

Physical and Chemical Transformations of Silver Nanomaterials in Textiles After Use and Disposal

D.E. Gorka*, J.M. Gorham*

*National Institute of Standards and Technology,
Mail Stop 8520, 100 Bureau Drive, Gaithersburg, MD, USA
danielle.gorka@nist.gov, justin.gorham@nist.gov

ABSTRACT

Silver nanomaterials (AgNMs) have been increasingly used in consumer products for their antibacterial properties. Textiles, including wound dressings, are just one of the many products which take advantage of AgNM's antimicrobial properties. To better understand realistic transformations that may occur to these materials upon entrance into the environment, more work needs to be performed to determine the chemical and physical properties of AgNM-containing consumer products throughout their lifecycle. Previous work demonstrated transformations to AgNM containing wound dressings during simulated use (e.g. wound fluid and sweat exposure). The aim of the current work is to evaluate transformations these same textiles undergo during modeled environmental exposure. To model textile disposal conditions, the pristine wound dressings were exposed to synthetic freshwater or artificial landfill leachate. All specimens were analyzed before and after exposure with the techniques dynamic light scattering (DLS), UV-Visible spectroscopy (UV-Vis), X-ray diffraction (XRD), X-ray photoelectron microscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and inductively coupled plasma mass spectrometry (ICP-MS). SEM-EDS showed the formation of chloride and phosphorous containing crystals on the surface of the commercial wound dressing after synthetic fresh water exposure. The surface was found to be heterogeneous with some areas showing increased granularity while other areas were similar to the pristine material. Wound dressing exposed to artificial landfill leachate showed increased granularity compared to pristine wound dressing. Unlike synthetic fresh water, no large crystals were found on the surface of the artificial landfill leachate exposed textile. Future studies will evaluate the transformations that occur to wound dressings exposed to simulated disposal conditions *after* being treated with test media for simulating use, thus representing more realistic end-of-use scenarios.

Keywords: silver, nanomaterials, characterization, textile, acticoat

1 INTRODUCTION

Nanomaterials are increasingly being used in consumer goods due to their unique properties. As a result of their antimicrobial nature, silver nanomaterials can be found in consumer products such as athletic clothing, stuffed animals, and food storage products.[1] Additionally, AgNMs are considered an attractive additive for biomedical products and devices such as bandages and wound dressing due to the antimicrobial properties they impart upon their products.[2]

However, increased use of AgNMs in consumer products will result in an increase in their entrance into the environment. This was demonstrated recently in a study by Courtemanche, et al., which found almost all silver remains in commercial wound dressings upon product disposal.[3]

Silver nanomaterials have been shown to have negative consequences on environmental organisms. Work by Arnaout and Gunsch found decreased nitrification by *Nitrosomonas europaea*, a bacteria necessary for nitrogen cycling in wastewater treatment plants.[4] Additionally, AgNMs inhibited anaerobic digestion of waste in lab-scale bioreactors used as a modelled landfill scenario.[5] Due to the potential negative consequences of AgNM-containing consumer products after disposal, it is necessary to understand what physical and chemical transformations these products will undergo throughout their lifecycle.

Here we evaluate the transformations to AgNM-containing textiles, specifically wound dressing, before and after exposure to simulated fluids consistent with disposal in landfills. In this work, wound dressings were exposed to synthetic fresh water and artificial landfill leachate. The resulting transformations have been examined by SEM-EDS with preliminary measurements reported in the following text.

2 METHODS¹

2.1 Exposure

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.

3 RESULTS AND DISCUSSION

3.1 Physical Transformations

The transformation of Acticoat after exposure to synthetic freshwater or artificial landfill leachate were visibly apparent. The pristine Acticoat was blue on the surface of the silver containing layers (Figure 1), however the color changed after exposure. At shorter exposure times (less than 2 h) there was little to no change in color from blue when exposed to the synthetic freshwater. Longer term synthetic freshwater exposure (> 2h), however, resulted in a gradual color change from blue to a dark brown color. This gradual process is perhaps best exemplified by the 24 h sample shown to the left (Figure 1, middle) which demonstrates how the majority of the Acticoat was dark brown, with the left side remaining blue. By 168 h the textile was completely dark brown. In contrast, exposure to artificial landfill leachate resulted in a color change to gray brown (Figure 1, right). At short exposure times, (less than 1 h) the wound dressing was a dark gray brown. As time increased the material became lighter in color, though it still remained gray brown. Interestingly, the white gauze layer (seen in the pristine wound dressing) between the active layers became yellowish/brown after exposure to either synthetic fresh water and artificial landfill leachate. One potential explanation is that silver redeposited and/or nucleated on this gauze layer after release from the blue wound dressing layers.

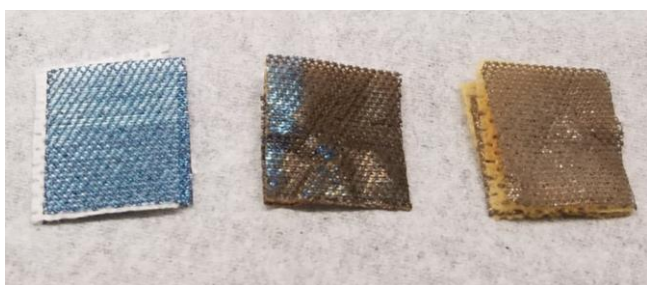


Figure 1: Photographs of Acticoat before (left) and after 24 h exposure to synthetic fresh water (middle) and artificial landfill leachate (right). The wound dressing becomes mottled blue and dark brown after exposure to synthetic fresh water and gray brown after exposure to artificial landfill leachate.

Solutions of synthetic sweat and simulated wound fluid were prepared. Artificial landfill leachate was prepared following United States Environmental Protection Agency (US EPA) guidelines Toxicity Characteristic Leaching Procedure (TCLP).[6] Briefly, 5.7 mL glacial acetic acid (Mallinckrodt, ACS grade) was added to 500 mL MilliQ water. Then 64.3 mL 1 N sodium hydroxide (Titrisar, MilliporeSigma) was added and the solution diluted to 1 L. The pH was adjusted to 4.98. EPA moderately hard water (MHW) was also prepared following EPA guidelines.[7] Briefly, 1.2 g magnesium sulfate (Sigma-Aldrich, 99.5%), 1.92 g sodium bicarbonate (Sigma, 99.5%), and 0.08 g potassium chloride (Mallinckrodt, ACS grade) were added to 19 L MilliQ water. The solution was aerated overnight. Next 1.2 g calcium sulfate dihydrate (Sigma-Aldrich, 98%) dissolved in 1 L MilliQ water was added and the solution was aerated overnight.

Ten mL exposure media was placed into a 30 mL low-density polyethylene plastic bottle and wrapped in foil (to prevent light exposure). A 2/3 inch x 2/3 inch of Acticoat (Acticoat 7, Smith & Nephews) was then added to the bottle, capped, and placed in a room temperature incubator, rotating horizontally at 50 rpm. The textile was removed at the following times after addition: 5 s, 1 h, 2 h, 6 h, 24 h, and 168 h. All solid samples were stored under vacuum until analysis. Liquid media was stored in the dark at 4 °C until analysis.

2.2 Characterization

A FEI Quanta 200 (Hillsboro, OR) environmental scanning electron microscope (SEM) with a Bruker XFlash 5030 (Billerica, MA) energy-dispersive X-ray spectroscopy (EDS) detector was used to image samples and to collect EDS spectra and mapping data. An operating voltage of 10 kV and a unitless spot size of 3 were used to image the samples and collect EDS data. EDS acquire times were 300 s and data was analyzed using Bruker Esprit v. 1.9.3 software. The middle layer of Acticoat (approximately 2 mm x 2 mm) was adhered to an Al stub with carbon tape.

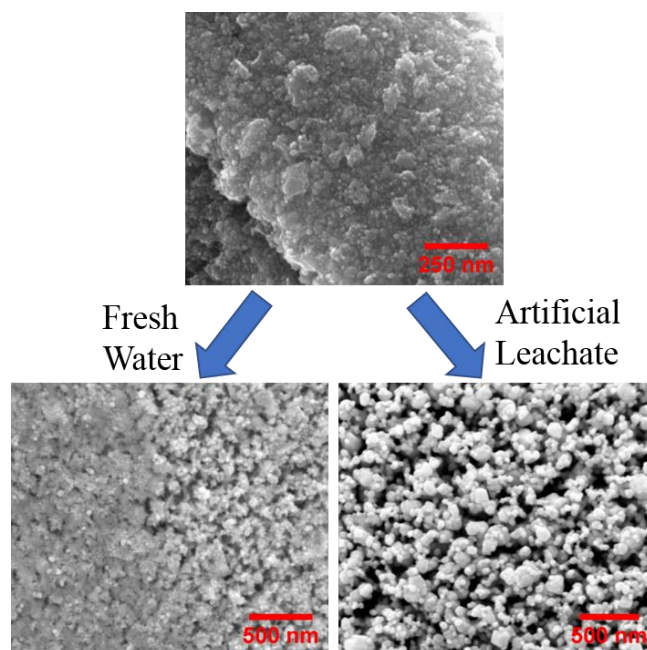


Figure 2: Scanning electron microscopy (SEM) images of pristine Acticoat (top) and Acticoat after 24 h exposure to synthetic fresh water (bottom left) and artificial landfill leachate (bottom right).

To further examine the physical transformations of Acticoat exposure to modeled environmental media, scanning electron microscopy images were taken (see Figure 2). Pristine Acticoat consisted of discrete spherical nanoscale particles deposited onto the substrate which agrees with previous studies.[8] After exposure to synthetic fresh water, the surface of Acticoat transformed in a non-consistent fashion (Figure 2, bottom left). Some areas showed increased granularity compared to the pristine wound dressing while other areas, sometimes in the same field of view, showed no change at all. Observations from other areas included the presence of submicron and micron-sized crystals on the surface of the silver layer (images in Figure 3A). These crystals were generally triangular or square in shape. In contrast, the surface of Acticoat after exposure to artificial landfill leachate was much more uniform with respect to the type of transformations that occurred. Compared to the pristine material, exposed Acticoat had increased granularity and space between the nanocrystals (Figure 2, bottom right). Particles still retained their spherical shapes. Chemical analysis was next performed to determine the chemical transformations of Acticoat after modelled environmental exposure.

3.2 Chemical Transformations

To better understand the elemental transformations that occurred as result of modeled environmental exposure, EDS

was used. Unsurprisingly, EDS mapping of pristine Acticoat revealed silver on the surface, and EDS spectra for the pristine material showed signatures predominantly of silver and also showed signatures for carbon and oxygen. After exposure to synthetic fresh water, EDS mapping showed that many of the micron-sized square crystals contained chloride while the triangular crystals contained phosphorous (Figure 3A). The EDS spectra for the entire mapped region displayed signatures for silver, as well as a signature for chloride. Signatures for phosphorous could be found in samples that contained several triangular crystals. EDS mapping for Acticoat after artificial landfill leachate exposure found silver on the surface. In some instances small crystals on the surface were found to contain chloride. The EDS spectra for Acticoat exposed to artificial landfill leachate contained signatures primarily for silver, with peaks for chloride and oxygen.

4 CONCLUSIONS

To better understand the chemical transformations that are occurring as a result of environmental exposure, further measurements will be performed using XRD and XPS. These techniques will determine the bonding environment and the oxidation states of the exposed textiles while corroborating the compositional information from EDS. This will then be used to help elucidate the effect of environmental exposure. Similarly, ICP-MS, DLS, and UV-Vis will be used to study the release of silver from the

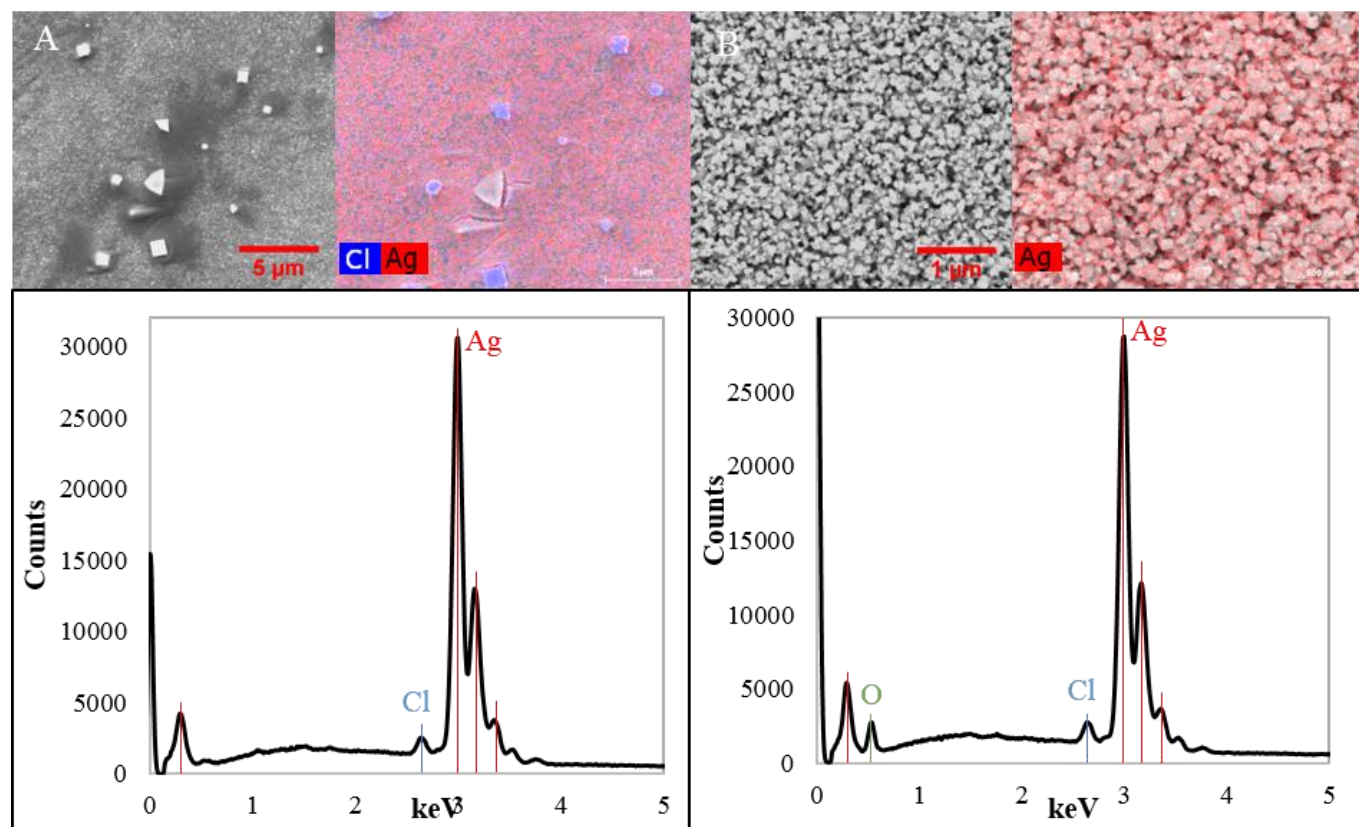


Figure 3: SEM images, energy dispersive X-ray spectroscopy (EDS) maps, and EDS spectra for Acticoat after 24 h exposure to A) synthetic fresh water and B) artificial landfill leachate.

commercial wound dressing. Knowing the amount of silver released under different environmental scenarios is necessary to determine the environmental impacts of commercial AgNM-containing textiles.

To examine more realistic use and disposal scenarios, the commercial wound dressing will be exposed to model human exposure media (e.g. synthetic sweat or simulated wound fluid) followed by model environmental exposure media. This will allow for more relevant data to be collected and for a more informed understanding of the physical and chemical transformations that occur to AgNM-containing textiles during their lifecycle.

Work here examined the physical and chemical transformations of AgNMs in consumer textiles that result after modeled environmental exposure. Exposure to synthetic freshwater resulted in the formation of chloride and phosphorous containing crystals on the surface of the textile. Additionally, exposure caused the surface to become heterogeneous, with some areas of the textile showing greater granularity than others. Exposure to artificial landfill leachate resulted in increased granularity of the commercial wound dressing compared to the pristine material. Future work will examine more realistic scenarios where the commercial AgNM-containing wound dressing is first exposed to model human exposure media (e.g. synthetic sweat or simulated wound fluid) before model environmental exposure. Data from this work will allow for a greater understanding of the transformations that will occur after disposal for AgNM-containing consumer textiles.

5 ACKNOWLEDGEMENTS

DE Gorka acknowledges funding and support from the National Academy of Science – National Research Council Postdoctoral Research Associateship Program.

REFERENCES

- [1] C. Marambio-Jones, E.M.V. Hoek, A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment, *Journal of Nanoparticle Research* 12(5) (2010) 1531-1551.
- [2] P.L. Taylor, O. Omotoso, J.B. Wiskel, D. Mitlin, R.E. Burrell, Impact of heat on nanocrystalline silver dressings. Part II: Physical properties, *Biomaterials* 26(35) (2005) 7230-40.
- [3] R.J. Courtemanche, N.S. Taylor, D.J. Courtemanche, Initiating silver recycling efforts: Quantifying Ag from used burn dressings, *Environmental Technology & Innovation* 4 (2015) 29-35.
- [4] C.L. Arnaout, C.K. Gunsch, Impacts of silver nanoparticle coating on the nitrification potential of *Nitrosomonas europaea*, *Environmental Science & Technology* 46(10) (2012) 5387-95.

[5] Y. Yang, M. Xu, J.D. Wall, Z. Hu, Nanosilver impact on methanogenesis and biogas production from municipal solid waste, *Waste Manag* 32(5) (2012) 816-25.

[6] U.S.E.P. Agency, METHOD 1311 TOXICITY CHARACTERISTIC LEACHING PROCEDURE, in: E.P. Agency (Ed.) 1992, p. 35.

[7] U.S.E.P. Agency, Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms, Environmental Monitoring Systems Laboratory, Office of Research and Development, US Environmental Protection Agency, 1991.

[8] L.S. Dorobantu, G.G. Goss, R.E. Burrell, Effect of light on physicochemical and biological properties of nanocrystalline silver dressings, *RSC Advances* 5(19) (2015) 14294-14304.