

Plasma treatment applied in the pad-dry-cure process for making rechargeable antimicrobial cotton fabric that inhibits *S. Aureus*

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Abstract

In this paper, variables in an environmentally friendly rechargeable antimicrobial finishing process were studied. Cotton fabric was treated with nitrogen plasma after padding with 5,5-dimethylhydantoin (DMH) when fabric was treated through the pad-dry-cure method, that is, pad-plasma-dry-cure. After that, fabric was chlorinated with sodium hypochlorite to impart antimicrobial property and function. An orthogonal array testing strategy was used in the finishing process for finding the optimum treatment condition. Ultraviolet spectroscopy, scanning electron microscopy and Fourier transform infrared spectroscopy were employed to evaluate the properties of treated cotton fabric, including concentration of chlorine on cotton fabric, morphological properties of the surface of cotton fabric and function groups on the cotton fabric. The results showed that cotton fabric finished with DMH with the help of plasma treatment followed by chlorination inhibits microorganisms effectively, the antimicrobial property against *Staphylococcus (S.) aureus* was rechargeable and durability of antimicrobial property was improved by plasma treatment.

Keywords

optimization, nitrogen plasma, rechargeable antimicrobial, cotton fabric, 5, 5-dimethylhydantoin

Sustainable textiles are the first choice for the development of the textile industry, because of the requirement of human health and environmental protection. The development of sustainable textiles needs innovations in technology.¹ Application of plasma treatment in the textile industry changes the traditional process for textile production.^{2,3} It satisfies the requirement of sustainable development of the environment and keeps the bulk properties of textiles at the same time.^{4–7} This is because the principle of plasma used for textile finishing is based on a simple physical principle, that is, matter changes its state when electrical energy is applied to it.¹ It will not affect the inherent nature of textiles⁴ and the whole process does not involve any water. Textiles are treated by plasma particles, such as electrons, free radicals, ions, photons and metastable species, generated with electrical energy from a plasma reactor.^{6,8,9} These particles affect the surface properties of fabric. The collision of plasma particles with the surface of

fabrics transfers electrical energy to the surface of fabrics, creating free radicals on the surface of fabrics.^{2,6,8,10–13} When these active radicals contact with chemicals, they will react with the chemicals and the new chemical groups will form on the surface of substrate.^{8,14} On the other hand, plasma treatment systems increase surface receptiveness and adhesion to chemicals.¹³ Surface modification of plasma provides

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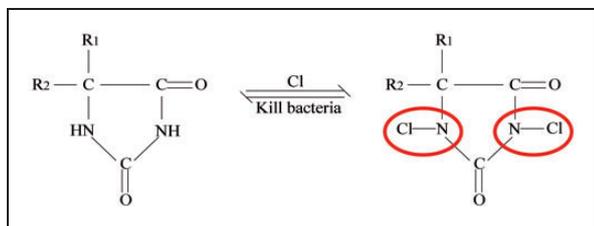


Figure 1. The reversible redox reaction of chemicals with halamine structures (red circle shows the N-halamine structure; color online only).

manufacturing, assembly and decorating advantages by cleaning, etching and functionalizing surfaces.^{8,15} This said, plasma treatment also can combine with traditional wet chemical finishing processes in some steps (e.g. the pad-dry-cure process) to enhance the treatment effect.^{16–18}

Antimicrobial textiles have been studied for numerous years. That is because it is necessary for textile goods, especially those made from natural fibers, to be antimicrobial. The reason is that they provide a large surface area to retain moisture, which is suitable for microorganisms to grow at appropriate temperatures.^{19–21} The microorganisms lead to two problems: firstly, the fiber may be degraded, discolored and smelly. In addition, the decomposed body secretions have a characteristic odor. Secondly, some germs may result in pruritus, inflammation and disease for humans.^{19,21–25} However, there are still some problems to be solved, for example, the toxicity of antimicrobial agents, the instability of antimicrobial activity of antimicrobial agents and the duration of antimicrobial effect of antimicrobial textiles.²⁶ Rechargeable antimicrobial textiles extend the service life of antimicrobial textiles. These kinds of antimicrobial textiles are finished with chemicals with N-halamine structures. The amine or imines groups in the N-halamine structures can be chlorinated by sodium hypochlorite to generate oxidative nitrogen-chlorine groups. The chlorine can kill microorganism effectively, and the lost chlorine can be recharged by chlorination of sodium hypochlorite.^{11,27–29} The reversible reaction of the chemical on a fabric makes the antimicrobial property of fabric rechargeable. The reaction principle is shown in Figure 1.

Previous research studied the antimicrobial effects of cotton fabrics finished with chitosan or 5,5-dimethylhydantoin (DMH) when plasma treatment was applied in different stages of the pad-dry-cure method.^{11,30} The current study focuses on the optimization of finishing conditions when cotton fabrics are finished with DMH with the pad-plasma-dry-cure process. In this study, parameters in the finishing process, such as concentration of DMH, temperature for curing, concentration of

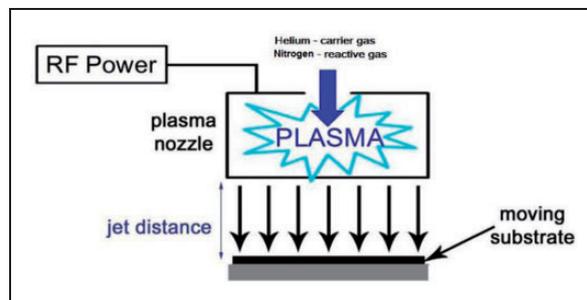


Figure 2. Schematic diagram of atmospheric pressure plasma treatment.

sodium hypochlorite and time for chlorination, will be optimized to strengthen the antimicrobial effect of cotton fabric finished with DMH with the aid of plasma treatment.

Experimental details

Preparation of materials

Desized, scoured and bleached 100% woven cotton fabric (54 yarns/cm in warp and 25 yarns/cm in weft, 261 g/m²) was used in this study (Supplied by Lai Tak Enterprises Ltd, Hong Kong). DMH (97%), sodium hypochlorite (5%, activated chloride), potassium iodide, glacial acetic acid (>99.8%) and a starch indicator (1% in H₂O) were purchased from Sigma-Aldrich. The fabric was first washed with a 2% non-ionic detergent (Diadavin EWN-T 200%) at pH 7 and 50°C for 30 min, and then rinsed with deionized (DI) water to remove detergent, oil or impurities and dried at 80°C for 20 min. After that, the fabric was washed with acetone for 10 min to remove detergent, oil or impurities thoroughly, and then washed adequately with DI water. The clean fabric samples were conditioned under a standard condition of 20 ± 2°C and 65 ± 2% relative humidity for at least 24 h prior to all experiments.

Plasma treatment

Atmospheric pressure plasma (APP) treatment was carried out after padding in a pad-dry-cure process. The plasma generator, Atomflo-200 series (Surf Technology, USA), was used for APP treatment of the fabric samples in this study. Gas discharge was ignited by low radio frequency (RF) (13.56 MHz). The plasma jet was placed vertically above the sample (Figure 2). The carrier gas used was helium, while the reactive gas was nitrogen. The discharge power of APP was 80 W, the flow rate of nitrogen was 0.15 L/min, the flow rate of helium was 9.6 L/min, the jet distance was 5 mm and the moving speed of fabric was 0.2 m/s.

Table 1. Parameters and levels used in the orthogonal array testing strategy.

Level	Parameters			
	concentration of DMH (%)	Temperature of curing (°C)	Concentration of sodium hypochlorite solution (%)	Time of chlorination (min)
I	2	120	0.8	20
II	4	140	1.0	40
III	6	160	1.2	60

DMH: 5,5-dimethylhydantoin.

Table 2. Experimental arrangement.

Test run	Parameters			
	Concentration of DMH (%)	Temperature of curing (°C)	Concentration of sodium hypochlorite solution (%)	Time of chlorination (min)
1	2	120	0.8	20
2	2	140	1.0	40
3	2	160	1.2	60
4	4	120	1.0	60
5	4	140	1.2	20
6	4	160	0.8	40
7	6	120	1.2	40
8	6	140	0.8	60
9	6	160	1.0	20

DMH: 5,5-dimethylhydantoin.

Parameters for optimizing treatment condition for cotton fabric finished with DMH

An orthogonal array testing strategy (OATS) technique was employed to analyze the optimum treatment condition of cotton fabric finished with DMH with plasma treatment.^{31–33} Four variables, that is, concentration of DMH, temperature of curing, concentration of sodium hypochlorite solution and time of chlorination, were investigated in the antimicrobial finishing process; the levels were selected by reference to other researchers' reports on the derivatives of DMH and based on some preliminary pilot tests carried out in this study.^{29,30,34} The experimental arrangements are shown in Tables 1 and 2.

The finishing process is such that cotton fabric was first padded with DMH with 80% pick up and then treated with plasma. After that it is dried at 80°C for 5 min as well as cured at 120°C for 7 min, 140°C for 5 min and 160°C for 3 min, respectively (i.e. pad-plasma-dry-cure). After curing, the fabrics were immersed in a sodium hypochlorite solution in beakers to chlorinate at room temperature, stirring with a glass rod every 2 min, to transform the amino groups in

DMH into N-halamines. After chlorination, to ensure there was no free chlorine left, these fabrics were washed with DI water until the water did not change to blue, which was tested with KI/starch solution. After antimicrobial finishing, the cotton fabrics were store under standard condition of $20 \pm 2^\circ\text{C}$ and $65 \pm 2\%$ relative humidity for at least 24 h prior to further evaluation.

After optimization of the cotton fabric finished with DMH through the pad-plasma-dry-cure process, in order to observe the effects of plasma applied in the DMH finishing process, the cotton fabric was finished with DMH under the optimum conditions with plasma treatment (termed as CWPD), and without plasma treatment (termed as CD), respectively.

Antimicrobial property

The antibacterial activity of samples was tested with reference to American Association of Textile Chemists and Colorists (AATCC) Test Method 147-2011 and *S. aureus* (ATCC 6538) was used as the model bacteria.^{25,35–38} The bacteria were inoculated in a blood

agar plate and incubated at 37°C for 24 h. A bacterial suspension was prepared in Brain-Heart Infusion (BHI) broth by harvesting the cells from the blood agar plate, and its optical density was measured with a spectrophotometer (wavelength at 660 nm) to 0.5 McFarland standard. Next, the suspension was diluted to 100-fold. After that, the diluted suspension was inoculated on new sterile blood agar plates using the Spiral Platter and freshly prepared samples (20 mm × 20 mm) were placed on the seeded agar surfaces. After standing still for 5–10 min, these plates were placed in an aerobic incubator and incubated at 37°C for 48 h. Finally, clear zones were observed to evaluate the antibacterial activity of samples.

The active chlorine content of the chlorinated DMH

The active chlorine content on the chlorinated cotton fabric finished with DMH was measured by the colorimetric method. In this study, 0.1 g of the chlorinated cotton fabric was cut into small pieces that were immersed completely in 40 mL of acetic acid aqueous solution (1%). One gram of potassium iodide was added and the mixtures were stirred vigorously for 1 h at room temperature with magnetic stirrers. Then, 0.5 mL of starch indicator was added into the solution. The complex of the formed iodine and starch made the solution blue. The same amount of un-chlorinated cotton fabric with DMH was treated under the same conditions as the control. The iodometric/thiosulfate method was not used because the concentration of chlorine was very low to be detected.

The available active chlorine content of the chlorinated sample was calculated according to the absorbance tested by ultraviolet (UV) spectrophotometer Lambda 18. Firstly, the absorbance of sodium hypochlorite was tested under spectrum ranging from 400 to 700 nm, and the wavelength of maximum absorption (λ_{\max}) was found. Secondly, the absorbance of three standard sodium hypochlorite solutions was tested and the standard curve was plotted. Then the regression equation was obtained: ($y = 30.401x - 50.84$; $R^2 = 0.9918$). Finally, the absorbance of samples was tested and concentration of chlorine on the sample was calculated based on the calibration curve. In this study, the λ_{\max} used was 427.60 nm.

Rechargeability

Chlorinated cotton fabrics were washed to test their rechargeability according to AATCC Test Method 61-1A. Before washing, the antimicrobial activity of chlorinated fabrics was tested. After washing over different times, the antimicrobial activity was tested again (termed as AW). After washing, these fabrics were chlorinated again with sodium hypochlorite. The time

for re-chlorination and the concentration of sodium hypochlorite were the same as when they were chlorinated for the first time. Then, the antimicrobial activity of these fabrics was tested (termed as AW + CH).

Fourier transform infrared spectroscopy with attenuated total reflection mode

A Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectrometer, Spectrum 100, was used to detect the chemical properties of finished fabrics. The spectra were collected using 16 scans with 4 cm^{-1} resolution between 650 and 4000 cm^{-1} . Then, the second derivative was calculated to remove the noise in the FTIR-ATR spectroscopy.

Scanning electron microscope

A JEOL Model JSM-6490 scanning electron microscope (SEM) was used for observation of the surface morphological changes. Magnification of the image was set at 4000x.

Weight change

The weight of all test specimens with the size of 200 mm × 100 mm was measured by using the AG204 DeltaRange Electronic Balance (METTLER TOLEDO) before and after treatment. A total of 40 samples were measured to obtain the averaged result for the treatment. A positive change implied a gain in the weight, while a negative change indicated a weight loss of the substrate. The percentage change of fabric weight was calculated by the following equation:

$$\text{Weight Change (\%)} = \frac{W - W_0}{W_0} \times 100 \%$$

where W (g) is weight of the substrate after treatment and W_0 (g) is initial weight of the substrate.

Tearing strength

An Elmatear Digital Tear Tester (James H. Heal & Co. Ltd, Halifax, England) was used to test the tearing strength of fabric according to American Society for Testing and Materials (ASTM D1424-09). The maximal capacity of the testing machine used in this test was 32 N.

Whiteness index

A Gretag Macbeth Color-Eye 7000A Spectrophotometer was used to evaluate the whiteness index of the samples based on ASTM E313.

Table 3. Orthogonal table for optimizing the antimicrobial property of cotton fabric finished with 5,5-dimethylhydantoin (DMH).

Test run	Parameters				Mean clear width against <i>S. aureus</i> (mm)
	Concentration of DMH (%)	Temperature of curing (°C)	Concentration of sodium hypochlorite solution (%)	Time of chlorination (min)	
1	2	120	0.8	20	1.487
2	2	140	1.0	4	1.101
3	2	160	1.2	60	0.610
4	4	120	1.0	60	1.245
5	4	140	1.2	20	1.597
6	4	160	0.8	40	1.364
7	6	120	1.2	40	1.439
8	6	140	0.8	60	1.711
9	6	160	1.0	20	0.955

Σ in mean clear width against *S. aureus* (mm)

	Parameters			
	Concentration of DMH (%)	Temperature of curing (°C)	Concentration of sodium hypochlorite solution (%)	Time of chlorination (min)
Σ I	3.198	4.171	4.562	4.039
Σ II	4.206	4.409	3.301	3.904
Σ III	4.105	2.929	3.646	3.566
Difference	1.008	1.480	1.261	0.473

Results and discussion

Optimum condition analysis

OATS is a convenient method to optimize experiments involved with variables or factors. The optimum condition and the importance of different factors in experiments are obtained easily through orthogonal experiments. The mean clear width of the sample against *S. aureus* (ATCC 6538) from the sample is used to evaluate antimicrobial activity of sample. The wider clear width means the antimicrobial activity is more active. Table 3 shows the mean clear width of the bacteria against *S. aureus* obtained from the nine specimens generated by the OATS technique.

Based on Table 3, it is observed that all four parameters in the finishing process, that is, concentration of DMH, temperature of curing, concentration of sodium hypochlorite solution and time of chlorination, cause different effects on the antimicrobial activity of cotton fabric finished with DMH. The order of importance of these parameters based on the orthogonal analysis is temperature of curing, concentration of sodium hypochlorite solution, concentration of DMH and time of chlorination. According to the results of the orthogonal analysis, the optimum condition for cotton fabric finished with DMH is concentration of DMH = 4%,

temperature of curing = 140°C, concentration of sodium hypochlorite solution = 0.8% and time of chlorination = 20 min. This optimum condition was used for cotton fabric finished with DMH for further evaluation.

Figures in bold in Table 3 exhibit the greatest value among all the values shown in the levels of different variables used, while the italic shows the level of importance of each variable.

As shown in Figure 3, the mean clear width of sample against *S. aureus* increases with the increase of the concentration of DMH in the beginning. However, when the concentration of DMH is up to 4%, the mean clear width against *S. aureus* changes slightly and it remains nearly stable. This is because DMH is finished onto cotton fabric mainly by the chemical reaction between the carboxyl group introduced onto fabric, and the amide groups in DMH. The concentration of DMH on fabric increases with the increase of concentration of DMH solution. However, when the amount of DMH on fabric is the same as the number of amide groups, the concentration of DMH on cotton fabric will keep constant. When the concentration of DMH is up to 4%, the fabric is saturated with DMH molecules. It is noteworthy that DMH cannot chemically bond with cotton fabric. This corresponds with

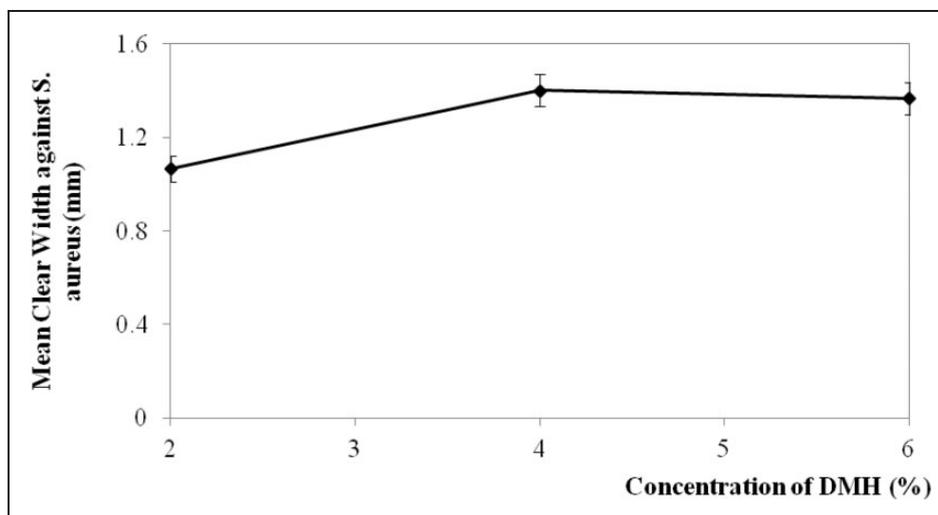


Figure 3. Effect of concentration of 5,5-dimethylhydantoin (DMH) on antimicrobial property of cotton fabric finished with DMH.

Langmuir's adsorption performance. Therefore, the optimum concentration of DMH finished onto cotton fabric is 4% in this study.

When the curing temperature is lower than 140°C, the mean clear width against *S. aureus* increases with the increase of curing temperature, as shown in Figure 4, that is, antimicrobial activity increases with increase of the curing temperature. However, as the curing temperature is higher than 140°C, the mean clear width against *S. aureus* decreases with the increase of curing temperature in Figure 4, that is, antimicrobial activity decreases. This is because the melting point is 130°C after chlorination and the flash point is around 175°C, which is not stable for DMH at high temperatures, and may result in poor fixation of DMH, meaning it may dissolve again in water during the subsequent finishing process.³⁹ Finally, the content of DMH and chlorine decreases with the increase of the curing temperature and the antimicrobial activity decreases.³³

As shown in Figure 5, when the concentration of sodium hypochlorite solution is lower than 1%, the mean clear width against *S. aureus* decreases with the increase of concentration of sodium hypochlorite solution. While the concentration of sodium hypochlorite solution is higher than 1%, the mean clear width against *S. aureus* increases with the increase of concentration of sodium hypochlorite. Generally speaking, the higher concentration of sodium hypochlorite solution provides more chlorine to interact with the DMH in the cotton fabric. However, this assumption does not verify the outcome seen in Figure 5. This may result from the strong oxidizing ability of chlorine solution, which is considered to be capable of damage functional moieties on fabrics. In addition, these damages correspond to the occurrence of decreased antimicrobial efficacy of treated fabrics. The N-containing groups can be

divided into two groups: some of them consist of DMH and they are not stable after chlorination; others are introduced into cotton fabric by nitrogen plasma treatment, because nitrogen plasma can functionalize the substrate with the N-containing group, such as $-\text{NH}_2$, $-\text{NH}$, $=\text{NH}$, CONH_2 or $\text{C}\equiv\text{N}$.⁴⁰ During chlorination, chlorine in sodium hypochlorite solution replaces hydrogen in the N-containing groups in DMH due to the steric hindrance. Moreover, the redundant chlorine will damage functional moieties on fabrics, because of the strong oxidizing ability of chlorine solution. After that, chlorine can react with N-containing groups on cotton fabrics introduced by the plasma treatment. That is why the mean clear width against *S. aureus* is smallest when the concentration of sodium hypochlorite solution is 1%.

As shown in Figure 6, the mean clear width against *S. aureus* decreases with the extension of the time of chlorination. This is because DMH is finished onto cotton fabric without any other binding agents and DMH is easy to dissolve into water. Thus, some chlorine will dissolve in sodium hypochlorite solution during chlorination. This said, with the extension of the time of chlorination, more DMH is dissolved into water.

Relationship between antimicrobial property and the concentration of chlorine on cotton fabric

The relationship between antimicrobial properties and the concentration of chlorine on cotton fabric is shown in Figure 7. From Figure 7, it can be seen that the mean clear width against *S. aureus* becomes wide with the increase of the concentration of chlorine on cotton fabric finished with DMH, which appears to be a linear relationship; the fitting linear equation is $y = 0.3069x - 0.882$ and the decisive coefficient $R^2 = 0.8688$. This is

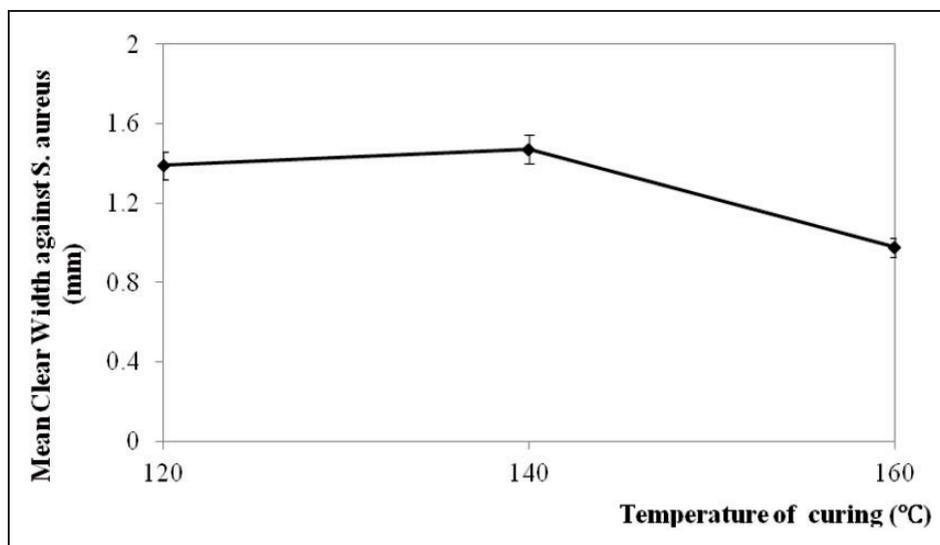


Figure 4. Effect of temperature of curing on the antimicrobial property of cotton fabric finished with 5,5-dimethylhydantoin.

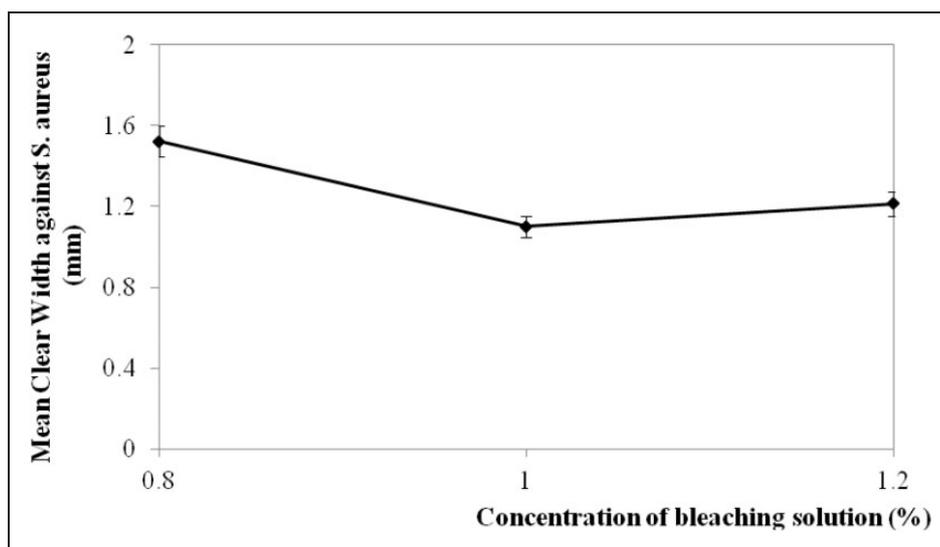


Figure 5. Effect of concentration of sodium hypochlorite solution on the antimicrobial property of cotton fabric finished with 5,5-dimethylhydantoin.

because the antimicrobial treatment principle of the cotton fabric finished with DMH is that chlorine is used to kill microorganism. When the quantity of chlorine increases, more bacteria can be killed. Therefore, an effective method to improve the antimicrobial property of cotton fabric is to increase the amount of chlorine on the cotton fabric.

Rechargeability

Rechargeability is extremely important for antimicrobial textiles. It extends the service life of antimicrobial textiles. Figure 8 shows the rechargeability of cotton

fabric finished with DMH with the aid of plasma treatment (coded as CWPD), and without plasma treatment (coded as CD) by comparing the antimicrobial activity of fabrics before washing, after washing (termed as AW) and after re-chlorination (termed as AW + CH). According to Figure 8, the mean clear width of cotton fabric with plasma treatment is approximately the same as that on fabric without plasma treatment before washing and after. However, the mean clear width of fabric with plasma treatment is higher than that on fabric without plasma treatment after re-chlorination. It was also found that, after re-chlorination, the antimicrobial activity of cotton fabric with plasma

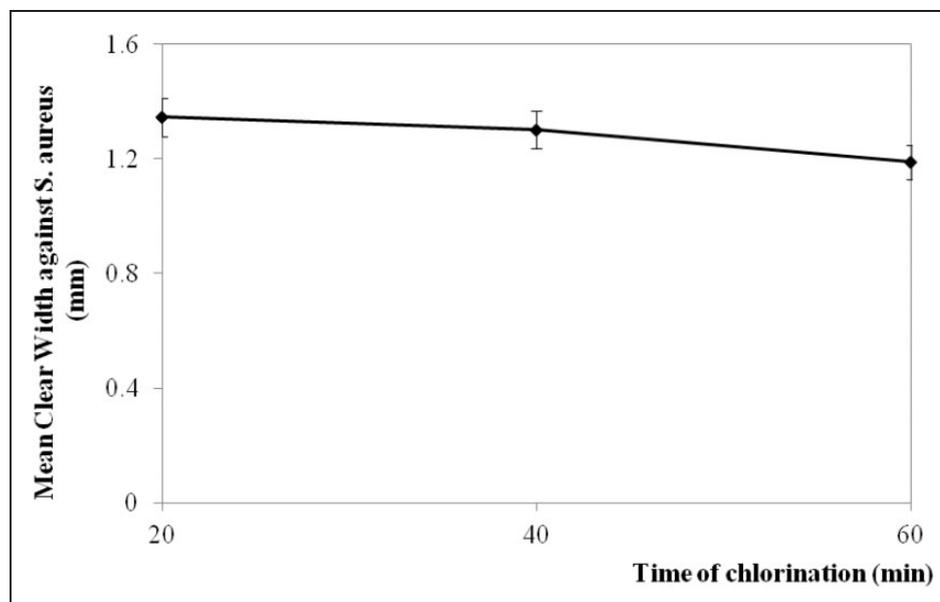


Figure 6. Effect of time of chlorination on the antimicrobial property of cotton fabric finished with 5,5-dimethylhydantoin.

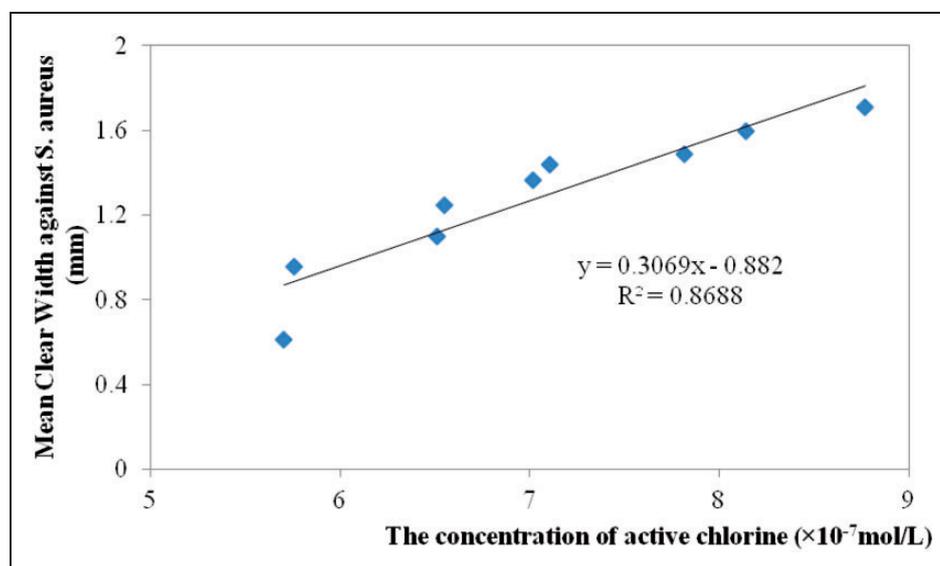


Figure 7. Relationship between antimicrobial property and the concentration of chlorine on cotton fabric.

treatment varies slightly with the increase of washing times, while the antimicrobial activity of cotton fabric without plasma treatment decreases significantly with the increase of washing times. Therefore, the plasma treatment increases adhesion of DMH on cotton fabric, as well as the durability of antimicrobial activity of cotton fabric. This is because DMH is attached on cotton fabric through physical adsorption while DMH is adsorbed on fabric through chemical reaction. The nitrogen plasma treatment provides carboxyl groups on the surface of cotton fabric, and these carboxyl groups

can react with the amide groups on the hydantoin ring in DMH to form a new amide group, which increases adhesion of DMH on the surface of cotton fabric.⁴¹ In addition, nitrogen plasma used in this experiment can functionalize the substrate with the N-containing group, such as $-\text{NH}_2$, $-\text{NH}$, $=\text{NH}$, CONH_2 or $\text{C}\equiv\text{N}$,⁴⁰ which also increases the antimicrobial activity of cotton fabric. Therefore, it is concluded that the antimicrobial property of cotton fabric finished with DMH with plasma treatment is rechargeable and the rechargeability is improved by plasma treatment

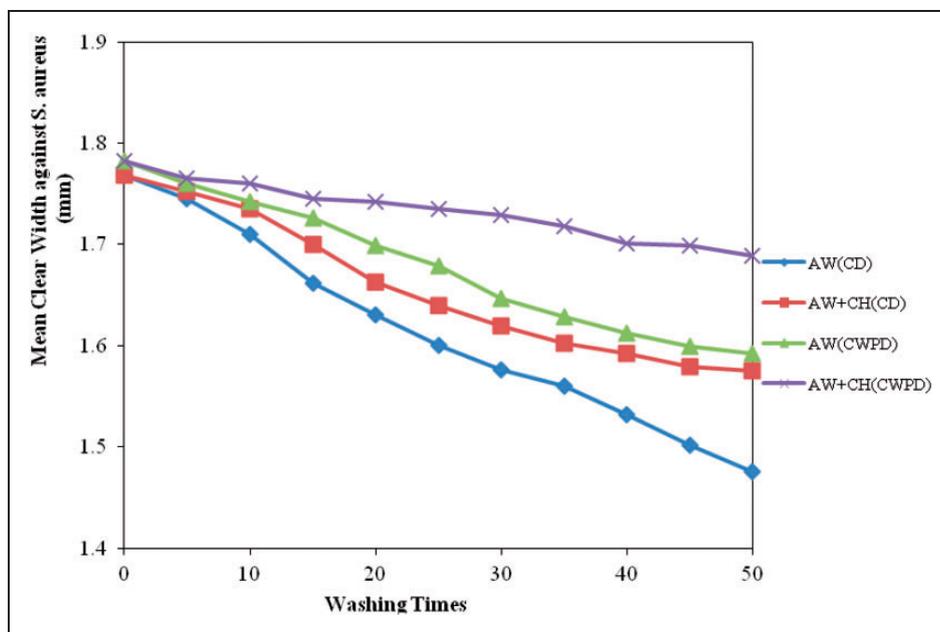


Figure 8. Rechargability of cotton fabric finished with 5,5-dimethylhydantoin.

compared with cotton fabric finished with DMH without plasma treatment.

FTIR-ATR

FTIR-ATR is used to determine the existing content of chemical groups on the finished substrates. In this experiment, characteristic groups of DMH, amide II and C=O and other chemical groups related to nitrogen plasma treatment will be determined. Figure 9 shows the second derivative FTIR-ATR spectrum of untreated cotton fabric (Figure 9(a)), cotton fabric treated with plasma (Figure 9(b)), cotton fabric finished with DMH with the aid of plasma (Figure 9(c)) and cotton fabric finished with DMH without plasma treatment (Figure 9(d)). Compared with Figure 9(a), the bands that appeared around 3740 cm^{-1} are attributable to N-H stretching vibrations and the peaks at around 1547 cm^{-1} are assigned to N-H (amine II) deformation in Figures 9(b)–(d). The absorbance peak at 1768 cm^{-1} is attributable to the stretching vibrations of C=O of the carboxyl group, which can react with amide groups on the hydantoin ring.³⁰ Absorbance bands in the 1754 cm^{-1} region of Figures 9(c) and (d) represent the stretching vibrations of C=O.^{42–46} Nevertheless, it is found that the absorbance peak of C=O in Figure 9(c) is higher than that in Figure 9(d), which means the content of DMH on the sample with plasma treatment is higher than that on the sample without plasma treatment. Therefore, the functionalization of nitrogen plasma treatment introduces N-containing groups into cotton fabric and the etching

effect of plasma treatment improves the content of DMH on cotton fabric.⁴⁰

In order to investigate the effect of plasma treatment in the pad-plasma-dry-cure finishing process, the second derivative FTIR spectrum of cotton fabric finished with DMH through the pad-dry-cure process (CD) is subtracted from the second derivative FTIR spectrum of cotton fabric finished with DMH through pad-plasma-dry-cure process (CWPD), as shown in Figure 10. In Figure 10, the absorbance peaks of C=O at 1755 cm^{-1} and N-H at 1542 cm^{-1} are present. Therefore, plasma treatment in the pad-plasma-dry-cure process can introduce functional groups to cotton fabric.

Weight change

The weight change of fabrics before and after finishing with DMH through CD and CWPD processes is shown in Table 4. According to Table 4, the weight of fabrics increased after finishing through CD and CWPD processes because of the existence of DMH on the surface of the fabrics. However, the increase of the weight of fabric finished through the CD process is higher than fabric finished through the CWPD process. This is caused by the etching effect of plasma treatment on cotton fabric. The etching effect of plasma treatment can lead to weight loss of substrates.^{47–50} In the rechargability test, antimicrobial activity of cotton fabric finished with DMH through the CWPD process is strong compared with cotton fabric finished with DMH through CD. This may demonstrate that the

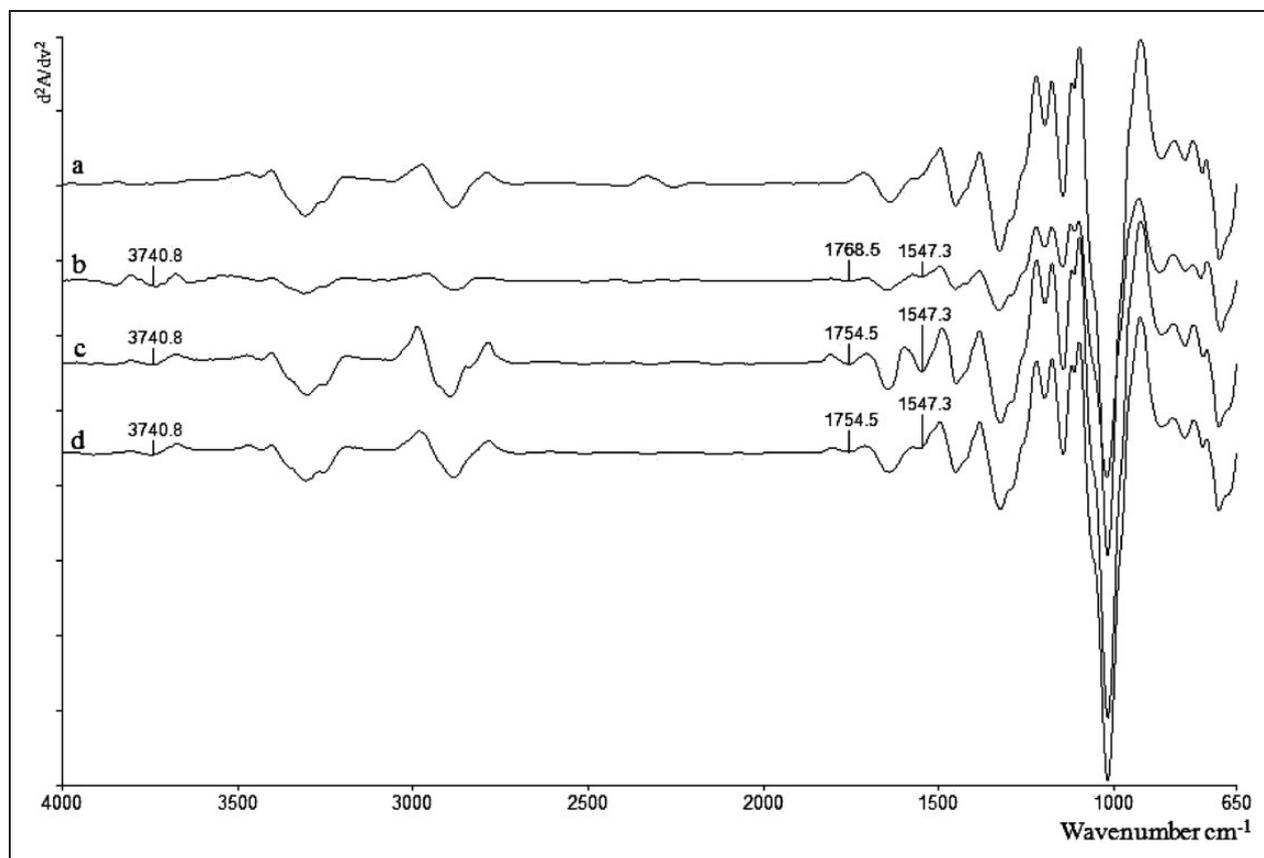


Figure 9. Second derivative Fourier transform infrared spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric finished with 5,5-dimethylhydantoin (DMH) through the “pad-dry-cure” method with the aid of plasma (CWPD), (d) cotton fabric finished with DMH through the “pad-dry-cure” method (CD).

weight of DMH on fabric finished through the CWPD process is higher than that on fabric finished with the CD process. Therefore, although the weight increase of cotton fabric finished with plasma treatment is small, plasma treatment increases the amount of DMH on cotton fabric.

Scanning electron microscopy

SEM is employed to observe the variations of the physical characteristics of the modified substrate surfaces. Figure 11 shows a SEM image of untreated cotton fabric (Figure 11(a)), cotton fabric finished with DMH through the “pad-dry-cure” method (CD) (Figure 11(b)) and cotton fabric finished with DMH through the “pad-plasma-dry-cure” method (CWPD) (Figure 11(c)). As shown in Figure 11, the surface of cotton fibers is smooth and even before antimicrobial finishing, while the surface of cotton fibers finished with DMH is no longer smooth and even. Comparing Figure 11(b) with Figure 11(c), it seems that DMH on the surface of fibers treated with plasma in Figure 11(c) is more than that on the surface of fibers

without plasma treatment seen in Figure 11(b). This corresponds with the results of comparison of weight change and antimicrobial activity of fabric finished with DMH through the CD and CWPD processes. Therefore, DMH can be finished onto cotton fabrics, and the distribution of DMH on the surface of cotton fibers is improved by plasma treatment. This is because the groves and cracks formed by the etching effect of plasma treatment make adhesion of DMH onto the surface of cotton fabrics easy.⁴¹

Tearing strength

The tearing strength of untreated fabric, fabric finished with DMH without plasma treatment (CD) and fabric finished with DMH with plasma treatment (CWPD) is shown in Table 5. Compared with untreated fabric, the tearing strength of cotton fabrics finished with DMH decreases. Nevertheless, the tearing strength of fabric finished with DMH without plasma treatment decreases more significantly than fabric finished with DMH with plasma treatment. When fabric is finished with DMH, the existence of DMH on the surface of

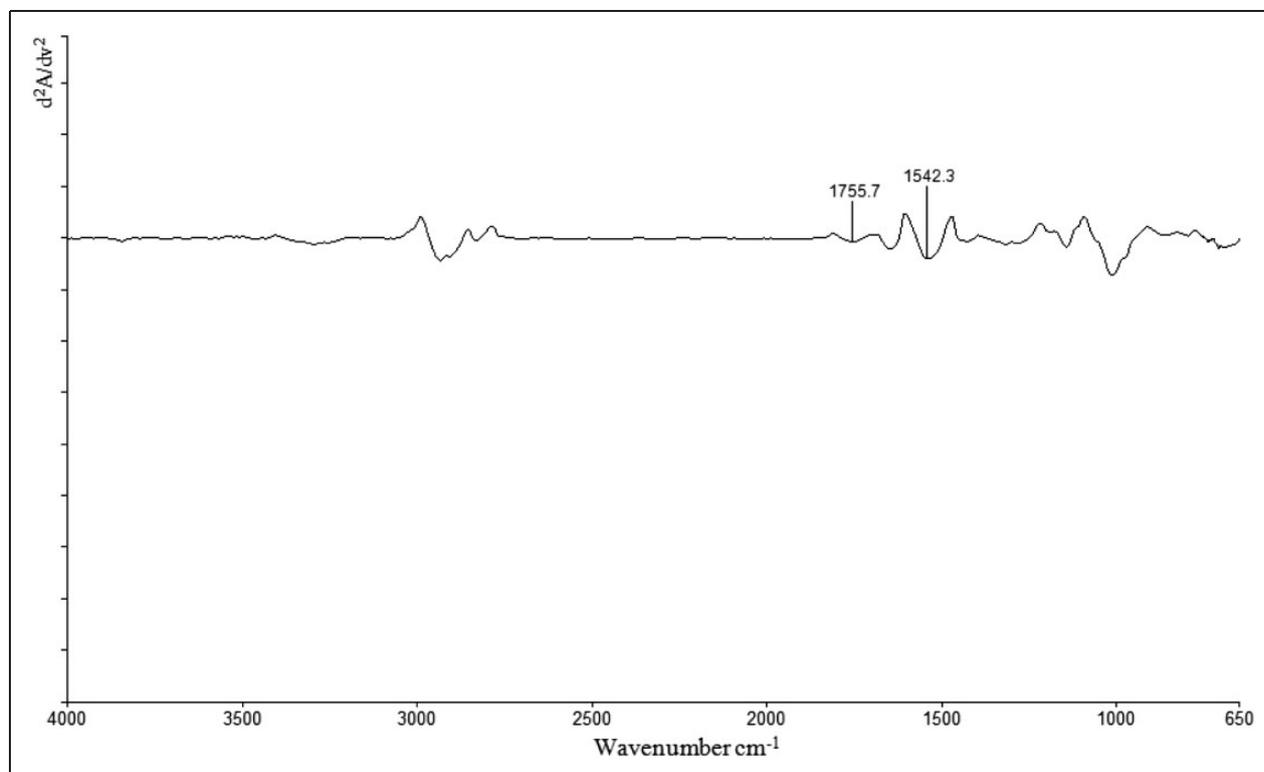


Figure 10. Spectral subtraction of second derivative Fourier transform infrared spectrum of cotton fabric finished with 5,5-dimethylhydantoin (DMH) through the pad-plasma-dry-cure process (CWPC) – cotton fabric finished with DMH through the pad-dry-cure process (CD).

Table 4. Weight change of fabrics before and after finishing.

Process	Before finishing (g)	After finishing (g)	Weight change (%)
CD	6.4236	6.5493	1.95
CWPD	6.4852	6.5288	0.67

fabric increases the surface friction and roughness, which restrict the sliding action of yarn during tearing. This said, the tearing strength of fabric should decrease after antimicrobial finishing,^{51,52} while plasma particles introduce reactive groups on the surface of fabric reacted with DMH, and etching effect decreases the friction between yarns.^{30,41,53} These increase the tearing strength of the fabric only a little. Therefore, plasma treatment is helpful for the tearing strength of fabric in functional finishing.

Whiteness index

The whiteness index is used to evaluate the whiteness of fabric after antimicrobial finishing and the results are shown in Table 6. A higher whiteness index means a lighter shade. According to Table 6, it is found that the

whiteness index value of cotton fabric with antimicrobial finishing (CD) is slightly whiter than untreated fabric. However, the cotton fabric finished with the pad-plasma-dry-cure process (CWPD) becomes much whiter than the untreated. The increase in whiteness is due to the use of sodium hypochlorite, which can serve as a bleaching agent to make materials white.

Conclusions

With the aid of plasma treatment, inserting in pad-dry-cure process for finishing DMH in cotton fabric followed by chlorination with sodium hypochlorite could inhibit the bacteria, *S. aureus*, effectively. The optimum conditions of the finishing process for obtaining the antimicrobial property in this research are concentration of DMH = 4%, curing temperature = 140°C, concentration of sodium hypochlorite solution = 0.8% and time of chlorination = 20 min.

The evaluations of cotton fabric finished with DMH with the aid of plasma treatment followed by chlorination show the antimicrobial activity can be recharged. In addition, the distribution, the content and the adhesion of DMH on cotton fabrics are improved by the plasma treatment. Nitrogen plasma also introduces a nitrogen-containing group onto the surface of cotton

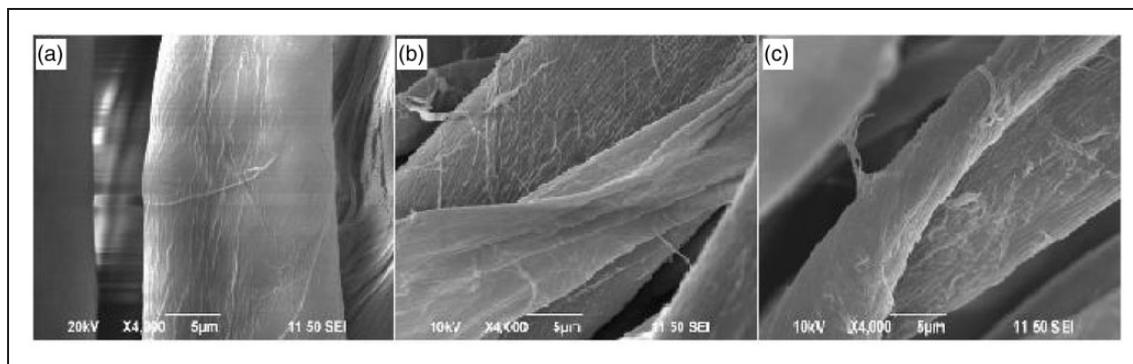


Figure 11. Scanning electron microscopy image of (a) untreated cotton fabric, (b) cotton fabric finished with 5,5-dimethylhydantoin (DMH) through the “pad-dry-cure” method (CD), (c) finished with DMH through the “pad-dry-cure” method with the aid of plasma (CWPD).

Table 5. The tearing strength of the cotton fabric in both warp and weft directions.

Sample	Untreated	CD	CWPD
Tearing strength in warp direction (N)	15.42	14.63	14.93
Tearing strength in weft direction (N)	10.4	9.42	9.69

Table 6. The whiteness index of cotton fabrics.

Sample	Untreated	CD	CWPD
Whiteness index	70	72	75

fabrics, which enhances the antimicrobial activity directly. Finally, the tearing strength and the whiteness of fabric are increased in the pad-plasma-dry-cure finishing method. Compared with the traditional pad-dry-cure process, there are no other chemicals, such as crosslinkers, to increase the antimicrobial effect in the finishing process in this study, which decreases the concentration and types of chemicals in waste water. This might be an environmentally friendly finishing method.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

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