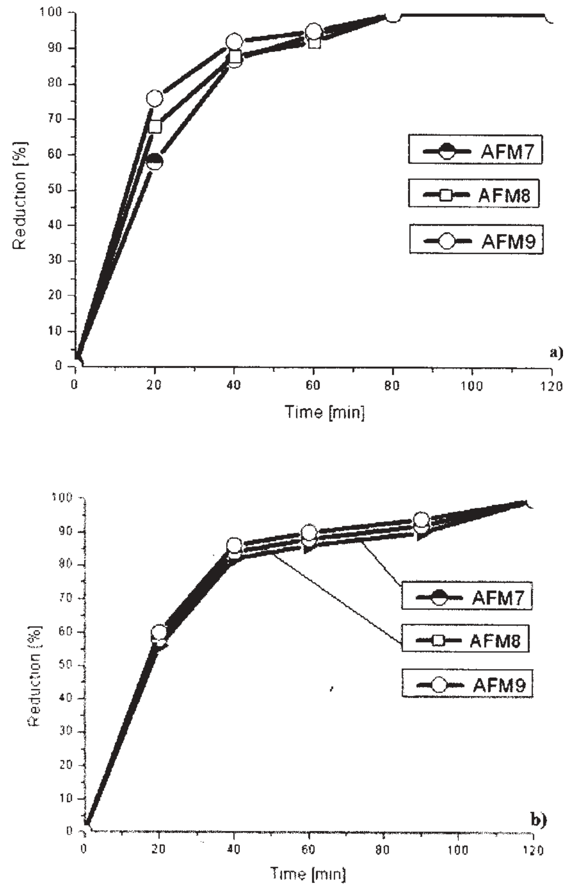


Fig. 3. Microbial population Percent Reduction of AMFF (after 200 washing cycles) - a) on *Klebsiella pneumoniae* (Gram-negative); b) on *Bacillus cereus* (Gram positive)

*Antibacterial properties*

The antibacterial activity of AMFF sample was assessed according to the ISO 27447 standard adapted. The number of samples tested for each kind of microorganism were 3 pieces of specimens. Film-forming materials were applied on the polyethylene and allowed to dry for 24 h. Were cut samples with sizes 2 x 2cm, then were placed in Petri dishes and inoculated with 0.38 mL of a bacterial suspension of ca 106 cfu/m. Antibacterial resistance of AMFF has been tested on the following species of microorganisms: *Bacillus cereus* (ATTC10876-Gram-positive) and *Klebsiella pneumoniae* (ATTC700603- Gram-negative) both cultured in Nutrient Broth Agar. The activity of the test material is quenched at specified sampling intervals (for example, 10, 20...120 min).

Results demonstrate that there was a significant reduction of bacterial populations for 2h (fig.2). The antibacterial activity was higher on *Klebsiella pneumoniae* with respect to *B. cereus*. AFFM9 samples induced the reduction (% reduction ≥ 99.98) on *Klebsiella pneumoniae* after 2h exposure (fig. 2). The antibacterial activity seems to correlate with content of AgNPs (samples AFFM7 and AFFM8), show lower activity than AFFM9.

AMFF are effective against gram-negative bacteria (*Klebsiella pneumoniae*) but for the gram-positive bacteria (*Bacillus cereus*), the effect is not so prominent (reduction 99.9%). It is believed that Gram-positive bacteria are not as sensitive to silver ions due to the thick layer of the peptidoglycan from the cell wall [26, 27].

Antimicrobial activity of film-forming materials that were subjected to 200 washing cycles was investigated by the same method and the results are shown in figure 3. Note that the antimicrobial activity is similar to that of film-forming materials which have not been subjected to washing. The antibacterial activity was higher on *Klebsiella pneumoniae* (% reduction -99.96) with respect to *B. cereus* (% reduction -99.89). We can say that AgNPs are well anchored in the film-forming material, and it is only released in a very small amount, which does not affect the antimicrobial properties and wet scrub resistance.

## Conclusions

Three antimicrobial materials AMFF1-AMFF3 with 100, 150 and 200ppm silver nanoparticles were obtained. The structure and morphology of coating materials were determined by XRF and scanning electron microscopy (SEM). It was proved that these formulations of film-forming materials with nanosilver in their composition have antimicrobial activity against *Bacillus cereus* and *Klebsiella pneumoniae*. The antibacterial activity seems to correlate with content of AgNPs (samples AFFM7 and AFFM8), show lower activity than AFFM9. Film-forming materials exhibit antibacterial activity even after 200 the repeated washing cycles.

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