Developing the functional cotton fabric with N-halamine antibacterial structure based on DA/PEI

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Abstract In this study, functional coatings with N-halamine structure were formed on cotton fabrics by dopamine (DA) auto-deposition and DA/Polyethylenimine (PEI) covalent co-deposition, respectively. SEM, UV-Vis and XPS had confirmed the deposition of DA and DA/ polydopamine (PDA) on the cotton fabrics. When the mass ratio of DA/PEI was 1:1.5, a uniform functional coating was formed. XRD had indicated that the coating and the oxidative sodium hypochlorite solution did not affect the crystal structure of cellulose. The DA/PEI co-deposited modified cotton fabric had excellent antibacterial property after chlorination, and the inactivation rate against *E. coli* and *S. aureus* could reach 100% with a contact time of 30 min. In vitro cell cytocompatibility studies demonstrated that the DA/PEI co-deposited modified cotton fabric has good biocompatibility. The functional coating on the cotton fabric remained stable after 50 washing cycles. The UPF values and the wrinkle recovery angle (WRA) tests showed that the DA/PEI co-deposited coating imparted great durable press and UV protective properties to the cotton fabric. The breaking strength loss rate of the modified cotton fabrics after chlorination was about 20%, which had little effect on the wearing property.
Introduction

As a natural fabric, cotton fabric has been popular with people because of its superior comfort, breathability, and hygroscopicty compared with synthetic fabrics, and is frequently used as underwear (Li et al. 2020). However, the porous structure of the cotton fabric can support bacterial growth, which harms human health (Zhou et al. 2021). In recent years, N-halamines stand out from many traditional antibacterial agents through their advantages of rapid inactivation, broad-spectrum antibacterial, long-term stability, renewable antibacterial properties, and safety for humans and the environment, and it has received more and more attention from researchers (Dong et al. 2017). N-halamines refer to organic compounds containing one or more \( \text{N}–\text{X} \) (\( \text{X} = \text{Cl}, \text{Br}, \text{or I} \)) covalent bonds. Usually, the precursor compounds containing amine, amide, or imide groups are oxidized to obtain N-halamines by exposure to dilute household bleach or halogen-releasing agents (Kaur et al. 2016). The halogen in N-halamines is usually Cl. Because N–Br and N–I are more active and unstable, these are difficult to apply in practice. The N–Cl bonds of N-halamines structures release oxidative chloride ions through the hydrolysis, and destroy the cell membrane and metabolism of bacteria to inactivate them. After bacteria inactivation, The N–Cl bond is deoxidized to the N–H bond, but after chlorination by household bleach solution, the N–Cl bond is regained, which brings renewable antibacterial properties to N-halamine antibacterial materials. This characteristic is not available in other antibacterial agents (Cerkez et al. 2016).

N-halamines have been generally combined with fibrous substrates by grafting or coating (Gao et al. 2015; Sun et al. 2012). The key to this surface modification is to find suitable methods to combine N-halamines with various fiber materials. Strategies of surface modification can be classified into chemical surface modification (Chien et al. 2019) and physical surface modification (Cerkez et al. 2011), according to whether there is a chemical bonding between N-halamine moieties and fibrous substrates. Although surface modification methods are versatile and efficient, these methods involve complex surface pre-treatment or a large number of reaction steps. To overcome this limitation, antibacterial polymers based on N-halamine modifications have been developed.

Dopamine (DA), an organic compound with functional catechol and amino groups, can spontaneously oxypolymerize into polydopamine (PDA) under aerobic conditions.
and weak alkaline conditions, and DA can be deposited on all types of the organic and inorganic materials and forms a functional coating (Hou et al. 2015; Lee et al. 2007; Zeng et al. 2013). This is most important that the N–H bond in the PDA structure is generated N–Cl bond after chlorination by household bleach solution, gives the coating certain antibacterial properties (Chien et al. 2020; Nazi et al. 2020; Nazi et al. 2022). However, the method still suffers from a long deposition time (Zhang et al. 2016), instability in the alkaline environment (Ball 2014; Ponzio et al. 2016a; Ponzio et al. 2016b; Wei et al. 2013), and inhomogeneous coating surface roughness (Kim et al. 2013). These limit application of DA. The groups in the PDA as secondary reactions platform react with amine- or thiol-containing molecules via Michael addition or Schiff-base reactions (Jegal et al. 2015). Co-deposition of amino-rich polyethyleneimine (PEI) with DA in solution, the covalent reaction occurs between oxidized dopamine and amino groups of PEI, significantly accelerates the deposition process, and covalent co-deposition also improves the coating chemistry stability (Yang et al. 2014). Meanwhile, the incorporation of PEI disrupts the non-covalent interactions (such as hydrogen bonding and π–π stacking) in the PDA, thereby reducing the particle size and making the co-deposited coating more uniform. The PEI chain contains a large number of N–H bonds, and the active chlorine content of the coating increases significantly after chlorination (Qiu et al. 2018).

In this work, functional coatings were prepared on the cotton fabrics by DA deposition and DA/PEI co-deposition. The morphology, chemical composition, and structures of modified fabrics surface were analyzed by SEM, UV-Vis, XPS, and XRD. The inhomogeneity of PDA coatings was solved by incorporating PEI, which brought great UV resistance and the durable pressing property for modified fabrics. The most major was to use the N–H bond on PEI to increase the active chlorine content of the coating after chlorination, thereby improving the antibacterial property. The washing stability, acid and alkali resistance stability, and storage stability of the modified fabrics were examined, and then the effect of modified cotton fabrics on the activity of Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) was analyzed. In vitro cell cytocompatibility test was conducted to assess biocompatibility of the DA/PEI coating cotton fabrics.

**Experimental**

**Materials**

Bleached woven cotton fabric (plain, 106 g/m², density: 440/10 cm for warp and 348/10 cm for weft, 60 × 60 s) were purchased from Zhongxin Shandong Textile Co., Ltd. 3-hydroxytyramine hydrochloride (dopamine hydrochloride) was purchased from Aladdin Shanghai Co., Ltd. Tris(hydroxymethyl) methyl aminomethane (Tris), Polyethyleneimine (Mw= 600 Da) and potassium iodide (KI) were obtained from Macklin Shanghai Co., Ltd. Sodium Thiosulfate Standard (Na2S2O3) Solution was produced in Yida Quanzhou Co., Ltd. Starch soluble and sulfuric acid

![Fig. 1 Schematic diagram of cotton fabrics modification and chlorination process](image-url)
were purchased from Damao Tianjin Co., Ltd. The sodium hypochlorite (NaClO) solution was provided by Kermel Tianjin Co., Ltd. The biological agents of *S. aureus* (ATCC6538) and *E. coli* (ATCC 25,922) were prepared in Guduo Shanghai Biological Technology Co., Ltd. 3T3 mouse fibroblasts were purchased from Shanghai Cell Bank.

Surface modification of cotton fabrics

0.2 g DA alone or DA/PEI with different mass ratios were dissolved in 100 mL Tris buffer (pH = 8.5, 10 mM). Then the cotton fabrics were immersed in the solution, the bath ratio was 1:30 (g: mL), and the cotton samples were taken out after 6 h at room temperature. Finally, the modified fabrics were rinsed with deionized water and dried in an oven at 45 °C to obtain PDA-Cotton and PDA/PEI-Cotton.

Chlorination of modified cotton fabrics

The NaClO solution was diluted (oxidative chlorine content ≥ 5.2%) by 10 times and its pH was adjusted with dilute sulfuric acid. Then, the modified cotton fabrics were immersed in 10% NaClO solution at a bath ratio of 1:30 and soaked at room temperature for 1 h. Finally, the chlorinated cotton samples were taken out and rinsed with deionized water to eliminate the residual solution on the samples, and then dried in an oven at 45 °C to obtain the PDA-Cotton-Cl and PDA/PEI-Cotton-Cl. The surface modification and chlorination process of cotton fabrics are shown in Fig. 1.

Characterizations

The surface morphology of cotton fabrics before and after modification was observed by scanning electron microscope (SEM, SM-7800 F, SHIMADZU, Japan). Ultraviolet-visible spectroscopy (UV-Vis, UV-8000, Shanghai, China) of the DA/PEI solution was measured with a scanning range of 800–00 nm. The elemental composition of the sample’s surface was evaluated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA), the diffraction source was Al Kα, the voltage was 12 kV and the current was 6 mA. The crystal structure of the samples was tested by X-ray diffraction (XRD-6100, SHIMADZU, Japan), the diffraction source was Cu Kα, the diffraction angle range was 10–80°, the scanning speed was 2°/min at 40.0 kV and 30 mA.

Determination of the active chlorine content

The active chlorine content of PDA and PDA/PEI coating cotton fabrics after chlorination was determined by the sodium thiosulfate/iodometric method. 0.25 g KI and 10 mL deionized water were placed in a conical flask and stirred for a period to dissolve the KI. Then 0.1 g of chlorinated cotton sample and 10 drops of 0.5% starch solution were added, and it shook gently to immerse the chlorinated sample in the solution. After stirring for a while, the color of solution turned dark blue, because the N–Cl bond on the chlorinated cotton fabric was hydrolyzed to generate oxidative Cl⁺, I⁻ was oxidized to I₂, and I₂ turned blue when met with starch. Finally, the dark blue solution was titrated with 0.001 N Na₂S₂O₃ standard solution until the solution became colorless, recorded the volume of Na₂S₂O₃ solution used, titrated three times in parallel for each group, and the weight% Cl⁺ on the samples was calculated by the following formula (1).

\[
Cl^+ (wt\%) = \frac{N \times 35.45 \times V}{2m} \times 100
\]

where Cl⁺ % is the wt percent of oxidative chlorine on the samples, N and V are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and m is the weight of the cotton swatch in g.

Washing stability

The washing stability of PDA and PDA/PEI coated fabrics was evaluated according to the standard AATCC 61-1996 Test Method. Two test samples with a size of 5.08 cm × 2.54 cm were placed in a stainless steel canister with 150 mL of 0.15% soap-solution and 50 stainless steel balls. The canister was rotated with 42 rpm at 49 °C. Every 45 min of washing is equivalent to 5 cycles of ordinary household washing. After the 5, 10, 25, and 50 cycles of water washing, a canister sample was taken out, washed with deionized water, and dried in an oven.
at 45 °C. The dried samples were chlorinated and their active chlorine content was measured, and the washing stability of the coatings was evaluated by the loss of active chlorine content.

Acid and alkali resistance stability

The modified fabrics were chlorinated for 1 h using 10% NaClO solution with different pH (pH = 5, 6, 7, 8, 9, 10). After chlorination, the samples were washed and dried and then titrated to calculate their active chlorine content. The loss of coatings in acid and alkali environments was evaluated by active chlorine content.

Storage stability

PDA-cotton-Cl and PDA/PEI-cotton-Cl were put into sealed bags and stored in a dark environment. After reaching the specified storage time (0, 5, 10, 15, 20, 25, and 30 d), the storage stability of the modified cotton fabrics was evaluated by the active chlorine content in the samples.

Biocidal efficacy testing

A modified AATCC 100–2004 Antimicrobial Testing Standard (called the “sandwich” test method) was used to evaluate the modified fabrics’ inhibitory properties against S. aureus and E. coli. 25 µL of bacterial suspension was added dropwise to a sample with a size of 2.54 × 2.54 cm, which was then covered with another sample of the same size, and finally, a sterile weight was used to ensure adequate contact between the two samples. After 30 min of contact time, the samples were immersed in a centrifuge tube containing 5 mL of 0.01 M sterile Na₂S₂O₃ solution to ensure complete quenching of the active chlorine. The solution with bacteria was diluted and added dropwise to the Trypticase agar and the number of colonies was counted after culturing at 37 °C for 24 h, and the antibacterial effect of each test sample was analyzed.

In vitro cytocompatibility evaluation

In vitro cytocompatibility of the fabric samples was estimated by using 3T3 mouse fibroblasts. 3T3 cells were cultured in DMEM medium containing 10% FBS and 1% Pentrip. After culturing, the cells were evenly seeded into 96 well plates, and then the medium was placed in a 37 °C incubator containing 5% CO₂ for 24 h. Then, 100 µL of sample extract or blank medium was used in place of the above medium, respectively. After culturing for 4 and 24 h, the cell proliferation was evaluated by measuring the absorbance (λ = 450 nm) by a microplate reader, and each sample was tested three times.

UV protective property

According to the AATCC183-2014 evaluation test standard for UV protection of textiles, a UV-2000 UV transmittance analyzer was selected to measure UVA, UVB, and UPF of cotton fabrics before and after modification.

Wrinkle recovery angle (WRA) measurement

The WRAs (warp + weft) of the modified cotton fabrics were tested according to the AATCC66-2008 standard. Three replicate experiments were performed for each group, and the results were averaged.

Physical mechanical property

According to the GB/T 3923 − 2013 test standard, the breaking strength of the test samples (20×5 cm) in the warp and weft directions was tested 3 times respectively, and the average value was calculated.

Results and discussion

Surface morphology and structural analysis

In order to determine the optimal mass ratio of DA and PEI, the SEM images of DA/PEI-cotton fabrics with mass ratios of 1:0.25, 1:1.5, and 1:3 were explored. The SEM images of the unmodified cotton fabrics, the DA deposition cotton fabrics, and the DA/PEI co-deposition cotton fabrics at the optimal mass ratios were compared, and the results are shown in Fig. 2.

The SEM images in Figs. 2A, B, and C show the surface morphology of modified cotton fabrics with PDA/PEI mass ratios of 1:0.25, 1:1.5, and 1:3 respectively. It can be seen that when the mass ratio of DA/PEI is 1:1.5, a uniform coating is formed on
the surface of the cotton fabric, while too little or too much PEI is not conducive to improving the uniformity of the coating. The SEM images in Fig. 2D and G show the surface of cotton fabrics. The surface of cotton fabrics is relatively smooth, with a certain degree of roughness and some natural impurity particles. In contrast, a large number of particles are formed on the surface of the DA modification cotton fabrics, and the distribution is inhomogeneous, as shown in Fig. 2E–H. This is due to the non-covalent interactions between the DA/PDA molecules, which cause the particles to agglomerate together. After co-deposition of DA and PEI on cotton fabrics are shown in Fig. 2F–I. It can be seen that there are no obvious aggregates on the surface of cotton fabrics, fine particles are formed and the co-deposited coating is more uniform. This is because PEI molecules are incorporated to the PDA aggregates, and the non-covalent interactions are destroyed by the covalent reaction between DA and PEI, and then inhibit the formation of particle aggregates.

The color change of the DA deposition and DA/PEI co-deposition solution at different times, and the UV-Vis absorption spectrum of the solution after 6 h reaction is shown in Fig. 3. It can be seen from the inset, that the color of DA and DA/PEI solutions gradually becomes darker with reaction time. After 6 h, the solutions are gray-black and brown-black, which is caused by the oxidation of DA and the reaction between catechol and amino groups (Zhao et al. 2015). The DA solution after the 6 h reaction is relatively turbid, and black suspended particles or precipitates can be seen with the naked eye, while the DA/PEI solution is relatively clear and transparent.
This indicates that the incorporation of PEI disrupts the non-covalent interactions in the PDA aggregates and effectively inhibits the formation of particles. In addition, the UV absorption spectra of the DA solution and the DA/PEI solution are observed. It can be seen that the DA solution has a weak absorption peak at $\lambda = 404$ nm, which comes from the quinone structure ($C\equiv C-O$) formation. However, the absorption peak of the DA/PEI solution shifts to $\lambda = 359$ nm, which is due to the Schiff-base reaction between DA and PEI. The $C\equiv C-N$ structure is formed, which results in a blue shift of the absorption peak (Yang et al. 2016).

The chemical bonding state of the modified cotton fabrics was analyzed by XPS characterization, and the results are shown in Fig. 4. Figure 4A shows that C 1s, O 1s, and N 1s characteristic peaks are detected on both PDA-Cotton and PDA/PEI-Cotton. The intensity of the N 1s characteristic peak gradually increases, indicating that DA and PEI are successfully modified on the cotton fabrics. However, a weak N 1s characteristic peak is detected on cotton fabrics, which may originate from the slurry on the raw cotton fabric. Split-peak fitting was performed on the C 1s and N 1s spectrum, and the results are shown in Fig. 4B and C. Figure 4B shows that the C 1s spectrum of the PDA-Cotton and PDA/PEI-Cotton fit new peaks at 284.8, 286.3, and 287.5 eV, which correspond to C–C, C–O, and O–C═O bonds (Chien et al. 2020). Figure 4C shows that the N 1s spectrum of PDA-Cotton and PDA/PEI-Cotton appears peak around 400.5 eV, which is caused by the vibration of the C–N bond. However, the intensity of the corresponding $C\equiv N$ peak of PDA/PEI-Cotton around 402.5 eV is significantly enhanced, which indicates that the Schiff-base reaction occurs between PEI and PDA (Tian et al. 2013).

The crystal structures of the cotton fabric samples were analyzed by XRD, and the results are shown in Fig. 5. It can be seen from Fig. 5 that four diffraction peaks appear in the cotton fabric at $2\theta = 14.6, 16.6, 22.7, \text{ and } 34.3^\circ$, these correspond to (1–10), (110), (200), and (004) crystal planes of cellulose, respectively (Cheng et al. 2018). The XRD patterns of PDA-Cotton, PDA/PEI-Cotton, PDA-Cotton-Cl, and PDA/PEI-Cotton-Cl display the same diffraction peaks. These indicate that the PDA/PEI coating and the oxidative NaClO solution do not affect the crystal structure of cellulose.

The stability of the modified cotton fabrics has a profound effect on their application. As shown in Fig. 6, because the PEI chain contains a large number of N–H bonds, the active chlorine content of the PDA/PEI coating will greatly increase after chlorination with NaClO. With the increase in the washing cycles, the active chlorine content of the PDA and PDA/PEI coatings decreases slightly. This is because a small part of the unreacted PDA and PEI adheres to the cotton fabrics and falls off after washing, resulting in active chlorine content loss. However, the active chlorine content of both coatings remains generally stable throughout the washing cycle. This is due to the functional catechol group of DA can interact with cotton fabrics to form “anchor points”. On the one hand, it forms covalent bonds with cotton fabrics through oxidative coupling reaction, and on the other hand, various non-covalent interactions also generate strong adhesion on the surface of cotton fabrics. Finally, the covalent bonds formed by the reaction of DA and PEI together provide a strong connecting network for the coating to promote its stability.

In order to examine the acid-alkalinity stability of PDA and PDA/PEI coatings, the modified cotton fabrics were chlorinated with different pH of NaClO solutions (pH = 5, 6, 7, 8, 9, and 10), and then the active chlorine content of the cotton fabrics was measured. Figure 7 shows that with the increasing pH of the solution, the active chlorine content of
the coating after chlorination decreases continuously. When the pH of the chlorinated solution is 10, the active chlorine contents of the PDA and PDA/PEI coatings remain 0.018 and 0.071 wt%. Compared with the active chlorine content at pH = 5, the content of the PDA and PDA/PEI coatings remains 32.4 and 38.6%, respectively. It shows that the coatings are more stable in acidic solution than those in alkaline solution and the addition of PEI can bring certain chemical stability to the coating. This is because under acidic conditions, the amine groups on the PDA are protonated, and each structural unit of the polymer carries a positive charge. However, under alkaline conditions, the catechol groups are negatively charged, so each structural unit of PDA carries two negative charges. Therefore, the electrostatic repulsion between polymer chains in alkaline solutions is stronger than that in acidic solutions, which leads to more coating detachment from cotton fabrics (Wei et al. 2013). At the same time, due to the oxidabil-ity of NaClO solution, the PDA coating is degraded. They both lead to the active chlorine content of PDA and PDA/PEI coatings cotton decrease (Frari et al. 2012). The pH of the NaClO solution declines and the active chlorine content of the chlorinated coating increases. At the same time, the strong acid solution will damage the cotton fabric, irritate the human skin, and affect health. Therefore, in this paper, the pH of

Fig. 4 Full XPS spectra of cotton, PDA-Cotton, and PDA/PEI-Cotton (A), XPS high-resolution C 1s bands of PDA-Cotton and PDA/PEI-Cotton (B), and XPS high-resolution N 1s bands of PDA-Cotton and PDA/PEI-Cotton (C)
NaClO solution was selected as 6 when the coated cotton fabrics were chlorinated.

In the process of storage at room temperature, the active chlorine content of the N-halamine antibacterial materials decreases due to the action of moisture in the air (Ma et al. 2019). Therefore, the storage stability of PDA-Cotton-Cl and PDA/PEI-Cotton-Cl was studied. The active chlorine content of PDA-Cotton-Cl and PDA/PEI-Cotton-Cl after 5, 10, 15, 20, 25, and 30 days of storage were tested respectively, and the results are shown in Fig. 8. Under dark conditions, the active chlorine content of the cotton fabric decreases slowly with the storage time. The active chlorine contents of PDA-Cotton-Cl and PDA/PEI-Cotton-Cl lost 51.8 and 50.8% after 30 days. This is because the hydroxyl and amino groups contain in the structure of PDA and PEI endow cotton fabrics with stronger hydrophilicity, which can easily absorb moisture in the air, resulting in the hydrolysis of the N–Cl bond. Hence, the active chlorine content decreases gradually (Gutman et al. 2014).
Coating functionality

The antibacterial activity of Cotton, PDA-Cotton, PDA/PEI-Cotton, PDA-Cotton-Cl, and PDA/PEI-Cotton-Cl was evaluated against S. aureus and E. coli (the inoculation concentration of E. coli was about $1.81 \times 10^7$ CFU/sample, and the inoculation concentration of S. aureus was about $1.104 \times 10^5$ CFU/sample). After contacting for 30 min, compared with the blank sample, the bacteria log reduction of different modified cotton fabrics was calculated. The results are shown in Fig. 9. Figure 9A shows that cotton, PDA-Cotton, and PDA/PEI-Cotton are unchlorinated and do not contribute to their antibacterial properties. It can be seen from Fig. 9B and C that small bacteria on the raw cotton are reduced, which is caused by the adhesion of bacteria on the cotton fabrics during the contact process, do not cause by the inactivation of bacteria. PDA-Cotton can inactivate 0.663 log S. aureus and 0.567 log E. coli within 30 min because PDA lends to bacterial inactivation by damaging cell membranes (Karkhanecchi et al. 2014; Su et al. 2016). PDA/PEI-Cotton can inactivate 0.964 log S. aureus and 1.915 log E. coli within 30 min. The high reactivity and hydrophilicity of the amino group further enhance its antibacterial properties compared with
However, the inactivation amount of bacteria does not satisfy the requirements of high-property antibacterial materials. The antibacterial properties of the modified cotton fabrics are significantly improved after chlorination. PDA-Cotton-Cl with 0.056 wt% active chlorine can inactivate 1.663 log \( S. \text{aureus} \) and 3.178 log \( E. \text{coli} \) within 30 min, and the antibacterial rate reached more than 97%. PDA/PEI-Cotton-Cl with 0.182 wt% active chlorine can inactivate 5.043 log \( S. \text{aureus} \) and 7.258 log \( E. \text{coli} \) within 30 min, and the antibacterial rate reached 100%. Through the chlorination, the N–H bonds on PDA and PEI are converted to N–Cl bonds, and then the N–Cl bonds are hydrolyzed to generate oxidative active chloride ions (Cl\(^+\)), which damage and inhibit bacterial cell membranes and metabolism. The addition of PEI provides a large number of N–H bonds, and more Cl\(^+\) are released after chlorination, and then inactivates all bacteria.

The Cytocompatibility test is one of the important indicators to measure the toxicity of prepared materials. 3T3 mouse fibroblasts were inoculated on the samples. The cell viability was tested after 4 and 24 h of culture, and the results are shown in the Fig. 10. After 4 and 24 h of culture, the cell viability of raw cotton and the blank control group was about 100%, which indicated that raw cotton had no inhibitory

### Table 1  UV resistance of Cotton, PDA-Cotton and PDA/PEI-Cotton

| Sample          | UVA (%) | UVB (%) | UPF   |
|-----------------|---------|---------|-------|
| Cotton          | 4.80    | 6.49    | 15.28 |
| PDA-Cotton      | 2.85    | 3.38    | 28.85 |
| PDA/PEI-Cotton  | 1.28    | 1.36    | 72.32 |

PDA (Nguyen et al. 2017; Zhang et al. 2019).
effect on cell survival. At 4 h, the cell viability of PDA/PEI-Cotton and PDA/PEI-Cotton-Cl was about 93 and 97%, respectively. And when the culture time increased to 24 h, the cell viability of PDA/PEI-Cotton and PDA/PEI-Cotton-Cl was about 83 and 85%, respectively. According to the ISO/EN 10993-5:2009 evaluation standard, when the cell viability is higher than 70%, the material is safe and nontoxic. So the prepared co-deposition-coated cotton fabrics have good cytocompatibility.

UV protective property and the UV transmittance in the UVA and UVB region of the unmodified Cotton, PDA-Cotton, and PDA/PEI-Cotton was tested, the results are shown in Table 1; Fig. 11.

It can be seen from Fig. 11 that the UV transmittances of PDA-Cotton and PDA/PEI-Cotton in the UVA and UVB region are significantly lower than that of cotton fabric. From Table 1, compared with the raw cotton fabric, the UPF value of PDA-Cotton is increased by 13.57 and its average UVA transmittance is reduced by 1.95%. Because the structure of polydopamine is similar to the melanin in the human body (d’Ischia et al. 2009), its conjugated structure has the ability to capture free radicals and can quench the active free radicals generated by UV rays (Ju et al. 2011). The UPF value of PDA/PEI-Cotton reaches 72.32, and the UV transmittance further reduces. This is because the PEI can destroy the non-covalent effect of PDA aggregates, and make the coating more uniform, increase the area of absorbing ultraviolet rays, and then significantly improve the anti-ultraviolet property of the coating. According to the test standard, when the UPF > 50, and UVA < 5%, the cotton fabric has great UV protective property. Therefore, the PDA/PEI-Cotton is an excellent UV-resistant textile.

Intermolecular hydrogen bonds formed by free hydroxyl groups in cotton fabrics are the main reasons for the poor wrinkle resistance of unmodified cotton fabrics. The disassembly-reconstruction phenomenon of hydrogen bonds in the cotton fabric structure occurs under the stretching effect. The newly formed hydrogen bonds can prevent the macromolecular chains from returning to the original state, or the recovery rate is too slow. And then this causes the wrinkled phenomenon of cotton fabric. The larger the WRA of the cotton fabric then the better its durable pressing property (Cai et al. 2021).

Figure 12 shows the WRAs of the cotton fabrics before and after modification. After DA and DA/PEI modification, the WRAs of cotton fabrics increase to 170 and 207 °, respectively. The wrinkle resistance of both cotton fabrics is improved. The DA connects tightly to the cotton fabrics through covalent and non-covalent interactions. The covalent interaction refers to the coupling reaction of the catechol group on the PDA with the free hydroxyl group on the cotton fabric to form an ether bond. The ether bond increases the initial modulus and tensile deformation of cotton fabrics, and then the WRAs of the coated cotton fabrics increase significantly (Talukder et al. 2016). The addition of PEI disrupts the non-covalent interaction of PDA aggregates and makes the PDA/PEI coating coverage uniform. More catechol groups and more free hydroxyl groups are coupled, and the intermolecular hydrogen bonds are reduced, which further improves the WRAs of DA/PEI coated cotton fabrics. During the chlorination process of the coating, the H on the N–H bond is replaced by Cl and releases hydroxyl ions, which increases the pH and degrades part of the coating (Nazi et al. 2020). At this time, some blocking hydroxyl groups are released again, resulting in the WRAs of the coated cotton fabrics after chlorination decreasing, but these are still greatly improved compared with the raw cotton fabric.
Physical mechanical property

Breaking strength is an important indicator to measure the wearability of cotton fabrics, and the production and chemical reagents in the modification process can affect the physical properties of the cotton fabric. For example, under high temperature and acidic conditions, the glycosidic bond of cellulose is broken, resulting in the strength of the cotton fabric decline (Li et al. 2013, 2014). Figure 1 shows the breaking strength of various modified cotton fabrics in the warp and weft directions. The warp and weft directions of the raw cotton are 623 and 379 N respectively. The breaking strength of DA and DA/PEI modified cotton fabrics only shows a slight decrease, this is because only aerobic and weak alkali conditions are required in the modification process, and high temperature and strong acid solution treatment are not involved. The slight drop in the breaking strength is due to that the covalent bonds are introduced on the macromolecular structure of the coated cotton to restrict the flow of the individual units. However, the NaClO solution has strong oxidizing properties, and the breaking strength of chlorinated cotton fabrics has a certain degree of loss. The warp breaking strength’s loss rates of PDA-Cotton-Cl and PDA/PEI-Cotton-Cl are 21.2 and 14.6%, and the weft breaking strength’s loss rates are 19.5 and 15.8%, respectively. It is obvious that the PDA/PEI-Cotton has better strength than that of PDA-Cotton, this may be because the uniformity of the PDA/PEI coating can effectively alleviate the oxidation effect of NaClO solution on the cotton fabric. In a word, the treatment process causes a loss of breaking strength, and the retention rate of strength is still about 80 and 85%, which has little effect on the wearing property of the cotton fabrics.

Conclusion

Through the co-deposition of DA and PEI, a uniform functional coating was formed on the cotton fabric. SEM and XPS confirmed that DA/PEI was successfully deposited on the cotton fabric surface. After chlorination, N-halamine structure was formed on cotton fabrics, which made cotton fabrics exhibit excellent antibacterial properties against \textit{S. aureus} and \textit{E. coli}. By adjusting the DA/PEI mass ratio of 1:1.5, the formation of PDA aggregates was suppressed and the PDA was uniformly distributed on the cotton fabrics. The DA/PEI coating cotton had great coating stability and UV protective property, and the durable pressing property of the cotton fabric was improved. The loss of physical and mechanical properties was also within the acceptable ranges. In vitro studies showed that DA/PEI coating cotton fabrics are nontoxic to mouse 3T3 fibroblast cells in vitro and have potential for biomedical applications.

Author contributions Jiansheng Wan, Hong Li, and Jun Yan designed the experiments and referenced conception. Xiaoyu Cai and Yongping Liao participated in the experiments. Jiansheng Wan analyzed the data. Jiansheng Wan, Hong Li, and Xiaoyu Cai wrote the paper. All authors had read and agreed to the published version of the manuscript.

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Declarations

Conflict of interest The authors have no conflicts of interest to declare.

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