Regenerable Antimicrobial Finishing of Cotton with Nitrogen Plasma Treatment


The effects of process variables on regenerable antimicrobial finishing of cotton fabric with nitrogen plasma treatment were investigated. Cotton fabric was treated with a mixture of nitrogen and helium plasma, and it was chlorinated with sodium hypochlorite to impart antimicrobial properties. An orthogonal array testing strategy (OATS) was used in the finishing process to determine the optimum treatment conditions. After finishing, the properties of cotton fabric, including concentration of chlorine, tearing strength, and presence of functional groups, were evaluated by ultraviolet spectroscopy (UV), tear testing, and Fourier transform infrared spectroscopy (FTIR). Cotton fabric treated with nitrogen plasma and chlorination effectively blocked microorganism growth. The resistance to Staphylococcus aureus bacteria was regenerable, and nitrogen plasma treatment showed no noticeable influence on the tearing strength of the cotton fabric.

Keywords: Optimisation; Nitrogen plasma; Regenerable antimicrobial; Cotton fabric

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INTRODUCTION

Textiles made from cotton fibers are breathable, adsorbent, and comfortable to wear because of their porous hydrophilic structures. Because the structure retains water and oxygen easily, it provides a suitable environment for microbial growth (Shahidi et al. 2007; Zhou and Kan 2014a,b, 2015). Therefore, it is necessary to impart antibacterial properties to cotton fabrics, particularly in view of the growing emphasis on health and hygiene care.

Conventional antibacterial finishing involves numerous chemicals, including antimicrobial finishing agents and cross-linkers that may be harmful to the environment. Environmental protection is an issue the textile industry has to address. Plasma technology alleviates this problem to some extent because plasma is a dry process for surface modification. During plasma application, the feed gas is converted into active particles by electrical energy applied from a plasma reactor. These active particles impinge on the surface of the fabric and rupture the chemical bonds to form free radicals on the surface. The free radicals react with oxygen and water to form an oxygenated surface, and these radicals also polymerise with other chemicals to introduce various functional groups onto the material surface (Inagaki 1984, 2000; Poll et al. 2001; Abidi and Hequet 2004; Virk et al. 2004; Narushima et al. 2007; Kuo et al. 2010; Zhou and Kan 2014b). The final treatment effect depends on the nature of the gases used (Kan et al. 1998). For example, nitrogen plasma introduces several N-containing groups on the
material surface, including –NH₂, -NH, =NH, -CONH₂, and -C≡N groups (Silva et al. 2008; Shahidi et al. 2010; Zhou and Kan 2014b). Plasma treatment changes only the uppermost atomic layers of material surface; most of the surface properties are unaffected (Bhat and Benjamin 1999; Poll et al. 2001).

Recently, regenerable antibacterial textiles have gained popularity. These fabrics are finished with N-halamines—chemicals containing amine, amide, and amide halamine bonds—that rapidly and totally inactivate a wide spectrum of micro-organisms (Sun and Sun 2001a,b,c, 2002). The chlorine in N-halamine is consumed during the bacterial inactivation, but it can be regenerated with sodium hypochlorite (Fig. 1). Wet chemical antimicrobial finishing can be combined with plasma treatment, which involves finishing agents (Zhou and Kan 2014a,b, 2015). To protect the environment and improve production efficiency, this study introduced N-halamine structures to the surface of cotton fabric via direct nitrogen plasma treatment without antimicrobial agents and related auxiliaries. The antibacterial properties of the fabric were then investigated.

\[
\begin{align*}
\text{NH}_2 & \quad \text{Cl} & \quad \text{NHCl} \\
\text{Kill bacteria} & \\
\end{align*}
\]

**Fig. 1.** Reversible redox reaction of N-halamine (red circle represents the N-halamine structure)

**EXPERIMENTAL**

**Materials**

Desized, scoured, and bleached 100% woven cotton fabric (54 yarns/cm in warp and 24 yarns/cm in weft, 261 g/m², white in colour) was supplied by Lai Tak Enterprises Ltd, Hong Kong. The fabric was washed with 2% non-ionic detergent Diadavin EWN-T 200% (Tanatex, Germany) at pH 7 and 50 °C for 30 min, rinsed with deionised water to remove detergent, oil, and other impurities, and dried at 80 °C for 20 min. The fabric was washed with acetone for 10 min to thoroughly remove detergent, oil, or impurities and then washed again with deionised water.

The clean fabric samples were conditioned under standard conditions of 20 ± 2 °C and 65 ± 2% relative humidity for at least 24 h prior to all experiments. Sodium hypochlorite (5% available chlorine), potassium iodide, glacial acetic acid (>99.8%), and starch indicator (1% in H₂O) used in this study were purchased from Sigma-Aldrich, USA.

**Plasma Treatment**

An Atomflo-200 series plasma generator (Surfx Technology, US) was used for atmospheric pressure plasma (APP) treatment of the samples. Gas discharge was ignited by low radio frequency (RF) (13.56 MHz). The plasma jet was placed vertically above the sample (Fig. 2).

The carrier gas was helium, and the reactive gas was nitrogen. The flow rate of helium was 15 L/min, and the jet distance was 5 mm. The flow rate of nitrogen was 0.2 litres per minute (LPM).
Chlorination

After plasma treatment, the fabrics were chlorinated at room temperature with sodium hypochlorite solution to transform amino groups on the finished fabric into N-halamines. After chlorination, the fabrics were washed with deionised water (DI) until the water did not change to blue to ensure there was no free chlorine; the presence of chlorine was tested with KI/starch solution. After antibacterial finishing, the cotton fabrics were stored under standard conditions of 20 ± 2 °C and 65 ± 2% relative humidity for at least 24 h prior to further evaluation.

Parameters for Optimisation of Treatment Conditions

An orthogonal array testing strategy (OATS) technique was employed to determine the optimum treatment conditions (Kan 2007; Kan et al. 2011; Zhou and Kan 2014a). Four variables, i.e., discharge power of APP, moving speed of fabric, concentration of sodium hypochlorite, and time of chlorination, were investigated in the antibacterial finishing process; OATS parameters and the experimental arrangements are shown in Tables 1 and 2, respectively.

Table 1. Parameters and Levels Used in OATS

<table>
<thead>
<tr>
<th>Level</th>
<th>Parameters</th>
<th>Discharge power of APP (W)</th>
<th>Moving speed of fabric (×10⁻³ m/s)</th>
<th>Concentration of sodium hypochlorite (%)</th>
<th>Time of chlorination (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>60</td>
<td>4.5</td>
<td>0.8</td>
<td>15</td>
</tr>
<tr>
<td>II</td>
<td>II</td>
<td>90</td>
<td>6.0</td>
<td>1.0</td>
<td>30</td>
</tr>
<tr>
<td>III</td>
<td>III</td>
<td>120</td>
<td>7.5</td>
<td>1.2</td>
<td>45</td>
</tr>
<tr>
<td>IV</td>
<td>IV</td>
<td>150</td>
<td>9.0</td>
<td>1.4</td>
<td>60</td>
</tr>
</tbody>
</table>

Antibacterial Property

Antibacterial activity of samples was tested according to AATCC Test Method 147-2011. *S. aureus* (ATCC 6538) was used as the model bacteria (Sun and Xu 1999; Scholz et al. 2005; Gouda and Ibrahim 2008; Mohammadkhodaei et al. 2010). The bacteria were inoculated in a blood agar plate (100 mm diam.) and incubated at 37 °C for 24 h.
Table 2. Experimental Arrangement

| Test run | Parameters                                      |
|----------|------------------------------------------------|---|
|          | Discharge power of APP (W) | Moving speed of fabric (×10^{-3} m/s) | Concentration of sodium hypochlorite (%) | Time of chlorination (min) |
| 1        | I                                              | I                                | I                                     | I                        |
| 2        | I                                              | II                               | I                                     | II                       |
| 3        | I                                              | III                              | III                                   | III                      |
| 4        | I                                              | IV                               | IV                                     | IV                       |
| 5        | II                                             | I                                | II                                     | III                      |
| 6        | II                                             | II                               | I                                      | IV                       |
| 7        | II                                             | III                              | IV                                     | I                        |
| 8        | II                                             | IV                               | III                                    | II                       |
| 9        | III                                            | I                                | III                                    | IV                       |
| 10       | III                                            | II                               | IV                                     | III                      |
| 11       | III                                            | III                              | I                                      | II                       |
| 12       | III                                            | IV                               | II                                     | I                        |
| 13       | IV                                             | I                                | IV                                     | II                       |
| 14       | IV                                             | II                               | III                                    | I                        |
| 15       | IV                                             | III                              | II                                     | IV                       |
| 16       | IV                                             | IV                               | I                                      | III                      |

A bacterial suspension was prepared in 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. And then, the suspension was diluted to 100-fold (5×10^3 cfu/mL). After that, 20 μL diluted suspension was deposited and inoculated on a new sterile blood agar plate (100 mm diam.) using the Spiral Platter, and fresh prepared samples (20×20mm) were placed on the seeded agar surfaces. After standing for 5 to 10 min, these plates were placed in the aerobic incubator and incubated at 37 °C for 48 h. Finally, clear zones were observed to evaluate the antibacterial activity of samples.

**Active Chlorine Content**

The active chlorine content on fabric was measured by a colorimetric method. A 0.1 g sample of chlorinated cotton fabric was cut into small pieces, which were immersed completely in 40 mL of acetic acid aqueous solution (1%). One gram of potassium iodide (KI) was added, and the mixture was stirred vigorously for 1 h at room temperature. Starch indicator (0.5 mL) was added, and the presence of starch-iodine complexes turned the solution blue. Active chlorine content was calculated according to the absorbance on
a UV spectrophotometer Lambda 18 (Perkin Elmer, USA). The absorbance of sodium hypochlorite was tested from 400 to 700 nm, and the wavelength of maximum absorption ($\lambda_{max} = 427.6$ nm) was determined. Next, the absorbance of three standard sodium hypochlorite solutions was tested, and the standard curve was plotted. The following regression equation was obtained: $y = 30.401x - 50.84$, $R^2 = 0.9918$. Finally, the absorbance of samples was tested, and the chlorine concentration in the sample was calculated based on the calibration curve.

**Regenerability**
Chlorinated cotton fabrics were washed to test their regenerability according to AATCC Test Method 61-1A before washing, the antimicrobial activity of the chlorinated fabrics was tested. After different washing times, the antimicrobial activity was tested again (denoted “AW”). After washing, the fabrics were chlorinated again with sodium hypochlorite. The time and the concentration of sodium hypochlorite for re-chlorination were the same as the first treatment. Finally, the antimicrobial activity of these fabrics was tested (denoted “AW+CH”).

**Durability of Antibacterial Activity on Cotton Fabric**
The active chlorine content of chlorinated cotton fabrics was tested after the process of antibacterial finish was completed. After these fabrics were stored in laboratory in darkness with BHT-free plastic bag for 1, 2, 3, 4, 5, and 6 months at 20 ± 2 °C and 65 ± 2% relative humidity, their active chlorine content (termed as AS) was tested again, separately. Meanwhile, they were chlorinated again and their concentrations of chlorine on fabric were tested (termed as AS+CH).

**Fourier Transform Infrared Spectroscopy with Attenuated Total Reflection Mode (FTIR-ATR)**
A Spectrum 100 model FTIR-ATR spectrometer (Perkin Elmer, USA) was used to detect the chemical properties of coated fabrics. The spectra were collected using 16 scans with 4 cm$^{-1}$ resolution between 650 and 4000 cm$^{-1}$. The second derivative was calculated to remove noise in the FTIR-ATR spectroscopy data.

**Tearing Strength**
An Elmatear digital tear tester (James H. Heal and Co. Ltd., Halifax, UK) was used to test tearing strength of fabrics according to ASTM D1424-09 (Dhiman and Chakraborty 2015). The maximal capacity of the testing machine was 32 N.

**Weight Change**
Cotton fabrics were treated separately with N$_2$/He plasma or He plasma. The conditions for plasma treatment were the same except for the presence or absence of N$_2$. The weight of all test specimens (200 mm × 100 mm) was measured with an AG204 DeltaRange Electronic Balance (Mettler-Toledo, OH) before and after treatment. A total of 40 samples were measured, and the average weight change was determined. Positive change implied a gain in the weight, while negative change indicated a loss of substrate. The percentage change in fabric weight was calculated by the following equation,

$$\text{Weight Change (\%)} = \frac{w-w_0}{w_0} \times 100\% \quad (1)$$
where \( W (g) \) is weight of the substrate after treatment and \( W_0 (g) \) is initial weight of the substrate.

**Colour Measurement**

A Gretag Macbeth Color-Eye 7000A Spectrophotometer (X-rite, MI, USA) was used to detect the change in fabric colour after antimicrobial finishing. The \( K/S \) value was used for evaluating the colour. A higher \( K/S \) value indicated a darker colour. In this study, the fabric colour was white, so a high \( K/S \) value indicated less whiteness.

**RESULTS AND DISCUSSION**

**Optimum Condition Analysis**

The OATS analysis is a convenient method to optimise experiments containing several variables or factors. It is easy to obtain the optimum conditions and to evaluate the importance of different experimental factors through orthogonal experiments.

**Table 3. Orthogonal Table for Optimizing the Antibacterial Property of Cotton Fabric Treated with Plasma**

<table>
<thead>
<tr>
<th>Test run</th>
<th>Mean Clear Width against S. aureus (mm)</th>
<th>Discharge power of APP (W)</th>
<th>Moving speed of fabric ( \times 10^3 ) m/s</th>
<th>Concentration of sodium hypochlorite (%)</th>
<th>Time of chlorination (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.329</td>
<td>5.314 (1.329)</td>
<td>5.970 (1.492)</td>
<td>5.495 (1.374)</td>
<td>5.277 (1.319)</td>
</tr>
<tr>
<td>2</td>
<td>1.285</td>
<td>5.152 (1.288)</td>
<td>5.590 (1.398)</td>
<td>5.462 (1.366)</td>
<td>5.714 (1.419)</td>
</tr>
<tr>
<td>3</td>
<td>1.300</td>
<td>6.511 (1.628)</td>
<td>5.580 (1.395)</td>
<td>5.325 (1.331)</td>
<td>5.676 (1.451)</td>
</tr>
<tr>
<td>4</td>
<td>1.400</td>
<td>5.492 (1.373)</td>
<td>5.329 (1.332)</td>
<td>6.187 (1.547)</td>
<td>5.802 (1.451)</td>
</tr>
<tr>
<td>5</td>
<td>1.307</td>
<td>1.359</td>
<td>0.641</td>
<td>0.862</td>
<td>0.525</td>
</tr>
<tr>
<td>6</td>
<td>1.336</td>
<td>5.495 (1.374)</td>
<td>5.462 (1.366)</td>
<td>5.325 (1.331)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.314</td>
<td>5.590 (1.398)</td>
<td>5.329 (1.332)</td>
<td>6.187 (1.547)</td>
<td></td>
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<tr>
<td>8</td>
<td>1.195</td>
<td>1.307</td>
<td>1.336</td>
<td>1.300</td>
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<tr>
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<td>1.667</td>
<td>1.307</td>
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<tr>
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<tr>
<td>11</td>
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<tr>
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<tr>
<td>14</td>
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<td>1.336</td>
<td>1.300</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.399</td>
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<td>1.336</td>
<td>1.300</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1.263</td>
<td>1.307</td>
<td>1.336</td>
<td>1.300</td>
<td></td>
</tr>
</tbody>
</table>

Figures in bold exhibit the greatest value among all the values shown in the levels of different variables used, while italics indicate the level of importance of each variable. The value inside the bracket is the mean clear width.
The mean clear width of a sample against *S. aureus* (ATCC 6538) was used as a measure of antibacterial activity. The clear width correlated with antibacterial activity. Table 3 shows the mean clear widths of samples from the nine OATS-generated conditions against *S. aureus*.

Four parameters in the finishing process—discharge power of APP, moving speed of fabric, concentration of sodium hypochlorite, and time of chlorination—caused different effects on antibacterial activity (Table 3). Based on the orthogonal analysis, the importance of these parameters (in descending order) was discharge power of APP, concentration of sodium hypochlorite, moving speed of fabric, and time of chlorination. The optimum conditions for cotton fabric treated with plasma were as follows: discharge power of APP = 120 W, moving speed of fabric = $4.5 \times 10^{-3}$ m/s, concentration of sodium hypochlorite = 1.4%, and time of chlorination = 60 min. When cotton fabric was treated under the optimum conditions, the mean clear width against *S. aureus* was 1.84 mm, which was the best result (Table 3). Therefore, the optimum conditions were verified. The optimised samples were used for further evaluation of regeneration ability, FTIR-ATR, and SEM.

The mean clear width against *S. aureus* fluctuated with increased discharge power (Fig. 3). When the discharge power was 120 W, the mean clear width was greater than under other discharge powers tested. The mean clear width fluctuated around $1.33 \pm 0.05$ mm when the discharge power was 60, 90, or 150 W. A higher discharge power is more effective in substrate surface breakage, which provides more active particles to form N-containing groups and, subsequently, enhances antibacterial activity. However, high discharge power substantially raises the temperature at the material surface, which deteriorates fibres and negatively affects free radical reactions with molecules on the material surface (Wong *et al.* 1999). Therefore, when discharge power was higher than 120 W, the antibacterial activity of the samples was reduced.

![Fig. 3. Effect of discharge power on antibacterial property](image)
The mean clear width against *S. aureus* decreased with increasing fabric moving speed (Fig. 4). The interaction time of plasma per unit area of fabric decreased with increased fabric moving speed; thus, a short plasma exposure time produced a lower density of free radicals on the fabric. Consequently, the fabric surface had fewer opportunities to react with free radicals, and fewer new functional groups were formed on the material surface.

**Fig. 4.** Effect of moving speed on antibacterial property

The mean clear width against *S. aureus* decreased as the concentration of sodium hypochlorite increased, up to 1.2%; after the concentration exceeded 1.2%, the mean clear width increased with increasing concentration (Fig. 5).

**Fig. 5.** Effect of concentration of sodium hypochlorite solution on antibacterial property
Concentrated sodium hypochlorite has strong oxidising power (Yu et al. 2012). With increasing concentration, sodium hypochlorite oxidised functional groups on the material surface, which reduced its chlorination efficiency in N-containing groups. However, at concentrations higher than 1.2%, sodium hypochlorite effectively chlorinated N-containing groups and oxidised other groups. Thus, the antibacterial activity was reduced initially but increased with increasing sodium hypochlorite concentration.

Figure 6 shows that the mean clear width against S. aureus increased markedly with chlorination time up to 30 min, beyond which the mean clear width remained relatively stable; there was a small increase at 60 min chlorination time.

This result, showing a plateau effect, reflects the quantitative limitations of N-containing groups on material surfaces. When fabric is chlorinated for 30 min, the fabric is saturated with chlorine. Thus, when chlorination time is longer than 30 min, antibacterial activity is nearly constant.

![Fig. 6. Effect of time of chlorination on antibacterial property](image)

**Relationship between Antibacterial Property and Concentration of Chlorine on Cotton Fabric**

The relationship between antimicrobial activity and concentration of chlorine on cotton fabric treated with nitrogen plasma was linear, with the mean clearance width against S. aureus increasing with increased chlorine concentration (Fig. 7; $y = 0.2039x + 0.3571$, $R^2 = 0.9614$).

The antimicrobial properties of the cotton fabric treated with nitrogen plasma result from chlorine, which kills microorganisms. When chlorine content increases, more bacteria are killed. Therefore, the antimicrobial activity of cotton fabric was improved when the amount of chlorine was increased.
FTIR-ATR

The FTIR-ATR spectra were employed to characterise variations on substrate surfaces after plasma treatment (Fig. 8). The second derivative FTIR-ATR spectrum was examined for untreated cotton fabric (Fig. 8a), cotton fabric treated with plasma (Fig. 8b), and cotton fabric treated with plasma and chlorination (Fig. 8c).

![Second derivative FTIR spectrum](image)

**Fig. 8.** Second derivative FTIR spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric treated with plasma followed with chlorination

\[ y = 0.2039x + 0.3571 \\ R^2 = 0.9614 \]
As shown in Fig. 8, absorption bands at approximately 3304 cm\(^{-1}\) indicated O-H stretching vibrations in cellulosic material, and the peaks observed at 2880 cm\(^{-1}\) corresponded to -C-H stretching (Zimmerley et al. 2010; Raghavendra et al. 2013; Kumar et al. 2014). Bands observed at around 1650 cm\(^{-1}\) were associated with the angular O-H bending of water molecules (Paschoal et al. 2015). Water molecules in cellulose are very difficult to extract because of the cellulose-water interaction (Abraham et al. 2011; Paschoal et al. 2015).

In contrast to untreated cotton fabric, cotton fabric treated with plasma exhibited a unique absorbance peak near 1550 cm\(^{-1}\) which represented the deformation of N-H, and the absorbance peak around at 1750 cm\(^{-1}\) is generally assigned to the presence of carbonyl band (C=O) (Figs. 8b, c) (Amick et al. 1980; Granja et al. 2001; Hui et al. 2005). These changes are caused by N\(_2^+\), N\(_2\) (excited), N, and N\(^+\) particles and electrons generated during nitrogen plasma treatment, which introduces nitrogen-containing groups in cotton fabrics and oxidises the primary hydroxyl group to a carboxyl group (Zhou and Kan 2015). The absorbance wavenumbers of -C-H, N-H, and C=O changed slightly after chlorination (Figs. 8b, c), which may have resulted from the introduction of chlorine.

**Regenerability**

Regenerability is extremely important for antimicrobial textiles, as it extends their service life. Figure 9 shows the regenerability of cotton fabric treated with N\(_2\)/He plasma. The antimicrobial activity of fabrics before washing, after washing (AW), and after re-chlorination (AW+CH) was compared.

The mean clear width of fabric against *S. aureus* decreased with the increase of washing times. While it increased again after re-chlorination after every washing (Fig. 9). Compared with the unwashed fabric, washing and re-chlorination decreased the mean clear width against *S. aureus*. Treatment with N\(_2\) plasma and sodium hypochlorite converts functional N-groups in cotton fabric to N-halamines, which have antimicrobial
properties; these antimicrobial properties are regenerable. In addition, the etching effect of plasma treatment decreases these properties substantially before washing. Because N-containing groups and cotton fabric are connected by chemical bonds, which are stable, the antimicrobial nature of the fabric is also stable. Thus, antibacterial activity in cotton fabric treated with nitrogen plasma is stable and regenerable.

**Durability of Antibacterial Activity on Cotton Fabric**

Durability is important for antimicrobial textiles. Antimicrobial textiles with long durability have long servicing life. Figure 10 shows the antimicrobial durability of cotton fabrics with nitrogen plasma treatment and chlorination with sodium hypochlorite. The concentration of active chlorinate on fabrics after storage (AS) and re-chlorination (AS+CH) were tested. It can be seen that active chlorine concentration decreased with the extension of time and that it could be recovered by re-chlorination with sodium hypochlorite. In the first three months, the active chlorine concentration decreased obviously, while it decreased slowly three months after samples are stored in laboratory in darkness with BHT-free plastic bag at 20 ± 2 °C and 65 ± 2% relative humidity. Meanwhile, the concentration of active chlorine after re-chlorination declined notably in first three months, and it remained nearly stable three months after. This may be caused by two reasons. The first one is that some of chlorine was not stable, because those atoms were on the functional groups formed by rearrangement of active particles activated by plasma treatment. Some of the functional groups were not stable, resulting in the chlorine, and even some of the functional groups on the fabric, becoming lost easily. The second reason is that the chlorine was used to kill bacteria in the enclosed environment during the first three months, leading to the quick decrease of chlorine on fabric, while there was no more bacteria to consume the chlorine on fabric in the following time, avoiding the decrease of chlorine. Therefore, the active chlorine concentration was decreased remarkably in the first three months, and then it stayed stable. That is to say, the antimicrobial activity of cotton fabric with nitrogen plasma treatment and chlorinated with sodium hypochlorite will be reduced, but it can be partly recovered by chlorination with sodium hypochlorite.

![Fig. 10. Duration of antimicrobial ability on cotton fabric](image-url)
Weight Change

Weight change was measured to evaluate the effect of plasma treatment on the properties of cotton fabric (Table 4). The weight of cotton fabric decreased a little after plasma treatment, and the weight loss of fabric treated with He plasma was obvious compared with cotton fabric treated with N2/He plasma. He is an inert gas, while N2 is a reactive gas. While He is not involved in chemical reactions on the surface of textiles, it acts during cleaning and etching by chain scissions or as a carrier gas for reactive gases and polymerising gases; reactive gases such as nitrogen introduce nitrogen-containing groups to the substrate surface (Shishoo 2007). The etching effect of He plasma treatment leads to weight loss in cotton fabric. In the N2/He mixed plasma, the etching effect of plasma is accompanied with plasma polymerisation of N-containing particles generated in plasma. In this study, the flow rate of helium remained unchanged, and N-containing active particles in the N2/He mixed plasma reacted with the material surface to form new groups, which partly offset the weight loss caused by the etching effect. Therefore, the N2/He mixed plasma treatment did not noticeably affect fabric weight, but it did introduce functional groups onto the fabric.

<table>
<thead>
<tr>
<th>Table 4. Effect of Plasma Treatment on Weight of Fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>He plasma</td>
</tr>
<tr>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>He plasma</td>
</tr>
<tr>
<td>N2/He plasma</td>
</tr>
</tbody>
</table>

Tearing Strength

The tearing strength of cotton fabrics with and without plasma treatment is shown in Table 5. After plasma treatment, the tearing strength decreased approximately 10% in both warp and weft directions. The etching effect of plasma treatment increases the surface friction and roughness, which restricts the sliding action of yarn during tearing. Therefore, the tearing strength decreases after plasma treatment (Kan et al. 2004; Cheng et al. 2010). Although the tearing strength of cotton fabrics declines after plasma treatment, it still satisfies the basic requirements of textiles (Zeng 2012). Therefore, plasma treatment for antibacterial finishing has no substantial effect on the tearing strength of cotton fabrics.

<table>
<thead>
<tr>
<th>Table 5. Tearing Strength of Cotton Fabric in Warp and Weft Directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>Tearing strength in warp direction (N)</td>
</tr>
<tr>
<td>Tearing strength in weft direction (N)</td>
</tr>
</tbody>
</table>

Colour Measurement

The whiteness of the fabric was evaluated by the K/S value across the visible spectrum (400 to 700 nm). Higher K/S values indicate darker (i.e., less white) fabric. The K/S values of cotton fabric with antimicrobial finishing were lower than those of untreated fabric (Fig. 11). Therefore, cotton fabric becomes whiter when it is treated with plasma and chlorination, probably because sodium hypochlorite is a bleaching agent.
CONCLUSIONS

2. Optimal antimicrobial properties were observed when the conditions for the finishing process included an APP discharge power of 120 W, a speed of fabric motion of $4.5 \times 10^{-3} m/s$, a sodium hypochlorite concentration of 1.4%, and a chlorination time of 60 min.
3. The antimicrobial activity was regenerable and durable, and re-chlorination was easy to perform.
4. FTIR, weight change measurements, and antimicrobial tests showed that nitrogen plasma introduced nitrogen-containing groups to the surface of cotton fabrics.
5. Antimicrobial finishing had acceptable effects on tearing strength and fabric colour.
6. As this finishing method does not involve other antimicrobial agents or auxiliaries, it is practical.

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