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In-situ photo-assisted deposition of silver particles on hydrogel fibers for antibacterial applications

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ABSTRACT

Silver nanoparticles (AgNPs) have attracted intensive research interest and have been recently incorporated in polymers, medical devices, hydrogels and burn dressings to control the proliferation of microorganisms.

In this study a novel silver antibacterial coating was deposited for the first time on hydrogel fibers through an *in-situ* photo-chemical reaction. Hydrogel blends obtained by mixing different percentages of silver-treated and untreated fibers were characterized by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Four different fluids, such as phosphate buffered saline (PBS), simulated body fluid (SBF), chemical simulated wound fluid (cSWF), and deionized water (DI water), were used for evaluating the swelling properties. The results obtained confirmed that the presence of silver did not affect the properties of the hydrogel. Moreover, the results obtained through inductively coupled plasma mass spectrometry (ICP-MS) demonstrated very low silver release values, thus indicating the perfect adhesion of the silver coating to the substrate. Good antibacterial capabilities were demonstrated by any hydrogel blend on *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) through agar diffusion tests and optical density readings.

1. Introduction

Recently, hydrogel and hydrogel-nanoparticle systems have opened a new skylight for different applications in biomedical engineering and these approaches are most effective and safe because they are compatible with most of biological molecules, cells and tissues [1,2].

Superabsorbent hydrogels are three-dimensional crosslinked hydrophilic, linear or branched polymers with the ability to absorb large quantities of water, saline or physiological solutions compared with general absorbing materials [3,4]. Because of their excellent hydrophilic properties, high swelling ratio and biocompatibility, hydrogels have been widely used in agriculture, biomedical area, tissue engineering, biosensors and sorbents for the removal of heavy metals and drug delivery [5]. Usually, most hydrogels are prepared from synthetic polymers by radical frontal or graft copolymerization, cross-linking and ionizing radiation [6].

The water holding capacity and permeability are the most important characteristic features of a hydrogel. The polar hydrophilic groups are the first to be hydrated upon contact with water, thus leading to the formation of primary bound water [7]. As a result, the network swells and exposes the hydrophobic groups, which are also capable of interacting with the water molecules. This leads to the formation of hydrophobically-bound water, also called 'secondary bound water' [7]. The primary and secondary bound water are often combined and called 'total bound water'. Because of their high absorption properties, hydrogels are very appealing materials for biomedical applications such as burn dressing or wound healing patches [8]. Recently, hydrogels have been used as scaffolds for guided bone regeneration in dental implants, and for osteogenesis when loaded with growth and differentiation factors [9,10].

Abbreviations: AgNPs, Silver nanoparticles; TGA, Thermogravimetrical analysis; FT-IR, Fourier transorm infrared; SEM, Scanning electron microscopy; EDX, Energy-dispersive X-ray spectroscopy; PBS, Phosphate buffered saline; SBF, Simulated body fluid; cSWF, Chemical simulated wound fluid; DI, Deionized; ICP-MS, Inductively coupled plasma mass spectrometry.

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Silver nanoparticles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving their bactericidal and fungicidal effectiveness [1].

Nano-sized silver particles provide a broad-spectrum antimicrobial effect through the inhibition of bacteria replication by interfering with DNA and RNA, the disruption of the cell membrane, interference with cell respiration, and inactivation and alteration of enzyme conformation [11].

Notoriously, silver ions have shown high toxicity to different species of bacteria including *Escherichia coli* and *Staphylococcus aureus* [12,13].

Silver is characterized by long-term activity against a broad spectrum of microorganisms [14]. This excellent antimicrobial agent [15] shows also a good resistance to sterilization techniques [16,17] and high biocompatibility [18].

The efficiency of nanosilver treated fibers in medical applications is widely reported in literature [19–24]. AgNPs are commonly used also in surgical fields, such as urology, dentistry, general surgery and orthopedics [20]. Hospital-acquired or nosocomial infections, particularly related to orthopedic fixation and artificial joint surgery, are normally hard to avoid infections [21–23]. The use of hydrogel fibers treated with silver nanoparticles in a slow release dressing would allow controlled bacteriostasis [24].

The aim of this work was the production and the characterization of advanced materials based on the combination of hydrogel and silver for application in biomedical fields, where a high absorption of sweat or exudate is required to improve comfort and welfare.

In this paper silver treated hydrogel fibers for application as biomaterial with improved antibacterial and superabsorbent properties are proposed.

The deposition of silver coatings on hydrogel fibers was performed through a technique based on the photochemical deposition of silver particles. This is a process developed and optimized at the University of Salento (Lecce, Italy) and widely applied to different substrates [25]. The novelty of this work is that the photochemical deposition of silver particles was carried out for the first time on synthetic hydrogel fibers. In order to reduce the costs and to develop a homogeneous product with good reproducibility, treated hydrogel fibers were mixed with untreated fibers in different percentages. The blends obtained were tested in terms of morphology, swelling properties and antibacterial capability on Gram positive and Gram negative bacteria, and the results were compared with the data obtained by neat hydrogel fibers and 100% silver treated hydrogel fibers. In this study, three blends have been obtained by mixing treated and untreated hydrogel fibers. Particularly, 50 wt.% (Blend A), 34 wt.% (Blend B) and 25 wt.% (Blend C) of silver treated hydrogel fibers were mixed with untreated fibers, in order to define the lowest concentration of silver treated fibers in the blend ensuring a good antimicrobial capability without altering the properties of the hydrogel blend, with evident advantages in terms of costs.

The different absorption properties of the blends in contact with biological fluids were evaluated through swelling tests with phosphate buffered saline, simulated body fluid and simulated wound fluid by using deionized water as control. Swelling properties were investigated by measuring the equilibrium swelling ratio in four different solutions, in order to evaluate the behavior of the material in simulated physiological conditions. The antimicrobial behaviors of the blends were also evaluated to afford important information for their application in the biomedical field.

The structure and properties of the material obtained were evaluated and studied. The morphological changes of the hydrogels were evaluated by SEM, while TGA and EDX were adopted to quantify the amount of silver deposited on the material. ICP-MS analysis was performed in order to evaluate the amount of silver release and to evaluate the adhesion of the silver coating on the substrate.

2. Materials and methods

2.1. Preparation of silver treated hydrogel fibers

The substrates used for the silver deposition were superabsorbent fibers named “Oasis Type 102/52/10” based on crosslinking copolymers of acrylic acid (acrylic acid, methyl acrylate and a silicone finish) commercialized by Technical Absorbents Limited, UK. The number 102 refers to the product code and indicates a standard product for carded non-woven/yarns with good absorbency properties, high wet integrity and increased wet mechanical strength. The number 52 indicates the length of the fibers in mm; the number 10 refers to the count in dtex.

In this work the deposition of silver particles was obtained by impregnation of fibers in an alcoholic solution made of 0.5 wt./v% silver nitrate (Alfa Aesar ACS 99.9%) dissolved in 4.5 v/v% of methanol (Carlo Erba 99.9%) and 95% deionized (DI) water.

Samples of hydrogels were weighted and placed in petri dishes. The silver solution was sprayed on the substrates by using a sprayer and by depositing four grams of solution per each gram of hydrogel fibers. Then, the wet spray-coated fibers were placed into a box containing a UV lamp (500 W) and exposed to UV irradiation (wavelength 365 nm, time 40 min, distance 20 cm) in order to induce the *in-situ* photoreduction of the silver ions and the formation of silver particles on the fibers surface. Methanol takes part to the chemical reaction as photo-reducing agent in the photoreduction process of silver nitrate and its percentage is defined according to the percentage of silver nitrate adopted. A low amount of silver (0.5 wt./v%) and also a low percentage of methanol were selected in order to minimize the costs of the treatment. Also, different blends of silver treated and untreated hydrogel fibers were prepared and tested in order to define the most advantageous system in terms of effectiveness, versatility and reproducibility.

After the treatment, the fibers were washed thrice using DI water in order to remove the unreacted salt. Then, the material was dried in oven at 45 °C overnight. After drying, the hydrogel blends were prepared by mixing the defined percentages of silver treated fibers with untreated fibers. Dry silver treated and untreated hydrogels were weighted and then the blends were manually prepared in the petri dish using a stainless steel spatula, by mixing at 1 Hz for 30 s. Particularly, sample “T” (treated) was prepared using 100% of silver-treated hydrogel fibers and 0% of neat hydrogel fibers. This sample used as positive control was adopted to obtain information about the change in properties of the hydrogel fiber associated to the presence of silver. The silver amount in treated and untreated fibers of each blend is reported in Table 1.

The untreated sample “NT” was used as negative control.

2.2. Preparation of fluids

SBF and cSWF were prepared according to the protocols reported in literature [26–29]. These fluids were used to evaluate the behavior of the material in a biological environment for biomedical applications.

Table 1
Percentages of silver-treated hydrogel fibers and untreated fibers in blends.

	% treated fibers	% untreated fibers
Sample T	100	0
Blend A	50	50
Blend B	34	66
Blend C	25	75
Sample NT	0	100