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N-Halamine-bonded Cotton Fabric with Antimicrobial and Easy-care Properties

Rong Li, Mingming Sun, Zhiming Jiang, Xuehong Ren*, and T. S. Huang[1]

Key Laboratory of Eco-textiles of Ministry of Education, College of Textiles and Clothing, Jiangnan University, Wuxi, Jiangsu 214122, China
[1]*Department of Poultry Science, Auburn University, Auburn, AL 36849, USA*

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Abstract: N-halamine precursor 2,2,6,6-tetramethyl piperidinol (TMP), a hindered amine light stabilizer, was bonded onto cotton fabric by using 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinking agent. A variety of treating conditions including TMP concentration, curing temperature and time, and catalyst were studied. The treated fabrics were characterized using FTIR spectra and scanning electron microscope (SEM). The cotton fabric treated with TMP precursor could be rendered biocidal upon exposure to dilute household bleach. The chlorinated cotton swatches showed great efficacy and inactivated 100 % of *Staphylococcus aureus* with 7.1 log reduction with 5 min of contact and 83.25 % of *E. coli* O157:H7 at 10 min of contact. In addition, the wrinkle recovery angle of the treated cotton fabrics increased from 229 ^{o} of untreated cotton fabrics to 253 ^{o}. This study provided a practical finishing process to produce cotton fabrics with easy care and antibacterial functionalities at the same time.

Keywords: Cotton, Antimicrobial, N-halamine, Easy-care, Biocidal

Introduction

People are more and more concerned about the function of their apparels with the improvement of living standards and consciousness of environmental protection. Apparel should not only be comfortable and beautiful, but also have good antibacterial properties in some specific applications. Cotton fibers are the most common and important natural materials in the apparel industry. Since cotton can absorb moisture, clothing made of cotton fabrics are the most comfortable garments. Despite the above advantages, cotton fabrics have disadvantages such as easy wrinkling in practical applications [1]. Extensive research works have been focused on the study of easy-care finishing of textiles. 1,3-dimethylo1-5,5-dimethylhydantoin (DMDMH), polycarboxylic acids such as 1,2,3,4-butanetetracarboxyic acid (BTCA) and citric acid, glyoxal, and inorganic phosphates have been used as the easy-care finishing agents of cotton [2-5]. However, the slow release of free formaldehyde from DMDMH limits their applications. Cross-linking agents, such as polycarboxylic acids which are free of formaldehyde, have been developed in easy-care finishing in the last decade [1,4,6-8].

On the other hand, cotton fabrics provide an excellent environment for microbial growth due to the large surface area and ideal substrates, which causes skin irritation and odor problems along with fabric deterioration [2,9]. Extensive researches have been reported on enhancing the antimicrobial functionalities of cellulose based-textiles using different antimicrobial agents, such as quaternary ammonium compounds [10], N-halamines [11-17], chitosan [18,19], polybiguanides [20], and nanoparticles of noble metals and metal oxides [21,22]. N-halamine materials have been developed and shown to be effective biocides in Dr. Worley's group during the past three decades [23-28]. These N-halamine compounds have advantages over other antimicrobial agents, such as durability and re-chargeablility, and high antimicrobial efficacy when these compounds are covalently bound to the substrates [29].

In this study, we attached 2,2,6,6-tetramethyl piperidinol (TMP), a hindered amine light stabilizer onto cotton fabric via the cross-linking agent 1,2,3,4-butanetetracarboxylic acid (BTCA) to impart multifunctional properties, i.e. easy-care and antibacterial functionalities by using the pad-dry-cure finishing technique after chlorinating with household bleach. The treated cotton swatches have been tested for antimicrobial activity against Gram-positive and Gram-negative bacteria, *Staphylococcus aureus* and *Escherichia coli* O157:H7, respectively. The wrinkle recovery angle and strength of treated cotton were also evaluated.

Experimental

Materials

Fabric of 100 % bleached cotton was provided by Zhejiang Guandong Printing & Dyeing Company, Zhejiang; 2,2,6,6-tetramethyl piperidinol (TMP) was purchased from Jiaxing SiCheng Chemical Co., Ltd, Zhejiang; 1,2,3,4-butanetetracarboxylic acid (BTCA) was purchased from Changzhou Chemical Industry Research Institute Co., Ltd, Jiangsu; Household bleach (the active chlorine content was 5 %) and sodium hypophosphite were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai. All reagents were used as received without further purification. The bacteria employed were *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* O157:H7 ATCC 43895 (American Type Culture Collection, Rockville, MD). The Trypticase soy agar

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*Corresponding author: xhren@jiangnan.edu.cn used was from Difco Laboratories, Detroit, MI.

Cotton Finishing Procedures

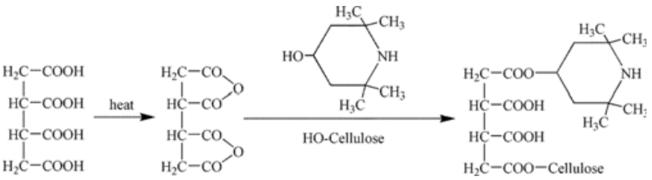
Equimolar quantities of BTCA and precursor TMP with or without sodium hypophosphite were dissolved in distilled water at concentrations of TMP ranging from 3 % to 7 % so as to load desired chlorine. Cotton swatches were soaked in the solution for 15 min, and then dried at 100 °C for 2 min, followed by curing at 150-190 °C for 20-180 s. Then the treated swatches were soaked in 0.5 % detergent solution for 15 min, washed with distilled water, and dried at ambient temperature. The attachment of TMP onto cellulose with the BTCA through the curing process was shown in Scheme 1.

Chlorination and Analytical Titration

The treated cotton swatches were immersed in a 10 wt % aqueous solution of household bleach (0.5% NaOCl) at room temperature for 1 h. The chlorinated cotton samples were washed thoroughly with distilled water and dried at 45 °C for 1 h to remove any remaining free chlorine from the surface of the fabric. The coated cotton fabrics were rendered antimicrobial by the above chlorination process (Scheme 2). The loaded chlorine concentration on the samples was determined by the iodometric/thiosulfate titration method. For example, about 0.2 g of chlorinated sample was suspended in a 50 m*l* water solution, then, 0.5 g of KI and 1 m*l* of 1 % of starch water solution were added. The solution was titrated with 0.0005 N sodium thiosulfate. The bonded active chlorine content on the cotton fabric swatch was calculated with the equation below:

$$Cl^{+}\% = \frac{N \times V \times 35.45}{W \times 2} \times 100 \qquad (1)$$

where N and V are the normality (eqv/l) and volume (l) of the $Na_2S_2O_3$ consumed in the titration, respectively, while W is the weight of the chlorinated cotton fabric.



Scheme 1. Attachment of TMP to cotton fabric.

Scheme 2. Production of antimicrobial cotton fabric.

Characterization

The FT-IR spectra of cotton fabric, treated cotton fabric, and chlorinated treated cotton fabric were recorded by a Nicolet Nexus 470 spectrometer in the optical range of 400-4000 cm^{-1} by 32 scans at a resolution of 4 cm^{-1}. The surface morphologies of cotton fabric and treated cotton fabric were characterized by scanning electron microscope (SEM) (Quanta 200, Holland).

Tensile Strength and Wrinkle Recovery Angle (WRA) Measurement

The tensile strength of cotton fabric was measured according to GB/T3923-1997 “Textiles—Tensile properties of fabrics—Part 1: Determination of breaking force and elongation at breaking force—Strip method”. The size of testing samples was 250×50 mm^2. Each sample was tested at least 3 times and average value was obtained. The tensile strength retention of cotton fabric was calculated with the equation as below:

$$\textit{Tensile strength retention (\%)} = \frac{\textit{tensile strength after treating (N)}}{\textit{tensile strength before treating (N)}} \times 100\ \% \qquad (2)$$

Wrinkle recovery angle of cotton fabric was determined according to GB/T3819-1997 “Textile fabric—Determination of the recovery from creasing of a folded specimen by measuring the recovery angle”. The recovery angles were measured in both warp (lengthwise yarns, abbreviated as WRA_W) and weft (widthwise yarns, abbreviated as WRA_F) directions, and the sum of these angles was reported as the $WRA_{(W+F)}$.

Antimicrobial Test

The *Staphylococcus aureus* ATCC6538 and *Escherichia coli* O157:H7 ATCC 43895 were used in this study. The individual cultures were inoculated in Trypticase® soy broth (TSB; Becton, Dickinson and Company, Sparks, MD) and incubated at 37 °C for 12 h. After incubation, the log phase bacteria were washed three times with 100 mM phosphate buffered (pH 7.0) by performing through centrifugation at 3,500×g for 10 min and re-suspended in phosphate buffer. The populations of bacterial cultures were estimated based on the absorbance at $O.D._{640\,nm}$ and diluted to working populations for use. The actual bacterial populations were also decided by spread-plate count method. Both chlorinated and unchlorinated treated cotton fabric samples were challenged with bacteria using a modified AATCC Test Method 100-1999 for antimicrobial efficacy testing. The testing began with the addition of 25 μl of the bacterial suspensions buffered at pH 7 to the centers of 6.45 cm^2 portions of cotton swatches in a sterile Petri dish, and with second identical swatches placed upon the first ones held in place by a sterile weight. Different swatches were exposed to the bacteria with contact times of 1, 5, and 10 min, respectively. Then they were placed in tubes containing 5.0 m*l* of sterile 0.02 N sodium thiosulfate and the tubes were vortexed 2 min to remove all oxidative chlorine. Quenched solutions were made 10-fold dilution with pH 7, 100 mM phosphate buffer, and each dilution was plated on Trypticase soy agar. The plates were incubated at 37 °C for 24 h. The bacterial colonies were recorded and enumerated for biocidal efficacy.

Results and Discussion

Effect of the Concentration of TMP on Chlorine Content

The concentration of finishing agents affects the physical properties, chlorine loading, and further antibacterial activity of cotton fabric. The increase of concentration of finishing agents will increase the cost of coating. Therefore, it is necessary to determine the optimal concentration of finishing mixture. The effect of the concentration of finishing agents on the active chlorine content is shown in Figure 1. The chlorine content increased from 0.06 % to 0.14 % with the increase of TMP concentration from 3 % to 4 %, and decreased with further increase of concentration. This indicates that the curing process favors the reaction of cotton fibers with TMP and BTCA when the concentration of TMP is lower than 4 %, which leads to the increase of chlorine loading with the increase of concentration of finishing agents. After the chlorine loading on cotton fabric reaches the maximum, the continuous increase of finishing agents might favor the reaction between cotton fibers and BTCA during coating due to more BTCA added into the solution. The solubility of BTCA in water is higher than that of TMP, which causes more BTCA penetrate into cotton fibers than TMP during treating. Therefore, there are fewer carboxylic acid groups of BTCA to react with TMP than with hydroxyl groups in cotton fibers. The increase of cross-linking between BTCA and cotton fibers results in the decrease of chlorine loading. Considering the economic cost and maximum chlorine loading, 4 % of TMP was used in the following treatment.

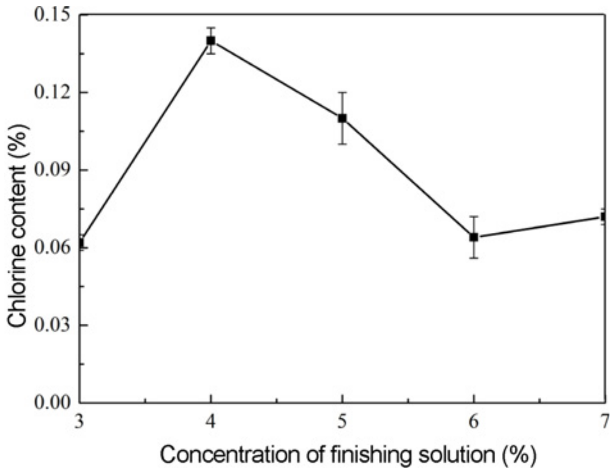


Figure 1. Effect of the concentration of finishing agents on chlorine content.

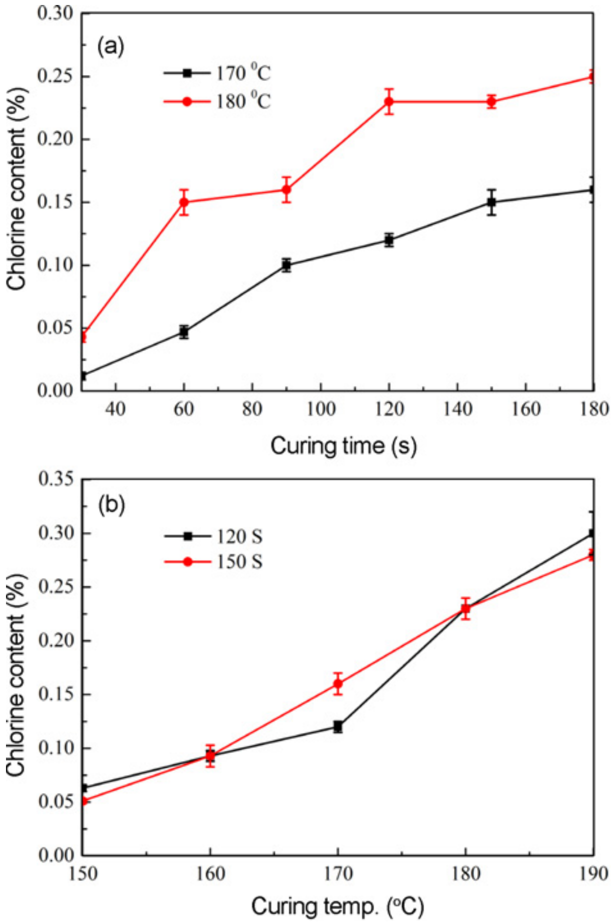


Figure 2. Effect of curing time (a) and temperature (b) on chlorine content.

Effect of Curing Condition on Chlorine Content

The effects of curing temperature and time on the chlorine loading are studied. As shown in Figure 2, longer curing time leads to higher chlorine content under the same curing temperature (Figure 2(a)), and the higher curing temperature leads to higher chlorine content with the same curing time (Figure 2(b)). This indicates that the curing temperature and time have a very important effect on the chlorine content. Higher temperature and longer curing time help in the formation of more covalent bonds of BTCA to cotton fibers and BTCA with TMP, which increase the chlorine content of cotton fabrics upon chlorination. When cured at 170 °C for 180 s or at 180 °C for 120 s, the chlorine loading is around 0.20 % which could provide efficient biocidal efficacy against bacteria.

Effect of Curing Condition on Strength of Cotton Fabric

The tensile strength of cotton fabric is shown in Figure 3. The warp and weft strengths of cotton fabric declined after finishing significantly. From the experimental data obtained at 170 °C, the warp strength of cotton fabric declines from 872 N to 532 N and the weft strength declines from 302 N to 178 N after 3 min of curing, and the tensile strength retentions are 61 % (warp) and 59 % (weft), respectively. When cured for 2 min at 180 °C, the warp strength of cotton fabric declines from 872 N to 519 N and the weft strength declines from 302 N to 159 N, and the tensile strength retentions are 60 % (warp) and 53 % (weft), respectively, which makes the fabric weaker.

The stability of the glycoside bond in macromolecule chains of cotton fibers is poor under acid conditions. The glycoside bond will hydrolyze under appropriate conditions such as appropriate hydrogen ion concentration, temperature, time *et al.,* leading to the breakage of the glycoside bond formed between carbon and oxygen atoms from two adjacent glucose monomers. The low pH of finishing solution at 4-5 in the experiment and high curing temperature will promote the breaking of glycoside bonds, resulting in strength loss in the treated cotton fabric. The higher curing temperature causes faster hydrolysis of the glycoside bond and the strength loss more serious. On the other hand, the cross-linking bonds between BTCA and cotton fibers formed during the treatment cause cotton fabrics to be stiff and brittle. A certain amounts of covalent bonds which are introduced between structural units and macromolecules of cotton fibers restrict the mobility of each unit, leading to the decrease of overall strength under external forces.

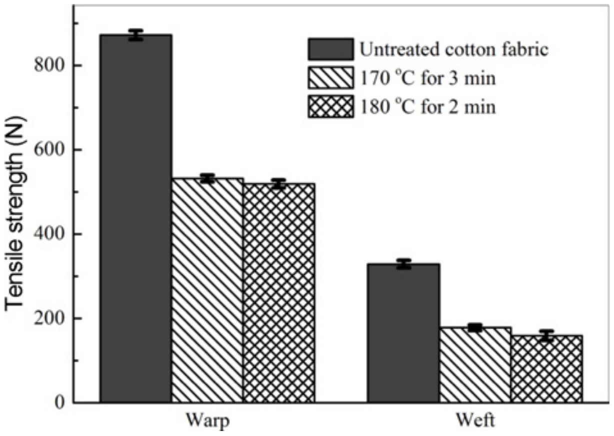


Figure 3. Effect of curing condition on tensile strength of cotton fabric.

Table 1. Effect of curing condition on WRA

Curing conditions	WRA_W (°)	WRA_F (°)	$WRA_{(W+F)}$ (°)
Untreated	57.9	53.8	111.7
170 °C for 3 min	102.8	111.7	214.5
180 °C for 2 min	109.8	113.1	222.9

Wrinkle Recovery Angle (WRA) and Tensile Strength Testing

The performance of easy-care and wrinkle recovery angle (WRA) of cotton fabrics treated with different curing conditions are investigated. The results are presented in Table 1. It shows that WRA of cotton fabric is improved significantly after treating. The improvement of WRA depends on the number of ester bonds formed between the hydroxyl groups of cotton fabric and the carboxyl groups in BTCA [1]. In addition, WRA of cotton fabric cured at 180 °C for 2 min is higher than that cured at 170 °C for 3 min, which indicates that the higher temperature benefits the cross-linking between BTCA and cotton fabrics.

A weak base is the common chemistry used as catalyst in the esterification reaction between anhydride and alcohol or cellulose hydroxyl. Sodium hypophosphite ($NaH_2PO_2{\cdot}H_2O$) is one of the best catalysts in BTCA easy-care finishing. The effect of the catalyst on chlorine content, tensile strength, and WRA performance are shown in Table 2. Compared to the control sample, the addition of 6 % sodium hypophosphite in the treatment causes the total WRA to increase from 222.9 ° to 251.6 °, the tensile strength decrease about 18 N for the warp and weft of fabrics, and the chlorine content of cotton fabric decreased slightly. The addition of the catalyst does not significantly change pH of the finishing solution, and has little effect on the hydrolysis of macromolecule glycoside of cotton fibers at high curing temperatures. On the other hand, the catalyst can facilitate the formation of cyclic anhydride in the BTCA molecule, and further promote the esterification reaction between anhydride and hydroxyl groups on cellulosic macromolecules, and more covalent bonds were formed between BTCA and cotton fibers. Thus, less TMP attached to the cotton fibers results in a slight decrease of chlorine loading. Generally, the cross-linking of cotton fabrics after finishing leads to the decrease of the tensile strength of treated cotton fabric with the increase of the wrinkle recovery property. The breaking of cotton fabric is caused by the breakage of macromolecule chains according to the fracture mechanism of cotton fibers. The certain degree of covalent bonds introduced intermolecularly between structural units

Table 2. Effect of catalyst on chlorine content, strength, and WRA

Sodium hypophosphite concentration	Chlorine content (%)	Tensile strength (N)		WRA (°)		
		warp	weft	WRA_W (°)	WRA_F (°)	$WRA_{(W+F)}$ (°)
0	0.19±0.01	519±9	159±11	109.8±5	113.1±4	222.9±5
6%	0.17±0.01	502±5	141±3	123.1±8	128.5±7	251.6±8

of cotton fibers further restricts the movement of macromolecule chains. The restricted movement of macromolecule chains after treatment and the stress concentration of fibers will lead to the decline of tensile strength.

Antibacterial Efficacy

The biocidal efficacy data for the unchlorinated and chlorinated of TMP/BTCA treated cotton fabrics against Gram-positive *S. aureus* and Gram-negative *E. coli* O157:H7 are presented in Table 3. The cotton fabrics were challenged with *S. aureus* and *E. coli* O157:H7 bacteria at 1.27×10^7 cfu/sample and 2.00×10^7 cfu/sample, respectively. The unchlorinated treated cotton fabric produced only a small log reduction for both bacteria, 0.90 log reduction of *S. aureus* and 0.03 log reduction of *E. coli* O157:H7 with 10 min of contact due to the adhesion of the bacteria to the surface of cotton fabric and perhaps a small degree inactivation of the bacteria. The reduction difference of unchlorinated cotton fabrics between the two bacteria is due to their different shape [23]. On the other hand, the ring opening reaction occurred in cyclic anhydride was not transferred into ester bonds, leading to the increase of polycarboxylic acid groups on the surface of cotton fabric surfaces. The inactivation of polycarboxylic acid against *S. aureus* are more effective than against *E. coli* O157:H7 [30]. The chlorinated cotton fabric inactivated 100 % of *S. aureus* within 5 min with log reductions of 7.10 and 83.25 % of *E. coli* O157:H7 within 10 min of contact. This indicates that *E. coli* O157:H7 is more difficult to be inactivated than *S. aureus*. There are hydrophobic pipes formed by pore protein in the outer membrane of Gram-negative bacteria. After chlorination, N-H bond in the TMP molecule was replaced by N-Cl bond which enhanced the hydrophobic properties of the treated cotton fabric. Therefore, the antimicrobial activity against Gram-negative bacteria is less effective than that against Gram-positive bacteria [31].

Characterization of Treated Fabrics

Cotton cellulose has numerous hydroxyl groups which can react with polycarboxylic acids such as BTCA by forming ester bonds. TMP contains one hydroxyl groups which can also react with BTCA through esterification. BTCA, acting as a cross-linking agent, links TMP to the cotton cellulose through the curing process (Scheme 1). The treated cotton fabrics contained numerous amine functional groups which could be rendered antimicrobial by exposure to diluted household bleach (Scheme 2).

The FTIR spectra of cotton, and cotton treated with BTCA and TMP before and after chlorination are shown in Figure

Table 3. Antibacterial property against *S. aureusa* and *E. coli* O157:H7

Sample	Contact time (min)	Bacterial reduction			
		S. aureus[a]		*E. coli* O157:H7[b]	
		%	Log reduction	%	Log reduction
Cotton-TMP-BTCA	10	87.34	0.90	6.20	0.03
Cotton-TMP-BTCA-Cl	1	89.45	0.98	9.55	0.04
	5	100	7.10	33.00	0.17
	10	100	7.10	83.25	0.78

[a] The inoculum population was 1.27×10^7 cfu/sample and [b] the inoculum population was 2.00×10^7 cfu/sample.

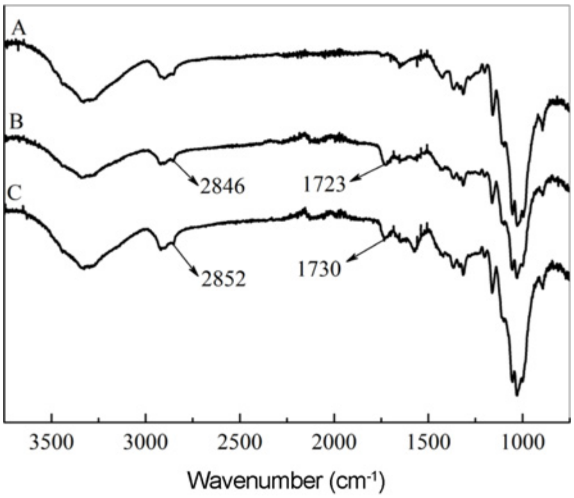


Figure 4. FTIR spectra of cotton fabric (A), cotton fabric treated with BTCA and TMP before (B) and after (C) chlorination.

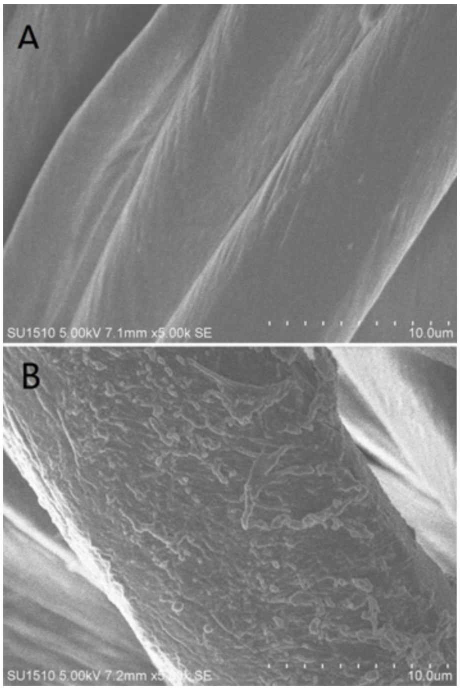


Figure 5. SEM pictures of (A) cotton fabric, and (B) cotton fabric treated with BTCA and TMP.

4. The characteristic vibration band of cotton treated with BTCA and TMP appears at 1723 cm^{-1} in Figure 4(B), which corresponds to the carbonyl vibration modes of BTCA. This band is not observed for the cotton in Figure 4(A). This vibration band shifts to 1730 cm^{-1} after chlorination (Figure 4(C)). The shift to higher wave number of the hydantoin carbonyl bands upon chlorination was reported from these laboratories for other N-halamines [14,23]. The band located at 2846 cm^{-1} shifts to 2852 cm^{-1} after chlorination. The shift is explained via the oxidative chlorine in TMP molecule has electrophilic inductive effect and causes the shift of neighboring -CH_3 bond.

Figure 5 shows the scanning electron microscopy (SEM) pictures of fabric surface. Clearly, the surface of untreated cotton fibers is smooth. While the surface of treated cotton fibers becomes rough indicating that the finishing agents attached to the surface of cotton fibers successfully.

Conclusion

N-halamine precursor 2,2,6,6-tetramethyl piperidinol (TMP) was successfully bonded onto cotton fabric by using 1,2,3,4-butanetetracarboxylic acid (BTCA) as crosslinking agent. The treated cotton fabrics were characterized using FTIR spectra and scanning electron microscope (SEM). The treated cotton fabric was found to have advantages of easy care and antibacterial functionalities despite of strength loss of fabrics. WRA of treated cotton fabrics was improved from 111.7° to 222.9° without catalyst and 251.6° with catalyst under the optimal finishing condition, while the tensile strength retentions were only 60 % (warp) and 53 % (weft), respectively. The cotton fabric treated with TMP precursor could be rendered biocidal after chlorination. The chlorinated cotton fabric completely inactivated *S. aureus* with log reductions of 7.1, and 83.25 % of *E. coli* O157:H7 within 5 and 10 min of contact, respectively. The future work will be focusing on the improvement of the treated cotton fabric strength.

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