Antibacterial finishing of flat textiles by ink-jet printing

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Abstract

The novel, original method of antibacterial finishing of flat textiles by ink-jet printing with application of nano-silver has been developed. The silver particles were prepared by direct reduction of silver salt-containing ink on and into the fibres (in-situ method). The one- or two-nozzles' system was used on an industial ink-jet printer equipped with the Xaar 128-360 printing head. Silver finished fabrics were subjected to the surface examination using the scanning electron microscopy (SEM) with energy disperse X-ray spectroscopy (EDX) booster. The chemical state of nanosilver deposited on textiles was determined using X-ray photoelectron spectroscopy (XPS). Also, the size and size distribution profile of silver particles extracted to water were estimated by the dynamic light scattering method (DLS). The changes in silver content on fabric finished after multiple washings were evaluated by an inductively coupled plasma spectroscopy (ICP-ToF-MS) as well as by the laser ablation mass spectroscopy (LA-ICP-ToF-MS). Antibacterial efficacy of silver finished textiles against Bacillus subtilis and Escherichia coli was examinated by a qualitative method (Agar Diffusion Test). The results obtained proved an excellent durablity of silver-finished textiles even after 50 alkaline washings. The method is protected by 2 patent applications.

Introduction

Recently, there is observed a significant increase in using of silver compounds to the antimicrobial finishing of the textile products, especially using silver nanoparticles. It is known that silver nanoparticles have antibacterial properties which enable to use them to antimicrobial textile finishing in production of protecting clothes and wound dressings. Its therapeutic property has been proven against a broad range of microorganisms, over 650 disease-causing organisms in the body, even at low concentrations [1-3]. Silver nanoparticles are a non-toxic and non-tolerant disinfectant [4].

Our research was mainly focused on the elaboration and implementation of antibacterial finishing of flat textiles using the ink-jet printing methods. To receive the long-lasting antibacterial properties of textiles, the ink-jet printing methods such as "1-nozzle with textile pre-treatment" and "2-nozzle" were developed [5,6]. The silver nanoparticles were prepared by direct reduction of silver salt-containing ink on and into the fibres (in-situ method). For this purpose, the especially prepared inks were elaborated and an industrial ink-jet printer equipped with the Xaar 128-360 printing head was used. In this paper the results of our research using the 2-nozzles' system are presented. Physicochemical phenomena taking place on the textiles' surface during the reduction process were subject to the surface examination using the modern instrumental methods and compared with the antibacterial efficacy as well as with its durability against washing in the alkaline bath.

Materials and methods

Woven cotton fabric BD22 - technical fabrics for work and safety clothing. Technical data: 100% cotton, surface mass : 245 g/m² (±5%), fabric construction: 3/1 twill (ISO 5081-1977).

All fabrics were printed using the Xaar digital printer with 4 nozzles, and done in cooperation with the Department for Clothing Technology and Textronics of TUL.

Antimicrobial finishing of textiles was made using the ink-jet printing 2-nozzles' method (1st nozzle - $AgNO_3$ containing ink; 2nd nozzle-reducer). Nano-silver particles were formed directly on the fabric during ink-jet printing process. Figure 1 shows scheme of the finishing process.

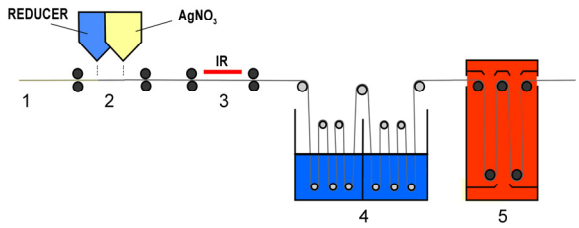

Figure 1*.Scheme of an antibacterial finishing process: 1.cotton fabric 2. 2-nozzles' ink-jet printing 3.IR- partly drying, 4. rinsing, 5.drying*

Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to determine nanoparticles shape and distribution on the textile surface. This method enabled to obtain the high-resolution, three dimensional-like images of solid samples. Variations in the surface topography of a material were depicted as variations in gray level of the image. Energy Dispersive X-Ray Spectroscopy (EDX) extended the usefulness of SEM in that the elemental analysis can be performed within the regions as small as a few cubic micrometers. The material studied was characterized by scanning electron microscopy with field emission S-4700 (Hitachi, Japan) equipped with energy dispersive spectrometer (Thermo-Noran, USA). Before SEM-EDX investigations, the analyzed samples were placed on carbon plasters and coated with carbon targets using Cressington 208 HR system (Cressington Scientific Instruments Ltd., UK).

DLS- Dynamic light scattering was used to determine the size and the size distribution profile of Ag-nanoparticles particles in dispersion. The Particle Sizing System NICOMP 380, a product of Nicomp, (Santa Barbara, USA) was used. The in-situ Ag- finished textiles were washed in double-distilled water with metal balls and then the size and the distribution profile of the nanoparticles washed out of the textiles were determined.

Evaluation of the chemical state of silver deposited on fabric was carried out using X-ray photoelectron spectroscopy (XPS). XPS data were obtained from a Vacuum Systems Workshop Ltd. instrument equipped with a Al-K X-ray radiation source (1486.6

eV, 200 W) and an 18-channel detector. Electron energies were determined in the fixed analyzer transmission mode with 22 eV electron pass energy. Spectral energies were referred vs. that of carbon (284.6 eV).

Washing fastness of silver-finished textiles was estimated according to the PN-EN ISO 105-C06:1996/Ap1:1999 standard; the method A1S with metal balls where ECE Standard Detergent of SDC Enterprises Ltd. was applied. After each laundering the samples were rinsed twice in double-distilled water and next dried at 80°C. The durability of an antimicrobial finishing of cotton samples was estimated after 1, 25 and 50 washings.

Quantitative determination of silver content in silver-finished cotton fabric before and after washing was carried out using the Optimass 8000, ICP-ToF-MS (Inductively Coupled Plasma-Mass Spectrometer with Time of Flight Analyzer), a product of GBC Scientific Equipment, Australia, after the process of mineralization of 0.2 g samples in the microwave system with nitric acid, a product of Baker.

The semi-quantitative determination of silver content in silver-finished cotton fabric before and after multiple washings was carried out using the laser ablation system CETAC LSX equipped with Nd:YAG laser and combined with ICP-ToF-MS, a product of GBC Scientific Equipment Australia, a non-destructive method to compare the results obtained with those obtained by the ICP-ToF-MS method. Application of laser ablation did not required any earlier sample preparation and enabled the direct analysis of the solid sample [7].

Using the data of the quantitative and semi-quantitative determination of silver content before and after washing, the washing fastness indicator (WFI) was calculated:

$$WFI_{\%} = \frac{C_{aw}}{C_{bw}} \cdot 100$$

where: C_{aw} – number of counts or content of silver [mg/kg] in the sa
C_{bw} - number of counts or content of silver [mg/kg] in the sample before washing.

The proposed indicator describes the percentage of silver content in fabric after the multiple washings and manifests the durability of silver-finished textiles against washing

The Agar Diffusion Test, according to the PN-EN ISO 20645:2007 standard was used for the evaluation of antimicrobial properties against *Escherichia coli* (Gram-negative bacterium-internal name: ŁOCK 0836 1998) and *Bacillus subtillis* (Gram-positive bacterium, internal name – ŁOCK 0816 1975, IBPRS, AATCC 6633).

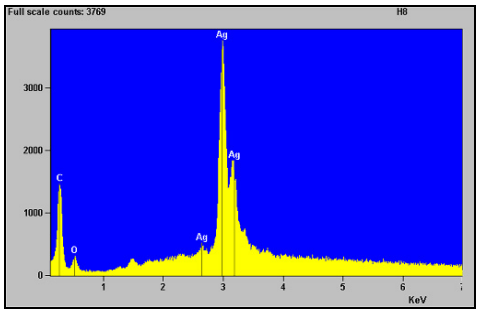

***Figure 2**. EDX spectra collected from single point of finished fabric.*

The carbon and oxygen peaks observed are the results of used substrate. Observations of X-ray images of samples have shown that on the surface of finished fabric the visible uniform thin layer of silver was detected.

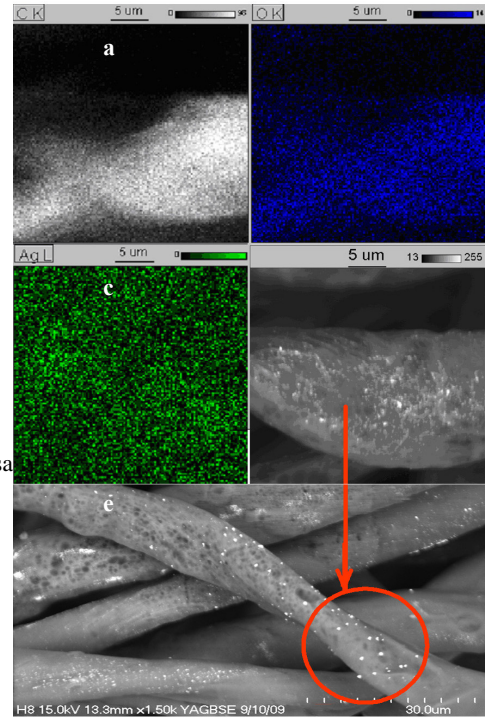

***Figure 3.** X-ray maps of detected elements (a-carbon ,b-oxygen, c-silver) and SEM micrograph (d) of silver particles present on the selected part of cotton fabric surface (e).*

Results and discussion

Surface examination of silver finished textiles

Silver finished sample was subjected to EDX survey analyses to determine the elements present and their distribution on fabric surface. The results of the element analysis of the silver finished fabric are shown in Figure 2. EDX studies revealed that the silver finished fabric contained C, O, and Ag mainly as well some impurities. The SEM images in Figure 3(d) proved that the silver deposits were compact and continuous on the modified fabric surface.

On the basis of the analysis of the SEM and EDX images can be concluded that many silver nanoparticles are visible on the cotton fabric and they are well distributed on the cotton fabric surface but sometimes some clusters can be created. Probably the silver nanoparticles' agglomeration occurred due to their high surface free energy during the finishing process.

Table 1. The volume and number weights of Ag-nanoparticles washed out of the antimicrobial finished textiles (DLS data)

Volume weight		Number weight	
Mean Diameter [nm]	Percent [%]	Mean Diameter [nm]	Percent [%]
23.7	82.4	23.3	97.4
118.3	8.5	116.2	2.1
454.4	9.1	451.1	0.5

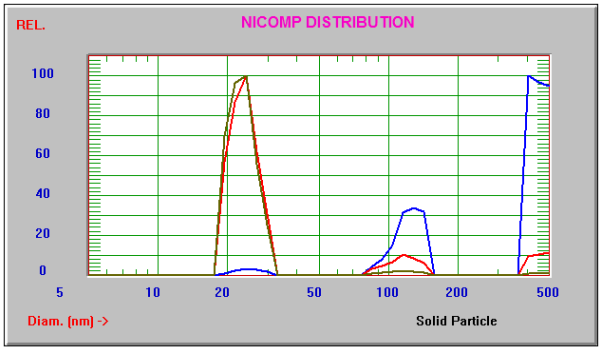

Figure 4. *Nicomp distribution profile of nano-Ag particles washed out of the finished textiles*

DLS analysis (Table 1, Figure 4) revealed that more than 94% of silver nanoparticles, having diameter about 24 nm were formed on the fabric surface.

To confirm the presence and to monitor the changes in the chemical state of the *in-situ* synthesized silver particles on the fabric surface, the XPS analysis was performed.

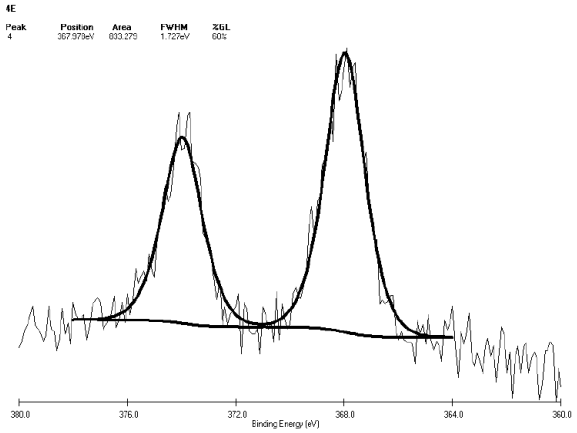

Figure 5. *XPS spectrum of a silver finished sample in the Ag region.*

Figure 5 shows the XPS spectra of Ag3d monitored on surface of the silver-finished cotton fabric. A double peak of Ag on the surface of silver-treated cotton fabrics was observed in the XPS spectra of nanosilver. The binding energies (B.E.) for these two peaks were found as 368.1 eV ($3d_{5/2}$) and 374.2 eV ($3d_{3/2}$), kinetic energy Ag-M_4VV (K.E.) of 356.9 eV and Auger parameter (Auger*= B.E.+K.E.) of 725.0 eV, respectively proving that the data obtained coincide very well with those published in literature indicating that the major chemical state of the silver present on the fabric surface is Ag^0. [4,8,9].

Washing fastness and the durability of antibacterial finishing

Silver content before and after washings, estimated by ICP-ToF-MS and LA-ICP-ToF-MS methods, was calculated and expressed as a Washing Fastness Indicator (WFI). The changes in the silver content determined by both the instrumental methods applied were shown in the Table 2 and 3.

Table 2. Silver content changes and the Washing Fastness Indicator (WFI) for silver finished fabric vs. washing

Number of washings	ICP-ToF-MS	
	Content of silver ± RSD% ($mg \cdot kg^{-1}$)	WFI [%]
0	195.11±2.27	-
1	144.69±1.21	74.16
25	119.17±0.19	61.01
50	99.66±0.8	51.08

Table 3. Changes in number of counts in the sample and Washing Fastness Indicator (WFI) for silver finished fabric

Number of washings	LA-ICP-ToF-MS	
	Number of counts in the sample	WFI [%]
0	1912660	-
1	1522410	74.37
25	1202520	62.87
50	853139	47.22

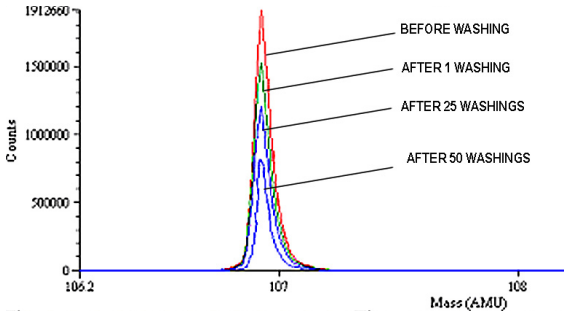

Figure 6. *Mass spectrum showing the changes in number of counts for* Ag^{107} *isotope for silver-finished fabric vs. multiple washings.*

The analysis of WFI values (Table 2 and 3) obtained suggests that silver particles are coupled well with the fabric structure and indicates a long-lasting washing durability. Quantitative results of silver content in cotton fabric after multiple washing process show unambiguously decrease in silver concentration with successive stage of washing cycle. This tendency presents a quite linear character, which was also confirmed by a direct solid analysis of

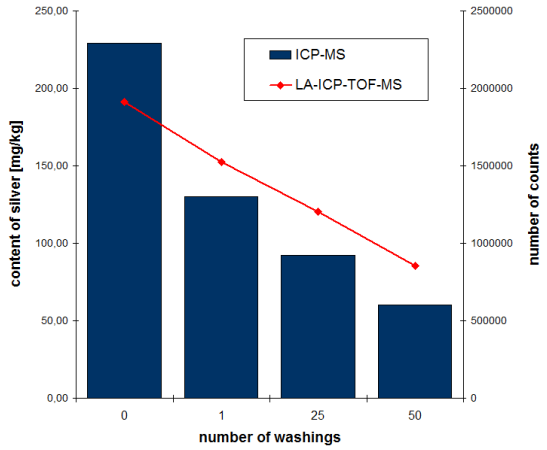

Figure 7. *Changes in the silver content in antibacterial finished fabric during the multiple washings as compared using the both instrumental methods.*

silver-finished fabric using LA-ICP-ToF-MS (Figure 7). The outcomes of semi-quantitative assessment of the nano-Ag content in cotton fabric during 50 washings' cycle were shown in the Figure 6. For all studied samples RSD did not exit 10%. It should be also mentioned that silver analysis using the LA system was performed on the relatively small area of sample while the determination of silver content after the sample mineralization concerns some volume of sample.

Nevertheless, data gathered from the both techniques applied in this work, are comparable. Moreover for all analysis the natural distribution of silver isotopes was retaining. In order to obtain such accordance a homogeneity of sample is necessary. As can be seen, the both ICP techniques can be applied as suitable methods for the determination of changes in the silver content on/in fabrics and the washing fastness calculation.

Antibacterial efficacy of silver finished fabrics

The silver-finished textiles exhibit long-lasting antibacterial activity even after 50 washing cycles. The results obtained confirmed that the ink-jet printing method developed of application of *in-situ* formed silver nanoparticles is very profitable method of antibacterial finishing of textiles. Table 4 shows the changes in inhibition zones of silver-finished fabric for both bacteria strains tested before washing and after 1, 25 and 50 washings (b.s. – beneath sample).

Table 4. Evaluation of antimicrobial properties against *Escherichia coli* and *Bacillus subtillis* - Agar Diffusion Test

Number of washings	Inhibition zone [mm]	
	Bacillus subtilis	*Escherichia coli*
0	3.0	4
1	2.5	3.5
25	2.0	3
50	b.s.	b.s.

Conclusion

This study confirmed that the proposed method of silver NPs' formation on cotton fabric via direct reduction of water-soluble silver salt using the 2-nozzles' ink -jet printing system at ambient temperature was a simple and efficient way to achieve the antibacterial properties of cotton fabrics. It is possible to obtain in these not restricted conditions, well- and uniform dispersed silver particles or clusters which was confirmed by SEM-EDX and DLS methods.

The results of the both instrumental methods applied in this work, namely: ICP-ToF-MS and LA-ICP-ToF-MS for silver content determination on cotton fabric in relation to those obtained for microbiological assessment of bactericidal efficacy indicate also that silver particles are coupled well with the fabric proving a long-lasting durability for washing (even to 50 washings). Data obtained from the chemical state analysis XPS revealed that the major state of the silver presented on the surface was Ag^0.

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Authors' Biography

Edward Rybicki is a Professor in the Chemical Technology and Textile Chemistry. Graduated from the Technical University of Lodz in the field of physical chemistry of polymers (1964). Ph.D. in radiation chemistry (1972) and D.Sc. (1992) in surface science from the Faculty of Chemistry. His research interests are adsorption at solid/liquid and liquid/air interfaces, surface chemistry, phenomena of the dyeing, washing and finishing processes.

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