# Using Plasma Treatment for Enhancing the Coating for Rechargeable Antimicrobial Finishing of Cotton Fabric

Chi-Wai Kan

***Abstract*—This paper focuses on the effects of plasma treatment applied to the rechargeable antimicrobial finishing for cotton fabrics. Nitrogen plasma treatment was used in the traditional pad-dry-cure finishing process of cotton fabric coated with 5, 5-dimethylhydantoin (DMH) with the aim of enhancing the coating effect and antimicrobial property. Then chlorine was introduced into nitrogen-containing groups on the coated cotton fabrics in order to make it antimicrobial by chlorination with sodium hypochlorite. FTIR was used to evaluate the surface properties, including the existence of DMH on cotton fabric and the content of DMH on cotton fabric after modification. The results showed that nitrogen-plasma introduces nitrogen-containing groups into cotton fabrics, the coating effect and adhesion of DMH on cotton fabric was enhanced with nitrogen plasma treatment, the successful introduction of chlorine on the coated fabric inhibits bacteria, *S. aureus*, effectively and the antimicrobial property is rechargeable.**

***Index Terms*—Antimicrobial, cotton fabric, DMH, plasma.**

## I. Introduction

Cotton is a natural cellulosic fiber consisting of numerous –OH groups and a small number of carboxylic acid groups providing a suitable environment for microorganisms to grow [1]. Therefore, the good moisture absorption ability leads to moist cotton easier attacked by bacteria. Rechargeable antimicrobial finishing for textiles has been developed recent year. N-halamines are the antimicrobial agents which make the antimicrobial property of textiles regenerable. N-halamines are defined as a compound containing one or more primary amine groups, secondary amine groups and/or imines groups which can be halogenated to generate oxidative nitrogen-halogen antibacterial moieties. During the process, amine or imines groups in N-halamine are changed to chloramines through chlorination. The bactericidal action of N-halamine is considered to be a manifestation of a chemical reaction involving direct transfer of positive halogen from N-halamine to appropriate receptors in the bacterial cells, which is attributed to the oxidative properties of halamine bonds (N-Cl) in contact with germs [2]-[4]. Though the bactericidal process consumes halogens, the lost halogens can be easily recharged by chlorination. DMH is a basic finishing agent which can be transferred into antimicrobial agent with N-halamine structure.

Plasma technology has been considered as an excellent mean to surface modification, because when it functionalizes surface of materials, it also keeps the original bulk properties of materials. In this study, DMH will be coated onto cotton fabric with the aid of plasma treatment. After chlorination, the coated cotton fabrics will be introduced N-halamine structure. In order to investigate the effect of plasma treatment on the antimicrobial activity of coated fabrics, plasma treatment is applied to the finishing process.

Manuscript received December 20, 2014; revised March 16, 2015. This work was supported by the Research Grants Council of The Hong Kong Special Administrative Region, China (Project No.: PolyU 5173/11E) and Hong Kong Polytechnic University.

Chi-Wai Kan is with the Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong (e-mail: tccwk@polyu.edu.hk).

## II. Experimental

### A. Materials

Desized, scoured and bleached 100% woven cotton fabric (138 yarns/inch in warp and 63 yarns/inch in weft, 261g/m$^2$) was used in this study. Nitrogen and helium gases were commercial grade. 5,5-Dimethyl hydantoin (DMH) (97%), sodium hypochlorite (5%, activated chloride), potassium iodide, glacial acetic acid (>99.8%) and starch indicator (1% in $H_2O$) were used.

### B. DMH Finishing Solution Preparation

To prepare a 6% of finishing bath, 48g DMH was dissolved in 800mL of deionized (DI) water with stirring for 1h.

### C. Plasma Treatment

The plasma generator, Atomflo-200 series (Surfx Technology, US), was used for APP treatment of the fabric samples in this study. Gas discharge was ignited by low RF frequency (13.56MHz). The plasma jet was placed vertically above the sample (Fig. 1). The carrier gas was helium, while the reactive gas was nitrogen. The discharge power of APP was 80W, the flow rate of nitrogen was 0.15 L/min, the flow rate of helium was 9.6 L/min, jet distance was 5mm and the moving speed of fabric was 0.2m/s.

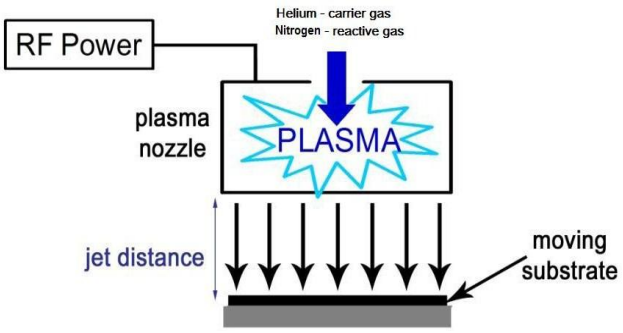


Fig. 1. Schematic diagram of APP treatment.

DOI: 10.7763/IJCEA.2015.V6.524

### D. Applying of DMH to Cotton Fabric

The process with plasma treatment, termed as DP, was that cotton fabric was first padded with DMH with 80% pick up and dried (80 ℃, 5 min). The fabric was then treated with plasma and cured at 160 ℃ for about 5 min. In order to observe the effect of plasma applied in the DMH finishing process, the control finishing process of cotton fabric, termed as DC, was that cotton fabric was first padded with DMH with 80% pick up and then dried at 80 ℃ for about 5 min as well as cured at 160 ℃ for about 5 min.

The fabrics treated with the same coating process were chlorinated at room temperature with 0.8%, 1.0% and 1.2% of sodium hypochlorite solution over 10, 20, 40 and 60 min, to transform some of the amino groups in DMH into N-halamines (Fig. 2). After chlorination, these fabrics were washed with DI water sufficiently to remove free chlorine; this was tested with KI/starch solution. Finally, these coated fabrics were dried and stored at 23±2 ℃ and 65±2% relative humidity.

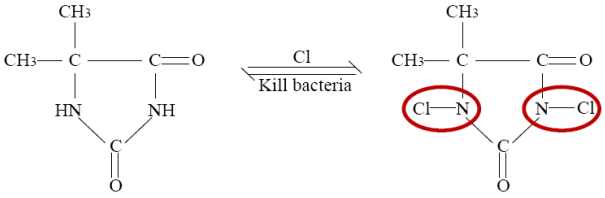


Fig. 2. The reversible redox reaction of DMH with halamine structures (red cycle shows the N-halamine structure).

### E. The Active Chlorine Content of the Chlorinated DMH

The active chlorine content of the chlorinated cotton fabric coated with DMH was determined by colorimetric method. The $\lambda_{max}$ was 427.60 nm and regression equation was $y$=30.401$x$-50.84; $R^2$=0.9918. 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 (KI) was added and the mixtures were stirred vigorously for 1 h at room temperature with magnetic stirrers. Then 0.5mL of starch indicator was added into the solution. The complex of the formed iodine and starch made the solution blue. Finally, the absorbance of samples was tested and concentration of chlorine on the sample was calculated based on the regression equation.

### F. Rechargeability

Chlorinated cotton fabrics were washed to test their rechargeability according to AATCC Test Method 61-1A. Before washing, active chlorine content of chlorinated fabrics was tested (termed as BW). After washing, the active chlorine content was tested again (termed as AW). After that, these fabrics were chlorinated again with sodium hypochlorite. The time for chlorination and concentration of sodium hypochlorite was the same as when they were chlorinated in the first time. Then, the active chlorine content of these fabrics was tested (termed as AW+CH).

### G. Antimicrobial Activity

Antimicrobial activity of samples was tested according to AATCC Test Method 147-2011. *S. aureus* (ATCC 6538) was used as the model bacteria.

### H. FTIR-ATR

FTIR-ATR spectrometer, Spectrum 100 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 $cm^{-1}$. Then, the second derivative calculated to remove the noise in the FTIR-ATR spectroscopy.

## III. Results and Discussion

### A. The Effect of Bleaching Conditions on Concentration of Active Chlorine on Fabrics

The amount of DMH on fabric can be estimated by testing the concentration of active chlorine on the fabric. Fig. 3 shows the effect of bleaching time on concentration of active chlorine on coated fabrics when concentration of sodium hypochlorite is 0.8%. According to Fig. 3, it can find that the concentration of active chlorine on fabrics with plasma treatment trends to be increased with the increase of bleaching time within 20 min, while the concentration of active chlorine on this fabric decreases when the bleaching time is longer than 20 min. That may be because the coating of DMH is not good enough; it dissolves in bleach solution when bleaching time is 60min. Therefore, the optimal chlorinated time is 20 min for cotton fabric coated with DMH to transfer the amino groups into N-halamine structures. When compare this fabric with the fabric without plasma treatment, it can be seen that the concentration of active chlorine of the cotton fabric with plasma treatment is higher, that is, plasma treatment enhances the coating effect of DMH and $N_2$ plasma treatment introduces nitrogen groups into the surface of cotton fabric, because the etching effect of plasma treatment makes the surface of fibers uneven which provides convenience for DMH coating, meanwhile, $N_2$ plasma can functionalize the substrate with N-containing group, such as $–NH_2$, -NH, =NH, $CONH_2$ or C≡N [5]. Fig. 4 shows the effects of concentration of bleach solution on concentration of active chlorine, when chlorination time is 40 min. In general, concentration of active chlorine of fabric increases with the increase of concentration of bleach solution in Fig. 4. The concentration of active chlorine on fabric treated with plasma is higher than that on fabrics finished without plasma treatment. This proves that plasma treatment can enhance the coating effect of DMH. This is because the unstable particles generated during the plasma treatment have a significant tendency to react to form free radicals, and these numerous free radicals interlock with each other easily which increases the chances of DMH coated onto cotton fabrics [6].

### B. FTIR-ATR

The FTIR-ATR spectra were employed to characterize DMH coated on the surface of cotton fabrics followed by chlorination. The characteristic absorbance band of DMH is amide II and C=O stretching of hydantoin ring. Fig. 5 shows the FTIR-ATR spectrum of untreated cotton fabric (Fig. 5a), cotton fabric treated with plasma (Fig. 5b), cotton fabric coated with DMH through ‘pad-dry-cure’ method (Fig. 5c), cotton fabric padded with DMH, dried, treated with plasma and cured (Fig 5d). In the spectra in Fig. 5b, 5c and 5d, the bands around 3750$cm^{-1}$ are attributable to N-H stretching

vibrations and the peaks at around 1547 $cm^{-1}$ are assigned to N-H (amine II) deformation. The absorbance bands in the 1761 $cm^{-1}$ region in Fig. 5c and Fig. 5d represent the stretching vibrations of C=O [7], [8]. Therefore, it can be concluded that nitrogen plasma treatment can introduce nitrogen-groups into cotton fabrics by comparing Fig. 5a and Fig. 5b. According to Fig. 5c and Fig. 5d, the appearance of peaks of C=O means DMH is coated onto cotton fabric. Moreover, the absorbance peak at 1761 $cm^{-1}$ in Fig. 5d is higher than that in Fig. 5c, which means plasma treatment improves the coating effect of DMH.

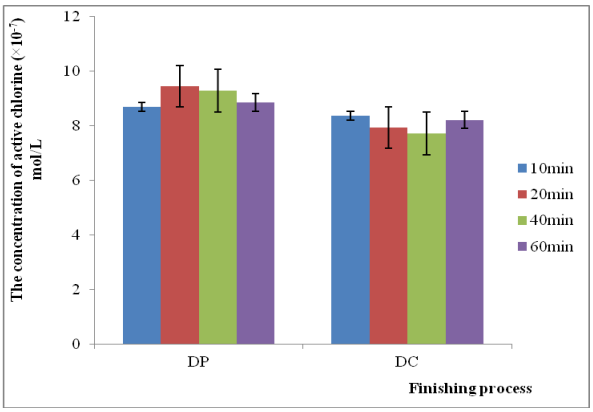


Fig. 3. The effect of bleaching time on the concentration of active chlorine on fabrics.

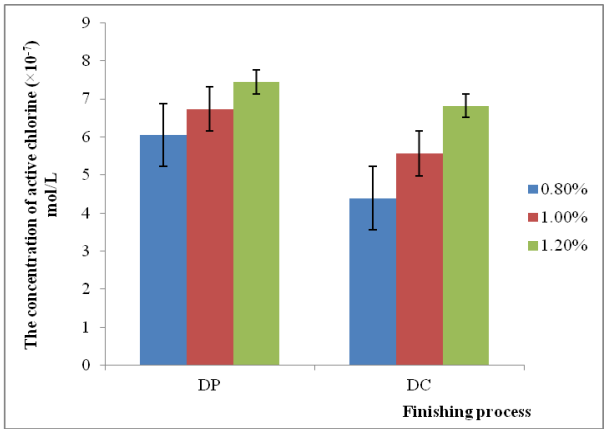


Fig. 4. The effect of the concentration of bleaching solution on the concentration of active chlorine on the fabrics.

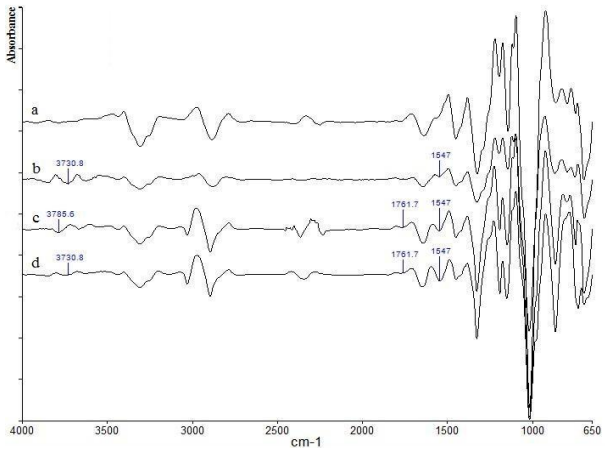


Fig. 5. FTIR spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric coated with DMH through 'pad-dry-cure' method (DC), (d) cotton fabric padded with DMH, dried, treated with plasma and cured (DP).

### C. Rechargeability

The rechargeability is very important for antimicrobial textiles. Those antimicrobial textiles with good rechargeability have long useful life. Fig. 6 shows the rechargeability property of cotton fabric coated with DMH with the aid of plasma treatment. It can be seen in Fig. 6 that almost all of samples coated with DMH with the aid of plasma treatment can be recharged after washing, because active chlorine concentration of these fabrics decreases after washing while active chlorine concentration increases after they are re-chlorinated. However, the active chlorine concentration on cotton fabrics after they are re-chlorinated is a little lower than they are on cotton fabric before washing. In addition, comparing with these samples with plasma treatment, the recharge ability of cotton fabric coated with DMH without plasma treatment is not very good. The active chlorine concentration decreases after washing, even after re-chlorination. That is because the adhesion of DMH on cotton fabric is not very good, DMH on cotton fabric is easily to dissolve into water, even in bleaching solution. Therefore, it can be concluded that plasma treatment is helpful for improving the rechargeability of cotton fabric coated with DMH and plasma treatment can enhance the adhesion of DMH on cotton fabrics that increase the durability of antimicrobial effect of cotton fabrics coated with DMH.

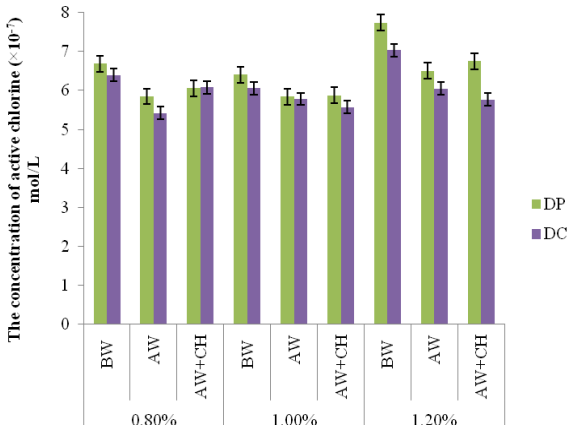


Fig. 6. The rechargeability of cotton fabric coated with DMH with plasma treatment.

### D. Antimicrobial Activity

In this part, the effect of concentration of DMH and content of sodium hypochlorite on antimicrobial activity of samples is studied. Clear zone of sample against *S. aureus* (ATCC 6538) from sample to bacteria is used to evaluate antimicrobial effect of sample. The growth of microorganism underneath the tested specimen was observed and the width of the clear zone was measured. The antimicrobial efficacy data are presented in Table I. The growth of *S. aureus* (ATCC 6538) underneath the tested specimen was not observed except in the sample without DMH coating. That means cotton fabrics coated with DMH can inhibit the growth of *S. aureus* (ATCC 6538) effectively. According to Table I, it can be seen that the clear zone of samples widens with the increase of concentration of sodium hypochlorite. It also can find clear zone of samples with plasma treatment is wider than that without plasma treatment (DC). Therefore, it can be concluded that plasma treatment is helpful for antimicrobial

effect of cotton fabrics coated with DMH.

TABLE I: THE MEAN CLEARANCE DISTANCE OF THE BACTERIA OBTAINED FROM THE SPECIMENS

| Treatment process | Concentration of DMH (%) | Concentration of sodium hypochlorite (%) | Mean Clear Width against *S. aureus* (cm) |
|---|---|---|---|
| Untreated fabric | 0 | 0 | 0 |
| DP | 6 | 0.8 | 1.67 |
| | 6 | 1 | 1.46 |
| | 6 | 1.2 | 1.80 |
| DC | 6 | 0.8 | 0.99 |
| | 6 | 1 | 1.28 |
| | 6 | 1.2 | 1.57 |

## IV. CONCLUSION

With the help of plasma treatment, cotton fabric coated with DMH gain durable and rechargeable antimicrobial function by chlorinating with sodium hypochlorite. The properties of finished samples have been tested by FTIR and the sample with plasma treatment during pad-dry-cure finishing method show durable and rechargeable antimicrobial activity which provides antimicrobial functions against *S. aureus* (ATCC 6538).

## ACKNOWLEDGMENT

Authors would like to thank the financial support from the Research Grants Council of The Hong Kong Special Administrative Region, China (Project No.: PolyU 5173/11E) and The Hong Kong Polytechnic University for this work.

## REFERENCES

[1] S. Lim and S. M. Hudson, "Application of a fiber-reactive chitosan derivative to cotton fabric as an antimicrobial textile finish," *Carbohydrate Polymers*, vol. 56, pp. 227-234, 2004.
[2] Y. Sun and G. Sun, "Novel refreshable N-halamine polymeric biocides: N-chlorination of aromatic polyamides," *Industrial and Engineering Chemistry Research*, vol. 43, pp. 5015-5020, 2004.
[3] Y. Sun, T, Chen, S. Worley, and G. Sun, "Novel refreshable n‐halamine polymeric biocides containing imidazolidin‐4‐one derivatives," *Journal of Polymer Science Part a: Polymer Chemistry*, vol. 18, pp. 3073-3084, 2001.
[4] L. Qian and G. Sun, "Durable and regenerable antimicrobial textiles: Improving efficacy and durability of biocidal functions," *Journal of Applied Polymer Science*, vol. 91, pp. 2588-2593, 2004.
[5] S. S. Silva, S. M. Luna, M. E. Gomes, J. Benesch, I. PashkulevaI, J. F. Mano JF, and R. F Reis, "Plasma surface modification of chitosan membranes: Characterization and preliminary cell response studies," *Macromolecular Bioscience*, vol. 8, pp. 568-576, 2008.
[6] M. Sanchis, O. Calvo, O. Fenollar, D. Garcia, and R. Balart, "Characterization of the surface changes and the aging effects of low-pressure nitrogen plasma treatment in a polyurethane film," *Polymer Testing*, vol. 27, pp. 75-83, 2008.
[7] L. Wang, J. Xie, L. Gu, and G. Sun, "Preparation of antimicrobial polyacrylonitrile fibers: Blending with polyacrylonitrile-co-3-allyl-5, 5-dimethylhydantoin," *Polymer Bulletin*, vol. 56, pp. 247-256, 2006.
[8] H. B. Kocer, S. Worley, R. Broughton, and T. Huang, "A novel N-halamine acrylamide monomer and its copolymers for antimicrobial coatings," *Reactive and Functional Polymer*, vol. 71, pp. 561-568, 2011.

**C. W. Kan** is an associate professor in the Institute of Textiles and Clothing, Hong Kong Polytechnic University. Dr. Kan earned his BSc and PhD in textile chemistry from the Hong Kong Polytechnic University. His research major is in the field of textile coloration and finishing, and surface modification of textile materials. Dr. Kan has worked extensively in the field of plasma treatment and has published more than 80 peer-reviewed journal and conference articles in this field.