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# SILVER NANOPARTICLES APPLICATION FOR TEXTILE CONSERVATION

**LITE Mihaela-Cristina[1,2], TĂNĂSESCU Elena-Cornelia[1,2], SECĂREANU Lucia-Oana[1], SĂNDULACHE Irina-Mariana[1], PERDUM Elena[1], IORDACHE George-Ovidiu[1]**

[1] National Research and Development Institute for Textiles and Leather, Bucharest (INCDTP), Department of Materials' Research and Investigation, 16 Lucretiu Patrascanu, 030508, Bucharest, Romania, E-Mail: office@incdtp.ro

[2] Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Gheorghe Polizu Street, 011061, Bucharest, Romania, E-Mail: secretariat@chimie.upb.ro

Corresponding author: Lite Mihaela-Cristina, E-mail: cristina.lite@incdtp.ro

***Abstract:*** *Silver is a metal well known for its antimicrobial properties and it is widely used in a broad range of applications (e.g., dyes, cosmetics, medicine etc.). Therefore, the attempt to use silver for textile cultural heritage conservation does not come as a surprise. However, the real challenge is to achieve a perfect fixation of these particles on textiles without altering the aesthetic aspect of the materials. In this context, the use of silver as nanoparticles is essential to ensure that none of the visual aspects is affected, such as color, texture, brightness etc. For the present work, different types of textile fibers were subjected to an accelerated aging process, using UV light, temperature, and humidity. The fibers selected for this study are natural, artificial and combination. In parallel, the textile fibers were treated with different dispersions containing silver nanoparticles and subjected to the same process. To make a comparison between the levels of degradation of the treated and non-treated fibers, they were characterized using different techniques. Electronic microscopy was used to observe the visual effect of the degradation. Infrared spectroscopy was performed to evaluate the changes in the functional groups of the polymeric structures and colorimetry measurements were carried out to quantify the color change of the fibers.*

***Key words:*** *silver nanoparticles, textiles, heritage, conservation***.**

## 1. INTRODUCTION

Textiles are indispensable objects for humankind. They reflect the evolution of society and the development of new technologies and materials [1]. Museums around the world include impressive collections of heritage textiles, in various stages of degradation [2,3]. The main method used to preserve them is to maintain a certain microclimate by adjusting the temperature, humidity, and brightness of the rooms where they are exposed or stored [4]. One of the main factors which has a strong impact on textile degradation is the contamination of microorganisms [5]. Silver compounds are well known for their biocidal properties against both bacteria and fungi [6-8]. The potential application of silver nanoparticle as antimicrobial treatment for cultural heritage conservation has been studied on limestones, paper, and cotton fabrics [9-11].

For this work, cotton, polyester, and mixture (50% cotton, 50% polyester) fabrics were subjected to an accelerated aging process, in a special chamber equipped with UV lamps with controlled temperature and humidity. In parallel, the textile fibers were treated with different dispersions containing silver nanoparticles and subjected to the same process. The fabrics were characterized using electronic microscopy and infrared spectroscopy. Also, colorimetry measurements were carried out to quantify the color change of the fibers, to evaluate the influence on the visual aspect of the fibers.

## 2. EXPERIMENTAL

### 2.1 Materials and methods

Five samples from each type of fabric, cotton (170 g/m$^2$), polyester (144 g/m$^2$), and cotton-polyester mixture (210 g/m$^2$), all measuring 11×9 cm were exposed to accelerated aging conditions, in a uv chamber (a QUV accelerated weathering tester device) following the working cycle reported in our previously study [12]. The instrument was equipped with fluorescent UV-B lamps (UVB-313), with a wavelength peak at around 313 nm, having nearly all their energy concentrated between 280 nm and 360 nm. All types of samples were collected every three days, having in the end five samples of each type at different degrees of degradation. These samples were characterized and compared to a reference sample (unexposed textile material). In parallel, all three types of fabrics were treated with two types of solutions: glycerol solutions in ethanol (1:1 volume ratio) and Arabic gum (AG) solution (2 g/L in water, prepared on a hot plate at 80$^o$C for 30 minutes). The fabrics were also treated with silver nanoparticles (AgNPs) (180 ppm), purchased from Sigma Aldrich, with the particle size < 100 nm, dispersed in the two previously prepared solutions. The dispersions with AgNPs were agitated in an ultrasound bath at 60$^o$C for 90 minutes. The fabrics were treated via pulverization, then they were left to air dry overnight. The treated fabrics were also exposed to the accelerated aging conditions mentioned above to make a comparison.

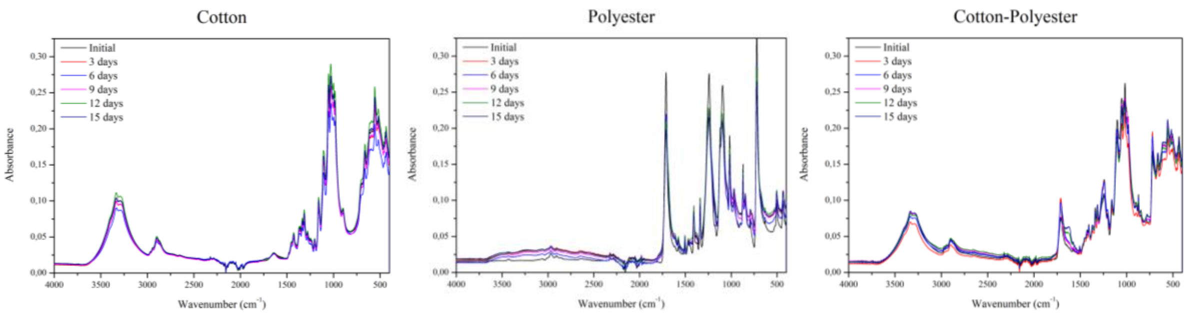
### 2.2 Characterization techniques

IR spectra were recorded using an FT-IR-ATR instrument from ThermoFisher, over a spectral range of 4000-400 cm-1. The fiber morphology of the samples was evaluated with a FEI Quanta 200 Scanning Electron Microscope (SEM), equipped with an ET detector. The chromatic parameters L*, a*, b* have been measured for each sample, using a Datacolor spectrophotometer Microflash 200d (with a D65/10 lamp).

## 3. RESULTS AND DISCUSSIONS

### 3.1 FTIR-ATR characterization

Fig. 1 shows the IR absorption spectra for the textile materials.




a. b. c.

**Fig. 1**: IR absorption spectra for a. cotton, b. polyester, c. cotton-polyester mixture

The spectra recorded at different exposure times are overlapped to assess the structural changes that might occur during and after the exposure. For all three types of textile fabrics there are no new bands in the IR absorption spectra of the exposed samples compared to the reference fabrics. Only slight changes in the intensity of the bands can be observed. This indicates that the changes at the structural level are minimal, and the fabrics are not significantly altered after exposing them to the mentioned conditions.

### 3.2 Scanning Electron Microscopy characterization

Tables 1 contain the SEM micrographs of the untreated and treated samples, collected before and after the artificial aging. All images were collected at 4000X magnification.

SEM images for the untreated fabrics do not indicate important changes of the fiber morphology after the exposure procedure, confirming the results obtained from FTIR characterization. The micrographs of the fabrics treated with dispersions 2 and 4 (containing AgNPs) illustrate the distribution of the nanoparticles on the fiber surfaces and show that they were uniformly spread. When analyzing the images of the treated fabrics with the first solution (Gly in EtOH), they seem to present signs of alteration, especially in the case of polyester fabrics, most probably due to the degradation of both textile fibers and glycerol. By applying Arabic gum solution, the integrity of the fibers is maintained after the exposure for cotton and cotton-polyester fabrics. Dispersion 4 (AgNPs in Arabic gum solution) seems to maintain the integrity of the fiber morphology for all three types of fabrics.

**Table 1:** SEM micrographs of the untreated fabrics before and after exposure to the mentioned conditions.

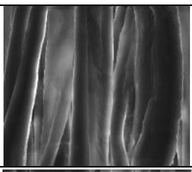
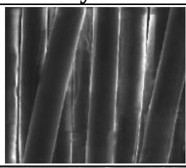
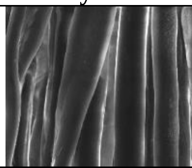
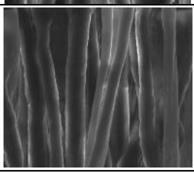
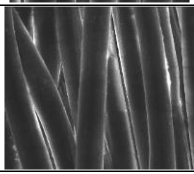
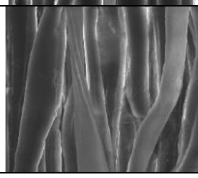
| Fabrics | Cotton | Polyester | Cotton-Polyester mixture |
|---|---|---|---|
| **Initial fabrics** |  |  |  |
| **Exposed fabrics** |  |  |  |

**Table 2:** SEM micrographs of the treated cotton fabrics before and after exposure to the mentioned conditions

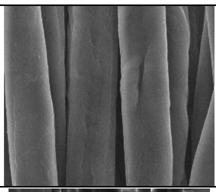
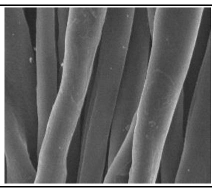
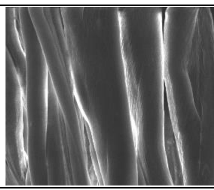
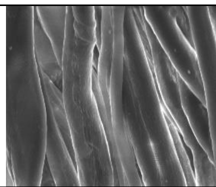
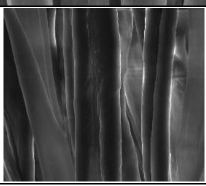
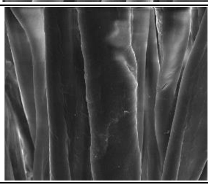
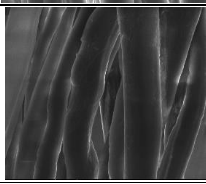
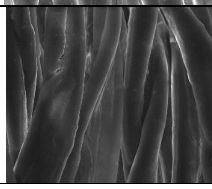
| Fabrics | Dispersions (1=Gly sol., 2=AgNPs in Gly sol., 3=AG sol., 4=AgNPs in AG sol.) | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| **Initial Cotton fabrics** |  |  |  |  |
| **Exposed Cotton fabrics** |  |  |  |  |

**Table 3:** SEM micrographs of the treated polyester fabrics before and after exposure to the mentioned conditions

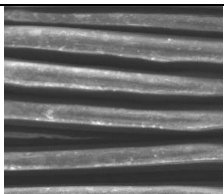
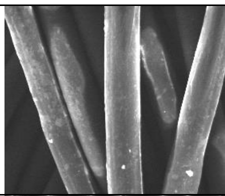
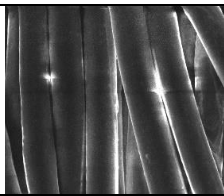
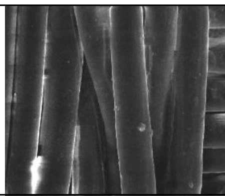
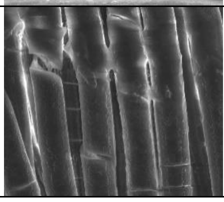
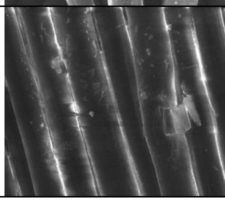
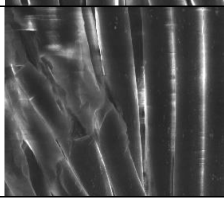
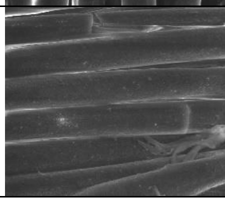
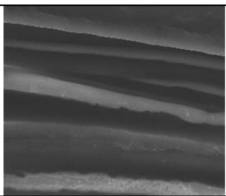
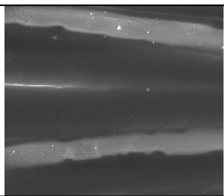
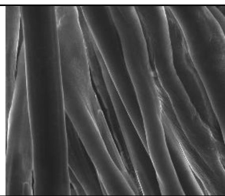
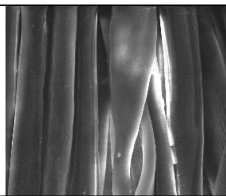
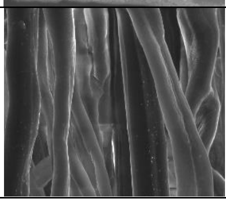
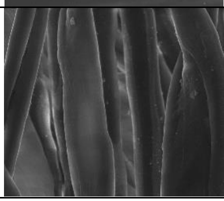
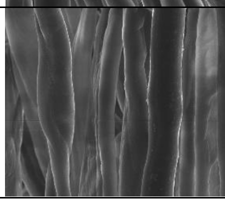
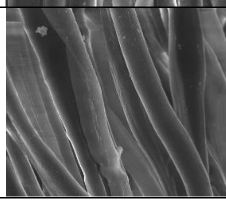
| **Fabrics** | **Dispersions (1=Gly sol., 2=AgNPs in Gly sol., 3=AG sol., 4=AgNPs in AG sol.)** | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| **Initial Polyester fabrics** |  |  |  |  |
| **Exposed Polyester fabrics** |  |  |  |  |

**Table 4:** SEM micrographs of the treated otton-polyester mixture fabrics before and after exposure to the mentioned conditions

| **Fabrics** | **Dispersions (1=Gly sol., 2=AgNPs in gly sol., 3=Arabic gum sol., 4=AgNPs in Arabic gum sol.)** | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| **Initial Cotton-Polyester mixture fabrics** |  |  |  |  |
| **Exposed Cotton-Polyester mixture fabrics** |  |  |  |  |

### 3.3 Colorimetric analysis

The chromatic parameters measured for each sample are listed in Table 5. The brightness of the samples is represented by the parameter L*, on a scale from 0 (for black) to 100 (for white). If a* and b* are positive, the color of the sample will be in the red-orange-yellow range. If a* is negative and b* is positive, the color of the sample will be in the yellow-greenish-green range. If a* and b* are negative, the color of the sample will be in the green-turquoise-blue range. If a* positive and b* negative, the color of the sample will be in the range of blue-purple-red. ΔE* represents the total color difference between the sample and the reference and is calculated according to the formula: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ [13].

The color of the untreated fabrics does not change significantly after exposure. The most affected seems to be the cotton-polyester mixture, for which the parameter b* increases from 1,42 to 11,13, indicating a color shift to yellow. Pure cotton presents increased resistance against degradation. When comparing the treated and unexposed fabrics, the dispersion which affects mostly the visual aspect of the textiles is the glycerol solution. Therefore, the glycerol-based dispersion is not suitable to be used for conserving textile cultural heritage. Also, it is observed that by adding AgNPs in the solution the color changes increase. The fabrics treated with Arabic gum solutions present the lowest values of ΔE, showing that these ones suffered the least changes of color. Furthermore, the change in color of these fabrics is minimal even after exposing them to the mentioned conditions. When studying the fabrics treated with the AgNPs dispersion in Arabic gum solution, it is observed that the changes in color after exposure are minimal compared to the case of the untreated fabrics and in the case of cotton-polyester mixture fabric the value of ΔE is even lower (from 9,93 to 8,17). The unexposed samples treated with dispersions 3 and 4 did not show visible changes in color. Even if ΔE exceeded the value of 1, in the case of dispersion 4, this change is not visible with the naked eye.

**Table 5:** Color change between the reference and the treated fabrics before and after exposure

| **Fabrics** | **Before exposure** | | | | **After exposure** | | | |
|---|---|---|---|---|---|---|---|---|
| | **L*** | **a*** | **b*** | **ΔE*** | **L*** | **a*** | **b*** | **ΔE*** |
| **Untreated cotton** | 92,06 | -0,02 | 2,60 | - | 91,6 | 0,05 | 2,58 | **2,02** |
| **Cotton$_1$** | 83,01 | 0,88 | 3,61 | **9,15** | 92,18 | 0,11 | 2,37 | **8,94** |
| **Cotton$_2$** | 78,24 | 0,71 | 3,64 | **13,88** | 89,29 | 0,18 | 4,38 | **11,02** |
| **Cotton$_3$** | 92,09 | 0,07 | 2,34 | **0,27** | 92,62 | 0,12 | 1,88 | **0,78** |
| **Cotton$_4$** | 89,52 | 0,10 | 1,85 | **2,64** | 88,83 | 0,18 | 4,72 | **3,01** |
| **Untreated polyester** | 92,74 | -0,12 | 1,27 | - | 88,88 | -1,43 | 5,94 | **6,1** |
| **Polyester$_1$** | 88,52 | -0,05 | 1,18 | **4,22** | 86,13 | -0,02 | 11 | **10,02** |
| **Polyester$_2$** | 83,53 | 0,17 | 0,11 | **9,29** | 85,11 | -0,76 | 8,33 | **7,76** |
| **Polyester$_3$** | 92,54 | -0,09 | 1,35 | **0,22** | 88,89 | -1,42 | 6,31 | **2,70** |
| **Polyester$_4$** | 90,25 | -0,02 | 1,08 | **2,50** | 86,90 | -1,10 | 8,41 | **8,06** |
| **Untreated cotton-polyester mixture** | 92,82 | -0,15 | 1,42 | - | 90,2 | -0,96 | 11,13 | **9,93** |
| **Cotton-Polyester$_1$** | 84,16 | 0,52 | 1,54 | **8,69** | 91,07 | -1,15 | 8,01 | **9,81** |
| **Cotton-Polyester$_2$** | 76,75 | 0,40 | 2,31 | **16,11** | 86,13 | -0,18 | 10,30 | **11,70** |
| **Cotton-Polyester$_3$** | 92,54 | -0,15 | 1,56 | **0,32** | 91,70 | -1,22 | 6,66 | **5,30** |
| **Cotton-Polyester$_4$** | 89,80 | -0,02 | 1,39 | **3,03** | 86,70 | -0,31 | 8,97 | **8,17** |

## 4. CONCLUSIONS

The three types of textile fabrics used for this study showed an increased resistance against degradation when subjected to an accelerated aging process involving UV light, temperature, and humidity. The IR spectra indicated that the changes at structural level are minimal. This information was confirmed by SEM micrographs and color change parameters. When applying the solution of glycerol, the fibers present signs of degradation after the exposure procedure. By adding AgNPs to the solutions and treating the fabrics with the resulting dispersions by pulverization, it can be observed that the nanoparticles are well dispersed over the surface of the fibers. The Arabic gum solution with dispersed AgNPs that was pulverized on the fabrics seems to have the best effect of maintaining the integrity of the fibers for all three types of fabrics. The visual aspect of the fabrics was the least modified when using the Arabic gum solution. Also, the presence of the AgNPs did not seem to have a significant effect on the color changes after the exposure. Given their tremendous antibacterial and antifungal effect and combined with the fact that they do not have an important impact over the visual aspect of the textile fabrics, silver nanoparticles represent a promising treatment for cultural heritage conservation.

## ACKNOWLEDGEMENTS

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