University of Sopron
Simonyi Karoly Faculty of Engineering, Wood Sciences and Applied Arts
Jozsef Cziraki Doctoral School of Wood Sciences and Technologies

THESIS OF PhD DISSERTATION

Changes in the amount of silver applied on textiles over usage

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Head of the Doctoral School: Prof. Dr. Levente Csóka

PhD program: Fiber technology and nanotechnology
Program leader: Levente Csóka
Discipline: Materials Science and Technologies

1 Topic of the doctoral thesis

My research deals with a well-defined part of the wide field of application of polymers, i.e. silver-coated textiles. The main topic of the research is centred on the following topics:
- Do commercially available silver-coated textiles have the characteristics expected by the customers prior to their use?
- Do the characteristics of silver-coated textiles change during normal use and if they do, to what extent?
After studying the background literature of the theme, the planned topics of my research had to be extended as I had found that:
- the research results provided in relation to the theme are not suitable for reproducing the results,
- the tools used for quickly, accurately and cost-efficiently examining the amount of silver on textiles under operating conditions are not available
- I had not found any background literature to compare the silver-coated textiles and the efficiency of treatments applied in medical practice

Therefore during the extension of my work:
- I developed and compared four different techniques to specify the amount of silver on silver-coated textiles,
- I studied the change of the silver content of various silver-coated textiles during use as I had originally intended,
- I studied the change of the silver content of the textiles and the antimicrobial effect during washing cycles and the change of silver amount
- during my research, I specified the test conditions necessary for the repetition and reproduction of the tests based on my experience
- I made a recommendation on the extension of the content of the consumer information brochures on silver-coated textiles
- I started to organise a comprehensive ring test on the theme
- I started to make a comparison with the pharmaceutical solutions as I find it necessary to include such information in the customer information brochures.

Taking into consideration the user expectations, I studied the changes of the characteristics of the silver-coated textiles during use, focusing on the change in the antibacterial effect.

I studied the following areas:
- the specification of the silver amount on silver-coated textiles
- the specification of the interrelation between the silver amount and the antimicrobial effect
- the specification of the change in the silver amount and the antimicrobial effect during use.

2 The purpose of the research

Based on the study, summary and synthesis of the background literature, my research aimed at specifying the silver content in the commercially available silver-coated textiles, examining its anti-microbiological effect and studying the impact of the textile washing cycles on these.

My research focused also on the specification of the interrelation between the silver content of the silver-coated textiles and the microbiological effect, and on the detection of changes.
My direct research goal is to develop a method during my work, enabling the comparison of silver-coated textiles and the simple specification of the amount of silver on the fabric.
I also aimed at developing a new test procedure making possible the direct specification of the silver content of textiles by weight or surface.
I intended to replace the previously known destructive testing methods, burning, dissolution in acid or alkali, and I primarily preferred non-destructive methods.
Two innovative methods were developed during my work, references for which had not been found in the scientific literature during our research:
- the method of the separation of silver on the fibres, and
- the detection of the silver amount on the fabric using a metal detector.

8 different, commercially available silver-coated fabrics were used in the research, including – based on the manufacturer's description – 4 samples of nanosilver textiles, 3 samples containing silver-coated fibres and 1 sample with silver on its surface. During the tests, the studied samples and the test methods were selected economically and within reasonable limits.

3 Research method

As the silver content of silver-coated textiles is in the order of mg/kg, the selection of the test methods required special attention.

Both the nanosilver fabrics and the fabrics containing silver-coated fibres were tested with the SEM-EDX (Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)) method after a proper sample preparation, and the silver amount was measured using the ICP-MS (Inductively coupled plasma mass spectrometry) device after the development of the acidic removal procedure. We developed a washing experiment which enables ICP-MS measurements after washing. Using microbiological and elemental analysis methods, I examined whether the silver content of the textiles changes after washing and to what extent the antimicrobial effects change after each washing cycle.

I examined the antimicrobial effect of the sample fabrics applying several methods, and I repeated the tests after the washing cycles, for comparison.

I could examine the resistance and conductivity of the fabrics containing silver-coated fibres and I separated the silver from the fibre with electrolysis. I examined the fabric and the change in the conductivity of the electrolyte solution during electrolysis.

In order to perform the measurements, I developed new measuring equipment enabling the detection of the change in the amount of metal on textiles. Complemented with spectroscopy, I can provide reliable data to accurately define the metal type with regard to how the amount of the metal (silver) changes on the textile between the washing cycles, as a result of various effects.

The thesis covers the historical overview of the topic, the summary of the scientific publications on the silver-coated textiles, as well as the description of the measuring and detection methods, the measurement results and also the description of the special metal detector developed by us.

The summary of the performed tests

I used commercially available textile products – that are silver-coated based on the manufacturer's description – to perform the research.

The parameters of the tested samples and the tests performed on the samples are included in Table 1.

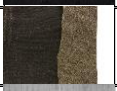
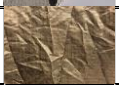
identifier	silver	photo	Scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDX)	X-ray fluorescence XStrata Atestor	Specification of the specific silver content of the textiles (ICP)	Microbiological test	Electrolysis, electrolyte solution concentration after 12 hours ppm	Metal detection method, voltage (V)	Electrical resistance (Ω)
ENZ-1	nanosilvered		✓	×	✓	✓	×	×	×
ENZ-2	nanosilvered		✓	×	✓	✓	×	×	×
ENZ-3	nanosilvered		✓	×	✓	✓	×	×	×
ENZ-4	nanosilvered		✓	×	✓	✓	×	×	×
ESZ-1	silver coating fibre		✓	×	✓	✓	×	×	×
ESZ-2	silver coating fibre		✓	✓	✓	✓	✓	✓	✓
ESZ-3	silver coating fibre		✓	✓	✓	✓	✓	✓	✓
EK-1	silvered on surface		×	×	✓	✓	✓	✓	✓

Table 1. Summary of the tests

During the research, in the course of the measurements and the measuring preparations, the number of experiments was kept within reasonable limits. Based on the first tests performed on the fabrics, I flexibly modified the experiments and selected the samples.

4 Research theses

When studying the scientific literature, I concluded that the examination of the commercially available silver-coated fabrics is barely dealt with. Fabrics are usually made under laboratory conditions with controlled silver content; the size and shape of the silver grains or the thickness of the coatings, and the exact physical and mechanical characteristics of the substrate materials, etc. are known.

During my research, I established the following:

THESIS 1

I established that the published scientific statements in relation to the theme cannot be reproduced. The description of the materials involved in the research works is inaccurate and the test conditions are not known exhaustively. Neither the maturity degree of the cotton fibre, nor the exact technological parameters of the artificial fibres are known. The customer information brochures of the commercially available textile products contain only minimum information concerning the instructions on composition and treatment indicated with textile icons. The manufacturers' information brochures do not include any specific information.
In my view, it is necessary to include more detailed customer information; I made recommendations in relation to this to the KERMI Department of ÉMI-TÜV SÜD Kft. and Innovatext Kft.

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THESIS 2

I established that in the case of textiles, it is not enough to use the silver textile label. The product has to be examined in every case in order to establish whether the commercially available product silvered in accordance with the manufacturer's information effectively contains silver and if it does, in what form (nanosilver, silver-coating on the fibre, etc.).
It was the first time to use X-ray fluorescence measurement for textile industry purposes. I established that, using the method, the metal coating on the textiles, fibres and filaments can be perfectly detected, however, the device is not suitable for detecting the nanoparticles. With this method, I could clearly establish in a non-destructive way what materials are included in the coating on the surface of fabrics and fibres.

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http://www.doksi.hu/get.php?lid=20723
http://testorg.eu/Testoreu/Megvalosult_tesztek/Reszletes_ismerteto.html

THESIS 3

I proved that the silver on silver-coated textiles can be separated with electrolysis. This self-developed method is based on the fact that the initial ppm of the electrolyte solution is permanent, and the fabrics subjected to various washing cycles change the ppm of the electrolyte solution during electrolysis. According to the method developed, during the 12-hour period the conductivity of the solution of the electrolysis cell shows a growing tendency;

during this period the silver coating on the fabrics, with the applied electrical parameters, can be separated.

I proved that if graphite electrodes are used for electrolysis, milky white mist is formed around the fabric at the beginning of the electrolysis and the electrolyte solution becomes opalescent. After 12 hours, the conductivity of the solution decreases and the silver settles to the bottom of the electrolysing container.

In the case of acid-resistant steel electrodes, the silver separating from the silver-coated fabric during electrolysis coats the cathode.

In both cases, I examined the fabrics and the sediment after electrolysis, using the SEM-EDX method. I established that after the 12-hour electrolysis the silver is not detectable on the fabrics, while the swab analysis shows 100% silver. By measuring the sediment, the amount of the silver can be specified, however, I did not apply this method due to the large losses. I established that a disadvantage of this method is that it cannot be applied in a non-destructive manner, and it is not suitable for measuring the amount of silver on nanosilver fabrics.

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Tünde Dudás, Balázs Ásványi, Stefan Ivanov Boyadjiev, Imre Miklós Szilágyi:
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Tünde Dudás, Teodóra Nagyné Kovács, Imre Miklós Szilágyi, Ferenc Mester:
MEASURING THE CHANGES IN THE QUANTITY OF SILVER IN SILVER-ENABLED TEXTILES BY A NEWLY DEVELOPED PORTABLE DEVICE
***AATCC Journal of Research-Textile Science** (before publication)*

THESIS 4

I established, using an electron microscope, that changes can be clearly detected on the fabric surface after the washing cycles. In the case of continuous silver coatings, the silver coating cracks on the fibre surfaces, the silver grains disperse, partially covering the non-silver-coated fibres. After the 10th washing cycle, the signs of wear could be observed, and using the EDX analysis, I proved the silver atom and m/m% change.
The surface silver coating and nanosilver on textiles and fibres can also be measured with this method. The disadvantage of this method is that it is not suitable for performing non-destructive tests.
I established that in the case of silver-coated textiles, a new control measurement has to be introduced after the 10th washing cycle, and its results have to be communicated to the customers.

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THESIS 5

Based on simple market research and a consumer survey, I established that for the customers of silver-coated products (socks) the most important

characteristics among the favourable product characteristics is the antibacterial effect.
I applied 6 methods for the testing of microbial effect; therefore I could prove that there is a sample fabric which showed no signs of any kind of inhibition in the case of a testing method, while under different test conditions inhibition could be observed. Based on the results, I proved using several methods that samples EK-1 and ESZ-2 contain silver in such a high concentration that – despite the decrease caused by the washing experiments – it is enough to reach the antimicrobial effect under the experimental circumstances applied by us. Sample ENZ-2 contained silver in a much lower concentration at the beginning of the tests compared to the other tested samples. During the washing cycles, the antimicrobial effect of sample ENZ-2 was nearly eliminated due to the decrease in the amount of silver, while in the case of tests performed with other methods antibacterial inhibition could not be observed.

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THESIS 6

Using the inductively coupled plasma mass spectrometry (ICP-MS), I established that the tested nanosilver textiles ENZ-1, ENZ-2, ENZ-3 and ENZ-4 contain silver specifically in significantly lower concentration (0.9-1.8 ppm) compared to fabrics ESZ-1, ESZ-2, ESZ-3 containing silver-coated fibres (12.2-137.7 ppm) and textile EK-1 made applying impregnation (846 ppm). The specific silver content of the individual sample types is highly different within the sample group. I established that the measured silver concentration of the 3 tested parallel samples varied significantly.
In order to check to what extent the silver concentration of the textiles changed as a result of washing, after 10 washing cycles we prepared the samples for ICP-MS measurement in accordance with the conditions optimised during the previously conducted removal experiments. We observed a substantial

decrease: the silver concentration on the textiles decreased by 77.5% in the case of EK-1, by 35.2% in the case of ESZ-2 and by 23.6% in the case of ENZ-2.
I established that, using this method, the silver content of fabrics and fibres coated on the surface, as well as nanosilver fabrics is measureable. The disadvantage of this method is that it cannot be applied in a non-destructive manner.

THESIS 7

I examined the fabrics after washing and abrasion cycles. The resistance of the tested fabrics showed a continuously growing tendency by the increase of the number of treatments. Complementing this test with SEM test results, I established that the resistance of fabrics with continuous silver coating constantly decreases as a result of the increasing number of washing cycles until the continuous fibre coating discontinues. After the discontinuity of the continuous coating, the resistance of the fabric cannot be measured, therefore this method is not suitable for specifying the amount of silver; however, the continuity of the coating can be checked in a non-destructive manner.

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THESIS 8

I proved that the silver on silver-coated textiles is detectable when above the quantity of 5 mg/kg, using metal detection methods.

The commercially available traditional metal detectors cannot perceive the small amount of metal that can be found on textiles. We developed a special metal detector with high sensitivity to detect the silver (metal) amount on textiles.

I established that the voltage generated by the fabrics at our disposal containing silver-coated filaments shows a decreasing tendency after the increasing number of washing cycles, which implies a decrease in the amount of metal (silver). The voltage generated by the impregnated silver-coated fabric decreases more moderately than in the case of fabrics containing silver-coated fibres, but after the 20th washing cycle, it nearly reaches the detectable limit, just like in the case of fabrics containing silver-coated fibres.

The direct measuring method (reading the voltage between values 0 and 7) with a manual and portable measuring device enables the quantification of the amount of silver on the fabric, and therefore, the amount of silver on the textile before and after washing or the silver content of two fabrics becomes comparable.

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5 Publications concerning the research topic:

Tünde Dudás, Bogdanka Ćurčić Tandi:
UTICAJ TEKSTILNIH PROIZVODA U OČUVANJU ZDRAVLJA
Časopis Tekstilna Industrija 2017/3 LXIV:(3) pp. 19-32. (2017) ISSN 0040-2389

Tünde Dudás, Ferenc Mester:
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Tünde Dudás, József Pitrik:
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The working title of the thesis was the following: The change of the amount of silver applied on polymers.