

Physical and Chemical Transformations of Silver Nanomaterial-containing Textiles After Use

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ABSTRACT

Nanomaterials have been increasingly used in consumer products and silver nanomaterials (AgNMs) especially have been used for their antimicrobial properties. As use of AgNMs in consumer products continues to increase, a corresponding increase in silver's presence in the environment will be observed due to disposal. To better understand what materials are entering the environment, work needs to be performed to determine the chemical and physical properties of AgNM-containing consumer textiles throughout their lifecycle prior to introduction into the environment through disposal. Therefore, the aim of this work is to evaluate chemical and physical transformations that AgNM-containing textiles undergo during modeled human exposure. A commercially available AgNM-containing wound dressing was studied as our model system. To model this textile during use, the material was exposed to synthetic sweat or simulated wound fluid for varied durations up to 7 days. The textile was extracted and stored under vacuum to minimize extraneous transformations after removal from test media. Both pristine and exposed wound dressings were characterized using a variety of analytical techniques including scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS), UV-Visible spectroscopy (UV-Vis), and dynamic light scattering (DLS). Electron microscopy revealed the formation of micron-sized structures on the surface of the commercial wound dressing after synthetic sweat exposure which spectroscopic and diffraction based techniques suggested were consistent with silver chloride. In contrast, wound dressing exposed to simulated wound fluid did not show any large structures on the surface of the material. In fact, the surface was similar, though less defined, than the pristine wound dressing. The release of silver from the wound dressing into the exposure media was also examined. Though ICP-MS found silver release, our DLS and UV-vis based results suggest that released silver was not detected in metallic form, aggregate, or on the nanoscale in the exposure media. A better understanding of the chemical and physical transformations of AgNMs in consumer products is necessary for manufacturers and

regulators to make more informed decisions on product design and use.

Keywords: silver, nanomaterials, characterization, textile, acticoat

1 INTRODUCTION

Due to their unique properties, nanomaterials have undergone increasing use in consumer products. For that reason, silver nanomaterials can be found in consumer goods including clothing, personal care items, and food storage products where they act as antimicrobial agents.[1] Moreover, their antibacterial property makes AgNMs an attractive additive for biomedical products and devices such as bandages and wound dressing.[2]

During use these AgNMs will undergo physical and chemical changes. These transformations are not well understood, though several studies have examined the release of silver from these textiles. Researchers suggest that soluble silver species will be released after the textile has been exposed to synthetic sweat or skin surface film liquid.[3, 4] Fewer studies have examined physical and chemical transformations that occur on the textile. One study that examined a commercial AgNM product called Acticoat Flex3 found the formation of silver and chloride containing crystals on the fibers after saline exposure.[5] These studies suggest transformations will occur on AgNM-containing textiles that may affect their chemical and physical properties after use. A greater understanding of the physical and chemical transformations that occur during the AgNM-containing textile use phase are necessary to better understand what forms are left on the textile and are entering the environment. This is important because a recent study suggests almost all of the silver present in a commercially available AgNM-containing wound dressing remains in the product upon disposal into the environment.[6]

The focus of this work was to examine the physical and chemical transformations that AgNM-containing textiles undergo during modeled human exposure. To do this, a commercial AgNM-containing wound dressing was examined quantitatively and qualitatively using various orthogonal analytical techniques including SEM-EDS, XRD, XPS, ICP-MS, UV-Vis, and DLS.

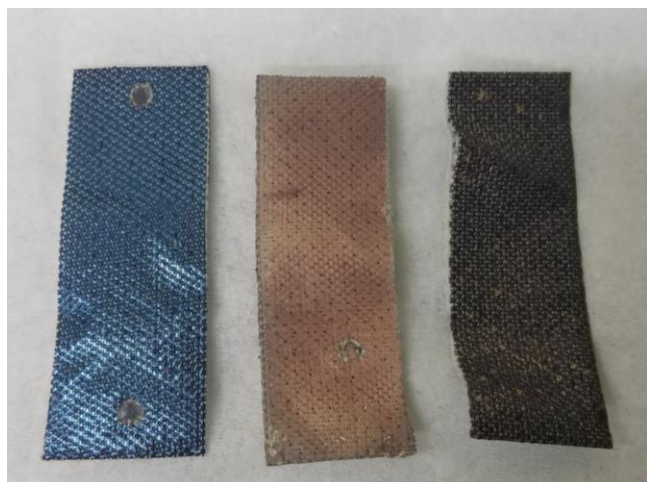


Figure 1: Photographs of Acticoat before (left) and after 168 h exposure to synthetic sweat (middle) and simulated wound fluid (right). Exposure results in a color change from blue to light brown (synthetic sweat) or dark gray (simulated wound fluid).

2 METHODS¹

Solutions of synthetic sweat and simulated wound fluid were prepared. Synthetic sweat was prepared following the International Standard Organization (ISO)105-E04-2008E acidic type synthetic sweat method.[7] Briefly, 0.5 g l-histidine monochloride monohydrate (VWR), 5 g sodium chloride (Alfa Aesar, 99%), and 2.2 g sodium dihydrogen orthophosphate dihydrate (Alfa Aesar, 99%) were mixed and diluted to 1 L with MilliQ water. For simulated wound fluid, an isotonic solution with an added 1% protein component was prepared.[8] Briefly, 8.27 g sodium chloride (Alfa Aesar, 99%), 0.37 g calcium chloride dihydrate (Amresco), and 10 g bovine serum albumin (BSA, SeraCare) were mixed and diluted to 1 L with MilliQ water.

A 2/3 inch x 2/3 inch of Acticoat (Acticoat 7, Smith & Nephews) was fully submerged in a 30 mL LDPE plastic bottle containing 10 mL of test solution. The bottle was wrapped in foil to prevent light exposure and rotated on a room temperature incubator at 50 rpm for varying amounts of time. The textile was removed at the following times after addition: 5 s, 1 h, 2 h, 6 h, 24 h, and 168 h. The textile was stored in a vacuum desiccator until analysis. The remaining test exposure solution was stored in the dark at 4 °C until analysis.

2.2 Characterization

¹ Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

Pristine and exposed samples were analyzed using a FEI Quanta 200 (Hillsboro, OR) environmental scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS). Samples were imaged at an operating voltage of 10 kV with a unitless spot size of 3. A Bruker XFlash Detector 5030 (Billerica, MA) was used to collect EDS spectra, with an acquisition time of 300 s. EDS data was analyzed using Bruker Esprit v. 1.9.3. A small piece approximately 2 mm x 2 mm was analyzed by adhering to an Al SEM stub with carbon tape. The middle silver-containing layer was imaged to minimize possible contamination of the outer layers.

Exposure media was analyzed by UV-Visible (UV-Vis) spectrophotometry using a PerkinElmer Lambda 750 spectrophotometer (Waltham, MA) to determine if particles were released from the Acticoat or AgNM textile into the synthetic sweat and simulated wound fluid after exposure. Absorbance data was collected from 200 nm to 800 nm using a plastic microcuvette with a pathlength of 1 cm. Dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS (Westborough, MA) was performed to determine the sizes of any particles released into the exposure media. Bulk silver optical density and refractive index were used and scattering was measured at 173°. Test exposure media samples were held at 23 °C for 180 s before the first run to equilibrate the temperature and were then held at that temperature during the run. For each sample, 8 measurements were made, each measurement consisted of 11 scans, and each scan was 10 s long.

3 RESULTS AND DISCUSSION

3.1 Physical Transformations

Exposure of Acticoat to either synthetic sweat or simulated wound fluid caused a visible change to the color of the product. As shown in Figure 1, the pristine Acticoat was blue in color, however exposure to either solution resulted in a noticeable color change. After exposure to synthetic sweat Acticoat was light brown (Figure 1, middle) and after exposure to simulated wound fluid Acticoat was dark gray in color (Figure 1, left). To better understand the physical transformations that were occurring, SEM images were acquired. Prior to exposure, discrete spherical crystals in the nanoscale range were found on the surface of pristine Acticoat (Figure 2, top) which agreed with previous work on the surface of Acticoat.[9] After 24 h exposure to synthetic sweat, submicron and larger micron-sized nonspherical crystals formed on the surface. This results agreed with Rigo, et al., where silver- and chloride-containing crystals were formed on Acticoat Flex3 after saline exposure.[5] In contrast to synthetic sweat, the surface of the simulated wound fluid exposed Acticoat looked similar to the pristine material. However, the

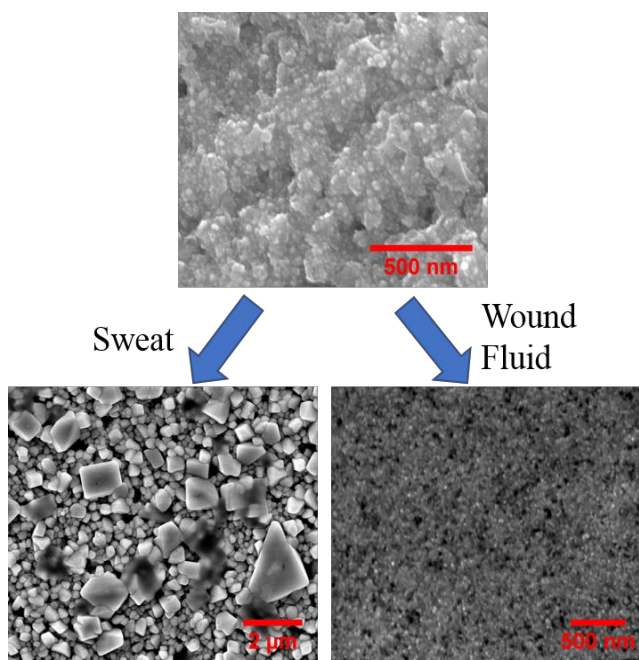


Figure 3: (SEM) images of Acticoat before (top) and after 24 h exposure to synthetic sweat (bottom left) and simulated wound fluid (bottom right).

features were less defined and the surface appeared to have less roughness than the pristine material. Importantly, there was no formation of submicron or micron-sized crystals on the surface of the wound dressing.

3.2 Chemical Transformations

To determine chemical transformations that may have occurred during modeled human exposure, EDS was first used. EDS mapping for pristine Acticoat indicated the presence of silver with peaks for carbon and oxygen present and minimal amounts of chloride. In contrast, the EDS spectra for synthetic sweat exposed Acticoat indicated both silver and chloride being present, as well as sodium (Figure 3A). The EDS map indicated overlap of both silver and chloride on the submicron and micron-sized crystals. Spots in the EDS map that indicated chloride but not silver also showed sodium, suggesting crystals containing sodium and chloride were present on the surface as well. The EDS spectra for simulated wound fluid exposed Acticoat showed the presence of silver, chloride, and sodium (Figure 3B). However, EDS mapping for this material showed almost complete overlap of silver and chloride. Other results by XRD and XPS (data not shown) suggest the presence of silver in metallic and silver chloride form after exposure to either test media suggesting a partial conversion of the

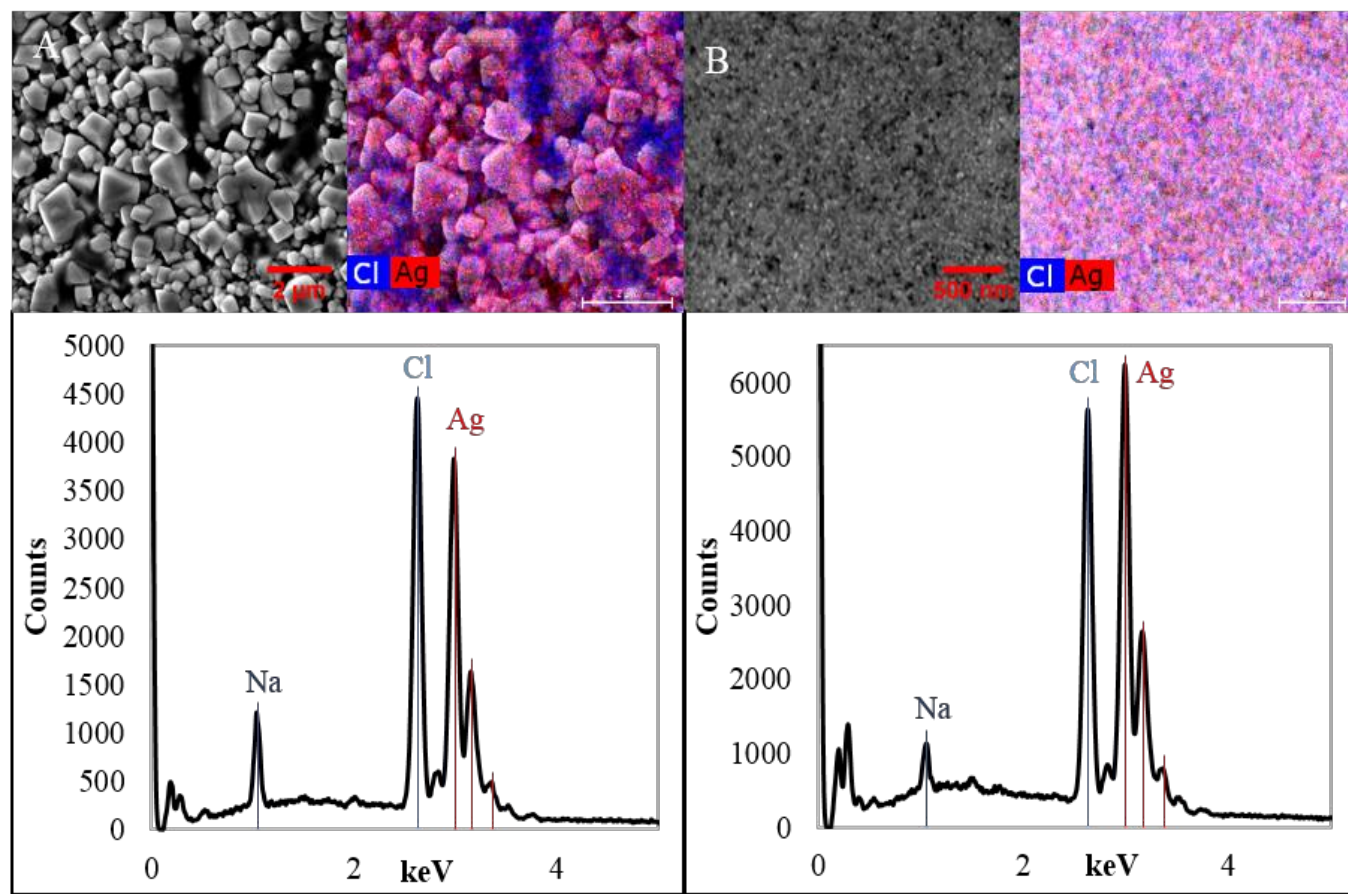


Figure 2: SEM images, energy-dispersive X-ray spectroscopy (EDS) maps, and EDS spectra of Acticoat after 24 h exposure to A) synthetic sweat and B) simulated wound fluid.

surface layer to the +1 oxidation state.

3.3 Evaluation of released silver

After the Acticoat was examined, the test media was studied to determine if any nanoscale particles were released into the fluids during exposure. Data to be published in future studies using ICP-MS revealed the presence of ppm levels of soluble silver in the wound fluid supernatant while the simulated sweat equivalent revealed only sub ppm levels.

DLS was used to determine if any nanoscale particles or aggregates were released into the test exposure solutions. Interestingly, Acticoat exposed synthetic sweat did not result in the appearance of any peaks in the DLS spectra, suggesting that any silver released was neither in a nanoscale particulate nor an aggregated form. Similarly, Acticoat-exposed simulated wound fluid supernatant did not display any new peaks in the DLS spectra compared to the unexposed simulated wound fluid. This again suggests that any silver released from the Acticoat during exposure was not in a nanoscale particulate form nor in an aggregated form.

UV-Vis was also performed to determine if any metallic silver was released from the textile during modeled human exposure. Consistent with the DLS-based findings, synthetic sweat and simulated wound fluid did not show any increases in absorbance or the appearance of any new peaks after interacting with Acticoat. This suggests that the silver released was not metallic or of a size sufficiently large enough to be detected by DLS. Therefore, the most likely form of released silver in the simulated wound fluid is as a complex with the added protein. This would agree with work by Rigo, et al., and Ostermeyer, et al. which found sequestration of silver in protein.[5, 10]

4 CONCLUSIONS

This work shows that modeled human exposure will result in both physical and chemical transformations of AgNMs on consumer textiles such as wound dressings. Exposure to synthetic sweat causes the formation of submicron and micron-sized silver and chloride containing crystals on the surface of the commercial wound dressing. Simulated wound fluid, in contrast, does not result in the formation of micron-sized crystals on the surface of the wound dressing. The wound dressing was found to release silver into the exposure media, with simulated wound fluid showing greater release than synthetic sweat. However, our results demonstrate that silver is not present in a metallic form, in aggregate, or on the nanoscale in the exposure media. The physical and chemical transformations found in this work necessitate the study of AgNM-containing consumer textiles under more realistic conditions. This will allow for better understanding of the chemical and physical transformations that AgNMs in consumer will undergo during use and allow for

manufacturers and regulators to make more informed decisions on product design and use.

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