Properties and Antimicrobial Efficacy of Cellulose Fiber Coated with Silver Nanoparticles and 3-Mercaptopropyltrimethoxysilane (3-MPTMS)

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ABSTRACT: Silver nanoparticles were coated onto cotton fabrics with 3-mercaptopropyltrimethoxysilane (3-MPTMS). The coating process was accomplished by soaking the cotton fabrics into silver colloid/3-MPTMS solution at 43°C for 90 min. The coated fabrics were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). SEM images showed a layer of silver nanoparticles and 3-MPTMS on cotton. The XPS data showed that distinguishable binding energy peaks of Ag 3d, Si 2p, Si 2s, S 2p were 368/374, 102, 153, and 162 eV, respectively, which confirms the existence of silver and 3-MPTMS on cotton fabrics. The treated cotton fabrics showed prominent antimicrobial effectiveness against *Staphylococcus aureus* (ATCC 6538) and *Klebsiella pneumonia* (ATCC 4352). Furthermore, the laundry test showed that 66% of silver nanoparticles were retained after five washing cycles. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2261–2267, 2011

Key words: coatings; colloids; polysiloxanes

INTRODUCTION

Numerous antimicrobial compounds are employed against bacteria. In general, quaternary ammonium compounds,[1–3] chitosan,[4–6] photocatalyst,[7,8] *N*-halamine materials,[9–11] and metal, especially silver nanoparticles are being used as antimicrobial compounds for textiles. Among these, currently, silver nanoparticles have been extensively researched due to their extremely large surface area, which can provide better contact with microorganisms.[12–15] In terms of mechanism of action, bacterial membrane possesses sulfur-containing proteins and silver nanoparticles connect with these proteins in the cell, silver nanoparticles combine with the cell membrane and penetrate inside the bacteria. After entering the bacterial cell, silver nanoparticles react with the respiratory chain of bacteria. Silver consequently inhibits the respiration process. In addition, silver nanoparticles release silver ions in the bacterial cell, which increase their antimicrobial efficacy.[12,16–19] Furthermore, the antimicrobial activities of silver nanoparticles have a relationship with surface area of the nanoparticles. Relatively smaller particles which have a larger surface area were more effective in the antimicrobial test.[12,20]

Silver nanoparticles for textile applications also have been studied in diverse areas. Polypropylene fibers were prepared with 30-nm silver nanoparticles in only the sheath-part (outside of the fiber), and provided sufficient antibacterial effects.[21,22] A padding process on cotton and polyester with silver nanoparticles (2 to 5 nm size) resulted in antibacterial effectiveness.[23] Silver nanoparticles were incorporated in cotton fabrics and the treated cotton fabrics inactivated *S. aureus* (Gram-positive bacteria) significantly.[14] Similar treatment of cotton fabrics with colloidal silver nanoparticles showed excellent inactivation against *E. coli* (Gram-negative bacteria), *S. aureus*, and *C. albicans* (Fungus).[15]

Cellulose fibers including cotton are an ideal substrate for the growth of microorganisms due to their hydrophilic properties. Interestingly hydroxyl groups on cellulose fibers which provide hydrophilicity, may help to render cellulose fibers antimicrobial when used with some reactive antimicrobial precursors.[10,24] However, little research regarding antimicrobial applications of silver nanoparticles on cotton fibers has employed a bonding agent to connect silver nanoparticles on cellulose. In general, pad-dry-cure process of silver nanoparticles has been used for cotton fibers.[14,15,25] In this study, 3-MPTMS containing thiol groups and siloxane groups which can react with silver nanoparticles and cotton,

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respectively, was used to attach silver nanoparticles onto cotton fabrics. Morphological change, thermal properties, washing fastness, and antimicrobial efficacy against *S. aureus* and *K. pneumoinae* were discussed.

EXPERIMENTAL

Materials

The 3-mercaptopropyltrimethoxysilane (3-MPTMS, 95%) was purchased from Aldrich. Silver colloid (Ag content: 5000 ppm, pH: 9.0 ± 0.5) was obtained from Miji Nanotech (Korea). Isopropanol (95%) was purchased from Duksan chemicals (Korea). All chemicals were used as received without further purification. Desized and bleached cotton fabric (KS K 0905-2008 rule) was obtained from Korea Apparel Testing and Research Institute.

Coating of cotton fabrics with silver nanoparticles and 3-MPTMS

A 0.1 mL of 3-MPTMS was added in 10 mL of isopropanol. Concurrently 2 mL of silver colloid was added in the 3-MPTMS and isopropanol solution to prepare an 830 ppm of silver colloid solution. Cotton fabric (5 cm × 5 cm) was soaked in the solution followed by shaking in a water bath at 43°C for 90 min. The treated samples were rinsed with 100 mL of propanol two times and then rinsed again with 100 mL of distilled water two times. Finally, the samples were air dried at ambient temperature.

Characterization

Transmission electron microscopy (TEM)

TEM was carried out with a Hitachi H-7600 at 120-kV accelerating voltage to observe the size of silver nanoparticles in silver colloid. The point-to-point resolution capable of 0.32 nm was employed.

Scanning electron microscopy (SEM)-Energy dispersive spectroscopy (EDS)

SEM-EDS was conducted with a Hitachi *S*-4100 for SEM at 15-kV accelerating voltage and Horiba EX-250 for EDS. Samples were coated with platinum by sputtering before examination.

X-ray photoelectron spectroscopy (XPS)

XPS spectra were determined using a ULVAC-PHI Quantera SXM. Monochromate Al was used as an X-ray source. Beam size, beam power, electron source, and pass energy were 100 μm, 100 W, 18 kV, and 26 eV, respectively.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was employed to inspect heat-stability of each film using a TGA 2950 (TA instruments). TGA was performed from 30 to 600°C at a heating rate of 20°C/min under nitrogen purge.

Laundering test

The ISO test method 105-C01:1989 was used to investigate the stability of silver nanoparticles on the cotton fabrics coated with 3-MPTMS. The concentration of detergent and washing temperature were 5 g/L and 40°C ± 2°C, respectively. The washing cycle was 30 min and five washing cycles were run.

Antimicrobial test

Cotton fabrics treated with 3-MPTMS only and treated with Silver nanoparticles/3-MPTMS were challenged with *Staphylococcus aureus* (ATCC 6538) and *Klebsiella pneumonia* (ATCC 4352), and total bacteria were 1.3×10^5 and 1.5×10^5 cfu/mL, respectively. To improve wetability between bacterial suspensions and samples, nonionic surfactant (Tween 80, 0.05%) was added. Bacterial suspensions (0.2 mL) were added to samples (0.4 g). The samples were incubated at 37°C for 18 h. After incubation, the samples were quenched with 20 mL of sterile 0.5% sodium chloride solution. The quenched samples were diluted using 0.5% sodium chloride solution and plated on Typticase soy agar. The plates were incubated at 37°C for 24 h, and the number of bacteria was counted to determine the presence or absence of viable bacteria.

RESULTS AND DISCUSSION

Characterization of cotton fabric coated with silver nanoparticles

The size of silver nanoparticles in colloid was measured by TEM and the results were shown in Figure 1. The image showed that the particle size of most nanoparticles is less than 5 nm; however, some larger sizes (5 to 10 nm) of silver nanoparticles are observed in the colloid. This may be due to the fact that nanoparticles aggregate in the silver colloid.

The morphological change of the cotton fabric treated with/without 3-MPTMS and silver nanoparticles is shown in Figure 2. The results demonstrate that the cotton treated with silver nanoparticles/3-MPTMS possesses a rough surface even though the control cotton has relatively smooth surface. The EDS spectrum [Fig. 2(b)] can explain that the composition on the surface of treated cotton contains silver and sulfur as well as silane. The

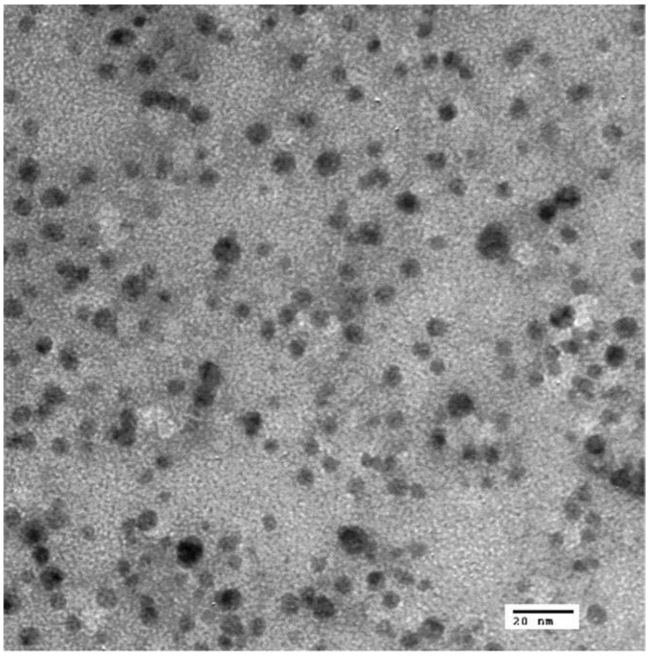

Figure 1 TEM image of silver nanoparticles in the silver colloid solution.

sulfur and silane are consistent with the presence of 3-MPTMS. To ensure the reaction between cotton, 3-MPTMS, and silver nanoparticles, further analysis of the cotton samples using XPS was employed and the broadscan spectra are shown in Figure 3. Specifically, the XPS spectra of Ag 3d region of treated and untreated cotton are depicted in Figure 4. The results show that the binding energy of silver on the treated cotton is $\sim$ 368 and 374 eV.[26] In addition, the XPS spectra of Si 2p and 2s region are demonstrated in Figures 5 and 6, respectively. The binding energy peak of Si 2p and Si 2s of the treated cotton appears around 102 and 153 eV, respectively.[27] The binding energy peak of sulfur can be found in Figure 6(b) and the peak of S 2p is shown at 162 eV.[28] Under EDS and XPS analysis, it is apparent that the silver and 3-MPTMS are combined on the surface of cotton fabrics.

Coating of silver nanoparticles on cotton fabric

The treatment of cotton fabrics under different concentration of silver colloid with/without 3-MPTMS are shown in Table I. The results show that when silver concentrations in the colloid had the values, 830, 2490, 3200, and 3600 ppm, the atomic% of silver on the coated layer of cotton are 0.11, 0.30, 0.28, and 0.29, respectively. The atomic% of silver on cotton fabric was enhanced with increased concentration of silver colloid; however, above 2490 ppm there is no significant increase. In previous research, Lee et al.

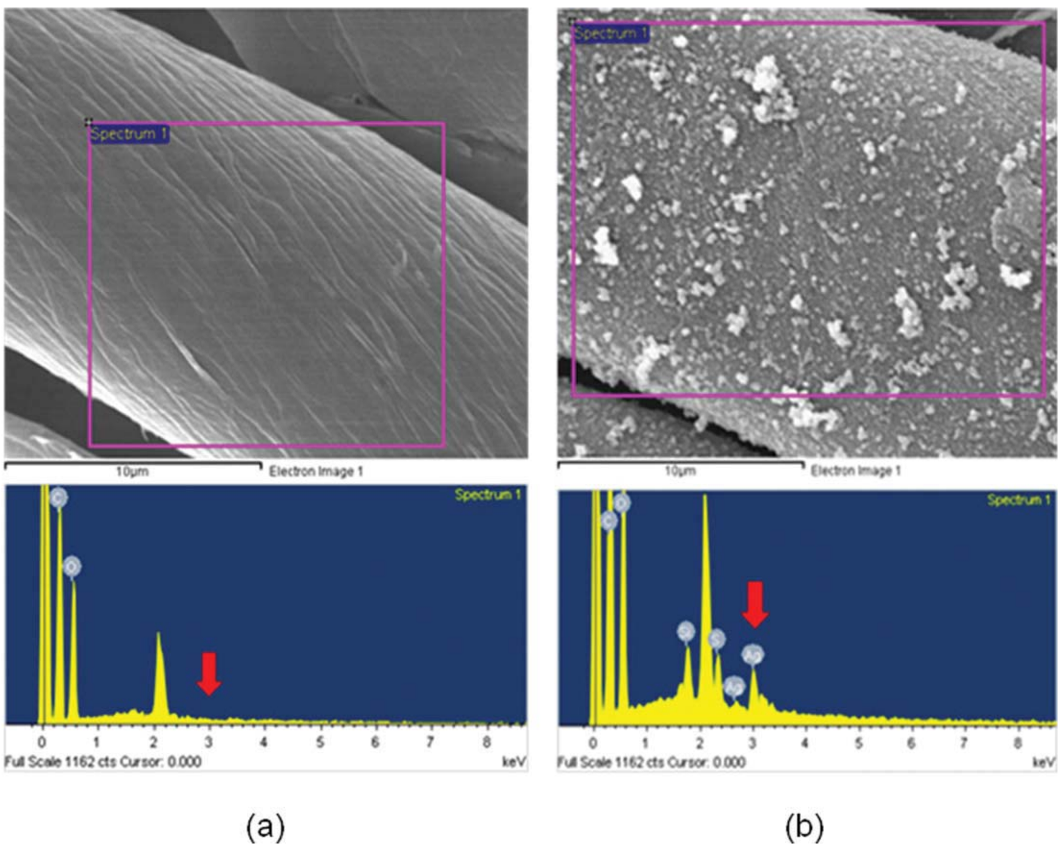

Figure 2 SEM-EDS micrograph of (a) untreated cotton and (b) treated cotton with silver and 3-MPTMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

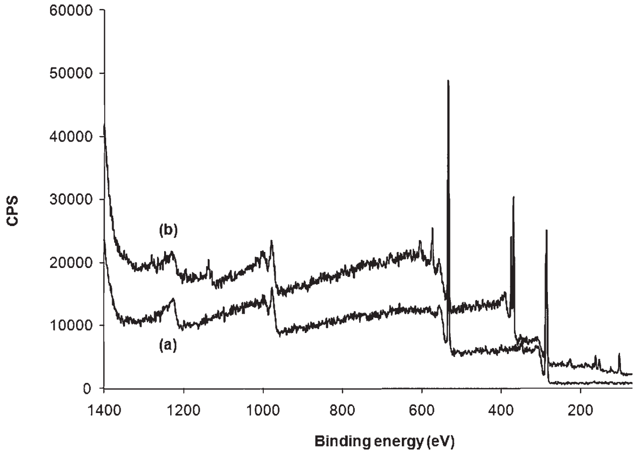

Figure 3 XPS spectra of (a) cotton and (b) silver colloid and 3-MPTMS-treated cotton.

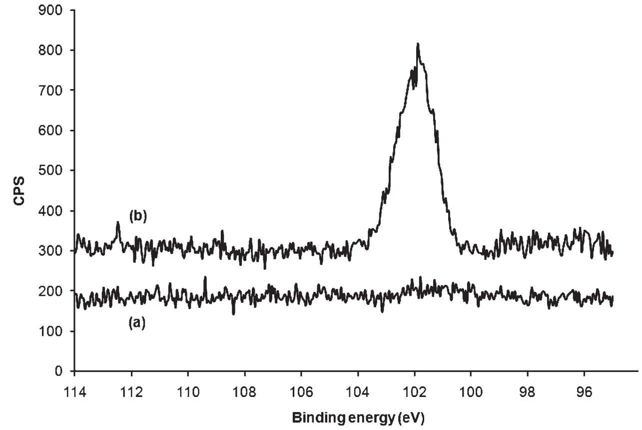

Figure 5 XPS spectra of Si 2p region in (a) untreated cotton and (b) silver colloid and 3-MPTMS-treated cotton.

considered 3-MPTMS as a binding bridge between silver nanoparticles and silica surface.[29] To confirm the role of 3-MPTMS in the reaction, the conditions with/without 3-MPTMS were applied and the results are shown in Table I. Silver colloid treatment without 3-MPTMS, reveals no silver remaining onto cotton fabric. Thus, in terms of attaching silver nanoparticles onto cotton, 3-MPTMS can be one of good binding agents. It is assumed that chemisorption between silver nanoparticles and thiol groups occurred. In addition, hydrolyzed siloxane may react with hydroxyl group in cellulose. The proposed reaction mechanism is demonstrated in Figure 7.

Since relatively lower ambient temperature could result in cost savings, specifically energy, processing temperature during treatment of materials is one of the significant factors for finishing industry. The treatment of 3-MPTMS and silver nanoparticles on cotton under different temperatures are shown in Figure 8. In case of 18°C as a treatment temperature, no silver is detected on cotton surface; however, at 43, 60, and 80°C as processing temperature, 0.31, 0.52, and 0.51 atomic% of silver are detected, respectively. Thus, it is assumed that condensation between siloxane in 3-MPTMS and hydroxyl group in cotton can be affected by temperature (heat) and the condensation could not occur under relatively low temperature, 18°C. When the temperature increased, the reactivity between siloxane and cotton also enhanced until 60°C. Since no further increase in atomic% appeared above 60°C, this temperature is suggested as an optimum temperature for the reaction between 3-MPTMS and cotton. In this research, 43°C was selected as a processing temperature for more energy efficient process and other tests were conducted at this temperature.

Thermal stability of the cotton fabric coated with silver nanoparticles

Thermal stability of untreated and treated cotton using thermogravimetric analysis (TGA) is depicted in Figure 9. The results show that a weight loss

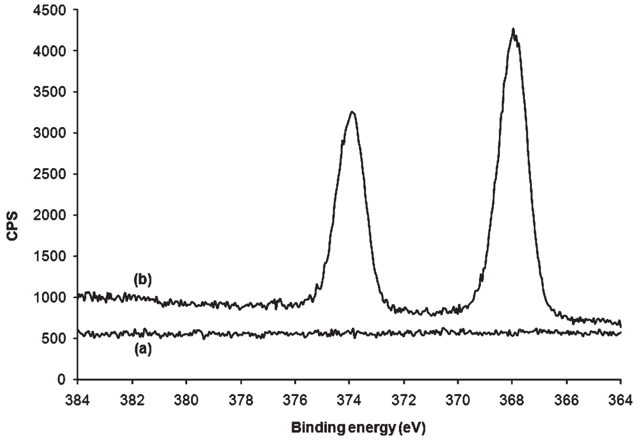

Figure 4 XPS spectra of Ag 3d region in (a) untreated cotton and (b) silver colloid and 3-MPTMS-treated cotton.

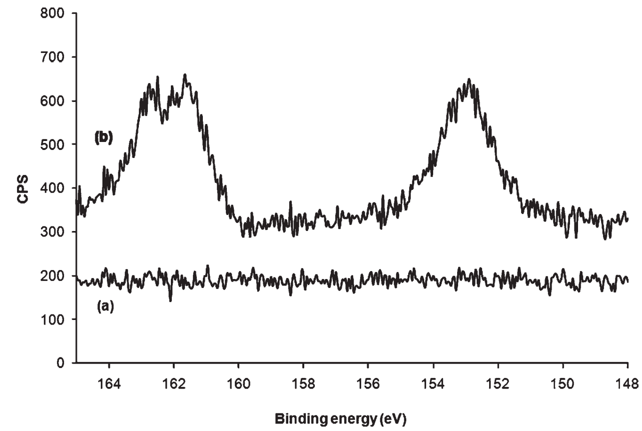

Figure 6 XPS spectra of Si 2s and S 2p region in (a) untreated cotton and (b) silver colloid and 3-MPTMS-treated cotton.

TABLE I
Atomic% of Silver on Cotton Samples Treated with/without 3-MPTMS at 43°C

Concentration of Ag in the solution (ppm)	Atomic % of Ag on treated samples	
	With 3-MPTMS[a]	Without 3-MPTMS
0	Undetected	Undetected
450	0.12	Undetected
830	0.11	Undetected
2490	0.30	Undetected
3200	0.28	Undetected
3600	0.29	Undetected

[a] The amount of 3-MPTMS (95%) was fixed at 0.1 mL.

occurred below 150°C which can be attributed to the evaporation of water on/into cotton fabrics. Untreated and Silver nanoparticles/3-MPTMS treated cotton fabrics reveal 354 and 348°C as an initial decomposition temperature (IDT), respectively. This IDT data is evidence that the treatment of cotton with silver nanoparticles and 3-MPTMS results in somewhat lower heat stability. In different research, cotton fabric also showed reduced IDT after treatment with dodecanethiol-capped silver nanoparticles.[25] After exposure under heat up to 600°C, the residue of the treated cotton remained 12% as compared to 7% for untreated cotton. The weight loss difference may be attributed to silane and silver nanoparticles on the treated sample.

Durability of the treated cotton fabric

In the case of functional finishing of fabrics for diverse applications, durability of functionality against repeated washing is one of major concerns. To investigate washing fastness of treated cotton with silver nanoparticles and 3-MPTMS, a laundry test was employed and results are shown in Table II. After five washing cycles, ~ 66% of silver was retained. This result may not be characterized as

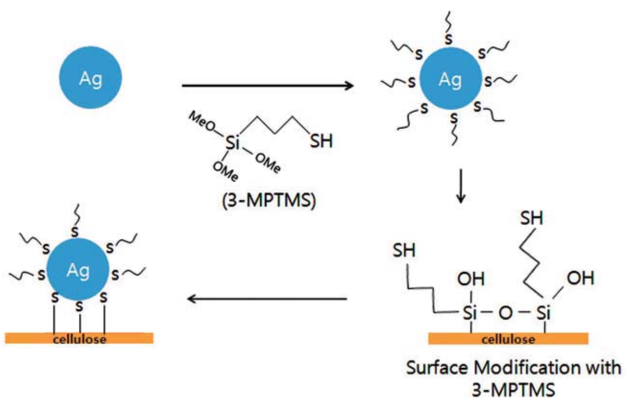

Figure 7 Proposed reaction scheme between silver nanoparticles, 3-MPTMS and cotton. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

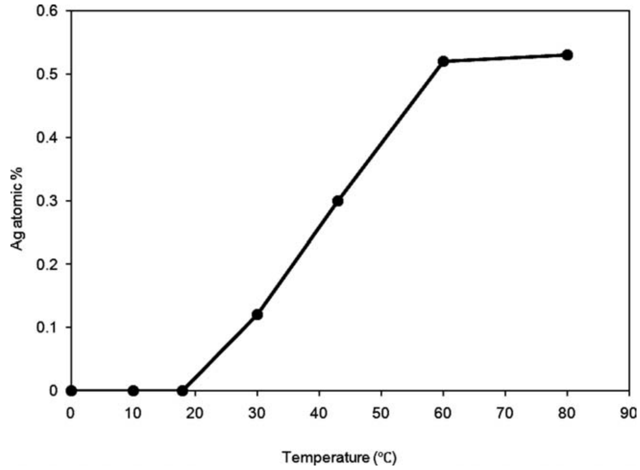

Figure 8 Amount of silver on cotton surface treated with silver colloid and 3-MPTMS at different temperatures.

excellent washing fastness; however, it could be considered that cotton fabrics treated with silver nanoparticles and 3-MPTMS possessed reasonable washing durability, especially since previous research showed that a silver nanoparticles treatment on cotton fabrics without 3-MPTMS was poorly retained (below 2% of original amount) after five washing cycles.[15] In addition, it is assumed that a larger size of silver nanoparticles may have relatively greater friction against water and other parts of the fabrics during washing. Thus, smaller size of silver nanoparticles attached on cotton with 3-MPTMS, might have increased washing fastness. In further research, this fact will be considered more precisely.

Antimicrobial efficacy

In this study, *S. aureus* as a Gram-positive bacterium and *K. pneumoinae* as a Gram-negative bacterium were used to measure antimicrobial activity and the

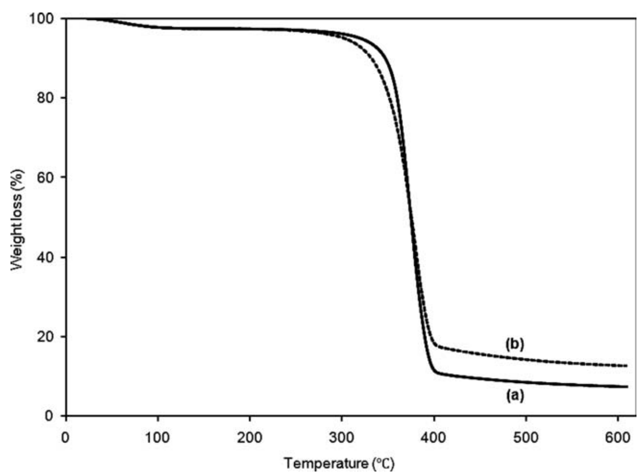

Figure 9 TGA pattern of (a) untreated cotton and (b) silver colloid and 3-MPTMS-treated cotton.

TABLE II
Washing Fastness of Cottons Treated with Silver Nanoparticles and 3-MPTMS

Washing cycles	Retaining of Ag (Atomic %)
0	0.30
1	0.29
2	0.26
3	0.23
4	0.23
5	0.20

test results are shown in Figure 10 and Table III. The results demonstrate that only 3-MPTMS-treated cotton did not show suitable antimicrobial effect; however, silver nanoparticles/3-MPTMS-treated cotton inactivated both bacteria. It is predicted that most of the silver nanoparticles may be connected with sulfur in 3-MPTMS, but the antimicrobial results explained that the surface of silver nanoparticles treated with 3-MPTMS on cotton still have some area available to inactivate bacteria and/or ionic silvers inactivate bacteria. In terms of antimicrobial activity, due to outer membrane of Gram-negative bacteria, they are normally less sensitive to disinfectants.[10] Thus, silver nanoparticles/3-MPTMS-treated cotton fabrics have sufficient antimicrobial efficacy against both bacteria, and it can be used as a broad-spectrum disinfectant.

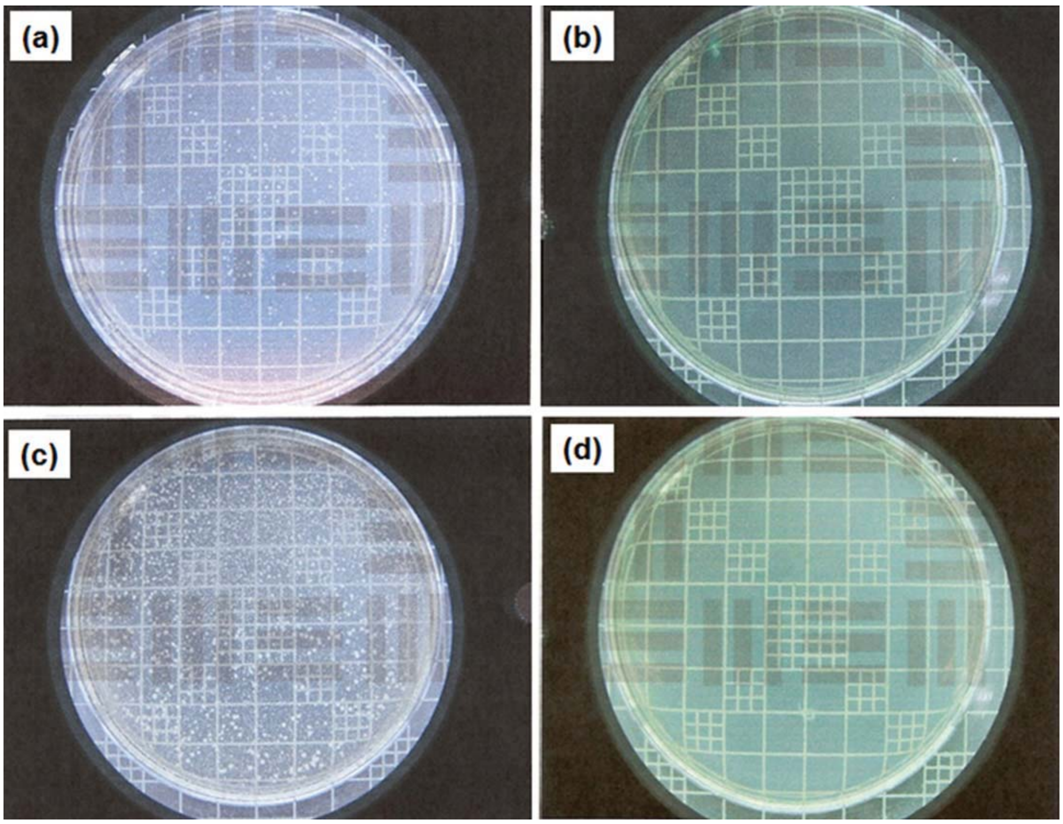

Figure 10 Antimicrobial activity of (a) cotton treated with 3-MPTMS against *S. aureus*, (b) cotton treated with Silver nanoparticles/3-MPTMS against *S. aureus*, (c) cotton treated with 3-MPTMS against *K. pneumoinae*, and (d) cotton treated with silver nanoparticles/3-MPTMS against *K. pneumoinae*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Antimicrobial Test Results of Cotton Fabrics Treated with 3-MPTMS and 3-MPTMS/Silver Nanoparticles

	Staphylococcus aureus			*Klebsiella pneumonia*		
Samples	Total bacteria (cfu mL^{-1})	Bacterial no. (cfu/sample)	Reduction (%)	Total bacteria (cfu mL^{-1})	Bacterial no. (cfu/sample)	Reduction (%)
Cotton treated with 3-MPTMS	1.3×10^5	6.7×10^4	48.2	1.5×10^5	1.5×10^5	<1
Cotton treated with Silver nanoparticles/3-MPTMS	1.3×10^5	0	100	1.5×10^5	0	100

CONCLUSIONS

Silver nanoparticles were successfully coated on cotton fabrics with 3-MPTMS. These treated fabrics were tested for washing fastness and showed reasonable and relatively enhanced durability than pad-dry-cure process which was used no bonding agent. The treated fabrics were also employed for antimicrobial test and the results released that excellent antimicrobial performance against *Staphylococcus aureus* and *Klebsiella pneumonia*.

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