Carbohydrate Polymers 78 (2009) 220–226

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

N-Halamine-coated cotton for antimicrobial and detoxification applications

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ARTICLE INFO

Article history:
Received 15 January 2009
Received in revised form 25 February 2009
Accepted 23 March 2009
Available online 28 March 2009

Keywords:
Biocidal
Cellulose
Bacteria
Antimicrobial
N-Halamine

ABSTRACT

A new *N*-halamine precursor, 3-(2,3-dihydroxypropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (TTDD diol), was synthesized and bonded onto cotton fabrics. Fabrics with variable amounts of chlorine loading were prepared by using several concentrations of TTDD diol. A second *N*-halamine precursor, 3-(3-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (TTDD siloxane), was also synthesized and bound to cotton for comparison purposes. The coated cotton fabrics contained two types of N–Cl moieties after chlorination of the amine and amide groups. Swatches with variable chlorine loadings were challenged with *Staphylococcus aureus* and *Escherichia coli* O157:H7 as a function of contact time. The biocidal test results showed that the chlorine loadings and surface hydrophobicities influenced the antimicrobial efficacies. The chlorinated swatches have also been employed to oxidize the simulant of chemical mustard to the less toxic sulfoxide derivative.

1. Introduction

Antimicrobial organic materials comprised of quaternary ammonium salts (Klibanov, 2007; Kurt, Gamble, & Wynne, 2008; Kurt, Wood, Ohman, & Wynne, 2007; Lewis & Klibanov, 2006; Murata, Koepsel, Matyjaszewski, & Russell, 2007; Park, Wang, & Klibanov, 2006; Sauvet, Fortuniak, Kazmierski, & Chojnowski, 2003; Waschinski & Tiller, 2005; Waschinski et al., 2008a, 2008b; Waschinski, Herdes, Schueler, & Tiller, 2005), phosphonium salts (Kenawy & Mahmoud, 2003; Kenawy, Abdel-Hay, El-Magd, & Mahmoud, 2006; Kenawy, Abdel-Hay, El-Shanshoury, & El-Newehy, 2002), and *N*-halamine compounds (Barnes et al., 2006; Chen et al., 2004a, 2004b, 2003a, 2003b; Chen & Sun, 2006; Grunzinger et al., 2007; Kocer et al., 2008; Kou et al., 2006; Lee, Broughton, Akdag, Worley, & Huang, 2008; Liang et al., 2007a, 2007b, 2006; Liu & Sun, 2008; Luo & Sun, 2006, 2008; Luo, Chen, & Sun, 2006; Makal, Wood, Ohman, & Wynne, 2006; Ren, Kocer, Worley, Broughton, & Huang, 2009; Ren et al., 2008a, 2008b; Sun & Xu, 1999a, 1999b, 1999c; Sun & Sun, 2001, 2002) have been used as antimicrobial agents in infection control. Among these, *N*-halamine materials have been extensively studied due to their stabilities, regenerabilities, and efficacies in inactivating bacteria. The infection of hospital personnel and patients with pathogenic microorganisms could be minimized if they were equipped with protective clothing containing these materials.

Cotton is an ideal medium for the growth of bacteria because of its composition. On the other hand, cotton can be easily modified to produce antimicrobial cellulose. Sun and coworkers have successfully employed wet finishing or grafting techniques to produce durable and regenerable antibacterial cotton fabrics (Liu & Sun, 2008; Sun & Xu, 1999a; Sun & Xu, 1999b; Sun & Xu, 1999c; Sun & Sun, 2001; Sun & Sun, 2002). Recently, a series of *N*-halamine siloxanes were synthesized and coated onto cotton to produce antimicrobial cellulose in these laboratories (Barnes et al., 2006; Kocer et al., 2008; Liang et al., 2007a; Liang et al., 2006; Liang et al., 2007b; Ren et al., 2008b). *N*-Halamine materials function as biocides through the direct contact of microbial cells with oxidative halogen. The hydrophobicities of *N*-halamine precursors and the increasing hydrophobicities of their halogenated derivatives influence the surface contact of the biocides and the cells, and in turn, may lower the rate of disinfection. On the other hand, an increase of oxidative N–X moieties provides more contact sites and can increase the disinfection rate. The work of Chen and Sun showed that an increase in alkyl chain length at the 3 position of the hydantoin ring can cause less contact sites with the cells and a lower rate of disinfection due to the increase of hydrophobicity on the surfaces of the antimicrobial materials. Kocer et al. have studied the effect of alkyl substitution at the 5 position of the hydantoin ring of *N*-halamine siloxanes on the rate of inactivation of microbes and reached the conclusion that hydrophobicity is one of the major factors that influence the disinfection rate. However, the *N*-halamine siloxanes reported above are only partially soluble in water and need the assistance of organic solvents for dissolution which can be a liability for industrial applications.

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0144-8617/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.03.029

Cross-linking agents, such as polycarboxylic acids, have been used to produce antimicrobial cellulose by bonding the hydroxylhydantoin- or aminohydantoin-containing precursors onto cotton (Kou et al., 2006; Lee et al., 2008; Ren et al., 2009). To attempt to explore the hydrophobicity effect on the rate of disinfection of bacteria and to address the solvent issues, a new *N*-halamine precursor, 3-(2,3-dihydroxypropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione (TTDD diol; see Fig. 1), was synthesized and coated onto cotton with the aid of the cross-linking agent 1,2,3,4-butanetetracarboxylic acid (BTCA). For comparison, 3-(3-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (TTDD siloxane; see Fig. 1) was synthesized and bound to cotton by a previously reported procedure (Liang et al., 2007a; Ren et al., 2008b). The coated cotton fabrics with different chlorine loadings were challenged with *Staphylococcus aureus* and *Escherichia coli* O157:H7 as a function of contact time. Akdag et al. had employed the *N*-halamine compound, 1,3-diochloro-5,5-dimethylhydantoin, in oxidation of organic sulfides (Akdag, Liang, & Worley, 2007). The chlorinated cotton fabrics coated with TTDD diol were also used in the current study to oxidize chloroethyl ethyl sulfide, a simulant of chemical mustard. The inactivation of bacteria and detoxification of the simulant of mustard make cotton fabrics coated with the *N*-halamine diol ideal for use in protective clothing.

2. Experimental

2.1. Materials and structural characterizations

Style 400 bleached 100% cotton print cloth was purchased from Testfabrics, Inc.(West Pittston, PA). 7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione and 3-(3-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (TTDD siloxane) were synthesized by a previously reported procedure (Ren et al., 2008b). All chemicals used in this research were purchased from Fisher Scientific (Fair Lawn, NJ) or Aldrich Chemicals (Milwaukee, WI) and employed without further purification. The NMR spectra of the synthesized compounds were recorded by a Bruker AV-250 (250 MHz) spectrometer. FTIR spectra of the samples were obtained with a Nicolet 6700 FT-IR spectrometer. Tensile strength testing was conducted in triplicate with an Instron 5565 instrument. The specimens were sized to 1 × 4 in, and the elongation speed was 1 in/min at a gauge length of 2 in.

2.2. Synthesis of 3-(2,3-dihydroxypropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione (TTDD diol)

Equimolar quantities of 7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-decane-2,4-dione and potassium hydroxide were mixed in ethanol and refluxed for 10 min. An equimolar amount of 3-chloropropanediol and 25 mL water were added to the above solution. The resulting mixture was stirred for 16 h at ambient temperature. Solvents ethanol and water were removed under reduced pressure. Acetone was added to the flask, and the potassium chloride produced in the reaction was removed by filtration. After removing acetone, the desired white solid compound was produced with a yield of 67%. Spectral data for a sample recrystallized from acetone are: ^{1}H NMR (250 MHz, DMSO-d_6): δ 1.13 (6H), 1.28 (6H), 1.60 (2H), 1.63 (2H), 3.30 (2H), 3.35 (2H), 3.68 (1H), 3.74 (1H), 4.61 (1H), 4.87 (1H), 8.51 (1H); ^{13}C NMR (DMSO-d_6), δ 28.99, 34.47, 42.33, 42.74, 50.08, 60.66, 64.42, 68.59, 156.74, 177.57.

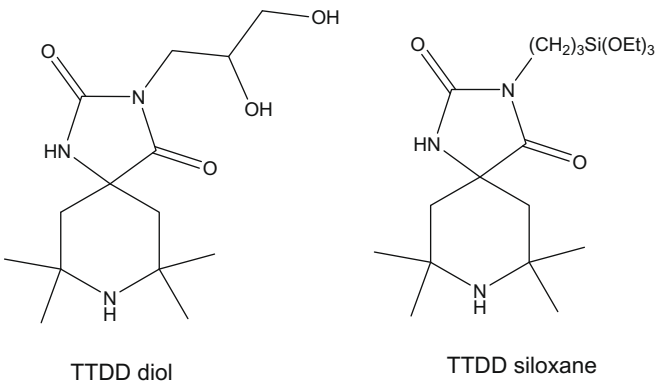

Fig. 1. Structures of the two compounds studied.

2.3. Coating procedures

The objective of this work was to prepare coatings with different chlorine loadings which might affect the biocidal efficacies. TTDD diol was dissolved in water at concentrations ranging from 1% to 5% with equimolar quantities of BTCA. Cotton swatches ware soaked in the solution for 15 min. These swatches were dried at 100 °C for 5 min and then cured at 170–180 °C for 2–3 min. The cured swatches were soaked in 0.5% detergent solution for 15 min, washed with water, and dried at ambient temperature. The coating of TTDD siloxane onto cotton was conducted by a previously reported procedure (Liang et al., 2007a; Ren et al., 2008b).

2.4. Chlorination and titration

The TTDD diol-coated cotton fabrics were chlorinated by exposure to 10% sodium hypochlorite solution (NaOCl)(0.6% Cl^+) at pH 11 at ambient temperature for 1 h. The free chlorine occluded to the surfaces of chlorinated cotton samples was removed by thoroughly rinsing with distilled water and heating at 45 °C for 1 h. The chlorine loading in the samples was determined by the iodometric/thiosulfate titration method.

2.5. Assessment of antibacterial activities

Biocidal efficacies of coatings against *S. aureus* (ATCC 6538) and *E. coli* O157:H7 (ATCC 43895) were determined using a modified AATCC 100-199 Test Method. 25 μL of the bacterial suspensions containing 8.3×10^6–1.7×10^7 CFUs buffered at pH 7 were added to the center of two pieces of 1 in square cotton swatches (chlorinated or unchlorinated control) which were held in place by sterile weights. The swatches were quenched with 5.0 mL of sterile 0.02 N sodium thiosulfate solution to remove all oxidative chlorine after the contact times of 1, 5, and 10 min. Plates with serial dilutions of the vortexed quenched samples on Trypticase soy agar were incubated at 37 °C for 24 h, and viable bacterial colonies were counted for biocidal efficacy analysis.

2.6. Assessment of coating durability

The AATCC Test Method 61-1996 was used to evaluate the stabilities of chlorine and the resistance to hydrolyses of the coatings. This test involved repeated washing cycles, each cycle being equivalent to three machine washings, in a Launder-Ometer at 49 °C for 45 min. Each test sample was rinsed three times with distilled water and dried at ambient temperature before the test.

2.7. Reaction of chloroethyl ethyl sulfide with chlorinated cotton swatches coated with TTDD diol

Mole ratios of 1:1 and 1:3 between 1-chloroethyl ethyl sulfide (1%) and Cl^+ of the chlorinated cotton coated with TTDD diol/BTCA

as determined by iodometric/thiosulfate titration were mixed in $CDCl_3$ and D_2O (10 drops). After specific reaction times the mixtures were then filtered and analyzed by ^1H and ^{13}C NMR.

3. Results and discussion

3.1. FTIR and tensile strength characterization of cotton coated with TTDD diol/BTCA

The synthesized TTDD diol which contains two hydroxyl groups and cotton which has numerous hydroxyl groups can react with BTCA by forming ester bonds under high temperature curing. In this work, it was found that adequate chlorination sites could be obtained for disinfection purposes without the use of an inorganic catalyst in the BTCA reaction. The cross-linking efficiency was thus adequate, although not measured in this study. The coated cotton fabrics contained amide and amine groups which were rendered antibacterial by exposure to diluted household bleach. The FTIR spectra of cotton, cotton coated with BTCA, and cotton coated with TTDD diol/BTCA before and after chlorination are shown in Fig. 2. The new bands at 1773 cm^{-1} (in Fig. 2C) and at 1785 cm^{-1} after chlorination (in Fig. 2D) were the carbonyl bands of TTDD diol for the unchlorinated and chlorinated cotton coated with TTDD diol and BTCA. The carbonyl bands of BTCA and a second carbonyl band of TTDD diol overlapped at 1702–1719 cm^{-1} (Fig. 2B, C, and D). A band corresponding to an N–Cl vibrational mode in the 500–670 cm^{-1} region could not be resolved due to the extensive overlap with C–H bending vibrational bands.

The measured loss of tensile strength of the coated samples even after chlorination was only 20–25% which is reasonable for any textile finishing process.

3.2. Antibacterial efficacies

Increased chlorine loadings on the coated swatches should increase the contact sites (N–Cl) on the cloth with the cells and result in an increase in the rate of inactivation of bacteria, but it could also cause poorer surface wetting due to an increase in hydrophobicity, thereby reducing the contact with the cells and lowering the rate of inactivation of bacteria. To evaluate this hypothesis, two *N*-halamine precursors were coated onto cotton fabrics and tested against bacteria after chlorination. The synthesized TTDD siloxane itself is not water soluble, and chlorination renders the cotton fabrics coated with TTDD siloxane even more hydrophobic. The effect of the chlorine loadings of swatches coated with TTDD siloxane on the rate of inactivation of bacteria was studied, and the biocidal results are shown in Tables 1 and 2. The biocidal tests were performed in duplicate. The coated swatches with chlorine loadings of 0.25% and 0.26% inactivated all of the *S. aureus* and *E. coli* O157:H7 within 5 min, and most of the bacteria were killed in a contact time of 1 min. When the chlorine loadings were increased to 0.49% (Table 1), the bacteria were inactivated completely within 30 min. The swatches with chlorine loadings of 0.52% in Table 2 inactivated all of the *S. aureus* and *E. coli* O157:H7 within 10 and 5 min, respectively. The swatches with higher chlorine loadings of 0.77% and 0.82% inactivated all of the *S. aureus* and *E. coli* O157:H7 within 10 min in the repeated tests. Apparently, the increase of chlorine loadings on the swatches coated with TTDD siloxane does not assist the inactivation of bacteria; this must be attributed to the increase of hydrophobicity and the resulting poorer surface wetting for the TTDD siloxane.

To minimize the hydrophobicity effect on the inactivation of bacteria, the N-halamine precursor TTDD diol/BTCA was coated onto cotton fabrics and tested against bacteria. The synthesized TTDD diol mixed with BTCA was soluble in water and could be coated onto cotton fabrics in aqueous solution. Another advantage of TTDD diol over TTDD siloxane is that the two hydroxy groups of TTDD diol render the coated swatches less hydrophobic even after chlorination which increases contact sites on the cloth with the cells. The biocidal test results against *S. aureus* are shown in Table 3. It was found that the coated swatches with chlorine loading of 0.20% inactivated all *S. aureus* with log reduction of 6.92 and 7.07 in a contact time of 10 min in the repeated experiments. When the chlorine loadings were increased to 0.56%, all *S. aureus* was inactivated within 5 min. When the chlorine loadings were increased to 0.82%, the coated swatches could inactivate all *S. aureus* in a contact time of 1 and 5 min in Exp1 and Exp2, respectively. The number of surviving *S. aureus* colonies from the control plate A was counted and the total bacteria on the swatches (for example, 1.30×10^5 CFUs/sample) was calculated based on the counted number (Fig. 3). As for the chlorinated swatches, no bacteria survived with 10 min contact which can be seen in plate B in Fig. 3.

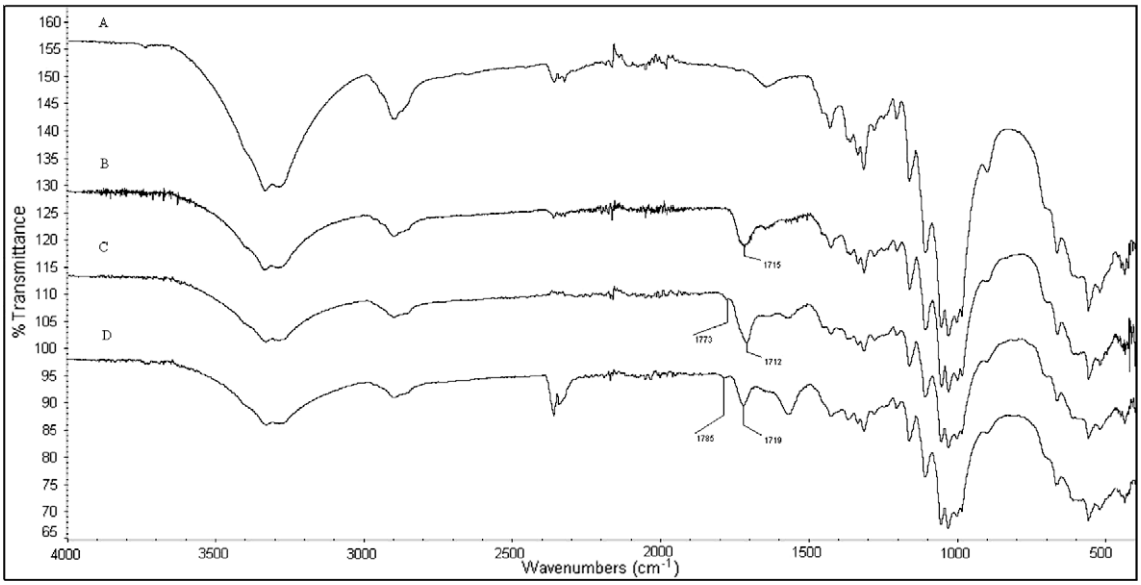

Fig. 2. FTIR spectra of (A) cotton, (B) cotton BTCA, (C) cotton-TTDD diol/BTCA, and (D) chlorinated cotton-TTDD diol/BTCA.

Table 1
Biocidal test I of cotton coated with TTDD siloxane against *S. aureus* and *E. coli* O157:H7.

Samples		*S. aureus*[a]		*E. coli* O157:H7[b]	
	Contact time (min)	% Reduction	Log reduction	% Reduction	Log reduction
Cotton-TTDD siloxane–Cl	1	99.998	4.63	99.999	5.28
(0.26% Cl^+)	5	100	7.16	100	7.10
	10	100	7.16	100	7.10
	30	100	7.16	100	7.10
Cotton-TTDD siloxane–Cl	1	99.98	2.91	99.998	4.68
(0.49% Cl^+)	5	99.99	4.05	99.998	4.68
	10	99.999	4.8	99.999	4.98
	30	100	7.16	100	7.10
Cotton-TTDD siloxane–Cl	1	99.99	3.90	99.996	4.43
(0.82% Cl^+)	5	99.99	3.95	99.999	5.28
	10	100	7.16	100	7.10
	30	100	7.16	100	7.10

[a] Inoculum concentration was 1.43×10^7 CFU.
[b] Inoculum concentration was 1.27×10^7 CFU.

Table 2
Biocidal test II of cotton coated with TTDD siloxane against *S. aureus* and *E. coli*.

Samples		*S. aureus*[a]		*E. coli*[b]	
	Contact time (min)	% Reduction	Log reduction	% Reduction	Log reduction
Cotton-TTDD siloxane–Cl	1	99.97	3.65	99.966	3.77
(0.25% Cl^+)	5	100	6.99	100	6.80
	10	100	6.99	100	6.80
	30	100	6.99	100	6.80
Cotton-TTDD siloxane–Cl	1	99.97	3.68	99.998	4.67
(0.52% Cl^+)	5	99.996	4.56	100	6.80
	10	100	6.99	100	6.80
	30	100	6.99	100	6.80
Cotton-TTDD siloxane–Cl	1	99.81	2.90	99.995	4.28
(0.77% Cl^+)	5	99.93	3.18	99.998	4.67
	10	100	6.99	100	6.80
	30	100	6.99	100	6.80

[a] Inoculum concentration was 9.67×10^7 CFU.
[b] Inoculum concentration was 6.33×10^7 CFU.

Table 3
Biocidal tests of cotton coated with TTDD diol/BTCA against *S. aureus*.

Samples		Exp1[a]		Exp2[b]	
	Contact time (min)	% Reduction	Log reduction	% Reduction	Log reduction
Cotton-TTDD diol (1%)	10	92.90	1.15	73.66	0.58
Cotton-TTDD diol (1%)–Cl	1	94.27	1.24	98.00	1.70
(0.20% Cl^+)	5	99.999	5.09	99.998	4.77
	10	100	6.92	100	7.07
Cotton-TTDD diol (2.5%)	10	94.35	1.25	61.63	0.42
Cotton-TTDD diol (2.5%)–Cl	1	99.998	4.79	99.99	3.99
(0.56% Cl^+)	5	100	6.92	100	7.07
	10	100	6.92	100	7.07
Cotton-TTDD diol (5%)	10	97.74	1.65	81.68	0.74
Cotton-TTDD diol (5%)–Cl	1	100	6.92	99.996	4.40
(0.82% Cl^+)	5	100	6.92	100	7.07
	10	100	6.92	100	7.07

[a] Inoculum concentration was 8.3×10^6 CFU.
[b] Inoculum concentration was 1.17×10^7 CFU.

Table 4 shows the biocidal test results of the coated swatches against *E. coli* O157:H7. The coated cotton swatches with chlorine loadings of 0.20%, 0.46%, and 0.80% inactivated all *E. coli* O157:H7 with log reduction of 7.23 in a contact time of 10, 10, and 5 min in Exp1, respectively. In Exp2, all *E. coli* were inactivated within 5, 10, and 5 min by the swatches with the same chlorine loadings as above. A small degree of inconsistency was found in the repeated experiment. This is probably due to the difficulty of performing reproducible bacterial testing on surfaces of textiles. The total number of *E. coli* O157:H7 surviving with a contact time of 10 min from the control sample was 2.46×10^6 CFUs/sample based on the bacteria number counted in plate A (Fig. 4). The chlorinated sample inactivated all of the bacteria (plate B, Fig. 4). The increase of chlorine loadings of the cotton coated with TTDD diol/BTCA did increase the contact sites with the cells and increase inactivation rate for both *S. aureus* and *E. coli* O157:H7. Hydrophobicity was not a factor for the TTDD diol in contrast to the TTDD siloxane.

3.3. Durability of the coatings

Data concerning the durability of the TTDD diol/BTCA coatings are presented in Table 5. It can be seen that the chlorinated coat-

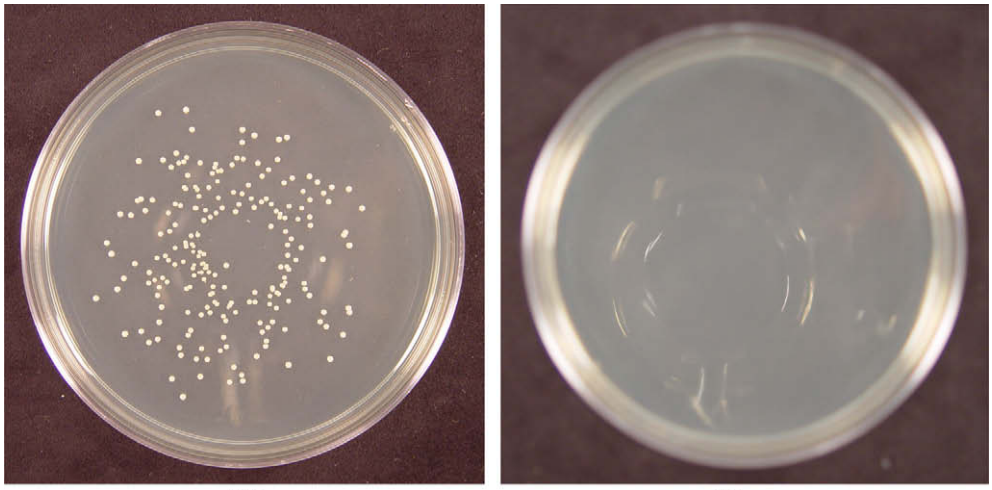

Fig. 3. Plates with colonies for cotton-TTDD diol/BTCA (5%) (A) and cotton-TTDD diol/BTCA–Cl (5%) (B). The challenge time of *S. aureus* was 10 min.

Table 4
Biocidal tests of cotton coated with TTDD diol/BTCA against *E. coli* O157:H7.

Samples		Exp1[a]		Exp2[a]	
	Contact time (min)	% Reduction	Log reduction	% Reduction	Log reduction
Cotton-TTDD diol (1%)	10	5.41	0.02	21.18	0.10
Cotton-TTDD diol (1%)–Cl	1	40.88	0.23	60.98	0.41
(0.20% Cl^+)	5	99.998	4.80	100	7.23
	10	100	7.23	100	7.23
Cotton-TTDD diol (2.5%)	10	13.29	0.06	5.41	0.02
Cotton-TTDD diol (2.5%)–Cl	1	81.08	0.72	56.65	0.36
(0.46% Cl^+)	5	99.999	4.93	99.99	4.06
	10	100	7.23	100	7.23
Cotton-TTDD diol (5%)	10	9.35	0.04	1.47	0.01
Cotton-TTDD diol (5%)–Cl	1	80.69	0.71	70.05	0.52
(0.80% Cl^+)	5	100	7.23	100	7.23
	10	100	7.23	100	7.23

[a] Inoculum concentration was 1.7×10^7 CFU.

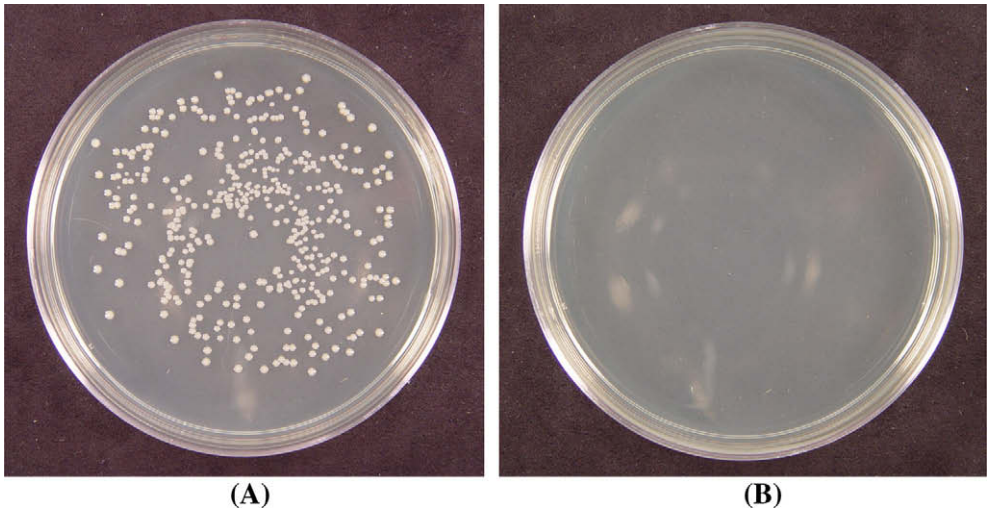

Fig. 4. Plates with colonies for cotton-TTDD diol/BTCA (5%) (A) and cotton-TTDD diol/BTCA–Cl (5%) (B). The challenge time of *E. coli* O157:H7 was 10 min.

ings do hydrolyze away from the surfaces of the coated cotton samples to some extent as washing cycles are extended. However, the samples did retain sufficient coating (0.07–0.16 weight percent Cl^+) to remain biocidal even after the equivalent of 50 machine washes.

3.4. Oxidation of chloroethyl ethyl sulfide by chlorinated cotton coated with TTDD diol/BTCA

The reaction between chloroethyl ethyl sulfide and chlorinated cotton coated with TTDD diol/BTCA was first prepared with 1:1

Table 5
Washing tests of cotton coated with TTDD diol/BTCA.

Machine washes	X	Y
0	0.38	0.38
5	0.11	0.17
10	0.10	0.17
25	0.08	0.18
50	0.07	0.16

X, chlorination (wt% Cl^+) before washing test.
Y, Chlorination (wt% Cl^+) before and after washing test.

mole ratio. The conversion rate of the reaction was low (13%) based on NMR analysis after 10 min contact. The extension of reaction time to 2 d increased the conversion rate to 59%. The long reaction time and low conversion rate was due to insufficient contact sites of oxidative chlorine. To increase the conversion rate, the mole ratio of chloroethyl ethyl sulfide and oxidative chlorine was adjusted to 1:3. After 60 min of reaction, virtually 100% of chloroethyl ethyl sulfide was oxidized to less toxic products. With higher mole ratios of chlorine to sulfide, the time for a complete conversion should decrease considerably. The major product was chloroethyl ethyl sulfoxide (Fig. 5) which was verified by NMR spectroscopy (^{1}H NMR (250 MHz), $CDCl_3$-d_6): δ 1.39 (3H), 2.80 (2H), 3.05 (2H), 3.58 (2H); ^{13}C NMR ($CDCl_3$-d_6), δ 6.82, 36.96, 46.17, 54.21, the chemical shifts being in accord with those reported previously (Hsu et al., 1990; Akdag et al., 2007). From Fig. 6, it can be seen that the signals corresponding to the chemical shifts for the simulant at δ values of 14.87, 26.19, 33.75, and 43.10 all completely vanish, with the concomitant appearance of the signals for the sulfoxide. The sulfoxide produced by oxidation of the sulfide is known to be considerably less toxic than are the sulfide or the further oxidized product sulfone (Yang, Baker, & Ward, 1992; Boring, Geletii, & Hill, 2001; Livingston, Kumar, & Landry, 2008).

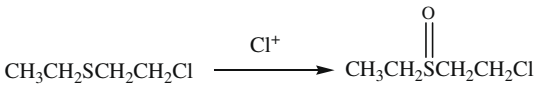

Fig. 5. Oxidation of chloroethyl ethyl sulfide by oxidative chlorine.

4. Conclusion

3-(2,3-dihydroxypropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro-[4.5]-decane-2,4-dione containing a diol functionality was synthesized and coated onto cotton fabric using a BTCA cross-linker at

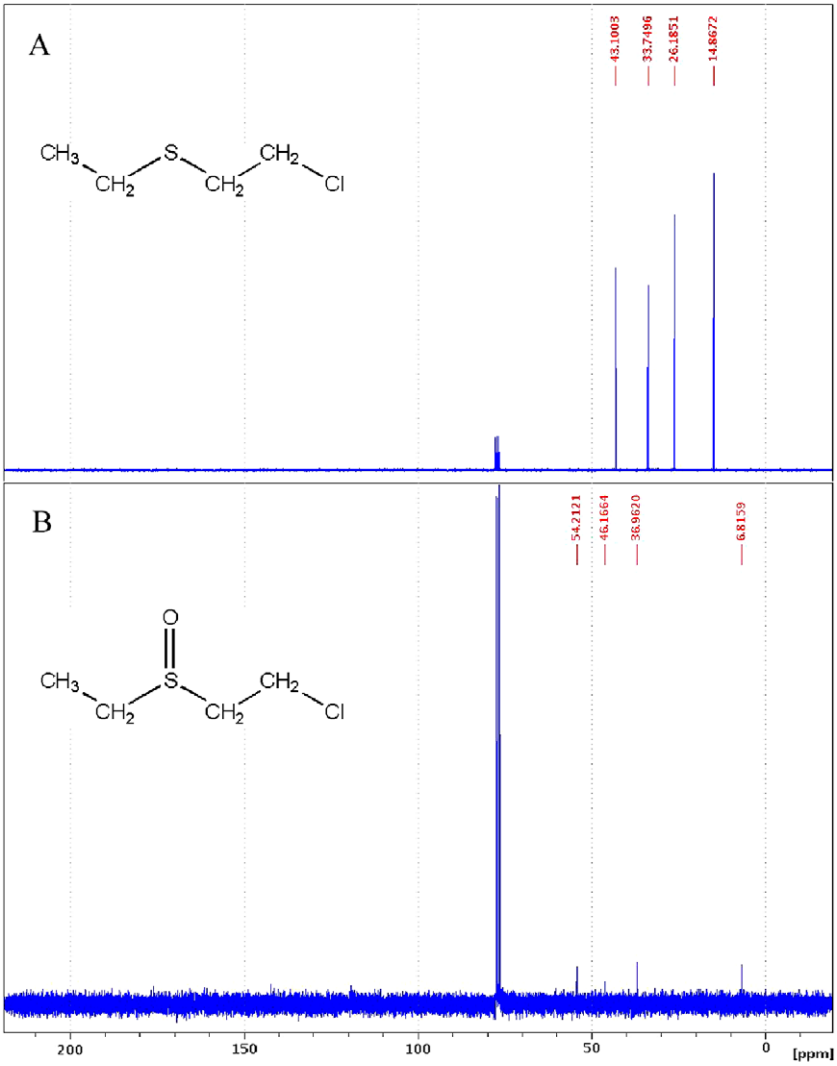

Fig. 6. ^{13}C NMR spectra ($CDCl_3$) showing the conversion of chloroethyl ethyl sulfide (A) to chloroethyl ethyl sulfoxide (B) over a 60 min period in contact with the chlorinated TTDD diol/BTCA cotton, the mole ratio being 3:1 oxidative chlorine to simulant.

different concentrations. The coated fabric was loaded with various amounts of chlorine upon exposure to dilute household bleach. The conversion of amide and/or amine groups into N–Cl moieties rendered the surface of the fabric more hydrophobic after chlorination, thus reducing the contact between the cells and oxidative chlorine and decreasing the biocidal activity against bacteria, as shown for the *N*-halamine siloxane-coated cotton fabrics. However, the diol groups on the surface of cotton fabrics coated with the *N*-halamine diol counter the hydrophobic effect shown for *N*-halamine siloxane coatings on the antimicrobial activity. The chlorinated cotton fabrics coated with TTDD diol/BTCA were also effective in oxidizing the mustard simulant to the less toxic sulfoxide product.

Acknowledgment

This work was supported by the US Air Force through Grant FA8650-07-1-5908.

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