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Surface chemical and biological characterization of flax fabrics modified with silver nanoparticles for biomedical applications

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ABSTRACT

Silver nanophases are increasingly used as effective antibacterial agent for biomedical applications and wound healing. This work aims to investigate the surface chemical composition and biological properties of silver nanoparticle-modified flax substrates. Silver coatings were deposited on textiles through the in situ photo-reduction of a silver solution, by means of a large-scale apparatus. The silver-coated materials were characterized through X-ray Photoelectron Spectroscopy (XPS), to assess the surface elemental composition of the coatings, and the chemical speciation of both the substrate and the antibacterial nanophases. A detailed investigation of XPS high resolution regions outlined that silver is mainly present on nanophases' surface as Ag_2O. Scanning electron microscopy and energy dispersive X-ray spectroscopy were also carried out, in order to visualize the distribution of silver particles on the fibers. The materials were also characterized from a biological point of view in terms of antibacterial capability and cytotoxicity. Agar diffusion tests and bacterial enumeration tests were performed on Gram positive and Gram negative bacteria, namely *Staphylococcus aureus* and *Escherichia coli*. In vitro cytotoxicity tests were performed through the extract method on murine fibroblasts in order to verify if the presence of the silver coating affected the cellular viability and proliferation. Durability of the coating was also assessed, thus confirming the successful scaling up of the process, which will be therefore available for large-scale production.

1. Introduction

Over the past years, the increasing phenomenon of the bacterial resistance to conventional antibiotics has strongly encouraged the interest in defining new routes for the formulation of novel safe and cost-effective biocidal materials [1–3]. Silver nanoparticles (AgNPs), in particular, have received great attention due to their unique bactericidal properties and have been widely applied to many consumer products and medical purposes [4–10].

Some authors have recently reported on the high degree of commercialization of nanosilver-related products for applications in electronics, disease diagnosis, imaging, treatment of infections etc. [11–14]. Particularly in the treatment of infected burns, wounds and chronic ulcers, AgNPs have received great attention for the formulation of topical dressings [15–18], as the risk of wound infection still remains the most common reason for impaired wound healing [19–23].

Traditional dressing cannot ensure protection against bacteria [24, 25], thus motivating the design of novel products for antibiotic or antimicrobial delivery in the wound site [26–28] and novel treatments of biofilm-associated infections [29]. Silver-containing dressings have been demonstrated to be effective in killing bacteria in mono- and poly-microbial biofilms, thus providing evidence of an effect on biofilm in recalcitrant chronic wounds [30–33]. Silver alginate dressings were found to be effective in inhibiting the growth of both Gram-positive and Gram-negative bacteria and yeast isolated and cultured from wounds [34]. A wide array of silver-based dressings is available on the market for application in acute and chronic wound care and in the treatment of diabetic ulcers [29,30]. Local application of several types of dressings including hydrocolloid, alginate, hydrogel, membrane and silver/alginate composites has also been proposed [35,36].

However, only few products involve the use of silver in the form of nanoparticles. Moreover, among natural textile fibers used as wound dressing, cotton has received the greatest attention in literature for the preparation of antibacterial fabrics. AgNPs immobilized on cotton fabrics were obtained by γ-irradiation [37], by sonochemical methods [38] or through the preparation of colloidal solutions [36,39] and physical deposition of AgNPs–alginate composites [40], with or without the use of binders.

This work aims to propose a different natural substrate, such as flax, in combination with silver in the form of nanoparticles. Flax has been used since ancient times for the production of linen cloth widely used in humid climates. Flax is an attractive material for wound dressing, as it may be useful in keeping the wound at the optimal moisture level

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[6,41–44]. In a previous work, wound-dressing biomaterials have been obtained by depositing flax substrates with a hydrogel embedding silver particles [45]; in this paper, flax has been directly treated with silver by translating the technology reported in previous works about cotton [46–48] to a different substrate and in a different production scale. In the previous cited works, the excellent adhesion of the particles to cellulosic fibers and the efficacy of silver-coated gauzes against fungi and bacteria were demonstrated even after conditioning in artificial exudate [47,48]. However, the novel technological approach to translate the process on large scale has not yet been investigated. In this work, the silver deposition technique was successfully scaled up through the design of a roll-to-roll apparatus allowing the treatment of large volumes of fabrics. Moreover, surface characterization such as X-ray Photoelectron Spectroscopy (XPS) of cellulosic fibers alone has already been proposed [49–51], but the investigation of modified fibers has not yet been deeply explored. Additionally, the XPS analysis of high resolution $Ag3d_{5/2}$ and Ag_{MNN} regions was carried out, to evaluate silver surface chemical speciation [52,53]. The surface chemical characterization of neat and treated flax samples, considering also the influence of the washing cycles and the nominal silver content, was also accomplished by XPS, corroborating results from SEM analysis performed to evaluate the stability of the silver coating and the strong adhesion of the particles to the fibers after laundries.

Cytotoxicity tests were performed on murine fibroblasts 3T3 through the extract method, in order to evaluate the influence of the silver coating on cellular viability and proliferation.

The antibacterial efficacy of nanosilver treated materials was demonstrated on Gram positive and Gram negative bacteria through qualitative and quantitative microbiological tests, even after the washing cycles.

2. Experimental details

2.1. Surface modification of flax fabrics

Textile materials kindly provided by Silvertech Ltd (Lecce, Italy) were flax substrates with density 1.5 g/cm^3, surface mass 0.02 kg/m^2, breaking tenacity 30 cN/Tex, produced without any chemical agent. They were treated with silver nanoparticles through the in situ photoreduction of silver nitrate [46]. While previous studies described the successful application of the technology to different materials on a laboratory scale, this work aimed to translate the process on a larger scale in order to evaluate the effectiveness of the silver deposition technique in providing durable antibacterial coatings on mass production. The technology consists of the deposition of a silver solution on the surface of the materials by dip or spray coating, and of the following exposure to UV irradiation ($\lambda = 365$ nm; 500 W) to induce the photo-reduction of the silver salt and the in situ synthesis of silver particles. Firstly, the silver solution is prepared by mixing silver nitrate, methanol and deionized water under magnetic stirring at room temperature until complete dissolution of the silver salt. Silver nitrate represents the precursor for metal silver, while methanol is used as both solvent and reducing agent in the photo-chemical reaction.

Then, the silver solution is deposited on the surface of the material through a proper method defined as function of the nature of the material, the application and the process scale-up. Finally, the wet materials are exposed to the UV source by defining the most appropriate distance from the lamp and minimum exposure time ensuring the complete reaction.

The conversion from silver salt to silver nanoparticles occurs through the following photo-chemical reaction

$$Ag_n + 2Ag^+ + CH_3OH + h\upsilon \rightarrow Ag_{n+2} + 2H^+ + CH_2O. \quad (1)$$

The process parameters are defined experimentally, by evaluating the loss of silver after washing cycles through thermo-gravimetric analysis (TGA) and energy dispersive X-ray spectroscopy (EDX). In this work, 0.1%$_{w/v}$ of silver nitrate in 10%$_{v/v}$ methanol/water has been selected for the preparation of the silver solution.

In order to allow the treatment of higher volumes of products, a roll-to-roll prototype apparatus designed for textile substrates has been adopted. The apparatus, consisting of an impregnation bath, a roll-to-roll transport system and a UV station, has been designed for the treatment of different textile materials, such as natural and synthetic yarns and fabrics. It is however well known that the treatment of natural and synthetic substrates with a silver-based antibacterial coating can cause the darkening of the substrate. As a result, one possible limitation of the work may be associated to the definition of the most appropriate process parameters in order to minimize the change in color of the fabric. For this reason, some parameters such as the impregnation time, the speed of the roll-to-roll system, the UV exposure time and the distance from UV lamp were properly set to contain the color variation and to ensure the absence of discoloration areas in the final product. In Fig. 1, pictures of the apparatus during the treatment of textile substrates are reported. In this work, flax fabrics (width 1 m) were impregnated in the bath containing the silver solution; then, the wet substrates were moved by the roll-to-roll system toward the UV station of the apparatus. The substrates were exposed to UV for a minimum time of 5 min at a distance of 30 cm from the UV lamps. Then, the substrates were washed with water to remove any presence of unreacted salt and samples were obtained for characterization. In order to test the durability of the coating and the resistance to laundries, the fabrics underwent ten washing cycles by adopting an Electrolux washing machine W4180H and a commercial soap, according to European Standard EN 26330:1993.

Then, the samples were again characterized.

2.2. Surface characterizations

Silver treated samples and untreated samples as control were analyzed through scanning electron microscopy SEM (Zeiss EVO) equipped

Fig. 1. Pictures of the prototype apparatus developed for the silver deposition treatment of textile substrates. a.) Textile substrates moving toward UV station; b.) UV exposure of the textile substrates.