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A study on multifunctional wool textiles treated with nano-sized silver

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Abstract We treated wool textiles with a sulfur nano-silver colloidal solution (SNSE) having Ag/S complex, which was a particle size of average 4.2 nm in ethanol base. The SNSE was a safe chemical agent having the perfect antibacterial efficacy with a very small amount of nano-sized silver and non-irritative solution to the skin. Antibacterial activity was evaluated by calculation of bacteria reduction against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Klebsiella pneumoniae*) bacteria. The treated wool textiles with the silver colloid were investigated the resistivity against insect pests through both calculation of the fiber loss weight and visible assessment attacked by larvae after 14 days in given conditions. Also, we confirmed the antistatic efficacy of the finished fabrics with silver particle on their surface. The static electricity of the treated wool fabric was increased more up to 50 ppm, then, it was decreased according to the silver content. Consequently, it was demonstrated that the finished wool fabrics with sulfur nano-silver colloid had various functionalities, such as mothproofing, antibiotic, and antistatic property.

Introduction

During rapid developments of technology in the textile industry in recent years, many researchers of worldwide have been vigorously investigated to functional textiles, because the functional textiles have long been recognized as the important characteristic in the textile industry [1]. However, a demand for end-use textile field such as antibacterial, antistatic, mothproofing, stain resistant, and others cannot be achieved by simple one-step processing [2, 3]. Particularly, it has been increased the interest in human living environment, then turn out various antibacterial textiles products.

Under proper temperature and humidity, wool textiles will be good media for generation and propagation of microorganisms [4, 5]. The microorganisms can be resulted in damages, skin irritations, and infections in wool products [6]. For these reasons, the wool materials of the high-grade clothes must be protected against microorganisms in order to suppress their growth and dissemination as well as fiber damage. Silver is one of non-toxic and safe antibacterial agents to the human body, and can kill many harmful microorganisms [7, 8]. The mechanism of antibacterial action of silver ions is closely related to their interaction with proteins, particularly at thiol (sulfydryl, –SH) groups, and are believed to bind protein molecules together by forming bridges along them. Since the proteins behavior often like as enzymes, the cellular metabolism is inhibited and the microorganism dies [9, 10]. When certain particles are very small size, nano size, the number of particles may be increased in unit area. The total surface area of the nano-sized silver particles is larger than that of large-sized silver in identity volume then antibacterial ability of the former is more effective than the latter [11–14].

The purpose of this research is to study the characterization of novel nano-silver colloid and its application for wool textiles. The wool textiles were prepared by a general padding method with the diluted SNSE colloidal solution. The wool textiles having nano-sized silver were investigated by means of their antibacterial, mothproofing, and electrical properties and surface observation with nano-particles.

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Experimental

Materials

The new nano-silver colloid (SNSE, Sulfur nano-silver ethanol based colloid) was supplied from NP-Tech Co., Ltd., Korea for this study. The SNSE was manufactured by a common wet chemical reduction method [15]. The SNSE was a new type of nano-silver colloid including a few sulfur compounds on nano-sized silver particles. Wool samples used in this study were a merino type and the length was 18–30 μm. All of the wool samples were provided from Suh Han Wool Textile Co., Ltd., Korea.

Finishing process

Before the finishing process, untreated wool fibers were cleaned with dichloromethane (40 °C, 30 min), rinsed with ethanol and water twice (25 °C, 10 min), and equilibrated in a conditioned room (20 °C, 60% RH). The fibers were treated with nano-silver colloid by a conventional pad-dry-cure (PDC) method. The silver concentrations on the surface were varied 5, 10, 20, and 30 ppm of the nano-sized silver particles depending on the pick-up ratio. The specimens were immersed in a fresh colloidal bath for 10 min and squeezed using a laboratory padder at the constant pressure. The samples were dried at room temperature for prevention of thermo-migration of metal particles for 30 min, and then the curing process of samples was performed at 120 °C, for 5 min. Worsted yarn and woven fabric used in the experiments were manufactured by the treated wool fiber using the diluted SNSE colloid of 20 ppm silver concentration. Wool knitted fabric was manufactured by the fiber, which dyed with a black acid dye followed by the treatment with the nano-sized silver particles. Wool/acryl blended fiber (50/50 in weight) was made up wool fibers treated with silver particles and untreated acryl fibers.

Measurements

Antibacterial test of treated wool textiles

The antibacterial properties of wool specimens were quantitatively evaluated against *Staphylococcus aureus* (*S. aureus*), ATCC 6538, a Gram-positive bacterium and *Klebsiella pneumoniae* (*K. pneumoniae*), ATCC 4352, a Gram-negative bacterium, according to the test method AATCC 100-1999. The test specimens were placed on germ containing agar plates, inoculated with *S. aureus*, and *K. pneumoniae*, and then incubated in an agar media. The prepared sample diameter was 4.8 ± 0.1 cm. Inoculum concentration was $1.3–1.6 \times 10^5$/ml. About 0.5% of non-ionic agent (Tween 20) was used to wet the wool samples with inoculum solution.

Bacteriostatic acitivity of wool textiles used in study was evaluated after certain contact time and calculated percent reduction of bacteria. Using the following equation:

$$R(\%) = \frac{A - B}{A} \times 100$$

where R is the bacterial reduction ratio, A is the number of bacterial colonies from untreated fabrics, and B is the numbers of bacterial colonies form treated fabrics.

Mothproofing test

For the determination of the resistance to the larvae of certain insect, mothproofing test was conducted on the wool fibers according to assessment of the visible damage and fiber weight loss procedure established by the International Standardization Organization 3998-1977. The untreated specimens were treated with 20 ppm silver particles on wool fiber surface using the SNSE colloid. Larvae in this experiment were *Tinea pellionella*, a type of moth. Conditioned voracity control specimens without silver and test specimens with silver of known mass were placed in contact with selected larvae for a period of 14 days. The loss in mass of all specimens, the extent of the attack on the test specimens and the condition of the test larvae were ascertained to assess the resistance. The loss in mass of each test specimen and voracity control, due to insect feeding, as following:

$$\Delta m = \frac{m_0 \times m_3}{m_2} - m_1$$

where, m_0 is the mass of the test specimen or control before exposure to larvae, m_1 is the mass of the test specimen or control after exposure to larvae, m_2 is the mean initial mass of appropriate moisture regain controls, and m_3 is the mean final mass of appropriate moisture regain controls. The visible damage of wool fiber was assessed the visible damage using the symbols given in Table 1. The larval conditions were confirmed by counting the number of larvae in live, dead, and pupating condition.

Electrostatic test

The electrostatic propensity of prepared samples was conducted in compliance with the test method KS K 0555-1996 for woven or knitted fabrics. Wool woven standard fabrics were settled with the nano-sized silver using the SNSE, which were diluted for 50, 100, 150, 200, 250, 300, 400, and 500 ppm of silver concentration on the wool fiber surfaces. The wool specimens were dried at room

Table 1 Visual assessment of mothproofness

Symbol	Cropping: Visible surface damage
1	No detectable damage
2	Very slight visible cropping
3	Moderate cropping
4	Very heavy cropping
Symbol	Estimation of holes
A	No detectable damage
B	Yarn or fiber partially severed
C	A few small holes: yarn or fiber severed
D	Several large holes

temperature, thereafter cured at 120 °C by passing through the mangle machine. The electrostatic voltages of wool fabric having the silver nano-particles were measured after rubbing with the specimens for 60 s at a rated of 400 rpm with a rotary static tester (Kyodai Kaken type Koa Shokai Co., Ltd., Kyoto). These experiments were done in a room kept at 20 ± 2°C and 40 ± 2% RH.

Result and discussion

SEM analysis

The surface of treated wool fabrics were observed by SEM. In Fig. 1, SEM images show on wool scales that were treated with 100 ppm of silver contents. The nano-silver particles bigger than 4.2 nm of particles in SNSE solution were observed in Fig. 1b. The agglomerated particles may attributable to the thermo-migration of the nano-sized silvers happened during curing process.

Antibacterial properties of treated wool with SNSE

The wool fibers were finished by 5, 10, 20, and 30 ppm of nano-sized silver particles with SNSE. These wool fibers were revealed to have an excellent antibacterial activity, as shown in Table 2. The antibacterial efficiency against *S. aureus* was consistent regardless of the silver contents. Against *K. pneumoniae*, the treatments by 5 ppm and 10 ppm showed 99.70% of bacterial reduction, which were comparatively lower than that by 20 ppm and 30 ppm treatments. The treated wool using SNSE showed the distinguished germicidal power against two bacteria. In the sequential test, the samples of undyed spun yarns, dyed woven and knitted fabrics, and dyed wool/acryl blends were used. These were manufactured by wool fiber treated with nano-sized silver 20 ppm on the scale. Among four types of sample, the woven fabric showed excellent activity on both bacteria. In particular, wool/acryl knit that was blended with untreated acryl fiber exhibited similar anti-bacterial efficacy (see Table 3).

Mothproofing property of treated wool with SNSE

The results of mothproofing tests with wool are shown in Table 4. The wool samples were processed by the SNSE

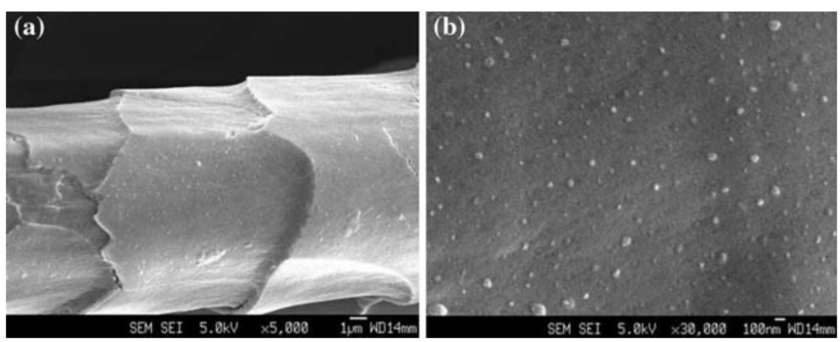

Fig. 1 Surface images of wool fiber having 100 ppm silver particles with sulfur nano-silver colloid; (**a**) 5,000 magnifications (**b**) 30,000 magnifications

Table 2 Assessment of antibacterial finishes on treated wool fiber with SNSE varying nano-sized silver contents

Bacteria		Silver concentration (ppm)				
		0	5	10	20	30
Staphylococcus aureus (CFU/mL)	Start	1.3×10^5	1.3×10^5	1.3×10^5	1.3×10^5	1.3×10^5
	After 24 h	3.6×10^7	<10	<10	<10	<10
	% reduction	–	99.99	99.99	99.99	99.99
Klebsiella pneumoniae (CFU/mL)	Start	1.4×10^5	1.4×10^5	1.4×10^5	1.4×10^5	1.4×10^5
	After 24 h	4.3×10^7	1.3×10^5	1.3×10^5	<10	<10
	% reduction	–	99.70	99.70	99.99	99.99

Table 3 Antibacterial assessment of wool textiles made of the wool fibers treated with 20 ppm silver particles on fiber surfaces

Bacteria		Sample type				
		Control	Yarn	Woven	Knitted	W/A knitted[a]
Staphylococcus aureus (CFU/mL)	Start	1.3×10^5	1.3×10^5	1.3×10^5	1.3×10^5	1.3×10^5
	After 24 h	6.0×10^5	1.2×10^4	<10	<10	1.2×10^4
	% reduction	–	98.00	99.9	99.9	98.00
Klebsiella pneumoniae (CFU/mL)	Start	1.6×10^5	1.6×10^5	1.6×10^5	1.6×10^5	1.6×10^5
	After 24 h	7.2×10^5	1.4×10^4	<10	1.4×10^4	1.4×10^4
	% reduction	–	98.06	99.99	98.06	98.06

[a] W/A knitted: 50% the wool fibers having 20 ppm silver + 50% the pure acryl fibers

Table 4 Resistance assessment to insect on treated wool fiber with 20 ppm silver particles on fiber surfaces

Sample	Loss weight (mg)	Average weight loss (mg)	Larvae condition		Grade
			Live	Pupation	
Control	40.06	40.54	15	0	–
	42.16		15	0	–
	39.57		15	0	–
	40.36		15	0	–
Specimen	2.28	6.32	0	0	2A
	1.94		0	0	2A
	10.93		1	0	3D
	10.11		0	0	3C

solution on the fiber surface of 20 ppm of silver nanoparticles. Larvae used in this study were an inhabitant moth of *Tinea pellionella* in the clothes. Fifteen larvae composed of test and voracity control specimens and test and specimens for moisture regain placed with wool specimens of known mass in covered container for a period. After 14 days, the larvae of control were all live without any pupation. On the other hand, the live larvae of test specimen were only one without any pupation in the container. The average loss in mass of voracity control of wool fiber due to insect feeding was 40.54 mg but that of treated wool on surface having silver particles was considerably reduced weight of 6.32 mg. The visible surface damage and estimation of holes were assessed with relatively good attack level as the results given in Table 1. The assessed grades of visible damaged were good levels relatively. We concluded that nano-silver colloid finishing had a high effectiveness on wool materials in mothproofing activity.

Electrostatic property of treated wool fabrics

Silver as a metal is an outstanding conducting material of electrical conductivity. We investigated the removal effect for static electricity by means of silver particles in SNSE. The wool fabric specimens were prepared by treatment of the diluted solution. The concentrations of silver particle on wool surface were varied from 50 ppm to 500 ppm. Figure 2 shows relative static electricity on wool fabrics measured by rotary static tester according with silver

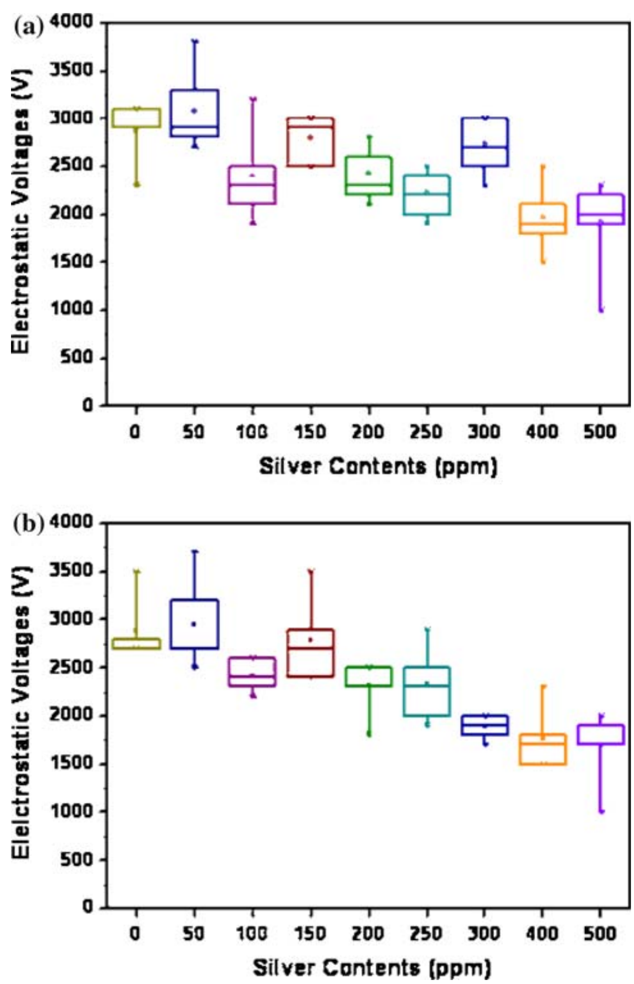

Fig. 2 Electrostatic voltages of the treated wool surface with sulfur nano-silver colloid varying silver contents; (**a**) against warp direction (**b**) against weft direction

contents. Electrostatic voltages of vertical axis were measured after rubbing with sample for 60 s at a 400 rpm and were recorded by oscilloscope. The values were initially increased to 50 ppm of silver content. This phenomenon was estimated that static electricity was generated due to small amounts for alteration of free electron. In Fig. 2b, similar tendency was observed like as that of warp direction, which the degree of electrification increased initially with decreasing of silver contents.

Conclusions

The sulfur nano-silver colloidal solution (SNSE) had perfect antibacterial efficacy with very small amount of the nano-sized silver against *S. aureus* and *K. pueumoniae.* Antibacterial efficacy on wool fibers was easily achieved by the conventional pad-dry-cure method using the nano-sized silver colloid including sulfur compound. The manufactured wool textiles using the treated fibers with the silver particle were showed as excellent antibacterial products. Insect resistance on the wool fibers was appeared to quantitative evaluation of average weight loss and qualitative evaluation of visual assessment of fibers. The weight loss of treated wool with silver 20 ppm significantly decreased compared with untreated fibers. The visual assessment of treated wool fiber was on the whole excellent. For anti-static propensity of wool fabric having silver particles, frictional electrostatic voltages of samples were measured varying the silver contents. The static electricity was slightly increased at 50 ppm silver, but it was deceased with increasing silver contents. The anti-static effect was displayed by treatment with SNSE in high concentration of silver on the wool fabric surfaces.

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