INVESTIGATION OF THE CHEMICAL DURABILITY AND EFFECTIVENESS OF TEXTILE PRODUCTS WITH SILVER COATING

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Abstract
We studied the silver content and the durability of the antimicrobial effect of commercially available silver-coated textiles. The effect of cleaning cycles on these attributions was in the focus of our work. Inductively coupled plasma mass spectrometry (ICP-MS) was used to monitor the silver content of samples, while the antimicrobial activity was tested by using four types of bacteria and four types of fungi.

Introduction
Nanotechnology is a very broad field, which incorporates research areas as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, microfabrication, molecular engineering, etc. [1]. Nanoparticles of silver are being used as antimicrobial agents in several ways, including the sterilization of wounds, embedding them in plastic coatings of storage containers (e.g. plastic boxes, inner walls of refrigerators, etc.) to prevent the fouling of food stored in them or incorporating silver nanowires into filter units used to purify drinking water [2].
Along the same concept, silver is also used in textiles (e.g. clothing, in the household, in cars, in furniture covers, etc.) to promote self-cleaning and odor-suppression. In these applications, silver is applied either in form of silver salts (e.g. silver chloride), elemental nanoparticles or nanoscale coatings on the surface of the textile fibers. The interlaced weaving of the fabrics from polymer and silver-coated fibers is also customary. In all cases, the antimicrobial effect is caused by the slow release of silver ions that reduces bacterial growth on the textile by releasing silver ions, which are active on the fiber surface [3,4].
The widespread use of silver nanoparticles in commercial products, especially textiles, will likely result in an increase of the environmental concentration levels of silver. The problem is further intensified by the fact that water plants persently are not well equipped to remove Ag nanoparticles from drinking water. Many researchers even consider silver to be more toxic than other metals when in nanoscale form also because these particles have a different toxicity mechanism compared to dissolved silver. Nanoparticles can also become airborne easily due to their size and mass. When inhaled, nanoparticles can go deeper into the lungs reaching more sensitive areas. The mentioned experience confirm why it is crucial to investigate the textiles treated with silver and compare their chemical durability and effectiveness to those of conventional textiles.

Samples and materials

The polymer textile samples studied were obtained from commercial circulation. Four textile samples were coated with Ag nanoparticles, three contained silver-coated fibers and one was given an undetermined treatment by the manufacturer which was referred as "silverization". The base fibers in these textiles are cotton, elastane, polyamide and poliesther.

For the quantitative determination of the silver content of textiles we used ICP-MS spectrometry on an Agilent 7700x instrument, The silver content of the textile samples was dissolved by using ultratrace purity HNO_3 (VWR). All solutions were prepared by using trace analytical purity deionized labwater (Millipore Elix Advantage 3+ Synergy). Cleaning (washing) cycles were modeled by using alkaline solutions prepared from with analytical grade Na_2CO_3 (Reanal). 0.22 μm poresize PVDF syringe filters (Labex) were used for the filtration of solutions. ICP-MS calibration solutions were prepared from ICP-MS multi-elemental stock solutions (Inorganic Ventures).

Optical microscopy images were recorded with an Optika Ti600-FL microscope equipped with a high-resolution color digital camera. All statistical and graphical evaluation of the data was made in OriginLab 8.6 and Microsoft Excel software.

Results and discussion

The optical microscopy images of the surface of the fabrics can be seen in Figure 1. The silver-coated fibers can be easily identified (ESZ-1, ESZ-2, ESZ-3). Even coatings (across the fabric) or nanoparticles of course can not be detected by optical microscopy. We also attempted to use scanning electron microscopy to detect these particles but it was not succesful due to the static charging of textiles. All in all, the presence of silver in the fabrics could only be partially confirmed by microscopy.

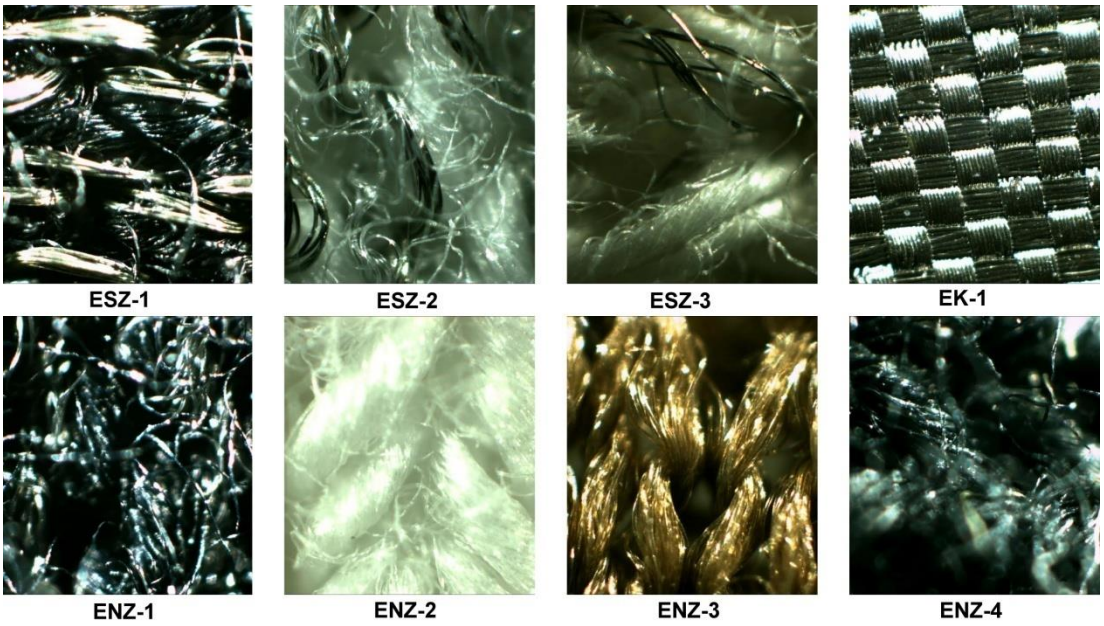

Figure 1. Optical microscope images of some silver-treated textiles (similar magnifications)

The initial microbiological activity of the textile samples was examined by preparing a suspension of suitable bacteria and fungi and incbuting sub-samples (30 x 30 mm) of the

textiles together with the suspension and in agar-agar gel at 30°C for 48 hours. The activity was estimated by measuring the size of colonies and comparing them to control colonies. The results showed that the antibacterial effects of the investigated textiles are intermediate. Three samples, a nano silverized (ENZ-2), a textile with Ag-coated fibers (ESZ-2) and the textile "silverized" (EK-1) showed the best antimicrobial activity. The activity was assumed to be caused by the presence of Ag.

In order to monitor the change of silver content of textiles during washing cycles, we developed a simple sample preparation method followed by ICP-MS analysis. Again, 30 x 30 mm pieces of textile were treated with 0.2 mol/dm^3 nitric acid for 10, 30, 60, and 120 minutes of time, during which shaking was also employed. This routine was followed in order to establish the optimal duration of acid treatment. As an illustration, this optimization curve for sample ESZ-2 can be seen in Figure 2. Based on these data, the area-specific silver content of the fabrics could be estimated; it was found to vary in a wide range from 0.5 to 850 mg/m^2.

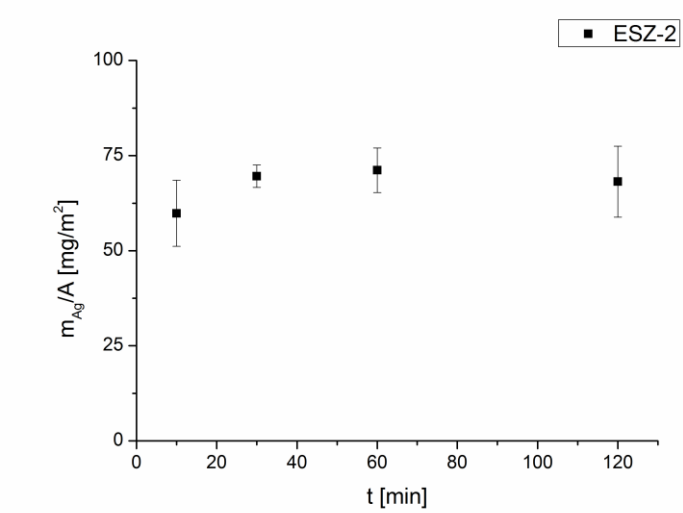

Figure 2. Optimization of the duration of nitric acid treatment of the sample ESZ-2 for the determination of the area-specific silver content. Error bars represent the standard deviation from three parallel measurements

We also performed model washing experiments, the purpose of which was to monitor the release (loss) of silver from these samples. Our first attempts with NP-treated samples involved washing with water and surveying the silver nanoparticles in the aqueous leachate by using single nanoparticle ICP-MS methodology. Unfortunately, no Ag NPs were detected, which is either the indication of that the Ag NPs used in the textile treatment are too small or that pure water can not easily remove the NPs. In further experiments we used a Na_2CO_3 solution (one spoonful of carbonate in 5 liter water) to model the washing procedure. 100 mL solution was poured on each sub-sample and the textiles were then shaked for 15 minutes. After each treatment, the sub-samples were carefully drained and rinsed thoroughly. Following this, the residual silver content of the fabrics was determined by the ICP-MS method, as described above. This washing procedure was then repeated several times, each time starting out with a fresh piece of fabric and continuing with the washing-rinsing cycles until the required, incremental number of steps.

In accordance with the expectations, the silver content of the samples decreased with the increase of washing cycles. The extent of the loss of silver was different for different samples,

probably because of differences in the base fiber composition and the silver treatment. Figure 3. shows the loss of silver after 10 washing cycles for three textile samples. The loss was greatest for ENZ-2, where it reached almost 77%, but even the most durable fabric lost 35% of its silver content.

The investigation of the remaining antimicrobiological activity of the washed samples is in progress now. We will present the detailed results in our poster contribution.

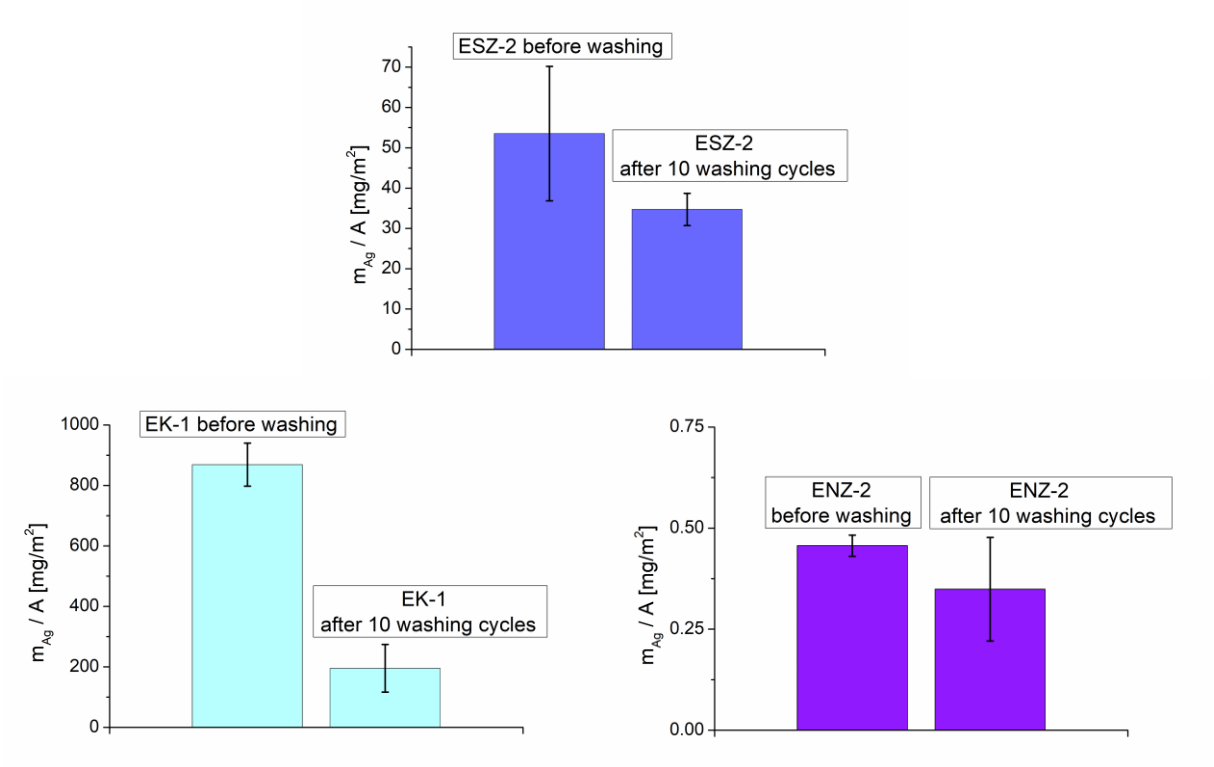

Figure 3. Change of the silver content of textiles as a result of Na_2CO_3 washing cycles. Error bars represent the standard deviation from three parallel measurements

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