Cellulose (2020) 27:6603–6615
https://doi.org/10.1007/s10570-020-03228-0

ORIGINAL RESEARCH

Naturally occurring betaine grafted on cotton fabric for achieving antibacterial and anti-protein adsorption functions

Panpan Duan · Qingbo Xu · Xujun Zhang · Jianing Chen · Weishi Zheng · Lin Li · Jing Yang · Feiya Fu · Hongyan Diao · Xiangdong Liu

Received: 12 January 2020 / Accepted: 9 May 2020 / Published online: 25 May 2020

Abstract In the textile industry, the use of naturally occurring antibacterial products in simple one-pot finishing processes is recommended. In this study, we present a clean technology using betaine (Bet) as the finishing reagent for preparation antibacterial fabrics. The reactive carboxyl group of Bet binds to the cellulosic fibers of fabrics via esterification, while the quaternary ammonium moiety of this compound exerts the antibacterial effect. Analyses show that the antibacterial efficiencies of Bet-modified cotton fabrics against *E. coli* and *S. aureus* are as high as 99.0 and 99.3%, respectively. Furthermore, these fabrics are highly durable against washing, with antibacterial activities greater than 91.5% after 20 washing cycles, and they display an excellent anti-protein adsorption property. The modification process proposed herein does not compromise the original properties of the fabric, and according to cytotoxicity tests, the modified fabrics are safe to wear against human skin. Overall, the fabric treatment process designed in this study constitutes a novel approach to the development of green finishing technologies in the textile field.

Keywords Natural betaine · Antibacterial fabric · Anti-protein adsorption · Cotton fabric

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10570-020-03228-0) contains supplementary material, which is available to authorized users.

P. Duan · Q. Xu · W. Zheng · L. Li · J. Yang · F. Fu · X. Liu (✉)
School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China
e-mail: liuxd@zstu.edu.cn

X. Zhang · J. Chen · H. Diao (✉)
State Key Laboratory for Diagnosis and Treatment of Infectious Diseases, Collaborative Innovation Center for Diagnosis and Treatment of Infectious Diseases, The First Affiliated Hospital, College of Medicine, Zhejiang University, Hangzhou 310003, China
e-mail: diaohy@zju.edu.cn

F. Fu · X. Liu
Institute for Smart Fiber Materials, Zhejiang Sci-Tech University, Hangzhou 310018, China

Introduction

Cotton is a very abundant natural polymeric material, which has a huge worldwide production more than 20 million tons every year. Cotton consists of nearly 99% cellulose, and the three hydroxyl groups on the pyranose rings of the cellulose backbone are energetically favorable for a variety of chemical reactions to impart a new functionality to cotton fabric. Textile is the main outlet of cotton because of its many desirable properties, which include low skin irritation, warmth, high breathability and good flexibility, offer excellent wearing comfort for the clothing that made of cotton fabric (Xu et al. 2020; Liu et al. 2017; Zhu et al. 2019; Yetisen et al. 2016). However, textile products made of cotton fabrics are prone to bacterial attack, resulting in discoloration, undesired odor, and health concerns (Pan et al. 2018; Xu et al. 2019a, b; Reshma et al. 2018). During the past few decades, several types of antibacterial agents have been assessed for use in the cotton textile industry (Reshma et al. 2018; Amini 2019; Shahidul Islam et al. 2016; Chatha et al. 2019; Fouda et al. 2013). However, most of these products are toxic towards humans, and the finishing processes that make use of them are generally complex (Rovira et al. 2019;Jurewicz et al. 2018; Windler et al. 2013; Wang et al. 2014). Indeed, the fabrication of antibacterial textile products consumes extensive energy, produces a lot of waste water, and is hygienically unsafe (Song et al. 2019; Chen et al. 2018; Rauytanapanit et al. 2018; Lu et al. 2018; Liu et al. 2018). This shows that more research is needed to develop "green finishing techniques" for the preparation of cotton textiles.

Betaine (Bet), also known as glycine betaine, is a non-hazardous natural compound that exists in almost all organisms (Zou et al. 2016; Cholewa et al. 2014; Kishitani et al. 2000). In fact, this compound possesses some medicinal activity and can be safely ingested by humans at a maximum supplementation of 400 mg/day (Craig 2004; Turck et al. 2017; Choi et al. 2018). Some reports claim that Bet is non-toxic towards bacteria (Zou et al. 2013, 2016; Cosquer et al. 1999; Su et al. 2018; Zhao et al. 2014; Xu and Xu (2014). Others demonstrate that this compound has bacteriostatic activity at high concentrations (Chambers et al. 1996;Huang et al. 2014; Peddie et al. 1998). Previously, a number of betaine analogues had been developed and proposed for use in antibacterial applications (Cosquer et al. 2004; Lindstedt et al. 1990; Cheng et al. 2009; Kritchenkov et al. 2019; Li et al. 2018; Pu et al. 2017); however, analyses showed that the toxicity of these compounds increased with increasing antibacterial activity (Cosquer et al. 1999; Burnett et al. 2018).

The grafting of betaine analogues on cotton fabrics has also been explored as a means to achieve antibacterial function (Chen et al. 2011a, b, c, 2016a, b; He et al. 2017; Zhang et al. 2018). Unfortunately, the procedures implicated in the preparation of Bet-modified fabrics are complex, and they require multistep operations. Moreover, relatively large quantities of waste water containing hazardous betaine derivatives generated in these procedures raise environmental risk, and thus, they are considered environmentally unfriendly. To overcome the toxicity, hazards, complexity, and high costs of traditional textile preparation procedures, simple one-pot finishing processes with non-toxic antibacterial reagents are proposed. Bet constitutes an antibacterial agent with great potential for use in the field of cotton fabric modification. The antibacterial activity of this compound is ensured by the quaternary ammonium moiety, whereas the carboxyl group allows it to bind to the cellulose chains on fiber surfaces via esterification reactions.

In this study, we report a novel non-hazardous technology for the fabrication of durably antibacterial fabrics using Bet as the finishing reagent. Experimental data show that the grafting of Bet on cotton fiber surfaces endows them with good antibacterial and anti-protein adsorption properties, without compromising the comfort features. Together with the simple process that may be easily scaled up to an industrial finishing production, this approach allows for the development of green finishing technologies for use in the textile industry.

Experimental section

Materials

Betaine monohydrate, methyl orange and bovine serum albumin (BSA) were purchased from Shanghai Aladdin Co., Ltd. (China). Cell counting kit-8 (CCK-8) was obtained from Dojindo (Japan) and Hacat cells were iGell Bioscince Inc. (China). Cotton fabric (109 g/m^2) was obtained from Suzhou Ke Chuan Textile Co., Ltd (China). Before modification, the fabrics (10 pieces, 5 cm × 5 cm) were cleaned by ultrasonic washing in sodium dodecyl sulfate solution (200 mL, 2 wt%) for 30 min, further washed using ethanol (200 mL, 95 wt%) for 1 h, rinsed with deionized water (100 mL, 30 min × 3 times), and dried at 80 ^{o}C.

Preparation of antibacterial cotton fabrics finished with betaine

Cotton fabrics (5 pieces, 5 cm × 5 cm) were immersed into a betaine monohydrate solution (100 mL, 20 wt%) at 80 °C for 30 min, and cooled to room temperature with the solution. After pH of the solution was adjusted to 1.8 using a HCl solution, the cotton fabrics were further dipped for 5 min, squeezed to wet weight of 90 ± 2 wt%, cured at 180 °C for 5 min, rinsed with deionized water (100 mL × 3 times), and dried at 80 °C for 1 h to obtain the Bet-Co-2 fabric sample. Other samples were prepared using a similar process but varied conditions (Table S1).

General characterizations

Surface morphologies of the cotton fabrics were observed using a field emission scanning electron microscope (FE-SEM) set (Ultra-55, Zeiss, Germany) with an energy dispersive X-ray spectrometer (EDS) after gold coating, adsorption of methyl orange and anti-serum protein adsorption were tested used UV–vis spectrophotometer (UV-2550, SHIMADZU). Water vapor permeability, water absorption capability, flexibility, tensile strength and laundering durability of the fabric samples were measured as our previous reports (Xu et al. 2019a, b), and the assay methods were described in the "Supporting Information" part. Other instruments such as attenuated total reflectance Fourier transform infrared (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) were same as in our previous reports (Xu et al. 2019a). *Escherichia coli* (*E. coli*, ATCC 1555) and *Staphylococcus aureus* (*S. aureus*, ATCC 547) were used as test microorganisms. Before the tests, the bacteria were activated with Letheen broth fluid nutrient medium for 24 h in a constant temperature incubator. The cotton fabric (0.24 g) was cut into pieces, added into the sterilized centrifuge tube with the activated bacteria of *E. coli* or *S. aureus* (10 μL, 10^6 CFU/mL) and the sterilized Letheen broth fluid nutrient medium (4 mL), and shaken at 25 °C for 18 h. The supernatant was diluted to an appropriate concentration, dispersed onto LB agar plants, and incubated at 37 °C for 24 h. The bacteriostatic reduction rate (BR) was calculated as following,

$$BR = \frac{B - A}{B} \times 100\%$$

where A and B are the number of colony-forming units (CFU) of the surviving microorganisms for the treated cotton fabric and the control sample (original cotton fabric), respectively.

Bacterial adhesion property of the Bet-Co fabrics

The fabric (one piece, 5 cm × 5 cm) was immersed in 20 mL of a bacterial solution (*S. aureus* or *E. coli*, concentration, 10^7 CFU/mL), incubated at 37 °C for 2 h, held vertically for 3 min to remove the excess bacterial solution, put into a fresh nutrient broth (20 mL) and incubated at 37 °C for 24 h with vibration at a 120 rpm. The sample was washed using sterile water (50 mL × 3 times) and sterile PBS (50 mL × 3 times) to remove the free bacteria, treated with 2.5 wt% glutaraldehyde aqueous solution for 1 h to fix the bacteria remained, washed using PBS (50 mL × 3 times) and distilled water (50 mL × 3 times). The fixed bacteria were dehydrated using a series of graded 50 mL ethanol solutions (50, 75, 90, and 100 wt%, for 15 min each), dried in a dessicator overnight, and subjected to FE-SEM observation.

Quantitative estimation of betaine moieties grafted on cotton fabrics

To estimate the quantity of Bet molecules grafting on the cotton fabrics, concentration decrease of a methyl orange solution that caused by a fabric adsorption was measured. The modified cotton fabric (5 cm × 5 cm) was immersed in a methyl orange solution (30 mL, 0.011 mmol/L) for 10 min. After removing the fabric, absorbance value at 460 nm of the solution was measured using the UV–Vis spectrophotometry to determine the concentration of methyl orange. This test was repeated for three times, and the adsorbed quantity of Bet was calculated according to the following formula (1):

$$m = \frac{C \times V}{M} \quad (1.)$$

where C (mmol/L) is the concentration decrease, V (L) is the solution volume, M (g) is the quality of the fabrics, and *m* (mmol/g) is the Bet quantity adsorbed by the cotton fabric. The quantity of Bet moieties grafted on the cotton fabric is its m difference value with original cotton fabric.

The anti-protein adsorption ability of the Bet-Co fabrics

To evaluate anti-protein adsorption ability of the Bet-Co fabric, two Bet-Co cotton fabrics (5 cm × 5 cm) were immersed into a BSA solution (20 mL, 0.2 mg/mL) and stirred for 10 min. The anti-protein adsorption ability was evaluated by measuring the decrease in light absorbance at 280 nm using the UV–Vis spectrophotometer.

Cytotoxicity analysis of Bet-Co fabrics

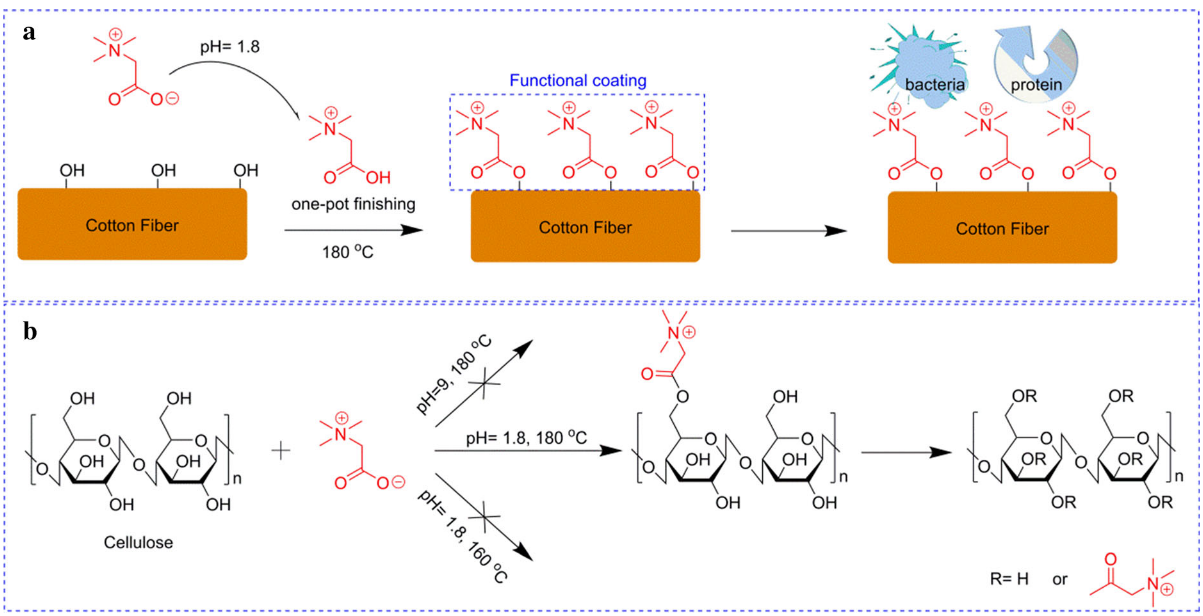
The cytotoxicity of the modified fabrics towards Hacat cells was evaluated using CCK-8 cell counting kit assays. Bet-Co-2 fabrics (2 pieces, 5 cm × 5 cm) were immersed in a physiological saline solution (10 mL) and stirred at 25 °C for 24 h. The resulting leachate solution was sterilized in an autoclave, diluted with physiological saline solutions for two and four times, which are named Bet-Co-2-2 and Bet-Co-2-4, respectively (Table S4), and then transferred to 96 well plates containing Hacat cells that had been cultured overnight. After incubation for 24 h, a CCK-8 reagent solution was also added to the wells, and the incubated mixtures were analyzed by a microplate reader and observed using an optical microscope. The physiological saline solution was used as a negative control. A CCK-8 reagent solution (10 μL) was further mixed in the wells and incubated for 1 h. Finally, the incubated mixtures were subjected to an absorbance measurement at 450 nm using a microplate reader (Epoch2, Biotek, America), and an observation using an optical microscopy (LX53, Olympus, Japan).

Results and discussion

Surface modification of cotton fibers using betaine

Bet molecules were simply grafted onto the surface of cotton fabric via a general pad-dry-cure process as shown in Scheme 1. Cotton fabrics were immersed in a betaine solution for 30 min followed by pH adjustment of the solution. Then, the cotton fabrics were squeezed, heated for several minutes, rinsed and dried to obtain the modified fabrics. The synthesis results suggest that the solution pH and the reaction temperature are important factors on the Bet coating grafted on the cotton fiber surface. The Bet layer was successfully constructed by adjusting pH at 1.8 and followed by heating the fabrics at 180 °C for 5 min, whereas, the modification was failed when the pH was 9.0 or the fabrics were heated at 160 °C for 30 min.

The successful binding of Bet to cellulose chains on the fiber surface was verified by ATR-FTIR analyses performed in the spectral range of 400–4000 cm^{-1}, as well as by XPS.



Scheme 1 **a** Schematic of the cotton fabric functionalized by Bet, and **b** the esterification reaction between Bet and the cellulose molecule on fiber surface

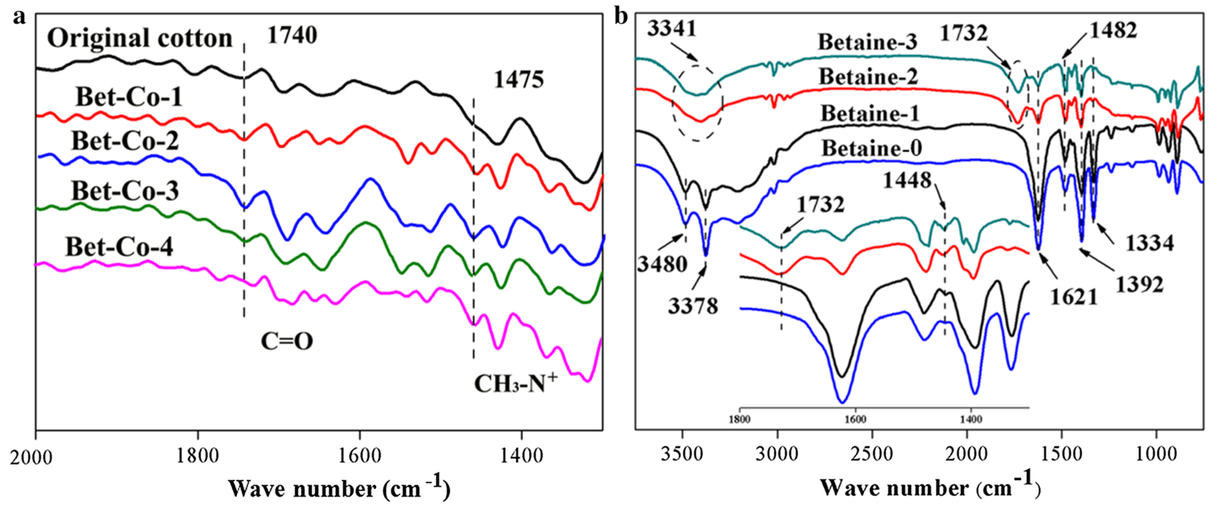


Fig. 1 **a** ATR-FTIR spectra of original cotton and the Bet treated fabrics, and **b** FTIR spectra of the products of Bet experienced the heating processes

As shown in Fig. 1a and S1, the modified cotton fabrics Bet-Co-1, Bet-Co-2, Bet-Co-3, and Bet-Co-4, exhibit new FTIR peaks that are not evident in the spectrum of the original fabric. These peaks are observed at around 1732 and 1475 cm^{-1}, and they are attributed to the C=O and CH_3-N^+ groups of Bet, respectively. Among the investigated fabrics, Bet-Co-2 showed the most intense peaks, which suggests that Bet grafting is most favored by pH and heating conditions of 1.8 and 180 °C (5 min), respectively. To confirm the effect of pH on grafting efficiency, four samples of Bet, processed under varying conditions of pH, were compared (Table S2). The results depicted in Fig. 1b show that the Bet powders dried at pH = 9.0 present the typical characteristic peaks of the carboxylate group at 1392 and 1621 cm^{-1} (Reinoso et al. 2012). Contrarily, the FTIR spectrum of the powders dried at pH = 1.8 exhibits significantly weakened carboxylate peaks; however, several new features that can be assigned to the carboxylic acid group are evident in this spectrum. These features include a broad band centered at 3341 cm^{-1}, an intense peak at 1732 cm^{-1}, and a weak absorption band at 1448 cm^{-1} corresponding to the O–H, C= O, and C–O stretching vibrations, respectively. The strong peak observed at 1334 cm^{-1} for betaine-0 and betaine-1 samples probably corresponds to the vibration of the bond between the $–CH_2N^+(CH_3)_3$ group of Bet and the OH^- ionic. This peak disappears after acidic treatment. Overall, the FTIR results suggest that acidic conditions favor the transformation of the carboxylate group into carboxylic acid, thereby promoting esterification reactions on cotton fiber surfaces.

The Bet-modified fabrics were further analyzed by XPS. Figure 2a and b compares the wide-range XPS spectra of the cotton fabrics before and after Bet modification. Unlike the spectrum of original cotton, the spectra of Bet-Co-1 and Bet-Co-2 fabrics exhibit characteristic N1s peaks at 400.6 eV. To confirm the existence of covalent bonds between Bet and the cellulose chains of cotton fibers, high-resolution C1s XPS spectra of the original and modified fabrics were also recorded. As shown in Fig. 2c, the C1s peak of the original cotton fabric is deconvoluted into three peaks, with binding energies of 288.0 (C–O–C), 286.5 (C–OH), and 284.6 eV (C–C). Meanwhile, the C1s peaks of Bet-Co-1 (Fig. S2) and Bet-Co-2 (Fig. 2d) are deconvoluted into four peaks, appearing at 287.9 (C=O/C–O–C), 286.5 (C–OH), 284.6 (C–C), and 285.7 eV (C–N). Combined with the FTIR analyses, the XPS results confirm the successful binding of Bet molecules onto cotton fiber surfaces via esterification reactions. In addition, the elemental composition data (Table S3) determined from XPS spectra indicated that Bet-Co-2 has more Bet molecules on the fabric surface than Bet-Co-1.

To determine the number of Bet molecules bound to the surface of a cotton fabric sample, adsorption tests were carried out. Modified fabrics immersed in methyl orange solutions adsorbed the methyl orange

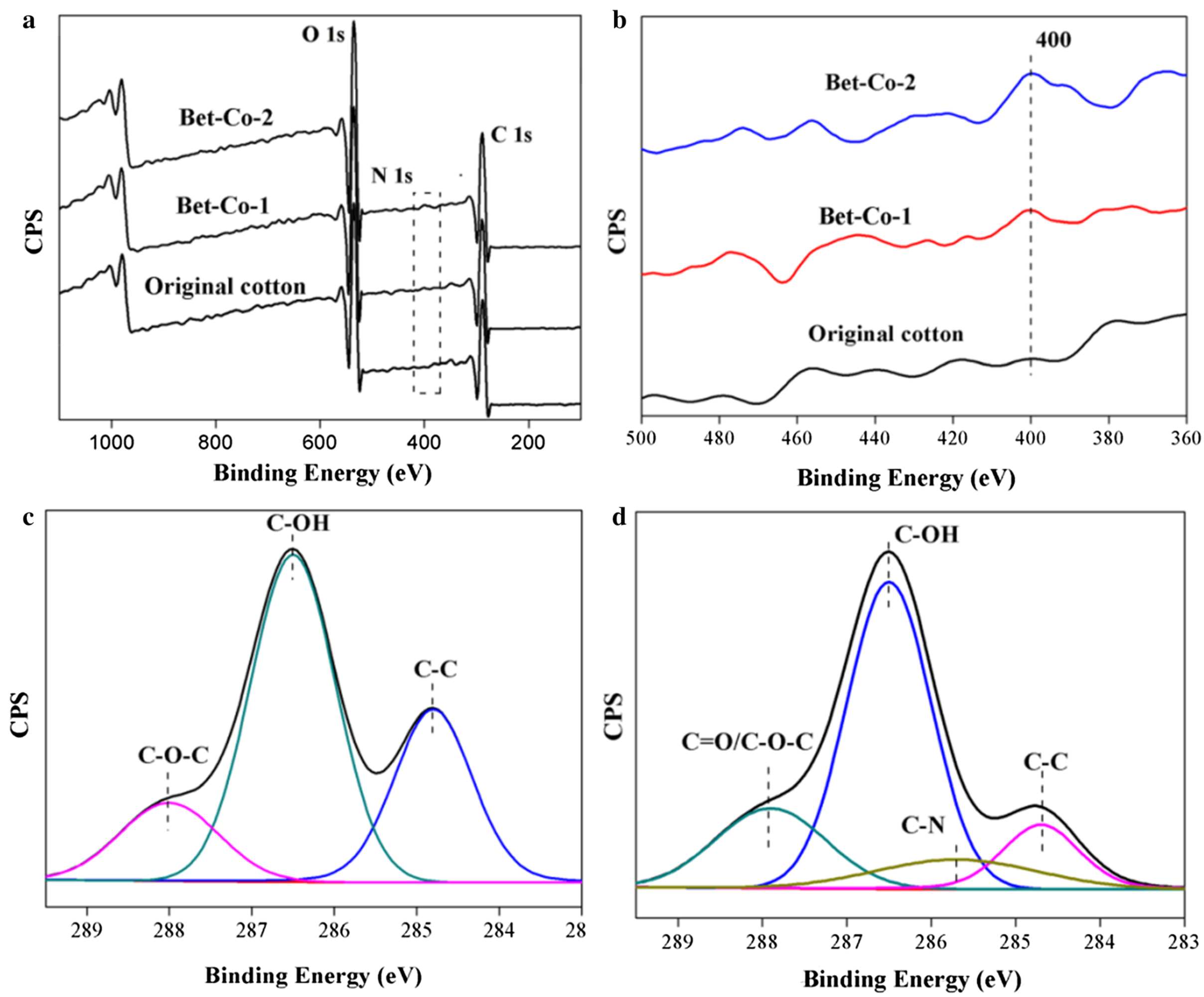


Fig. 2 XPS survey spectra of the cotton fabric samples on **a** wide range and **b** partly detailed range of binding energy, the deconvoluted Cls XPS spectra of **c** original cotton fabric and **d** Bet-Co-2 fabric

molecules by ionic effect, resulting in reduced concentrations that were measured using UV–Vis spectrophotometry. The spectra depicted in Fig. S3 show that the absorbance of methyl orange at 460 nm is only slightly reduced upon the immersion of original cotton (Fig. S3c), Bet-Co-3 (Fig. S3e), or Bet-Co-4 (Fig. S3f) fabrics. Repeated immersions do not appreciably enhance the adsorption of methyl orange on the fabric surfaces. Meanwhile the Bet-Co-1 (Fig. S3a) and Bet-Co-2 (Fig. S3b) fabrics provoke significant reduction in methyl orange absorbance. The quantities of grafted Bet molecules were estimated using Eq. (1) and the calibration curve of methyl orange presented in Fig. S4. The values listed in Table 1 show that approximately 0.35 mmol of Bet

Table 1 Estimated quantities of Bet molecules that grafted on the cotton fabrics

Sample	MOD[a] (mmol/L)	BMF[b] (mmol/g)
Original cotton	20×10^{-4}	71×10^{-6}
Bet-Co-1	86×10^{-3}	31×10^{-4}
Bet-Co-2	10×10^{-2}	35×10^{-4}
Bet-Co-3	80×10^{-4}	22×10^{-5}
Bet-Co-4	30×10^{-4}	39×10^{-6}

[a]Decrease in methyl orange concentration

[b]Estimated Bet moieties that grafted on the fabrics

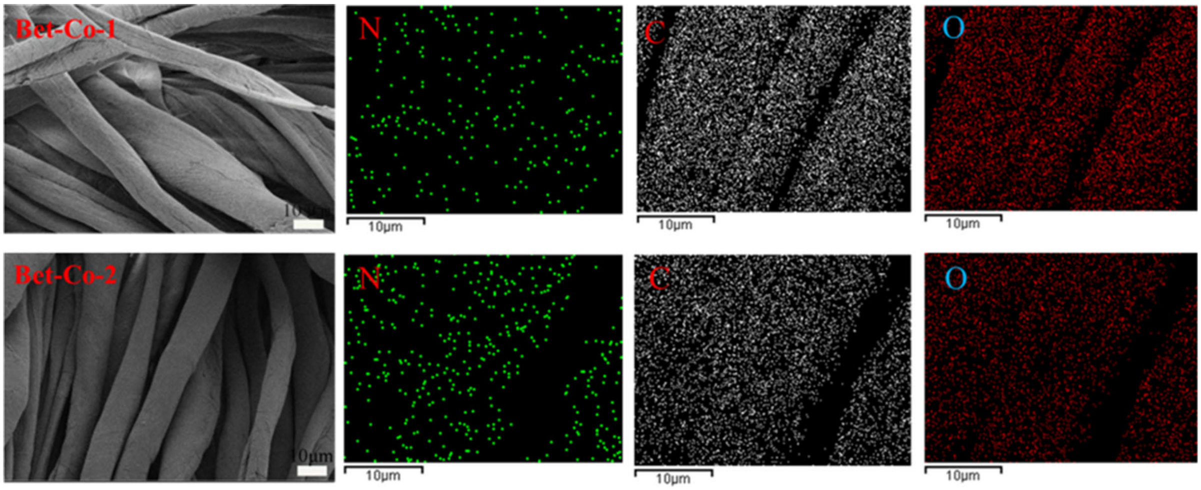


Fig. 3 SEM images and elemental mapping (N, C, O) of the fiber surfaces in Bet-Co-1 and Bet-Co-2 fabrics

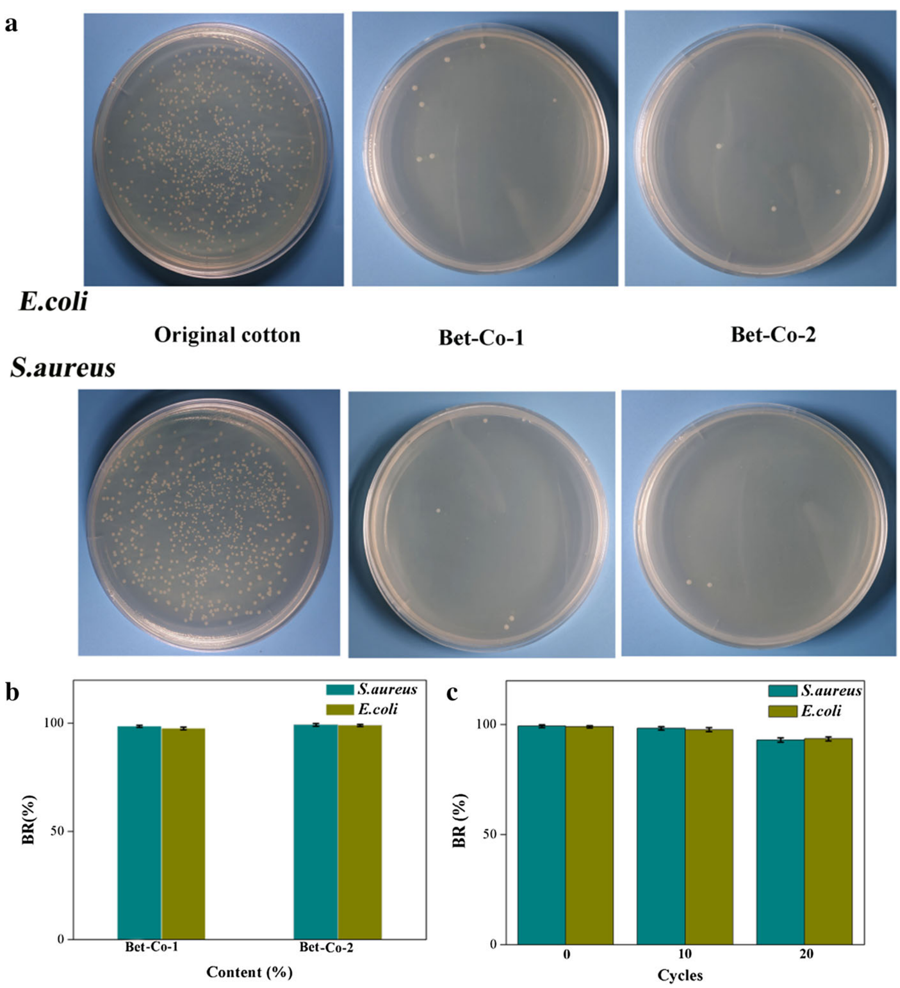


Fig. 4 **a** Optical images of the antibacterial tests against *S. aureus* and *E. coli*, **b** antibacterial rates of the Bet treated fabrics, and **c** antibacterial durability of Bet-Co-2 fabric

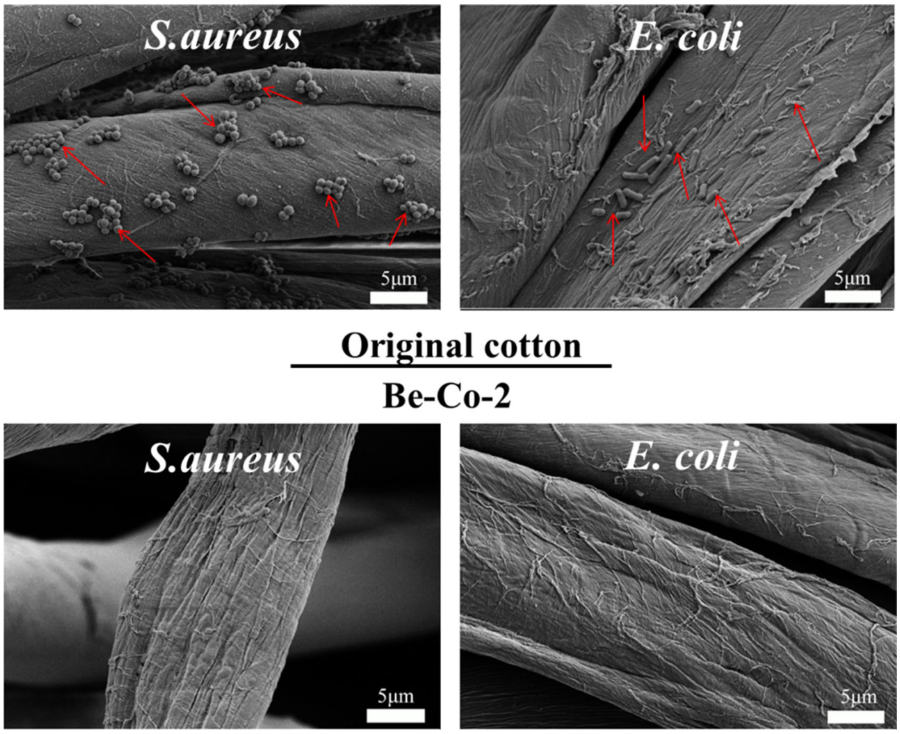


Fig. 5 SEM images of the adhered bacteria on the original cotton and Bet-Co-2 fabrics

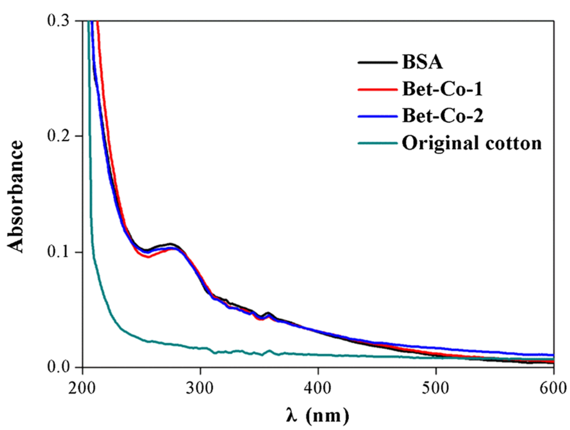


Fig. 6 UV–Vis absorbance changes of the BSA solutions caused by the immersion of the fabric samples

are bound to one kilogram of the Bet-Co-2 cotton fabric, compared to only 0.039 mmol bound to one kilogram of Bet-Co-4. Based on these results, it is concluded that temperature and pH conditions are very important factors affecting the grafting reaction.

The SEM images depicted in Figs. 3, S5, and S7 show that Bet modification induces no significant changes in the morphology of the original cotton fabric (Fig. S5). Furthermore, EDS spectra of the investigated samples demonstrate that in addition to the carbon and oxygen elements present in the original fabric (Fig. S6a), the modified fabrics are composed of nitrogen (Fig. S6b and c). Mapping images (Figs. 3 and S7) show that the micro distribution of N atoms on the surfaces of modified cotton fabrics is relatively uniform, and that the distribution density increases with increasing Bet concentration (Table S3). The optical images shown in Fig. S8 indicate that the Bet-modification provokes insignificant changes in fabric color, which renders it favorable for use in the clothing industry. Comparatively, silver nanoparticle treatment leads to substantial color changes (Fig. S8c) and is thus, unsuitable for the engineering of clothes fabrics

XRD analyses were also performed in order to detect the structural damage evoked by Bet modification. As shown in Fig. S9, the XRD pattern of the modified Bet-Co-1 and Bet-Co-2 sample is very similar to that of the original cotton fabric, with typical diffraction peaks observed at 2θ values of 14.7°, 16.4°, 22.6°, and 34.3° (Xu et al. 2019a, 2020) are all observed in the XRD spectrum. This indicates

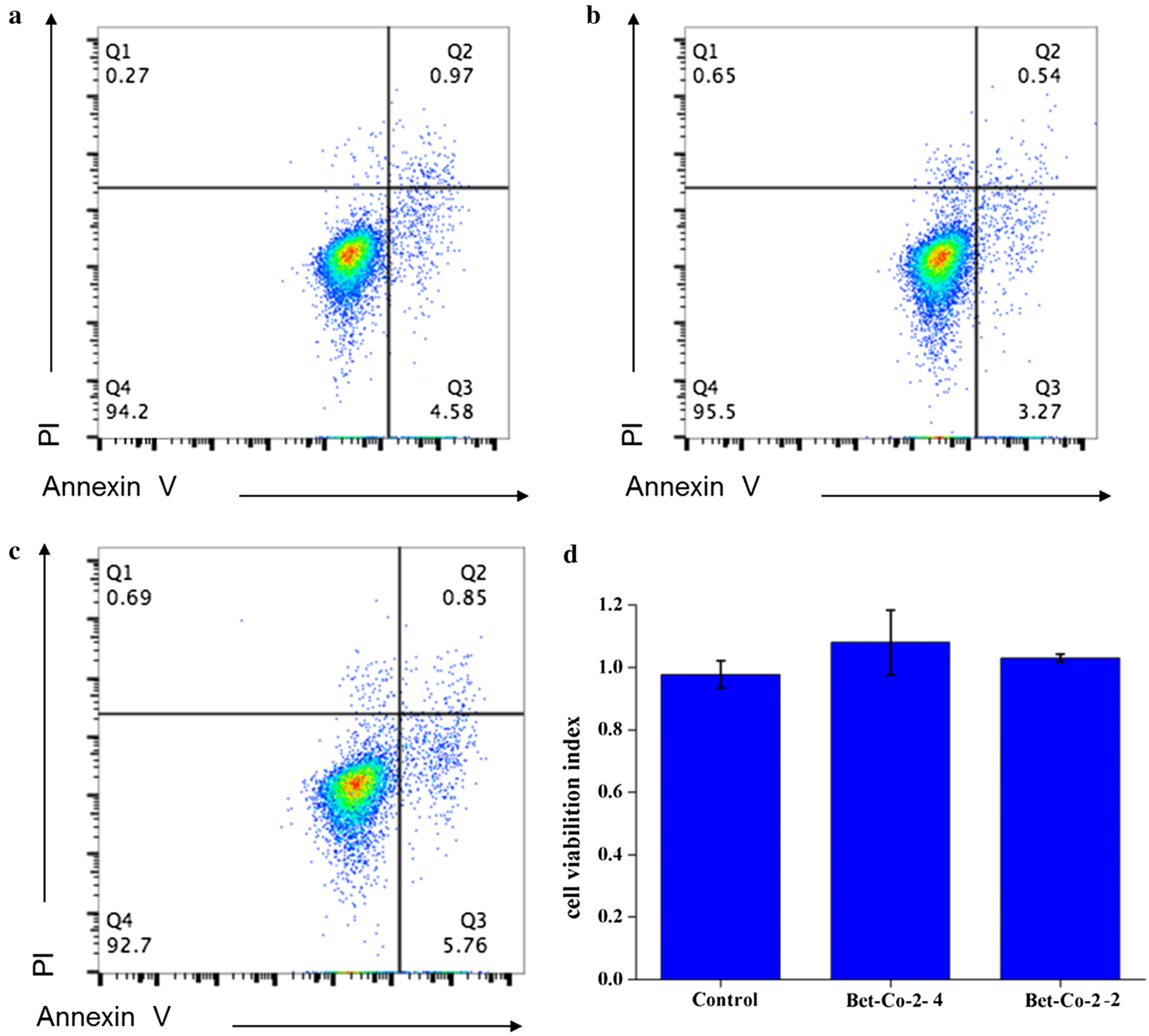


Fig. 7 **a**–**c** Apoptosis assays and **d** in vitro cytotoxicity (CCK-8) assessments of the leachate solution from Bet-Co-2 fabric. Results are presented for **a** control, **b** Bet-Co-2-4, and **c** Bet-Co-2-2

that the modification process does not significantly damage the crystalline structure of cellulose.

Antibacterial effects of the Bet-Co fabrics

The images showing the antibacterial activity of the original cotton, Bet-Co-1, and Bet-Co-2 fabrics against *S. aureus* and *E. coli* are shown in Fig. 4a. Meanwhile, Fig. 4b compares the statistically calculated BR values. The results indicate that Bet-Co-1 and Bet-Co-2 possess excellent antibacterial activity (BR $>$ 99%) compared to the original cotton fabric (control sample). Furthermore, the antibacterial function of the modified fabrics is durable (Figs. 4c and S10), with *E. coli* and *S. aureus* BR values maintained above 90%, even after 20 cycles of laundering.

The images showing the antibacterial activity of the original cotton, Bet-Co-1, and Bet-Co-2 fabrics against *S. aureus* and *E. coli* are shown in Fig. 4a. Meanwhile, Fig. 4b compares the statistically calculated BR values. The results indicate that Bet-Co-1 and Bet-Co-2 possess excellent antibacterial activity (BR $>$ 99%) compared to the original cotton fabric (control sample). Furthermore, the antibacterial

function of the modified fabrics is durable (Figs. 4c and S10), with *E. coli* and *S. aureus* BR values maintained above 90%, even after 20 cycles of laundering.

To understand the bacterial adhesion behavior of Bet-modified fabrics, SEM images showed the adhesion of bacteria to different fiber surfaces were recorded and compared. *S.aureus* and *E.coli* were used as bacterial models in this investigation. The images presented in Fig. 5 show that a number of bacteria, with relatively pristine shapes, are adhered to the surface of the original cotton fibers (Fig. 5), whereas no bacteria are detected on Bet-Co-2 (Fig. 5). Considering that the bacterial morphologies observed herein are consistent with those reported previously for cationic bactericides (Hoque et al. 2012; Qiao et al. 2019). It is suggested that the antibacterial effect of Bet-modified fabrics is due to the quaternary ammonium group of Bet.

The anti-protein adsorption performance of the modified (Bet-Co-1 and Bet-Co-2) and original cotton fabrics was also evaluated. The light absorbance data illustrated in Fig. 6 demonstrate that the amounts of BSA present in solution after the immersion of the original cotton fabric is below the detection limit. However, the concentration of BSA (absorbance at 280 nm) remains relatively the same before and after the immersion of the modified fabrics. This indicates that unlike the original cotton sample, the Bet-modified fabrics do not significantly adsorb proteins. Therefore, Bet grafting enhances the anti-protein fouling property of fabrics, thereby blocking the nutritional source needed for bacterial growth and preventing biofilm formation (Dang et al. 2015; Harris et al. 2011).

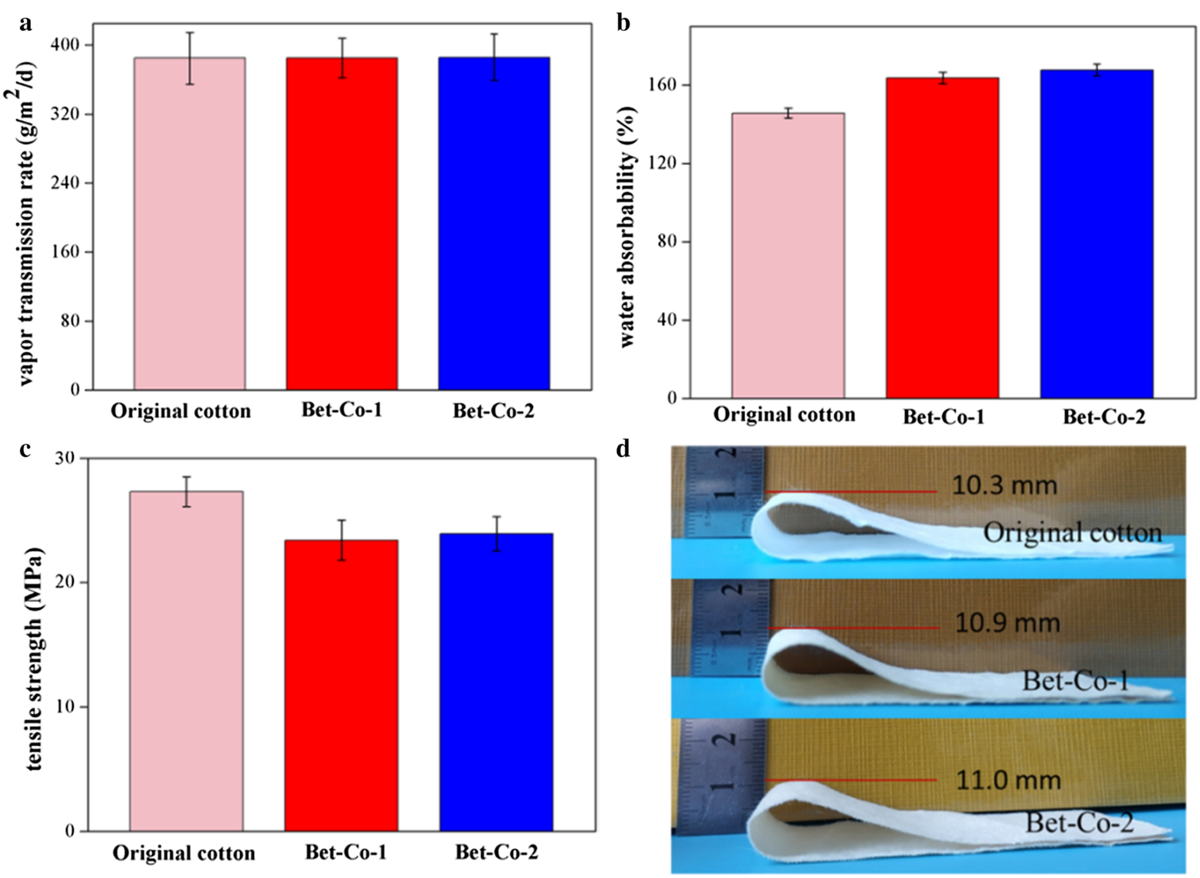


Fig. 8 **a** Water absorbability, **b** vapor transmissibility, **c** tensile strength, and **d** flexibility of the original cotton fabric and Bet treated fabrics

Safety and wearing comfort properties of Bet-Co fabrics

To evaluate the safety of fabrics that are in direct contact with human skin, cytotoxicity measurements are commonly carried out. In this work, cell viability was assessed using leachates (Table S4) of fabrics immersed in physiological saline solution. The apoptosis assays presented in Fig. 7 show no obvious differences between the original and modified cotton fabrics. In fact, both fabrics exhibit good cell viability, meaning that the compounds leached from them are non-toxic against Hacat cells.

Water vapor permeability, water absorbability, mechanical strength, and flexibility are typical wearing comfort properties of cotton fabrics. To ensure that the modification process does not appreciably damage these features, they were measured and compared for all investigated fabrics. As shown in Fig. 8a, the vapor transmissibility of the modified cotton is similar to that of the original sample. However, Bet grafting increases water absorbability from 145.9% in original cotton to 163.6 and 167.7% in Bet-Co-1 and Bet-Co-2 fabrics, respectively (Fig. 8b). Such increase is attributed to the highly hydrophilic nature of Bet. As for tensile strength, it decreases slightly upon modification, probably due to the effect of esterification reaction in increasing acidity (Fig. 8c). Finally, the original and modified fabrics possess comparable flexibilities, with the former presenting a maximum loop height of 10.3 mm, compared to 11 mm for the latter (Fig. 8d).

The thermal stability of fabrics was studied by thermogravimetric analysis (TGA). Based on the results depicted in Fig. S11, the thermal decomposition profiles of modified fabrics are consistent with those of the original cotton, which indicates that the Bet coating layer is sufficiently stable under drying and ironing conditions.

Conclusion

In this study, betaine, an antibacterial agent, was covalently bonded to cotton fiber surfaces via the esterification reaction between the carbonyl groups of the modifier and the hydroxyl groups of cellulose. This modification endowed the fabric with excellent antibacterial and anti-serum protein adsorption capacities, without compromising its wearing comfort properties, such as water absorbability, vapor transmissibility, and flexibility. The experimental results indicate that the Bet-modified fabrics exhibit inhibition rates of *E. coli* and *S. aureus* ($> 99\%$) much greater than those of the original cotton fabric. Furthermore, the antibacterial effect of the former is largely maintained, even after 20 washing cycles. Cytotoxicity tests confirm that the modified fabrics pose no health hazards and are thus safe to wear against human skin. The harmless nature of betaine and the simplicity of the grafting process render the proposed modification strategy an advantageous and environmentally friendly approach for the fabrication of antibacterial textiles.

Acknowledgments This study was funded by National Natural Science Foundation of China (Grant Numbers 51873195 and 51573167).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Amini SM (2019) Preparation of antimicrobial metallic nanoparticles with bioactive compounds. Mater Sci Eng C Mater Biol Appl 103:109809

Arza CR, Ilk S, Demircan D, Zhang B (2018) New biobased non-ionic hyperbranched polymers as environmentally friendly antibacterial additives for biopolymer. Green Chem 20(6):1238–1249

Burnett CL, Bergfeld WF, Belsito DV, Hill RA, Klaassen CD, Liebler DC, Marks JG, Shank RC, Slaga TJ, Snyder PW, Andersen FA, Heldreth B (2018) Safety assessment of alkyl betaines as used in cosmetics, safety assessment of alkyl betaines as used in cosmetics. Int J Toxicol 37:28–46

Chambers ST, Lever M (1996) Betaines and urinary tract infections. Nephron 74(1):1–10

Chatha SAS, Asgher M, Asgher R, Hussain AI, Iqbal Y, Hussain SM, Bilal M, Saleem F, Iqbal HMN (2019) Environmentally responsive and anti-bugs textile finishes-recent trends, challenges, and future perspectives. Sci Total Environ 690:667–682

Chen S, Chen S, Jiang S, Mo Y, Luo J, Tang J, Ge Z (2011a) Study of zwitterionic sulfopropylbetaine containing reactive siloxanes for application in antibacterial materials. Colloid Surface B 85(2):323–329

Chen S, Chen S, Jiang S, Mo Y, Tang J, Ge Z (2011b) Synthesis and characterization of siloxane sulfobetaine antimicrobial agents. Surf Sci 605(11):25–28

Chen S, Chen S, Jiang S, Xiong M, Luo J, Tang J, Ge Z (2011c) Environmentally friendly antibacterial cotton textiles finished with siloxane sulfopropylbetaine. ACS Appl Mater Interfaces 3(4):1154–1162

Chen S, Yuan L, Li Q, Li J, Zhu X, Jiang Y, Sha O, Yang X, Xin J, Wang J, Stadler F, Huang P (2016a) Durable antibacterial and nonfouling cotton textiles with enhanced comfort via zwitterionic sulfopropylbetaine coating. Small 12(26):3516–3521

Chen Y, Li J, Li Q, Shen Y, Ge Z, Zhang W, Chen S (2016b) Enhanced water-solubility, antibacterial activity and biocompatibility upon introducing sulfobetaine and quaternary ammonium to chitosan. Carbohydr Polym 143:246–253

Chen Y, Zhang Q, Ma Y, Han Q (2018) Surface-oriented fluorinated pyridinium silicone with enhanced antibacterial activity on cotton via supercritical impregnation. Cellulose 25(2):1499–1511

Cheng G, Li G, Xue H, Chen S, Bryers JD, Jiang S (2009) Zwitterionic carboxybetaine polymer surfaces and their resistance to long-term biofilm formation. Biomaterials 30(28):5234–5240

Choi YJ, Na JD, Jun DS, Kim YC, Funct J (2018) Protective effect of betaine against galactosamine-induced acute liver injury in rats. J Funct Foods 44:65–73

Cholewa JM, Guimaraes-Ferreira L, Zanchi NE (2014) Effects of betaine on performance and body composition: a review of recent findings and potential mechanisms. Amino Acids 46(8):1785–1793

Cosquer A, Pichereau V, Le Mee D, Le Roch M, Renault J, Carboni B, Uriac P, Bernard T (1999) Toxicity and osmoprotective activities of analogues of glycine betaine obtained by solid phase organic synthesis towards *Sinorhizobium meliloti*. Bioorg Med Chem Lett 9(1):49–54

Cosquer A, Ficamos M, Jebbar M, Corbel JC, Choquet G, Fontenelle C, Uriac P, Bernard T (2004) Antibacterial activity of glycine of betaine analogues: involvement osmoporters. Bioorg Med Chem Lett 14(9):2061–2065

Craig SA (2004) Betaine in human nutrition. Am J Clin Nutr 80:539–549

Dang Y, Xing CM, Quan M, Wang Y, Zhang S, Shi S, Gong Y (2015) Substrate independent coating formation and antibiofouling performance improvement of mussel inspired polydopamine. J Mater Chem B 3(20):4181–4190

Fouda MM, Abdel-Halim ES, Al-Deyab SS (2013) Antibacterial modification of cotton using nanotechnology. Carbohydr Polym 92(2):943–954

Ghartavol MM, Aziz SGG, Babaei G, Farjah GH, Ansari MHK (2019) The protective impact of betaine on the tissue structure and renal function in isoproterenol-induced myocardial infarction in rat. Mol Genet Genom Med 7(4):579

Harifi T, Montazer M (2015) A review on textile sonoprocessing: a special focus on sonosynthesis of nanomaterials on textile substrates. Ultrason Sonochem 23:1–10

Harris CA, Resau JH, Hudson EA, West RA, Moon C, Black AD, McAllister JP (2011) Reduction of protein adsorption and macrophage and astrocyte adhesion on ventricular catheters by polyethylene glycol and *N*-acetyl-L-cysteine. J Biomed Mater Res A 98(3):425–433

He L, Gao C, Li S, Chung CTW, Xin JH (2017) Non-leaching and durable antibacterial textiles finished with reactive zwitterionic sulfobetaine. J Ind Eng Chem Mater 46:373–378

Hoque J, Akkapeddi P, Yarlagadda V, Uppu DS, Kumar P, Haldar J (2012) Cleavable cationic antibacterial amphiphiles: synthesis, mechanism of action, and cytotoxicities. Langmuir 28(33):2225–2234

Huang Z, Li Y, Ai Z, Wang N, Pan Z, Xie X, Fan H, Suo B (2014) Effects of betaine on the growth of Staphylococcus aureus and the establishment of inactivation model. J Chin Inst Food Sci Technol 14:42–48

Jurewicz J, Radwan M, Wielgomas B, Kaluzny P, Klimowska A, Radwan P, Hanke W (2018) Environmental levels of triclosan and male fertility. Environ Sci Pollut Res Int 25(10):5484–5490

Kishitani S, Takanami T, Suzuki M, Oikawa M, Yokoi S, Ishitani M, Alvarez-Nakase AM, Takabe T (2000) Compatibility of glycinebetaine in rice plants: evaluation using transgenic rice plants with a gene for peroxisomal betaine aldehyde dehydrogenase from barley. Plant Cell Environ 23:107–114

Kritchenkov AS, Egorov AR, Dysin AP, Volkova OV, Zabodalova LA, Suchkova EP, Kurliuk AV, Shakola TV (2019) Ultrasound-assisted Cu(I)-catalyzed azide-alkyne click cycloaddition as polymer-analogous transformation in chitosan chemistry. High antibacterial and transfection activity of novel triazol betaine chitosan derivatives and their nanoparticles. Int J Biol Macromol 137:592–603

Lever M, Slow S (2010) The clinical significance of betaine, an osmolyte with a key role in methyl group metabolism. Clin Biochem 43(9):732–744

Li L, Jin Y, Zhou H, Wang H (2018) Synthesis of zwitterionic *N*-chlorohydantoins for antibacterial applications. Bioorg Med Chem Lett 28(23):3665–3669

Lindstedt M, Allenmark S, Thompson RA, Edebo L (1990) Antimicrobial activity of betaine esters, quaternary ammonium amphiphiles which spontaneously hydrolyze into nontoxic components. Antimicrob Agents Chemother 34(10):1949–1954

Liu S, Zhou H, Wang H, Yang W, Shao H, Fu S, Feng Z, Lin T (2017) Argon-plasma reinforced superamphiphobic fabrics. Small 13(40):1701891

Liu G, Xiang J, Xia Q, Li K, Lan T, Yu L (2018) Superhydrophobic cotton gauze with durably antibacterial activity as skin wound dressing. Cellulose 26(2):1383–1397

Lu L, Hu C, Zhu Y, Zhang H, Li R, Xing Y (2018) Multifunctional finishing of cotton fabrics by water-based layer-by-layer assembly of metal–organic framework. Cellulose 25(7):4223–4238

Pan Y, Yang P, Moloney MG, Wang L, Ma F, Wang Y (2018) Ag NP-loaded cotton fiber materials: preparation, surface deposition, and antibacterial activity with different chemical structures. ACS Appl Biol Mater 2(1):510–517

Peddie BA, Wong-She J, Randall K, Lever M, Chambers ST (1998) Osmoprotective properties and accumulation of betaine analogues by Staphylococcus aureus. Fems Microbiol Lett 160(1):25–30

Pu Y, Hou Z, Khin MM, ZamudioVazquez R, Poon KL, Duan H, ChanPark MB (2017) Synthesis and antibacterial study of sulfobetaine/quaternary ammonium-modified star-shaped poly[2-(dimethylamino)ethylmethacrylate]-mased copolymers with an inorganic core. Biomacromol 18(1):44–55

Qiao Z, Yao Y, Song S, Yin M, Luo J (2019) Silver nanoparticles with pH induced surface charge switchable properties for antibacterial and antibiofilm applications. J Mater Chem 7(5):830–840

Rauytanapanit M, Opitakorn A, Terashima M, Waditee-Sirisattha R, Praneenararat T (2018) Antibacterial cotton fabrics based on hydrophilic amino-containing scaffolds. Colloid Surface B 164:42–49

Reinoso DM, Damiani DE, Tonetto GM (2012) Zinc carboxylic salts used as catalyst in the biodiesel synthesis by esterification and transesterification: study of the stability in the reaction medium. Appl Catal A Gen 449:88–95

Reshma A, Priyadarisini VB, Amutha K (2018) Sustainable antimicrobial finishing of fabrics using natural bioactive agents—a review. Int J Life Sci Pharma Res 8(4):10–20

Rovira J, Domingo JL (2019) Human health risks due to exposure to inorganic and organic chemicals from textiles: a review. Environ Res 168:62–69

Shahid M, Mohammad F, Chen G, Tang RC, Xing T (2016) Enzymatic processing of natural fibres: white biotechnology for sustainable development. Green Chem 18(8):2256–2281

Shahidul I, Shahid M, Mohammad F (2013) Green chemistry approaches to develop antimicrobial textiles based on sustainable biopolymers—a review. Ind Eng Chem Res 52(15):5245–5260

Shahidul Islam SUI, Butola BS, Mohammad F (2016) Silver nanomaterials as future colorants and potential antimicrobial agents for natural and synthetic textile materials. RSC Adv 6(50):44232–44247

Song L, Sun L, Zhao J, Wang X, Yin J, Luan S, Ming W (2019) Synergistic superhydrophobic and photodynamic cotton textiles with remarkable antibacterial activities. ACS Appl Biol Mater 2(7):2756–2765

Su Y, Guo Q, Wang S, Zhang X, Wang J (2018) Effects of betaine supplementation on L-threonine fed-batch fermentation by Escherichia coli. Bioproc Biosyst Eng 41(10):1509–1518

Turck D, Bresson J-L, Burlingame B et al (2017) Safety of betaine as a novel food pursuant to regulation. Efsa J 15(11):1831–4732

Wang B, Zhang Y, Mao Z, Yu D, Gao C (2014) Toxicity of ZnO nanoparticles to macrophages due to cell uptake and intracellular release of zinc ions. J Nanosci Nanotechnol 14(8):5688–5696

Wehrs M, Wehrs JM, Liu Y, Platz L, Prahl JP, Moon J, Papa G, Sundstrom E, Geiselman GM, Tanjore D, Keasling JD, Pray TR, Simmons BA, Mukhopadhyay A (2019) Green Chemistry Sustainable bioproduction of the blue pigment indigoidine: expanding the range of heterologous products in R toruloides to include non-ribosomal peptides. Green Chem 21:3394–3406

Windler L, Height M, Nowack B (2013) Comparative evaluation of antimicrobials for textile applications. Environ Int 53:62–73

Xu K, Xu P (2014) Betaine beet molasses enhance L-lactic acid production by *Bacillus coagulans*. Plos One 9(6):100731

Xu Q, Li R, Shen L, Xu W, Wang J, Jiang Q, Zhang L, Fu F, Fu Y, Liu X (2019a) Enhancing the surface affinity with silver nano-particles for antibacterial cotton fabric by coating carboxymethyl chitosan and L-cysteine. Appl Surf Sci 497:143673

Xu Q, Zheng W, Duan P, Chen J, Zhang Y, Fu F, Diao H, Liu X (2019b) One-pot fabrication of durable antibacterial cotton fabric coated with silver nanoparticles via carboxymethyl chitosan as a binder and stabilizer. Carbohydr Polym 204:42–49

Xu Q, Shen L, Duan P, Zhang L, Fu F, Liu X (2020) Superhydrophobic cotton fabric with excellent healability fabricated by the "grafting to" method using a diblock copolymer mist. Chem Eng J 379:122401

Yetisen AK, Qu H, Manbachi A, Butt H, Dokmeci MR, Hinestroza JP, Skorobogatiy M, Khademhosseini A, Yun SH (2016) Nanotechnology in textiles. ACS Nano 10(3):3042–3068

Zhang S, Yang X, Tang B, Yuan L, Wang K, Liu X, Zhu X, Li J, Ge Z, Chen S (2018) New insights into synergistic antimicrobial and antifouling cotton fabrics via dually finished with quaternary ammonium salt and zwitterionic sulfobetaine. Chem Eng J 336:123–132

Zhao S, Zhang Q, Hao G, Liu X, Zhao J, Chen Y, Zhang H, Chen W (2014) The protective role of glycine betaine in Lactobacillus plantarum ST-III against salt stress. Food Control 44: 208–213

Zhu C, Chalmers E, Chen L, Wang Y, Xu B, Li L, Liu X (2019) A nature-inspired, flexible substrate strategy for future wearable electronics. Small 15(35):1902440

Zou H, Wu Z, Xian M, Liu H, Cheng T, Cao Y (2013) Not only osmoprotectant: Betaine increased lactate dehydrogenase activity and L-lactate production in *Lactobacilli*. Bioresour Technol 148:591–595

Zou H, Chen N, Shi M, Xian M, Song Y, Liu J (2016) The metabolism and biotechnological application of betaine in microorganism. Appl Microbiol Biol 100(9):3865–3876