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Environmentally Friendly Antibacterial Cotton Textiles Finished with Siloxane Sulfopropylbetaine

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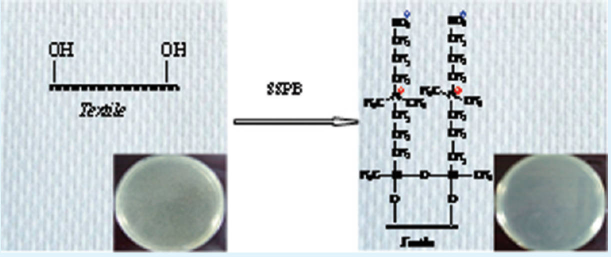
S *Supporting Information*

ABSTRACT: This paper reports a novel environmentally friendly antibacterial cotton textile finished with reactive siloxane sulfopropylbetaine(SSPB). The results show that SSPB can be covalently bound onto the cotton textile surface, imparting perdurable antibacterial activity. The textiles finished with SSPB have been investigated systematically from the mechanical properties, thermal stability, hydrophilic properties and antibacterial properties. It is found that the hydrophilicity and breaking strength are improved greatly after the cotton textiles are finished with SSPB. Additionally, the cotton textiles finished with SSPB exhibit good antibacterial activities against gram-positive bacteria *Staphylococcus aureus* (*S.aureus, ATCC 6538*), gram-negative bacteria *Escherichia coli* (*E.coli, 8099*) and fungi *Candida albicans* (*C.albicans, ATCC 10231*). Moreover, SSPB is nonleachable from the textiles, and it does not induce skin stimulation and is nontoxic to animals. Thus, SSPB is ideal candidate for environmentally friendly antibacterial textile applications.



KEYWORDS: siloxane, antimicrobial, betaine, finishing, textile, environmentally friendly

1. INTRODUCTION

Recently, textiles with antibacterial activity or antiviral activity have become extremely important in the health protection of human body. The antibacterial activity of textiles can be obtained through the antibacterial finishing of textile using antibacterial agents or by incorporating them into synthetic fibers during extrusion.[1] The number of antibacterial agents that are suitable for textile applications on the market has increased dramatically in the past decades. The main antibacterial agents include metals or metal salts,[2−5] quaternary ammonium compounds (QACs),[6−8] polybiguanides,[9] N-halamine,[10−12] chitosan,[13−15] and triclosan.[16] These antibacterial agents have expanded greatly the use of textiles in pharmaceutical, medical, engineering, agricultural and food industries. However, most of the antibacterial agents still have some disadvantages which limit their applications greatly. For instance, the uptake and durability of metals in textiles are the two big problems of treatment for the metal antibacterial agents. Many heavy metals are even toxic to environment.[1] The QACs also have some inherent weakness, such as leaching from the textiles, incompatibility with the anion surfactant.[17] Dow Corning Company had produced one kind of QACs antibacterial finishing agent with alkoxysilanes (AEM 5700) for covalently binding onto the textile surface, imparting durable antibacterial activity.[18] However, the antibacterial activity of this durable QACs was also decreased or even expired because of the absorption of dirt, deadly microorganisms or complex formation between the positively charged QACs and the negatively charged anionic detergent during repeated laudering[17] In addition, the low antibacterial activity to epiphyte and the weak light tolerance influences the applications of polybiguanides greatly. The bacterial resistance to triclosan has been well-documented and is of great concern. Triclosan has been banned in textiles and some other products by many countries because of its produced toxic polychlorinated dioxins upon exposure to sunlight.[1] The chitosan tends to be environmentally friendly in the antibacterial applications. However, the antibacterial activity of chitosan is pH-sensitive and limits to acidic conditions.[19,20] The chitosan also shows weak adhesion to cellulose fibers and is leached gradually from the fiber surface by repeated laudering.[17] These disadvantages motivate researchers to actively explore new antibacterial agents and technologies for antibacterial textiles finishing. In addition, antibacterial efficiencies and durability, environmental friendliness, health, and safety are also important to the antibacterial agents.

On the other hand, betaines represent a specialized family of zwitterionic materials that bear both cationic moiety like QACs and anionic functional groups like sulfo-, carboxy-, and phosphobetaines on the same repeat unit.[21,22] Recently, synthetic betaines have attracted a significant amount of interest because of their antipolyelectrolyte characteristics,[23,24] electrolyte-response,[25] bio/blood compatibility,[26,27] and antibiofouling properties.[28]

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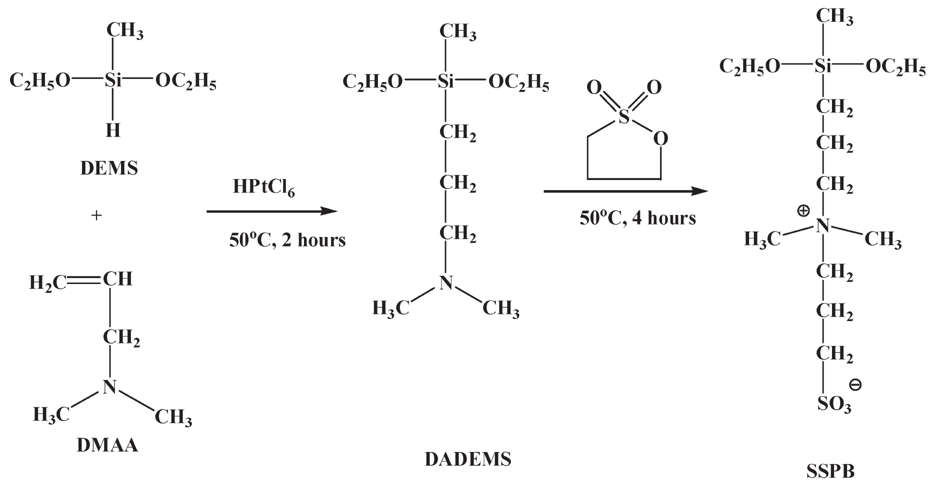
Scheme 1. Synthetic Routine of DADEMS and SSPB



Several betaines had been developed that show good antibacterial activity and a broad range of inhibition.[21,29−31] For example, ward et al. reported the polymethacrylic sulfopropylbetaine copolymers exhibiting good antibacterial activity against both gram-negative and gram-positive bacteria.[21] Cheng et al. demonstrated that surfaces treated with long-chain zwitterionic poly(sulfopropylbetaine methacrylate) were highly resistant to bacterial adhesion and biofilm formation.[29] Liu et al. reported that the chitosan/betaine derivative complex showed stronger antibacterial activity and a broader range of inhibition as compared with chitosan acetate alone.[32] These studies suggested that the betaines would be good antibacterial agents. However, previous studies mainly connect the betaine groups with the polymer backbone through ether,[28] amide,[26] imide,[22] or other hydrolyzable chemical bonds. These structures lead to the removal of the betaine groups in water by hydrolysis. Additionally, previous betaines have no reactive groups available to form strong bonds with the substrate. These disadvantages lead to the leaching from the substrate and the decrease of antibacterial activity during the utilization process. However, to the best of our knowledge, few reports have been published about the antibacterial textiles finished with betaines. Tuyoshi et al. had reported a novel alkoxysilane compound synthesized from propane sultone with N-propyl trimethoxysilane-N,N-dimethyl-N-(2-Carboxyethyl ammonium betaine. They proposed that the products can impart hydrophilicity to the surfaces of various base materials.[33] However, they do not investigate the antibacterial activity of the treated textiles with the alkoxysilane betaines.

Therefore, antibacterial agent sulfopropylbetaine containing reactive alkoxysilane group (SSPB) is synthesized and used for antibacterial finishing of cotton textiles in this work. Thereafter, the SSPB-finished cotton textiles have been investigated systematically from the mechanical properties, thermal stability properties, hydrophilic properties, and antibacterial properties. For environmentally friendly textile applications, the skin stimulation and acute toxicity of SSPB are also presented.

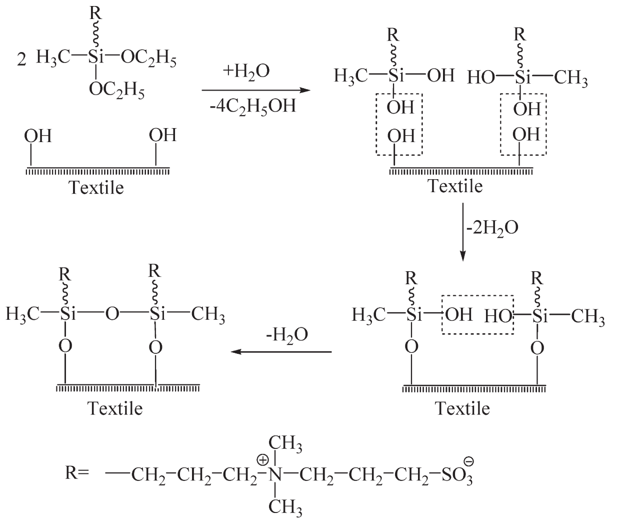
2. EXPERIMENTAL SECTION

2.1. Materials. Diethoxymethylsilane (DEMS, >99.0%, Qufu Chenguang Chemical Co. Ltd., China), hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, Tianjin Kermel Chemical Reagent Co. Ltd., China), and N,N-dimethylallylamine(DMAA, 99.5%, Huangshan Chemical Industry Co. Ltd., China) were purified by distillation before use. 1,3-Propanesultone (1, 3-PS, 99%, Quzhouxinteng Chemical Co. Ltd., China) was used without any pretreatment. Tetrahydrofuran (THF, AR, Guangzhou Chemical Reagent Factory, China) was dried with 4 Å molecular sieves over one week. Gram-positive bacteria *Staphylococcus aureus* (*S. aureus, ATCC 6538*), gram-negative bacteria *Escherichia coli* (*E. coli, 8099*), and fungi *Candida albicans* (*C.albicans, ATCC10231*) were purchased from Guangdong Institute of Microbiology, and were incubated at 30 °C on a nutrient agar plate for 24 h before use.

2.2. Synthesis of Siloxane Sulfopropylbetaine. The synthetic route of SSPB is presented in Scheme 1. Diethoxymethylsilane (0.1 mol), *N, N*-dimethylallylamine (0.1 mol), and chloroplatinic acid (0.01 mmol, dissolved in isopropanol) were added to a 250 mL three-necked flask equipped with a reflux condenser and a thermometer. Under the continuous stirring and N_2 condition, the reaction had been carried out at 50 °C for 2 h and the intermediate compound dimethylamine diethoxymethylsilane (DADEMS) was obtained. Thereafter, 0.1 mol 1, 3-propanesultone (dissolved in 100 mL THF) was added to the mixture and the reaction proceeded at 50 °C for another 4 h. Finally, the SSPB was obtained after extracting with absolute THF and drying under vacuum. The SSPB is hydrolyzed easily by water in air. Thus, the condensation product of SSPB, poly (siloxane sulfopropylbetaine) (PSSPB), was obtained by the hydrolysis−condensation reaction for further analysis like Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance(NMR). ^1H NMR of PSSPB (400 MHz, D_2O): δ(ppm) 0.26($C\underline{H}_3{-}Si$, 3H), 0.68($C\underline{H}_2{-}Si$, 2H), 1.85($C\underline{H}_2 - CH_2{-}Si$, 2H), 2.24($C\underline{H}_2$-−$H_2{-}SO_3$, 2H), 3.0($C\underline{H}_2{-}SO_3$, 2H), 3.1($(C\underline{H}_3)_{\underline{2}}{-}N^+$, 6H), 3.4($Si{-}CH_2{-}CH_2{-}C\underline{H}_2{-}N$, 2H), 3.7-($C\underline{H}_2{-}CH_2{-}CH_2{-}SO_3$, 2H). ^{13}C NMR of PSSPB (100 MHz, D_2O):δ(ppm) 1.49($\underline{C}H_3{-}Si$),15.3($\underline{C}H_2{-}Si$), 18.0($\underline{C}H_2{-}CH_2{-}Si$), 20.7($\underline{C}H_2{-}CH_2{-}SO_3$), 49.6($\underline{C}H_2{-}SO_3$), 49.7($(\underline{C}H_3)_2{-}N$), 64.3-($\underline{C}H_2{-}CH_2{-}CH_2{-}SO_3$), 68.6($\underline{C}H_2{-}CH_2{-}CH_2{-}Si$). Additionally, ^1H NMR,^{13}C NMR, and H−C COSY spectra of PSSPB are provided in the Supporting Information (see Figure S1).

2.3. Preparation of Cotton Textile Finished with SSPB. The resultant SSPB is a sol−gel precursor containing ethoxide groups (Si-OEt) that can easily hydrolyze to form silanol groups (Si−OH). The silanol groups further condense among each other or react with the hydroxyl group(−OH) of cotton fiber. The formation of covalent bonds between −SiOH groups of the hydrolytic SSPB and −OH groups of cotton fibers during the finishing process imparts the cotton textile with

Scheme 2. Reactive Principle of Cotton Textile Finished with SSPB



perdurable antibacterial activity.[17,34] The reactive principle of cotton textile finished with SSPB is presented in scheme 2. The typical finishing process of cotton textiles using the SSPB is described as follows. A commercial cotton textile is ultrasonic washed with dimethylacetamide and water in sequence for 10 min(mins) before it is dried in air. Thereafter, the clean textile is dipped in 2.0 wt % SSPB/alcohol finishing agent (liquor ratio 20:1). After being dried in air, the SSPB finished cotton textile can be obtained. The amount of SSPB on the surface of cotton textile is about 0.03 mg/cm^2. No unwanted color is observed in this SSPB finished cotton textiles.

2.4. Characterization. FT-IR spectra of samples were recorded with a Perkin-Elmer 1000 FT-IR spectrometer. Ten scans at 4 cm^{-1} resolution were signal averaged and stored as data files for further analysis. ^{1}H NMR, ^{13}C NMR and H−C COSY spectra of PSSPB were recorded on a 400 MHz spectrophotometer (AVANCE AV400, Bruker) at room temperature using D_2O/NaCl as the solvent (0.1 M NaCl) and tetramethylsilane (TMS) as an internal standard(as seen in Supporting Information in figure S1). The surface composition of the SSPB, cotton textile and cotton textile finished with SSPB was analyzed by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI 1800) using an Al Kα as the radiation source. A survey scan was collected over the range of 0−1300ev, and a high-resolution spectrum was collected for N1s. The take off angle of the photoelectron was set at 75°. Thermo-gravimetric analysis was conducted with thermo-gravimetric analyzer (TGA, Q50, TA Instruments, USA) under O_2 atmosphere with a flow capacity of 40 mL/min. The scan was carried out at a heating rate of 10 °C/min from 40 to 600 °C. The thermal transitions of samples were investigated using a differential scanning calorimetry (DSC, Q200, TA Instruments, USA) at a heating rate of 10 °C/min under continuous nitrogen flow. Scanning electron microscope (SEM) measurements were performed with Hitachi S-4800 scanning electron field-emission microscope. The samples were coated with gold before SEM scanning.

2.5. Evaluation of Fabric Mechanical Properties. The mechanical properties of the cotton textiles finished with SSPB and the raw cotton textiles were evaluated using a universal testing machine according to the standard test method of ISO 9073 part 3 (Strip Method).[35] All the tensile tests were carried out under the standard atmosphere with a temperature of 20 ± 2 °C and a relative humidity of 65 ± 2%. Five specimens (5 cm wide and 15 cm long) were cut and tested at a constant cross-speed of approximately 100 mm/min. The preload was 2 N and the distance between clamps was 100 mm. Finally, the mean values of tensile strength and elongation were recorded for further analysis. Standard error (S) was calculated using the following formula:

$$S = \sqrt{\frac{\sum(X_i - \bar{X})^2}{n-1}} \tag{1}$$

Where X_i is the experimental value, $\bar{X}$ is the mean value, and n is the total number of experiments.

2.6. Evaluation of Hydrophilicity of Cotton Textile Finished with SSPB. The hydrophilicity of raw cotton textiles and cotton textiles finished with SSPB was evaluated according to FZ/T 01071(2008) and ISO 9073−6(2000) textile-test method for capillary effect.Typically, three specimens (250 mm length, 30 mm width) were cut from the textiles in the right, middle and left direction, respectively. After conditioning at standard air condition with temperature of 25 ± 2 °C and relative humidity of 65 ± 3%, one side of the specimens was fixed on the backbone while the other side of the specimens was loaded vertically with a suitable clamp. The bottom of specimen was put below 15 mm ±2 mm of the zero point of ruler. Thereafter, deionized water with red ink was added to the vessel and the specimens were put into the water below zero point of the ruler. Finally, the water wicking height of specimens at different time was recorded for analysis. Each experiment was carried out in triplicate and the mean results were reported for analysis

2.7. Evaluation of Antibacterial Properties of Textiles. The antibacterial properties of raw cotton textiles and cotton textiles finished with SSPB against *E. coli*, *S. aureus* and *C.albicans* were quantitatively evaluated using viable cell count method.[34,36] To investigate the washing durability of antibacterial activity, the antibacterial rate of cotton textile finished with SSPB was evaluated after 50 washes according to FZ/T 73023−2006 standard method. The leachability of SSPB from cotton textile was determined by diffusion method on agar plate after washing one time according to FZ/T 73023−2006 standard method. In a typical washing cycle, the textile sample was first washed for 5 min in the washing machine with a common washing agent and 40 °C water (2 g/L). Thereafter, the sample has been rinsed for two times. In each cycle, the textile was washed for 2 min and dehydrated for 30 s. The above steps were repeated to the predetermined washing times. To avoid the interrupt of washed agent, the textile sample should be washed with a large amount of water and dried in air before the antibacterial testing. The colonies of the bacterium on the agar plate were counted and the reduction in number of the bacterium was calculated using the equation below.[37]

$$\text{reduction rate } (\%) = \frac{A - B}{A} \times 100 \tag{2}$$

Where A is the number of bacterial colonies after 18 h contact on the raw cotton textile (control, unfinished textile), and B is the number of bacterial colonies after 18 h contact on the cotton textile finished with SSPB. Each experiment was carried out in triplicate and the mean results were reported for analysis. Antibacterial kinetics of raw cotton textiles (control) and the cotton textiles finished with SSPB were investigated by studying the dependency of antibacterial rate on the contact time.

2.8. Skin Stimulation and Acute Toxicity of SSPB. Skin stimulation of SSPB was carried out on three New Zealand rabbits (1 male and 2 female). The rabbits were treated with 0.5 mL of 5 times of the used concentration solution of SSPB(100 g/L) layered on one side of the vertebral column (with hair removed), with the other side used as a control. These animals were regularly observed for 7 days after receiving according to technical standard for disinfection (Ministry of healt of P.R.China, 2002).[38] In this experiment, the integral skin irritation (I_t) is defined as

$$I_t = \frac{\sum(S_{eri} + S_{edi})}{n} \tag{3}$$

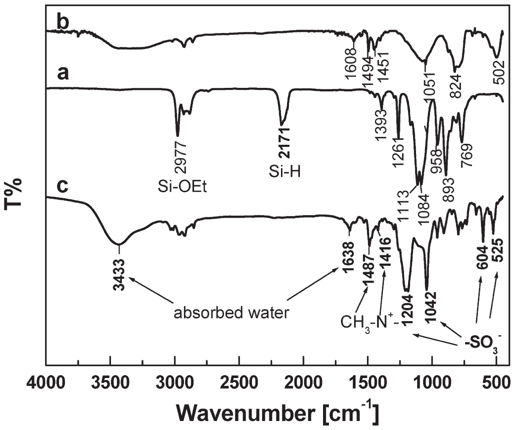


Figure 1. FT-IR spectra of (a) DEMS, (b) DADEMS, and (c) PSSPB.

Where, S_{er} is scores of erythema, S_{ed} is scores of edema, i is number of the tested rabbit (i = 1, 2, 3), t is the time of stimulation (t = 1, 24, and 48), and n is the numbers of tested rabbits. The class of skin stimulation for the tested sample is evaluated according to the maximum integral skin irritation (I_{tmax}). The evaluation criteria of S_{er}, S_{ed}, and the intensity of skin irritation are provided in the Supporting Information (Tables S1 and S2).

To test the acute toxicity of SSPB, we used Horn's method. Twenty SPF level NIH rats were housed and maintained at 22 °C with free access to water and no food for 16 h; 5000 mg SSPB/kg BW by oral gavage was used. The experimental animals were observed immediately after receiving the drug over the exposure time of 14 days. The change of organs or the numbers of killed rats are used for evaluation of acute toxicity of sample.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis of SSPB. Figure 1 presents the FT-IR spectra of DEMS, intermediate compound DADEMS and the hydrolysis product PSSPB. The band at about 2171 cm^{-1} in the spectrum of DEMS is characteristic of the Si—H stretching vibration and this band is not observed in the DADEMS and PSSPB spectra, this indicates that the reaction between DEMS and *N,N*-dimethylallylamine went to completion. As compared with the FT-IR spectra of DEMS and DADEMS, new absorption peaks at 1042 and 1204 cm^{-1} can be observed in the spectrum of PSSPB. These bands are ascribed to the symmetric and asymmetric stretching vibration of SO_3^- group. The presence of the absorption peaks at 604 and 528 cm^{-1} also indicate the existence of the SO_3^- group.[39,40] In addition, the stretching vibration of C—N and methyl group of quaternary ammonium salt (N^+—CH_3) are also observed at 1416 and 1487 cm^{-1}, respectively, in the spectrum of PSSPB.[41] It indicates that the resultant PSSPB contains both quaternary ammonium and sulfonic salts. Additionally, the absorption peak at 2977 cm^{-1} assigned to the ethyl group of Si-OEt disappears in the spectrum of PSSPB. Thus, this confirms that SSPB is completely hydrolyzed into PSSPB in presence of water due to the hydrolysis—condensation reaction. Furthermore, the ^{1}H NMR, ^{13}C NMR and H—C COSY spectra also show the exact structure of PSSPB (as seen in the Supporting Information in Figure S1). Additionally, the PSSPB spectrum also has new peaks at 3433 and 1638 cm^{-1}. These bands are ascribed to the stretching vibration and bending vibration of O—H group of adsorbed water. This implies that the obtained PSSPB should have good hydrophilic properties. Moreover, it is observed during the DSC testing (as seen in the Supporting Information in Fgure S2) that the glass transition temperature (Tg) of dried PSSPB is measured at 57 °C, and the T_g shifts to lower temperature range after it absorbs water or moisture. It is very consistent with the results observed in literature.[42] Thus, it is confirmed that PSSPB has good hydrophilic properties, which may improve the hydrophicity of SSPB finished textile.

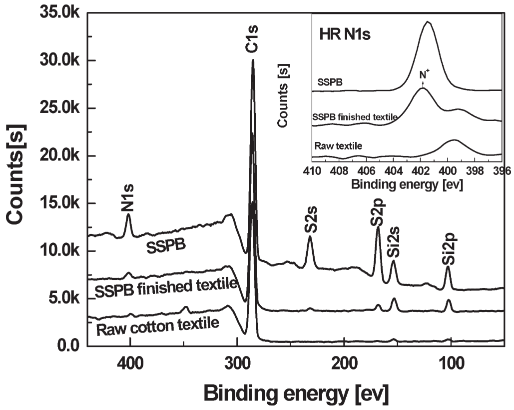


Figure 2. XPS spectrum of SSPB, raw cotton textile and cotton textile finished with SSPB.

3.2. XPS Analysis. Figure 2 shows the XPS spectra of SSPB, raw cotton textile and cotton textile finished with SSPB. The surface elemental composition of SSPB was identified by a survey scan using the XPS spectrum of SSPB. It is known that the XPS signals at 169 eV, 285 eV and 402 eV are attributed to S2p, C1s and N1s, respectively.[43,44] In this case, the experimental molar ratio of S, N and Si is 1.3:1.1:1, which is very close to the theoretical values (1:1:1). The S atomic percentage is higher than the Si atomic percentage, indicating that the surface is enriched in sulfobetaine groups.[45] It confirms that the resultant product is the siloxane sulfopropylbetaine. Additionally, only one nitrogen peak at 402 eV is presented, corresponding to the C—N group of quaternary ammonium salt, in the high-resolution N1s spectrum of SSPB.[46] This indicates that the tertiary ammonium of DADEMS is completely converted into quaternary ammonium of SSPB. In addition, the attachment of SSPB on the cotton textile surface can be ascertained through the comparison study of XPS spectra between the raw cotton textile and the cotton textile finished with SSPB. It is found in Figure 2 that there is a new peak at 168 eV attributed to S2p in the cotton textile finished with SSPB. However, no such peak can be found in the XPS spectrum of raw cotton textile. As compared with the raw cotton textile, the N1s and Si2p peaks are much higher in the cotton textile finished with SSPB. Moreover, in the high-resolution N1s spectra of SSPB, cotton textile and cotton textile finished with SSPB as shown in figure 2, a new peak at 401.8 eV attributed to the positively charged nitrogen (N^+) of SSPB appears in the cotton textile finished with SSPB. Thus, it is confirmed that the SSPB is covalently bound to the cotton textile successfully.

Additionally, it is found that the ratio of N1s/S2p in the cotton textiles finished with SSPB is 1.4/1.0. The percentage of N^+ (cation) in the N1s of SSPB finished textile is about 71% as determined *via* XPS testing. Thus, the ratio N^+ (cation)/SO_3^- (anion) of textiles finished with SSPB is 1.01 (the calculation is provided in the Supporting Information, Figure S3a,b). This result is expected if charge neutrality is maintained.[47] Therefore,

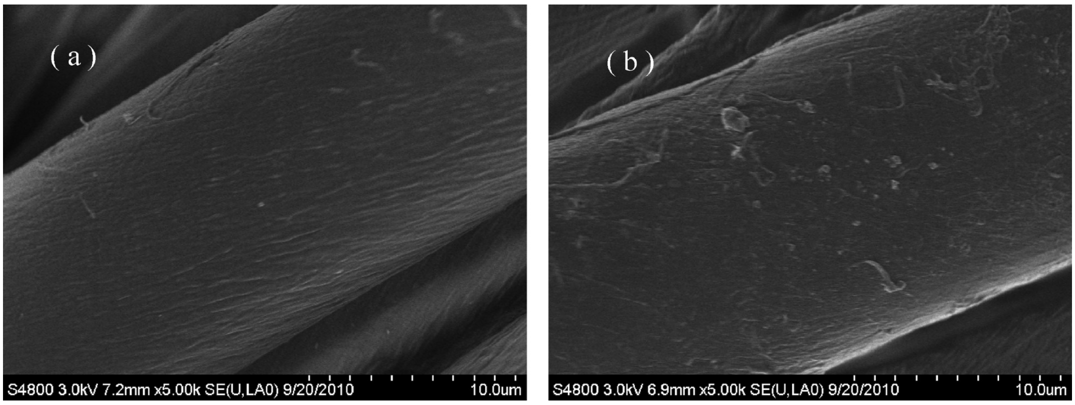


Figure 3. SEM images of (a) raw cotton textile and (b) cotton textile finished with SSPB.

it indicates that the cotton textiles finished with SSPB show charge neutrality.

3.3. Surface Morphology of Cotton Textile Finished with SSPB. SEM technique was used to investigate the surface morphology of raw cotton textile and cotton textile finished with SSPB. According to the SEM observation, one can get direct information about the nature of coating, the compatibility between the surface of fabric with the coating, and the distribution of coating along the surface.[48] Figure 3 presents the SEM images of cotton textile finished with SSPB comparing with raw cotton textile. It is observed obviously that a discontinuous thin film and some nanoscale attachment are bound to the surface of cotton fiber finished with SSPB, whereas there is no attachment on the surface of raw cotton textile. This confirms again that SSPB is bound successfully to the cotton textile. The SSPB finishing process of cotton textile is carried out in the aqueous medium. It is proposed that the SSPB finishing process of cotton textile is an environmentally compatible process having the potential for scaling up manufacturing of antibacterial textiles.[35]

3.4. Hydrophilicity of Cotton Textile Finished with SSPB. To investigate the hydrophilicity of textiles, we measured water contact angle and water absorption rate in this experiment. It is found that the initiative contact angle of raw cotton textile is 60°, and it gradually declines to 0° within about 10 s because of the smooth surface of raw cotton textile. However, the water contact angle on cotton textile finished with SSPB is reduced to 0° within less than 0.1 s. This is due to the fact that the surface becomes rough after the discontinuous SSPB layer is coated on the surface of cotton textile as observed in the SEM images. In addition, it is also found that the water absorption rate of cotton textile finished with SSPB is very fast. The possible mechanism to the hydrophilicity can be explained as follows. When water is absorbed onto the surface of hydrophilic fabric like SSPB finished cotton textile, it transfers on the fabric. This process is caused by capillary penetration. The original force for capillary penetration is the hydrophilicity of the fabric, which strongly depends on the surface energy and the surface roughness.[49]

To further study capillary penetration of cotton textile, we investigated the hydrophilicity of raw cotton textile and cotton textile finished with SSPB according to the procedure described in standard method FZT/T 01071(2008). Figure 4 presents the capillary effect of cotton textile finished with SSPB comparing with the raw cotton textile. It is well-known that the higher the water wicking height, the better hydrophilic. It is found in Figure 4 that the water wicking height of cotton textile finished with SSPB and raw cotton textile within 5 min is 80 and 35 mm, respectively. Continuously, the water wicking height of cotton textile finished with SSPB reaches 105 mm within 10 min, and 140 mm within 30 min. However, the water wicking height of raw cotton textile is only 50 mm within 10 min, and 65 mm within 30 min. After 120 min, the water wicking height of raw cotton textile and cotton textile finished with SSPB reaches 92 and 192 mm, respectively. Thus, it confirms that the hydrophilicity of cotton textile finished with SSPB is better than that of the raw cotton textile. i.e., the hydrophilicity of cotton textiles is improved through the SSPB finishing.

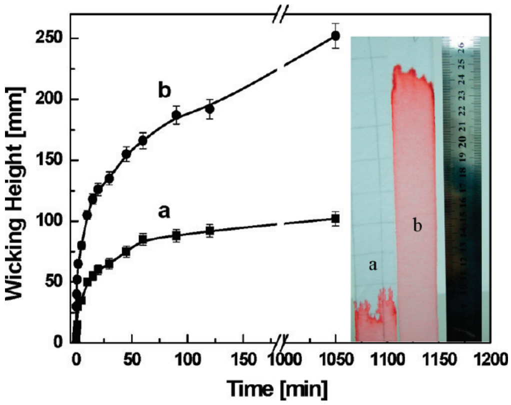


Figure 4. Capillary effect of (a) raw cotton textile and (b) cotton textile finished with SSPB. Each symbol indicates the means ± error limits for three observations.

3.5. Thermal Stability. In this experiment, the thermal stability of cotton textile finished with SSPB comparing with the raw cotton textile was investigated by thermagravimetric (TG) analysis and derivative thermogravimetry (DTG) analysis under an oxygen atmosphere(60 mL/min) at a heating rate of 10 °C/min. The TG and DTG curves are presented in Figure 5. It is observed that the degradation in both samples takes place in two stages. The start decompose temperature of raw cotton textile is 223 °C, and the raw cotton textile loses its 70.3% weight rapidly before the temperature is raised to 320 °C. The temperature for 95% residual weight is 278 °C and the maximum rate of weight loss occurs at 314 °C in the raw cotton textile. These weight loss at the first stage could be attributed to a complex process, including degradation of the saccharide rings and the disintegration of macromolecule chains of cotton fiber.[50] After the temperature is raised to above 320 °C, the weight loss is slow down and only 1.73% residual weight is left at 600 °C. However, in the cotton textile finished with SSPB, the decomposition at the first stage starts at 189 °C and proceeds at a faster rate until 267 °C. Within this temperature range, the cotton textile finished with SSPB has lost its 43.4% weight. Similarly, this process is resulted from a combination of decomposition of macromolecular chain carrying sulfopropylbetaine groups, the degradation of saccharide rings and the disintegration of macromolecule chains of cotton fiber. Beyond this temperature, the degradation proceeds at a relatively slow rate until 600 °C. At this stage, the maximum rate of weight loss occurs at 449 °C. Finally, there is only 3.0% residue at 600 °C. According to the TG and DTG plot of two samples, it is found obviously that the initial decomposition temperature (T_i) and the temperature for the maximum rate of weight loss (T_{max}) are lower in the cotton textile finished with SSPB as compared with the raw cotton textile. However, the T_i and T_{max} of cotton textile finished with SSPB at the second stage are higher than that of raw cotton textile. It indicates that the degradation of raw cotton textile takes place at a higher temperature as compared with the cotton textile finished with SSPB, i.e., the SSPB finishing reduces the thermal stability of cotton textile. This is due to the fact that the thermal stability of SSPB is lower than that of raw cotton textile.

3.6. Mechanical Properties of Cotton Textile Finished with SSPB. Figure 6 shows the mechanical properties of cotton textile finished with SSPB as compared with the raw cotton textile. The mechanical properties of cotton textile in particular breaking strength are usually damaged during the antibacterial finishing process. For example, the breaking strength of raw fabrics was decreased by 11.93% (from 24.57 to 21.64%) after bleaching with hydrogen peroxide and a fluorescent brightening agent. To acquire the antibacterial activity, the bleached fabrics were finished with triclosan through a conventional pad−dry process using polycarboxylic acids as cross-linking agents and phosphorus-containing acids as catalysts. The breaking strength of antibacterial cotton textiles was further reduced by 6.9−55.0%.[16] In addition, Soares and co-workers prepared a antibacterial cotton by polymerization of glycidyl methacrylate (GMA) with 1,4-diazabicyclo(2,2,2) octane monocationic salt (MS) derivative in the presence of free radical initiators sodium bisulfite and potassium persulfate. They found that the tensile strength was reduced from about 300 to 265 N in the warp direction (decreased by about 12%) and reduced slightly in the weft direction.[35] In the present work, it is noted that the breaking strength of cotton textile finished with SSPB is improved significantly from about 265N to 322N in the weft direction and from about 586N to 652N in the warp direction as shown in Figure 6a, i.e., the breaking strength of cotton textile finished with SSPBs is increased by about 21.5% in the weft direction and about 11.3% in the warp direction. At the same time, it is found in Figure 6b that the maximum breaking elongation is reduced slightly from about 68 to 64% in the weft direction (decreased by 5.9%) while it is improved from about 32.9 to 37.7% in the warp direction (increased by 14.5%). Therefore, the mechanical properties of cotton textile finished with SSPB are improved significantly as compared with the raw cotton textile.

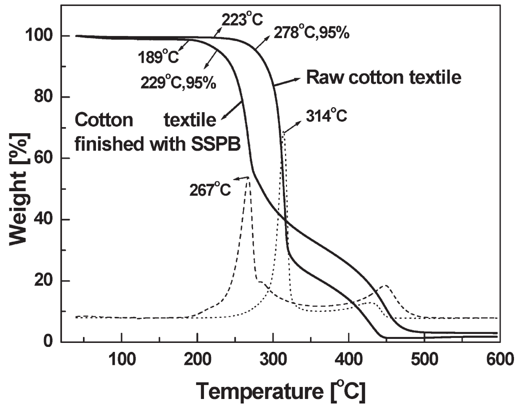


Figure 5. TG and DTG curves of raw cotton textile and cotton textile finished with SSPB under an O_2 atmosphere.

3.7. Antibacterial Properties of Cotton Textile Finished with SSPB. The antibacterial activities of cotton textile finished with SSPB were evaluated according to the protocols described in literature.[34] The raw cotton textile without SSPB was used as a control sample. The bacterial colonies were allowed to grow on the surface of the cotton textile finished with SSPB. The antibacterial activity was then evaluated according to their antibacterial rate. Figure 7 shows the antibacterial activities of cotton textile finished with SSPB against *S.aureus* and *E.coli* as compared with the raw cotton textiles. It is found that the count for viable colonies of both bacterial is decreased sharply after 24 h in the cotton textile finished with SSPB. The antibacterial rate of cotton textile finished with SSPB reaches more than 99.99% against *S.aureus* and 99.92% against *E.coli.* This implies that the resultant cotton textile finished with SSPB has excellent antibacterial activity against both gram-positive *S.aureus* and gram-negative *E.coli*.

As mentioned above, antibacterial textiles are usually produced by adding antibacterial agents to textiles through finishing process. The advantages of such application are high productivity and relatively low processing costs. However, many textiles

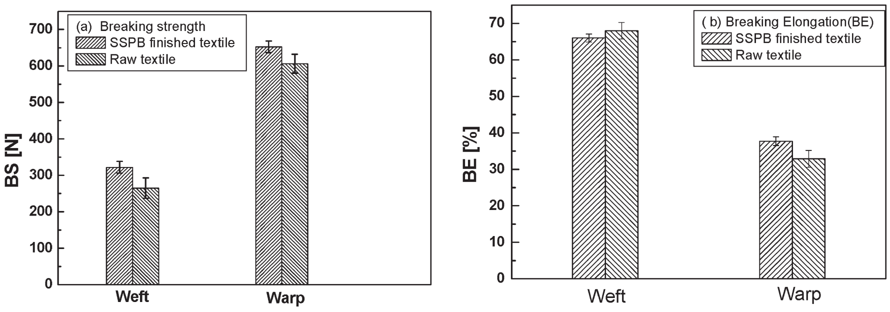


Figure 6. Mechanical properties of the raw cotton textile and the cotton textile finished with SSPB: (a) breaking strength and (b) breaking elongation. Each symbol indicates the means ± standard errors for five observations.

finished in this way exhibit low durability against repeated laundering. The performance and washing durability of antibacterial functions depend on the amount of the agents imparted on the textiles and interactions between the agents and the fibers.[16] In this experiment, to evaluate the durability of antibacterial, the samples had been laundered 50 times and their antibacterial activity was further evaluated using the same method. The antibacterial activities of cotton textile finished with SSPB after 50 washes are summarized in table 1. It is found that the antibacterial rate against gram-negative bacteria *E.coli*, gram-positive bacteria *S.aureus* and fungi *C.albicans* are 90.30%, 92.14% and 92.62%, respectively. It is known that the reference values of AAA class antibacterial textiles for antibacterial rate are 70, 80, and 60%, respectively. Thereafter, the antibacterial rates of cotton textile finished with SSPB are still higher than the reference value. This indicates that cotton textile finished with SSPB has a good washing durability in antibacterial activity against repeated laundering. In addition, the zones of inhibition around the pellet after washing one time are summarized in Table 1. It is found that the diameters of inhibition zone for cotton textile finished with SSPB against *E.coli*, *S.aureus* and *C. albicans* are all 0 mm. This implies that no antibacterial agent is leached from the cotton textile finished with SSPB. It can also confirm that the SSPB is very good immobilized antibacterial agent for antibacterial textile applications.

It is well-known that the pH value can influence the charge on the polymer bearing ionizable groups like QACs, which may influence its ability to inhibit bacterial growth.[51,52] In our earlier report, we had investigated the influence of pH on the antibacterial activity of SSPB against *E.coli*. The results show that the SSPB had good antibacterial activity against *E.coli* within the pH range of 4.0−9.0.[53] This result means that ionization behavior or the charge have no influence on the antibacterial activity of SSPB.

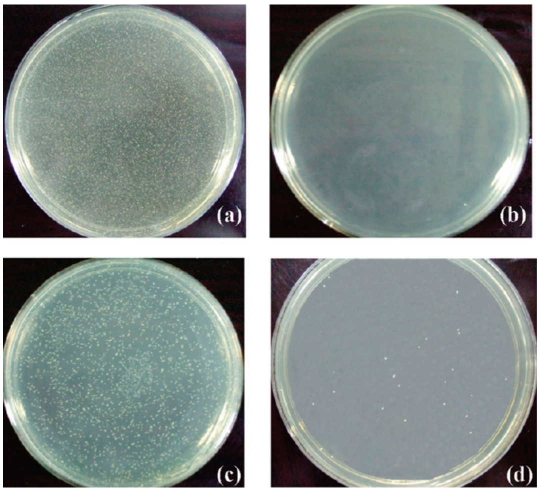


Figure 7. Antibacterial activities against the test microorganisms after 24 h contact time of samples. (a) *S.aureus*, raw cotton textile; (b) *S. aureus*, cotton textile finished with SSPB; (c) *E.coli*, raw cotton textile; (d) *E.coli*, cotton textile finished with SSPB.

The bactericidal kinetics of cotton textile finished with SSPB was investigated with the viable cell count method. Figure 8 presents the antibacterial kinetic of raw cotton textile and cotton textile finished with SSPB. As expected, comparing with the raw cotton textiles (control-2), the antibacterial activities of cotton textiles finished with SSPB against *E. coli* increase as the contact time goes by. Within the first 1 h, the antibacterial rate is increased by 89%. After 2 h, the antibacterial rate is increased rapidly by 99.9%. Finally, more than 99.95% of viable colonies are vanished when the contact time is extended up to 4 h. However, the survivors in QACs are usually decreased by several times within several minutes.[54] Thus, it implies that the antibacterial mechanism of SSPB should be quite different from that of conventional QACs, which exerts its antibacterial activity by destroying the cell membranes.[55]

It is well-known that β-D-galactosidase specifically hydrolyzes the *O*-nitro phenol, β-D-galactosidase−glycoside (ONPG) bond in sugar, fat and lactose. β-D-galactosidase from *E. coli* has particular substrate specificity for the hydrolysis of ONPG. If the cells of *E. coli* break, β-D-galactosidase will leak out of the cells and catalyze the hydrolysis of ONPG in solution. Because the product of ONPG hydrolysis, *O*-nitro phenol (ONP), has a characteristic absorption at 420 nm, spectroscopy can be used to determine whether the *E. coli* cells are disrupted.[55] Recently, the destroying mechanism of SSPB on *E. coli* cells has been investigated by determining the change of β-D-galactosidase. The cells membranes have also been checked using the SEM after the

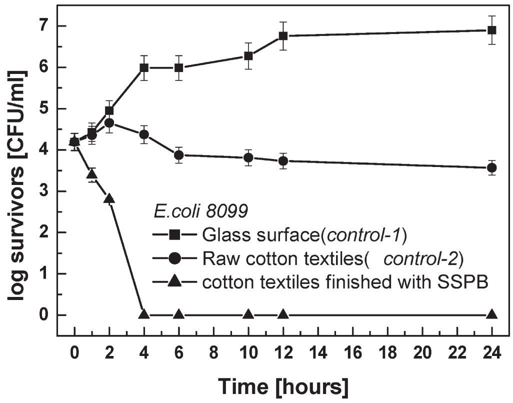


Figure 8. Antibacterial kinetic of raw cotton textile (control-2) and cotton textile finished with SSPB. Each symbol indicates the means ± error limits for three observations.

Table 1. Antibacterial activities of cotton textile finished with SSPB after washing

	antibacterial rate[a]		diameter of inhibition zone[b]	
microorganisms	exp value (%)[c]	ref value (%)[d]	exp value (mm)	ref value (mm)[d]
E.coli (8099)	90.30 ± 3.2	≥70	0	≤5
S.aureus (ATCC 6538)	92.14 ± 3.0	≥80	0	≤5
C.albicans (ATCC 10231)	92.62 ± 5.0	≥60	0	≤5

[a] Test method:FZ/T 73023−2006 D7 absorption. the sample was laundered 50 times. [b] Test method:FZ/T 73023−2006 E7 inhibition zone method, the sample was laundered one time. [c] Each symbol indicates the means ± error limits for three observations. [d] Reference value of AAA class antibacterial textiles.

Table 2. Skin Stimulation Test Results of SSPB[a]

	number		1	2	3		
	sex		male	female	female		
	weight (kg)		2.1	2.0	2.1	integral skin irritation(I_t)	intensity of skin irritation
1 h	sample	S_{er}	0	0	0	0	no stimulation
		S_{ed}	0	0	0		
	control	S_{er}	0	0	0	0	
		S_{ed}	0	0	0		
24 h	sample	S_{er}	0	0	0	0	
		S_{ed}	0	0	0		
	control	S_{er}	0	0	0	0	
		S_{ed}	0	0	0		
48 h	sample	S_{er}	0	0	0	0	
		S_{ed}	0	0	0		
	control	S_{er}	0	0	0	0	
		S_{ed}	0	0	0		

[a] S_{er}, scores of erythema, S_{ed}, scores of edema. The intensity of skin irritation for the tested sample is evaluated according to the maximum integral skin irritation. No simulation is defined as an intensity of skin irritation lower than 0.5.

Table 3. Acute Oral Toxicity Test Results of SSPB Antibacterial Agents

	female		male	
dose (mg/kg)	no. of tested rats	no. of killed rats	no. of tested rats	no. of killed rats
5000	10	0	10	0

E. coli cells are contacted with SSPB for 5 h. The results show that the SSPB antimicrobial agent does not cause rupture of *E. coli* cells. Thus, it is confirmed that the antibacterial mechanism of SSPB is bacteriostasis rather than bactericide, indicating that the SSPB may interfere with the bacterial metabolism or with the ability of bacteria to reproduce.[53] The intrinsic antibacterial mechanism of SSPB will be further investigated in a future study.

3.8. Skin Stimulation and Acute Toxicity. It is very important to consider the toxicity of compounds before they can be used to treat humans. The toxicity of materials could arise not only from the cations they contain but also the reactive vinyl groups present in monomers.[38] In this experiment, the safety of SSPB was investigated by skin stimulation test and acute oral toxicity test. Their results are summarized in Table 2 and 3, respectively. It is found in Table 2 that the scores of erythema (S_{er}) and the scores of edema (S_{ed}) are 0 in all tested rabbits after they are contacted with SSPB as well as control sample for more than 48 h. According to the evaluation criteria of S_{er} and S_{ed} for skin simulation, it is known that no erythema or edema were observed in any of the tested rabbits.Thus, the integral skin irritation (I_t) is 0, and the maximum integral skin irritation (I_{tmax}) is also 0 as shown in Table 2. Accordingly, the intensity of skin irritation for the tested specimen is no simulation. This means that the SSPB antibacterial agent is a nonirritant to the skin. In addition, the acute oral toxicity test conducted on twenty rats also shows that the tested animals treated with 5000 mg SSPB/kg BW develop well and their body weights increase normally. No rats are killed among the 10 female rats as well as among the 10 male rats as shown in Table 3. No obvious pathological changes in various organs were observed in any of the tested rats. This indicates that the SSPB antibacterial agent is nontoxic to animals. Thus, the results of this study suggest that SSPB is an environmentally friendly safe antibacterial agent for textile applications.

4. CONCLUSION

In this paper, a reactive environmentally friendly antibacterial agent SSPB is synthesized and used for antibacterial textiles finishing. On the basis of the analysis of structure of SSPB, the SSPB finished antibacterial textiles were investigated systematically from the mechanical properties, thermal stability, hydrophilic properties, and antibacterial properties. The following conclusions can be obtained.

1 SSPB contains both sulfopropylbetaine groups and reactive siloxane groups, which can be covalently bound onto the cotton textile surface during the finishing process.

2 The hydrophilicity and the breaking strength of cotton textile are improved greatly through SSPB antibacterial finishing.

3 SSPB are very good immobilized antibacterial agents for environmentally friendly antibacterial textile applications. The cotton textile finished with SSPB show good antibacterial activities against *E.coli, S.aureus* and *C.albicans.* The SSPB is nonleachable in the cotton textile and it shows no skin stimulation and no toxicity to animals.

ASSOCIATED CONTENT

Supporting Information. 1H-NMR (a), 13C-NMR (b), and H−C COSY (c) spectra of PSSPB in D2O, DSC curves of PSSPB, XPS N 1s spectrum of SSPB finished cotton textile, and evaluation criteria for skin simulation. This material is available free of charge via the Internet at http://pubs.acs.org

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