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Enhancing the Antimicrobial Efficacy of Polyester Fabric Impregnated with Silver Nanoparticles Using DBD Plasma Treatment

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Abstract. The functionalization of polyester fabric (PES) with antimicrobial agents presents huge number of potential applications in advanced products. However, the lack of functional groups and the high PES hydrophobicity make the functionalization processes costly, prolonged and requires the use of polluting chemical compounds. In this work, dielectric barrier discharge (DBD) plasma treatment, an affordable and environmental-friendly method, was used to introduce new chemical groups, increase the surface energy and roughness of PES in order to improve the adhesion of silver nanoparticles (AgNPs) in its surface. The PES functionalization was evaluated by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and antimicrobial efficacy against *Staphylococcus aureus* and *Escherichia coli*. Despite some additional oxidation, the DBD plasma-treated PES showed superior adhesion of AgNPs and excellent antimicrobial efficacy even after 10 washing cycles (WC).

Introduction

Polyester is one of the most applied synthetic fibers in the textile industry holding more than 50 % of the market share [1]. It has been preferred due to its good mechanical strength, processability, quick-drying, and dimensional stability [2]. This fiber strongly resists to the direct attack of microorganisms due to their molecular structure. However, it also induces higher perspiration, which commonly results in discomfort and microbial growth when it is used in direct contact with the skin [3]. In particular, textiles used in medical applications are in close contact to the human body for a long time, hence they are prone to increase the risk of infection [4]. Thus, it is essential to improve the antibacterial property of polyester for the production of advanced medical, protective and hygienic textiles [5]. New properties that are not intrinsic on textiles can be incorporated by chemical, physical or biological functionalization [6]. The incorporation of nanomaterials to generate nanocomposites has been a common strategy to introduce antimicrobial activity into textiles. Silver nanoparticles (AgNPs) has received huge attention due to the emergence of antibiotic-resistant strains and their low propensity to develop resistance. AgNPs exhibited a broad-spectrum antibacterial capability and demonstrated the potential to overcome some aspects of microbial resistance [7]. Nanoengineered textiles can be produced through several processes such as exhaustion, padding, dip coating, electroless, screen printing, dropwise, immersion, sonication and electrospinning [8, 9]. Some methods involve several steps and high temperature that are not cost-effective [10, 11]. Using the exhaustion method, the textiles are in constant contact with the nanoparticles-containing dispersion. The NPs are firstly moved from the dispersion to the fabric and then by adsorption and diffusion into the fiber interior. In this process, the temperature, time, NPs concentration, pH and auxiliary agents

are crucial parameters to control a suitable NPs deposition [12]. In addition, decreasing the difference between the surface energy of the particles and the material when they are incorporated may also improve their affinity [13].

Plasma treatments have been considered as promising tools to functionalize the surface of fabrics, whereby using a defined selection of plasma gas and treatment conditions can introduce novel properties and functionalities. It has been presented as an alternative to conventional wet-chemical treatments, since it does not require water and chemicals. Plasma consists of an ionized gas, where ions, electrons and radicals are created and may interact. The formed species react with the topmost atomic layers of the materials producing new reactive species [14]. Dielectric barrier discharge (DBD) plasma treatment has shown to enhance NPs adhesion. DBD plasma treatment activates the fabric surface, increasing the surface energy of the fabrics by the introduction of new functional groups according to the used gases. It also promotes the creation of micro-roughness that improves the NPs fixation [15, 16]. In previous works of our research group, the deposition of AgNPs onto polyamide was improved by the pre-functionalization of the fabrics with plasma treatments and using AgNPs dispersed in ethanol, allowing a deposition at low temperature [17]. In this work, the functionalization of PES fabric with AgNPs, also using the exhaustion process at low temperature, was tested by combining the DBD plasma treatment at atmospheric pressure in air to increase the surface energy and roughness of the polyester fabric using a low-cost and environmentally friendly method.

Materials and Methods

Materials. Commercial PES fabric with a weight per unit area of 100 $g \cdot m^{-2}$ was used in this work. First, the fabric was washed using a solution of 1.0 $g \cdot L^{-1}$ of a non-ionic detergent at 60 °C for 60 minutes, rinsed with distilled water and dried. Commercial polyvinylpyrrolidone-coated (PVP) AgNPs (20-30 nm) were obtained from SkySpring Nanomaterials Inc, Houston, TX, USA. All the other reagents were purchased from Sigma-Aldrich without any purification.

Redispersion of AgNPs. AgNPs were dispersed in ethanol with a concentration of 1.0 $mg \cdot mL^{-1}$ using an ultrasonic bath for 30 minutes and ultrasound tip for more 30 minutes.

DBD Plasma treatment DBD plasma treatment was executed in a semi-industrial machine (Softal GmbH/University of Minho) that works at room temperature and atmospheric pressure in air. It uses a system of two metal electrodes coated with ceramic and counter electrodes coated with silicon with 50 cm of width, a gap distance of 3 mm and produces the discharge at high voltage 10 kV and low frequency 40 kHz. The machine was operated at 1 kW of power and velocity of 4 m min^{-1}. The plasma was applied 10 times in each side of the PES fabric that corresponds to a dosage of 5.0 kW $min \cdot m^{-2}$.

AgNPs deposition The AgNPs were applied onto PES fabric samples (sample non-treated and sample pre-treated with DBD plasma) by an exhaustion process at 30 °C using a dispersion of NPs (1 $mg \cdot mL^{-1}$), with a liquor ratio of 1:100. The process was carried out in a laboratory machine (Ibelus) that uses infra-red heating. The program started at room temperature and the temperature was increased to 30 °C at a rate of 3 $°C \cdot min^{-1}$. After remaining at this temperature for 60 min, the samples were dried at 40 ºC.

Scanning electron microscopy (SEM). The SEM analyses were carried out with an ultra-high resolution FEG-SEM, NOVA 200 Nano, FEI Company. Secondary electron images were carried out with an acceleration voltage at 5 kV. Backscattering electron images were performed with an acceleration voltage of 15 kV. Samples were covered with a film of Au-Pd (80-20 weight %) (208HR Cressington Company, coupled to a MTM-20 Cressington High Resolution Thickness Controller).

X-ray photoelectron spectroscopy (XPS). XPS analyses were carried out using a Kratos AXIS Ultra HAS. The VISION software was used for data acquisition and CASAXPS software for data analysis. The analysis was performed with a monochromatic Al Kα X-ray source (1486.7 eV), operating at 15kV (150 W), in FAT mode (Fixed Analyser Transmission), with pass energy of 40 eV for regions ROI and 80 eV for the survey. Data acquisition was performed with a pressure lower than $1x10^{-6}$ Pa and it was used a charge neutralization system. Spectra have been charged corrected to give the adventitious C1s spectral component (C–C, C–H) binding energy of 285 eV. High-resolution spectra were collected using an analysis area of ≈1 mm^2. This process has an associated error of ±0.3 eV. Deconvolution into sub-peaks was performed by least-squares peak analysis software, XPSPEAK version 4.1, using the Gaussian/Lorenzian sum function and Shirley-type background subtraction.

Antimicrobial test. The antibacterial efficacy of PES samples containing AgNPs and pristine PES fabric was determined following the standard ASTM-E2149. Bacteria pre-inoculums of *Staphylococcus aureus* (ATCC25923) and *Escherichia coli* (ATCC 25922) were prepared in tryptic soy broth (TSB) and, after 12 h of incubation at 37 °C and 120 rpm, the inoculum of each bacterium was centrifuged, the supernatant discarded and the bacteria washed with sterile phosphate buffer saline (PBS). Then, the initial concentration of each bacterium was adjusted to 1.5–3.0 × 10^7 CFUs·mL^{-1} in PBS. The PES samples (2x1 cm) were inserted into falcon flasks of 10 mL and 5 mL of the diluted inoculum was transferred for each falcon. The samples were incubated for 24h at 37 °C and 120 rpm. Each of these dispersions was used to prepare 7-fold serial dilutions, which were plated out before (0 h) and after contact with the fabrics (24 h). The number of CFU was counted and the results were presented as log reduction. The antibacterial activity was performed in triplicates in two independent experiments.

Results and Discussion

PES samples impregnated with AgNPs presented in this work were developed using two distinctive particularities, being one of them related to the pre-functionalization of the textile with DBD plasma treatment. The applied DBD plasma treatment dosage was 5.0 kW min·m^{-2} with the goal to induce modifications onto PES fabric surface and improve the AgNPs adhesion. DBD plasma treatment has shown the ability to increase the fibre surface roughness and increase the availability of COOH chemical groups [18]. The second particularity of this work was the functionalization of PES using a low-temperature exhaustion method (30 °C), able to decrease the economic impact of high-temperature processes. Thus, PES samples with and without DBD plasma treatment were functionalized with AgNPs by exhaustion at 30 °C and characterized. SEM images were collected to understand the differences in the distribution, shape and quantity of AgNPs onto PES fabric surface (Fig. 1). The enlarged view of the SEM micrographs (magnification of 1000 x) showed the superior adhesion of AgNPs on DBD plasma-treated sample, with a more uniform and dense distribution. Using a higher magnification (5000 x) it was possible to perceive some agglomeration in both samples but even more in samples with DBD plasma treatment.

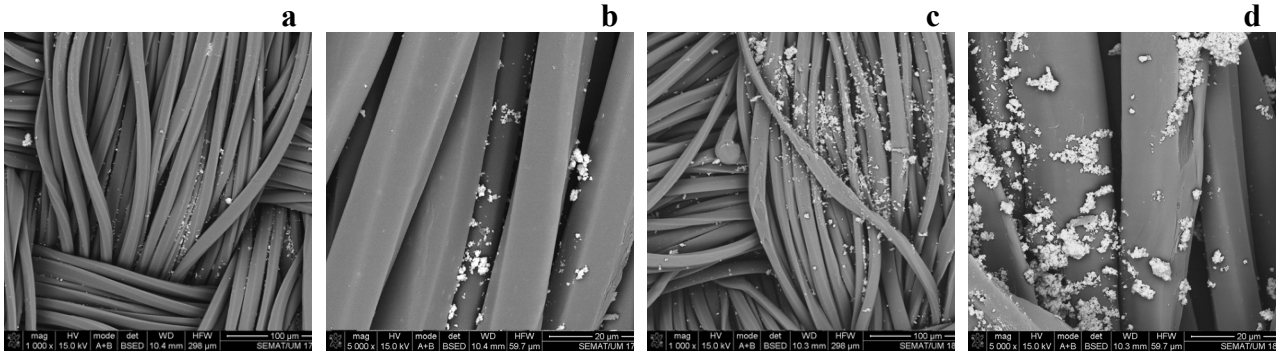

Fig. 1. SEM images of untreated (a and b) and DBD plasma-treated (c and d) PES samples with AgNPs with magnifications of 1000 x (a and c) and 5000 x (b and d).

The chemical modifications on the PES fabric surface induced by the functionalization with AgNPs and DBD plasma treatment, as well as the availability and oxidation state of Ag in the fabrics, was studied by XPS. DBD plasma treatment in air can create several species comprising atomic oxygen, nitrogen oxides, ozone, neutral and metastable molecules, radicals and ultraviolet radiation. The surface energy of materials treated with DBD increases by the introduction of oxygen polar group, due to the dissociation of oxygen molecules by electron impact. In addition, the excitation and dissociation of nitrogen molecules also can lead to other reaction paths able to produce extra atomic species [19]. In the deconvolution spectra of C 1s high-resolution spectra it was possible to observe three different peaks at 285.0 eV (C-C/C-H), 286.5 eV (C-O) and 288.9 eV (O=C) attributed to common chemical bonds in PES [20, 21]. The superior area in the O=C peak in DBD plasma-treated samples is in accordance with the reported increase in double bonded oxygen content (in the form of carboxylic groups) due to the plasma using air. This is also supported by the deconvolution's spectra of O 1s at 533.6 eV, where the C=O peak increased from 28.7 to 41.3 % (Fig. 2 and Table 1).

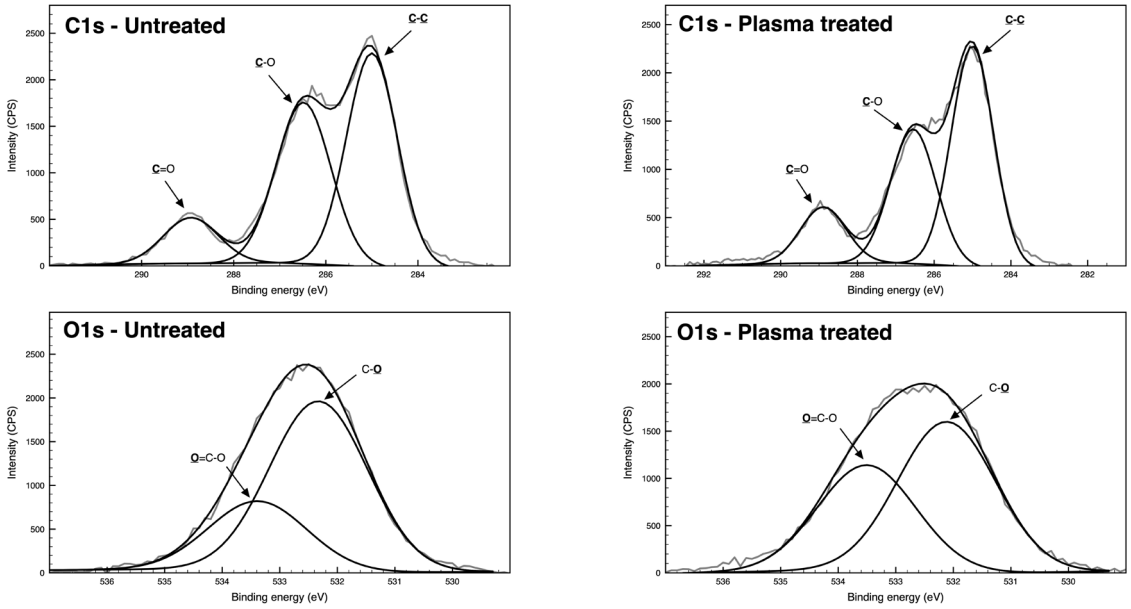

Fig. 2. Deconvolutions of the high-resolution XPS spectra of the C 1s and O 1s binding energy regions of PES fibers surface before and after DBD plasma treatment.

Lastly, the deconvolutions of the Ag 3d showed the presence of silver in untreated and DBD plasma-treated samples but a superior intensity in the treated sample. The deconvolution of the untreated PES sample showed the peaks with the binding energy of the Ag 3d5/2 and Ag 3d3/2 at 367.9 eV and 373.9 eV, respectively. These peaks were attributed to silver metals (Ag^0) on polyester fabric [22, 23]. The Ag 3d deconvolution spectra of plasma-treated samples showed the same peaks as untreated samples with small deviations, where the peaks appeared at 368.2 eV and 374.3 eV. These peaks displayed an intensity 4 times higher in the DBD plasma-treated sample, proving a far superior content of AgNPs when DBD plasma treatment was applied. Moreover, in the DBD plasma-treated sample two different and lower peaks emerged at the binding energies of 369.4 eV and 375.5 eV (relative area of 6.2 and 4.0%, respectively) (Fig. 3 and Table 1). The new peaks demonstrated the presence of oxidated Ag species on the AgNPs surface when DBD was applied [24, 25].

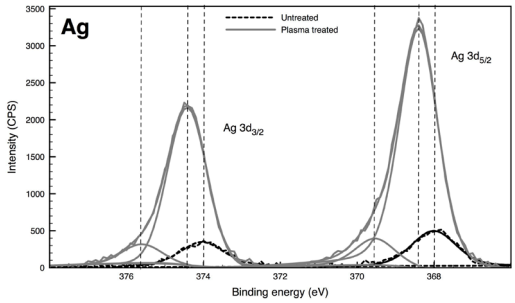

Fig. 3. Deconvolutions of the high-resolution XPS spectra of the Ag 3d binding energy region of PES fibers surface before and after plasma treatment.

Table 1. The relative percentage of chemical bonds in PES samples with and without DBD plasma treatment.

	Relative area of chemical bonds (%)								
	C1s			O1s		Ag3d			
	C-C/ C-H	C-O	C=O	C-O	O=C	Ag^0	Ag^+	Ag^0	Ag^+
	285.0 eV	286.5 eV	288.9 eV	532.6 eV	533.6 eV	367.9 - 368.2 eV	369.4 eV	373.9 - 374.3 eV	375.5 eV
Untreated PES	48.9	39.8	11.3	71.3	28.7	44.5	-	55.5	-
Plasma-treated PES	51.8	34.0	14.2	58.7	41.3	56.9	6.2	32.9	4.0

The antibacterial efficacy of the DBD plasma-treated and not treated PES fabric containing AgNPs was assessed using *S. aureus* and *E. coli* by shake flask method. The DBD plasma-treated samples showed superior antimicrobial activity when compared with the untreated sample against both tested bacteria (Fig. 4). The untreated sample showed a log reduction of 2.23±0.06 and 3.40±0.34 against *S. aureus* and *E. coli*, respectively, and the DBD plasma-treated sample showed a log reduction of 2.83±0.08 in *S. aureus* and the complete reduction of *E. coli*. The superior action of DBD plasma-treated samples can be due to the higher concentration of AgNPs onto fabric surface observed in the SEM images and deduced by the superior intensity of the peaks in the XPS analysis. This can also be a result of the reactive oxygen species formed during the plasma process. Even after 5 and 10 washing cycles (WC) the antimicrobial activity showed to be similar or higher than the initial samples. During the washing processes, the AgNPs that were inside the fabric can be directed to the textile surface, being the availability of nanoparticles higher than the initial one onto the surface of the fabric. On the other hand, the oxidation state of nanoparticles could be changed during the washing steps, generating a different action against different bacteria. This may explain the different results in the antimicrobial results after the washing processes. Accordingly, the efficacy of PES samples against *S. aureus* increased using plasma-treated samples after 5 and 10 WC and decreased in the untreated samples. Nevertheless, against *E. coli*, the activity increased in both samples. In general, AgNPs are more effective against Gram-negative than Gram-positive bacteria due to their structural differences. The AgNPs bind to the thin layers of peptidoglycan in Gram-negative bacteria, changing the permeability and penetrating it. In this case, although the concentration of nanoparticles in the untreated samples was lower than the DBD plasma-treated one, the washing process provided enough AgNPs with the suitable oxidation state to the surface of the fabric to improve the antibacterial activity against *E. coli*.

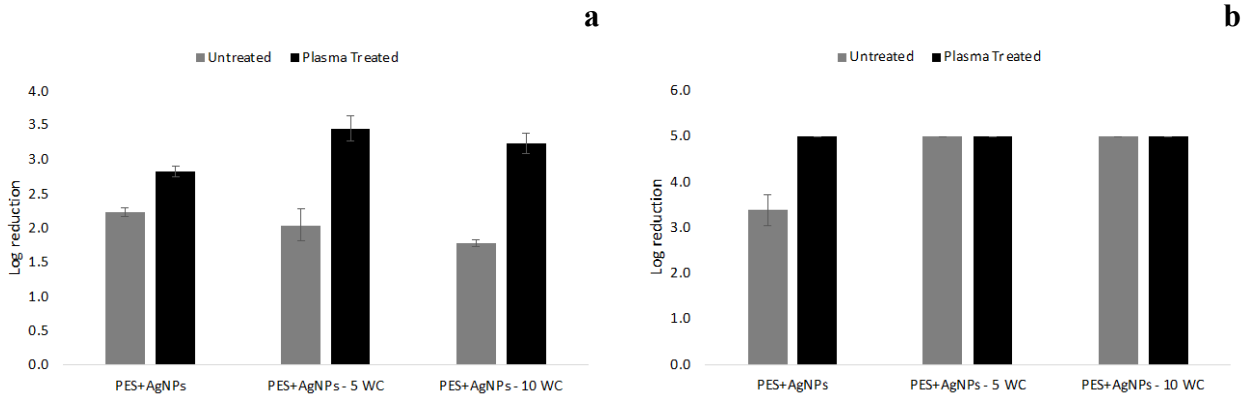

Fig. 4. Antimicrobial activity of PES samples against *S. aureus* (a) and *E. coli* (b) before and after 5 and 10 washing cycles (WC).

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