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Non-leaching and durable antibacterial textiles finished with reactive zwitterionic sulfobetaine

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ABSTRACT

An antibacterial finishing protocol using a reactive sulfobetaine was reported to fabricate safe and durable antibacterial textiles. The specifically designed sulfobetaine contains highly reactive triazine group acting as an anchor to fix the antibacterial betaine group on textiles via covalent bond formation. After the finishing, the textiles were endowed durable antibacterial activities of 98.0% against gram-negative *Escherichia coli* and 95.2% against gram-positive *Staphylococcus aureus* even after they were laundered for 30 times. The safety evaluation showed that the reactive sulfobetaine had no skin irritation and cytotoxicity. These results indicate that the developed antibacterial finishing is safe and durable on textiles.

Introduction

Pathogenic bacteria cause numerous severe infections and deaths every year, which has become a growing threat to public health. An efficient approach to enhance human body protection from pathogenic bacteria is to construct antibacterial textile surfaces. Currently, several types of agents including metals/metal salts, quaternary ammoniums and triclosans were used as antibacterial agents on textiles [1–4]. However, because of the unsafe risk to human body and environment, metal/metal salts and triclosans are already limited in the application on textiles [1]. Quaternary ammoniums show cumulative toxicity and hemolytic activity to mammalian cells, indicating low biocompatibility [5,6]. And they easily absorb dead microorganisms, which may induce inflammation on skin and the loss of antibacterial activity from the covering of the antibacterial functional sites by the accumulation of the dead microorganisms [7,8]. Furthermore, these antibacterial agents exist on textiles only through physical interactions, which is leachable. In the recent study, it was found that these antibacterial agents except triclosan showed a pronounced decrease in their antibacterial activities due to their leaching in the laundering processes [9]. In addition to antibacterial durability, the environmental friendship of the antibacterial agents is another important issue need to be paid more attention. There are still constant needs to develop environmentally-friendly and non-leaching antibacterial agents for healthcare textiles.

Zwitterionic compounds are a kind of innocuous and neutral materials with a positive/negative charge balance within the same segment [10]. According to their chemical structures, the zwitterionic compounds developed so far include sulfobetaines, sulfabetaines, carboxybetaines, phosphobetaines and zwitterionic amino acids [11–14]. Among them, sulfobtaines and carboxybetaines are the two predominant classes of zwitterionic compounds studied. Due to their good biocompatibility, zwitterionic compounds have attracted considerable research interests in the field of biomaterials [11,12]. They have been widely reported for the applications as biocidal micelles [15,16], electrospun nanofibers [17,18], switches and brushes [19–22], stealth interfaces [23,24], modification agents [25,26] and antifouling hydrogels [27–29]. The succeeded results in these studies showed that the zwitterionic compounds had good antibacterial activity [19]. But, most zwitterionic compounds in these studies are polymers, which are not suitable for the antibacterial application on porous substrates like textiles. Otherwise, the coated polymer layers would block the pores of textile fibers and thus adversely influence the textile air permeability, which is significantly important for healthcare and wound dressing. Although zwitterionic compounds showed excellent biocompatibility and antibacterial ability, very few of them were reported for the antibacterial application on textile materials [30,31]. Therefore, their applications on textile material show promising developing prospects.

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In this work, a kind of reactive zwitterionic sulfobetaine containing triazine group (CSPB, Fig. 1) was designed and synthesized to fabricate non-leaching and durable antibacterial surfaces on textile materials. Triazine group is highly reactive with cellulosic textiles [32] and thus was used to permanently fix the antibacterial sulfobetaine groups on textiles through covalent bond formation. The covalent binding with textiles is expected to prevent CSPB leaching off the textile surfaces in the laundering process and endow textiles a durable antibacterial activity. In addition to antibacterial durability, the hydrophilicity and air permeability of the treated textiles by CSPB were also investigated. Considering the application safety on textiles, skin stimulation and cytotoxicity of CSPB were also studied.

Experimental

Materials

N,N-dimethylethylenediamine, di-*t*-butyl dicarbonate (BOC), 1,3-propanesultone (PST) and cyanuric chloride (CC) were purchased from Sigma–Aldrich. Gram-positive bacteria *Staphylococcus aureus* (*S. aureus,* ATCC 6538) and gram-negative bacteria *Escherichia coli* (*E. Coli,* ATCC 25922) were purchased from Guangdong Institute of Microbiology. Human skin HaCaT cells were purchased from Kunming Cell Bank of Type Culture Collection, Chinese Academy of Sciences. All other regents (analytical grade) and solvents (spectroscopic grade) were commercially available and used as received.

Characterizations

High resolution mass spectra were recorded using a Micromass Q-TOF 2 mass spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian 400 spectrometer using TMS as an internal standard. Field emission scanning electron microscopy (SEM, JEOL JSM-6335F) was applied to look into the micromorphology of cotton textiles before and after the finishing with CSPB. The chemical compositions of the cotton textiles finished with CSPB were determined by X-ray photoelectron spectroscopy (XPS) on a SKL-12 X-ray photoelectron spectrometer (Shenyang, China) equipped with a VG CLAM 4MCD electron energy analyzer. XPS is configured with a dual anode source from VG (type XR3E2) and non-monochromatic Mg Kα radiation (1253.6 eV) at a current of 15 mA with an ultrahigh vacuum ($<8 \times 10^{-10}$ Torr). To compensate for surface charging effects, all binding energies were referenced to the C 1s hydrocarbon peak at 284.6 eV.

Synthesis of CSPB

In a typical procedure, BOC (2.6 g, 11.9 mmol) in DCM (5 mL) was added into the solution of compound **1** (1.0 g, 11 mmol) in DCM (20 mL) at room temperature under stirring. 5 h later, the mixture in flask was washed using saline water (250 mL) and the oil solution was collected. After the solvent was removed under vacuum at 50 °C, compound **2** was obtained as yellowish oil. The obtained oil was dissolved in chloroform (25 mL) and PST (1.47 g, 12 mmol) was added into the solution. The solution was refluxed at 60 °C for 4 h and then cooled to room temperature. After filtration, compound **3** was obtained as white powder. Next, the powder was dissolved in D. I. water (30 mL) and the solution was adjusted to pH < 1 using hydrochloride acid. Stirred at room temperature for 3 h, the water was removed to collect compound **4** as yellowish powder. Thereafter, the yellowish powder and potassium carbonate (1.66 g, 12 mmol) were added into acetone (100 mL) and stirred for 30 min in an ice bath. CC (2.33 g, 12.6 mmol) in acetone (20 mL) was added into the abovementioned solution. Then, the solution was kept stirring for another 6 h in the ice bath. After filtration and washing with acetone, CSPB was obtained as white powder (Yield: 73.7%). HRMS (ESI positive): *m/z* 402.0135 ($[M+2Na-H]^+$). ^{1}H NMR (D_2O, ppm): δ 3.80 (t, *J* = 8.0, 2H), 3.46 (m, 4H), 3.07 (s, 6H), 3.02 (s, 1H), 2.86 (t, *J* = 8.0, 2H), 2.13 (m, 2H); ^{13}C NMR (D_2O, ppm): δ 170.10, 165.51, 62.83, 60.75, 51.15, 47.15, 34.84, 18.17. These spectra were also provided in the Supporting information (Fig. S1).

Fabrication of antibacterial textile surfaces

The antibacterial surfaces on cotton textiles were fabricated through a typical padding-curing process. Before use, commercially available cotton textiles were washed in 5 g L^{-1} sodium dodecyl sulfate solution at 60 °C for 20 min to remove possible surface impurities. Then it was rinsed thoroughly in deionized water and dried in air. A piece of textile (30×40 cm^2) was padded in 20 g L^{-1} CSPB aqueous solution containing 10 g L^{-1} sodium bicarbonate at the pressure of 3 kg and followed by curing at 90 °C for 3 min. Then, the finished textiles were rinsed in tap water and air dried for the test.

Hydrophilicity and air permeability of textiles finished with CSPB

The hydrophilicity of the textiles was evaluated according to the standard method ISO 9073-6:2000 for textile capillary effect. Typically, a piece of sample (25×3.0 cm^2) was fixed on the backbone and then conditioned at 25 °C and 70% relative humidity. The site at the height of 2 cm from the sample bottom was as the zero point. Then, it was put into the water containing red colorant vertically with the zero point just contacting with water. Thereafter, the water mark height of the sample was read at different time. The average of three measurements was used in the analysis.

Air permeability of the textiles provides an indication of their breathability and was determined based on the rate of air flow passing perpendicularly through the textiles. A textile sample with

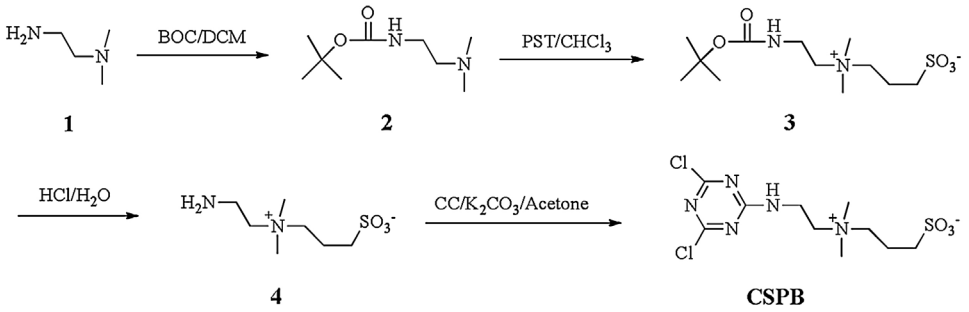

Fig. 1. Synthesis route of CSPB.

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