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Antibacterial functionalization of cotton fabrics by electric-beam irradiation

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ABSTRACT: An *N*-halamine precursor monomer, 2,2,6,6-tetramethylpiperidinyl acrylate (TMPA), was synthesized and successfully grafted onto cotton fibers via an impregnation process (IP) and electron-beam irradiation (EB). The grafted cotton fibers could provide antibacterial efficacy after chlorination through a dilute sodium hypochlorite solution. The antibacterial efficacy was challenged against *Staphylococcus aureus* and *Escherichia coli*. The cotton fibers grafted with TMPA and acrylic acid by EB inactivated all of the bacteria within 30 min of contact, whereas the samples grafted with TMPA via an IP could not completely kill the bacteria with 60 min. The breaking strength and UVA light stability also improved significantly. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42023.

KEYWORDS: cellulose and other wood products; coatings; fibers; grafting

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INTRODUCTION

With the development of antibacterial textile materials, nonharmful, ecofriendly, and highly efficient antibacterial agents and manufacturing methods have attracted researchers' attention. In the preparation of antibacterial materials, the choice of antibacterial agents is particularly important. Several antibacterial materials, including metals, quaternary ammonium salts,[1–3] chitosan,[4–8] triclosan,[5,8–10] and *N*-halamine,[11–15] have been widely applied in antibacterial materials. However, the drawbacks of some agents limit their practical application. Inorganic antibacterial agents, such as Ag and Cu, can cause environmental pollution. Quaternary ammonium salts have a low antibacterial efficacy and degradability problems. Chitosan treatment affects the texture of fabrics.[16] Among these antibacterial agents, *N*-halamines have been studied extensively and are considered to be ideal agents because of their superior antibacterial properties against a broad spectrum of bacteria, their nontoxicity, and their rechargability.[17] Materials, such as cellulose,[15] polyester,[18] nylon,[19] polypropylene,[20,21] polyacrylonitrile,[22] polyurethane,[23] cellulose acetate,[24] and chitosan,[25,26] have been functionalized with *N*-halamine to obtain antibacterial activity.

Recently, polymeric antibacterial *N*-halamines, such as poly [1,3-dichloro-5-methyl-(4′-vinyl phenyl) hydantoin], have been synthesized and have been shown to have good antibacterial efficacy.[27] *N*-Halamine polymers might be superior to other antibacterial polymers, such as polymeric phosphonium materials and polymeric quaternary ammonium compounds, in terms of their antibacterial efficacy, stability, rechargeability, and lack of toxicity.[1,28–30] To bond the polymeric antibacterial agents to existing polymeric backbones, both conventional chemical grafting techniques and radiation grafting methods have been used. Radiation grafting has some advantages over conventional chemical grafting methods in the modification of fibers.[31] Normally, conventional chemical grafting requires higher temperatures and initiators to increase the activities of molecules. In addition, a longer reaction time is necessary. Most of the initiators are oxidizers, which can seriously damage the breaking strength of the fibers, especially cotton fibers. Greatly different from the traditional grafting, electron-beam irradiation (EB) supplies high-energy rays and produces highly reactive intermediates; this can cause the grafting reaction to occur. Furthermore, the irradiation reaction can be carried out at room temperature without any initiators, and the reaction can be completed within several seconds. Recently, radiation grafting has been used to manufacture materials with special functionalities, such as flame retardancy,[32] water repellency,[33] anticreasing properties,[34] antibacterial efficiency, and rot resistance, for biomedical applications.[35]

In this study, the *N*-halamine precursor monomer, 2,2,6,6-tetramethylpiperidinyl acrylate (TMPA), was synthesized with acryloyl

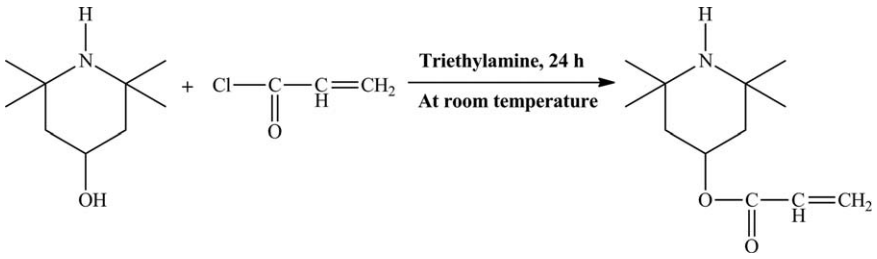

Figure 1. Synthetic route for TMPA.

chloride and 2,2,6,6-tetramethyl-4-piperidinol. The synthesized TMPA was grafted to cotton fibers via a conventional chemical grafting technique and by EB. The grafted cotton was characterized by Fourier transform infrared (FTIR)–attenuated total reflectance (ATR) spectroscopy, X-ray measurements, and scanning electron microscopy (SEM). The antibacterial efficacies of the chlorinated grafted cotton fabrics against *Staphylococcus aureus* and *Escherichia coli* O157:H7 were evaluated. The breaking strength and UV stability of the treated cotton were also investigated.

EXPERIMENTAL

Materials

The specification of plain-weave cotton fabrics were 133 × 72/40^S × 40^S, as provided by Zhejiang Guangdong Printing & Dyeing Co. (Zhejiang, China). Acryloyl chloride and 2,2,6,6-tetramethyl-4-piperidinaol were purchased from J&K Chemicals Co., Ltd. Other chemicals used in this research were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Instruments

An EB150/20–250S1 electron accelerator was provided by Hubei Eray Nuclear Technology Co., Ltd. The NMR spectra of the compounds were tested by an AVANCE III 400-MHz digital NMR spectrometer. The FTIR spectra of the cotton fibers were recorded with a Nicolet NEXUS 470 spectrometer.

Synthesis of TMPA

Acryloyl chloride (0.01 mol) was added to a solution of 2,2,6,6-tetramethyl-4-piperidinol (0.011 mol) and triethylamine (0.01 mol) in tetrahydrofuran (50 mL) at 0–5°C. The mixture was stirred at room temperature for 24 h, and the solution was concentrated by evaporation after the filtration and removal of the triethylamine hydrochloride produced in the reaction. The resulting solution was extracted with deionized water. The organic phase was dried in a vacuum oven overnight. The product was a light yellow oil (yield = 78.6%). The synthetic route is shown in Figure 1. TMPA was dissolved in $CDCl_3$ for NMR analysis. The spectral data for the sample are shown as follows.

^{1}H-NMR (400 MHz, $CDCl_3$-d1, δ): 6.54 (dd, 1H), 6.12 (dd, 1H), 5.52 (dd, 1H), 5.26 (m, 1H), 1.96 (d, 2H), 1.94 (d, 2H), 1.50 (s, 12H).

Grafting of TMPA onto Cotton by the Impregnation Process (IP)

In a typical run, TMPA was dissolved in distilled water containing equimolar acetic acid to prepare a 100 g/L (0.47 mol/L) TMPA solution. An amount of 0.25 g of cotton fabric was placed in a 250-mL, three-necked flask equipped with a condenser and magnetic stirrer. Then, 100 mL of TMPA solution and 0.20 g (0.94 mmol) of ammonium persulfate were added to the previous flask. After purging with N_2 for 30 min, the reaction was kept at 70–75°C for 8 h with constant stirring under a nitrogen atmosphere. After grafting, the cotton fabrics were washed thoroughly with alcohol and distilled water to remove any polymer of TMPA that might have adhered to the cotton. The grafted cotton fabrics were dried in a desiccator.

Grafting of TMPA onto Cotton by EB

TMPA was dissolved in distilled water containing an equimolar quantity of acetic acid and acrylic acid (AA; 1:1 w/w) to prepare a 100 g/L (0.47 mol/L) TMPA solution. An amount of 0.25 g of cotton fabrics was placed in a 150-mL beaker. After constant stirring for 30 min, the padded cotton fabrics were irradiated in N_2 by an electron beam at room temperature. The irradiation dose was 43 GKy. The average beam voltage and current were maintained at 130 kV and 1 mA, respectively.

Chlorination and Titration

The grafted cotton fabrics were immersed in a 10% sodium hypochlorite solution at room temperature for 2 h. The pH value was adjusted to 7 by diluted sulfuric acid. After chlorination, the cotton fabrics were washed thoroughly with distilled water and dried at 45°C for 1 h to eliminate unreacted chlorine. The active chlorine content of the cotton fabrics was measured by an iodometric/thiosulfate titration method.[14,36,37] The chlorinated cotton fabrics (0.2 g) were immersed in 20 mL of an ethanol/acetic acid solution in a Erlenmeyer flask; this was followed by the addition of 0.5 g of KI. The solution was titrated with a standardized $Na_2S_2O_3$ aqueous solution. The chlorine content (Cl^+) released from the cotton fabrics was calculated according to eq. (1):

$$Cl^+(\%) = \frac{nv \times 35.45}{w \times 2} \times 100 \quad (1)$$

where n and v are the normality (equiv·L^{-1}) and volume (L) of the titrant standardized sodium thiosulfate and w is the weight of the chlorinated cotton fibers (g).

Crystallinity Index

The X-ray diffraction spectra of the cotton fibers were recorded at room temperature from 10 to 65° with Cu/Kα irradiation (λ = 0.15406 nm) at 40 kV and 40 mA. The scan speed was 0.4°/min with a step size of 0.02°. The crystallinity index (*CrI*) was calculated from the X-ray spectra with the peak-height method:[38]

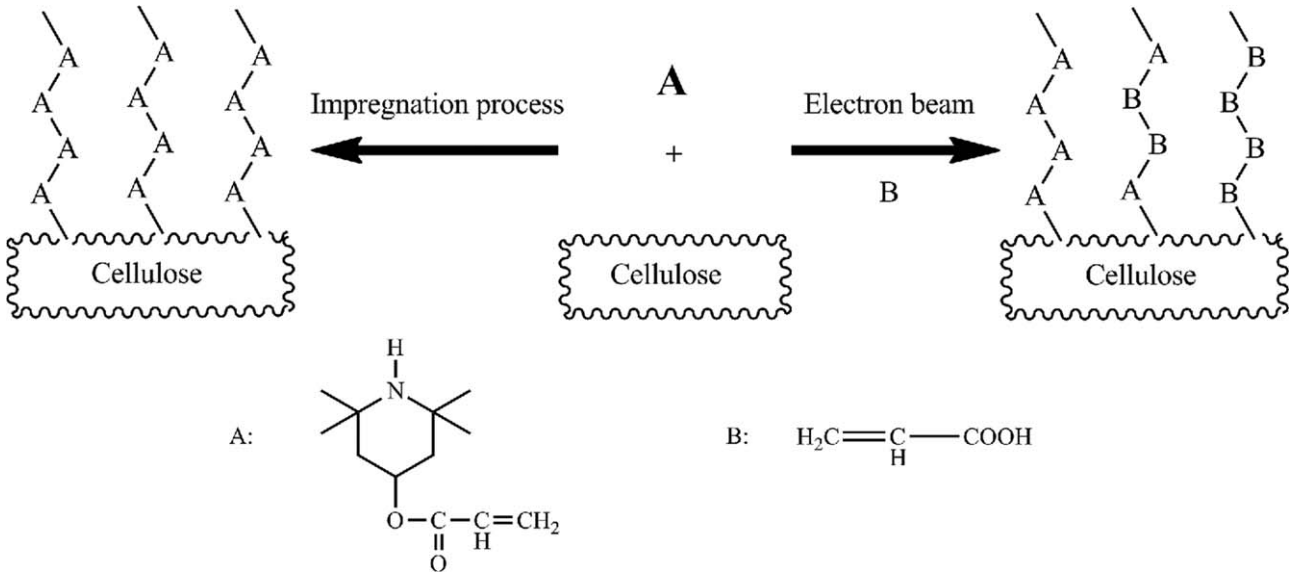

Figure 2. IP and EB used in this research.

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (2)$$

where I_{002} was the maximum intensity above baseline at $2\theta = 22.5°$ and I_{am} was the minimum in intensity above baseline corresponding to the amorphous region at $2\theta = 18.5°$.

Breaking Strength Testing

The breaking strength of the cotton fibers was determined by an electronic fabric strength tester according to the GB/T3923-1997 method. The warp direction of the breaking strength was tested. The cotton fabrics were cut into pieces with dimensions of 25 × 6 cm^2. Triplicates were produced for each sample, and their averages are reported.

Contact Angle Measurement

The contact angles were tested with water at room temperature with a JC2000D static contact angle goniometer. Each sample was tested at 10 different spots on the sample. A water drop volume of 1 μL was selected. The contact angles images were captured with a video camera and estimated by the software according to the Young–Laplace equation.

Antibacterial Test

The cotton fabrics grafted with the two methods were challenged with *S. aureus* (ATCC 6538) and *E. coli* (ATCC 43895) with a modified version of AATCC Test Method 100–1999. A volume of 25 mL of bacterial suspensions mixed with pH 7 phosphate buffer was placed in the middle of one piece of a cotton swatch, and another piece was sandwiched over it to ensure close contact between the bacterial suspension and the cotton swatches. After contact times from 10 to 60 min, the samples were quenched with 5.0 mL of 0.02*N* sodium thiosulfate to remove active chlorine. Serial dilutions were made with pH 7 phosphate buffer and plated on Trypticase soy agar. After incubation at 37°C for 24 h, the viable microorganisms were counted.

UVA Light Stability

An accelerated weathering tester was used in the UVA light stability test of the cotton fabric. Chlorinated cotton fabrics treated with the two methods were irradiated by UVA light in the range from 1 to 24 h. After exposure to the UV light, the cotton fibers were titrated or rechlorinated and titrated. The chlorine content retentions were calculated with eq. (3) as follows:

$$\text{Chlorine content retention (\%)} = \frac{\text{chlorine content retention after UVA light irradiation (\%)}}{\text{chlorine content retention before UVA light irradiation (\%)}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Preparation of the Antibacterial Cotton Fabrics

TMPA, an *N*-halamine precursor monomer containing an amino group (N—H), was synthesized. The N—H bond could be converted into an N—Cl bond after chlorination.[39] TMPA could be grafted onto cotton fibers via initiation at the unsaturated double bond. However, the cotton fibers grafted with TMPA turned into hydrophobic materials. The results of the antibacterial tests show that the hydrophobic materials could not kill all of the bacteria in a short time.[7,11,31] To improve the hydrophilicity of the treated cotton fibers, AA was added to the grafting solution. Meanwhile, AA was easily initiated for grafting because it contained an activated terminal alkene, which minimized steric hindrance.[22]

To obtain antibacterial cotton fabrics, two grafting methods were used in this study: IP and EB (Figure 2). In IP, cotton fabrics were immersed in TMPA or TMPA/AA solutions with ammonium persulfate as the initiator, and the temperature was

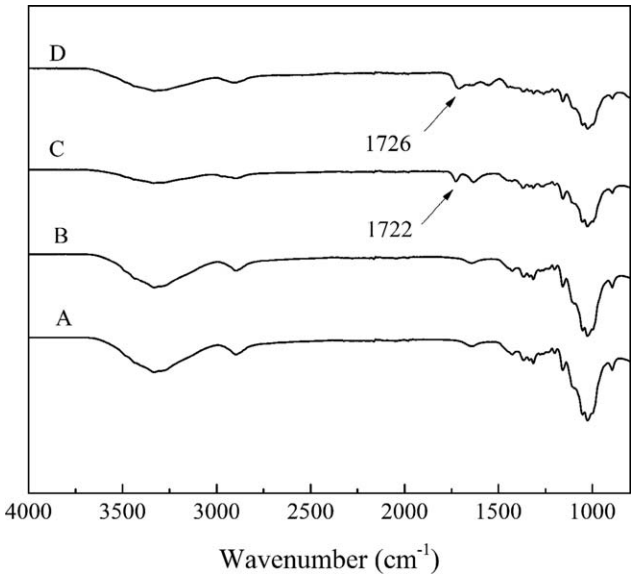

Figure 3. FTIR–ATR spectra for (A) cotton, (B) cotton irradiated with 43 kGy, (C) cotton–IP–Cl, and (D) cotton–EB–Cl.

kept at 70–75°C for 8 h under a nitrogen atmosphere. The chlorine contents of the cotton fibers grafted with TMPA (cotton–IP–Cl) and TMPA/AA were 0.11 and 0.03%, respectively, and their graft yields were 9.3 and 3.2%, respectively. The reason for the lower chlorine content of the cotton grafted with TMPA/AA was that the initiated AA aggregated easily,[30–32] and the poly(acrylic acid) prevented the monomers from grafting onto the cotton fibers in the extended time reaction.

The other grafting method was EB. In the reaction, the cotton fibers were padded with the solution containing TMPA or TMPA/AA. Then, the wetted cotton fibers were irradiated by an electron beam at room temperature under an N_2 atmosphere. More active groups on cotton cellulose chains could be initiated by the electron beam, such as at the positions of the 2,3 carbon atoms of the glucose ring and glycosidic bond.[22,33] The monomer could graft onto these positions. Meanwhile, because AA easily aggregated, the chlorine content of cotton fibers grafted with TMPA/AA (cotton–EB–Cl) reached 0.16% and was higher than that of the cotton fibers grafted with TMPA (0.08%). Their graft yields were 15.1 and 7.4%, respectively.

Characterization of the Grafted Cotton Fibers

In IP, only the hydroxymethyls on the units of cellulose could be converted to radicals by initiators.[40] Plenty of initiated monomers in solution could form homopolymers. By contrast, more positions, such as hydroxyl groups and carbon–carbon bonds on cellulose, could be converted to radicals by EB;[31] this led to the grafting of more monomers onto cellulose.

FTIR spectroscopy was used to confirm and characterize the grafting reaction of cotton with the monomers. The FTIR–ATR spectra of the untreated cotton fibers and cotton only irradiated

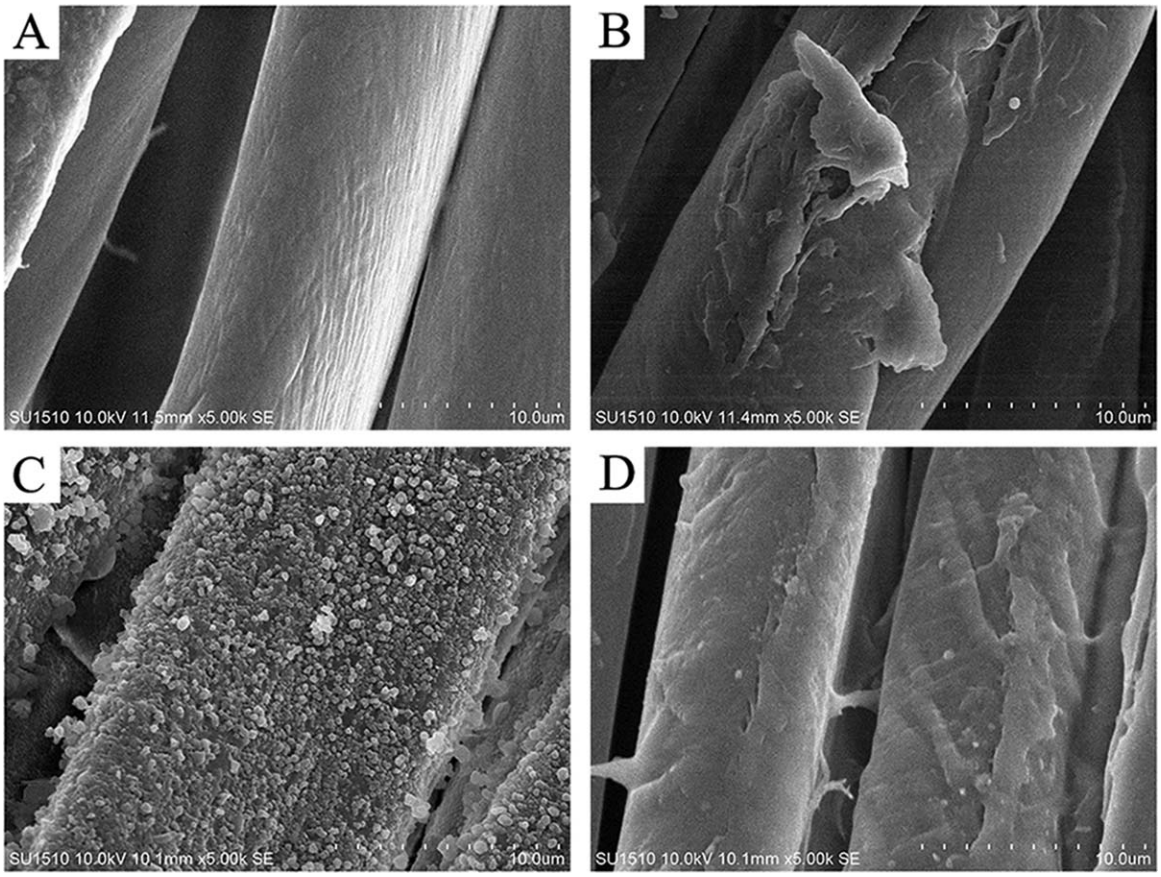

Figure 4. SEM micrographs of (A) cotton, (B) cotton irradiated with 43 kGy, (C) cotton–IP–Cl, and (D) cotton–EB–Cl.

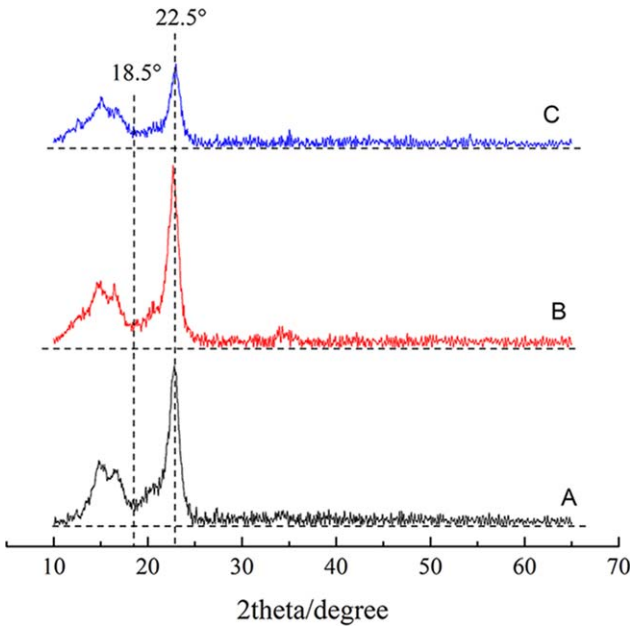

Figure 5. X-ray diffraction patterns of the cotton fibers: (A) cotton, (B) cotton–IP, and (C) cotton–EB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by EB are shown in Figure 3(A,B), respectively. There was no new peak or distinctive changes on the cotton after EB. However, the cotton grafted with TMPA or TMPA/AA showed new peaks at 1726 and 1722 cm^{-1} [Figure 3(C,D)]; these were attributable to the vibration of the carbonyl group in TMPA or AA.[34]

SEM was also used to investigate the surface morphologies of the cotton fibers and treated cotton fibers at 5000× magnification. The surface of the irradiated cotton swatches [Figure 4(B)] seemed to be corroded roughly, whereas the untreated cotton looked smooth [Figure 4(A)]. Meanwhile, the cotton grafted with TMPA [Figure 4(C)] or TMPA/AA [Figure 4(D)] became uneven; this indicated that the monomers were grafted onto the fibers successfully.

Figure 5 shows the X-ray diffraction pattern of the untreated cotton fibers and treated cotton fibers via IP and EB. It was clearly observed from the pattern that the maximum intensity above the baseline of the cotton irradiated with EB [Figure 5(C)] sharply decreased, whereas the X-ray pattern of the cotton fibers treated by IP did not show any difference from the control sample. The changes in the cotton fibers were expressed by the crystallinity index. According to eq. (2), the crystallinity index of the untreated cotton fibers was 54%, cotton–IP–Cl was 53%, and cotton–EB–Cl was 48%. After irradiation, the cotton fibers gained more amorphous regions to absorb monomers; this resulted in a higher chlorine content of the chlorinated grafted cotton fibers.

Breaking Strength Testing and Contact Angle Measurement

According to the GB/T3923-1997 method, the breaking strengths of the cotton, cotton–IP–Cl, and cotton–EB–Cl were tested. The warp breaking strengths of the cotton–IP–Cl and cotton–EB–Cl decreased from 851 to 215 and 617 N, respectively. The cotton fabrics were immersed in the solutions containing acetic acid during grafting, and the glycoside bonds of the cotton fibers were unstable under acidic conditions. With constant heating, the glycoside bonds of the cotton fibers accelerated hydrolysis in the IP; this caused a severe strength loss in the cotton. Although EB occurred at room temperature for only a few seconds, the breaking strength of the cotton–EB–Cl was much higher than that of the cotton–IP–Cl.

TMPA's four methyl groups made it hydrophobic. The treated cotton fibers became hydrophobic after grafting. The contact angle of the cotton grafted with TMPA was 108.7° [Figure 6(A)]. The addition of hydrophilic AA in grafting caused the contact angles to decrease to 97.4° [Figure 6(B)]. The cotton treated with TMPA/AA was easier to wet and put into contact with the bacterial suspensions.[41]

Antibacterial Efficacy

The antibacterial efficacy of the grafted cotton fabrics challenged against *S. aureus* and *E. coli* O157:H7 is summarized in Table I. As presented, the antibacterial efficacy of the cotton–EB–Cl was much better than that of the cotton–IP–Cl. We observed that the cotton–EB–Cl samples provided the complete inactivation of *S. aureus* within 30 min and *E. coli* O157:H7 within 10 min, respectively. However, the cotton–IP–Cl swatches showed only a 1.6 log reduction of *S. aureus* and 1.4 log reduction of *E. coli* after 60 min of contact time. The unchlorinated cotton samples showed small log reductions of both bacteria, mainly because of

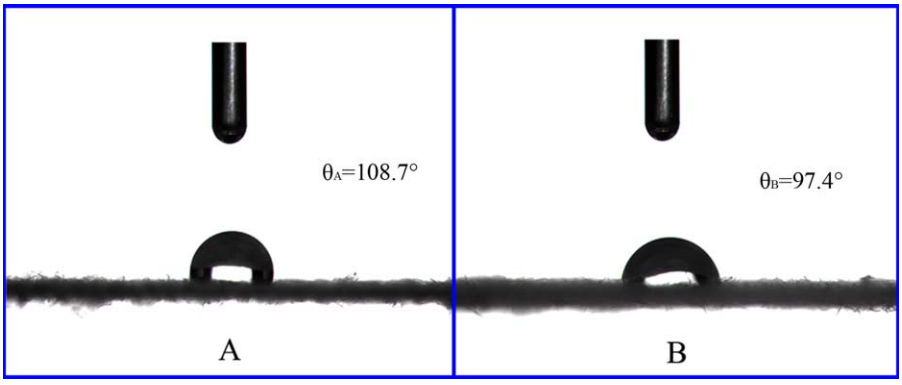

Figure 6. The contact angles of (A) cotton–IP–Cl, (B) cotton–EB–Cl (θ_A: the contact angle of cotton–IP–Cl, θ_B: the contact angle of cotton–EB–Cl). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Antibacterial Efficacy of the Grafted Cotton

Sample	Contact time (min)	Log bacterial reduction	
		S. aureus[a]	*E. coli* O157:H7[b]
Cotton–IP	60	0.64	0.02
Cotton–IP–Cl	10	0.82	0.06
	30	0.98	0.29
	60	1.60	1.40
Cotton–EB	60	1.45	0.81
Cotton–EB–Cl	10	3.86	6.05
	30	5.99	6.05
	60	5.99	6.05

[a] Inoculum concentration = 9.67×10^5 cfu.
[b] Inoculum concentration = 1.13×10^6 cfu.

the adhesion of the bacteria to the fiber surfaces. The cotton–EB–Cl samples were easier to wet and bring into contact with the bacteria during testing because of the addition of the hydrophilic group of AA, which resulted in higher inactivation rates.[18,41]

UVA Light Stability Testing

The results of the treated cotton fibers challenged with UVA light are shown in Table II. Under UVA light, most of the chlorine in the cotton–IP–Cl was lost after 4 h irradiation, whereas the chlorine content of the cotton–EB–Cl was 0.12% with the same exposure time under UV light, and it decreased to 0.03% after 24 h irradiation. After 24 h of irradiation, the treated cotton was rechlorinated. More than 90% of the chlorine content of the treated cotton could be recovered for both IP and EB; this indicated that the bonds between the cotton and the grafted polymer were very stable under UV light. The stability of the cotton fibers coated with *N*-halamines with a similar structure and containing amine groups was reported to be poor, and only 40% of the chlorine could be recovered upon rechlorination.[15] Therefore, the regenerability of the antibacterial grafted cotton treated by EB was improved significantly. A thin layer of film on the cotton treated by EB and containing poly(acrylic acid) might have reflected or absorbed UVA light to protect the cleavage of N—Cl bonds from irradiation,[42–44] and this led to the gradual decrease of chlorine.

Table II. UVA Light Stablity Test

Irradiation time (h)	Chlorine content (%)	
	Cotton–IP–Cl	Cotton–EB–Cl
0	0.11	0.16
1	0.04	0.15
2	0.02	0.13
4	0	0.12
8	0	0.11
12	0	0.07
24	0	0.03
Rechlorination	0.10	0.15

CONCLUSIONS

A *N*-halamine precursor monomer, TMPA was synthesized and successfully grated onto the cotton fibers via IP and EB. X-ray diffraction patterns showed that the crystallinity index of the grafted cotton fibers via EB decreased from 54 to 48%, whereas that of cotton treated with IP was almost the same as that of the untreated cotton. Compared with IP, EB processing was undertaken at room temperature within a few seconds without the addition of initiators; this could reduce processing costs in an industrial setting. The chlorinated cotton treated with TMPA/AA by EB could kill six logs of the *S. aureus* and *E. coli* within 30 and 10 min, respectively. However, the samples grafted with TMPA via IP could not completely kill the bacteria within 60 min of contact. In addition, the UVA stability of the cotton treated with EB was much better than that treated with IP, and over 90% of the chlorine could be regained after 24 h of irradiation and rechlorination.

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