

Silver Nanoparticle Deposition on Hydrophilic Multilayer Film Surface and Its Effect on Antimicrobial Activity

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ABSTRACT: Silver nanoparticles were deposited on the surface of the external polyamide 6 (PA6) layer of a multilayer film, by spraying and ultrasound-assisted methods. The effect of silver nanoparticles content and deposition method on the mechanical and optical properties of the multilayered films as well as the efficiency of silver ion release and their fungicidal characteristics were evaluated. Itaconic (IA) and Maleic anhydride (MA) were used as adhesion promoter agents for preventing the agglomeration of the silver nanoparticles and for improving the adhesion to the PA6 polymer surface. With IA, a homogeneous distribution of silver nanoparticles on the

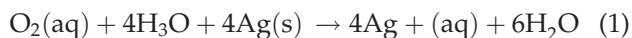
PA6 surface was achieved. The silver ion release and biocide effect of the multilayered films was found to be dependent on the anhydride type and on the deposition method used. The multilayer films with a layer of PA6-silver nanocomposite demonstrated good fungicidal activity, specifically against fungus *Aspergillus niger*. The observed results could be applied in the design of industrial films for packaging. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2643–2650, 2012

Key words: multilayered films; silver nanoparticles; nanocomposites; fungicidal properties; sonochemical

INTRODUCTION

Antibacterial agents can be broadly classified into two types, organic and inorganic. Organic antibacterial materials are often less stable particularly at high temperatures and/or pressures compared to inorganic antibacterial agents.¹ On the other hand, inorganic materials such as metal and metal oxides have attracted a lot of attention because of their ability to withstand harsh processing conditions.

It has been demonstrated that in aqueous environments metallic silver can release silver ions and inhibit the microbial activity.² Elemental silver particles can provide a large reservoir of antimicrobial silver ions, because in contact with hydronium ions in water and dissolved oxygen [O₂(aq.)] they release small amounts of silver ions according to eq. (1).³



The oxidation of elemental silver into ions according to eq. (1) occurs on the surface of the particles, only. For that reason, the concentration and rate of the silver ion release can be controlled by the surface to volume ratio of the silver particles that means by the particle size.

Since an aqueous environment is a critical condition for the ions release to occur, the water diffusion through a hygroscopic polymer matrix is essential. It is well known that water can diffuse through the crystalline layers of a Polyamide (PA) matrix.⁴ Water molecules can interact with carbonyl groups of the PA by hydrogen bonding and swell the PA matrix structure, enhancing the silver nanoparticles oxidation.

Silver has been used in various polymers^{5,6} to generate antimicrobial properties. Some commercial filler, such as zirconium phosphate, titanium dioxide, and some zeolites have been used as silver carriers. Silver-substituted zeolites are one of the most widely used antimicrobial additives in food packaging materials.

One example is the inorganic composite with a slow silver release rate, currently used as preservative in a variety of products.⁷ Another current application includes compounds with silica gel microspheres, which contain a silver thiosulfate complex, which is mixed into plastics for long-lasting antibacterial protection.⁸

The exact antimicrobial mechanism of silver is not known; however, it has been determined that the

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active agent is the ionic silver, which combines with the thiol (SH) groups, leading to the protein inactivation.⁹ There is evidence that the antibacterial and antifungal potency of silver is directly proportional to the concentration of silver ions in the solution.^{10,11} In this respect, the nanosized silver particles will have a larger surface area per unit mass and hence a higher ion release efficiency than bulk materials.^{12,13}

Dispersion of silver nanoparticles into a polymer matrix will therefore produce a polymer nanocomposite with antibacterial and antifungal properties. In this respect, the properties of nanocomposites are greatly influenced by both the nanoparticles dispersion degree within the polymer matrix and the interfacial adhesion between the components. However, the fine dispersion of nanoparticles in a polymer using conventional compounding techniques is a very difficult task, due to the strong tendency of nanoparticles to agglomerate and aggregate, losing the benefits of the nanometric size.^{14,15}

The polymer–nanoparticle interface plays an important role. Thus, the polymer modification with alkoxy silane groups has been applied in some studies to provide the covalent bonding to inorganic nanomaterials.^{16,17} Controlling the level of dispersion through intermolecular interactions, and exploiting these interactions to enhance the thermomechanical behavior, provides a broad field for polymer research.¹⁸ The homogeneous dispersion of silver nanoparticles on solid polymers, for example, is still a challenging area of research.

To protect the silver nanoparticles from oxidation, polar, water-soluble polymers such as poly(vinyl alcohol) (PVOH)¹⁹ and poly(vinyl pyrrolidone) (PVP)²⁰ are frequently used as protective coatings. The synthesis of silver nanoparticles, with an average particle size of ~ 8 nm homogeneously dispersed in PVP, has been achieved by the polyol reduction of silver nitrate with ethylene glycol (EG), using a sonochemical process.²¹

Different methods have been used to produce polymer–silver nanoparticles composites, including; *in situ* polymerization,²² sol–gel synthesis,²³ solid-state polymer transformation,²⁴ cosputtering silver nanoparticles into a polymer,²⁵ magnetron sputter coating of polymer with nanosilver,²⁶ and so forth.

The sonochemical method enables the synthesis of nanoparticles and their deposition on various substrates in a one-step procedure. The cavitation process of bubble growth and the subsequent explosive collapse of these bubbles, which take place during the sonochemical method of nanoparticle synthesis, help to avoid the agglomeration and force the penetration of the silver nanoparticles into the surface of the supporting substrate.²⁷

The preparation of multilayer films containing silver nanoparticles via layer by layer assembly of chi-

tosan–silver complex²⁸ and the deposition and immobilization of silver nanoparticles on different polymer surfaces,²⁹ have been reported, in both cases for antimicrobial purposes. However, the use of MA and IA as aids for the immobilization of the silver nanoparticles after its deposition on a polymer surface has not been reported.

Sonochemical irradiation has proven to be an effective aid for the synthesis of nanosized materials,²⁷ as well as for the deposition of nanoparticles into different substrates.³⁰

The present work deals with the study of the ion release capability of silver nanoparticles deposited, either sprayed or ultrasonically sputtered, on the external PA6 surface of a multilayer film structure, previously treated with itaconic or maleic anhydride for promoting the silver nanoparticles adhesion/immobilization.

The films ion release efficiency and antifungal properties are discussed as a function of the silver deposition method and the anhydride type used.

EXPERIMENTAL

Materials

The polymers used were linear low density polyethylene (LLDPE, Dowlex 2045), from Dow Chemical with a melt index of 1.0 g/10 min, a graft copolymer of maleic anhydride onto polyethylene (PEgMA), Fusabond E-MB226 from Du Pont, and a polyamide 6 (PA6), Tebenyl-6 3100 from Engineering Resins. Prior to processing, PA6 was dried in a vacuum oven for 10 h at 85°C. The silver nanoparticles were from *Nanostructured and Amorphous Materials Inc.* These nanoparticles had a polyvinylpyrrolidone (PVP) oxidation protective coating. Ethylene Glycol (EG) with a boiling point of 197.1°C, Itaconic Anhydride (IA) with a boiling point of 114°C and Maleic Anhydride (MA) with a boiling point of 202°C from Aldrich Chemicals were used as received.

Preparation of multilayer film

The film used for the study was prepared by coextruding polyethylene and PA6 as the two external layers and PEgMA as adhesive layer, in a three-layer 40 ± 2 μm thick flat film, "PE/Adhesive/PA6," using three-single-screw extruders ($L/D = 24$, KTS-100 from Davis Standard, USA) connected to a multilayer feed block fitted with a flat die. The die temperature was fixed at 250°C. The film layer thicknesses were: PE = 15 ± 1 μm , Adhesive = 5 ± 1 μm and PA6 = 20 ± 1 μm .

Preparation of the silver nanoparticles suspensions in a water–ethylene glycol 10 : 1 solution with each of the two different anhydrides (Ag/EG/IA and

Ag/EG/MA suspensions) were carried out using ultrasonic irradiation. A sonicator, AMCR-5118 from Industronic, Mexico, at 300 W and 20 kHz was used for this purpose. Previous to the ultrasonic irradiation, the silver nanoparticles were thoroughly rinsed with water to remove the water soluble PVP oxidation protective coating.

The silver nanoparticles suspension was sprayed using a metallic sprayer to form a thin layer over the external PA6 layer of the coextruded film structure. The silver suspension was also ultrasonically sputtered on the PA6 layer, introducing the film structure into a sonicator and irradiating it for 30 min with a high-intensity ultrasonic horn. The coated films were thoroughly washed with water to remove loose and poorly adhered silver nanoparticles.

Characterization of the multilayer films

The mechanical properties of the resulting multilayer films were measured according to ASTM D 882 with an Instron Model 4301, USA. Light transmission and haze were determined according to ASTM D1003, using a Hazegard Plus from BYK Gardner, USA. Film surfaces were studied with a Jeol-JSM7104F with a STEM modulus and a field emission gun at an accelerating voltage of 200 kV. To monitor the silver ion release, the composites were introduced in bottles containing distilled and deionized water and continuously shaken. The analytes collected were used to quantify the silver ion released by the composites at various time intervals, up to 14 days, using a Thermo Jarrel-ASH, USA IPC spectrophotometer.

The microbiological tests were performed for qualitative purposes, in PDA medium and for quantitative purposes, according to ASTM E 2149-01. The samples were tested against a fungus *Aspergillus niger* (ATCC 6275), supplied by American Type Culture Collection (ATCC). The strains were grown and multiplied in PDA medium, at 28°C for 72 h.

The test was made by inoculating the *A. niger* in PDA, then a film of 2.5 cm diameter previously sterilized with ethanol was placed in a Petri dish that was immediately incubated at 28°C for 72 h. After this, the samples were visually analyzed for the inhibition of fungi growth. Three replicas were examined for each treatment.

An autoclave (Tuttnauer BRINKMANN 2540E) was used for the broth medium sterilization, at 121°C for 15 min. The films formulated with silver nanoparticles were previously sterilized with ethanol. A strain concentration of 10^6 CFU was used in the antifungal tests. The antifungal activity was evaluated by inoculating *A. niger* in potato-dextrose broth at 28°C, followed by the addition of each one of the films. The flasks were then immediately incubated in a rotary shaker (at 150 rpm) at 28°C for

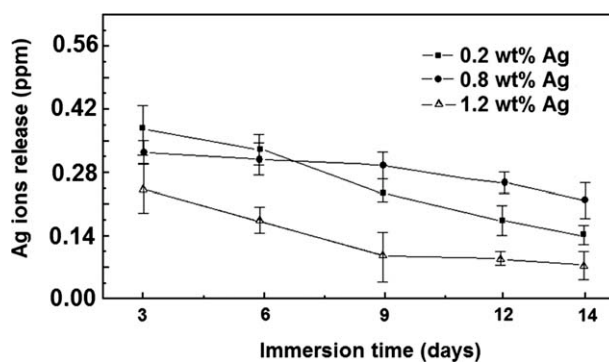


Figure 1 Silver ion release as a function of immersion time for samples with different silver contents and IA contents equivalent to 2.5 times the silver content. Silver deposited by spraying.

72 h. Five replicas were examined for each treatment. In all cases, a control sample (broth medium) and a reference multilayer film without silver nanoparticles were tested as references.

The inhibition percentage in the fungus growth was evaluated by comparing the biomass between the tests and reference samples after 72 h of incubation.

RESULTS AND DISCUSSION

Effect of silver content and stabilizing agent type and content

Figure 1 shows the silver ions (Ag^+) release from film samples onto which the silver nanoparticles suspension (Ag/EG/IA) was sprayed, with different silver contents and IA contents equivalent to 2.5 times the silver content. It is observed that in all cases, the amount of released Ag^+ decreases with the immersion time in distilled and deionized water. In addition, at all immersion times, the sample with the higher silver concentration shows the least amount of released Ag^+ .

It can be assumed that at 0.2 and 0.8 wt % Ag, the nanoparticles still maintain their homogeneous distribution without agglomeration, but at 1.2 wt % Ag, the concentration became sufficiently high as to surpass a saturation point and present agglomeration, which would appear as having microparticles, with less surface area able to liberate Ag^+ .

Figure 2 shows the silver ions (Ag^+) release from film samples onto which the silver nanoparticles suspension (Ag/EG/IA), with an IA concentration equivalent to 1.0, 2.5, and 3.0 times the silver content and 0.8 wt % of Ag was sprayed. At 1.0 and 3.0, the Ag^+ release decreases markedly after nine days of immersion times. In general, the largest Ag^+ release was obtained with an IA content of 2.5 times that of silver for almost all the immersion times, probably because this IA content is sufficient to stabilize this

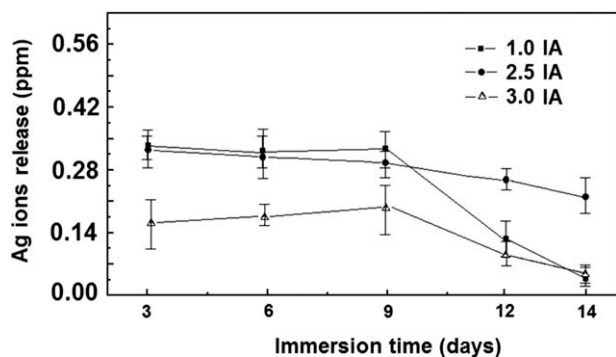


Figure 2 Silver ion release as a function of immersion time for samples with 0.8 wt % of silver nanoparticles and IA contents of 1.0, 2.5, and 3.0 times the Ag content. Silver deposited by spraying.

silver nanoparticle content (0.8 wt %). This IA content would avoid silver nanoparticle agglomeration which would offer higher surface area, and thus increase the amount of released Ag^+ . Considering the results presented above, 0.8 wt % of silver nanoparticles and 2.5 wt % of IA or MA (2.5×0.8) were the selected concentrations for the rest of the study.

Silver ion release

Figure 3 shows the Ag^+ release at different times for samples with 0.8 wt % silver nanoparticles prepared by spraying and ultrasonic sputtering. All nanocomposite samples present Ag^+ release. This indicates that the silver oxidation on the polymer surface is taking place. Samples with silver but without MA or IA show the lowest level of Ag^+ release. On the other hand, it can be observed that: (a) samples with IA as stabilizing agent presented a higher amount of Ag^+ release as compared with those with MA, no matter if prepared by spraying or ultrasound; and (b) samples prepared via the ultrasonic method presented a much higher amount of Ag^+

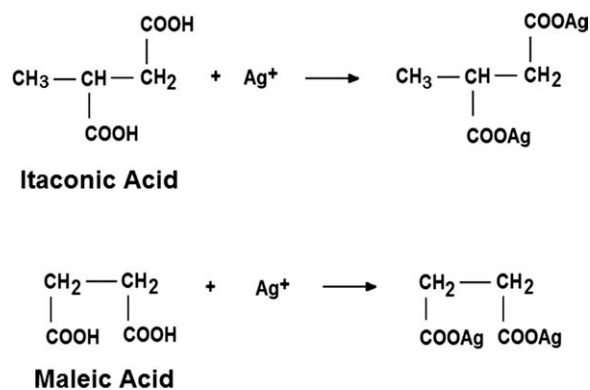


Figure 3 Silver ion release as a function of immersion time for samples with 0.8 wt % of silver nanoparticles and IA or MA contents of 2.5 times the Ag content. Silver deposited by different methods.

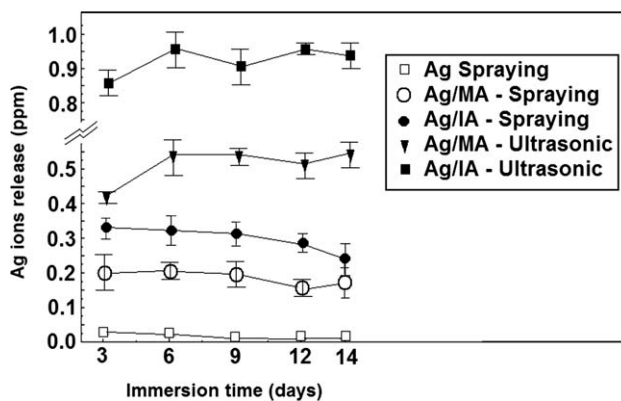


Figure 4 Scheme of the possible interactions between silver nanoparticles and Maleic acid (MA) or Itaconic acid (IA).

release as compared with those prepared by spraying, no matter the anhydride used. Finally, the highest amount of Ag^+ release was presented by those samples prepared via the ultrasonic deposition method, using IA as stabilizing agent.

This indicates that the ultrasonic method improves the particle dispersion by exposing the Ag particles to alternate compression and expansion modes that fragment the silver agglomerates, greatly increasing the surface area to volume ratio of the nanoparticles and positively affecting the ions release. Both IA and MA can form silver salts according to the reaction scheme on Figure 4.

The better performance on Ag^+ release, observed by the IA over the MA on these silver complexes, may be explained on the basis that the position of the carboxylic groups in the IA facilitate the fast Ag^+ release from the compound (Scheme in Fig. 4) which is not the case with MA compound in which the carboxylic groups are closer to each other in its formula (Scheme in Fig. 4). So, the silver ions release was lower due to the difficult mobility of these ions into the medium. These results are in good agreement with those reported by other authors.³¹

Stem analysis

Figures 5 and 6 show the STEM images and the silver particle size distributions for the samples prepared via the spraying and the ultrasonic sputtering methods respectively, for each case, with MA and IA. The silver nanoparticles size distribution is quite different when comparing the two different agents. The MA-treated samples show many agglomerates which appear in the STEM images as a few particles of a very large size whereas the IA samples show much less agglomeration which appear in the STEM images as many particles of a smaller size.

In the case of samples prepared via the spraying method, samples with MA showed an average silver

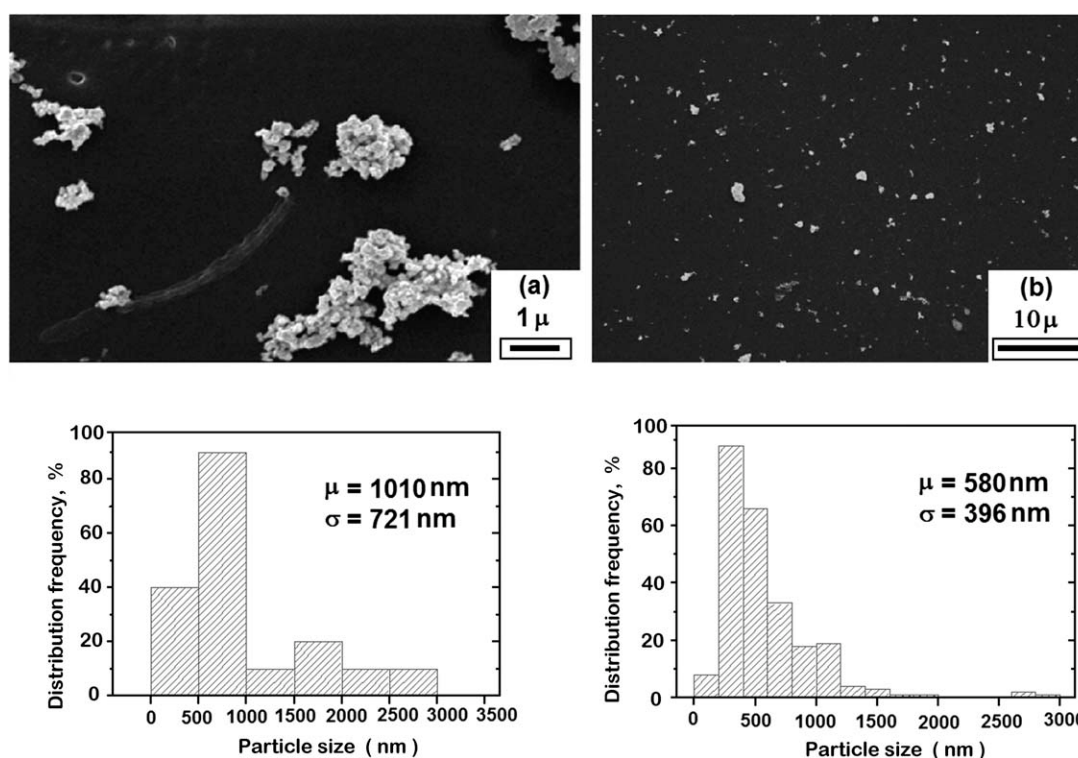


Figure 5 STEM images and the histograms of silver particle size distribution, showing the average particle size (μ) and standard deviation (σ) of PA6-silver nanocomposite with: (a) MA and (b) IA, prepared using spraying method.

particle size of 1010 nm, whereas samples with IA showed an average particle size of 580 nm. In the case of samples prepared via the ultrasonic sputtering method, samples with MA showed an average particle size of 540 nm, whereas samples with IA showed an average particle size of 140 nm.

That is, independently of the silver deposition method, samples with IA showed the smaller average particle size; and independently of the stabilizing agent used, samples prepared via the ultrasonic sputtering method, showed the smaller average particle size.

This indicates that the ultrasonic method improves the particle dispersion by exposing them to alternate compression and expansion modes that would fragment the silver agglomerates and result in a much lower particle size.³² These results are in agreement with those reported by several authors that found that ultrasound uniformly disperses nanoclay particles and helps in the process of clay exfoliation.^{31,33} This suggests that a well distributed particle deposition on the polymer surface could be obtained when using the ultrasonic deposition method and IA as the compatibilizer.^{34,35}

When using ultrasonic method, the Ag nanoparticles are bombarded at very high speeds by the micro jets and shock waves created near solid surfaces after the collapse of the bubbles,³⁴ This bombardment will cause the sintering of nanometer-sized particles onto the polymer surface.³⁵

During the sonication processing silver does not form any chemical bond with the PA, but rather, it penetrates the polymer surface and it is adhered to the polymer via the sintering process described above.

Mechanical properties

Table I presents the tensile properties of film samples with 0.8 wt % of silver nanoparticles deposited on its surface by spraying and ultrasonic methods. It is observed that the modulus and tensile strength of samples treated with IA remain approx equal to those of the reference sample, irrespective of the deposition method used, whereas those treated with MA present a reduction in modulus and tensile strength, attaining only $\sim 80\%$ of that of the reference. This difference in properties was attributed to the difference in the silver nanoparticles dispersion, which is more improved when using IA as stabilizing agent and when using ultrasonic sputtering as the silver deposition method.

Optical properties

Table I also presents the light transmission and haze properties of the reference and treated films. It can be observed that: the samples prepared via the ultrasonic method, either treated with IA or MA, as well as the samples prepared via the spraying method

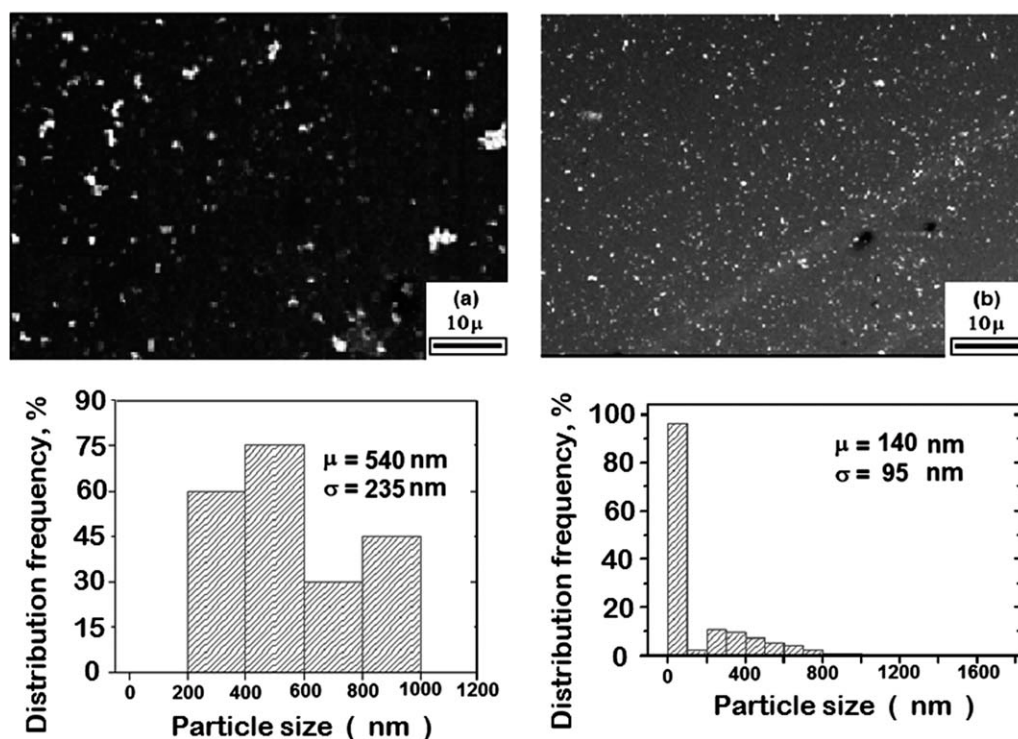


Figure 6 STEM images and the histograms of silver particle size distribution, showing the average particle size (μ) and standard deviation (σ) of PA6-silver nanocomposite with: (a) MA and (b) IA, prepared using ultrasonic irradiation method.

with IA, present a light transmission practically equal to that of the reference film. The sample prepared via the spraying method with MA, present a reduced light transmission and an increased haze.

This suggests that the ultrasonic deposition method as well as the IA tend to produce the best nanoparticle dispersion and the least nanoparticle agglomeration which in turn will produce the least interference with the visible light transmission.

Antifungal activity

It can be observed in Figure 7, that all samples containing silver nanoparticles [Fig. 7(b–e)], show a certain degree of antifungal activity, as can be inferred

from the “clean” inner disk in each sample. On the other hand, this inner disk is completely covered by fungi in the reference sample [Fig. 7(a)]. In addition, within samples containing silver, the “cleanest” inner disk, i.e., the strongest antifungal activity, is observed when using the ultrasonic method for the silver deposition and IA as stabilizing agent.

The tests for the growing inhibition against fungus “*A. Niger*” were performed in analytes collected after maintaining the samples in deionized water for 14 days with continuous shaking. It can be seen (Fig. 8) that after 14 days, the biocide effect of the samples is maintained, since all samples containing silver nanoparticles showed a strong fungus growing inhibition as compared to the reference sample.

TABLE I
Mechanical and Optical Properties of the Multilayer Films

Sample	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Light trans-mission ^a (%)	Haze ^b (%)
Reference film	130 ± 6	37 ± 3	730 ± 25	92.2 ± 6	14 ± 4
Ultrasonically deposited Ag					
Itaconic Anhydride	135 ± 5	38 ± 4	600 ± 25	91.5 ± 5	14.1 ± 3
Maleic Anhydride	103 ± 4	28 ± 4	565 ± 20	89.0 ± 8	16.0 ± 5
Sprayed Ag					
Itaconic Anhydride	121 ± 7	39 ± 3	580 ± 20	90.5 ± 4	15.4 ± 4
Maleic Anhydride	99 ± 5	32 ± 2	585 ± 25	81.5 ± 8	21.0 ± 5

^a Ratio of total transmitted light to incident light.

^b Transmitted light that deviates from the incident beam by more than 2.5° on average.

Samples prepared via the ultrasonic deposition method present a greater inhibition, especially the one using IA, which showed a remarkable 45% inhibition.

Considering that the inhibition effect is directly related to the Ag⁺ release, the above-mentioned results can be assumed to be due to the better distribution and dispersion of the silver nanoparticles attained when using the ultrasonic deposition method with IA as stabilizing agent. In such case, the silver nanoparticles will present a large surface area, which in turn will result in a high Ag⁺ release (0.93 ppm). These results are in good agreement with those reported by other authors.³⁶

CONCLUSIONS

Coextruded polymer films were prepared, with an external PA6 layer, onto which silver nanoparticles were deposited either via the ultrasonic or the spraying methods, using either IA or MA as stabilizing agents, as described above.

The best antifungal properties, combined with a negligible effect on the mechanical and optical properties were obtained when using the ultrasonic method for the silver deposition and IA as stabilizing agent. The combination of ultrasonic method

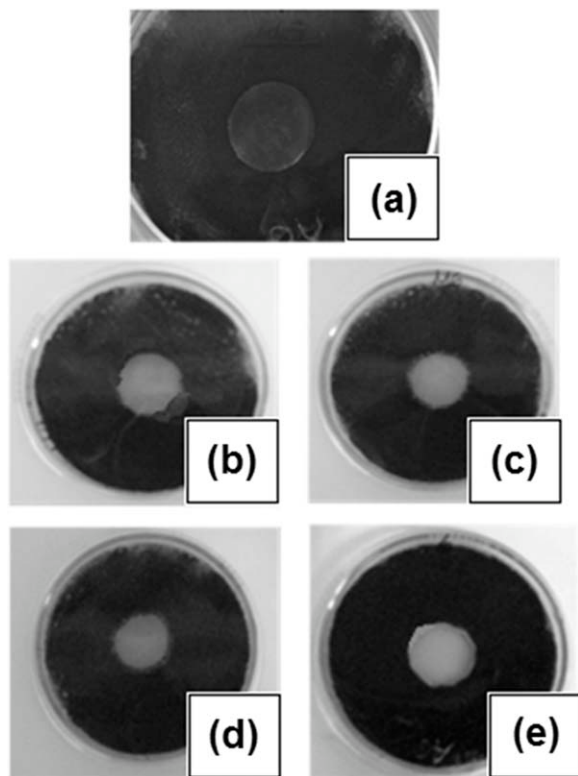


Figure 7 Photographic image of the incubation of fungus *A. Niger*, after 72 h on: (a) reference multilayer film, (b) sample with MA by spraying, (c) sample with IA by spraying, (d) sample with MA by ultrasonic, and (e) sample with IA by ultrasonic.

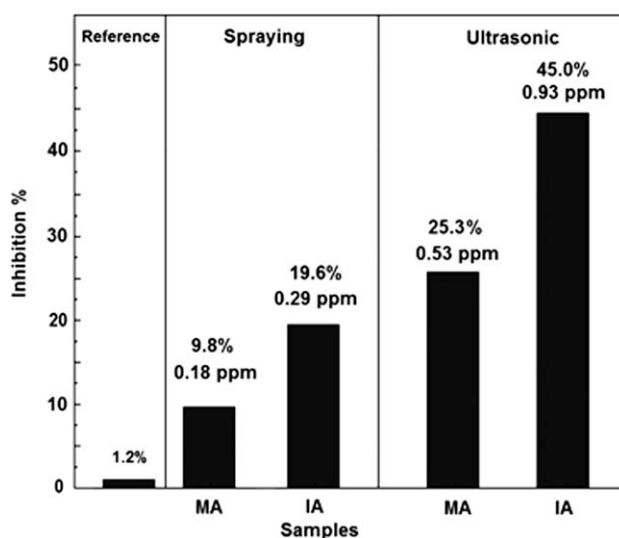


Figure 8 Reduction of inhibition power against fungus *A. Niger*, of samples of the silver nanoparticles studied, after 14 days.

and IA produced the smallest silver average particle size, 140 nm. The spraying method and MA, on the other hand, produced the largest particle size, 1010 nm. The difference was attributed to the cavitation process generated during ultrasonic exposition, in which the Ag nanoparticles are bombarded at very high speeds towards the polymer surface, providing their strong adhesion to the polymer substrate, without giving chance for agglomeration. The great difference in the size of the deposited silver particles (nanosized versus microsized) had a tremendous effect on the antifungal, as well as in the mechanical and optical properties.

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