Chemical analysis of plasma-assisted antimicrobial treatment on cotton

C W Kan[1*], Y L Lam[1], C W M Yuen[1], A Luximon[1], K W Lau[1] and K S Chen[2]

[1]Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
[2]Department of Materials Engineering, Tatung University, 40 Zhongshan North Road, 3rd Section Taipei 104, Taiwan

E-mail: tccwk@inet.polyu.edu.hk or tccwk@polyu.edu.hk

Abstract. This paper explores the use of plasma treatment as a pretreatment process to assist the application of antimicrobial process on cotton fabric with good functional effect. In this paper, antimicrobial finishing agent, Microfresh Liquid Formulation 9200-200 (MF), and a binder (polyurethane dispersion, Microban Liquid Formulation R10800-0, MB) will be used for treating the cotton fabric for improving the antimicrobial property and pre-treatment of cotton fabric by plasma under atmospheric pressure will be employed to improve loading of chemical agents. The chemical analysis of the treated cotton fabric will be conducted by Fourier transform Infrared Spectroscopy.

1. Introduction

Cotton fabric is highly popular due to their excellent properties such as regeneration, bio-degradation, softness, affinity to skin and sweat-absorbing property [1, 2]. However, cotton fabric is very prone to be attacked by certain microorganisms, insects and fungi causing functional, hygienic and aesthetic difficulties [3-5]. Extensive efforts have been made to control emerging disease infections. Therefore, a large demand exists for anti-microbial finished textiles [6, 7] and there are three methods of applying anti-microbial agents to textiles, i.e. (i) the anti-microbial agents are directly adsorbed onto fibres; (ii) the anti-microbial agents are confined to the network structure of a reactive synthetic resin formed on the fibre surface; and (iii) the anti-microbial agents are covalently bound to cellulosic fibres [8]. Bacteria have different membrane structures which are classified as Gram negative or Gram positive [9]. Gram negative bacteria exhibit only a thin peptidoglycan layer of around 2–3 nm between the cytoplasmic membrane and the outer membrane, while Gram positive bacteria lack the outer membrane but have a peptidoglycan layer of about 30 nm thick [9]. The anti-microbial finishing can inhibit the growth or kill the invading bacteria by several ways including (i) cell wall damage and/or inhibition of cell wall synthesis, (ii) changing the chemical or physical state of proteins and nucleic acid inside the cell, (iii) inhibition of enzymes inside the cell and consequently retarding the normal biological activities and metabolism of bacteria, and (iv) inhibition of synthesis of protein or nucleic acids thereby interrupting the ability of bacteria to grow and reproduce [10].

* To whom any correspondence should be addressed

In this paper, antimicrobial finishing agent will be used for treating the cotton fabric for improving the antimicrobial property and pre-treatment of cotton fabric by plasma under atmospheric pressure will be employed to improve loading of finishing agent.

2. Experimental

2.1. Materials

100% desized, scoured and bleached cotton fabric was used. The fabric was further cleaned with 2% non-ionic detergent at pH 7 and 60°C for 30 minutes and then rinsed thoroughly with deionised water for 15 minutes. The cleaned fabric was conditioned at 65±2% relative humidity and 21±1℃ for 24 hours prior to all experiments.

2.2. Atmospheric pressure plasma (APP) treatment

APP treatment was conducted by an atmospheric pressure plasma jet (APPJ, Surfx Technologies LLC, CA) with a rectangular nozzle. The substrate was exposed at a constant speed of 2mm/s to the afterglow plasma generated by a radio frequency of 13.56 MHz. Helium (He) and oxygen (O_2) were used as carrier and reactive gas respectively. Plasma operation parameters were set as: jet distance = 3mm, oxygen concentration = 1%, substrate speed = 10 mm/s and ignition power = 120W. Schematic diagram of the experimental setup was shown in Figure 1.

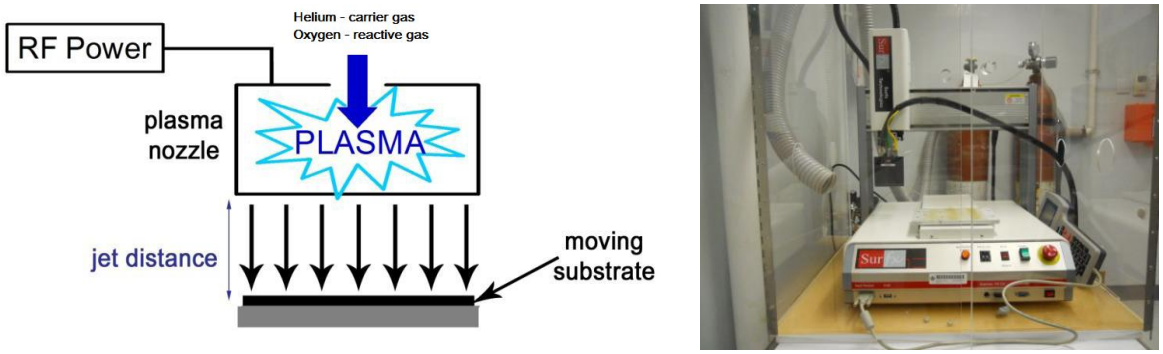

Figure 1. Schematic diagram of APP treatment

2.3. Antimicrobial finishing

The anti-microbial finishing agent (halogenated phenoxy compound, Microfresh Liquid Formulation 9200-200) compound (MF, 0.25%) and a binder (polyurethane dispersion, Microban Liquid Formulation R10800-0) (MB, 0.5%) were used together with a melamine resin. They were applied to the fabric by pad-dry-cure process with an 80% wet pick up. The fabric was dried and cured at 100℃ and at 140℃ for 5 minutes respectively. Finally, the fabrics were conditioned at 21±1℃ and 65±2% relative humidity for 24 hours prior to any further treatment.

2.4. Parallel streak method

The anti-microbial function of the treated cotton materials (five samples) was evaluated by AATCC 147-2004 (Using *S. aureus*, American Type Culture Collection No. 6538 as received) in which the size of specimens was modified to 10mm x 50mm. The preparation and maintenance of the culture medium were conducted according to AATCC 147-2004.

2.4. Fourier transform infrared spectroscopy

Surface chemical composition of the cotton specimens was studied by Fourier Transform Infrared spectrophotometer (Perkin Elmer Spectrum 100) with the scanning range between 4000 cm^{-1} and 700 cm^{-1} and the resolution of $4nm^{-1}$, using the attenuated total reflection with 256 scans.

3. Results and Discussion

3.1. Antimicrobial activity

The parallel streak method determines the anti-microbial activity of the treated textile materials against Gram positive bacteria, *S. aureus*. During the test, specimens were placed in contact with nutrient agar which had been previously streaked with an inoculum of *S. aureus*. After incubation, a clear area, i.e. the zone of inhibition, of the interrupted growth underneath and along the sides of the test material indicated the anti-microbial activity of the specimen. Figures 2(a) and 1(b) illustrate the growth inhibition of *S. aureus* conducted on the untreated (control) and anti-microbial-treated fabric specimens (M1) respectively. Figures 1(c) and 1(d) illustrate the growth inhibition of *S. aureus* conducted on the plasma-treated alone (PM0) and plasma pretreated follow by anti-microbial-treated (PM1) specimens respectively. Table 1 summarises the mean clearance distance of the bacteria obtained from the specimens.

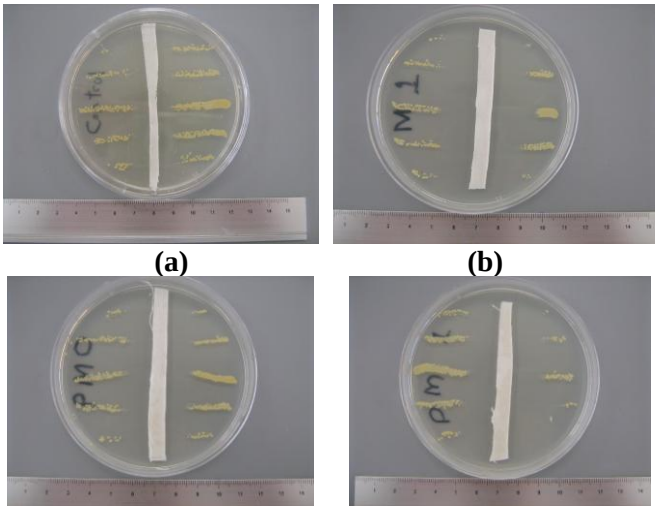

Figure 2. Growth inhibition of *S. aureus* conducted on (a) control, (b) M1, (c) PM0 and (d) PM1

Table 1. The mean clearance distance of the bacteria obtained from the specimens

Sample Symbol	Mean Clearance Distance (cm)
Control	1.2
M1	1.5
PM0	1.3
PM1	1.6

In general, *S. aureus* has a relatively thick wall of 20-80 nm [11], which is composed of many layers of peptidoglycan polymer and one plasma membrane. These layers of peptidoglycan are composed of a fairly open network polymer of N-acetylmuramic acid and N-acetylglucosamine polysaccharide chains with peptide bridges [12]. Hence, the Gram positive bacteria are less resistant to many chemical agents than Gram negative cells [13]. Figure 2(a) shows that the control fabric inhibited the growth of *S. aureus* with an average of 1.2cm ZOC in the agar plate. This was due to the fact that the semi-bleached control cotton fabrics might contain some bleach residues, i.e. H_2O_2, which was used to remove the natural coloration and the remaining trace impurities obtained from the cotton in the pre-finishing stage. Although H_2O_2 was less harmful as compared to other reactive oxygen species such as hydroxyl radicals and superoxide ions, it could still enter the cell exhibiting anti-microbial activity [11]. At a very low concentration of MF, the anti-microbial activity of M1 specimen was enhanced as

reflected by a slightly larger zone of inhibition when compared with the control specimen. The result proved that the MF agent does exhibit anti-microbial activity against *S. aureus.*

From Figure 2(a), it was showed that the control fabric (averaged 1.2cm ZOC) inhibited the growth of *S. aureus* because of the bleach residues on fabric surface which could enter the cell exhibiting anti-microbial activity [13]. Moreover, the anti-microbial activity of M1 specimen (averaged 1.5cm ZOC) was enhanced providing a slightly larger zone of inhibition when compared to control specimen. Table 1 shows that plasma treatment may provide anti-microbial activity, i.e. fabric specimen PM0, when compared with the control fabric. The hydrophilic nature of carbonyl groups present in the oxygen plasma pretreated fabric specimen also increases the anti-microbial activity after treatment with MF-MB (PM1) [15-17]. Therefore, PM1 specimen had an average of 1.6cm ZOC which was slightly higher than that of M1 specimen.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR was used to characterise the bonding present in the anti-microbial-treated cotton fabric in order to confirm the reactions presented in Figure 3. With regard to M1 specimen, it was observed that there were strong hydroxyl stretching bands at 3420-3250cm^{-1} [18] representing the presence of triclosan on the fabrics. However, the terminal hydroxyl group of triclosan molecule might react with cellulose. Hence, there was no new characteristics peak being formed as shown in Figure 3. On the other hand, Figure 4 (FTIR spectra of control and M1 specimen focused at 2000-1400cm^{-1}) shows two medium sharp bands at 1670 and 1510 cm^{-1} respectively which were due to the presence of benzene ring in aromatic compounds [18]. Therefore, it was confirmed that the MF agent applied was successfully bonded with cotton fabrics.

Figures 5 and 6 show the FTIR spectra of the MF-MB-treated fabric with or without plasma pre-treatment (M1 and PM1) at 4000-700cm^{-1} and 2000-1400cm^{-1} respectively. It was found that the characteristic bands related to the benzene rings at 1670 and 1510 cm^{-1} were also observed in the PM1 specimen as illustrated in Figure 6 [18]. In general, FTIR can be used for quantitative analysis because the strength of the absorption is proportional to the concentration. It was confirmed that the PM1 specimen contained more MF-MB chemical agents than that of the M1 specimen, i.e. PM1 had higher % absorption as shown in Figure 5.

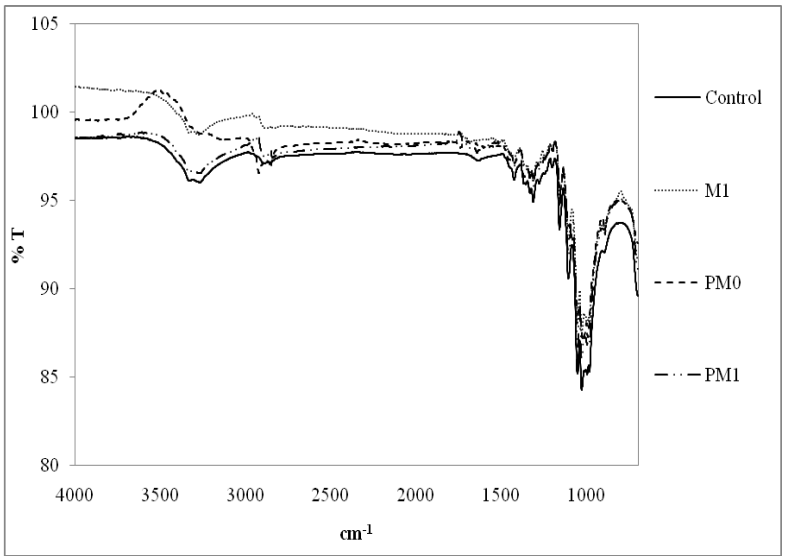

Figure 3. FTIR spectra of control, M1, PM0 and PM1

Figure 4. FTIR spectra of control and M1 at 1400-2000cm^{-1}

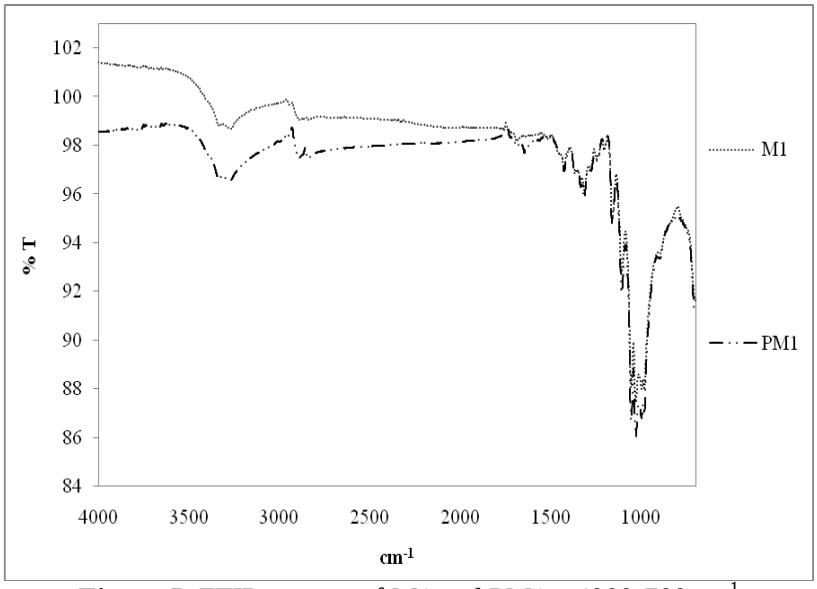

Figure 5. FTIR spectra of M1 and PM1at 4000-700cm^{-1}

Figure 6. FTIR spectra of M1 and PM1at 2000-1400cm^{-1}

4. Conclusion

In the present study, the control fabric slightly inhibited the growth of *S. aureus* because of the bleach residues left on fabric surface, while the anti-microbial activity of the MF-MB-treated specimen was enhanced as reflected by a slightly larger zone of inhibition. Moreover, the fabrics pre-treated with oxygen plasma only could further enhance the anti-microbial property of the fabric because the plasma gas containing reactive oxygen species which could enter the cell and eventually cause the death of cell. The hydrophilic nature of carbonyl groups present in the oxygen plasma pre-treated specimens also increased the anti-microbial activity when treating it with MF-MB.

FTIR was used for analysing the chemical composition of the fabrics. Two strong hydroxyl stretching bands at 3700-3600cm^{-1} and 3420-3250cm^{-1} respectively were observed in the MF-MB-treated specimen which was representing the presence of triclosan on the fabrics. Based on the FTIR results, it was noted that plasma pre-treated cotton fabric more MF-MB chemical agents than that of one without plasma treatment. Therefore, it could conclude that plasma pre-treatment could enhance the absorption of antimicrobial finishing agent by the cotton fabric and hence increased cotton antimicrobial ability.

Acknowledgements

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] Zhang F, Wu X L, Chen Y Y and Lin H 2009 *Fibers and Polymers*. **10**(4) 496.
[2] Chen C Y and Chiang C L 2008 *Materials Letters* **62**(21-22) 3607.
[3] Chen H L and Burns L D 2006 *Clothing and Textile Research Journal* **24**(3) 248.
[4] Gao Y and Cranston R 2008 *Textile Research Journal* **78**(1) 60.
[5] Daoud W A, Xin J H and Zhang Y H 2005 *Surface Science* **599** 69.
[6] Parthasarathi K and Borkar S P 2007 *Colourage* **54**(7) 43.
[7] Mahltig B, Haufe H and Böttcher H 2005 *Journal of Materials Chemistry* **15** 4385.

[8] Nakashima T, Sakagami Y, Ito H and Matsuo M 2001 *Textile Research Journal* **71**(8) 688
[9] Morones J R, Elechiguerra J L, Camacho A, Holt K, Kouri J B, Ramirez J T and Yacaman M J 2005 *Nanotechnology* **16**(10) 2346.
[10] Abo-Shosha M H, El-Hosamy M B, Hashem A M and El-Nagar A H 2007 *Journal of Industrial Textiles* **37**(1) 55.
[11] Blake D M, Maness P C, Huang Z, Wolfrum E J and Huang J 1999 *Separation and Purification Methods* **28**(1) 1.
[12] Page K, Palgrave R G, Parkin I P, Wilson M, Savinc S L P and Chadwick A V 2007 *Journal of Materials Chemistry* **17** 95.
[13] Fu G F, Vary P S and Lin C T 2005 *Journal of Physical Chemistry B* **109**(18) 8889.
[14] Rajpreet K V and Gita N R 2004 *Textile Research Journal* **74**(12) 1073.
[15] Radetic M, Llic V, Vodnik V, Dimitrijevic S, Jovancic P, Saponjic Z and Nedeljkovic J M 2008 *Polymers for Advanced Technologies* **19**(12) 1816.
[16] Vaideki K, Jayakumar S, Thilagavathi G and Rajendran R 2007 *Applied Surface Science* **253**(17) 7323.
[17] Chen C C, Chen J C and Yao W H 2010 *Textile Research Journal* **80**(8) 675
[18] Chalmers J M and Griffiths P R 2002 *Handbook of Vibrational Spectroscopy, **Vol. 4**,* (New York: Wiley).