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Synthesis of nanosilver on polyamide fabric using silver/ammonia complex

Majid Montazer [a,*], Ali Shamei [b], Farbod Alimohammadi [b]

[a] Textile Department, Functional Fibrous Structures & Environmental Enhancement (FFSEE), Amirkabir University of Technology, Hafez Avenue, Tehran, Iran
[b] Young Researchers Club, Tehran South Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

In this paper, a novel synthesis method for nanosilver has been introduced on or within the polymeric chains of polyamide 6 fabric by using silver/ammonia complex $[Ag(NH_3)_2]^+$. The silver complex was reduced directly by functional groups of polyamide chains without using any additional chemical reducing agents. The polyamide fabric was also stabilized with formation of new linkages between the polymeric chains of the nylon fabric through silver nanoparticle synthesis. The presence of nanosilver on the fabric was confirmed by UV–vis spectra, EDX patterns and XRD patterns. In addition, X-ray photoelectron spectroscopy (XPS) was utilized to identify the chemical state of silver in a range of silver oxide and silver metal. The SEM images confirmed the presence of nanosilver on the polyamide within the size of 20 and 150 nm. Excellent antibacterial properties were achieved with the treated fabrics against *Staphylococcus aureus* and *Escherichia coli*. Further, the antibacterial properties of the polyamide fabric treated with 35 mg/L silver/ammonia were durable against washing as they only decreased to 98.6% after 20 washes. In addition, some other properties of the treated fabrics including color changes, dimensional stability, water droplet adsorption, and reflectance spectrum are reported and thoroughly discussed.

1. Introduction

Silver nanoparticles are considered to be the most widely used nanoparticles in the textile industries as antibacterial. Their application increases in protective wear for medical and military personnel to reduce infection in wound dressings [1–4]. Ag ions and Ag based compounds are highly toxic to microorganisms with strong biocide effects on various species of bacteria such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *Klebsiella mobilis* [5,6]. Silver as a non-poisonous material in low concentration with antimicrobial properties can be used in different textile fabrics [7–11]. However, few studies have been published regarding the reaction of silver nanoparticles on the human body and the possible effect of incompatibility, dispersion, accumulation in body organs and their toxicity on the body and their release to the environment requires the assessment of environmental risks associated with these particles [12,13].

Silver nanoparticles are among the most commercialized nanoparticles worldwide and clinical compounds include the treatment of external infections or in medical appliances. Wound sutures, artificial tendons and medical packaging, which are prepared by polyamides, preferably should possess an antimicrobial efficacy to minimize the risk of device related infections. Besides, silver particles can be used as an additive or coating material for the preparation of antimicrobial polymers [14].

There are several synthesis methods introduced for the production of silver/polyamide composites or polyamide fibers containing silver nanoparticles. The preparation of polyamide/Ag nanocomposite is reported via thermal reduction of silver acetate through melting [14]. Also, syntheses of silver nanoparticles have been introduced using silver nitrate, ethylene glycol and poly(N-vinylpyrrolidone) (PVP) by electrospinning [15]. In addition, silver nanoparticles are synthesized on different fabrics including polyamide through the sonochemical method in water with ethylene glycol as a reducing agent [16–18]. In this process, a strong adhesion, and a uniform coating of silver nanoparticles on the fibers are confirmed using ultrasound irradiation [18].

Most of the reported studies on the synthesis of silver nanoparticles are based on using reducing and stabilizing agents on the textile fabrics. However, the current work is aimed to synthesize silver nanoparticles on polyamide fabric without using any reducing and/or stabilizing agents. This process was carried out in water at boil using the inherently reducing and the stabilizing properties of polyamide chains of the nylon fabric. The swelling of fabric at the boil induced Ag ions to penetrate into the intramolecular chains, and reduced the silver/ammonia complex to silver nanoparticles also oxidized the polyamide molecular chains.

* Corresponding author at: Textile Department, Functional Fibrous Structures & Environmental Enhancement (FFSEE), Amirkabir University of Technology, Hafez Avenue, Tehran, Iran. Tel.: +98 21 65542657; fax: +98 21 66400245.
E-mail address: tex5mm@aut.ac.ir (M. Montazer).

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2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$) 99.9%, sodium hydroxide (NaOH), ammonium solution 25%, Tryptic soy agar (TSA), and sodium chloride (NaCl) 99.9% were from Merck Co. (Germany), and polyamide 6 (nylon 6) knitted fabric with 85 g/m^2 was purchased from the local market. Also, deionized water was used in the synthesis processing. The samples were washed in a bath containing a 2 g/L nonionic detergent with L:G (liquor to good ratio) = 50:1 at 50 °C for 15 min. Next, it was rinsed with distilled water.

2.2. Instrumentation

X-ray photoelectron spectroscopy (XPS) via Twin Anode of XR3E2 (model 8025-BesTec) was applied to determine the chemical state of both silver and oxygen, and a Philips X-ray Diffraction (model X'Pert PRO MPD) was used to assess the crystallinity of the silver nanoparticles on the polyamide fabrics, the active data plot was smoothed by the average adjacent data points via OriginPro data analysis and graphing software. The SEM images were taken using a scanning electronic microscopy model XL30 from Philips Co. A spectrophotometer Varian Carry 5000 was employed to obtain the reflectance spectrum of the treated fabric. The color coordinates (L^*, a^*, and b^*) of CIELAB color system were obtained using a Color eye 7000 calorimeter with observer 10°, and illuminant D65.

2.3. Synthesis of silver nanoparticles on the polyamide knitted fabric

The mixture of silver nitrate solution (0.5 M) and NaOH (0.5 M) was sonicated in an ultrasonic bath for 5 min, resulting in brown Ag_2O powder precipitation (Eq. (1)). Next, the precipitate was washed with deionised water for 3 times and then dried. It was subsequently mixed with 2% ammonia, molar ratio of 4:1, forming a stable aqueous solution complex $[Ag(NH_3)_2]^+$ (Eq. (2)) [17,19,20]. The precautions were made for disposal of dilute acid to prevent formation of the explosive silver nitride [21].

$$2Ag^+ + 2NO_3^- + 2Na^+ + 2OH^- \rightarrow Ag_2O\downarrow + 2NaNO_3 + H_2O \quad (1)$$

$$Ag_2O + NH_3 \cdot H_2O \xrightarrow{Sonication} [Ag(NH_3)_2]^+. \quad (2)$$

The polyamide fabric was then treated with three diverse concentrations of Ag_2O including 10 mg/L, 25 mg/L, and 35 mg/L and required ammonia in L:G = 20:1 at room temperature. The temperature was increased to boil with 4 °C/min for 30 min. The color of the treated fabric changed from white to light yellow. However, the color changes were much more intense on the fabric loaded with more silver nanoparticles. Subsequently, the treated fabrics were extracted from the bath, washed and dried at the room temperature.

2.4. Washing fastness of polyamide fabric treated by Ag-NPs

The washing fastness was conducted according to AATCC 61(2A)-1996 test method as each washing is equivalent to five launderings at medium or warm setting in 38 ± 3 °C. This test is used to investigate the stability of nanoparticles on the surface of the polyamide through antibacterial tests after 10, 20 and 30 washes.

2.5. Color changes of polyamide fabric treated by silver nanoparticles

Three coordinates (L^*, a^*, and b^*) of CIELAB color system were obtained using a Color eye 7000 [22]. The overall color differences between the untreated and treated samples are designated by the term ΔE which was calculated based on Eq. (3) [22–24]:

$$\Delta E = \sqrt{(L_o^* - L^*)^2 + (a_o^* - a^*)^2 + (b_o^* - b^*)^2}. \quad (3)$$

In this system, L^* shows the lightness of the fabric and a^* and b^* indicate red–green (redder if positive; greener if negative) and yellow–blue colors (yellower if positive; bluer if negative), respectively.

2.6. Dimensional stability measurement

AATCC test method 179-2004 was used to specify the deformation level of the knitted fabric after washing. A square with a side of 25 cm was marked on the fabric sample and its diameters were then measured after washing. AATCC test method 124-2006 was used for washing. Finally, the deformation level was obtained from the difference in the length of diameters using Eq. (4).

$$X = 100 \times \left[\frac{2(AC - BD)}{(AC + BD)}\right] \quad (4)$$

where, X is the deformation change percentage.

In most garments, the acceptable shrinkage level after washing is 2–3%. However, the type of fiber, fabric structure and final end-use influence the acceptable shrinkage level. The allowed shrinkage level for knitted fabrics is usually higher than that of woven fabrics and maximum shrinkage is up to 5% [25].

2.7. Water droplet adsorption time

This test (BS 4554) is considered for the fabrics containing hydrophilic fibers. The necessary time by seconds taken for a water droplet or water sugar solution to be adsorbed up to 50% in the fabric is defined as wettability.

In this test, the sample is closed and leveled in a frame to a diameter of 15 cm. A burette with a standard tip is placed above the horizontal level of the sample with a 6 mm interval. A light source is placed in a 45° and the vision angle is placed in a 45° direction to the light source. Once no liquid is seen on the surface, the time is recorded. Three samples are tested in 5 areas and the mean value was reported [25,26].

2.8. Antimicrobial testing on treated polyamide fabrics

Staphylococcus aureus, ATCC 6538, as Gram-positive bacteria and *E. coli*, ATCC 11303, as Gram-negative bacteria were tested. Some colonies of each bacterium were suspended in a physiologic saline solution (NaCl 0.9% in distilled water at pH 6.5) with a concentration of 0.5 McFarland. The vials of bacterial suspensions were then incubated with agitation at 37 °C ± 2 °C, 220 rpm for 2 h. A homogenous suspension of bacteria was prepared. Then, a serial dilution was prepared in 5 steps (dilution of 1:100000) and a concentration of about 1.5–2 × 10^3 CFU/mL was used for the antibacterial testing. The bacteriological culture tubes containing one piece of polyamide fabric (10 mm × 10 mm) were sterilized by an autoclave device in moisturized heat (121 °C, 15 lb) for 15–20 min. Subsequently, an aliquot of 1 mL bacterial suspension and 2 mL TSB broth was added to each tube and 3 mL in each tube was detected. To ensure that any decrease in bacterial count was due to the exposure to the polyamide fabrics, one control of the saline solution with TSB broth, and one control of aliquot with the untreated fabrics including the tubes containing the polyamide fabrics treated with the bacterial suspensions and the control tubes were incubated at 37 °C for 24 h. Next, some samples of 10 μL from each tube were taken and counted by pour plate method. In this method, samples are mixed with melted agar (that decreases temperature to 45 °C) and poured. The plates were incubated at 37 °C for 24 h and the colonies of