Silver-Coated Wool Yarns with Durable Antibacterial Properties

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ABSTRACT: The use of fabrics with antibacterial properties for commodity applications can provide numerous advantages such as a reduction in the release of odors due to bacterial proliferation in sweat and a reduction in the development of skin hypersensitivity reactions due to microorganisms trapped into the fabrics. Silver is one of the most effective antibacterial agents used for the high degree of biocompatibility and for its long-term antibacterial effectiveness against many different bacterial strains. In this study, an innovative technique for the deposition of nanosilver antibacterial coating on woolen fiber was analyzed. In particular, fabrics woven with different percentages of silver-treated fibers were compared to determine the best ratio preserving the antibacterial activity and optimizing the cost-effectiveness of the final product. Scanning electron microscopy revealed a uniform distribution of silver nanoclusters on the fibers. The impressive silver coating stability and durability were demonstrated after several washing cycles through thermogravimetric analysis. The antimicrobial activity of the silver-treated substrates was evaluated by antibacterial tests on *Escherichia coli*. A very strong antibacterial activity was found even in presence of the lower silver content; therefore, a blend of coated and uncoated fibers is proposed for practical applications. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2239–2244, 2012

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INTRODUCTION

There is a growing interest toward the use of fabrics characterized by nontoxic and durable antimicrobial finishing for the production of medical devices, personal hygiene or healthcare products, and consumer goods.[1–3] Surface treatments on fibers or fabrics can significantly increase their functional performances. Antibacterial properties are strictly related to the surface properties of the fibers. Bad odors in presence of sweat and the development of allergic reactions triggered by microorganisms trapped in fabrics can be avoided by reducing the bacterial proliferation.[2,4] However, the selection of nontoxic and nonallergenic chemical agents with antimicrobial activity is very limited, thus restraining the choice of available treatments.[5] Notoriously, silver ions have shown high toxicity to different species of bacteria including *Escherichia coli*.[6,7] Silver is characterized by long-term antimicrobial properties, excellent resistance to all sterilization techniques, effectiveness on many different bacteria,[8] and high biocompatibility.[9] Furthermore, silver does not induce skin irritation,[10,11] and it is characterized by low toxicity to human cells.[12–15] Sol-gel technique,[16] microwave irradiation,[17] and sonochemical deposition of silver nanoparticles[18] are among the methods developed so far to produce silver-based antibacterial coatings.

A previous study described the development and the characterization of an innovative and patented technology[20] for coating with silver cotton yarns and polyester fibers.[19] The present study utilized a similar technology for the treatment of wool fibers to develop antibacterial fabrics for standard clothes. Different percentages of silver-treated fibers were used to produce antibacterial fabrics. This aimed to determine the minimum amount of treated fibers necessary to preserve the antibacterial activity, thus optimizing the cost-effectiveness of the final material. The analysis of the adhesion of silver clusters onto the substrate was conducted to verify if the use of the fabrics under normal conditions could compromise the presence of silver on the surfaces. The initial amount of silver and the durability of the treatment were evaluated by thermogravimetric analysis (TGA) performed on samples even after several washing cycles. The morphology of the silver nanoclusters deposited on the fibers was analyzed by scanning electron microscopy (SEM). The antimicrobial capability of the silver-treated substrates was

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investigated by antibacterial test against *E. coli*, according to Standard "*SNV 195920-1992*."

MATERIALS AND METHODS

Silver-coated woolen fibers were obtained by using *in situ* photoreduction of silver clusters, a patented process[20] developed by Silvertech. The substrates used for silver deposition is extra fine merino wool named "Hercosett" (Fig. 1). This particular type of wool is treated with chlorine and resin to improve the resistance of yarns to both washing and hot air drying. Knitwear realized with this type of wool is called "Total easy care," and it can be used for technical applications and for daily clothing. The silver deposition[20] was obtained by impregnation of wool in a water/alcoholic solution of silver nitrate made of 2 wt % silver nitrate, 18 wt % methanol, and 80 wt % deionized water. The wet substrates were then exposed to UV-rays to induce the formation of metal silver clusters on the surface of the material. After treatment with silver, the wool was sent to a textile company to produce three different types of fabrics each characterized by a different amount of silver-coated woolen fibers. This aimed to detect the minimum amount of silver that ensures a strong antimicrobial capability even after several washings. Sample "A" was prepared using 50% of silver-treated woollen fibers and 50% of neat wool. Sample "B" was prepared using the 30% of silver-treated woolen fibers and the 70% of neat woolen fibers. Finally, sample "C" was made with 10% of silver-treated fibers and 90% of neat wool.

Morphological analysis was performed by SEM, using a Jeol JSM-6550F. Particularly, both the treated wool before the spinning process and the antibacterial fabrics (samples A, B, and C) were analyzed. The same analysis was also performed on neat wool as control.

Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 409 operating in air to measure the amount of silver deposited on the woolen fibers. The presence of silver was identified by the presence of a solid residue above 900°C. To investigate the stability of the antibacterial agent on the substrate after several washing cycles, the TGA analysis was also performed on samples A, B, and C after 1, 10, and 50 washing cycles. Washing tests were conducted according to the European Standard EN 26330:1993.

Diffusion tests in agar (Aldrich) were performed according to the Standard SNV 195920-1992 to evaluate the antibacterial activity of the samples. The procedure consists in placing samples on agar plates[19] in contact with bacteria and evaluating the bacterial growth inhibition near and under the sample after incubation in oven at 37°C for 24 h. The standard defines different levels of antibacterial capability. When an inhibition zone is observed both close and under the fabric, the antibacterial property is defined as "good." When growth inhibition area is observed under the sample only, the antibacterial property is defined as "sufficient." If the sample is totally covered by the bacteria as well as the area under the fabric, the antibacterial property is defined as "not sufficient." Samples A, B, and C and the untreated wool were tested.

Figure 1 Extrafine merino wool used as substrate for silver deposition.

RESULTS AND DISCUSSION

SEM analysis was performed on woolen fibers before the spinning process (Fig. 2) and on fabrics realized with different percentages of silver-treated fibers (Fig. 3). This aimed to determine whether the industrial process used to obtain the fabrics affected the presence of silver particles on the textile samples and hence their antimicrobial capability. Figure 2(a,b) shows respectively images of untreated and silver-treated woolen fibers before the spinning process. The neat fiber [Fig. 2(a)] presented a smooth surface alternated with areas of roughness. Silver-treated fibers [Fig. 2(b)] showed a uniform distribution of submicron silver clusters on the surface of fibers with bigger clusters forming in the areas of increased roughness. This result provided evidence

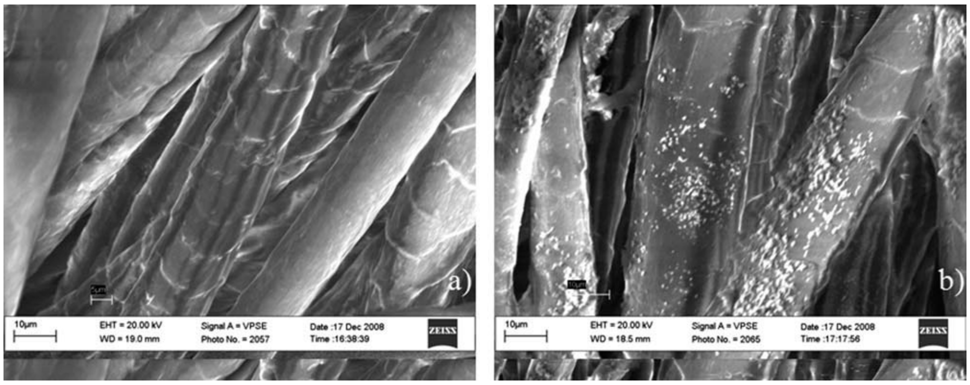

Figure 2 SEM images of wool fibers before the spinning process: (a) neat wool at 3000× magnification and (b) silver-treated wool at 3000× magnification.

of the influence of surface structure on the deposition of silver.

SEM images of the antibacterial fabrics (samples A, B, and C) in comparison with the untreated sample are shown in Figure 3 at a lower magnification. As expected, sample A showed the highest amount of silver coated fibers [Fig. 3(a)]. The amount of fibers treated with silver gradually decreased as shown in Figure 3(b,c) and completely disappeared in the untreated sample [Fig. 3(d)]. The uniform distribution of silver particles within the fabrics suggests that the industrial process does not affect the distribution of silver within the substrate, also confirming the very strong adhesion of the coating to the substrate. To check the adhesion of silver onto the textile substrate after the common condition of use, samples underwent several washing cycles. The amount of silver was then evaluated by TGA on the fibers before the spinning process and on the fabrics A, B, and C, before and after 1, 10, and 50 washing cycles. The initial amount of silver found in the treated fibers before the spinning process was equal to 1.61 wt %, whereas for the fabrics were equal to 0.78 wt % for sample A, 0.48 wt % for sample B, and 0.14 wt % for sample C.

As reported in Table I, only after the first washing cycle, it is possible to observe a small decrease in the amount of silver for all the samples and

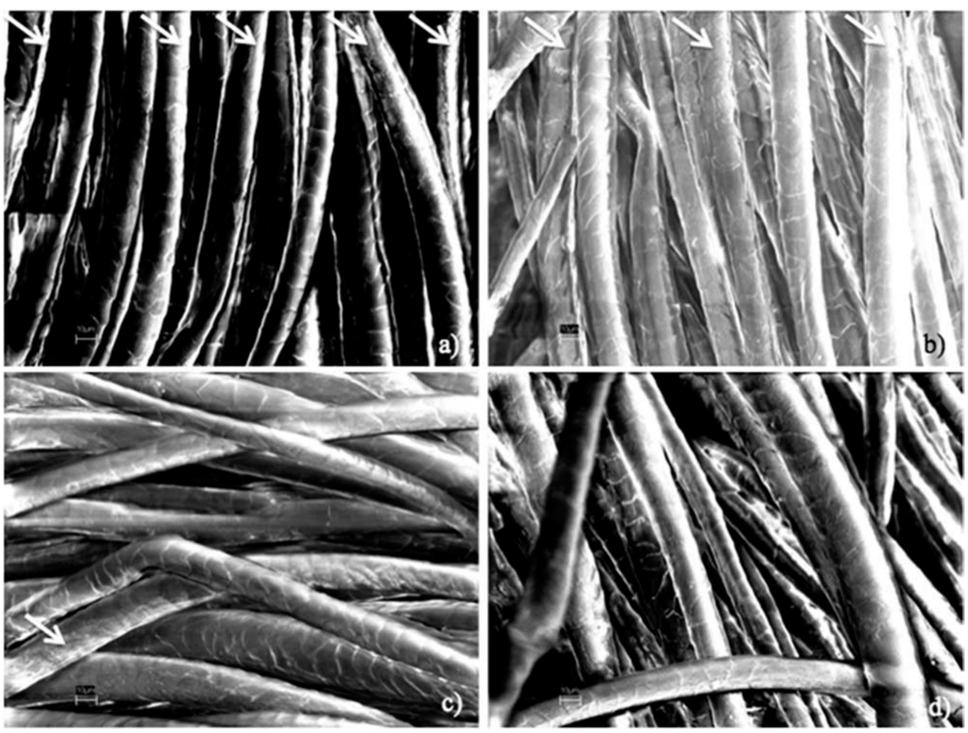

Figure 3 SEM images of unwashed fabric samples at 500 magnifications of: (a) sample "A" made of 50% of silver treated wool fibers, (b) sample "B" made of 30% of silver treated wool fibers, (c) sample "C" made of 10% of silver treated wool fibers, and (d) untreated wool. The arrows indicate the fibers treated with silver.

TABLE I
Amount of Silver for the Silver-Treated Wool Fabrics Before and After Washing Cycles

	Starting silver amount (%)	Silver amount after 1 washing cycle (%)	Silver amount after 10 washing cycles (%)	Silver amount after 50 washing cycles (%)
Sample A	0.78	0.67	0.67	0.67
Sample B	0.48	0.41	0.41	0.41
Sample C	0.14	0.12	0.12	0.12

probably due to the detachment of silver clusters not perfectly bonded to the fibers. Following the first cycle, the amount of silver is stable for all the samples for up to 50 cycles, thus confirming the good adhesion and stability of silver clusters on the wool substrate.

As reported in literature, silver exhibits antibacterial capability against *E. coli*.[19,21,22] The results of the antimicrobial tests performed on samples A, B, and C after 50 washing cycles compared with the control fabric are reported in Figure 4. Antibacterial capability was evaluated by analyzing the presence of bacteria under [Fig. 4(a–d)] and around [insets in Fig. 4(a–d)] each sample. The neat wool sample, after incubation in oven at 37°C for 24 h, as expected, does not show any antibacterial capability, associated with a complete growth of *E. coli* colony around [inset in Fig. 4(a)] and under the fabric [Fig. 4(a)]. An inhibition zone of bacterial growth both around and under the sample was observed only in the

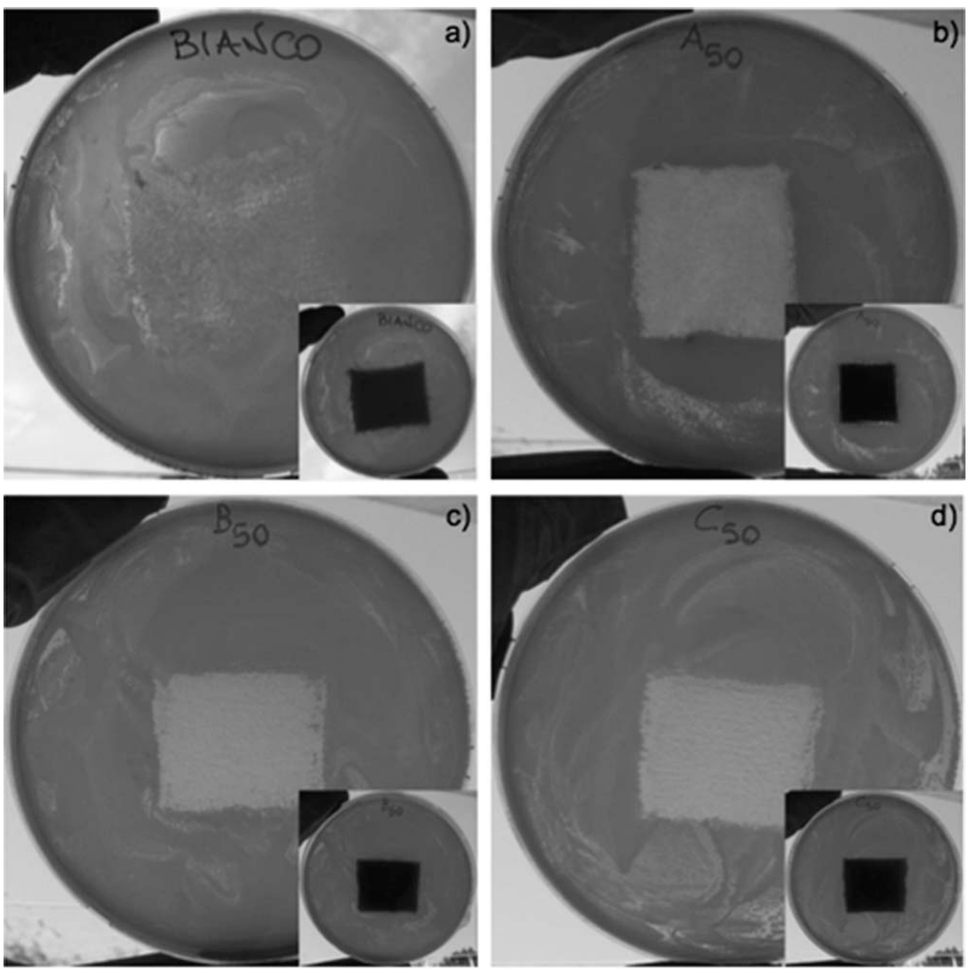

Figure 4 Antibacterial tests on *E. coli*. Samples were removed from the agar plate to evaluate the inhibition of bacterial growth under the fabrics containing the 50, 30, and 10% of silver-treated wool (respectively, b, c, and d) after 50 washing cycles in comparison with the neat sample (a). The insets in each picture show images of the same plates before removal of the fabric samples to verify the bacterial growth around the samples. Only around sample A (inset in b) an inhibition zone can be observed.

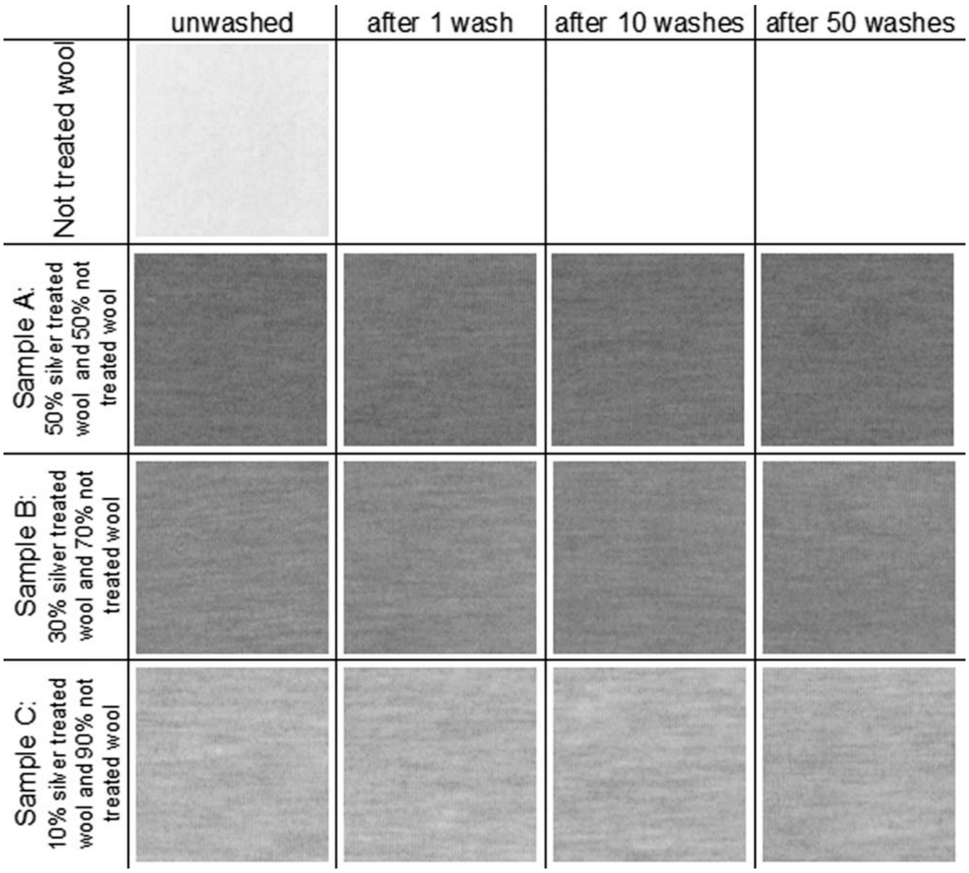

Figure 5 Visual comparison of samples A, B, and C made with the different compositions of wool and sample of untreated wool.

fabric A [inset in Fig. 4(b,d)], which contains the highest amount of silver-treated fibers. The extent of the inhibition zone around sample A was of 1.2 mm; therefore, the antibacterial effect associated with this sample can be labeled as "good," according to the level of antibacterial activity provided by the Standard "*SNV 195920-1992*" confirming the growth inhibition effect induced by silver.

All the silver-treated samples showed inhibition of bacterial growth under the fabric and no differences could be detected between the bacteria-free zone under samples B and C, [Fig. 4(c,d)]. This indicated that both the 10 and 30% of silver-treated fibers ensured an antibacterial capability classified as "sufficient." These results suggested that fabrics produced with the 10% of silver-treated fibers could represent the ideal choice for the control of the cost of the final product.

Figure 5 shows images of fabrics produced with different percentages of silver-treated fibers (samples A, B, and C as described above) and of neat wool in function of the number of washing cycles. The visual comparison confirmed that all the samples, both washed and unwashed, had a clean and regular aspect even after 50 washing cycles. All the fabrics showed a good fastness of the color without discoloration confirming a very good adhesion of silver on the substrate.

CONCLUSIONS

Antibacterial woolen fabrics were obtained by using a patented deposition technology of silver nanoparticles. Fabrics were obtained with different percentages of silver-treated fibers to investigate the minimum amount of silver ensuring a good antibacterial capability. Antibacterial activity of samples was checked against *E. coli* and the amount of 10% of silver-treated fibers demonstrated a good antibacterial capability even after several washing cycles. SEM analysis confirmed that the industrial process to obtain fabrics did not alter the strong adhesion of silver particles to the fibers and their uniform distribution. The high stability and durability of the coating was also confirmed by TGA performed after a significant number of washing cycles to reproduce the conditions of use for the fabrics.

References

1. Czajka, R. Fibers Text East Eur 2005, 13, 13.
2. Gao, Y.; Cranston, R. Text Res J 2008, 78, 60.

3. Wong, Y. W. H.; Yuen, C. W. M.; Leung, M. Y. S.; Ku, S. K. A.; Lam, L. I. Autex Res J 2006, 6, 1.
4. Gorenšek, M.; Recelj, P. Text Res J 2007, 77, 138.
5. Mucha, H.; Hofer, D.; ABflag, S.; Swere, M. Melliand Textilberichte 2002, 83, 53.
6. Zhoo, G.; Stevent, S. E. Biometals 1998, 11, 27.
7. Maliszewska, I.; Sadowski, Z. J Phys: Conf Ser 2009, 146, 012024.
8. Alcamo, I. E. Fundam Microbiol 1991, 748, 61.
9. Williams, R.; Doherty, P.; Vince, D.; Grashoff, G.; Williams, D. Crit Rev Biocompatibility 1989, 5, 43.
10. Joeger, T. K.; Joeger, R.; Olsson, E.; Granqvist, C. G. Trades Biotechnol 2001, 19, 15.
11. Lee, H. J.; Yeo, S. Y.; Jeong, S. H. J Mater Sci 2003, 38, 2199.
12. Dastjerdi, R.; Mojtahedi, M. R. M.; Shoshtari, A. M.; Khosroshahi, A. J Text Inst 2010, 101, 204.
13. Jia, X.; Ma, X.; Wei, D.; Donga, J.; Qiana, W. Colloids Surf A Physicochem Eng Asp 2008, 330, 234.
14. Yang, S. Y.; Seo, J. Y. Colloids Surf A Physicochem Eng Asp 2008, 313, 526.
15. Durán, N.; Marcato, P. D.; Souza, G. I. H. D.; Alves, O. L.; Esposito, E. J Biomed Nanotechnol 2007, 3, 203.
16. Mahltig, B.; Textor, T. Fibers Polym 2010, 11, 1152.
17. Yin, H.; Yamamotob, T.; Wada, Y.; Yanagida, S. Mater Chem Phys 2004, 83, 66.
18. Hadad, L.; Perkas, N.; Gofer, Y.; Calderon-Moreno, J.; Ghule, A.; Gedanken, A. J Appl Polym Sci 2007, 104, 1732.
19. Pollini, M.; Russo, M.; Licciulli, A.; Sannino, A.; Maffezzoli, A. J Mater Sci: Mater Med 2009, 20, 2361.
20. Pollini, M.; Sannino, A.; Maffezzoli, A.; Licciulli, A.Antibacterial surface treatments based on Silver clusters deposition 2008, EP20050850988.
21. Xing, Y.; Yang, X.; Dai, J. J Sol-Gel Sci Technol 2007, 43, 187.
22. Pollini, M.; Paladini, F.; Catalano, M.; Taurino, A.; Licciulli, A.; Maffezzoli, A.; Sannino, A. J Mater Sci: Mater Med 2011, 22, 2005.