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Chemical, mechanical and antibacterial properties of silver nanocluster/silica composite coated textiles for safety systems and aerospace applications

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ABSTRACT

This work describes the chemical, mechanical and antibacterial properties of a novel silver nanocluster/silica composite coating, obtained by sputtering, on textiles for use in nuclear bacteriological and chemical (NBC) protection suites and for aerospace applications.

The properties of the coated textiles were analyzed in terms of surface morphology, silver concentration and silver release in artificial sweat and synthetic tap water, respectively. No release of silver nanoparticles was observed at given conditions.

The water repellency, permeability, flammability and mechanical resistance of the textiles before and after sputtering demonstrated that the textile properties were not negatively affected by the coating.

The antibacterial effect was evaluated at different experimental conditions using a standard bacterial strain of *Staphylococcus aureus* and compared with the behavior of uncoated textiles.

The coating process conferred all textiles a good antibacterial activity. Optimal deposition conditions were elaborated to obtain sufficient antibacterial action without altering the aesthetical appearance of the textiles.

The antibacterial coating retained its antibacterial activity after one cycle in a washing machine only for the Nylon based textile.

1. Introduction

Bacterial contamination is a problem for several applications such as medical devices and everyday life surfaces and objects used by the general public [1–5]. Applications in which this problem often is underestimated are protection garments for nuclear bacteriological and chemical (NBC) protective suits, health monitoring vests, antiseptic storage containers, and all related textile accessories used in the production of safety systems designed for harsh environments.

The newly developed NBC suit consists of a novel concept of a multi-layered antibacterial, permeable NBC protective textile. It can be used in emergency escape life-vests with integrated respiration and anti-flash textiles, or be integrated with conductive and/or anti-electrostatic textiles for a new generation of personal protective equipment (PPE) for fire-fighters, chemical and mining rescuers.

The elaboration of enhanced, stable and anti-septic textiles for applications in safety systems, designed for harsh environments, is of extreme importance as they should protect the user from infections or improve the security and well-being of personnel operating

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in difficult areas (war, natural disaster, third world countries, *etc.*), in which garments are worn for long time-periods.

Other plausible fields for exploitation of antibacterial coatings are in aerospace applications, in garments for astronauts that spend long time periods in closed environments, and to preserve antiseptic conditions of textiles (*e.g.* parachute and airbag subsystems) installed on interplanetary exploration probes, thus avoiding proliferation of bacteria from Earth or the external environment [6]. As an example, the next ESA ExoMars exploration mission will land an exploration rover on the surface of Mars, for which all materials and surfaces must be sterilized and sterile conditions maintained throughout the whole mission. Parachutes and airbags, typically made of textiles, are currently sterilized to reduce microbial charge by employing a dry heat microbial reduction process with thermal cycles at 126 °C for 35 h. The possibility to provide such items with a thermal resistant, long lasting anti-septic coating will allow multiple uses, and increase the efficiency of the exploration mission.

Silver antimicrobial activity and ability to inhibit polymicrobial/fungal colonization are well documented [7], even though the mechanism(s) still are debated [8]. In addition to its broad spectrum antibacterial activity silver presents a low bacterial resistance. This feature is extremely important considering the increasing development and spreading of bacterial resistance to antibiotics, as recently evidenced by international communications [9]. Several techniques such as sol-gel [10], chemical and physical vapor deposition [11], silver absorption on zeolites [12], biological synthesis [13] and ion exchange [14] have been explored to generate antibacterial coatings on different textile substrates. The fabrication methods of antimicrobial textiles are classified in two main categories; (a) addition of the antimicrobial agent to the fiber prior to its spinning or extrusion, and (b) post-treatment of the fiber or fabric during stages of finishing. Examples of commercial products fabricated using these methods are; (i) silver-coated polyester (Polyethylene terephtalate, PET) and cotton yarns, produced via the patented (Silvertech) *in situ* photo-reduction process of silver clusters [15,16] in which silver is deposited via silver nitrate impregnation in a water/alcoholic solution, (ii) nanostructured silver films of different thickness deposited on surfaces of polypropylene by magnetron sputtering [11], (iii) nanosized silver deposited on cellulosic and synthetic fabrics by colloidal processes [17], and (iv) antibacterial polymer textile fabric prepared by surface functionalization using RF-plasma or vacuum-UV, followed by immersion in $AgNO_3$ solutions of different concentration and silver reduction at a given pH using a weakly reducing agent [18]. Technologies such as Agiene®, Agion® and Trevira Bioactive® are available on the market to provide antibacterial functionality to textiles [19–21].

A novel antibacterial silver nanocluster/silica composite coating has recently been developed possible to deposit by means of RF co-sputtering on several substrates including glasses [22–24], metals and polymers [25,26]. The technique allows the thermal, chemical and mechanical stability of silica to be combined with the antibacterial characteristics of silver. According to literature findings are its main advantages, compared with other coatings, (i) its one-step coating process, (ii) its production without solvents or toxic chemicals, (iii) the lack of nanoparticle manipulation, (iv) the embedment of silver nanoclusters in a silica matrix, (v) its suitability for large scale production, (vi) its possibility to coat selected areas on almost any substrate, (vii) its possibility to tune the silver concentration and coating thickness, and (viii) its high thermal and mechanical stability, as evidenced in [26].

The aim of this paper is to present the chemical, mechanical, and antibacterial characteristics and performance of a novel silver nanocluster/silica composite coating applied on innovative textiles for use in nuclear bacteriological and chemical (NBC) protection suites, health monitoring vests, antiseptic storage containers and textile accessories for aerospace applications.

2. Experimental

2.1. Materials and coating

The study comprises three different textiles; (i) a white Nylon fabric PIA-44378D,Type I (denoted “Nylon”) used in parachutes and airbag subsystems and for use in aerospace environments, (ii) a black textile with active carbon (woven fabric: 59% cotton, 41% polyester; activated carbon spheres; non-woven fabric: 100% polyamide; 280 g/m^2) (denoted “Black”) used to absorb dangerous chemicals, and (iii) a camouflage Suit Tissue “Defender M, 210 g/m^2” (65% Lenzing FR^{TM} [27], 25% Para-aramidic fiber, 10% polyamide) (denoted “Camouflage”) used in NBC (Nuclear, Bacteriological, Chemical) suits.

The textiles were coated with the silver nanocluster/silica composite coating by means of a RF co-sputtering process (Microcoat MS450), using silver- (Sigma–Aldrich 99.99% purity) and silica (Franco Corradi S.r.l. 99.9% purity) targets. The coating was applied via a co-deposition process applying 200 W to a 6 in. silica target, and 1 W (in pulsed DC mode) to a 1 in. silver target. All process parameters are given in Table 1. Details on the nanocluster/silica composite coating are given elsewhere [22–26].

2.2. Physical, chemical and mechanical properties

Coating morphology and composition were analyzed for all coated textiles by means of field emission scanning electron microscopy and energy dispersive X-ray spectroscopy, FEG-SEM-EDS (QUANTA INSPECT 200, EDAX PV 9900, Zeiss SUPRATM 40). Compositional analyses of the outermost surface (a surface area of approximately 1 mm^2) of coated Nylon and Camouflage textiles were performed by means of X-ray photoelectron spectroscopy, XPS (Kratos AXIS Ultra^{DLD}, Kratos Analytical, Manchester, UK) using a monochromatic Al X-ray source.

Overall surface topographies of the coated Camouflage and Nylon textile surfaces were investigated by means of tapping mode atomic force microscopy, AFM (Digital Instruments Dimension 3100), imaging of 1–8 μm^2 large areas.

Coating thicknesses (on glass substrate) were determined by means of stylus profilometry (Tenkor^{TM} P16, US).

The total amount of silver in the coating was determined for each textile by means of atomic absorption spectroscopy (AAS) (air-acetylene flame, Varian AA240FS) after extraction in 20 mL heated (100 °C) nitric acid (HNO_3)/and fluoric acid (HF) mixtures (10% HNO_3/0.1% HF) for 2 h. The determination limit varied between 0.5 and 2.0 mg/L in the measured range.

The amount of released silver in solution (non-precipitated) was determined using atomic absorption spectroscopy (PerkinElmer AAnalyst 800) upon exposure in artificial sweat, in compliance with the EN1811 standard [28] (NaCl (5.0 g NaCl/L, 1.0 g urea/L, and 1.0 g lactic acid/L), and in synthetic tap water (0.099 g $CaCO_3$/L), 0.033 g NaCl/L, and 0.0298 g Na_2SO_4/L), respectively. Coated samples (approximately sized 1 cm × 1 cm) were immersed with an area/solution volume ratio of 1 cm^2/10 mL for 2, 4, 24 and 168 h at dark conditions at 37 °C and pH 6.5 for artificial sweat (determination limit – 0.5 μg/L), and at pH 7.5 for synthetic tap water (determination limit – 0.5 μg/L). Triplicate coated samples and one uncoated sample were exposed for each time period and solution.

Parallel measurements of the released amount of silver from the coated textiles (by means of AAS, air-acetylene flame, Varian AA240FS) were made after soaking in tap water and artificial sweat respectively at 37 °C (stirring conditions – 10 rpm). The samples