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# Efficient silver nanoparticles deposition method on DBD plasma-treated polyamide 6,6 for antimicrobial textiles

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**Abstract.** Several methods for silver nanoparticles (AgNPs) deposition on dielectric barrier discharge (DBD) plasma treated and not treated polyamide 6,6 fabric were tested for the production of durable antibacterial textiles. Ultrasound-assisted, dip-coating, exhaustion at 70°C and spray deposition methods were applied. The treated fabrics were analysed in terms of coating uniformity, plasma effect, nanoparticles concentration onto the fabrics and nanoparticles release. Scanning electron microscope (SEM), energy dispersive X-ray (EDX), atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and reflectance spectroscopy(%R) were performed. In the fabrics impregnated with AgNPs by dip coating or spray methods there are no significant differences in the plasma treated and untreated samples. Ultrasound tip and exhaustion at 70°C presented higher AgNPs loading. Better AgNPs distribution, higher concentration and less agglomeration were observed in the plasma treated samples and an improved controlled release as well. The plasma treated fabrics with AgNPs deposited with the ultrasound method showed the highest concentration of nanoparticles onto the fabrics as well as the lowest NPs agglomeration. However, this deposition is limited to certain areas of the fabric, the samples were not uniform. The exhaustion method showed the best equilibrium between the NPs distribution and state of agglomeration.

## 1. Introduction

The World Health Organization and the European Centre for Disease prevention are really concerned about the growing healthcare-associated infections. Over 4 million people developed an infection associated to this environment and their treatment contributed for the intensification of microbial resistance worldwide [1,2]. Therefore, the increasing concern in the widespread use of biocides leads to the development of new strategies [3,4].

The study of antimicrobial fabrics with silver nanoparticles (AgNPs) incorporation has shown excellent properties in medical, pharmaceutical, cosmetics and electronics applications due to their good action against pathogens, preventing and treating infections [5]. The high surface-to-volume ratio from



AgNPs promotes an easy release of silver ion, responsible for the antimicrobial effect [6]. Three different mechanisms are proposed. The first hypothesis is linked to contact killing surfaces by the generations of reactive oxygen species (ROS) and Ag<sup>+</sup> ions release that degrade bacteria cell membranes. The second theory is related with oxidative intracellular reactions. The last hypothesis is associated with the bonds between Ag<sup>+</sup> ions and sulphur, oxygen or nitrogen atoms in biological molecules in bacteria [7]. Unfortunately, NPs could penetrate cells and display cytotoxicity and genotoxicity in human body limiting practical applications. Properties including size, agglomeration and chemical structure are responsible for NPs toxicological effect [8]. Thus, it is important to develop a new class of antibacterial surfaces with firmly nanoparticles loading and with precise local release of antibacterial effect.

The most traditional method for nanoparticles deposition onto fabrics is the pad-dry-cure technique [9]. Other methods were developed such as dip coating, electrochemical methods and layer-by-layer depositions. However, these methods showed several limitations for nanoparticles depositions [10-12].

Dielectric barrier discharge (DBD) plasma-assisted deposition of AgNPs has shown to enhance the NPs adhesion prepared in water dispersions dispersions. DBD plasma is a dry environmental friendly technology that evenly modifies textile surfaces without conventional chemical procedures [13]. DBD plasma treatment activates the fabric surface by the introduction of new polar functional groups such as carbonyl, carboxyl, ether, amine and hydroxyl according to the used gases (e.g. air, helium, nitrogen or oxygen) [14]. These polar groups are able to increase the surface energy thus altering wettability. It can also promote etching and cross-linking, without deteriorating the bulk properties of the material [15]. In addition, the attractiveness of plasma treatment for AgNPs deposition is also due to the formation of micro-roughness that associated to the chemical changes on the surface improves the AgNPs fixation. AgNPs can be deposited on different parts of the textile substrate being mechanically locked by attractive forces such as Van der Waals or electrostatic ones. Moreover, it can also be assisted by chemical interactions such as ionic, covalent, metallic and hydrogen bonds [16].

In this work, several methods for the AgNPs deposition on DBD plasma pre-treated polyamide 6,6 (PA66) were tested for the production of durable antibacterial textiles. Ultrasound-assisted deposition, dip-coating, spray and exhaustion at 70°C methods were tested in terms of coating uniformity, plasma effect, nanoparticles concentration onto the fabrics and nanoparticles release. Scanning electron microscope (SEM), energy dispersive X-ray (EDX), atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and reflectance (%R) were performed.

## 2. Methods and Procedures

### 2.1. Materials

Commercial PA66 (warp density of 50 threads cm<sup>-1</sup>, a weft density of 32 threads cm<sup>-1</sup> and an areal density of 110 g m<sup>-2</sup>) fabric was used. The samples were pre-washed with a 1 g L<sup>-1</sup> of non-ionic detergent solutions at 60°C for 60 min and then rinsed with water and dried at 40°C before DBD plasma treatment, in order to minimize contaminations of manufacture. All the other reagents were analytical grade purchased from Sigma–Aldrich, St. Louis, MO, USA and used without further purification.

### 2.2. DBD plasma treatment

The DBD plasma treatment was performed in a semi industrial prototype machine (Softal GmbH/University of Minho) working at room temperature and atmospheric pressure in air, using a system of metal electrode coated with ceramic and counter electrodes coated with silicon with 50 cm effective width, gap distance fixed at 3 mm and producing the discharge at high voltage 10 kV and low frequency 40 kHz. The discharge power supplied by the electrodes and the speed may change, with maximum discharge of 1.5 kW and speed of 60 m min<sup>-1</sup>. The dosage applied onto PA66 fabric was 5 kW min m<sup>-2</sup>. The machine was operated at optimized parameters: 1 kW of power and velocity of 4 m min<sup>-1</sup>. The plasmatic dosage (D) was calculated according to the following equation 1 [17]:

$$D = \frac{P \cdot N}{V \cdot W} \quad (1)$$

Where,

P = power (kW); N = number of passages; V = velocity (m min<sup>-1</sup>); W = width of treatment (m).

### 2.3. Preparation of AgNPs dispersions

Water dispersions of AgNPs with 20 nm as particle size (10 mg L<sup>-1</sup>) were prepared in an ultrasonic bath for 30 min followed by an ultrasonic tip for more 30 min.

### 2.4. AgNPs deposition

AgNPs dispersions were deposited onto untreated and plasma treated PA66 (0.3 g per sample) by i) ultrasound tip assisted deposition, ii) dip coating iii) spray and iv) exhaustion at 70°C: i) The fabrics were immersed in 250 mL of nanoparticle dispersion for 5 minutes with an intensity of ultrasound tip at 50%, 60%, 70% or 80% with different geometries. The samples were removed and dried at 30°C; ii) The fabrics were immersed in 50 mL of nanoparticle dispersion for 10 minutes. The samples were removed and dried at 30°C; iii) AgNPs dispersion was applied by spray directly. The system was pressurized at 1.5 bar and maintained at the distance of 5 cm to the substrate. AgNPs were applied in both sides. The samples were dried at 30°C; iv) AgNPs dispersion was applied by exhaustion for 60 min, 100 rpm, a 1:100 ratio bath, at 70°C. Then, the samples were removed and dried at 30°C.

### 2.5. Reflectance

The samples with AgNPs were analysed by Datacolor Spectraflash SF 600 Plus CT spectrophotometer with D65 light, over the range of 390–700 nm and expressed in reflectance (%R). Reflectance measurements were made three times in different positions of the fabric and the average was calculated.

### 2.6. SEM and EDX

Morphological analyses of fabrics were carried out with an Ultrahigh Resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company. Secondary electron images were performed with an acceleration voltage at 5 kV. Backscattering Electron Images were realized with an acceleration voltage of 15 kV. Samples were covered with a film of Au-Pd (80-20 weight %) in a high-resolution sputter coater, 208HR Cressington Company, coupled to a MTM-20 Cressington High Resolution Thickness Controller. Atomic compositions of the membrane were examined with the energy dispersive spectroscopy (EDX) capability of the SEM equipment using an EDAX Si(Li) detector and an acceleration voltage of 5 kV.

### 2.7. AAS and ICP-OES analysis

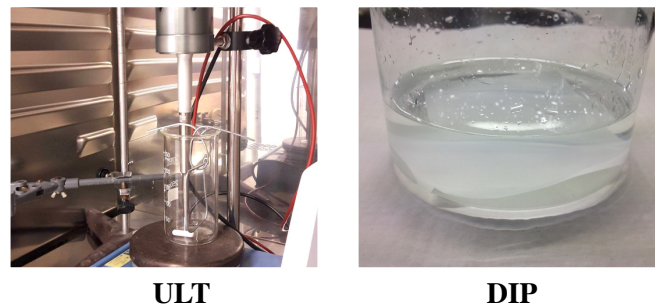
Prior to analysis for AAS and ICP the AgNPs dispersions were digested in 10.00 mL of concentrated nitric acid at 95°C for 30 minutes with magnetic stirring. The samples were cooled, transferred to a 30.00 mL falcon and diluted to 30 mL of distilled water. The procedure was made in triplicate.

A flame atomic absorption spectrophotometer Analytic Jena model nova 350 was used to perform AAS analyses. Silver nanoparticles concentration in the dispersions was measured before and after the deposition in samples with and without DBD plasma treatment by exhaustion at 70°C.

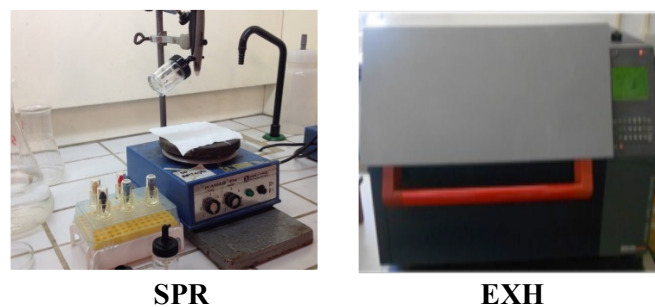
ICP-OES was performed for study of AgNPs release with time. Seven samples, 5x5 cm, without and with 5 kW min m<sup>-2</sup> of DBD plasma dosage with AgNPs deposited by exhaustion at 70°C were immersed separately in a flask with 20.00 mL of distilled water. After 1, 3, 5, 7, 10, 15 and 30 days, the respective sample was removed and AgNPs in the liquid were digested. A single-element standard solution was diluted to prepare the calibration curve of silver with 1, 0.750, 0.500, 0.25, 0.100, 0.075 and 0.050 mg L<sup>-1</sup>. The analyses were performed in a ICP-OES spectrometer PERKIN ELMER OPTIMA 8000 equipped with an auto-sampler S10. WinLab software was used to process and for data acquisition.

### 3. Results

AgNPs agglomeration and its uncontrollable release represent an important limitation in their application. In this work, it was intended evaluate different methods for AgNPs deposition in order to obtain a higher and strong attached concentration of NPs onto the fabric surface and a controlled release of the NPs. The impregnation of PA66 with AgNPs was performed by i) ultrasound tip assisted deposition, ii) dip coating iii) spray and iv) exhaustion at 70°C according to figure 1 and 2.

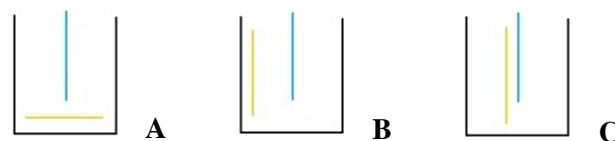


**Figure 1.** Methods for AgNPs deposition. ULT: ultrasound; DIP: dip coating.



**Figure 2.** Methods for AgNPs deposition. SPR: Spray; EXH: Exhaustion at 70°C.

The effect of ultrasonic tip was tested with 50%, 60%, 70% and 80% power intensity in an ultrasound bath with different geometries of the tip/sample positions as schematized in the figure 3.



**Figure 3.** Main geometries of ultrasound tip tested.

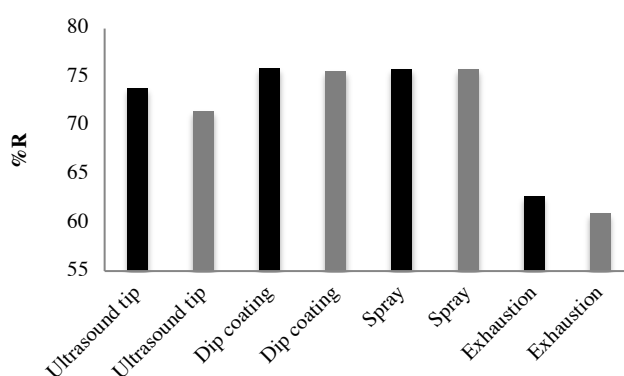
All tested configurations did not show uniform AgNPs distribution on the fabric surface. However, significant differences between plasma untreated and plasma treated samples were observed. Plasma sample showed higher local AgNPs dispersion but only in some specific spots of the PA66 fabric (Fig. 4). The ultrasound tip method pointed out the importance of the mass transfer in the AgNPs adhesion on the plasma treated fabric surfaces. The best sample obtained at 70% of ultrasound intensity and geometry B was used to the characterization measurements.



**Figure 4.** Tip ultrasound-assisted AgNPs deposition at 70% of ultrasound intensity using geometry B. Left sample: without plasma treatment. Right sample: with plasma treatment.

All the other tested methods showed uniform distribution of AgNPs on the fabrics. Visually the fabrics are less colored than the ultrasound spots. However, the exhaustion method displayed more intense coloration suggesting higher AgNPs deposition.

Reflectance measurements were made to estimate AgNPs concentration onto the fabrics. The decrease in specular reflection could be considered a direct measure of the AgNPs abundance in the topmost layer of the material since the NPs act as radiation absorbers on the entire visible spectra [18]. It is expected that a higher concentration of AgNPs on the fabrics would decrease reflectance values at 420 nm (figure 5). In the fabrics impregnated with AgNPs by dip coating or spray methods there are no significant differences in the plasma treated and untreated samples. In these cases due to the lower temperature and mechanical action of the system, the mass transfer is lower than ultrasound and exhaustion methods limiting the firmly AgNPs loading on the surface. Ultrasound tip and exhaustion at 70°C presented higher AgNPs loading due to the both mechanical action and higher temperature. Different exposition time was also tested (data not shown) and no significant difference was observed in the dip coating method. The best reflectance value was obtained with the exhaustion method at 70°C and 100 rpm for 60 minutes of treatment.

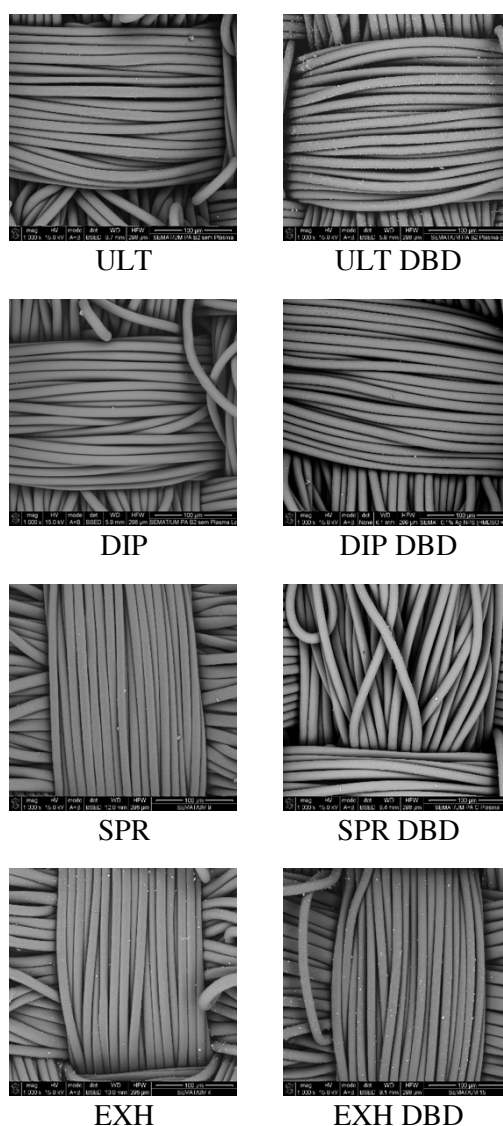


**Figure 5.** Reflectance measurements at 420 nm of PA66 samples impregnated with AgNPs using different deposition methods: Black bars: samples without plasma treatment. Gray bars: plasma treated samples.

The SEM images of PA66 untreated and DBD plasma treated samples shows AgNPs in all the tested methods (figure 6). However, better distribution, higher concentration and less agglomeration were observed in the plasma treated samples. The plasma treated fabrics with AgNPs deposited with the ultrasound method showed the highest concentration of nanoparticles onto the fabrics as well as the lowest NPs agglomeration due to the cavitation effect that is able to maintain the NPs well separated. However, this deposition is limited to certain areas of the fabric limiting its application as medical dispositive. The SEM images of the dip coating and spray methods showed very low amount of AgNPs for both plasma-treated and untreated fabrics. Moreover, the few AgNPs observed on the surface are present in the form of big agglomerated clusters. These methods are the most simple but also the worse

in term of NPs application. The exhaustion method showed the best equilibrium between the NPs distribution and state of agglomeration. The SEM images showed AgNPs good distribution in the plasma treated sample. Some agglomeration is present but it is not so dramatic as in the DIP and spray methods. As previously observed at this relatively low concentration ( $\sim 10 \text{ mg L}^{-1}$ ) the AgNPs tend to aggregate in clusters on the surface of the DBD-treated PA66 fibers due to the thermo-migration of the nanoparticles during the application of the exhaustion method and to the chemical changes induced by DBD plasma treatment [19, 20].

Despite the deep probe depth of EDX technique, the peak of silver was detected on the surface of the AgNPs-loaded fabrics (data not shown). Moreover, clear differences between the samples untreated and plasma treated as well as among the different methods can be noted in the silver peak intensity. The exhaustion method confirms as the best solution.



**Figure 6.** SEM images of the different deposition methods without and with (DBD) plasma treatment. ULT: Ultrasound; DIP: dip coating; SPR: Spray; EXH: Exhaustion at 70°C.

AgNPs concentrations in the liquid dispersions were measured before and after the exhaustion deposition method by AAS (table 1). The initial concentration was  $8.0 \text{ mg L}^{-1}$ . After the deposition, the

AgNPs concentration in the dispersion was significantly lower in the plasma treated sample. These results confirm the higher AgNPs adsorption due to the DBD plasma treatment effect onto the fabric surface.

**Table 1.** AAE results

Dispersion	[AgNPs] (mg L <sup>-1</sup> )
Initial concentration	8.00
After deposition no DBD	3.50
After deposition with DBD	0.87

In order to estimate the kinetic of the release of AgNPs from the fabrics, the amount of silver released from AgNPs-loaded fabrics by exhaustion method at 70°C was measured using the ICP-OES technique. AgNPs-loaded fabrics were immersed in water and liquid samples were collected after 1, 3, 5, 7, 10, 15, 30 days. From the collected data it is clear that the plasma treated samples are releasing more silver in the solutions (table 2). Moreover, it seems that plasma treated samples are able to better control the release of silver ions over time showing a higher stability in the released concentrations.

**Table 2.** ICP-OES results

Collect time (days)	[AgNPs] (mg L <sup>-1</sup> ) Samples no DBD	[AgNPs] (mg L <sup>-1</sup> ) Samples with DBD
1	0.10	0.12
3	0.00	0.20
5	0.08	0.20
7	0.05	0.20
10	0.06	0.15
15	0.05	0.08
30	0.14	0.20

#### 4. Conclusion

The results obtained in this study showed that the mass transfer controls the AgNPs deposition onto PA66 fabric surface. Temperature and mechanical agitation are preponderant factors that influenced the loading of NPs. The DBD plasma application enhances NPs adhesion and adsorption for all the used methods demonstrating to be a promising waterless and chemically free surface modification technique. The ultrasound method displays an irregular distribution despite its local good deposition. The dip coating and spray methods did not reach the minimum amount of AgNPs on the fabric surface and showed high AgNPs agglomeration. The exhaustion method showed the best results for both NPs distribution and reduced agglomeration. The AAS and ICP method prove the good plasma-promoted adsorption of AgNPs and their controlled release during time. The next experiments will be conducted to test different temperature, plasma dosage and time of application in the exhaustion method including the use of polymeric barrier layers to tune the controlled release of AgNps.

#### 5. Acknowledgment

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