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Characterization of antibacterial silver coated yarns

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Abstract Surface treatments of textile fibers and fabrics significantly increase their performances for specific biomedical applications. Nowadays, silver is the most used antibacterial agent with a number of advantages. Among them, it is worth to note the high degree of biocompatibility, an excellent resistance to sterilization conditions, antibacterial properties with respect to different bacteria associated with a long-term of antibacterial efficiency. However, there are only a few antibacterial fibres available, mainly synthetic with high production cost and limited effectiveness. Cotton yarns with antimicrobial properties are most suitable for wound healing applications and other medical treatments thanks to their excellent moisture absorbance while synthetic based fibres are most suitable for industrial applications such as automotive tapestry and air filters. The silver-coated fibers were developed applying an innovative and low cost silver deposition technique for natural and synthetic fibers or yarns. The structure and morphology of the silver nanoclusters on the fibers was observed by scanning electron microscopy (SEM), atomic force microscopy analysis (AFM) and XRD analysis, and quantitatively confirmed by thermogravimetric analysis (TGA) measurements. Good silver coating stability has been confirmed performing several industrial washing. Antimicrobial tests with *Escherichia coli* were performed.

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1 Introduction

Nowadays silver is the most adopted antibacterial agent on various supports [1, 2], due to its high biocompatibility [3], excellent resistance to sterilization conditions, effectiveness on different bacteria [4] and long-term durability of its antibacterial effect. Silver has been known as a purifying agent since the Egyptian age when it was employed to purify water to be stored for a long period of time. When released by the fiber surface, silver ions interact with the bacteria leading to its death crossing the cell wall [5, 6]. Modern medicine makes use of silver as an antibacterial agent in the treatment of burns or eye infection in new-born babies [5]. Anti-inflammatory properties of silver have also been proved by a reduced reddening of infected wounds edges.

Cellulose and cotton fibers with antimicrobial properties are usually chosen for wound healing and other medical treatments [7–10] thanks to their excellent moisture absorbance, while synthetic based fibres are most suitable for industrial applications such as automotive tapestry and air filters. However, coating and/or incorporating silver into the fibres is challenging. Synthetic fibres such as polyester, polyamide and polypropylene are mostly used as a host fiber material, and silver antibacterial agent is usually added in metallic form during melt-spinning. This increases production complexity and costs of final products, mainly due to the presence of solid metallic silver particles. Recently different procedures have been progressed to deposit metallic silver on different substrates [11–16].

In these papers mild reducing conditions are applied, all involving a silver salt and a reducing agent. In some cases fiber pre treatment after improved silver adhesion is also proposed.

Even if the demand of cellulose fibers for wound healing and other medical treatments is increased in the last years, due to their excellent moisture absorbance [17–19], cotton fibres do not exhibit any antibacterial property. In this work silver coated fibres produced applying a patented silver deposition technique were used [11]. Antibacterial properties of silver treated substrates were demonstrated using *Escherichia coli*. These tests confirmed that deposited silver nanoclusters, examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM), present a good antibacterial efficacy, comparable to the one shown by kanamicina antibiotic. Thermogravimetric analysis (TGA) on treated cotton fibers demonstrated a good silver coating stability, even after several industrial washings, thus confirming the durability of the innovative silver treatment on the cotton substrates.

2 Materials and methods

Silver coated polyester (Polyethylene terephtalate, PET) and cotton yarns, produced applying a patented silver deposition technique, were kindly provided by Silvertech Ltd. Silver deposition is obtained by UV reduction of a silver salt dissolved in an alcoholic solution. This solution is used to impregnate the yarns.

Antibacterial tests were carried out following the Standard '*SNV 195920-1992*' sketched in Figs. 1, 2. The

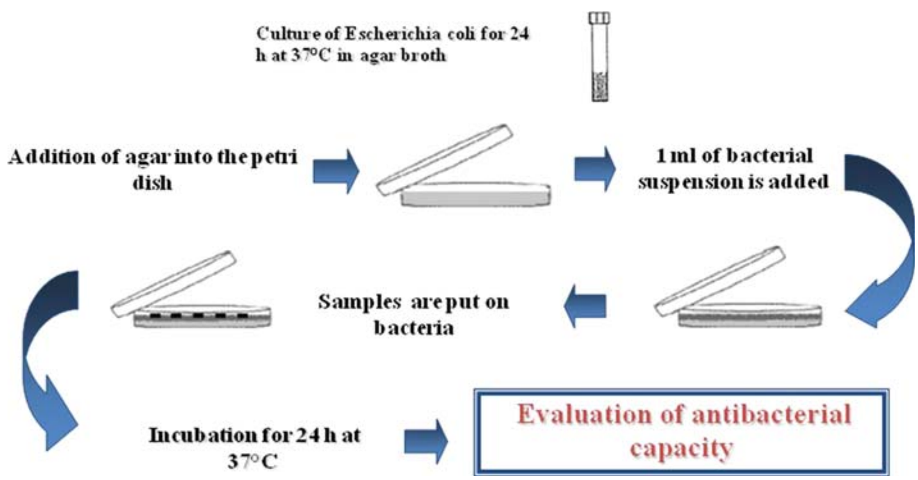

Fig. 1 Experimental control method of antibacterial activity through diffusion test in Agar (Standard '*SNV 195920 -1992*')

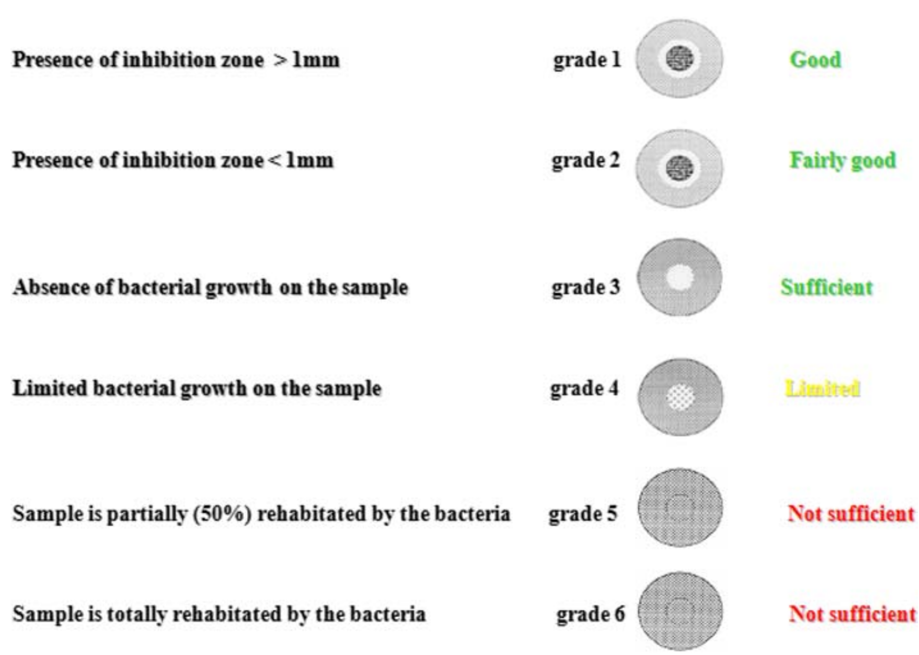

Fig. 2 Different levels of antibacterial capacity as a function of the presence and size of inhibition growth area around the sample (Standard '*SNV 195920 -1992*')

antibacterial activity was assessed through a diffusion test in Agar (from Aldrich). Following this method, an *E. coli* colony is positioned in a petri dish filled with agar gel. A yarn or a few fibres was placed over the colony and the whole dish was incubated in oven at 37°C for 24 h. After this period, the dish is removed from the oven and the area covered by the bacteria colony with respect to the samples was evaluated. If a growth inhibition area was observed close to the sample (characteristic size >1 mm), antibacterial property is labeled as 'good'. If the sample is totally rehabitated by the bacteria, the antibacterial property is labelled as 'not sufficient'. Different levels of antibacterial capacity are related to the dimension of the growth inhibition area around the sample, as reported in Fig. 2.

The size and morphology of silver nano-cluster present on antibacterial fibers were examined by scanning electron microscopy (SEM) Jeol JSM-6550F and atomic force microscopy (AFM) in contact mode by using an EXPLORER-VEECO system equipped with a Si_3N_4 pyramidal tip. X-ray diffraction was performed in order to detect the crystal structure of silver nanoclusters on the fibers substrate. XRD measurements were carried out using a Cu-Kα radiation on a Rigaku Ultima$^+$ equipment operating at 40 kV and 20 mA, between $10° \leq 2\theta \leq 100°$.

The stability of silver treatment on the cotton substrates was analysed by thermogravimetric analysis (TGA) using a NETZSCH STA 409 operating in air. The solid residue above 800°C is attributed to the incombustible silver coating. The TGA analysis was also performed after 0, 1, 5, 15 and 20 industrial washing cycles at 40°C for 30 min by using an Electrolux washing machine model W4180H with the use of a softening agent (Morbisol Eco from Anco Ltd) followed by drying cycles with an Electrolux dryer model T4350.

3 Results and discussion

As reported in the literature, either polyester either cotton fibers coated by silver exhibit antibacterial capability for *E. coli* [20]. In this study antibacterial tests were performed on a sample of spun cotton previously impregnated with kanamicina antibiotic, and on a sample of untreated spun cotton for comparison purposes. The effect of silver compared with the control samples was determined by measuring the size of the area of inhibition growth close to each sample.

As clearly shown in Fig. 3a, the *E. coli* colony seeded in the petri dish filled with agar grows on the neat cotton sample after incubation in oven at 37°C for 24 h: neat cotton does not display any antibacterial activity, as expected.

The antibacterial effect of a silver coated cotton yarn is shown in Fig. 3b. It can be observed a clearly defined bacterial free zone around each sample which confirm the growth inhibition effect induced by silver ions. A similar antibacterial behaviour is shown in Fig. 3c, where a sample of spun cotton impregnated with kanamicina antibiotic is tested: it is evident that the silver coating leads to an antibacterial effect comparable or even improved compared with those of a specific antibiotic.

Antibacterial behaviour of synthetic polymers-based fibers was also investigated. Four samples of a polyester woven made using a different amount of silver-treated

Fig. 3 Test of *Escherichia coli* growth on **a** neat spun cotton, **b** antibacterial fiber, **c** a sample of spun cotton impregnated with kanamicina antibiotic

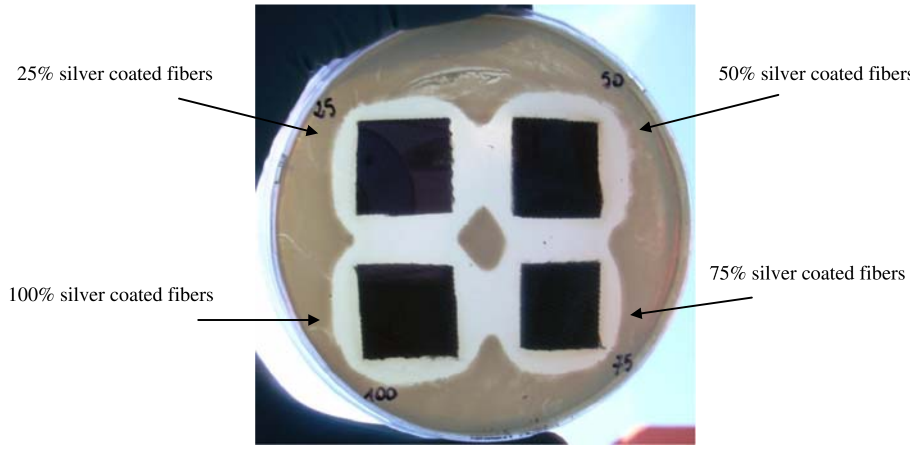

Fig. 4 Test of *Escherichia coli* growth on antibacterial polyester fibers

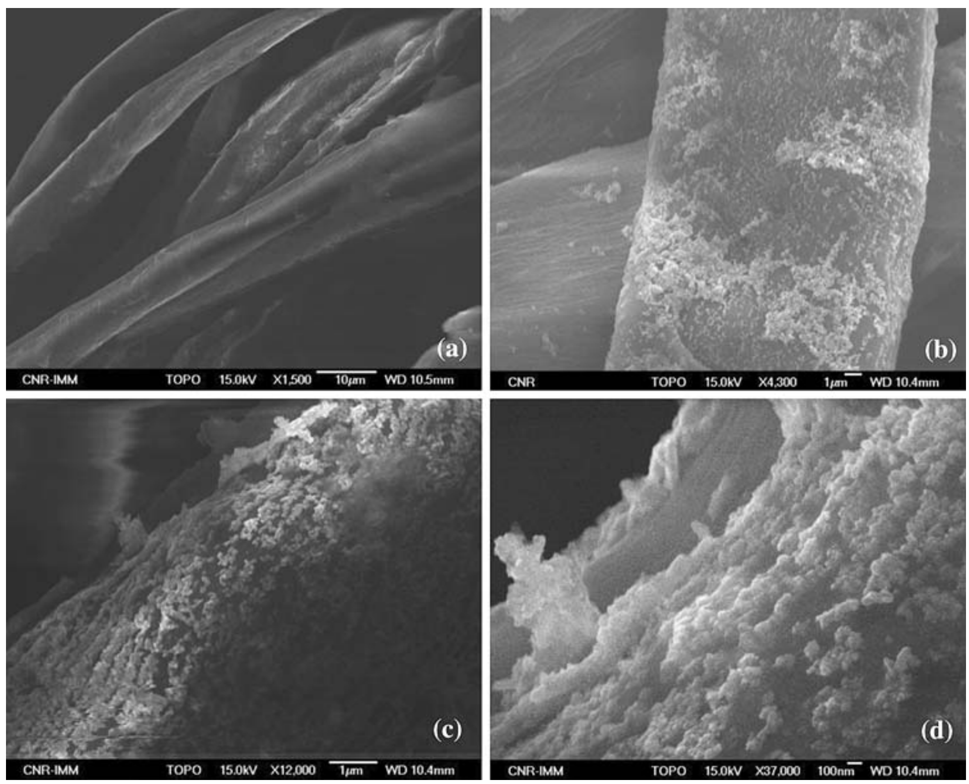

Fig. 5 SEM images of **a** neat spun cotton fiber at 1500× magnification, **b** silver-treated cotton fiber at 4300× magnification, **c** silver-treated cotton fiber at 12000× magnification, d silver-treated cotton fiber at 37000× magnification

fibers were placed in the E-Coli bacteria colony. The picture obtained after 24 h incubation at 37°C in back-light observation is shown Fig. 4. A high antibacterial effect is clearly evident by the growth inhibition zone which is present around all the samples. Moreover, it is worth noting that even the samples with the lower percentage of antibacterial fibers (25% in the yarn) displays a high antibacterial capacity, indicating that a low amount of silver-coated fibers in the yarn can be successfully used with a clear advantage in terms of device costs.

The SEM pictures reported in Fig. 5 were obtained on a silver treated cotton sample and on a sample of neat spun cotton used as control (Fig. 5a). As shown in Fig. 5a, a neat spun cotton fiber at 1500 magnification is characterized by a smooth surface. A non uniform layer of silver was deposited as shown in Fig. 5b–d. In particular Fig. 5b shows an image of silver-treated cotton fiber at 4300 magnification which is characterized by a non uniform layer of silver in cluster form; it is possible to observe that in some cases silver clusters aggregate. Fig. 5c, d, acquired respectively at 12000× and 37000× magnification, clearly indicate that silver clusters, made of nanocrystals of quite regular shape characterized by dimensions of the order of 100 nm, are present.

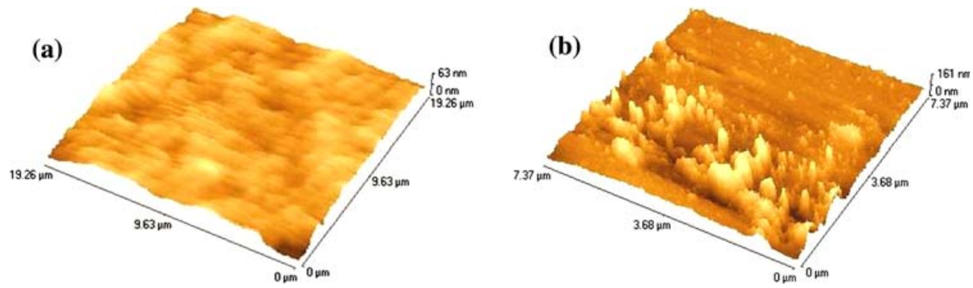

Fig. 6 3D AFM image of **a** neat polyester fiber, **b** silver-treated polyester fiber

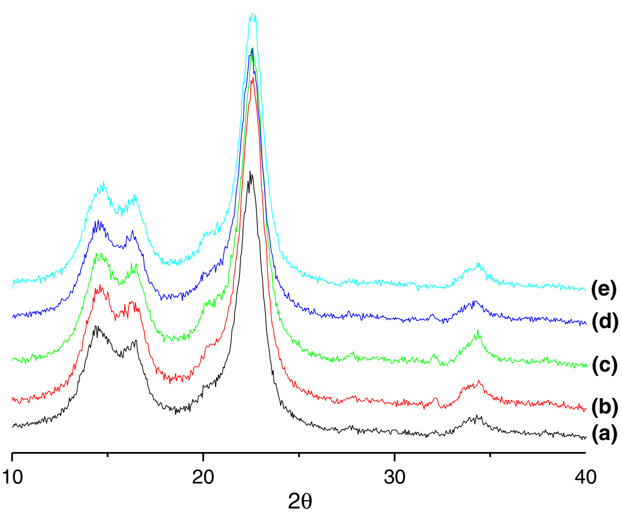

Fig. 7 X-ray patterns of silver-treated cotton (*a*), after 1 time washing (*b*), after 5 times washing (*c*), after 10 times washing (*d*), after 20 times washing (*e*)

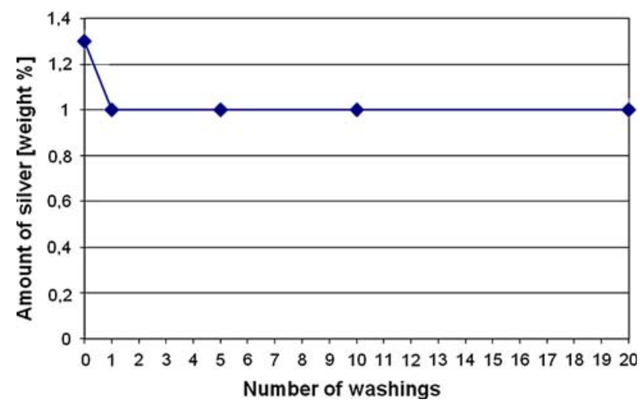

Fig. 8 Results of thermogravimetric analysis conducted on silver-treated cotton and on treated cotton industrially laundered 1, 5, 10, 20 times respectively

The surface topography was conducted on polyester fiber by AFM microscopy in order to point out the morphological change obtained after the silver deposition treatments.

In Fig. 6a is shown AFM analysis conducted on neat polyester fiber characterized by a smooth surface.

A silver treated polyester fiber reveals a different morphology, as shown in Fig. 6b, where silver aggregates are randomly distributed on the surface. The same characteristic dimensions of 100 nm, also observed in SEM pictures, can be easily recognized.

The results of the XRD analysis performed on fabrics made with silver-treated cotton, before and after several industrial washing cycles (1, 5, 10, 20 cycles), are reported in Fig. 7. The XRD patterns are typical of the cellulose [21], showing the main diffraction signals at 2θ values of 14.9°, 16.3°, 22.5°, and 34.6°, attributed to the diffraction planes 101, 101, 002, and 040, respectively [22]. Interestingly, the XRD patterns do not show any characteristic diffraction peak of silver, for all of the fabrics. This finding might be ascribed to the very limited amount of silver deposited, and is consistent with similar literature results [23].

Thermogravimetric analysis (TGA) was carried out on silver-treated cotton before and after 1, 5, 10 and 20 industrial washing cycles. Figure 8 shows the results of thermogravimetric analysis; the initial amount of silver was equal to 1.3 wt%, and after 1 cycle and up to 20 cycles it remains at 1 wt%, indicating a good adhesion and stability of silver clusters on the substrate.

4 Conclusions

Antibacterial silver based fibers are suitable for many different applications ranging from medical (such as surgical clothes, wound healing etc.) to woven and non-woven fabrics.

The studied fibers and fabrics were developed by means of a patented silver deposition technique suitable for natural and synthetic fibers or yarns.

SEM and AFM analysis show a non uniform layer of silver clusters made of crystals with a characteristic dimension of about 100 nm. Silver treated fibres show strong antibacterial activity against *E. coli* colony as confirmed by antimicrobial test even if a limited amount of silver fibers are used to fabricate a yarn. The high stability of antibacterial treatment, even after a significant number of industrial washing and drying cycles, was demonstrated with thermogravimetric analysis (TGA).

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