



Antimicrobial silver coating using PVD-PECVD system

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Physical vapor deposition - plasma enhanced chemical vapor deposition (PVD-PECVD) system has been used exclusively for deposition and doping of carbonaceous films [silver nanoparticles (Ag-NPs)] on cotton fabrics and the findings are compared, in terms of technical efficiency and microbial inhibition, with those of the magnetron sputtering (MS) technique. It is found that the proposed technique presents promising characteristics for the deposition of silver nanoparticles (Ag-NPs) on textiles, which meet the industrial demand.

Keywords: Antimicrobial properties, Active plasma screen, Magnetron sputtering, Plasma enhanced chemical vapor deposition, Physical vapor deposition, Silver nanoparticles

1 Introduction

In hospitals, cotton textiles comprise several products, such as masks, catheters, gowns, hygiene products and curatives^{1,2}. With heat and moisture from the skin, these materials become prolific for pathogens, such as *Staphylococcus hominis*, and this may compromise the prognosis of immunosuppressed patients^{1,3,4}.

In view of this problem, the textile industry has sought efficient ways to incorporate Ag-Ps, classically recognized for its antimicrobial effect, into textiles⁵. Due to its methodological simplicity and to require a low investment in equipment, the dip-coating method has been expressively used by the industry. However, this technique has disadvantages, such as use of Ag-Ps may be susceptible to loss in quality, and sensitive to small vibrations in the environment, which completely compromise the homogeneity of the films generating losses^{1,6-8}.

Numerous researchers have searched for methods capable of overcoming this technique, and have obtained interesting results by means of systems based on electric plasmas, such as MS techniques and discharge dielectric barrier (DBD)^{9,10}. Because they are based on the use of electric plasmas, these techniques

generate small amounts of process residues, are economical, as well as efficient in depositions. The DBD technique has been used successfully only to fix Ag-Ps by batching in the textiles, something that the system MS is not able to do so, although it is the only option, so far studied, capable of producing the particles it deposits on textiles.

Recently, Capote *et al.*¹¹ modified the system plasma-enhanced chemical vapor deposition (PECVD) including an additional cathode "Active screen plasma (ASP)", which made it potentially capable of meeting the demand for a highly versatile, economical, efficient technique that offers unique control over the variables of the film deposition process. The PVD (physical vapour deposition) modified PECVD process (PVD-PECVD) is based on the interaction among different types of chemical specimens (electrons, ions, atoms, molecules) generated by the plasma, and the exchange of energy between them and the ASP. Unlike an original PECVD because it contains a variable composition of ASP, the modified systems (PVD-PECVD) can produce diversified films without the use of solvents, depending only on the composition of ASP, which acts similar to the targets of MS systems. In addition, ASP raises the deposition rate of PECVD by making the plasma denser, and thus represents an advance in relation to the original technique, for making

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evaporation / sputtering depositions in a system originally designed for another purpose¹².

This technique is widely used for the deposition of thin films of semiconductors, amorphous materials, transparent films and carbon films. However, its application has been neglected to textile industry till date^{12,13}. Therefore, the present work aims at producing Ag-Ps coatings on cotton fabrics using PVD-PECVD system to determine their physical, chemical and antimicrobial effects, and to compare the results with the conventional magnetron sputtering technique.

2 Materials and Methods

2.1 Preparation of Samples

A set of 80 samples of raw cotton fabrics (1.5 cm² and 1 mm thickness) has been produced and then equally distributed in 16 groups. Each group consisted of 5 elements which were intended for plasma treatment. The sample set was subjected to a mechanical cleaning process with neutral detergent and water, and then to an acetone bath for 10 min on a QUIMIS Q335D ultrasound system. The cleaning procedures were terminated by drying the samples for one hour at 60 °C inside a sterilifer digital oven (model SX 1.0 DTME), and with ozone plasma

2.2 Silver Deposition Process

All procedures were performed in a pulsed DC source PECVD system, produced by nanomaster (model NPE-4000), using a silver ASP as an additional cathode. The samples were placed on the original cathode of the PECVD, while the ASP, as a hollow cathode, was positioned on the samples. Table 1 shows the general parameters maintained during deposition process, of which only the deposition time and the plasma power were varied as a function of the group produced.

2.3 Characterization of Film

The characterization of the films began with the morphological analysis of the cotton fibers, using

Table 1 — Parameters kept constant during the silver deposition

| Parameter | Set |
|-------------------|-----------|
| Pressure | 0.03 torr |
| Pulse | 100 kHz |
| Reverse pulse | 0.8 μs |
| Voltage | 650 V |
| Current | 0.6 A |
| Temperature range | 18-50 °C |
| Gas | Oxygen |

high resolution images produced by scanning electron microscopy (SEM, model Inspect F50). Images were produced by backscattered electrons and secondary electron emission respectively with an acceleration voltage of 20 kV and 3 kV. Ag-Ps were quantified by the percentage by weight of silver atoms (PWAg) present in the total chemical composition of the films. The samples were then coated with an Au-Pd conductive film (80-20% by mass), and then a total of 80 spectra were taken per quintuplet of the sample groups, obtained by X-ray spectroscopy by dispersion in power (EDX). The PWAg was determined by the arithmetic mean of the values found in the quintuplicates of each group. The amount and diameter of the Ag-Ps were determined by means of computational image analysis of the samples produced by SEM. In order to read this data, the images were processed in the Image J software.

The thickness of the films and the maximum amplitude of the roughness of the samples were determined by 3D optical profilometry in a KLA-Tencor system, capturing data by means of 21 and 11 traces of 199.797 μm respectively in the groups covered and not covered by Ag-Ps, at a speed of 100 μm/s and a frequency of 200 Hz. The thickness of the films was directly measured by the equipment, the maximum amplitude of the roughness of the samples was determined by calculating the difference between the roughness of the group with higher PWAg, and the roughness of the fabrics not covered by the film. Therefore, the measurements were made in 10 samples, corresponding to the quintuplets of each group, and expressed by mean ± standard deviation of root mean square value (RMS) of each group, which express the statistical measure of magnitude of the roughness variation along the surface of the samples.

The wettability of the surface of the samples was determined on the basis of the sessile drop principle by analyzing the static contact angle (CA) of the water droplet (polar liquid). The volume of the droplets was kept constant at 2 μL. All five replicates of the samples were analyzed in the Kruss DSA 100 equipment for a period of 3-14 days after the production of the coatings. The data collected were reported as a function of the arithmetic averages ± standard deviation determined.

2.4 Determination of Deposition Rate of PVD-PECVD System

The average deposition rate of the PVD-PECVD technique was calculated based on the ratio of the film

thickness to the elapsed time to produce it. The results were expressed in $\mu\text{m}/\text{min}$.

2.5 Microbiological Test

Different samples coated with Ag-Ps were positioned in 16×60 mm petri dishes seeded with *Staphylococcus hominis* (ATCC 700586) at the concentration of 9×10^8 cells / mL. The cells were cultured in 5 mL tryptone soy agar (TSA) medium. The culture plates were incubated at 37°C for 7 days with the faces coated with the quintuplets of each group facing the culture medium. The antimicrobial effect was observed when the colony growth was limited to the edge of the samples; however, the other cases no antimicrobial effect was observed.

2.6 Antimicrobial Effect Test

The set of samples, that presented the highest efficiency in the microbial test was used for the antimicrobial effect test. This test was designed to elucidate whether the inhibition of microorganisms caused by Ag-Ps results from a microbiostasis, or cell death process. The set of samples selected was sterilized in a vertical model braslact autoclave at 120°C , 1 atm for 15 min. Then, the group was immersed in 5 mL of 10% saline, contaminated with 9×10^8 cells/ mL of *S. hominis*. At the end of this step, the samples were placed in Petri dishes

containing 5 mL of sterile TSA medium, and incubated for 5 days at 37°C .

The microbicidal effect was verified in the cases where there was no growth in microbial cultures; however, in the other cases microbiostasis effect was observed.

2.7 Comparison between MS and PVD-PECVD Techniques

PVD-PECVD and MS deposition techniques were compared in terms of Ag-Ps concentration, film thickness, size of Ag-Ps, and antimicrobial effect, in order to answer the following hypotheses:

(i) Null hypothesis (H_0) —there are no statistically significant differences between films produced by PVD-PECVD or Magnetron Sputtering.

(ii) Alternative hypothesis (H_a) —there are statistically significant differences between films produced by PVD-PECVD and Magnetron Sputtering.

The results produced by the present study were compared to those obtained by three authors^{2,10,14} who conducted experiments under similar conditions, using cotton textiles.

3 Results and Discussion

3.1 Production of Ag-Ps Films

Initially the white cotton [Fig. 1(A)] becomes silvery [Fig. 1 (B)] due to the presence of Ag-Ps on

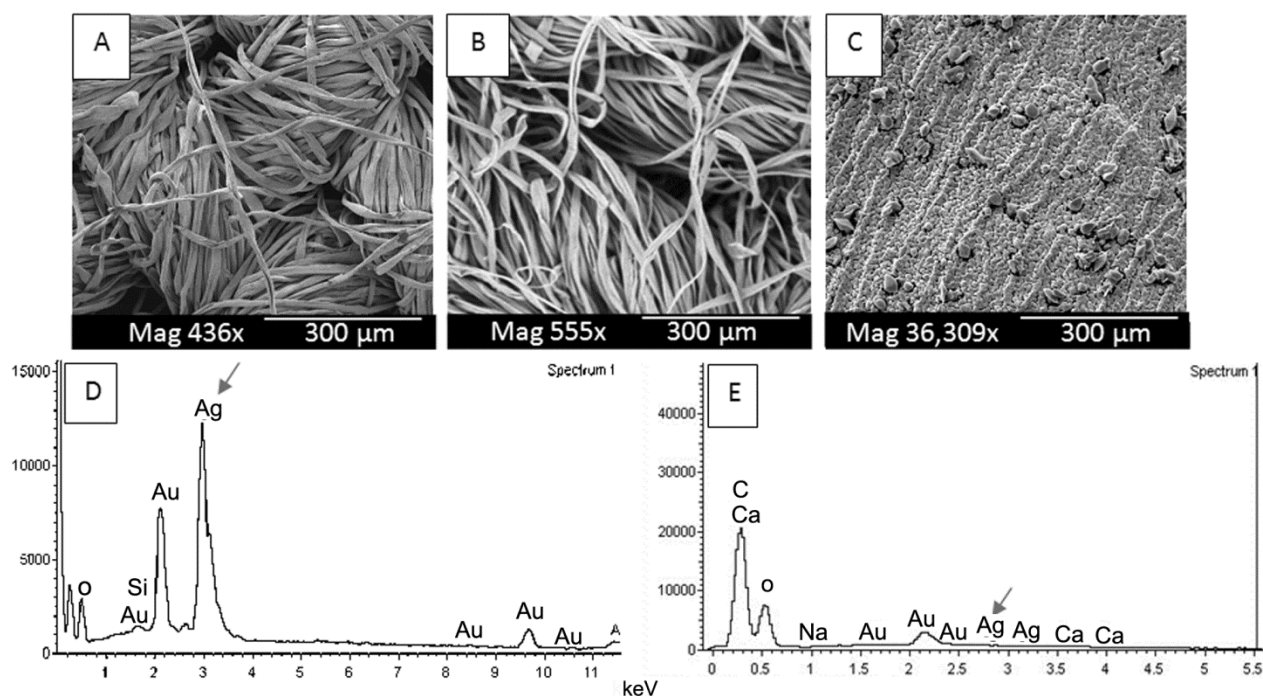


Fig. 1 — Comparison between coated and uncoated cotton with Ag-P: (A) cotton in natural state ($\times 436$), (B) cotton coated with Ag-P ($\times 555$), (C) Ag-P on cotton surface ($\times 36,000$), (D) EDX spectra of natural cotton and (E) EDX spectra of Ag-P coated cotton

the textiles [Fig. 1 (C)]. As indicated by the reading of the EDX spectra, the coated groups [Fig. 1 D] show prominent peaks corresponding to the silver atoms; which are not present in the uncoated groups spectra [Fig. 1 (E)]. This result corroborates with the hypothesis that the PVD-PECVD technique is able to produce Ag-Ps films on cotton textiles.

3.2 Morphology of Film

The films have been studied in both region, and also in the central region. According to the analysis by “Image J” software, the Ag-Ps present in the central region [Fig. 2 (A)] has diameter ranging from 1nm to 20nm. The particles of 1 nm are expressive in the total composition of the film, corresponding to approximately 60% of the coating. The dimensions of Ag-Ps varies according to their distance from the massive film, since more distant / isolated particles are larger than those closest to the coating [Fig.2 (B)].

The phenomenon described is based on the principle of mass / energy conservation, since the clusters arose from the collision of newly ejected ASP atoms, with others previously deposited on the

substrate. Therefore, the energy resulting from the collisions is accumulated in the clusters till reaches the melting point of the silver, redistributing the masses of the clusters evenly on the surface of the fabric. Consequently, the films produced by PVD-PECVD are structured similarly to those produced by MS systems^{14,15}. This phenomenon can be easily understood by observing an ice cube melting on a flat surface, since the observed phase change in this material stems from the increased kinetic energy of the water molecules, liquefying the ice cube, and provoking the uniform redistribution of its mass, as occurs with the clusters of Ag-Ps in the formation of the films. Evidences, such as the occurrence of carbonation points on the substrates of the 200 W / 5-10 min groups [Figs 3(A), (B), (D), (E)], corroborate with the analysis provided hereunder. Considering that the samples do not expose to exogenous heat source during the film production, the only cause of their carbonization is the release of excess energy accumulated in the clusters. According to the present hypothesis, the other groups do not present carbonation points because the amount of energy

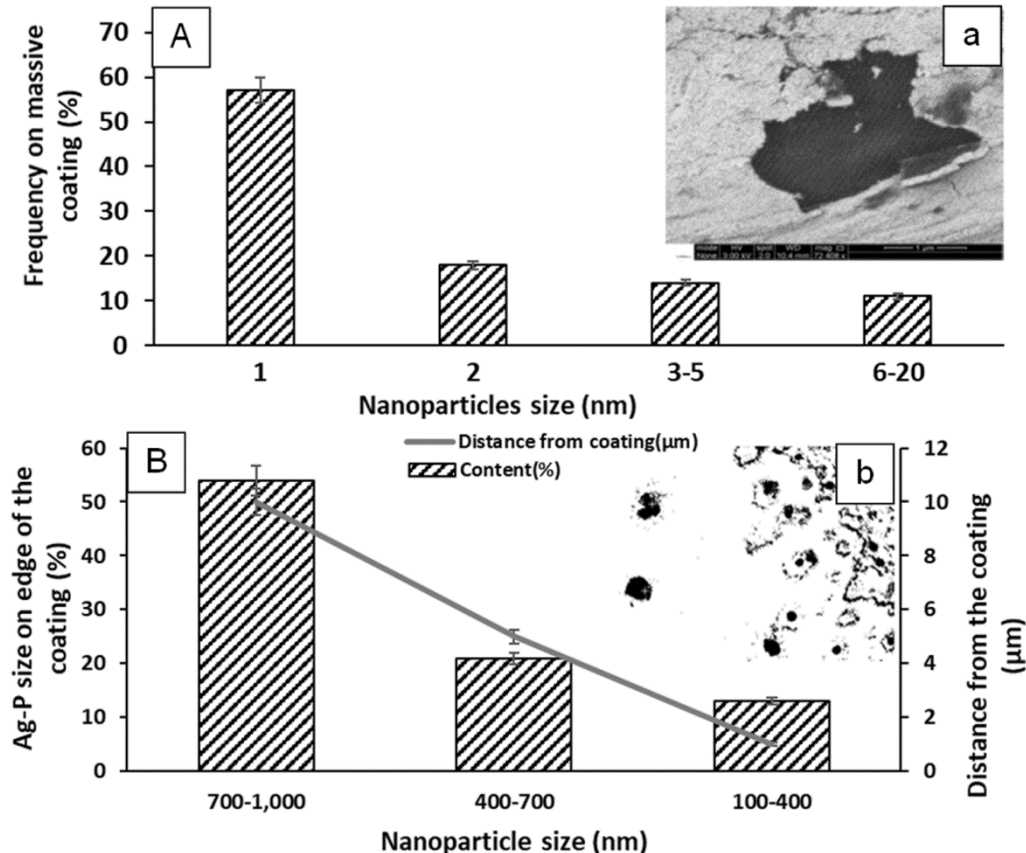


Fig. 2 — Relations of Ag-P sizes with the film edge and massive coating (A) relation between Ag-P sizes on edge of samples and its distance from the massive coating (insert a) $\cong \times 72,400$ and (B) frequency of Ag-P sizes on massive coating (b) $\cong \times 10,000$

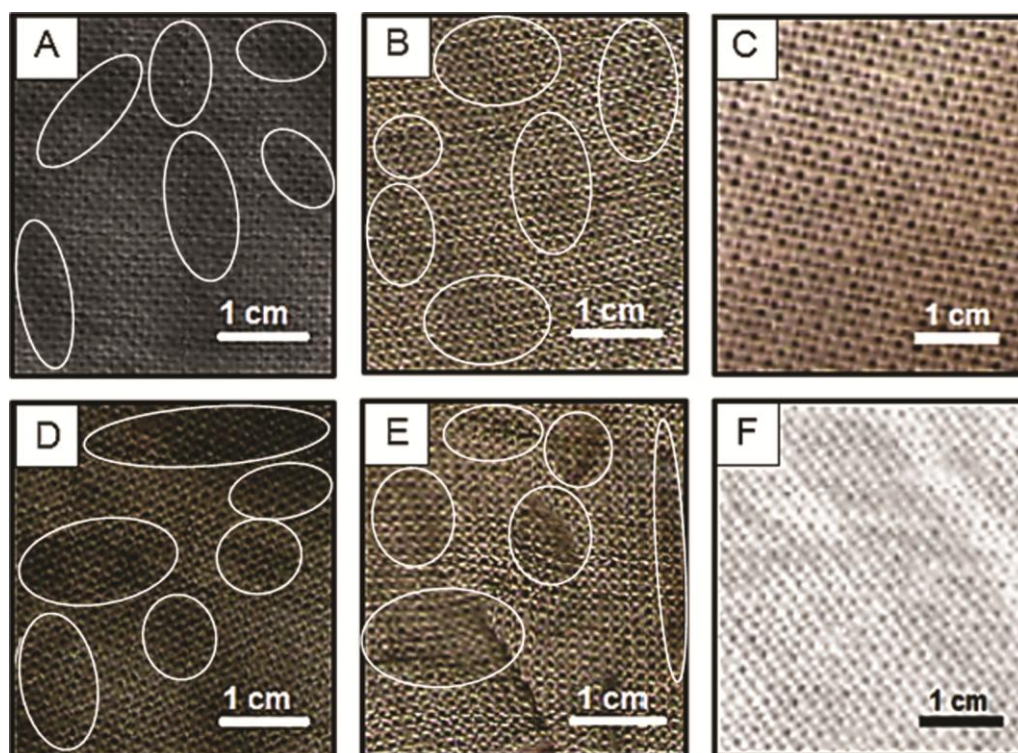


Fig. 3 — Representative images of groups with/without carbonization points: 200 W 10 min [front (A) and back (D)]; 200W 5 min [front (B) and back (E)]; other groups [front (C) and back (F)]. The presence of white circles highlights carbonized regions in samples (A) / (D), and (B) / (E); not present in sample (C) / (F).

accumulated in their clusters is not excessive [Figs 3(C) and (F)].

Morphological analysis also shows that the subprocesses, through which the particles are ejected from the ASP, determine the size of the clusters. It is observed that the variation in Ag-Ps diameters is a consequence of the deposition subprocesses deriving from the PVD-PECVD techniques (sputtering and evaporation). The particles from sputtering presented higher energy and lower grain size in comparison to those produced by evaporation, which present low energy and larger size grain^{16,17}. Thus, the portion of the samples directed towards the center of the ASP receives more particles from the evaporation process, whereas the parts facing its edge receive more particles from the sputtering process, since the region of the plasma sheath around the ASP extends ~ 60 mm, from its surface. Therefore, the uniformity observed on coatings is understood as a consequence of both the aggregation of the Ag-Ps isolated by the fusion clusters and the redistribution of their mass in equal parts by the substrate.

The large difference between the Ag-Ps diameters of each group corroborates the position of Kelly¹⁵ and Mejía¹⁴, adapted to the PVD-PECVD technique, that

the Ag-Ps are ejected from the ASP through the sputtering and evaporation subprocesses. According to the definition of these subprocesses, the smaller Ag-Ps, formed by particles ejected by sputtering, receive matter from the larger Ag-Ps. These are formed by particles from the evaporation, and found in the size of 1 nm, the point of equilibrium between their redistributed dimensions, because this size is the most frequent in the massive portion of the film. This effect occurs similar to two ice cubes of different sizes held in contact, which level off in terms of volume when the water resulting from their liquefaction mixes. If this volume of water loses enough energy to solidify, a single ice stone is formed whose dimensions are the average of the dimensions of the cubes that preceded it.

3.3 Physical Properties

From the analysis of the values expressed by the EDX spectra (Table 2), it is observed that the PWAg deposited on the samples, does not show an expressive variation, since it is started from a PWAg of approximately 0%, on average for the group 75 W / 0.5 min, reaching a PWAg of ~ 17%, on average for the group 200 W / 10 min.

This result suggests the existence of a correlation between the PWAg in the films, the duration of the depositions, and the plasma power. In fact, the correlation between these variables is found extremely strong, since the Pearson (r) correlation coefficients calculated are above 0.9 for all groups. The only exception is with respect to the groups produced during 0.5 min and the group 75W / 1 min, for which the value of (r) not can be determined. The calculated " r " coefficient is also submitted to the two-tailed hypothesis test, which ensures its significance for a (α) equal to 95%, indicating that the observed correlation is not accidental. Considering that the concept of "power" in its simplest expression is the amount of work performed by a force as a function of time, the observed association between plasma power and PWAg is expected even with respect to the small amount of silver deposited in the processes executed during 0.5 min and 75 W / 1 min. However, this information cannot be statistically verified since these groups presented PWAg values very close to 0%; values close to 0 cannot be calculated. The low content of Ag-Ps perceived in these samples is resulted from the insufficient amount of silver atoms ejected from the ASP to form a film at appreciable levels. Thus, the presence of the few Ag-Ps on the surfaces of the groups of 0.5 min, and also of the group 75W / 1 min is observed in an unpredictable way and quite isolated by different regions of the substrates. On the other hand, in the other groups the

contribution of Ag-Ps is large enough to form a film, which is resulted from the progressive reduction of free spaces on the sample surface as the deposition time and plasma power become larger.

With respect to the thicknesses of the coatings (Table 3), a variation from 0.3 μm ($\pm 0.02 \mu\text{m}$) to 12 μm ($\pm 0.94 \mu\text{m}$) is observed as a function of the parameters used. The growth profile of this variable follows that of PWAg, since the accumulation of Ag-Ps in superimposed strata is what constituted the film effectively. Consequently, the determinant parameters in PWAg, together with the rate of deposition of Ag-Ps from the reactor, are equally important to understand the growth of the thickness of the coatings.

In above study, the causes of variation in PWAg deposited in the sample, film thickness, and deposition rate of the PVD-PECVD system, have been presented. From these data a conflict has been verified regarding the determination of the maximum deposition time that the system would support, since the deposition rate, which ranges from 0.2 $\mu\text{m} / \text{min}$ ($\pm 0.04 \mu\text{m} / \text{min}$) to 1.2 $\mu\text{m} / \text{min}$ ($\pm 0.085 \mu\text{m} / \text{min}$), increases inversely the duration of the depositions, while the PWAg is increased proportionally to this variable. From this analysis two observations are made, viz (i) by concerning the growth of the deposition rate suggests the existence of a maximum time limit from which deposition would cease, and (ii) by relating to the growth of PWAg, it suggests that the parameter "deposition time" is the most important to reach previously determined thicknesses. Although the maximum deposition time limit has not been the subject of the present study, the empirical experience of working with PVD-PECVD systems suggests that the electric discharge would not be stable for times much longer than 10 min due to the appearance of metastable voltaic arcs.

With respect to wettability of the sample surface, analysis of the contact angle (CA) of the water droplet (Table 4) reveals that the groups produced in 0.5 min

Table 2 — PWAg in the samples and the Pearson correlation coefficients, considering the intersections of variables "time" and "power"

| Power, W | Pearson coefficient correlation (r) | | | |
|----------|---|---------------------|---------------------|--------------------|
| | 0.5 min | 1 min | 5 min | 10 min |
| 75 | 0 | 0 (+0.22) | 0.07(± 0.004) | 0.3 (± 0.1) |
| 100 | 0 | 0.6 (± 0.02) | 0.7 (± 0.05) | 1.1 (± 0.17) |
| 150 | 0 (+0.2) | 2.1 (± 0.005) | 3 (± 0.08) | 8 (± 0.5) |
| 200 | 0 (+0.1) | 2.3 (± 0.02) | 5 (± 0.3) | 17 (± 1) |

Values in parentheses are standard deviation.

Table 3 — Thickness of films deposited on the samples and system deposition rates, considering the intersections of variables "time" and "power"

| Power, W | Thickness, μm | | | | Deposition rate, $\mu\text{m}/\text{min}$ | | | |
|----------|--------------------------|--------------------|--------------------|--------------------|---|--------------------|----------------------|----------------------|
| | 0.5min | 1min | 5min | 10min | 0.5min | 1min | 5min | 10min |
| 75 | 0 | 0 | 0.3 (± 0.02) | 0.5 (± 0.03) | 0 | 0 | 0.06 (± 0.034) | 0.05 (± 0.007) |
| 100 | 0 | 0.6 (± 0.03) | 1.4 (± 0.05) | 1.7 (± 0.07) | 0 | 0.6 (± 0.05) | 0.28 (± 0.058) | 0.17 (± 0.01) |
| 150 | 0 | 0.8 (± 0.04) | 2.3 (± 0.03) | 3 (± 0.17) | 0 | 0.8 (± 0.05) | 0.46 (± 0.09) | 0.3 (± 0.091) |
| 200 | 0 | 7.7 (± 0.4) | 9.7 (± 0.6) | 12 (± 0.94) | 0 | 7.7 (± 1.02) | 1.94 (± 0.087) | 1.2 (± 0.085) |

Values in parentheses are standard deviation.

depositions for all potencies, and the group produced during 75 W / 1 min, show CAs statistically equivalent to that of the control group (not covered by the film). On the other hand, it is observed that the CA of the other groups decreases as the PWAg is increased in the samples. Consequently, the 200 W / 10 min group presents lower CA ($89.3^\circ \pm 4.5^\circ$) than the others. The reverse growth profile between the PWAg and CA variables is observed in Ag-Ps films deposited on cotton fabrics produced by different techniques^{9,18}. In general, the scientific community chooses the increase of the substrate roughness due to the different sizes of Ag-Ps in the film as the primary cause of this effect^{9,19-21}. In this aspect, the present study ratifies this premise, since the deposition of Ag-Ps is increased the roughness of the uncoated substrates by up to 110.5%.

3.4 Antimicrobial Effect Produced by Film

The results of the microbiological test indicate that the culture grows on all control group [Fig. 4 (A)], and that there is no growth of the culture on the samples produced in the potencies of 150 W and 200 W during the times of 1 min, 5 min and 10 min, which are therefore considered effective in terms of inhibition of growth of microorganisms [Fig. 4 (B)],

because the colony grows only on to the border of these samples, which presents a narrow inhibitory halo. In all other cases the samples are partially or totally covered by the culture, and therefore ineffective with respect to the microbicidal property. With respect to the observed effect, the present results are in agreement with published works involving not only *S. hominis*, but also *Escherichia coli*, *S. aureus*, *Klebsiella pneumoniae* and *C. albicans*^{3,4,20-22}.

Due to the effectiveness of the 150 W / 1min group in combating *S. hominis*, and the low input consumption as compared to equally efficient but produced groups for 5 and 10 min, it is chosen to undergo the antimicrobial test. The results show no growth of *S. hominis* on textiles coated by the film [Fig. 4 (C)], but the bacteria culture grows on TSA medium. This result indicates that the presence of the Ag-Ps on the textiles dipped in the saline solution does not prove the death of the bacteria. Therefore, the present film causes a bacteriostatic effect.

The antimicrobial effect achieved by the Ag-Ps is closely associated with the physical characteristics of the coatings. In this sense, the concentration of 2.1% ($\pm 0.005\%$) of Ag-Ps in the samples is marked as the minimum limit from which efficacy is obtained. The analysis of this result shows that, as reported by

Table 4 — Arrangement of water contact angle values measured in the samples, considering the intersections of variables "time" and "power"

| Power, W | Contact angle, deg | | | |
|----------|---------------------|---------------------|---------------------|---------------------|
| | 0.5 min | 1 min | 5 min | 10 min |
| 75 | 142.6 (± 3.1) | 142.6 (± 5.7) | 125.9 (± 5.3) | 116.9 (± 4.5) |
| 100 | 142.6 (± 5.1) | 131.9 (± 4.6) | 125.7 (± 4.9) | 113.2 (± 5.6) |
| 150 | 142.6 (± 5.8) | 125.7 (± 5.3) | 118.9 (± 4.9) | 110.9 (± 4.8) |
| 200 | 142.6 (± 6.0) | 110.9 (± 6.5) | 110.6 (± 4.5) | 89.3 (± 4.5) |

Values in parentheses are standard deviation.

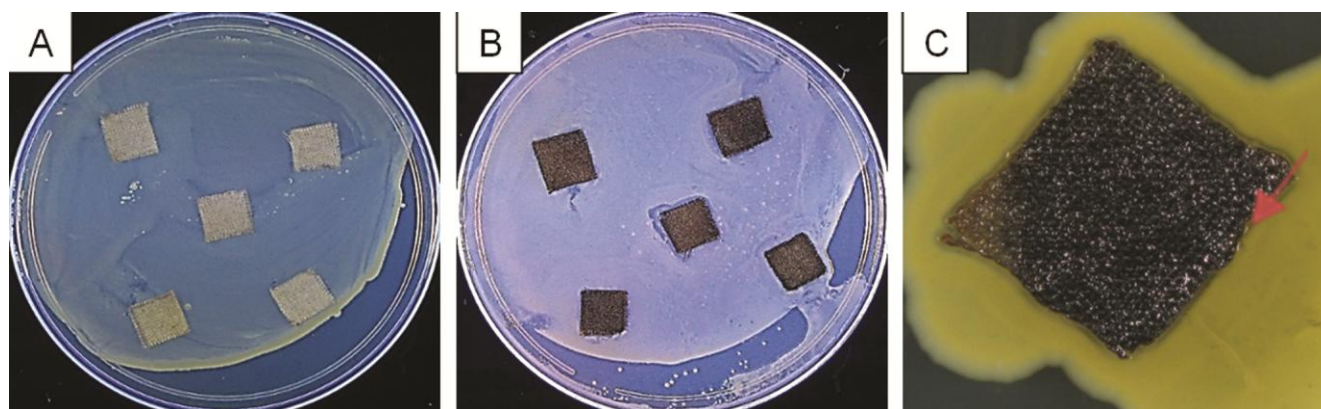


Fig. 4 — Antimicrobial assay. The culture medium is partially covered by *S.hominis*, observed by the region of milky aspect: (A) control group; (B) representative image of microbicidal groups; and (C) result of "type of antimicrobial effect" test [The red arrow indicates the presence of an inhibitory halo around the edge of the sample]

Budama²³, Ag-Ps demonstrate antimicrobial efficiency even in small amounts. Regarding the diameter of Ag-Ps, various studies have highlighted the microbicidal power of particles ranging from 1 nm to 100 nm^{1,20,21,23,24}. In this aspect, the present methodology corroborates with the literature, since the Ag-Ps present in massive region of the coatings are limited to the range of 1-20 nm. Although, there are no studies demonstrating particle effects greater than this amplitude, the edge of the coatings presents 100% of its Ag-Ps greater than 100 nm (\cong 100 to \cong 1000 nm), and also demonstrates efficiency to inhibit microorganisms.

In addition to the present associations, several researches have related the antimicrobial effect of Ag-Ps with the thickness of the silver films. However, there is no consensus found regarding this property in terms of efficacy, because there are studies such as Sataev²⁵, which presents microbicidal coatings with 0.5-0.6 μ m, while in other works, Chadeau² and Wang¹⁰ obtained the same effectiveness with silver coatings extremely thin from 0.001 μ m to 0.4 μ m. The combination of these findings supports the assumption that coatings of Ag-Ps are microbicides within a wide range of thicknesses, which in the case of this study shows lower limit 0.8 μ m (\pm 0.04 μ m), and upper limit 12 μ m (\pm 0.94 μ m). In contrast to findings in the literature^{2,10,14}, the present work also produces coatings with 0.3 μ m (\pm 0.02 μ m) of thickness and no microbicidal effect is detected. These results suggest that the association between microbicidity and thickness of the coatings is purely fortuitous.

According to Chadeau², Ag-Ps films deposited on cotton fabrics by MS, promote an expressive reduction in the number of colony forming units (UFC) after 24 h. On the other hand, still with respect to the MS technique, Mejía¹⁴ produced antimicrobial samples from depositions of 1 min of duration. Compared to these findings, the PVD-PECVD methodology is found more efficient than the Chadian MS, and it shows presented efficiency equivalent to Mejía's MS, since samples produced from 150 W / 1 min per PVD-PECVD show antimicrobial properties.

Till date, few studies have related the microbicidal effect of textiles coated with Ag-Ps, with wettability and roughness of textiles^{9,18}. However, various studies have demonstrated that high RMS surfaces have numerous peaks and valleys, which confer favorable sites for eukaryotic cell adhesion^{26,27}. As the chemical composition of the cell membrane is

essentially the same throughout the biosphere, it is reasonable to assume that the same effect would occur with bacteria^{26,28-30}. However, the present study is in contradiction to this logic, since the groups with the highest RMS value are the most antimicrobial. Consequently, from this result it is found that the direct relationship between the roughness and the antimicrobial effects is causal, since the observed phenomena is resulted from the alteration in CA of the samples, which is a variable dependent on the RMS value. Therefore, the incorporation of Ag-Ps into the substrates makes them more hydrophilic, and consequently more repulsive to hydrophobic structures such as the plasmatic membrane and the cell wall of the microorganisms. This hypothesis effectively associates and corroborates the understanding of the results of the antimicrobial test, which reveals that the films produced by the present methodology are ineffective in the extermination of the colonies, except in cases of prolonged bacteriostasis³¹, but they act with great efficiency in prophylaxis of infections by avoiding the fixation of microorganisms^{20,21}. However, there is no consensus on "what effectively inhibits microbial growth", because there are studies that associate this effect with the inherent microbicidity of silver, and others that associate it with the gradual and persistent release of Ag-Ps from the coated material^{2,22,31}.

3.5 Comparison Between PVD-PECVD and MS

Table 5 shows the comparison between characteristics values of films produced by both PVD-PECVD and MS techniques. It is observed that the minimum average thickness of microbicide films is 98% higher in PVD-PECVD films than in MS. The minimum average PWAg is 91% higher in MS microbicide films than in PVD-PECVD. The Ag-P average diameter presents two different behaviors as a function of the region where the particles were deposited on sample (edge or center). On the edge of microbicide films, it is noticed that the Ag-P diameter is 99% higher in PVD-PECVD than in MS. On the other hand, on center region, the PVD-PECVD demonstrates Ag-P diameters 75% less than by MS. Both techniques (PVD-PECVD and MS) demonstrate the ability to produce coatings equally efficient in terms of microbicidity.

As the differences between the characteristics of the films are quite significant, there is no need to use any statistical hypothesis test to assure that the production of Ag-Ps films on textiles by PVD-

Table 5 — Comparison of values of films produced by both PVD-PECVD and MS techniques

| Parameter | PVD-PECVD | MS (Ref. 14) | MS (Ref. 2) ² | MS (Ref. 10) |
|--|-----------|--------------|--------------------------|--------------|
| Minimum time to produce microbicidal samples, min | 1 | 1 | NA | 5.7 |
| Power, W | 150 | 60 | NA | 40 |
| Pressure, torr | 0.030 | 0.0075 | 0.0015 | 0.0160 |
| PWAg, % | 2.1 | 23.36 | NA | NA |
| Intensity of microbicidal effect, % | 100 | 100 | 100 | 100 |
| Minimum thickness of microbicidal films, μm | 0.8 | 0.04 | 0.001 | 0.002 |
| Maximum size of Ag-Ps, nm | 960 | 5.8 | NA | NA |
| Minimum size of Ag-Ps, nm | 1 | 4 | NA | NA |
| NA--Data not available | | | | |

PECVD would result in coatings with characteristics quite different from produced by MS. Therefore, based solely on the present results it is not possible to determine advantages of one system with respect to the other. However, the versatility of the PVD-PECVD system, much larger than that of the MS, makes it easy to overcome its disadvantages (lower deposition rate and higher minimum thickness than MS) by enabling:

- to diversify plasma configurations, using different precursor gases alone or concomitantly;
- to use ASP made of silver alloys or other metals;
- to readjust ASP dimensions, and other modifications that would allow to optimize the efficiency of PVD-PECVD systems.

In addition, the total lifetime of the PVD-PECVD process is about 2 min, or 10%, less than in the MS process. This difference is a consequence of the ideal working pressure of the MS system being smaller than that of the PVD-PECVD system, thus MS systems require a longer time to achieve the ideal conditions for depositing the film, and for reopening the chamber at the end of the process. This provides an important technical advantage of the PVD-PECVD system, since it works with higher pressures and reduces the expense with electricity.

4 Conclusion

4.1 The results lead to the conclusion that the PVD-PECVD technique is an effective alternative for producing Ag-Pcoatings on cotton textiles. The films produced show good uniformity regardless of the initial size of the ASP particles ejected. This characteristic results both from the aggregation of Ag-Ps isolated by the fusion clusters and from the redistribution of their mass in equal parts on the substrate by the "ice cube" effect.

4.2 The size of the Ag-Ps deposited by this technique shows the variation of the diameter as a

function of the distance with which they are located in relation to the solid film, and also as a function of the type of subprocess by which the particles are ejected from the ASP (sputtering or evaporation). The largest Ag-Ps produced by PVD-PECVD have a diameter of 960 nm, and decrease in size until reaching about 100 nm before they merge to the solid film, where almost 60% of the Ag-Ps has 1 nm. The simple frequency with which these particles occur in the coatings is in favor of smaller Ag-Ps limited to the range 40- 960 nm.

4.3 With respect to the silver concentration in the films, the PWAg presents a maximum variation of 17% of the total mass of the sample. Among the variables configured in the system, the duration of deposition and plasma power are highlighted in the determination of PWAg in the samples, and consequently in the determination of the other properties of the films.

4.4 In relation to the antimicrobial effect, it is found that the deposition of small amounts of Ag-Ps, about 2.1% ($\pm 0.005\%$), makes the textiles 100% effective in inhibiting microorganisms.

4.5 Both MS and PVD-PECVD techniques differ significantly from one another. The PVD-PECVD system is slightly less efficient than MS. On the other hand, the MS technique operates longer and therefore is more expensive processes and less versatile processes than PVD-PECVD. Both techniques demonstrate equivalent efficiency with respect to the microbicity of the films produced.

4.6 The findings of the present work assure that the PVD-PECVD technique is an economical, versatile, sustainable alternative to produce coatings of Ag-Ps on textiles. As time is a decisive factor in large-scale production, PVD-PECVD technique proves to be an interesting option for industrial use in processes that require rapid production and continuous innovation of the products. This versatility

is especially interesting for the industry, which inevitably needs to innovate and continually improve its products to remain competitive in the market.

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References

- 1 Radetić M, *J Mater Sci*, 48(1)(2013)95.
- 2 Chadeau E, Oulahal N, Dubost L, Favergeon F & Degraeve P, *Food Control*, 21(1) (2010)505.
- 3 Egbuta M A, Mwanza M & Babalola O O, *Int J Environ Res Public Health*, 14 (2017).
- 4 Mitra C, Phani M, Gummadidala Kamelia A, Ruth C, Merrifield M, Jamie R & Anindya C, *Environ Sci Technol*, 51 (2017) 8085.
- 5 Sudip S, Ipsita K, Amitava M, Tugrul A, Yakup U, Ebru Ş, Ahmet K, Ayse D & Amit K, *Mater Res Express*, 6(2019).
- 6 Nofar D, Yaniv D, Nathaniel K, Michael M, Daniel A, Marina B & Elizabeth A, *Polym Adv Technol*, 28 (2017) 583.
- 7 Zhang J, Li B, Wu L & Wang A, *Chem Commun*, 49 (2013) 11509.
- 8 Tang X, Zhang X, Zhang H, Zhuang X & Yan X, *Text Res J*, 88 (22) (2017). doi:10.1177/0040517517725120.
- 9 Andrea Z, Margarida F, Antonio F, Tzanko T, Marta F, Fernando O, Luís A, Teresa A, Noémia C, Maria E & António S, *ACS Appl Mater Interfaces*, 7(2015) 13731.
- 10 Hongbo W, Jinyan W, Jianhan H & Qufu W, *J Coatings Technol Res*, 4 (2007) 101.
- 11 Capote G, Mastrapa G C & Trava-Airoldi V J, *Surf Coat Technol*, 284 (2015) 145.
- 12 Capote G, Ramirez M A da Silva, Lugo D C & Trava-Airoldi V J I, *Surf Coat Technol*, 308(2016) 70.
- 13 Lugo C, Silva P, Ramirez M, Pillaca M, Rodrigues C, Fukumasu N, Corat E, Tabacniks M & Trava-Airoldia V, *Surf Coatings Technol*, 332 (2017) 135.
- 14 Mejía M, Restrepo G, Marín J, Sanjines R, Pulgarín C, Mielczarski E, Mielczarski J & Kiwi J, *ACS Appl Mater Interfaces*, 2 (2010) 230.
- 15 Kelly P J & Arnell R D, *Vacuum* 56 (2000) 159.
- 16 Ohring M, Thin-film evaporation process materials science of thin films, in *Materials Science of Thin Films*, (Academic Press) 2002. doi:https://doi.org/10.1016/B978-012524975-1/50006-9.
- 17 Ohring M, Discharges, plasmas, and ion-surface interactions, in *Materials Science of Thin Films*, (Academic Press) 2002. doi:https://doi.org/10.1016/B978-012524975-1/50007-0.
- 18 Vu N K, Zille A, Oliveira F R, Carneiro N & Souto A P, *Plasma Process Polym*, 10 (2013) 285.
- 19 Li XM, He T, Crego-Calama M & Reinhoudt D N, *Langmuir*, 24 (2008) 8008.
- 20 Lee H J, *J Mater Sci*, 38 (2003) 2199.
- 21 Duran N, Marcato PD, De Souza G I H, Alves OL & Esposito E, *J Biomed Nanotechnol*, 3 (2007) 203.
- 22 Ilana P, Guy A, Nina P & Geoffroy G, *Nanotechnology*, 19 (2008) 245705.
- 23 Budama L, Çakır B A, Topel Ö & Hoda N, *Chem Eng J*, 228(2013) 489.
- 24 Dubas ST, Kumlangdudsana P & Potiyaraj P, *Colloids Surfaces A Physicochemical Eng Asp*, 289 (2006) 105.
- 25 Sataeva M, Koshkarbaeva S, Tleuova A, Perni S, Aidarova S & Prokopovich P, *Colloids Surfaces A Physicochem Eng Asp*, 442 (2014) 146.
- 26 Santos E, Luqueta G, Ramu R, Santos T, Doria A, Polyana Radi, Pessoa R, Vieira L & Maciel H, *Res Biomed Eng*, 32 (2016) 144.
- 27 Bendavid A, Martin PJ, Comte C, Preston EW, Haq AJ & Magdon FS, *Diam Relat Mater*, 16 (2007) 1616.
- 28 Silva P, Santos E, Gonçalves C, Cardoso M, Soares C & Beltrame M, *Laser Phys*, 26 (2016) 105601.
- 29 Santos T, Vieira A, Paula L, Santos E, Gonçalves P, Khouri S, Maciel H, Pessoa R & Vieira L, *J Mech Behav Biomed Mater*, 68 (2017) 239.
- 30 Luqueta G R, Santos ED, Pessoa R S & Maciel H S, *Res Biomed Eng*, 33 (2017) 58.
- 31 Sun N, Wang T & Yan X, *Carbohydr Polym*, 172 (2017) 49.