

Durable antimicrobial cotton fabrics containing stable quaternarized *N*-halamine groups

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Abstract A novel *N*-halamine precursor with tertiary amino group (5,5-dimethylhydantoinyl-3-ylethyl)-dimethylamine (DEADH), was synthesized and then covalently bonded onto cotton fabrics modified by 3-chloropropyltrimethoxysilane to form quaternarized *N*-halamine precursor grafted cotton fabrics which could be transferred to *N*-halamine structure upon exposure to dilute sodium hypochlorite solution. The grafted cotton fabrics were characterized by FT-IR, X-ray photoelectron spectroscopy, and field emission scanning electron microscope. The antimicrobial test showed that the cotton fabrics grafted with the quaternarized *N*-halamine were capable of 7-log inactivation of *Staphylococcus aureus* and *Escherichia coli* O157:H7 within 1 min of contact time. Very interestingly, it was found that the grafting process and following chlorination had almost no adverse effect on the tensile strength of cotton fabrics.

Furthermore, the antimicrobial cotton fabrics exhibited good washing durability and stability.

Keywords Durable · Antimicrobial · Cotton fabric · Quaternarized *N*-halamine · Tensile strength

Introduction

Microbial contamination of polymeric materials plays an important role in the transmission of infectious diseases (Binder et al. 1999; Larson and Olmsted 2001; Neely and Maley 2000). Among these materials, textile materials, particularly natural fibers, with the favorable conditions such as humidity, warmth, and nutrients, are prone to microbial growth (Ren et al. 2009). Use of contaminated medical textiles is an important contributor to cross-infection. However, cotton does possess many functional groups, such as hydroxyl groups, which make it easily modified to render it antimicrobial. In that sense, quaternary ammonium salts (Colak and Tew 2008; Lin et al. 2003; Tiller et al. 2005; Wynne et al. 2011; Fulmer and Wynne 2011; Klivanov 2007; Waschinski et al. 2008; Eren et al. 2008), metal ions (El-Shishtawy et al. 2011; Takano et al. 2011), and *N*-halamines (Sun and Sun 2001; Liu et al. 2010; Makal et al. 2006; Cao and Sun 2009; Dong et al. 2011; Wang et al. 2011; Luo et al. 2011; Zhao et al. 2011), have been immobilized onto surfaces of cotton materials to reduce the risk of spreading pathogenic microorganisms.

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As one of the most effective biocides, *N*-halamine materials have created a great deal of interest in recent years for several reasons including their durability, recharge ability, and high antimicrobial efficacy against a broad spectrum of microorganisms. Among various *N*-halamine compounds, heterocyclic structures such as hydantoins, imidazolidinones, triazines, and oxazolidinones have been studied extensively to achieve higher stability in a wide range of temperatures and pH values as compared to noncyclic structures (Worley et al. 1999). Moreover, antimicrobial activity rates increase from amine halamine to amide halamine to imide halamine, whereas their stability decreases in that order (Qian and Sun 2004). 5,5-dimethylhydantoin, a commercially available cyclic *N*-halamine precursor containing both amide and imide groups, can react with halogenated siloxanes or epoxides through its imide group to form hydantoinyl siloxanes or epoxides which can be grafted onto the cotton fibers. It was reported that a powerful antimicrobial cotton fabric material was successfully prepared by covalently bonding a hydantoinyl siloxane onto cotton fabric and then chlorinating the grafted one (Ren et al. 2008a). However, the hydantoinyl siloxane was water-insoluble and the organic solvent was used to prepare the grafting solution. To avoid the use of organic solvents in grafting process, water-soluble *N*-halamine precursors are desirable.

In this study, a novel water-soluble *N*-halamine precursor with tertiary amino group, (5,5-dimethylhydantoinyl-3-ylethyl)-dimethylamine (DEADH), was synthesized by a dehydrochlorination reaction between 5,5-dimethylhydantoin and (2-chloroethyl)dimethylamine in ethanol. DEADH can not be directly grafted onto untreated cotton fabrics since it does not have coupling groups. To solve this issue, we grafted hydrolyzed 3-chloropropyltrimethoxysilane onto cotton fabric first and then bonded DEADH onto the modified cotton fabric through a quaternarization between DEADH and the grafted hydrolyzed 3-chloropropyltrimethoxysilane. After a convenient chlorination process, DEADH grafted on cotton fabric was converted to amide *N*-halamine structure. The whole procedure was shown in Fig. 1. Since DEADH was water-soluble and 3-chloropropyltrimethoxysilane could be hydrolyzed in water, no organic solvents were needed in the grafting process. Moreover, the coexistence of quaternary ammonium group and

N-halamine group in the surface of the as-prepared antimicrobial cotton fabric might lead to an enhancement of antimicrobial efficacy.

Experimental

Chemicals and reagents

Fabric swatches (Bleached 100 % Cotton Print Cloth) were obtained from Shanghai Luyang Window Decoration Co., Ltd. Gram-positive bacteria *Staphylococcus aureus* (*S. aureus*, ATCC 6538P) and gram-negative bacterial *Escherichia coli* (O157:H7 ATCC 11229) were purchased from Shanghai Institute of Materia Medica of the Chinese Academy of Sciences. The Trypticase soy agar used was from Sinopharm Chemical Reagent. Co., Ltd. 5,5-Dimethylhydantoin was obtained from Shanghai Yinghan Chemical Co., Ltd. Other chemicals and solvents were purchased from Aladdin Chemical Company.

Instruments

The NMR spectra were obtained using Bruker Avance 400. The IR spectra were obtained using Mattson PK-60000 infrared spectrometer. Elementary analysis was performed on Elementar Vario El III elemental analyzer. The X-ray photoelectron spectroscopy (XPS) spectra were obtained using Perkin Elmer PHI 5000 ESCT System. Field emission scanning electron microscope (FE-SEM) pictures were obtained using Hitachi S4800 scanning electron microscope.

Synthesis of (5,5-dimethylhydantoinyl-3-ylethyl)-dimethylamine (DEADH)

12.83 g (0.11 mol) of 99 % thionyl chloride was added to a 250 mL flask in the ice bath and then 8.91 g (0.10 mol) of 2-aminoethanol was slowly added under stirring. The mixture was heated to 35–50 °C while being stirred for 1 h, then 150 mL of ethanol was added and heated to its boiling. After cooled to ambient temperature, the intermediate compound (2-chloroethyl)dimethylamine hydrochloride was collected by filtration and purified by recrystallization from ethanol (Burckhalter et al. 1950). The obtained intermediate was mixed with 10.24 g (0.08 mol) of 5,5-dimethylhydantoin and 12.76 g (0.18 mol) of

covalently bonded to the amide nitrogen atom of DEADH in the grafted cotton fabrics was determined by a modified iodometric/thiosulfate titration procedure (Liang et al. 2006a). In this procedure, a small chlorinated cotton fabric sample (about 0.40 g) was suspended in a solution of 45.0 mL ethanol and 5.0 mL 0.1 N acetic acid. After addition of 0.30 g of KI, the solution was titrated with 0.10 N of sodium thiosulfate solution until the orange color disappeared at the end point. The weight percentage of oxidative chlorine in the cotton fabrics could then be calculated using the following equation.

$$Cl^+\% = \left[\frac{N \times V \times 35.45}{2 \times W} \right] \times 100\%$$

Where $Cl^+\%$ is the weight percent of oxidative chlorine on the sample, N and V are the normality (equiv/L) and volume (L) of the $Na_2S_2O_3$ consumed in the titration, respectively, and W is the weight of the cotton sample (g).

Evaluation of fabric mechanical properties

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 $250 \times 50 \text{ mm}^2$. Each sample was tested at least 3 times and average value was obtained.

Evaluation of antibacterial properties of textiles

2.54 cm^2 of square cotton fabrics, some untreated to serve as controls, others treated with DEADH, but unchlorinated, to serve as a second type of controls, and others treated with DEADH, but chlorinated, served as samples for antimicrobial efficacy testing. Dried fabrics were challenged with either *S. aureus* ATCC 6538P or *E. coli* O157:H7 ATCC 11229 using a modified AATCC 100-199 Test Method. $25 \mu\text{L}$ of bacterial suspensions buffered to pH 7 were placed in the center of a pair of cotton fabrics held in a place by a sterile weight to ensure good contact of the fabrics. After contact times of 1 and 5 min, the various fabrics were placed in sterile conical centrifuge tubes containing 9.5 mL of phosphate buffer and 0.5 mL of sterile 0.05 M sodium thiosulfate to quench any oxidative free chlorine which might have been present,

and vortexed for 250 s to remove bacteria. Then the swatches were removed, and serial dilutions of the quenched solutions were plated on Trypticase soy agar. The plates were incubated at $37 \text{ }^\circ\text{C}$ for 24 h and then counted for viable CFU of bacteria.

Evaluation of washing durability and stability

In this study, we adopted a standard washing test according to AATCC Test Method 61-2007 to measure the washing durability of both unchlorinated and chlorinated DEADH treated cotton fabrics (Ren et al. 2008b). Stainless steel canisters containing 150 mL of 0.15 % AATCC detergent water solution and 50 stainless steel balls and fabrics (1 in. \times 2 in.) were fixed in a Launder-Ometer (Darong Textile Instrument Co., Ltd., Zhejiang, China) and rotated at 42 rpm and $49 \text{ }^\circ\text{C}$ for 45 min. After 1, 2, 5, 10 washing cycles, samples were taken out and rinsed three times with distilled water and then dried at ambient temperature. Each cycle of washing in this method is equivalent to five machine washings. For unchlorinated DEADH treated cotton fabrics, one set of samples were chlorinated after 1, 2, 5, and 10 washing cycles, respectively. The percentages of oxidative chlorine (Cl^+) were measured by the modified iodometric/thiosulfate titration procedure to assess the durability of DEADH moieties bonded on cotton fabrics. For chlorinated DEADH treated cotton fabrics, the percentages of Cl^+ after 0, 1, 2, 5, and 10 washing cycles were measured to assess the stability of amide N–Cl bonds during washing. Also, chlorinated DEADH treated cotton fabrics were rechlorinated after each washing cycle and then the percentages of Cl^+ were measured to assess the durability of DEADH moieties on chlorinated cotton fabrics.

For stability test, 10.00 g of chlorinated DEADH treated cotton fabrics was stored at room temperature and then the percentages of Cl^+ were measured after a period of time to assess the stability of *N*-halamine antimicrobial moieties of chlorinated DEADH treated cotton fabrics during storage.

Results and discussions

Synthesis of DEADH

5,5-dimethylhydantoin is an important *N*-halamine precursor containing both cyclic amide and imide

groups. Its active imide group can react with some organic halides to form the derivatives of 5,5-dimethylhydantoin which can be grafted on the surfaces of materials and its amide group can be easily transferred to *N*-halamine functional group upon exposure to dilute sodium hypochlorite solution (Ren et al. 2008a; Liang et al. 2006b; Liang et al. 2007a). In this study, (2-chloroethyl)dimethylamine was used to react with 5,5-dimethylhydantoin to form (5,5-dimethylhydantoinyl-3-ylethyl)-dimethylamine (DEADH), a water-soluble hydantoinyl tertiary amine. It was found that ethanol is suitable solvent for this reaction. After reaction was over, the solvent could be collected by evaporation for reuse. The structure of DEADH was confirmed by $^1\text{H-NMR}$ spectrum, shown in Fig. 2.

Grafting DEADH onto the surface of cotton fabrics

3-Chloropropyltrimethoxysilane is a useful coupling agent which can react with tertiary amines or *N*-halamine precursors containing imide groups to form siloxane quaternary ammonium salts or siloxane *N*-halamine precursors. So far, many siloxane quaternary ammonium salts and siloxane *N*-halamine precursors have been synthesized and grafted onto cotton fabrics (Shao et al. 2004; Liang et al. 2007b). However, the

syntheses of such kinds of siloxanes required higher reaction temperature, longer reaction time, and high boiling solvent such as DMF. After reaction, the evaporation of DMF consumed more energy and took longer time. To overcome these disadvantages, we adopted an innovative grafting process to bond DEADH onto the surface of cotton fabrics. 3-Chloropropyltrimethoxysilane was hydrolyzed in water and then grafted onto cotton fabrics through a dehydration reaction. The chloropropyl groups on the surface of grafted cotton fabrics can react with tertiary amino groups of DEADH to form the quaternarized *N*-halamine precursor grafted cotton fabrics. In this paper, the immersion-dry-cure process was used to covalently bond DEADH onto the surface of hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabrics. It was found that the key parameters for grafting were curing temperature and time. After immersed in 6 % DEADH aqueous solution for 1 h, the wet cotton fabrics were dried at 95 °C for 1 h, and further cured at different temperatures for various times.

After curing, 0.10 % NaOCl aqueous solution was used to chlorinate the treated cotton fabrics to form antimicrobial quaternarized *N*-halamine on the cellulose. The mass-on of DEADH grafted onto cellulose

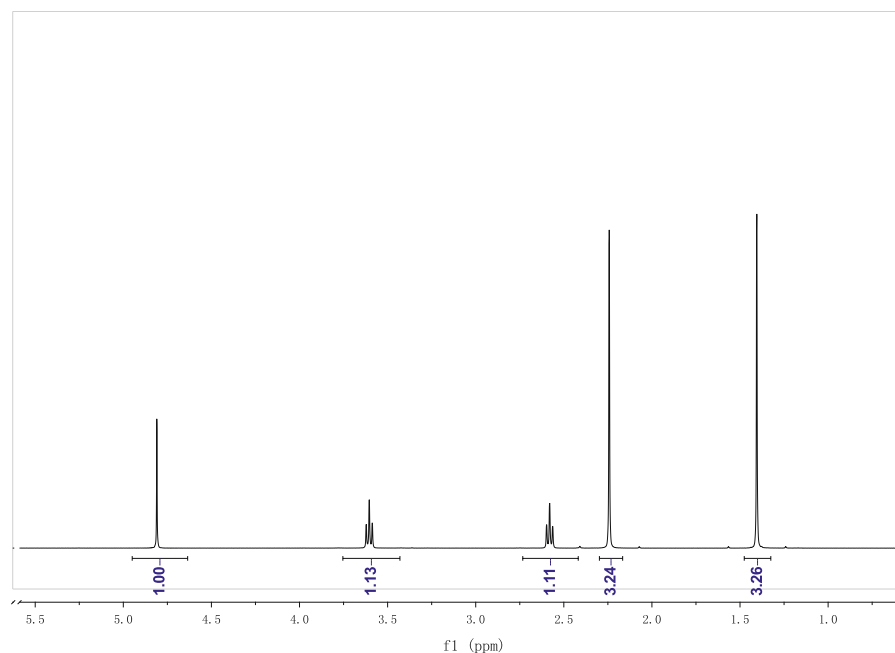


Fig. 2 $^1\text{H-NMR}$ spectrum of DEADH

can be estimated from oxidative chlorine percentage (Cl^+ %) in the cotton fabrics. Higher Cl^+ % indicates more DEADH grafted on the cotton fabrics. Figure 3 shows the effect of curing time on Cl^+ % in the cotton fabrics under 170 and 180 °C. It was found that longer curing time leads to higher Cl^+ % in the cotton fabrics under the same curing temperature. As shown in Fig. 4, higher curing temperature leads to a higher Cl^+ % in the cotton fabrics. However, too high curing temperature may lead to deterioration of cotton fabrics. Considering this factor, we chose 180 °C as optimistic curing temperature and 3 min as curing time.

Characterization of treated cotton fabrics

FTIR spectra were recorded and used to conform the effective grafting of DEADH onto cellulose. As shown in Fig. 5, Compared to untreated cotton fabric and hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, the DEADH treated one has two strong peaks at 1,712 and 1,769 cm^{-1} which are ascribed to the C=O stretching vibration on the hydantoinyl ring of DEADH (Wei et al. 2010; Cerkez et al. 2012). It clearly demonstrated that DEADH should have been covalently bonded onto cellulose because non-grafted water-soluble DEADH could be easily washed off from the surface of cotton fabric after curing.

The successful grafting of hydrolyzed 3-chloropropyltrimethoxysilane and then DEADH onto the surface of cotton fabrics can be ascertained by comparing the XPS spectra before and after the treatment of them.

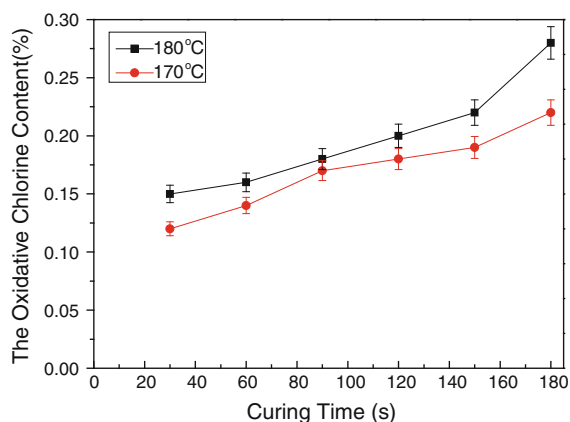


Fig. 3 Effect of curing time on Cl^+ % in the cotton fabrics

Figure 6 shows the XPS wide scans of untreated cotton fabric, hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, and DEADH treated one. In the case of untreated cotton fabric (a), the appearances of a C 1 s signal at a binding energy of 284 eV and an O 1 s signal at 532 eV verify the existence of carbon and oxygen in the untreated cotton fabric. In the case of hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric (b), except C 1 s peak and O 1 s peak, the appearances of a Cl 2p signal at a binding energy of 197 eV, a Si 2s signal at a binding energy of 154 eV, and a Si 2p signal at a binding energy of 103 eV conform the existence of chlorine and silicon which are characteristic elements of hydrolyzed

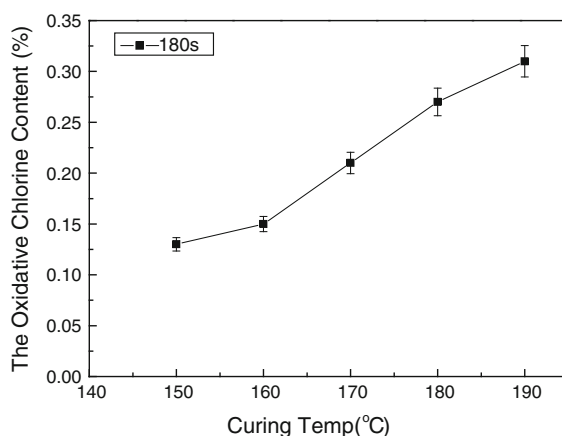


Fig. 4 Effect of curing temperature on Cl^+ % in the cotton fabrics (curing time: 3 min)

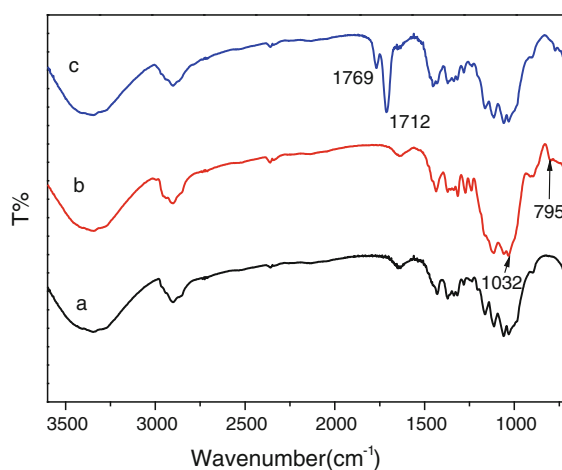


Fig. 5 FTIR spectra of (a) untreated cotton fabric, (b) hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, and (c) DEADH treated cotton fabric

3-chloropropyltrimethoxysilane. It means that hydrolyzed 3-chloropropyltrimethoxysilane has been successfully grafted onto the surface of cotton fabric. In the case of the DEADH treated cotton fabric (c), a new peak at about 400 eV corresponds to N 1s signal. From the inset of Fig. 6, it was found that a weak peak at 402 eV, corresponding to the nitrogen element of quaternary ammonium salt, almost merges with the peak at 400 eV which is ascribed to the nitrogen element of amide and imide groups in the hydantionyl ring of DEADH (Cheng et al. 2005; Yao et al. 2008; Tamura et al. 2012). It demonstrates that DEADH has been covalently bonded onto the cellulose and a quaternization reaction has occurred during curing process.

Surface morphologies of cotton specimens were investigated by the scanning electron microscopy (SEM). Figure 7 reveals the SEM images of untreated cotton fabric, hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, and DEADH treated cotton fabric. It seems that the curing process might cause slight damage on the cotton fabrics.

Antimicrobial efficacy evaluation

The antimicrobial efficacies for untreated cotton fabric, hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, DEADH treated cotton fabric,

and chlorinated DEADH treated cotton fabric against Gram-positive *S. aureus* and Gram-negative *E. coli* O157:H7 are presented in Table 1. As can be seen from Table 1, the chlorinated DEADH treated cotton fabric provided more than 7 log reduction of both *S. aureus* and *E. coli* O157:H7 within a contact time of 1 min. The super powerful antimicrobial efficacy of the chlorinated DEADH treated cotton fabric is probably due to synergistic enhancement of quaternary ammonium salt and *N*-halamine functional groups. For untreated cotton fabric, the log reductions of *S. aureus* and *E. coli* are 0.22 and 0.58 with a contact time of 1 min, 0.19 and 0.67 with a contact time of 5 min, respectively. For hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, the log reductions of *S. aureus* and *E. coli* are 0.64 and 0.61 with a contact time of 1 min, 0.74 and 0.79 with a contact time of 5 min, respectively. These small log reductions are possibly due to the adsorption of bacteria on the surface of cotton fabrics (Kang et al. 2013). For DEADH treated cotton fabric with quaternary ammonium salt groups on the surface, the log reductions of *S. aureus* and *E. coli* are 0.61 and 1.45 with a contact time of 1 min, 0.86 and 1.95 with a contact time of 5 min, respectively. It means that quaternary ammonium salt groups have much weaker antimicrobial efficacy than *N*-halamine groups.

Tensile strength

Figure 8 shows the tensile strength results of weft and warp yarns received from untreated cotton fabric, DEADH treated cotton fabric, and chlorinated DEADH treated cotton fabric. Statistically significant difference was not found on the tensile strength values after curing and chlorination processes. According to these results, it can be concluded that the curing and chlorination processes of the cotton fabrics did not cause any significant damage to the structure of the yarns.

Washing durability and stability

The greatest challenge to antimicrobial textiles is the durability of the antimicrobial moieties. For *N*-halamine grafted textiles, the washing durability mainly depends on the stabilities of covalent bonds between *N*-halamine molecules and the textile and *N*-halamine functional groups (N–Cl) during washing

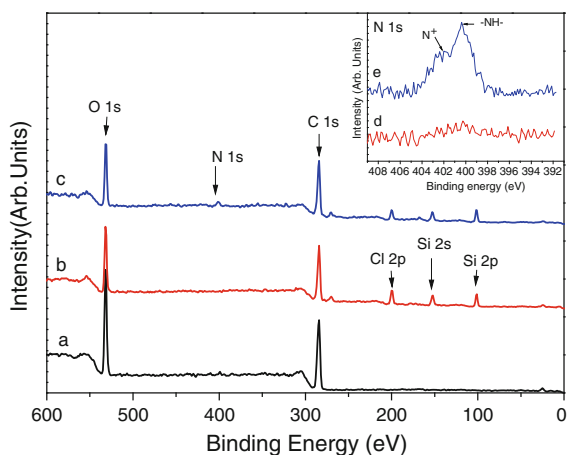


Fig. 6 XPS spectra of untreated cotton fabric (a), hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric (b), and DEADH treated cotton fabric (c). Inset: XPS spectra of hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric (d) and DEADH treated cotton fabric (e) between 410 and 390 eV

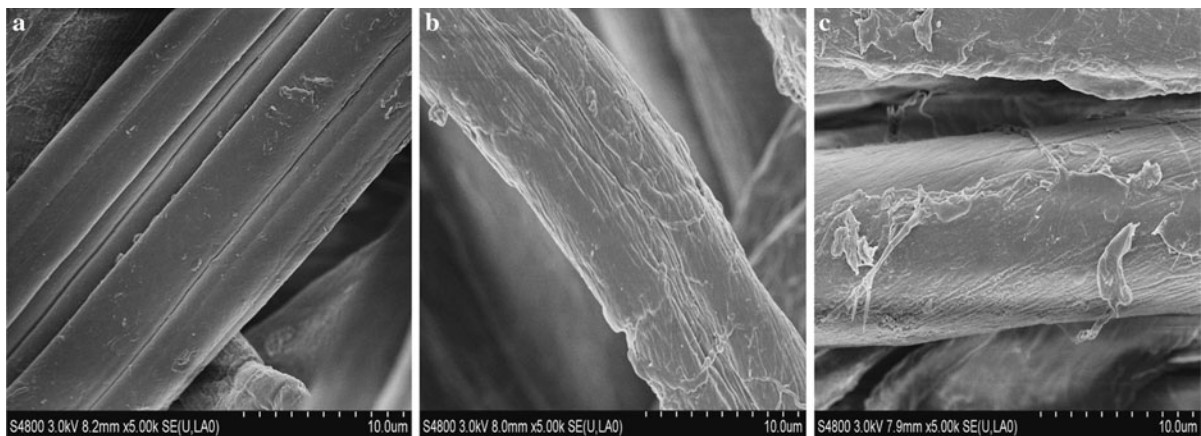


Fig. 7 FE-SEM images of (a) untreated cotton fabric, (b) hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, and (c) DEADH treated cotton fabric

Table 1 Antimicrobial efficacies against *S. aureus* and *E. coli* O157:H7 for untreated cotton fabric, hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric, DEADH treated cotton fabric, and chlorinated DEADH treated cotton fabric

	Contact time (min)	Log reduction of <i>S. aureus</i> ^a	Log reduction of <i>E. coli</i> O157:H7 ^b
Cotton control ^c	1	0.22	0.58
	5	0.19	0.67
Cotton grafted ^d 0 wt% Cl ⁺	1	0.64	0.61
	5	0.74	0.79
Cotton grafted ^e 0 wt% Cl ⁺	1	0.61	1.45
	5	0.86	1.95
Cotton grafted and chlorinated ^f 0.25 wt% Cl ⁺	1	7.42	7.15
	5	7.42	7.15

^a The sample was inoculated with 25 μ L of bacterial suspension at 2.61×10^7 CFU/mL

^b The sample was inoculated with 25 μ L of bacterial suspension at 1.41×10^7 CFU/mL

^c Untreated cotton fabric

^d Hydrolyzed 3-chloropropyltrimethoxysilane treated cotton fabric

^e DEADH treated cotton fabric

^f Chlorinated DEADH treated cotton fabric

process. In this study, we adopted a standard washing test to measure the washing durability of DEADH treated cotton fabrics. The results were shown in Table 2. For unchlorinated DEADH treated cotton fabrics, they were chlorinated after 1, 2, 5, and 10

washing cycles. The percentages of oxidative chlorine (Cl⁺) were 0.27, 0.22, 0.17, and 0.11 %, respectively. Based on the original 0.33 % of Cl⁺, it can be calculated that the Cl⁺% of DEADH treated cotton fabrics after 1, 2, 5, and 10 washing cycles decreased by 18.19, 33.34, 48.49, and 66.67 % which was caused by the departure of the whole DEADH moieties from cotton fabrics due to the disconnection of covalent bonds between DEADH moieties and cotton fabrics. For chlorinated DEADH treated cotton fabrics, the percentages of Cl⁺ after 1, 2, 5, and 10 washing cycles were 0.12, 0.05, 0.03, and 0.01 %, respectively. However, the percentages of Cl⁺ reached 0.27, 0.25, 0.18, and 0.14 % by rechlorination after 1, 2, 5, and 10 washing cycles. It clearly demonstrates that the decrease of Cl⁺% on chlorinated DEADH treated cotton fabrics during washing is caused by both the conversion of N–Cl to N–H groups and the departure of the whole DEADH moieties from cotton fabrics. Also, after 10 washing cycles, the lost percentages of the whole DEADH moieties for the chlorinated and unchlorinated DEADH treated cotton fabrics are 57.57 and 66.67 % according to the differences of Cl⁺% between original Cl⁺% and the Cl⁺% after 10 cycles. It means that the chlorinated DEADH treated cotton fabrics are more resistant to washing than the unchlorinated DEADH treated cotton fabrics, probably due to the increase of the surface hydrophobicity through the transformation of N–H to N–Cl groups (Cerkez et al. 2011).

N–X(X=Cl, Br, I) bonds in N-halamine compounds may change to N–H bonds during storage due to their

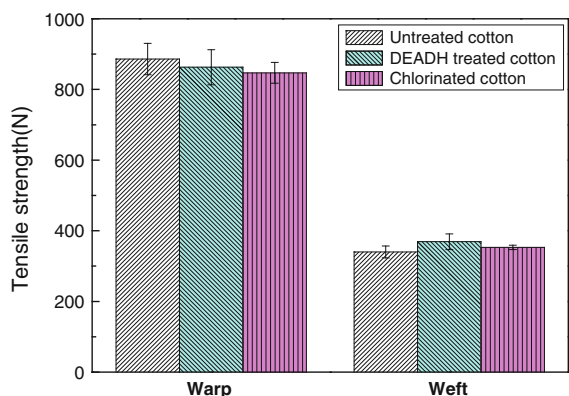


Fig. 8 Tensile strength results of weft and warp yarns received from untreated cotton fabric, DEADH treated cotton fabric, and chlorinated DEADH treated cotton fabric

Table 2 Washing durability testing results of DEADH treated cotton fabrics

Washing cycles*	X	Y	Z
0	0.33		
1	0.12	0.27	0.27
2	0.05	0.25	0.22
5	0.03	0.18	0.17
10	0.01	0.14	0.11

X chlorination before washing (Cl^+ wt%)

Y rechlorination after each washing cycle (Cl^+ wt%)

Z chlorination after each washing cycle only (Cl^+ wt%)

* Each cycle of washing in this method is equivalent to five machine washings

interaction with microorganisms, moistures, etc. Figure 9 shows the stability of N–Cl bonds in chlorinated DEADH treated cotton fabric under room temperature. After 5 days storage, the Cl^+ % of chlorinated DEADH treated cotton fabric decreased by 7.14 % from initial 0.28 to 0.26 %. From 5 to 30 days storage, the Cl^+ % of chlorinated DEADH treated cotton fabric kept almost constant. It means that the amide N–Cl bonds in chlorinated DEADH treated cotton fabric are very stable under room temperature. Also, as mentioned above, the lost Cl^+ during storage can be easily regained by rechlorination. In fact, most textiles need regular washing and the diluted bleach solution (NaOCl solution) can be added to washing machine to run in situ rechlorination for *N*-halamine textiles after a period of time.

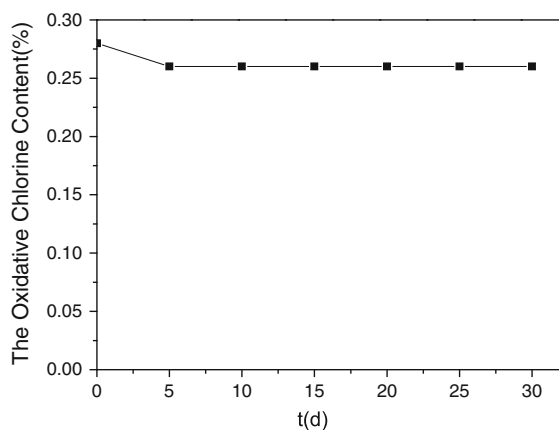


Fig. 9 Stability of N–Cl bonds in chlorinated DEADH treated cotton fabric under room temperature

Conclusions

DEADH, a new water-soluble hydantoinyl derivative, was synthesized by a dehydrochlorination reaction between 5,5-dimethylhydantoin and (2-chloroethyl)-dimethylamine. In order to avoid the time-consuming and energy-consuming synthesis of a quaternarized hydantoinyl siloxane between DEADH and 3-chloropropyltrimethoxysilane to form a quaternarized *N*-halamine precursor containing a coupling group for grafting, we developed a useful method to covalently bond DEADH onto the surface of cotton fabrics by the aid of 3-chloropropyltrimethoxysilane. DEADH is water-soluble and 3-chloropropyltrimethoxysilane can be hydrolyzed in water, so the two-step immersion-dry-cure process does not require any organic solvents. Very interestingly, the as-prepared antimicrobial cotton fabrics exhibited super strong capacity to kill harmful micro-organisms. Washing durability test indicated that 43.43 % of DEADH moieties remained on the surface of chlorinated DEADH treated cotton fabrics after 10 washing cycles (equivalent to 50 machine washings) and 0.14 % of Cl^+ could be reached by rechlorination which could still quickly kill bacteria. More importantly, the *N*-halamine moieties of the as-prepared antimicrobial cotton fabrics are very stable under storage condition due to the amide *N*-halamine structure and the tensile strength of them are almost the same as the untreated ones. With above-mentioned advantages, the as-prepared antimicrobial cotton fabrics will have potential applications in sports and leisure clothing,

home furnishings, hotel industry product, and particularly medical and healthcare textiles.

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