PLASMA-BASED REGENERABLE ANTIMICROBIAL FINISHING FOR CELLULOSIC TEXTILE MATERIALS

ZHOU CHANGE

Ph.D

The Hong Kong Polytechnic University

2016

The Hong Kong Polytechnic University

Institute of Textiles and Clothing

Plasma-based Regenerable Antimicrobial Finishing for Cellulosic Textile Materials

Zhou Change

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

August, 2015

CERTIFICATE OF ORIGINALITY

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

_____

Zhou Change

ABSTRACT

Owing to the advance in hygroscopicity and permeability, cotton fabrics are considered as paramount textiles. Just because of the good hygroscopicity, cotton fabrics are attacked easily by microorganism. This drawback can be made up by antimicrobial finishing of cotton fabrics. The ideal antimicrobial materials should be regenerable and safe for human and environment. This study investigates the application of nitrogen plasma treatment in antimicrobial finishing processes for cotton fabrics to impart cotton fabrics with regenerable antimicrobial property.

In this research, nitrogen plasma treatment used independently to provide antimicrobial finishing for cotton fabrics was firstly studied. Then plasma treatment was combined with pad-dry-cure process of fabrics coated with chitosan and 5, 5 - dimethylhydantoin (DMH), separately. In all of these finishing processes, the fabric was chlorinated with sodium hypochlorite to impart antimicrobial properties and functions. The finishing processes were optimized by an orthogonal array testing strategy (OATS). The influences of parameters, e.g. discharge power of plasma, flow rate of nitrogen, moving speed of fabrics, concentration of finishing agent, curing temperature, concentration of sodium hypochlorite, and time of chlorination, in the antimicrobial finishing processes on the regenerable antimicrobial activity of cotton fabrics were studied. Ultraviolet-visible spectroscopy (UV-vis), Scanning electron microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were employed to characterize the properties of cotton fabric, including concentration of chlorine, morphological properties and functional groups on the cotton fabrics.

Tearing strength and weight loss of treated fabrics were also evaluated to study the interaction of plasma treatment with cotton fabrics. The antimicrobial results showed that cotton fabrics treated with plasma independently or finished with the combination processes of plasma and pad-dry-cure process had inhibition of bacteria, *Staphylococcus (S. aureus),* and the antimicrobial property was regenerable.

LIST OF PUBLICATIONS

Refereed Journal

(1) Zhou CE, Kan CW and Yuen CWM, Regenerable Antimicrobial Finishing of Cotton with Nitrogen Plasma Treatment, (preparing).

(2) Zhou CE, Kan CW and Yuen CWM, Optimizing plasma-assisted regenerable antibacterial performance of cotton fabric, (submitted).

(3) Zhou CE, Kan CW and Yuen CWM, Orthogonal analysis for rechargeable antimicrobial finishing of plasma pretreated cotton, Cellulose, (Accepted).

(4) Zhou CE, Kan CW and Yuen CWM, Plasma treatment applied in the pad-dry-cure process for making rechargeable antimicrobial cotton fabric that inhibits S. Aureus, Research Textile Journal, (Under Revision).

Conference papers

(1) Zhou CE, Kan CW and Yuen CWM, Plasma-based Regenerable DMH Antimicrobial Finishing for Cotton Fabric. Textile Summit and Research Student Conference, Leeds, UK. Apr. 23-27, 2014.

(2) Zhou CE and Kan CW, Review of Rechargeable Antimicrobial Function and Its Application. The 12th Asian Textile Conference, Shanghai, China. Oct. 23-26,2013.

ACKNOWLEDGMENTS

First of all, I would like to express my deepest appreciation to my chief supervisor Dr. Chi-wai Kan and co-supervisor Prof. Chun-wah Marcus Yuen for academic guidance, efficient instruction, constructive advice, valuable help and encouragement during the planning and development of my research.

All the faculty and staff in the ITC, HK PolyU, who have gave instruction in courses and helped in my study, are sincerely thanked.

Great thanks are also extended to Ms Joyce Yau and Dr James Tsoi in HKU, who gave me a lot of help on my research.

I also 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.

Finally, thanks must go to my families for their unlimited support, love and sacrifice.

CONTENTS

LIST OF ABBREVIATIONS

-OH	hydroxyl group
λ_{max}	wavelength at maximum absorption
A6M	after 6 months
ACHT	2-amino-4-chloro-6-hydroxy-s-triazine
ACN	ammonium cerium (IV) nitrate
ACTMIO	1-acryloyl-2,2,5,5-tetramethylimidazolidin-4-one
ADMH	3-allyl-5,5-dimethylhydantoin
Ag^+	silver ion
AN	acrylonitrile
APP	atmospheric pressure plasma
AW	after washing
AW+CH	chlorination after washing
B6M	before 6 months
BHI	Brain-Heart Infusion
BTCA	1,2,3,4- butanetetracarboxylic acid
BW	before washing
CC	cotton fabric coated with chitosan through pad-dry-cure process
CD	cotton fabric coated with DMH through pad-dry-cure process
CDDMH	chlorinated 3-dodecyl-5,5- dimethylhydantoin
CDMH	chlorinated 5,5- dimethylhydantoin
CDPC	cotton fabric coated with chitosan through pad-dry-plasma-cure

	process
CDPD	cotton fabric coated with DMH through pad-dry-plasma-cure process
CPC	cotton fabric coated with chitosan through plasma-pad-dry- cure process
CPD	cotton fabric coated with DMH through plasma-pad-dry-cure process
CTAB	cetylmethylammonium bromide
CTMIO	chlorinated 2,2,5,5-tetramethyl-imidozalidin-4-one
Cu^{2+}	copper ion
CWPC	cotton fabric coated with chitosan through pad-plasma-dry-cure process
CWPD	cotton fabric coated with DMH through pad- plasma-dry- cure process
DA	N-(1,1-dimethyl-3-oxobutyl) acrylamide
DCDMH	1, 3-dichloro-5, 5-dimethyl hydantoin
DI	deionized
DMDMH	dimethylol-5,5-dimethylhydantoin
DMH	5,5-dimethylhydantoin
FTIR-ATR	fourier transform infrared spectroscopy with attenuated total reflection mode
GH	3-glycidyl-5, 5-dimethylhydantoin
GH’s	3-glycidyl-5,5-dialkylhydantoins
HA	hydantoin acrylamide
HDI	1, 6-hexamethylene diisocyanate

HTCC	N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride
KI	potassium iodide
LPM	liter per minute
MIC	minimum inhibitory concentration
MMA	methyl methacrylate
MTMIO	3-methylol-2,2,5,5-tetramethylimidazolidin-4-one
N-Cl	halamine bond
NMAHTCC	O-acrylamidomethyl-N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride
OATS	orthogonal array testing strategy
PET	polyester
PHMB	polyhexamethylene biguanide
Poly-CTD	poly(1,3,5-trichloro-6-methyl-6-(4'-vinylphenyl)-1,3,5-triazine-2,4-dione)
PU	polyurethane
QACs	Quaternary ammonium compounds
QAS	quaternary ammonium salts
RSGP	Rapid Step-Growth Polymerization
SEM	Scanning Electron Microscope
VAC	vinyl acetate
VBDMH	3-(4’-vinylbenzyl)-5,5-dimethylhydantoin
VDAT	2-vinyl-4, 6-diamino-1, 3, 5-triazine
Zn^{2+}	zinc ion

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 INTRODUCTION

1.1 Background of study

With economic growth and improvement in people's lives, compared with immediate improvement of human living, more and more people are beginning to pay more attention to creating more comfortable and safer living conditions, especially in the context of health and hygiene (Sparavigna, 2008). Therefore, the growing global concern of contact transmissions of infectious diseases and personal protection has greatly stimulated research activities on biocides and healthcare textiles in several areas, particularly in medical, health care and apparel products (Lymberis & Olsson, 2003; Rigby, Anand, & Horrocks, 1997; Virk, Ramaswamy, Bourham, & Bures, 2004). Antibacterial finishing for textiles, especially those made from natural fibers, is becoming increasing necessary as demand for protective, decorative and technical textiles is growing. Cotton, natural cellulose fiber consisting of β-1, 4-D-glucose, has numerous –OH groups and a small number of carboxylic acid groups (Abidi, Hequet, & Cabrales, 2010). Therefore, cotton fabrics have good hygroscopicity which makes it comfortable for dressing and popular with the public. However, because of its excellent moisture absorption ability and large surface area, moist cotton easily gets attacked by bacteria such as pathogenic bacteria, odor-generating bacteria, molds, fungi and viruses, which can lead to two problems: firstly, the fiber may be degraded, discolored and smelly and decomposed body secretions have a characteristic odor; secondly, some germs may result in pruritus, inflammation and disease for humans (Gouda & Ibrahim, 2008; Kenawy & Abdel‐Fattah, 2002; Kim, Nam, Choi, & Jang,

2003; Lim & Hudson, 2004; Neeta et al., 2007; Thanh & Phong, 2009). Therefore, antimicrobial finishing for cotton is an important subject for the development of healthcare textiles.

Researchers have focused on antimicrobial polymers and textiles in the past few decades due to the growing concern about contact transmissions of infectious diseases and personal protection from undesirable effects. A number of chemicals are used to impart antibacterial properties to textiles, such as phenols, organic and inorganic acid sand salts, aromatic diamidines, biguanides, aldehydes, heavy metal derivatives, alcohols, anilides and miscellaneous preservatives. Antibacterial property of textile goods finished with these chemicals, however, is not regenerable (Simoncic & Tomsic, 2010). Durable and regenerable antimicrobial functions on textile materials have been developed based on halamine chemistry and the structural properties of chemicals by incorporating halamine structures (Huang & Sun, 2003; Liu & Sun, 2006). These biocidal polymers and textiles satisfy the requirement of the optimum antimicrobial effect and environmental friendliness. N-halamine is a regenerable and refreshable antibacterial agent which can kill a wide spectrum of micro-organisms fast, without resistance from micro-organisms and much environmental concern (Y. Sun & Sun, 2001a; Y. Sun & Sun, 2001b; Y. Sun & Sun, 2001c; Y. Sun & Sun, 2004). This kind of textile materials provides effective biocidal ways for reusable clothing which enhance a level of antimicrobial protection.

Numerous methods for incorporating antimicrobial functions into textile materials have been developed elsewhere (Badrossamay & Sun, 2008; Badrossamay & Sun,

2009; Ren et al., 2008). Despite the variety of systems reported in the literature, most of the finishing methods are not environmentally friendly enough and those methods change the intrinsic characteristics of fabrics. Functional finishing for textiles with plasma is an advanced method for textile industry to alleviate the pressure of cleaner production. Low pressure plasma (LPP) used for surface modification of polymer substrates is a well-developed technology for the alteration of surface chemistry and physical property, such as hydrophilicity, reactivity, and morphology. Plasma surface modification can introduce various functional groups onto a polymer surface, which achieve enhanced wettabilities, facilitated graft polymerization and improved adhesion with other materials and so on (Narushima et al., 2007; Noeske, Degenhardt, Strudthoff, & Lommatzsch, 2004). Compared with conventional wet surface modification methods for polymer substrates, the processes with plasma are cost efficient, environmentally friendly, uniform, shorter treatment time and higher reactivity, and applicable to many materials and can keep the bulk properties of the treated substances (Abidi & Hequet, 2004; Abidi & Hequet, 2005). The popularities of cotton fabric and plasma treatments in the textile industry make the antibacterial finishing processes with plasma for cotton more attractive. Therefore, regenerable antimicrobial finishing and cleaner production can be combined with plasma, which should be a part of the new product development strategy.

1.2 Objectives

With the development of commodity products, the textile industry competes for the consumer's attention on the basis of product quality, price and defining attribute.

History has also shown that consumer will pay more for clothing with a defining and desirable attribute. The project is aimed to develop an atmospheric pressure plasma (APP) treatment for changing the concept of textile wet processing and enhancing competitiveness of textiles on the aspect of antimicrobial finishing. The followings are the objectives of this study.

(1) To explore the possibility of application of plasma treatment in antibacterial finishing for cotton fabric and make the finishing process environmentally friendly.

(2) To implement the APP treatment on cotton fabrics under different processing conditions, e.g. gas flow rate, plasma discharge power and fabric speed for studying the effects of these process parameters on the surface properties of cotton fabrics.

(3) To evaluate the physical and topographical properties, chemical and antibacterial properties of the cotton fabrics with respect to different process parameters for developing an APP treatment optimization model for achieving the desired antibacterial effect of cotton fabrics.

(4) Combine plasma treatment with traditional finishing process to improve antibacterial finishing processes and antibacterial property of cotton fabrics with antibacterial finishing.

(5) To evaluate the physical and topographical properties, chemical and antibacterial properties of the cotton fabrics after antibacterial finishing and optimize the finishing process.

1.3 Scope of study

The scope of this study is the application of plasma treatment in antibacterial finishing process for cotton fabric to improve antibacterial activity of cotton fabric and alleviate environmental pollution of antibacterial finishing. The present work includes:

(1) The influences of different condition parameters in plasma treatment process, such as flow rate of gases, discharge power, fabric speed, and concentration of bleaching solution and time of chlorination during chlorination.

(2) The effects of different condition parameters for plasma-assist chitosan antimicrobial finishing process, such as concentration of chitosan, curing temperature, and concentration of bleaching solution and time of chlorination during chlorination.

(3) The effects of different condition parameters for plasma-assist 5, 5-dimethylhydantoin (DMH) antimicrobial finishing process, such as concentration of DMH, curing temperature, and concentration of bleaching solution and time of chlorination during chlorination.

(4) The comparison of antimicrobial activity of plasma-based antimicrobial finishing cotton fabric with plasma treatment, plasma-assist chitosan-based antimicrobial finishing cotton fabric and plasma-assist DMH-based antimicrobial finishing cotton fabric.

1.4 Research Methodology

The following research methodologies are adapted according with the objectives of this study.

(1) A comprehensive literature review was conducted to consolidate the background knowledge concerning the recent development in textile antimicrobial finishing and the application mechanism of antimicrobial agents. Application of plasma treatment in textiles was also reviewed in order to enhance antimicrobial activity of cotton fabric with its assistance.

(2) The preliminary trials on antimicrobial agents with different structure were conducted to select the suitable antimicrobial agents for the objective of this study. The reactions occurred in the finishing processes were characterized by fourier transform infrared spectroscopy (FTIR). The feasibility of plasma-assist antimicrobial finishing process to improve the performance of antimicrobial cotton fabrics was studied using different evaluation methods.

(3) Variation of condition parameters in finishing process might result in different textile performance. Condition parameters such as flow rate of gases, discharge power of plasma, fabric speed, concentration of finishing bath, time of curing, and concentration of bleaching solution and time of chlorination during chlorination were studied with orthogonal analysis to obtain optimal condition parameters and improve the effect of antimicrobial finishing.

(4) The performance of antimicrobial fishing cotton fabrics was evaluated with a

series of authoritative evaluation methods to verify the effectiveness of the antimicrobial finishing process. And the mechanism of the functional finishing for cotton fabrics was also studied with instrumental methods such as scanning electron microscope (SEM) and FTIR.

1.5 Significance of Study

(1) Regenerable antimicrobial textiles provide an important role in the development of innovation functional finishing. It extends the working life of antimicrobial textiles.

(2) Textile industry is always a high-polluting industry because of the heavy use of chemicals. Plasma treatment applied in regenerable antimicrobial finishing is an environmentally friendly method to reduce the use of textile auxiliary in the finishing processes.

(3) Chemicals with N-halamine structure have been applied to numerous materials to provide an antimicrobial property by traditional methods. This study combine the regenerable antimicrobial agents with plasma treatment is an alternative to improve the antimicrobial activity of antimicrobial textiles.

1.6 Chapter summary

Based on the objectives, the thesis consists of seven chapters.

Chapter 1 outlines the background, objectives, scope, methodology and significance of this study.

Chapter 2 is the literature review that presents an introduction of plasma treatment and the development of antimicrobial finishing. In this Chapter, application of plasma treatment on surface modification, parameters affecting the finishing effect in plasma treatment, antimicrobial mechanism of antimicrobial finishing, antimicrobial agents, methods for antimicrobial finishing and evaluation of antimicrobial property will be summarized.

Chapter 3 covers the details of antimicrobial finishing experiments. The materials and apparatus used in experiments are provided. Detailed experimental procedures including antimicrobial finishing and evaluation of finished fabrics are described.

Chapter 4 focuses on optimizing the condition parameters of plasma-based antimicrobial finishing for cotton fabric in terms of flow rate of gases, discharge power of plasma generator, fabric speed, and concentration of bleaching solution and time for chlorination during chlorination using orthogonal analysis technique. The variations of physical and chemical properties of cotton fabrics after plasma treatment are evaluated.

Chapters 5 and 6 study the optimal chitosan regenerable antimicrobial finishing and DMH regenerable antimicrobial finishing conducted on cotton fabrics with assistance of optimal plasma-based antimicrobial finishing process. The condition parameters such as concentration of finishing bath, time for curing, and time for chlorination and concentration of bleaching solution during chlorination are discussed. The physical and chemical properties of the finished cotton fabrics are investigated.

Chapter 7 summarizes the present thesis and proposes recommendations for future study.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

2.1.1 Introduction of plasma treatment

Use of plasma technology for surface modification has drawn much attention in extant research (Abidi & Hequet, 2004; Abidi & Hequet, 2005; Gorjanc, Bukošek, Gorenšek, & Vesel, 2010; Sun & Stylios, 2006; Zhang et al., 2003). Plasma was first discovered by Sir William Crooks, an English physicist, and identified it as the forth state of mater in 1879. It was named as plasma by Irving Langmuir, an American chemist and physicist, in 1927. Since their introduction in 1960s, the main application of plasma is in the micro-electronic industries and exploited in material science (Luo & Van Ooij, 2002; Vohrer, Müller, & Oehr, 1998). With the development of plasma, research work regarding plasma treatments applied in textile field has been going on since the early 1980 in many laboratories across the world (Luo & Van Ooij, 2002; Shishoo, 2007).

Plasma treatment is divided into thermal plasma and cold plasma according to the relative temperatures of the electrons (Luo & Van Ooij, 2002). Because of thermal stability of textile materials, thermal plasma is not suitable for the modification of textile materials. Cold plasmas are also classified into low-pressure plasmas and atmospheric pressure plasmas (APP). Although low-pressure plasma is a highly mature technology in microelectronics industry, its vacuum vessel goes against continuous production in textile industry (Shishoo, 2007). Therefore, APP is compatible with various treatments in textile industry.

Plasma is partly ionized gas consists of neutral and charged particles: positive ions and negative electrons or ions, neutrons, free radicals, meta-stable excited species and molecular and polymeric fragments (Hegemann, Brunner, & Oehr, 2003; Kuo, Chang, Hung, Chen, & Inagaki, 2010; Virk et al., 2004). These active particles impinge on the material surface to modify the properties of materials. The free radicals react with oxygen and water to form oxygenated surface and these radicals also polymerize with other chemicals to introduce various functional groups onto the material surface (Abidi & Hequet, 2004; Inagaki, 1984; Inagaki, 2000; Kuo et al., 2010; Narushima et al., 2007; Poll, Schladitz, & Schreiter, 2001; Virk et al., 2004; Zhou & Kan, 2014b). The final treatment effect largely depends on the nature of gases used (Kan, Chan, Yuen, & Miao, 1998; T. Yasuda, Gazicki, & Yasuda, 1984). Plasmas used for textile modification are generic surface processes including surface activation by bond breaking to create reactive sites, grafting of chemical moieties and functional groups, etching, cleaning and deposition of conformal coatings (Sun et al., 2010; Virk et al., 2004). New functional groups such as –OH, –C=O, –COOH formed on textile materials during plasma treatment improve wettability and graft polymerization of textile materials (Shahidi et al., 2010; Silva et al., 2008; Virk et al., 2004). The effects of plasma treatment, surface cleaning, etching, cross-linking of near-surface molecules and modification of surface-chemical structure enhance the adhesion of textile materials with in finishing (McCord et al., 2002; Virk et al., 2004). All of plasma treatment processes provide new and desirable properties to textiles without affecting their bulk properties, because the chemical and physical transformation of textile

materials resulted from plasma treatment occur in the uppermost atomic surface layers (< 100 Å) (Chen et al., 2010; Kuo et al., 2010; Virk et al., 2004). Plasma treatment as a uniquely effective surface modification method is not concerned with any water. This provides an environmentally friendly surface modification method for textile industry.

2.1.2 Antibacterial finishing of cotton fabric

Cellulose is a homopolymer consisting of β-1, 4-D-glucose as shown in Figure 2.1 (Ren et al., 2008; Satyamurthy, Jain, Balasubramanya, & Vigneshwaran, 2011). The repeat unit is glucose which is linked by β-1, 4- glycoside bonds in cellulosic molecular. Primary hydroxyl groups and secondary hydroxyl groups in cellulosic molecule have same characteristic as them are in alcohol form. Glucose in the right of cellulosic molecular has a latent aldehyde group shown in red circle in Figure 2.1 makes cellulose reducible, but the amount of aldehyde groups is small because every cellulosic molecular has one latent aldehyde group. Therefore, the reducibility of cellulose is not significant. However, it becomes obvious with the decrease of molecular weight of cellulose. Numerous hydroxyl (–OH) groups and a small number of carboxylic acid groups in cellulosic molecular result in porous hydrophilic structure which makes textiles made from cellulosic fibers breathable, absorbent and comfortable to wear (Ren et al., 2008). Since the structure is such that it retains water and oxygen easily, it provides a suitable environment for microorganisms to grow. This makes cellulosic textiles susceptible to bacteria (Kenawy & Abdel‐attah, 2002; Neeta et al., 2007; Shahidi, Ghoranneviss, Moazzenchi, Rashidi, & Mirjalili, 2007;

Thanh & Phong, 2009; Zhou & Kan, 2014b; Zhou & Kan, 2015). Cotton is natural cellulosic fiber, which contains the highest percentage of cellulose among various sources in nature (Satyamurthy et al., 2011). Therefore it is necessary to impart antibacterial property to cotton fabrics, particularly in view of the growing emphasis upon health and hygiene nowadays.

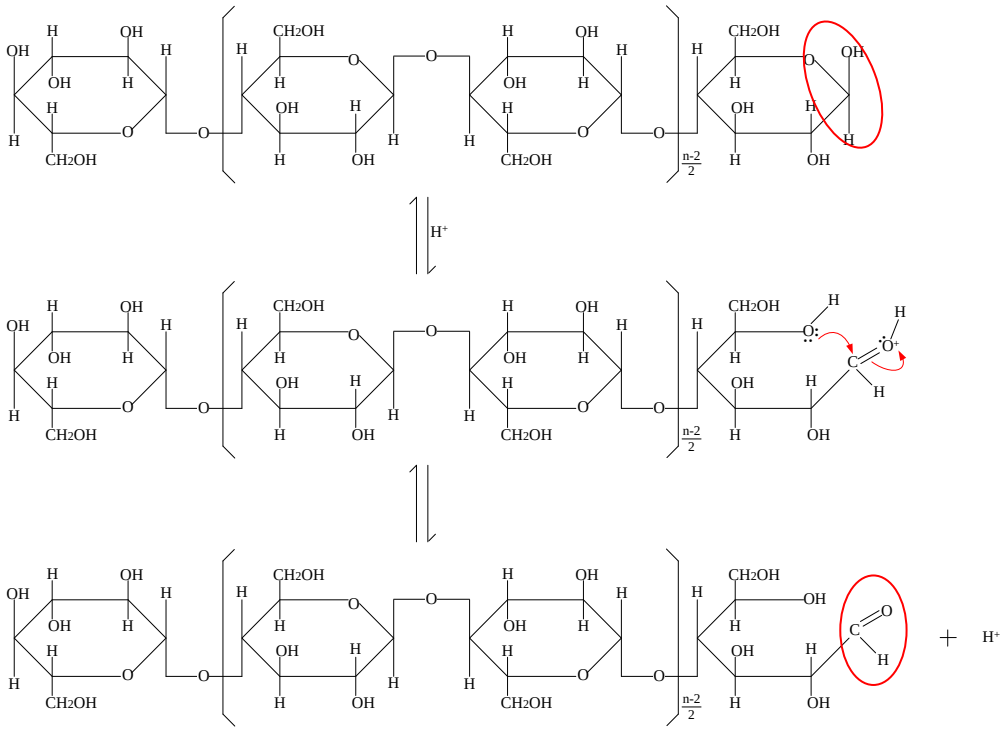

Figure 2.1 Structural formula of cellulose and reaction of cellulose in acids

For safety and health properties, antibacterial cotton fabric is grafted or coated with bactericides (chitosan, quaternary ammonium salts, chlorine, chloramines, etc.) (Chen et al., 2011; Lim & Hudson, 2004; Liu & Sun, 2006; Son, Kim, Ravikumar, & Lee, 2006; Sun, Xu, Bickett, & Williams, 2001; Ye, Xin, Li, Lee, & Kwong, 2006), loading heavy metal ions (silver, copper, zinc) (Hebeish et al., 2011; Jia, Mei, Cheng, Zhou, & Zhang, 2012; Lee, Yeo, & Jeong, 2003; Perelshtein et al., 2009). However, the uptake

and durability are difficult to manage because they leach from the textiles easily (Chen et al., 2011). These chemicals are always loaded on cotton fabrics with the help of other chemicals, including cross-linking agents, initiators and catalysts, etc. Incompatibility of antibacterial agents with other chemicals and toxicity of chemicals to environment and humans are also important weaknesses that need to be improved (Chen et al., 2011). The ideal antimicrobial textiles should be processed these features: (I) rapid and powerful inactivation of a wide spectrum of microorganisms including bacteria and fungi; (II) non-selective and non-mutable to pathogens; (III) non-toxic to human body and environment at concentration used-safe to handle and use; (IV) durable to usage, repeated washes and prolonged storage; (V) compatible with other textile chemical processes (VI) capable of being recharged or regenerated in laundering; (VII) colorless and odorless; (VIII) no unfavorable effect on handle and other physical properties of textiles; (IX) reasonable cost and effective at low concentration (Gao & Cranston, 2008; Qian & Sun, 2004; Shahidi & Wiener, 2012; Sun & Worley, 2005).

2.2 Application of plasma treatment on surface modification

2.2.1 Principle of plasma treatment

Plasma technology is based on a physical principle, that is, matter changes its state when energy is supplied to it. With the increase of energy, the state of matter changes from solid to liquid to gaseous, and then it turns into plasma. The generation of plasma is shown in Figure 2.2.

Accordingly, plasma is gases which can be dissociated into electrons, ions, photons and metastable species by electrical energy applied from the plasma reactor. The free radicals and other metastable particles generated in the plasma collide with the material surface and rupture the covalent bonds, creating free radicals on the substrate surface. These free radicals can form new groups on matrix after rearrangement or react with other chemicals to introduce functional groups onto the material surface (Abidi & Hequet, 2004; Inagaki, 1984; Inagaki, 2000; Kuo et al., 2010; Narushima et al., 2007; Poll et al., 2001; Virk et al., 2004; Zhou & Kan, 2014b). The formation of new material surface after plasma treatment possesses new functional groups which improve the properties of materials and are convenient for the further functional finishing.

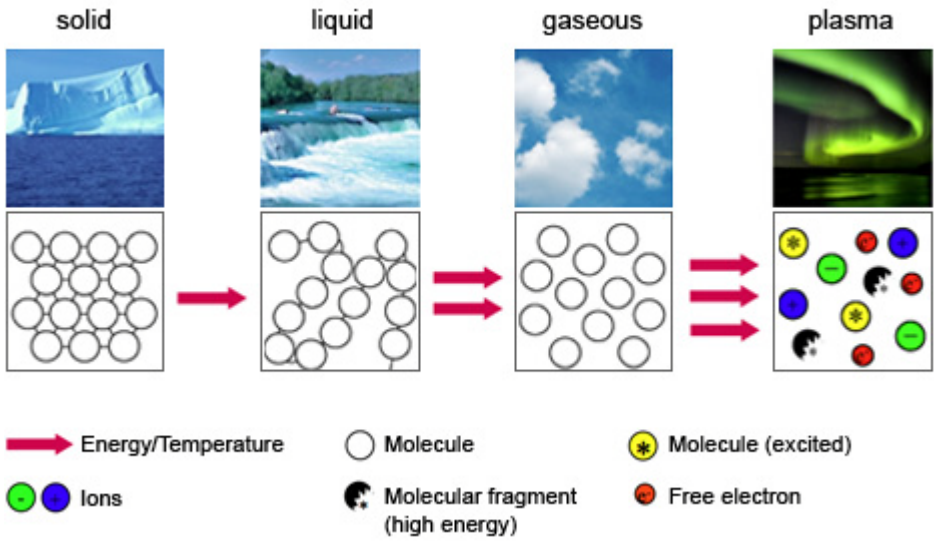

Figure 2.2 Generation of plasma (Anonymity, 2013)

2.2.2 Plasma-textile surface interactions

Although it is intuitively assumed that plasma treatments enable different kinds of

functional properties without affecting the bulk properties of substrate. However, the plasma treatment process is an interactive process of gas-phase particles with the top surface of materials, and the nature and the extent of the interaction are quite important factors of plasma treatment (Yasuda, 2005). To explore the potential applications of plasma treatment in textiles, it is necessary to study the interactions between the plasma particles and the textiles. The final treatment effect of plasma on material surface depends on the interactions between the plasma particles and the textile substrate. When these exited and energetic particles impinged the surface of textiles, they induce various reactions. Normally, these reactions bring out two types of interactions between plasma particles and material surface shown in Figure 2.3. One is chain scission on the surface resulting in surface cleaning, etching or activation. Another one is initiation of polymerization or co-polymerization on material surface forming highly crosslinked structures (Kale & Desai, 2011; Morita & Park, 1992). These interactions result in the chemistry variations of textile surfaces, which enable their improvements of adhesion, biocompatibility, hydrophilicity, dyeability, etc.

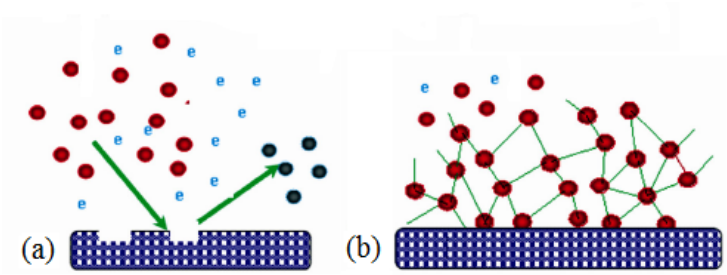

Figure 2.3 Interaction of plasma with material surface: (a) Plasma Ablation, (b) Plasma deposition (Kale & Desai, 2011)

2.2.3 Factors affected plasma treatment

The final treatment effect of plasma on substrates can be affected by the factors involved in plasma treatment processes. The first and direct factor affected final treatment effect is the nature of gases used for plasma treatment (Kan et al., 1998; Yasuda et al., 1984). According to the interactions of plasma with material surface, the gases used for plasma treatment can be classified into two types. The first type is non-polymerizing gases including simple monoatomic and diatomic gases, i.e. helium, argon, oxygen, nitrogen, carbon dioxide and air. The second type is polymerizing gases which are mainly organic molecules like fluorocarbons, hydrocarbons and silicone containing monomers. Non-polymerizing gases can be divided into two groups: inert gases and reactive gases. Inert gases, such as helium or argon, are not involved in chemical reaction on the surface of textiles directly but cleaning and etching by chain scissions, whereas reactive gases like oxygen or nitrogen can introduce oxygen or nitrogen containing groups. Inert gases can also be carrier gas for reactive gases and polymerizing gases except be plasma for etching and cleaning. Helium is preferred gas over the others because of its high energy metastable state and excellent heat conductivity (Kale & Desai, 2011; Shishoo, 2007). Diversity of plasma treatment effect leads to its various applications in textile industry. In summary, the nature of gases used for plasma modification plays a critical role as it can incorporate different kinds of functional groups on the surface of textiles.

Besides nature of gas, discharge power, flow rate of gases, sample distance and exposure time are also important factors which affect the effect of plasma treatment.

Normally, plasma applied with higher discharge power carries more kinetic energy resulting in strong intensity of plasma action (Švorčík et al., 2006; Yasuda et al., 1984). However, in order to avoid over-heating, the discharge power should be controlled in a range (Wong, Tao, Yuen, & Yeung, 1999). Influence of flow rate of gases on the effectiveness of plasma treatment is complicated. When the flow rate is not high, the effectiveness of plasma treatment strengthens with the increase of flow rate of gases. While the flow rate is high, the effectiveness of plasma treatment weakens with the increase of flow rate of gases. The reason is that when the flow rate is high, the density of plasma particles increases and they have more opportunities to collide with each others, and the kinetic energy will be transferred to the internal energy of particles because of inelastic collisions (Shishoo, 2007; Yasuda et al., 1984), weakening the effectiveness of plasma treatment. Sample distance should be in 2-5mm. The first reason is that when sample distance is too small, the flow of the gas from the nozzle is almost blocked by fabric, and the gases could be only be bounced off the surface and flew out in a direction more parallel to the fabric surface. This greatly reduced the effectiveness of the plasma treatment. Another reason is that when the distance is too large, the velocity and the activity of the active species in the plasma jet greatly decrease when they reach the top side of the fabric and thus are not effective (Yasuda et al., 1984). Longer exposure time leads to more severe modification of material surface, because a longer exposure time provided more opportunity for the plasma particles to penetrate into the interior region of material. However, too long exposure time also adversely affects the properties of material. Therefore, exposure time should be

controlled carefully (Yasuda et al., 1984).

2.2.4 Classifications of modification methods of plasma treatment

Based on the interactions between plasma particles and textiles, plasma is used to modification of material by two ways, that is, ablation and deposition processes. These plasma treatment processes can be independently applied to textile finishing imparting textiles functional properties. Meanwhile, plasma treatment also can combine with traditional wet chemical finishing processes (e.g. pad-dry-cure process) to enhance treatment effect (Chen, Chen, & Yao, 2009; Ilic et al., 2010; Yen, Chen, Hong, & Chen, 2006).

2.2.4.1 Plasma ablation

Plasma ablation is used to modify surface of fibers. Ablation of materials by plasma treatment can be achieved by two principal processes physical modification and chemical modification. The physical modification is the surface roughening of the fiber through the sputtering effect, enlarging contact area, voids and spaces (Luo & Van Ooij, 2002; Tourrette et al., 2009; van Ooij, Luo, & Datta, 1999). Meanwhile, it enables a complete cleaning of textiles from manufacturing residuals (oil, dust, oxides, biological and chemical agents) (Tendero, Tixier, Tristant, Desmaison, & Leprince, 2006). The chemical modification involves the chemical reaction of impinging species with dislodging element, increasing the concentration of functional groups on the fiber surface (van Ooij et al., 1999; Wong et al., 1999). Both physical and chemical modifications are proceeding by the etching effect of active particles in plasma,

decomposing the fibers' surface partly. Energetic particles can cut the molecular chain and initiate the crosslinking reaction on the surface of fibers. These kinds of plasma activation and etching processes are carried out with non-polymerizing gases. Inert gas plasma provides high energy for physical modification of material surface, while reactive gas plasma not only plays an important role on physical modification but introduces chemical groups on the surface of fibers, such as oxygen containing groups and nitrogen containing groups. Energetic particles in plasma clean the surface of fibers, change the surface roughness and improve the surface performance including hydrophilicity, shrink resistance, biocompatibility, chromaticity, and affinity between dyestuffs and fibers (Belin, 1976; Gregorski & Pavlath, 1980; Hesse, Thomas, & Höcker, 1995; Inagaki, 2000; Kan et al., 1998; Kral et al., 2007; Morent, De Geyter, Leys, Gengembre, & Payen, 2007; Narushima et al., 2007; Shishoo, 2007; Sun & Stylios, 2004; Wei, Liu, Hou, & Huang, 2007; Wong et al., 1999).

2.2.4.2 Plasma deposition

Deposition can be controlled to achieve new functionalities in the nanometer through plasma metallization, plasma polymerization and plasma co-polymerisation while the intrinsic bulk properties remain unchanged (Shishoo, 2007; Tendero et al., 2006).

(1) Plasma metallization

Plasma metallization is actually a sputter-based process. Sputtering is initiated by the impact of energetic particles on a target material, that is, metal. The incident particles collide with the surface of target material through a multiatom kinetic collision process,

and atoms near the surface can be dislodged with enough energy to overcome the surface binding energy and emitted from target material. These atoms are known as sputtered atoms, and they can deposit on some other surface. This is plasma metallization process shown in Figure 2.4. In general, the energetic particles used for the sputtering of metals is inert gas plasma such as argon, while reactive sputtering, metal oxides or nitrides, is motivated with an addition of reactive gases yield such as oxygen, nitrogen, etc. The energy of the incident particles can be enhanced by electrical and magnetic fields to avoid collisions. Thus, the plasma metallization can be obtained using magnetron sputtering to transfer metal to textiles (Hegemann, Amberg, Ritter, & Heuberger, 2009; Shishoo, 2007). Numerous kinds of textiles have been finished with various metals through plasma polymerization process (Chadeau, Oulahal, Dubost, Favergeon, & Degraeve, 2010; Crowther & Badyal, 1998; Hossain, Hegemann, Fortunato, Herrmann, & Heuberger, 2007; Kiwi & Pulgarin, 2010; Koprowska, Ziaja, & Janukiewicz, 2008). Shahidi et al. deposited copper on cotton fabrics using plasma polymerization process achieved the antimicrobial textiles with good antimicrobial activity and wash fastness without any chemical and wet process (Shahidi et al., 2007). Hegemann et al. gained uniform, nanoscaled Ag coated fibers through plasma polymerization used magnetron sputtering in a continuous process, which maintains the textile character of the fibre, yet allows a sufficient electrical conductivity and shows higher wash fastness (Hegemann et al., 2009). Ziaja et al. obtained metallization of polypropylene fabric with good adhesion by plasma polymerization using magnetron sputtering process (Ziaja, Koprowska, &

Janukiewicz, 2008). Plasma metallization is an alternative approach to produce textiles with conductive coat, especially for heat-sensitive, three-dimensional substrates. This method eliminates wastage of the metal precursor greatly during application, especially for precious metals, silver or gold etc. (Crowther & Badyal, 1998; Koprowska et al., 2008).

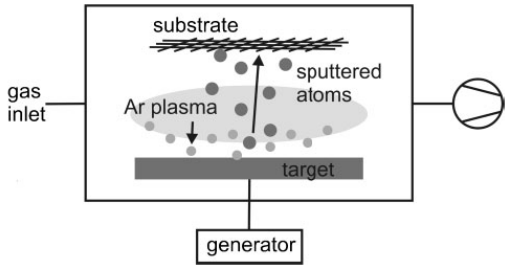

Figure 2.4 Example of plasma metallization process (Hegemann et al., 2009)

(2) Plasma polymerization

Plasma polymerization is known as a process that converts monomers into plasma particles and recombines them at radical sites into film at the surface of substrates. It, radical-dominated plasma chemical vapor deposition process, enables the deposition of thin coatings forming amorphous, more or less cross linked structures on all kinds of substrates using electrical monomer discharges. It is performed using different kinds of plasma polymerizing gases including organic, organosilicone, organo-metallic or hetero-atomic organic vapors (Hegemann, 2006; Sparavigna, 2008; Vohrer et al., 1998). The mechanism of plasma polymerization is different from traditional polymerization, because some monomers might not be activated by traditional ways. The fundamental growth mechanism is known as Rapid Step-Growth Polymerization (RSGP) illustrated with the concept of chemical quasi-equilibrium in

Figure 2.5, which enables a macroscopic approach to plasma polymerization (Hegemann, Hossain, Körner, & Balazs, 2007; Rutscher & Wagner, 1993). It is supposed that reactive gases or monomers enter an active zone (bulk plasma and plasma/sheath boundary region), where they are activated by hot discharge electrons and form into reactive particles including radicals, excited species, ions etc., and then these particles flow into a passive zone (plasma sheath and surface growth region) yielding recombination and stable products, such as deposition on substrates (Hegemann et al., 2007; Rutscher & Wagner, 1993). According to Figure 2.5, the recombination of reactive particles and the reactivation of reaction products determine the plasma polymerization. Cycle 1 is the reactions of reactive particles with a single reactive site and cycle 2 is based on divalent reactive particles. Cross-cycle reactions from 2 to 1 can proceed. Moreover, the surface takes part in plasma polymerization by radical sites, third-body reactions, and etching processes that lead to ablation and re-deposition (Hegemann, 2006; Hegemann et al., 2007; Rutscher & Wagner, 1993).

Relying on the macroscopic approach, plasma polymerization can be described by the composite parameter power input per gas flow *W/F*, which represents the energy invested per particle within the active plasma zone. Thus, the mass deposition rate R_m can be derived by the following equation:

$$\frac{R_m}{F} = G\exp\left(-\frac{E_a}{W/F}\right) \quad \text{Equation 2.1}$$

Where *G* is reactor depending geometrical factor; *W* is the power input; *F* is the gas flow; E_a is the monomer-dependent activation energy (Hegemann, 2006; Shishoo,

2007).

The equation by variation of *W/F* can be handled with Arrhenius-type plot to obtain a straight line, where E_a is slope corresponds, proving the validity of this approach. Deviations from this straight line might be found at low and at high energies because of oligomers taking part in film growth and energetic particle interactions, respectively (Hegemann, 2006; Shishoo, 2007).

Generally speaking, plasma polymerization does not affect even enhances the mechanical properties of fibers and fabrics, whereas it always adversely affect the wettability of fibers, because of the dense cross-linked chain structures of plasma-polymerized polymers with poor wettability or large water contact angle normally (Luo & Van Ooij, 2002).

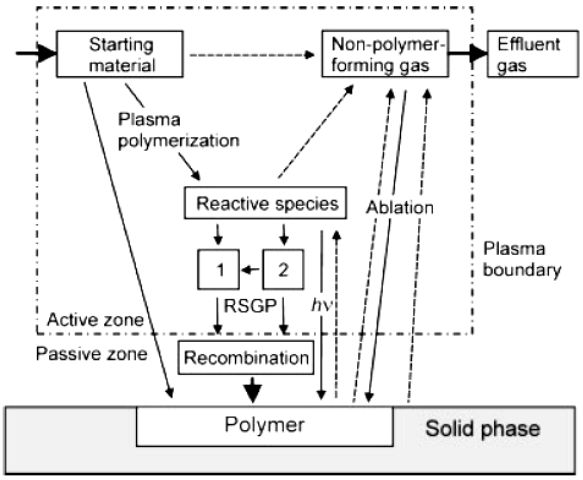

Figure 2.5 Schematic diagram of plasma polymerization processes (Hegemann et al., 2007)

(3) Plasma co-polymerization

The difference between plasma polymerization and plasma co-polymerization is that

plasma polymerization uses the vapor of one monomer to form the feed gas, whereas plasma co-polymerization uses a mixture of the vapors of more than one monomer, usually two. Plasma co-polymerization provides an exciting opportunity to produce coatings with mixtures of functional particles which are different to achieve from single monomer systems (Beck et al., 2005). The variation of the proportion of monomers in the feed gas can increase the variety of plasma polymers (Beck, Jones, & Short, 1996). And the additional process parameter is important to control the chemical and physical properties of plasma polymers. In plasma co-polymerization, a second monomer is co-polymerised alongside the monomer containing the functional group of interest. That is to say, plasma co-polymerization is obtained by adding additional gases in plasma polymerization process, which also can be investigated with Equation 2.1 (Hegemann, 2006). Actually, plasma-co-polymerization can be used successfully with a wide range of precursors including not only non-polymerizing gases and polymerizing gases but metals (Beck et al., 1996; Beck et al., 2005; Daw et al., 1998; Shishoo, 2007). When the second monomer is metal, the plasma co-polymerization can be described as a mixed process including plasma deposition and plasma polymerization (Shishoo, 2007). With the development of plasma finishing process, metals, such as silver, can be coated onto polymers to form metal nano-clusters/plasma polymers which are possible to allow for an *in situ* immobilization of nano-particles during plasma deposition. This provides a one-step coating process that eliminates the necessity of direct handling of nano-particles (Balazs et al., 2005; Favia et al., 2000; Shishoo, 2007).

2.2.5 Advantages of plasma treatment

The dry and environmentally friendly plasma technology aims as replacing wet-chemical process steps and adding new values to textile products (Hegemann, 2006). Plasma treatments almost can be applied to all textiles without altering their key characteristic with low quantities needed of monomers and energy (Buyle, 2009; 'Massimo Perucca', 2006). The reactive particles of plasma produced from ionization, fragmentation and excitation processes are with high enough energy to dissociate various chemical bonds leading to a significant number of simultaneous recombination mechanisms. It is benefit in semiconductor physics in producing pore-free, uniform thin films with superior physical, chemical, electrical and mechanical properties (Sparavigna, 2008). This opens up new possibilities for polymer industrial applications. The plasma treatment processes also avoid higher water consumption in wet chemical process. This is helpful for environmental protection. Meanwhile, it has an important effect on cost, because it needs not to clean the polluted water coming from the production process (Massimo Perucca, 2006). Therefore, plasma technology is becoming more attractive for surface modifications of textile substrates (Abidi & Hequet, 2004; Abidi & Hequet, 2005) .

2.3 Antibacterial finishing of cotton fabrics

2.3.1 Mechanism of antimicrobial action

A quintessential living microbe has an outermost cell wall which is mainly composed of polysaccharides (Gao & Cranston, 2008). The wall with rigidity and strength offers

cells integrity of cellular components and protects the cell against mechanical stress from the extracellular environment. Actually, the cell wall is a semi-permeable membrane which encloses intracellular organelles and a multitude of enzymes and nucleic acids. The enzymes are responsible for the chemical reactions that occur within the cell, and the nucleic acids reserve the entire genetic information of the organism. The survival or growth of microorganisms depends on the integrity of the cell and the concerted action and suitable state of all of these components (Gao & Cranston, 2008). Antimicrobial agents work by destroying the cell wall synthesis or altering the permeability of cell membrane, denaturing proteins, inhibiting enzyme activity or inhibiting lipid synthesis, disrupting metabolic pathway or interfering with nucleic acid synthesis, all of which are indispensable for cell survival (Anonymity, 2015; Byarugaba, 2010; Gao & Cranston, 2008; Tenover, 2006).

2.3.2 Antimicrobial agents used for textiles

A multitude of chemicals are used as strength the antimicrobial properties of materials. According to the antimicrobial action, antimicrobial agents can be categorized into two groups, biocides and biostats. Biocides refer to kill microbe and eliminate their growth, while biostats are able to inhibit the growth of microorganism (Simoncic & Tomsic, 2010; G. Sun & Worley, 2005). Almost all antimicrobial agents used in commercial textiles, e.g. silver, triclosan, polyhexamethylene biguanide (PHMB) and quaternary ammonium compounds, are biocides (Gao & Cranston, 2008). Antimicrobial agents offer special protection against the various microbes on textiles. They act selectively on vital microbial functions with minimal effects or without

adverse effects on host functions. Different antimicrobial agents act in different ways. The understanding of the chemical properties of antimicrobial agents and their antimicrobial mechanisms is crucial in the study of antimicrobial finishing (Byarugaba, 2010). Here it is principally focused on some antibacterial agents that are commercially used in textile finishing.

2.3.2.1 Metals and metallic salts

Metal ions used as antimicrobial agents have a long history in many fields. They have been used in textiles since the early 1940 s (Fouda, 2012; Kawabata & Taylor, 2007). It is well known that metal ions, such as silver ion(Ag^{+}), copper ion (Cu^{2+}) and zinc ion(Zn^{2+}), have strong ability to kill the microbe, because most of heavy metals are toxic to microbes at very low concentrations both in free states and in compounds (Gao & Cranston, 2008; Shahidi & Wiener, 2012). This often attributes to their affinity for protein material and the insolubility of the metal proteinate formed (Capelli, 1990). They bind to intracellular proteins, react with nucleophilic amino acid residues inproteins and attach to sulphydryl, amino, imidazole, phosphate and carboxyl groups of membrane or enzyme proteins leading to denaturation of protein ans cell death (Dastjerdi, Montazer, & Shahsavan, 2009; Gao & Cranston, 2008; Shahidi & Wiener, 2012). Among these various metal antimicrobial agents including silver, zinc, copper and cobalt, silver is the most widely used in general antimicrobial finishing of textiles (Gao & Cranston, 2008; Shahidi & Wiener, 2012; Windler, Height, & Nowack, 2013). The uptake and durability need to be enhanced at the finishing stage, especially for natural fibers. And as biocidal, the bactericidal sensitivity of metal ions varies

depending on the microbial species (Delgado, Quijada, Palma, & Palza, 2011; X. Wang, Du, Fan, Liu, & Hu, 2005). Therefore, transition metals and heavy metals can be complex with other organic antimicrobial agents to provide effective antimicrobial activity. For example, Wang et al. combined different kinds of metals with chitosan together and the antimicrobial activities of these complexes are much higher than free chitosan and metal salts (Wang et al., 2005). Another method to improve the application performance of metal salts is to produce highly ionic nano-particulate metals (Au, Ag, Cu and Ga) and metal oxides (TiO_2, ZnO and CuO) which possess extremely high surface areas and unusual crystal morphologies which provide numerous edge/corner and other reactive surface sites displaying unique physical and chemical properties (Shahidi & Wiener, 2012; Stoimenov, Klinger, Marchin, & Klabunde, 2002). Meanwhile, nano-particles can impart new properties to fibers. For example, nano-sized metal particles can be can be added into spinning solution to produce thin solid polymer strands with special properties which depends on the required applications, because the diameter of fibers produced through electrospinning is less than 100nm (Fouda, 2012). A multitude of strategies are used to improve the antimicrobial activities of metals and metallic salts. However, their cost is still a problem need to be solved because most of them are noble metals. Another problem is environmental problem, due to the release of metal ions into environment.

2.3.2.2 Quaternary ammonium compounds

Quaternary ammonium compounds (QACs), particularly those cationic surface active agents containing chains of 12–18 carbon atoms, have been used broadly as sterilizing

agents. These compounds carry a positive charge at the N atom and they accumulate in the cell driven by the membrane potential inflicting types of detrimental effects on microbes, including damage to cytoplasmic membranes, denaturation of proteins and disruption of the cell structure (Gao & Cranston, 2008; Gilbert & Moore, 2005; Ma, Sun, & Sun, 2003). The antimicrobial activity of QACs depends on the number of cationic ammonium groups and the length of the alkyl chain in the molecule. The cationic ammonium group of the QACs attractively interacts with the negatively charged cell membrane of the microbe to take effect resulting in the formation of a surfactant–microbe complex. This causes the interruption of protein activity and all essential functions of the cell membrane. QACs also affect bacterial DNA, causing a loss of multiplication ability. If the long alkyl chain is bonded to the cationic ammonium in the structure of the QACs, two types of interactions between the agent and the microorganism can occur: a polar interaction with the cationic nitrogen of the ammonium group and a non-polar interaction with the alkyl chain. Consequently, the alkyl group penetrates into the microorganism enabling the alkylammonium group to physically interrupt all key cell functions (Simoncic & Tomsic, 2010). During inactivation of bacterial cells, the quaternary ammonium group remains intact and retains its antimicrobial ability as long as the compound is attached to textiles (Gao & Cranston, 2008). However, there are no reactive functional groups in the structure of the QACs to allow its chemical bonding to the fibers. The physical bonding leads to easy leaching of the QACs from textiles resulting in a fast decrease in concentration to below the minimum inhibitory concentration (MIC) (Simoncic & Tomsic, 2010).

2.3.2.3 Polybiguanides

Polybiguanides are polymeric cationic amines including 8-15 cationic biguanide repeat units separated by hydrocarbon chain linkers of identical or dissimilar length (Fouda, 2012). It has been employed for a wide range of applications as antimicrobial agent since 1957. It exhibits greater antimicrobial activity against a broad spectrum of organisms (Foulkes, 1973). The most remarkable antimicrobial agent of polybiguanides is polyhexamethylene biguanide (PHMB) with an average of 11 units shown in Figure 2.6 (Blackburn, Harvey, Kettle, Payne, & Russell, 2006; Chen-Yu, Eberhardt, & Kincade, 2007; Fouda, 2012; Kawabata & Taylor, 2007). It can interact with membrane-bound anionic phospholipids to kill virus (Krebs et al., 2005). It can bind to textiles with anionic groups because of its cationic groups. The weak ion-ion linkages result in slow release of free antimicrobial agent by dissociation (Blackburn et al., 2006; Chen-Yu et al., 2007; Fouda, 2012; Kawabata & Taylor, 2007). Blackburn et al studied the relationship between the concentration of PHMB and the interaction of PHMB with cellulose (Blackburn et al., 2006; Blackburn et al., 2007). The result of adsorption isotherms is that these were typical Langmuir isotherms at low concentrations, while at higher concentrations, they were more indicative of Freundlich isotherms. The reason is that at lower concentrations of PHMB, electrostatic interactions dominate a contribution to binding through hydrogen bonding between PHMB and carboxylic acid groups in the cellulose; at high PHMB concentrations, increasing PHMB adsorption are attributed to a combination of electrostatic and hydrogen-bonding forces, that is, monolayer aggregation and

multilayer stacking of PHMB through electrostatic interactions with counterions and hydrogen bonding of biguanide groups (Blackburn et al., 2006; Blackburn et al., 2007). The anionic groups on cellulose are anionic carboxylic groups forming by oxidation of glucose rings during pretreatment processes such as bleaching, mercerizing, plasma treatment and dyeing (Fouda, 2012; Kawabata & Taylor, 2004).

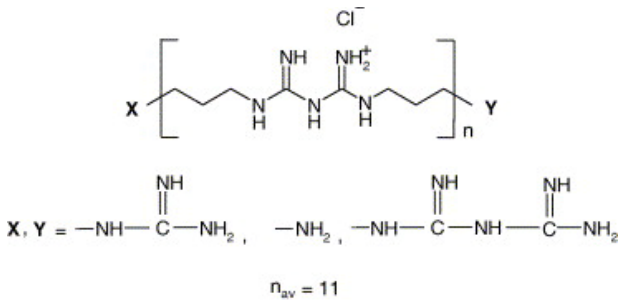

Figure 2.6 Chemical structure of Polyhexamethylene biguanide. n_{av} is the average number of repeat units (Fouda, 2012)

2.3.2.4 Triclosan

Triclosan (2, 4, 4'-trichloro-2'-hydroxydiphenyl ether), a chlorinated phenolic compound (Figure 2.7), is a synthetic, non-ionic and broad-spectrum antimicrobial agent. It has been considered to have multiple mechanisms of action and numerous cellular targets. However, it acts mainly by inhibiting fatty acid biosynthesis through blocking lipid biosynthesis at sublethal concentrations (Orhan, Kut, & Gunesoglu, 2007; Yazdankhah et al., 2006). Although triclosan have positive effect on against both Gram-positive and Gram-negative bacteria, the antimicrobial activity against Gram-positive bacteria is greater than that on Gram-negative bacteria (Orhan et al., 2007; Yazdankhah et al., 2006).

Triclosan, as antimicrobial agent, also has disadvantages. Its antimicrobial action

against microorganisms is quite slow. It needs to take more than 10 hours to contact and exhibit its maximum antimicrobial functions. Meanwhile, it was found that triclosan can cause mutations of drug-resistant strains in microorganisms, which has been well documented and is of great concern (Gao & Cranston, 2008; Sun & Worley, 2005).

Triclosan has poor water solubility, but it is soluble in the flavor/surfactant phase. Several methods have been used to triclosan finishing onto textiles. It can be grafted onto cellulosic fabrics with the assist of crosslinking agents. It also can act as a disperse dye on polyester and nylon fabrics. To achieve a more durable finishing, triclosan can be finished onto fabrics by hosting cavities or carrier, such as cyclodextrins and polylactide (Gao & Cranston, 2008; Nostro, Fratoni, & Baglioni, 2002; Simoncic & Tomsic, 2010). Triclosan can also be directly incorporated into synthetic polymers through melt-mixing or suspension polymerization (Gao & Cranston, 2008; Simoncic & Tomsic, 2010).

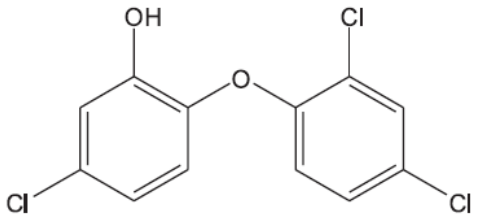

Figure 2.7 Chemical structure of triclosan (Gao & Cranston, 2008)

2.3.2.5 Chitosan

Chitosan is a natural nontoxic biopolymer used widely in various fields due to its excellent biocompatibility, biodegradability and non-toxicity. Chitosan is a poly-β

(1-4)-D-glucosamine (Figure 2.8) which can be produced by deacetylation of chitin, a linear N-acetyl-β (1-4)-D-glucosamine that exists in the exoskeleton of crustaceans and the cell walls of fungi (Cao & Sun, 2009; Chang, Tu, Wu, Hsueh, & Hsu, 2008; Lv, Luo, Deng, & Sun, 2013). The nature of chitosan is polycation because the amino groups at the C-2 atoms of the glucosamine units can be protonated. Amino groups with positive charge can be adsorbed to the negatively charged bacterial surface inducing the disruption of the cell membrane and an increase in its permeability. Chitosan can also interact with the DNA of microorganisms to prevent protein synthesis (Rabea, Badawy, Stevens, Smagghe, & Steurbaut, 2003; Simoncic & Tomsic, 2010). Accordingly, it possesses positive antimicrobial properties against varieties of microorganisms through ionic interaction at a cell surface, which can kill the cell (Rabea et al., 2003; Shahidi & Wiener, 2012). The $–NH_2$, -OH groups in chitosan molecule are regarded as the dominating reactive sites (Lim & Hudson, 2003; Rabea et al., 2003; Wang et al., 2005). Therefore, it can react or chelate with other chemicals to form new antimicrobial agents which possess more powerful antimicrobial properties.

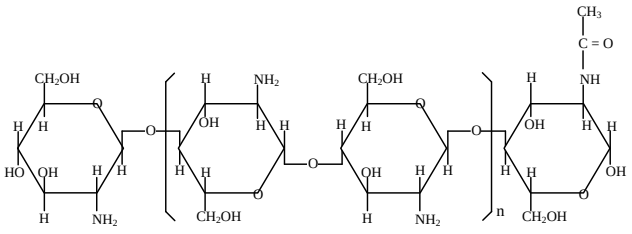

Figure 2.8 Chemical structure of chitosan

2.3.2.6 Dyes

For the requirement of energy conservation and environmental protection, researchers

explored to combine antimicrobial finishing with other treatment in one process, for example dyeing. However, the combination is designed usually based on a simple mixing of dyes, antimicrobial agents and other auxiliaries. Therefore, the compromise of dyeing and antimicrobial finishing conditions is required and the final effects of the resultant fabrics are usually sacrificed. Accordingly, the only way to satisfy the requirement is to get dyes with antimicrobial property. Natural dyes with tannins or naphthoquinones are reported by researchers possessing antimicrobial property. Some commercially available dye powders, such as Acacia catechu, Kerria lacca, Quercus infectoria, Rubia cordifolia and Rumex maritimus are reported against common pathogens Escherichia coli, Bacillus subtilis, Klebsiella pneumoniae, Proteus vulgaris and Pseudomonas aeruginosa when applied to textile materials (Singh, Jain, Panwar, Gupta, & Khare, 2005). Moreover, antimicrobial dyes can be designed and synthesized by incorporating biocidal quaternary ammonium salts (QAS) into dyes shown in Figure 2.9 (Ma et al., 2003; Simoncic & Tomsic, 2010). For example, acid dyes can be used as bridges to link antimicrobial agents such as QAS to nylon (Kim & Sun, 2001). Some synthetic dyes are made with antimicrobial property specifically. For example, a new series of azo disperse dyestuffs, prepared by the reaction of sulphanilamidodiazonium chloride derivatives with indan-1,3-dione, gave excellent dyeing and antimicrobial results on wool and nylon (Gao & Cranston, 2008; Sayed & El‐aby, 2001). These dyes with antimicrobial property largely reduce the consummation of quantities of energy and the production of amounts of wastewater which are necessary in textile dyeing and finishing in separate steps.

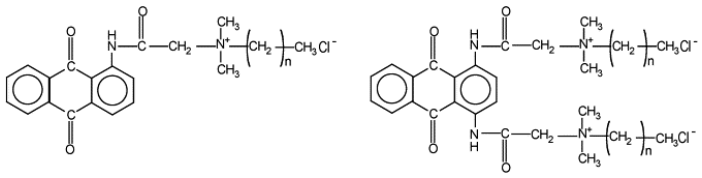

Figure 2.9 The structures of antimicrobial cationic dyes (*n*=3, 7, 11) (Ma et al., 2003)

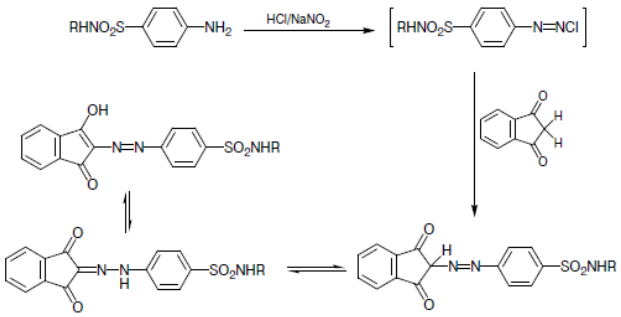

Figure 2.10 Scheme of synthesis of antimicrobial disperse dyestuffs (Sayed & El−aby, 2001)

2.3.2.7 Regenerable N-halamine

N-halamine can be 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, that is, amine or imines groups in N-halamine are changed to chloramide through chlorination. The bactericidal action of N-halamine is believed 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 bond (N-Cl) in contact with germs (Qian & Sun, 2004; Y. Sun & Sun, 2004). Though the bactericidal process consumes halogens, the lost halogens can be easily

recharged by chlorination. This is a reversible redox reaction (Figure 2.11). Insoluble polymers coated with N-halamine produce a substantial reservoir of combined halogen for enhanced disinfection purposes (Liang et al., 2007a). They are active for a wide spectrum of bacteria, fungi and viruses. As one of the most effective biocides, N-halamine structures possess several useful features including good stability for long-term use in aqueous solution and in dry storage over a broad temperature range, ability to regenerate in a chlorine solution repeatedly after loss of activity from extensive usage, lack of corrosion of surfaces, low toxicities, and relatively low expense. It satisfies the requirements of ideal antimicrobial textiles on some extent. The monomers of regenerable antimicrobial agents with N-halamine structures include chitosan, hydantoin derivatives, polycarboxylic acids, acrylamide and its derivatives, imidazolidinone derivatives, N-halamine siloxanes and triazine derivatives. In addition, some other chemicals are used as carriers of released antibiotics which could be repeatedly recharged to regenerate the antimicrobial activities, which provides another innovative approach to the production of refreshable antimicrobial agents. N-halamine can be used to various textiles including cellulose, polyester and polyamide (Simoncic & Tomsic, 2010). This kind of textile materials provides effective biocidal ways for reusable clothing which enhance a level of antimicrobial protection. Here lists some kinds of chemicals with N-halamine structure.

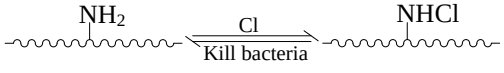

Figure 2.11 The reversible redox reaction of N-halamine

(1) Hydantoin and Its Derivatives

Hydantoin and its derivatives have been grafted to cellulose, polyester, polyamide, polyacrylonitrile, and polypropylene fabrics, and the grafted hydantoin rings are then converted to the N-halamine structures after chlorination (Y. Sun & Sun, 2001b; Y. Sun & Sun, 2001c; Wang, Xie, Gu, & Sun, 2006). The grafted textiles exhibited powerful antimicrobial efficacy against both gram-positive and gram-negative microorganisms, and the antibacterial functions of the modified textiles are durable and regenerable through chlorine bleaching.

The halogenated 5, 5-dimethyl hydantoin is always used as antimicrobial. 1, 3-dichloro-5, 5-dimethyl hydantoin (DCDMH) had been used as disinfectant in circulating-water system since 1979 in America (X. Wang & Wang, 2000). Sun et al. covalently linked 5, 5-dimethyl hydantoin to the surface of polyurethane (PU) with 1, 6-hexamethylene diisocyanate (HDI) as the coupling agent (X. Sun, Cao, Porteous, & Sun, 2012). After chlorination, the antimicrobial materials could kill a broad range spectrum of microbial. The antimicrobial effects of the new polymers are both durable and regenerable. Actually, the antimicrobial activity of 5, 5-dimethyl hydantoin varies with the species of the tested organisms (El-Newehy, Al-Deyab, Kenawy, & Abdel-Megeed, 2011). With the development of technology, several kinds of functional groups, such as allyl-, methyl-, methylol-, are introduced into the ring of 5, 5-dimethyl hydantoin to improve its antimicrobial effect. Thus, 5, 5-dimethyl hydantoin is always used as precursor to synthesize regenerable antimicrobial agents. Several hydantoin derivatives are developed in recent years, such as

3-triethoxysilylpropyl-5,5-dimethylhydantoin (Liang, Wu, Huang, & Worley, 2005), 3-(3-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro-[4.5] decane-2,4-dione (Liang et al., 2007b), 3-glycidyl-5,5-dialkylhydantoins (Liang, Chen et al., 2007), 3-hydroxymethyl-5,5-dimethyl- hydantoin (Li & Worley, 2001), 3-(4'-vinyl benzyl)-5, 5-dimethylhydantoin, dimethylol-5, 5-dimethyl- hydantoin (Y. Sun & Sun, 2004) and 3-allyl-5, 5-dimethylhydantoin (Qian & Sun, 2004). All of these antimicrobial agents can be grafted onto many kinds of textiles, such as cotton fabrics and different synthetic fabrics. All of these textiles show excellent antibacterial efficiencies, durable antimicrobial properties, environmental friendliness, and they are safe to use. Nevertheless, imide moiety of the hydantoin ring in compounds **A**, **B**, **C** and **D** shown in Figure 2.12 is used to covalently tether the compound to the textile's surface instead of providing additional biocidal property. Usually, the order of bond strengths of N-chloramines in three different forms is amine > amide > imide, while the antimicrobial activity is in reverse order (Kocer, Worley, Broughton, & Huang, 2011; Worley, Eknoian, & Li, 1999). Thus, use of the imide nitrogen of the hydantoin ring would be beneficial for antimicrobial applications. A hydantoin acrylamide (HA) can be synthesized by the reaction of N-(1,1-dimethyl-3-oxobutyl) acrylamide (DA), potassium cyanide, and ammonium carbonate in the condition of the mixed solvent of water and ethanol, which is shown in Figure 2.13. During the reaction, the vinyl group in acrylamine monomer is not disturbed and there are three N-H sites in HA, which offer many opportunities for HA to copolymerize with other monomers to provide an antimicrobial property. Kocer et al. reported HA was copolymerized with a siloxane

monomer and the copolymer inactivated the germs efficiently (Kocer et al., 2011). The inherent disadvantage of hydantoin and its derivatives is the slow release of formaldehyde during wearing and using (Ren, Kocer, Worley, Broughton, & Huang, 2009). This is a weakness should be improved for hydantoin and its derivatives as antibacterial monomers.

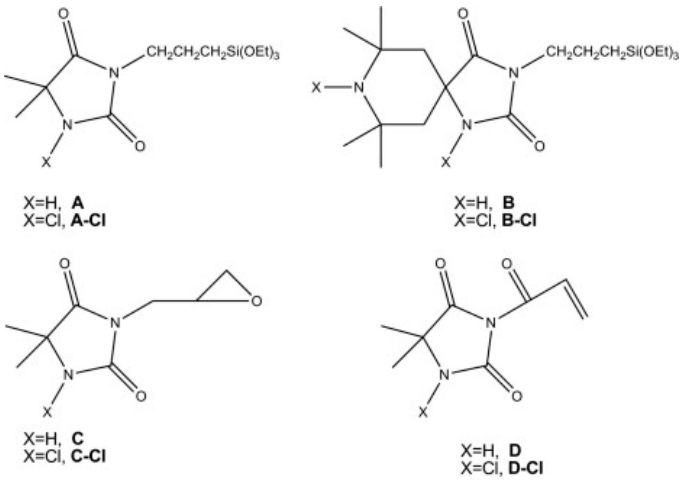

Figure 2.12 Structure of previously synthesized N-halamine compounds (Kocer et al., 2011)

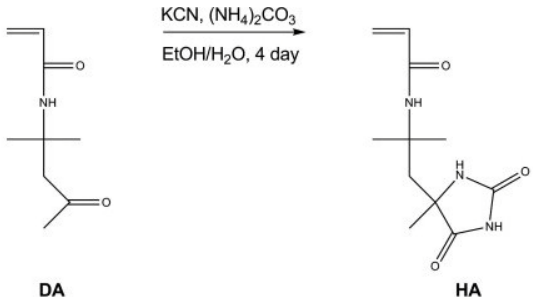

Figure 2.13 Synthesis of hydantoin acrylamide (Kocer et al., 2011)

(2) Imidazolidinone and Its Derivatives

The stability of antimicrobial agents is an important factor which affects the durability of antimicrobial agents. The stability of N-halamines is determined by their structures,

which are imide, amide and amine bonds. The imide halamine is the least stable structure which loses active chlorine and return to precursor quickly. Thus, more imide bonds result in relatively less durable antimicrobial properties of materials, which is the reason that most of fabrics treated with hydantoin and its derivatives have relatively low durability, especially in washing (Qian & Sun, 2003). Imidazolidinone and its derivatives provide amine and amide structure which can be incorporated to the fabrics to solve that problem. Sun et al. grafted 3-methylol-2,2,5,5-tetramethylimidazolidin-4-one (MTMIO) onto cellolose to bring the amine halamine structure into antimicrobial textiles. The reaction beween MTMIO and cellulose is shown in Figure 2.14. After the TMIO ring is grafted onto cellulose, the amine bond can be converted to the stable amine halamine, which then will provide the desired durable antimicrobial functions (Qian & Sun, 2003). Ren et al. synthesized and attached 3-(2,3-dihydroxypropyl)-5,5-dimethylimidazolidine- 2,4-dione, an N-halamine precursor with two hydroxyl groups, onto cotton fabrics with the assistance of the suitable cross-linking agent. After exposure to dilute hypochlorite solutions, the coated fabric showed excellent antimicrobial efficacy and stability (Ren et al., 2009). Sun et al. synthesized 1-acryloyl-2,2,5,5-tetramethylimidazolidin-4-one (ACTMIO) which could copolymerize with several vinyl monomers such as acrylonitrile (AN), methyl methacrylate (MMA), and vinyl acetate (VAC) and graft onto cotton, polyester (PET), nylon and polypropylene fabrics. After regular chlorine bleach, the amine groups in treated fabrics transformed into stable N-halamine group and provided powerful, durable and regenerable antimicrobial functions (Y. Sun, Chen,

Worley, & Sun, 2001).

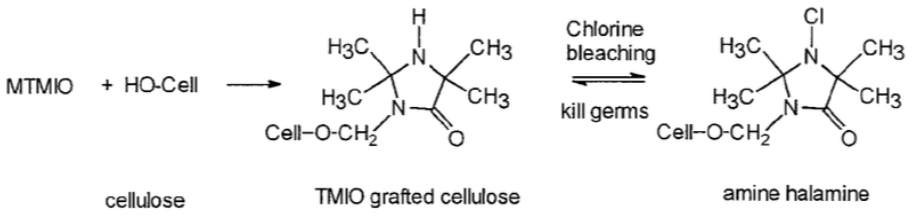

Figure 2.14 Chemical modification of cellulose with MTMIO (Qian & Sun, 2003)

The biocidal speeds of derivatives of imidazolidinone were low because of their amine halamine structures, although they provided excellent durable antimicrobial efficacy (Qian & Sun, 2004). Thus, in order to produce biocidal fabrics that can inactivate microorganisms rapidly and survive after repeated laundering and long duration of storage, many researchers combined the derivatives of imidazolidinone and the derivatives of hydantoin in different ratios in chemical modification of fabrics, which could bring a hybrid of imide, amide and amine halamine structures on fabrics. Qian et al. mixed 3-methylol-2,2,5,5-tetramethylimidazolidinone and dimethylol-5,5-dimethylhydantoin together, and the mixing biocide systems could provide improved antibacterial efficacy against microorganisms and washing durability. Bounding N-halamine precursors chemically to fibers is not only way to prepare antimicrobial textiles (Qian & Sun, 2004). Tan et al. introduced chlorinated 5,5-dimethylhydantoin (CDMH), chlorinated 2,2,5,5-tetramethyl-imidozalidin-4-one (CTMIO) and chlorinated 3-dodecyl-5,5- dimethylhydantoin (CDDMH) introduced into the electrospinning dope of nylon 6. All of these electrospun nylon 6 membranes

with the three different N-halamines killed all of bacteria at 40 min showed effective antimicrobial functions. It was also found that with the same active chlorine contents, electrospun nylon6 membranes with CDMH resulted in faster antimicrobial actions while the membranes with CDDMH acted much slower because of both the slower reaction of chloroamide group and the attached long alkyl chain. The antimicrobial action of CTMIO containing electrospun nylon 6 membranes was of similar rate as that of CDDMH containing electrospun nylon 6 membranes (Tan & Obendorf, 2007). This result demonstrated that N-halamine with imide has best antimicrobial activities again.

(3) Triazine Compounds

Monomeric chloromelamine derivatives, namely, triazine compounds have potent antimicrobial activity, excellent stabilities and low toxicities (Chen & Sun, 2005). As an insoluble biocidal material in water and all organic solvents, they have already been safely and extensively used as water and food disinfectants (Braun & Sun, 2004; Chen, Luo, & Sun, 2007). Sun et al. investigated poly(1,3,5-trichloro-6-methyl-6-(4'-inylphenyl)-1,3,5-triazine-2,4-dione)(Poly-CTD) as a biocide against the bacterium in a water-filter application in 1990s. Not only did the polymer inactivate microorganism efficiently with brief contact time, but also it was very stable in storage at room temperature for at least one month (Sun, Chen, & Worley, 1996). Sun et al. synthesized a reactive triazine derivative, 2-amino-4-chloro-6-hydroxy-s-triazine (ACHT), through the controlled hydrolysis of 2-amino-4,6-dichloro-s-triazine and attached it to cellulose fabric via nucleophilic substitution by four different methods, including

cold-pad-batch, pad-dry-cure, pad-steaming and exhaustion. The result showed the pad-dry-cure method provided the highest ACHT content on fabrics, and the treated fabrics provided powerful, durable and refreshable antimicrobial functions after chlorination (Braun & Sun, 2004; Chen et al., 2007; Sun, Chen, & Braun, 2005). However, the disadvantage of ACHT is that it only can treat the materials with reactive sites such as hydroxyl groups or amino groups. To solve this problem, Sun and his co-workers found a polymerizable triazine derivative, 2-vinyl-4, 6-diamino-1, 3, 5-triazine (VDAT), which could readily form homopolymers and copolymers. They synthesized a series of polymeric chloromelamines via conventional free-radical polymerizations. Because of the existence of triazine structure in VDAT, the polymerization activity is very high. And the results demonstrated that the antimicrobial functions of antimicrobial polymers containing VDAT against multidrug-resistant bacteria are powerful, durable and regenerable (Chen & Sun, 2005).

(4) Siloxane Derivatives

It has been mentioned that the order of bond strength is amine N-Cl > amide N-Cl > imide N-Cl and the order of the reactivity of oxidative chlorine with receptors on the biological cells is contrary. The stability order of the imide and amide moieties could be changed based on steric effects of the substituents on the 5 position of a hydantoin ring, and then amide N-Cl exhibit both fast inactivation rates and exceptional stability. Siloxanes are very useful surface coupling agents, and several N-halamine precursors attached with siloxanes successfully have been employed in industrial settings.

N-Chlorohydantoinyl silanes and siloxanes are prolific N-halamine compounds which can be applied to a variety of surfaces such as cellulose, PET to render the surfaces antimicrobial (Kou et al., 2009). In recent years, a series of N-halamine siloxane antimicrobial compounds have been studied. Worley et al. prepared a trialkoxysilylpropylhadantoin derivative, 3-triethoxysilylpropyl-5,5-dimethylhydantoin, and then polymerized it into hydantoinylsiloxane precursor polymer (Worley et al., 2005). Liang et al. employed 5,5-dimethyl- 3-(3'-triethoxysilylpropyl) hydantoin and its hydrolysis product polymer poly[3-(5,5- dimethylhydantoinylpropyl)hydroxysiloxane] in either monomeric or polymeric form to functionalize particles of silica gel through covalent bonding, which improved the biocidal efficacy because of the larger surface area of silica gel. The results showed that these coatings were very stable in flowing water and could be recharged with aqueous solution of household bleach once the oxidative chlorine lost. Thus, biocidal silica gel could be applied in sterilization of flowing water in any industries (Liang, Owens, Huang, & Worley, 2006). Several N-halamine compounds, imidazolidinone, hydantoin and their derivatives, have been used to functionalize many commercial polymers, such as cellulose, nylon, PET, polyurethane and Kraton rubber which were rendered biocidal once the surface contact with pathogens. Liang et al. coated hydantoinyl siloxane and a quaternary ammonium salt siloxane monomers and polymers onto various surfaces including sand particles, paint and cotton fabric, which showed good stability against water and effective biocidal activity. It can be concluded from this investigation that N-halamine siloxane

monomers and polymers are very important for the construction of biocidal surface coatings (Liang et al., 2006; Liang et al., 2007a). N-halamine siloxane monomers and polymers as antimicrobial materials enriched the variety of antimicrobial agents largely. The existence of alkyl groups substituted on the heterocyclic rings adjacent to the oxidative N-Cl moiety make N-halamine compounds quite stable in long period in aqueous solution and in dry storage, because they hinder the release of “free halogen” into water (Liang et al., 2007a). Therefore, researchers started to observe the effect of alkyl derivatization on the other performances of this kind of antimicrobial materials. Kocer et al. investigated the stabilities towards water and ultraviolet light exposure of a series of hydantoinyl siloxanes including 3-Triethoxysilylpropyl-5,5-dimethylhydantoin, 3-Triethoxysilyl-propyl-5-methyl-5-propylhydantoin, 3-Triethoxysilylpropyl-5-methyl-5-pentyl-hydantoin, 3-Triethoxysilylpropyl-5-heptyl-5-methylhydan-toin, 3-Triethoxysilyl-propyl-5,5-diethylhydantoin, and 3-Triethoxysilylpropyl-5,5-dibutylhydantoin which contained variation in alkyl substitution at the 5 position of the hydantoin ring. The result showed that the variation of alkyl substitution in hydantoinyl siloxanes had no significant effects on either hydrolytic stability or ultraviolet stability of siloxane antimicrobial materials. Finally, the author recommended that the dimethyl derivative was the first choice for a potential application among all of those hydantoinyl siloxane derivatives, because it was the cheapest one to prepare (Kocer et al., 2008). The application of siloxanes N-halamine antimicrobial monomers or polymers not only improved the performance of antimicrobial function and enriched the varieties of

antimicrobial materials but also extended the application range of materials, such as silica gel.

(5) Acrylamide and Its Derivatives

All the antimicrobial agents mentioned above, hydantoin and its derivatives, imidazolidinone and its derivatives, triazine compounds as well as siloxane derivatives are cyclic halamine precursors, while acyclic halamine precursors with vinyl groups, acrylamide and its derivatives, as antibacterial agents also show excellent antibacterial efficiency. Sun et al. grafted acrylamide and methacrylamide onto cotton fabric in high yields by using a free radical polymerization process, and both the antimicrobial efficacy and the durability of the grafted fabric are comparable to cyclic halamine antibacterial agents; its store stability is also as good as cyclic halamine antibacterial agents except in alkaline conditions (Liu & Sun, 2006). To achieve multipurpose textiles, polymethacrylamide is coated onto Kevlar fabrics by Luo et al (Luo & Sun, 2008). After bleaching, the coated Kevlar fabrics not only keep its original thermal and mechanical properties, but possess potent, durable, and regenerable antibacterial, antifungal, antiviral, and antispore functions (Luo & Sun, 2008). Badrossamay et al. employed the acyclic halamine precursors, acrylamine and methacrylamine, on the antibacterial modification of polypropylene through a reactive extrusion process. The modified PP provides powerful antimicrobial properties and shows great potential to be used as medical devices and nonwoven textiles (Badrossamay & Sun, 2008; Badrossamay & Sun, 2009). However, acrylamine and methacrylamine as antimicrobial agents are easy to leak from the textile because of

their low molecule weight. Yildiz et al. grafted a bifunctional monomer N-(hydroxymethyl) acrylamide onto cotton fabric through the etherification reaction providing cotton fabrics with stable and regenerable biocidal functionality. That is because N-methylol groups in N-(hydroxymethyl) acrylamide substitute the cellulosic hydroxyl groups making it covalently attach onto cotton and then it can be homopolymerized or copolymerized via free radical polymerization because of the existing of vinyl groups (Yildiz et al., 2012). During the application of antimicrobial materials, photolytic decomposition or hydrolysis will shorten their service life if they are not stable towards UV light or water. Cerkez et al. observed the effect of different tethering groups on the UV stabilities and washing stabilities of cotton fabrics coated with hydantoin acrylamide copolymers which were got by copolymerizing hydantoin acrylamide with different kinds of monomers containing silane-, epoxide- or hydroxyl group. The results demonstrated that all of these chlorinated samples were remarkably stable against both of repeated launderings and UV light exposure, especially the epoxide group-containing copolymer (Cerkez, Kocer, Worley, Broughton, & Huang, 2012). Acrylamine and its derivatives broaden the variety of antibacterial agents. Meanwhile their properties of acrylamine and its derivatives are excellent for the usage of antimicrobial materials in lots of industries.

(6) Chitosan and Its Derivatives

As mentioned above, there are amino groups in chitosan molecule. Researchers found it can be transformed into N-halamine shown in Figure 2.15. Sun et al. found that upon chlorine bleach treatment, some of the amino groups in chitosan were transformed into

N-halamine structures, and the antimicrobial functions of N-halamine-based chitosan against both gram-negative and gram-positive bacteria were potent durable and regenerable (Cao & Sun, 2008). The derivatives of chitosan also can become regenerable antibacterial agents. Ren et al. synthesized N-halamine precursor 3-glycidyl-5, 5-dimethylhydantoin (GH), and then bonded it onto chitosan by a ring opening reaction between chitosan and GH. After chlorination, the chitosan derivative on the surface of fabric shows excellent antimicrobial functions against both Gram-negative bacteria and Gram-positive bacteria. This is because the addition of stable cyclic N-halamine with a hydantoin ring into chitosan significantly increases the active chlorine loadings on the films, which enhances the antimicrobial activity and durability (Li, Hu, Ren, Worley, & Huang, 2012). Chitosan also can be used as carriers of anionic antimicrobials to prolong antimicrobial actions because it a cationic polymer which can bind anionic molecules through the formation of ionic complexes (Cao & Sun, 2009). The released antibiotics could be repeatedly recharged to regenerate the antimicrobial functions.

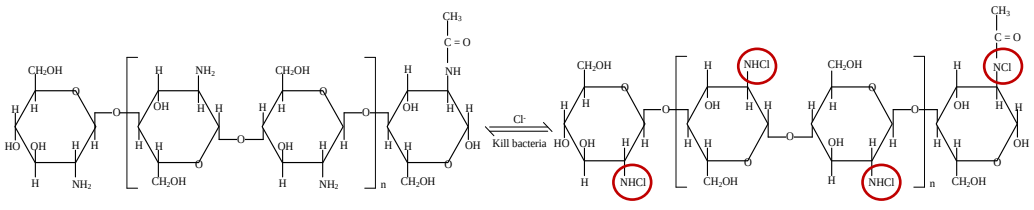

Figure 2.15 The reversible redox reaction of chitosan with halamine structures (red cycle shows the N-halamine structure).

(7) Other Antimicrobial Materials

There are some other kinds of antimicrobial materials with N-halamine structure

which shows amazing durable and refreshable antimicrobial effects. For example, carboxyl groups have been introduced into the surface of textiles, and then they are transformed into N-halamine structures or biocidal peroxyacid structures which make their antimicrobial functions regenerable (Chen & Han, 2011; Huang & Sun, 2003). A series of N-halamine oxazolidinones have also been studied, such as 4-[(Acryloxy)methyl]-4-ethyl-2-oxazolidinone, 4-(Crotonoxymethyl)-4-ethyl-2-xazolidinone, 4-[[(2'-Methylacryl)-oxy]methyl]-4-ethyl-2-oxazolidinone, 4-[[(3',3'-imethylacryl)oxy]methyl]-4-ethyl-2-oxazolidinone, Poly[4-[(acryloxy)methyl]-4-ethyl-2-oxazolidinone]. These kinds of monomers can be used as water-soluble disinfectants independently as well as polymeric disinfectants via polymerizing (Eknoian, Putman, & Worley, 1998).

2.3.3 Methods for antibacterial finishing

Various methods available for antimicrobial finishing of different textiles, depending on the mechanisms of antimicrobial finishing, can be divided into two types. One type is that antimicrobial agents are physically embedded in the structure of the fiber forming a controlled-release system. The antimicrobial agents release slowly from a reservoir on the surface of fabrics or in the interior of the fibers. This finishing method is suitable for synthetic fibers, the reason is that the antimicrobial agents can be incorporated into the polymer prior to extrusion or blended into the fibers during their formation (Delgado et al., 2011). Such processing provides the best durability of antimicrobial activity. This method of fabrication has been adopted by some manufacturers, such as the silver-containing Bioactive polyester fibers developed by

Trevira and the triclosan-containing Silfresh cellulose acetate fibers manufactured by Novaceta (Gao & Cranston, 2008; Yeo, Lee, & Jeong, 2003). For natural fibers, hosting cavities introduced by grafting of chemicals with cavities provide a way to forming the controlled-release system. Among numerous chemicals, cyclodextrin is the best choice, because of its hydrophilic outer surface and internal hydrophobic hollow interior, which can entrap a vast number of lipophilic compounds into their hydrophobic cavity. Polybiguanides, triclosan, etc. have been used to antimicrobial finishing of cellulosic textiles through this method (Denadai et al., 2007; Qian et al., 2009). The antimicrobial textiles with 'leaching' antimicrobial property are very effective against microorganisms on textiles or in the surrounding environment. However, the antimicrobial agents will run off eventually and the antimicrobial activity will not be effective any more. Moreover, the antimicrobial agents released to the environment may interfere with other desirable microorganisms. Another type is that antimicrobial agents are chemically bounded to the surface of fibers. This can be realized by pad-dry-cure method easily on natural as well as synthetic fibers for the biocides such as triclosan, PHMB, chitosan,QACs, etc (Chung, Lee, & Kim, 1998; Gao & Cranston, 2008; Lim & Hudson, 2004; Orhan, Kut, & Gunesoglu, 2009). Chemical modification of the biocide for covalent bond formation with the fiber, crosslinking of the active agent onto the fiber using a crosslinker and polymerization grafting occur during pad-dry-cure process. Except pad-dry-cure method, admicellar polymerization and sol-gel also have been reported in antimicrobial finishing of textiles and obtain desired functionality (Attia, 2002; Fouda, 2012; Mahltig, Fiedler, &

Böttcher, 2004; Mahltig, Haufe, & Böttcher, 2005; Ren et al., 2008; Simoncic & Tomsic, 2010). In addition, nanotechnology is applied to the finishing processes to improve the antimicrobial effect (Fouda, 2012). Nanosized colloidal solutions and nanoscale particles enable antimicrobial textiles with excellent antibacterial activity and long durability (Ye et al., 2005; Ye et al., 2006). Antimicrobial finishing of textiles through chemically bounding only inhibits the microorganisms on the surface of fibers, not in the surrounding environment (Shahidi & Wiener, 2012).

2.3.4 Evaluation of antibacterial property

Evaluation of antimicrobial effect of antimicrobial materials is extremely important for the development of antimicrobial textiles. Various methods have been explored to examine the antimicrobial effect of antimicrobial materials in recent years. The most representative methods fall into two categories: (1) qualitative methods: AATCC-30, AATCC-90, AATCC-147, JIS L 1902-Halo method, SN 195920 and ISO 20645 (2) quantitative methods: AATCC-100, ASTM E2149, JIS L 1902-Absorption method and, ISO 20743 (Gao & Cranston, 2008; Gomes, Mano, Queiroz, & Gouveia, 2010; Hofer, 2006; Pinho, Magalhães, Henriques, & Oliveira, 2011).

The qualitative methods are that textile samples are placed in contact with nutrient agar plates inoculated with bacterial cells and then incubated under moist conditions at 37 ºC for 24-48 hours. Thus, this kind of methods also can be called agar diffusion methods. The intimate contact of the textiles with the bacteria and the growth medium will result in the inhibition of bacterial growth directly underneath the textiles and

immediately around the edges of the textiles (Gomes et al., 2010). The diameter of the inhibit zone give an indication of the potency of the antimicrobial activity or the release rate of the diffusive compound. Although these methods are only qualitative, they are simple to perform and are most suitable when a large number of samples are to be screened for the presence of antimicrobial activity.

The quantitative methods are also known as absorption. That is because textile samples in these test methods are placed in direct contact with a certain small volume of bacterial inoculums and the bacterial inoculums must be fully absorbed into samples without leaving any free liquid. After incubation under humid conditions at 37 ºC for a specified contact time, bacteria from the samples are eluted and the total bacterial number is determined by serial dilution. Antimicrobial activity can be assessed by calculating the percentage of reduction through comparing the size of the initial population with that following the incubation (Gao & Cranston, 2008; Gomes et al., 2010; Pinho et al., 2011). These test methods provide quantitative values on the antimicrobial finishing. However, they are more time and material consuming than the qualitative methods.

These test methods are performed under artificial conditions (e.g. rich nutrients in the inoculum and saturating moisture in the testing fabrics) which are beneficial for bacterial growth. The exaggerated conditions are far from the conditions during the normal use of a textile product. To date, very few studies have examined the antimicrobial effects under normal wearing conditions. But these test methods offer a standard to assess the antimicrobial effectiveness of the treated textiles. The textiles

must pass antimicrobial test before marketing, which insure the safety of the textiles used (Gao & Cranston, 2008).

2.4 Conclusion

Cotton textiles with antimicrobial function are essential for people to use them safely and healthily. Duration and safety are very important for desirable antimicrobial cotton textiles. Cotton textiles finished with regenerable antimicrobial agents possess long antimicrobial work life, which extend the duration of antimicrobial property. Meanwhile, antimicrobial finishing processes must insure the safety of human during manufacturing and usage and have to satisfy the requirement of environmental protection and energy saving. In addition, many standards are used to evaluate the antimicrobial textiles to insure its safety during usage.

Plasma treatment is an alternative method whether used for antimicrobial finishing for cotton textiles independently or combined with other wet chemical treatment. When it imparts antimicrobial property to textiles, it enhances the duration of antimicrobial activity and keeps the bulk properties of textiles. Moreover, plasma treatment applied to antimicrobial finishing of textiles is efficient and environmentally friendly as well as energy saving. Therefore, combination of plasma treatment and regenerable antimicrobial finishing is a good way for producing regenerable antimicrobial cotton textiles in this study.

CHAPTER 3 EXPERIMENTAL

3.1 Introduction

This chapter describes the details of experiments, including materials, apparatus, experimental procedures and test methods used in this study.

3.2 Materials

3.2.1 Preparation of cotton specimens

Desized, scoured and bleached 100% twill woven cotton fabric (128 yarns/inch, yarn count 20 S, in warp; 60 yarns/inch, yarn count 16 S, in weft; fabric weight 261g/m^2) supplied by Lai Tak Enterprises Ltd was used.

The fabric was first washed with 2% non-ionic detergent Diadavin EWN-T 200% (TANATEX Chemicals) at pH 7 and 50 ºC for 30 min in a dyeing and finishing machine (Samuel Pegg & Son Ltd), rinsed with deionised water to remove detergent, oil and other impurities, and then hydro-extracted in a Nyborg C260R Hydro-extractor (HERKA GmbH & Co.) for 2 min. The fabrics were dried in a Nyborg T4350 tumble dryer (HERKA GmbH & Co.) at moderate temperature around 80 ºC for 20 min. After that, the fabric was cut into 100 mm x 200 mm and washed with acetone (ACS Reagent grade, supplied by VWR international) in fume cupboard for 10 min to remove detergent, oil or impurities on the fabric surface thoroughly and then again washed with deionised water adequately. After that, the fabrics were hydro-extracted in a Nyborg C260R Hydro-extractor (HERKA GmbH & Co.) for 2 min. Lastly, the fabrics were dried in a Nyborg T4350 tumble dryer (HERKA GmbH & Co.) at

moderate temperature around 80 ºC for 20 min. The cleaned fabric samples were conditioned at 20±2 ºC and 65±2% relative humidity for at least 24 hours prior to all experiments.

3.2.2 Chemical used in this study

Antimicrobial agents used in this study were chitosan and 5, 5-Dimethyl hydantoin (DMH) (97%) purchased from Sigma-Aldrich Co. Chitosan used in this research was low molecular weight (50 to 190 kDa) and its deacetylation was higher than 75%.

Acetic acid glacial (reagent A.C.S. grade) was purchased from International Laboratory with purity of 99.8+%.

Sodium hypochlorite (5% free chlorine) was got from Acros Organics.

Potassium iodide (KI) (analytical reagent grade) was obtained from Fisher Scientific with purity of 99+%.

Sodium hydroxide (reagent A.C.S. grade) was bought from Sigma-Aldrich Co. with purity of 99+%.

Starch solution used as indicator was purchased from Fluka Analytical with concentration of 1% in water.

Sodium carbonate (analytical reagent grade) (99.8%), Potassium dichromate (analytical reagent grade) (99.8%), Sodium thiosulphate 5-hydrate (analytical reagent grade) (99%) were bought from Accu-Chem Industries, Inc.

Sulphuric acid (98.0%) was bought from VWR International Ltd.

Nitrogen was obtained from Hong Kong Industrial Gas LTD with purity of 99.999+%.

Helium was obtained from Linde HKD Ltd with ultra-high grade.

3.3 Determination of active chlorine in sodium hypochlorite solution

In order to get precise concentration of active chlorine in sodium hypochlorite used in this research, the active chlorine in sodium hypochlorite must be determined by iodometric titration.

Firstly, $Na_2S_2O_3$ standard solution (0.1 mol/L) was prepared. 12.5g $Na_2S_2O_3 \cdot H_2O$ was dissolved in 500mL cool boiled water, added 0.1g Na_2CO_3 and stored in brown bottle in dark place for one week.

Second, $K_2Cr_2O_7$ standard solution (0.1 mol/L) was prepared to titrate with $Na_2S_2O_3$ solution to find its molarity. $K_2Cr_2O_7$ was dried at 120 ^oC to constant weight and cooled to room temperature in dryer. 1.2258 g $K_2Cr_2O_7$ was dissolved in deionized (DI) water in beaker, and then the solution was transfered into 250mL volumetric flask, diluted to volume and mixed adequately. After that, 25mL of the solution was transfered to iodine flask, 1g KI and 10mL H_2SO_4 (1:8) were added into it, and then the iodine flask was sealed and stored in dark place for 10min after mix. Then, it was diluted with 120mL deionized water, and titrated to pale yellow-green with $Na_2S_2O_3$ solution prepared one week ago. At that time, 3mL starch indicator was added, and the titration was continued until the solution turned into bright green from blue. Finally, the concentration of $Na_2S_2O_3$ can be calculated according to Equation 3.1.

$$C_{Na_2S_2O_3} = \frac{6\times(CV)_{K_2Cr_2O_7}}{V_{Na_2S_2O_3}} \quad \text{..... Equation 3.1}$$

Where: $C_{Na_2S_2O_3}$ is concentration of $Na_2S_2O_3$ standard solution; $V_{Na_2S_2O_3}$ is volume of $Na_2S_2O_3$ standard solution; $C_{K_2Cr_2O_7}$ is concentration of $K_2Cr_2O_7$ standard solution; $V_{K_2Cr_2O_7}$ is volume of $K_2Cr_2O_7$ standard solution.

Finally, 2mL sodium hypochlorite solution was dissolved in 100mL deionized water in iodine flask, and 20 mL KI solution (10%) and 10mL H_2SO_4 (1:10) were added. And then it was titrated to light yellow with $Na_2S_2O_3$ solution standardized above. After adding 3mL starch indicator, the titration was continued until the blue disappear. Finally, the concentration of $Na_2S_2O_3$ can be calculated according to Equation 3.2..

$$C_{\text{active chlorine}} = \frac{C_{Na_2S_2O_3}\times V_{Na_2S_2O_3}\times 0.03545\times 100\%}{V_{NaClO}} \text{.....Equation 3.2}$$

Where: $C_{Na_2S_2O_3}$ is concentration of $Na_2S_2O_3$ standard solution; $V_{Na_2S_2O_3}$ is volume of $Na_2S_2O_3$ standard solution; V_{NaClO} is volume of sodium hypochlorite; $C_{\text{active chlorine}}$ is concentration of active chlorine in sodium hypochlorite solution.

3.4 Plasma treatment

Atmospheric pressure plasma (APP) treatment was carried out at different stages of the traditional process in order to enhance the coating of antimicrobial agents on fabric. The Atomflo-200 series (Surfx Technology, US) plasma generator was used for APP treatment of the fabric samples. Gas discharge was ignited by low RF frequency (13.56 MHz). The plasma nozzle was mounted vertically above the sample (Figure 3.1). The carrier gas was helium, while the reactive gas was nitrogen. Flow rate of gases, discharge power, jet-to-substrate distance and fabric moving speed were designed

according to different experimental procedures.

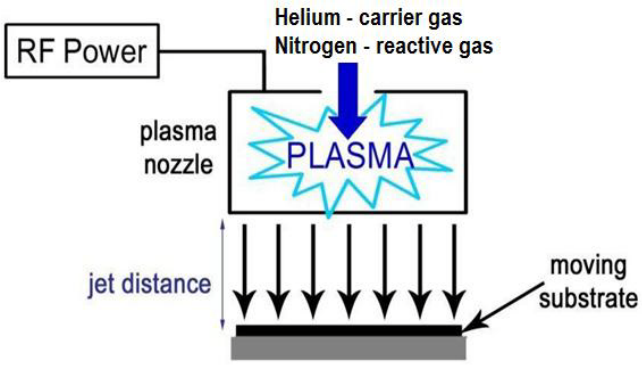

Figure 3.1 Schematic diagram of APP treatment.

3.5 Antimicrobial finishing

3.5.1 Plasma-based antimicrobial finishing

3.5.1.1 Orthogonal experimental procedure

The plasma-based antimicrobial finishing experiments proceeded through orthogonal array testing strategy (OATS) (Kan, 2007; Kan, Yuen, & Wong, 2011; Zhou & Kan, 2014a). Parameters, i.e. discharge power of APP, moving speed of fabric, concentration of sodium hypochlorite and time of chlorination involved in this experiment were investigated; OATS parameters and the experimental arrangements are shown in Tables 3.1 and 3.2. The optimal process parameters could be used in the later antimicrobial finishing process with the coating of antimicrobial agents.

Fabrics were treated with mixture of helium and nitrogen plasma. The flow rate of helium was 15 liter per minute (LPM), the flow rate of nitrogen was 0.2 LPM, and jet-to-substrate distance was 5 mm. The discharge power of APP and the fabric

moving speed were optimized through orthogonal analysis shown in Tables 3.1 and 3.2.

After plasma treatment, fabrics were chlorinated in beaker with stirring at room temperature with sodium hypochlorite to transform some of the amino groups on the finished fabrics into N-halamines and impart antimicrobial properties to cotton fabrics in the plasma-based antimicrobial finishing process. The chlorination was carried out according to orthogonal experiments, and the parameters were shown in Table 3.1. After chlorination, to ensure there was no free chlorine, these fabrics were washed with DI water until the water did not change to blue; this was tested with KI/starch solution. After antibacterial finishing, the cotton fabrics were dried and stored under standard conditions of 20±2ºC temperature and 65±2% relative humidity for at least 24 prior to further evaluation.

Table 3.1 Parameters and levels used in OATS

Level	Parameters			
	Discharge power of APP (W) A	Moving speed of fabric ($\times 10^{-3}$ m/s) B	Concentration of sodium hypochlorite (%) C	Time of chlorination (min) D
Ⅰ	60	4.5	0.8	15
Ⅱ	90	6.0	1.0	30
Ⅲ	120	7.5	1.2	45
Ⅳ	150	9.0	1.4	60

Table 3.2 Experimental arrangement

Test run	Parameters			
	Discharge power of APP (W) A	Moving speed of fabric ($\times 10^{-3}$ m/s) B	Concentration of sodium hypochlorite (%) C	Time of chlorination (min) D
1	Ⅰ	Ⅰ	Ⅰ	Ⅰ
2	Ⅰ	Ⅱ	Ⅱ	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

3.5.1.2 Effect of flow rate of gas on antibacterial activity of cotton fabric

Flow rate of secondary gas should be adjusted according to discharge power of plasma machine shown in Table 3.3. Based on optimal finishing process of plasma-based antimicrobial finishing for cotton fabrics obtained from above experiment, effects of flow rate on antimicrobial activity was investigated. The experiment was designed according to combinations between discharge power and flow rate of secondary gas. The discharge power of plasma treatment for cotton fabrics was 120W; moving speed

of fabrics was 3×10^{-3} m/s; flow rate of nitrogen was 0.2, 0.3 and 0.4 LPM; concentration of sodium hypochlorite was 1.4%; and chlorination time was 60min.

Table 3.3 Combinations between discharge power and flow rate of secondary gas

Discharge power (W)	Flow rate of secondary gas (LPM)
30	≤0.1
60	≤0.2
90	≤0.3
120	≤0.4
150	≤0.5

3.5.2 Plasma-assist 5, 5-dimethylhydantoin (DMH) antimicrobial finishing

3.5.2.1 DMH finishing solution preparation

Finishing bathes with three different concentrations were prepared. To prepare three finishing bathes with concentrations of 2%, 4% and 6%, 16g, 32 g, 48g DMH was dissolved in784mL, 768mL and 752mL de-ionized water separately with stirring for 1 h for complete dissolution.

3.5.2.2 Experimental procedure

Cotton fabrics coated with DMH could be carried out through four finishing processes by combining plasma treatment with pad-dry-cure process. In every finishing process, the parameters of plasma treatment are the optimum conditions obtained from the experiments of plasma treatment for antimicrobial finishing of cotton in Section 3.5.1. The importance of concentration of DMH solution, curing temperature, concentration of sodium hypochlorite and time for chlorination were evaluated by design of

experiments. In the whole antimicrobial finishing processes, samples were immersed in the DMH finishing bath for 10 min before padding. The fabrics were dried at 80ºC for about 5 min. Concentration of DMH solution, curing temperature, concentration of sodium hypochlorite and time for chlorination in each finishing process were arranged with orthogonal technique. These parameters were selected according to properties of DMH and cotton fabrics.

The first process involves first treating the fabric with plasma. After that, the fabric was padded with 80% pick up of DMH solution with Rapid padder (Labortex Co., LTD.). The fabric was then dried and cured with labdryer (Mathis, Switzerland) (i.e. plasma-pad-dry-cure, termed as CPD). In the second process, DMH was first padded on cotton fabric with 80% pick up of DMH solution with Rapid padder (Labortex Co., LTD.). After that, the fabric was treated with plasma and dried as well as cured with labdryer (Mathis, Switzerland) (i.e. pad-plasma-dry-cure, termed as CWPD). In the third process, fabric was first padded with DMH with 80% pick up of DMH solution with Rapid padder (Labortex Co., LTD.) and dried with labdryer (Mathis, Switzerland). The fabric was then treated with plasma and cured with labdryer (Mathis, Switzerland) (i.e. pad-dry-plasma-cure, termed as CDPD). In order to observe the effects of plasma applied in the DMH finishing process, the finishing process of cotton fabric was carried out with traditional “pad-dry-cure” process without plasma treatment, that is, cotton fabric was first padded with DMH with 80% pick up of DMH solution with Rapid padder (Labortex Co., LTD.) and then dried and cured with labdryer (Mathis, Switzerland) (termed as CD).

After these procedures, fabrics were chlorinated in beaker with stirring at room temperature with sodium hypochlorite to transform some of the amino groups on the finished fabrics into N-halamines and impart antimicrobial properties to cotton fabrics. After chlorination, to ensure there was no free chlorine, these fabrics were washed with de-ionized water until the water did not change to blue; this was tested with KI/starch solution. After antibacterial finishing, the cotton fabrics were dried and stored under standard conditions of 20±2ºC temperature and 65±2% relative humidity for at least 24 prior to further evaluation.

3.5.2.3 Parameters for optimization of treatment conditions through OATS

An OATS technique was employed to analyze the optimum treatment conditions. Four process parameters, i.e. concentration of DMH, temperature of curing, concentration of bleaching solution and duration of chlorination were investigated; experimental arrangements were as shown in Tables 3.4 and 3.5 (Zhou & Kan, 2014a).

Table 3.4 Parameters and levels used in OATS

Parameters		Concentration of DMH (%)	Temperature of curing (ºC)	Concentration of bleaching solution (%)	Time of chlorination (min)
Sign		A	B	C	D
Level	Ⅰ	2	120	0.8	20
	Ⅱ	4	140	1.0	40
	Ⅲ	6	160	1.2	60

Table 3.5 Experimental arrangement

Test run	Parameters			
	Concentration of DMH (%) A	Temperature of curing (ºC) B	Concentration of bleaching solution (%) C	Time of chlorination (min) D
1	Ⅰ	Ⅰ	Ⅰ	Ⅰ
2	Ⅰ	Ⅱ	Ⅱ	Ⅱ
3	Ⅰ	Ⅲ	Ⅲ	Ⅲ
4	Ⅱ	Ⅰ	Ⅱ	Ⅲ
5	Ⅱ	Ⅱ	Ⅲ	Ⅰ
6	Ⅱ	Ⅲ	Ⅰ	Ⅱ
7	Ⅲ	Ⅰ	Ⅲ	Ⅱ
8	Ⅲ	Ⅱ	Ⅰ	Ⅲ
9	Ⅲ	Ⅲ	Ⅱ	Ⅰ

3.5.2.4 Comparison of antimicrobial cotton finished with DMH with plasma treatment at different stage

Four different processes mentioned above in Section 3.5.2.2 were used for coating cotton fabric with DMH. In these four finishing processes, concentration of DMH solution used in the finishing processes are 4%, fabrics were cured at 160ºC for about 5 min, concentration of sodium hypochlorite for chlorination is 0.8%, 1.0% and 1.2%, and fabrics were chlorinated about 10, 20, 40 and 60 min, respectively.

3.5.3 Plasma-assist chitosan antimicrobial finishing

In order to observe the differences of antimicrobial cotton fabric finished with different antimicrobial agents, cotton fabric was finished with chitosan with plasma treatment.

3.5.3.1 Chitosan finishing solution preparation

To prepare three finishing bathes with concentrations of 4%, 32g chitosan was dissolved in 768mL de-ionized water and added 2.4mL glacial acetic acid with stirring for 1 h for complete dissolution.

3.5.3.2 Experimental procedure

Cotton fabrics coated with chitosan were carried out through four finishing processes by combining plasma treatment with pad-dry-cure process. The parameters of plasma treatment are the optimum conditions obtained from the experiments of plasma treatment for antimicrobial finishing of cotton in Section 3.5.1. The parameters in the finishing processes were selected according to the properties of chitosan and cotton fabrics.

The first process involved first treating the fabric with plasma. After that, the fabric was padded with 80% pick up of chitosan solution with Rapid padder (Labortex Co., LTD.). The fabric was then dried at 90 ºC for about 5 min and cured at 140 ºC for about 10 min with labdryer (Mathis, Switzerland) (i.e. plasma-pad-dry-cure, termed as CPC). In the second process, chitosan was first padded on cotton fabric with 80% pick up of chitosan solution with Rapid padder (Labortex Co., LTD.). After that, the fabric was treated with plasma and dried at 90 ºC for about 5 min as well as cured at 140 ºC for about 10 min with labdryer (Mathis, Switzerland) (i.e. pad-plasma-dry-cure, termed as CWPC). In the third process, fabric was first padded with chitosan with 80% pick up of chitosan solution with Rapid padder (Labortex Co., LTD.) and dried at 90 ºC for

about 5 min with labdryer (Mathis, Switzerland). The fabric was then treated with plasma and cured at 140 ºC for about 10 min with labdryer (Mathis, Switzerland) (i.e. pad-dry-plasma-cure, termed as CDPC). In order to observe the effects of plasma applied in the chitosan finishing process, the finishing process of cotton fabric was carried out with traditional “pad-dry-cure” process without plasma treatment, that is, cotton fabric was first padded with chitosan with 80%pick up of chitosan solution with Rapid padder (Labortex Co., LTD.) and then dried at 90 ºC for about 5 min and cured at 140 ºC for about 10 min with labdryer (Mathis, Switzerland) (termed as CC).

After these procedures, fabrics were washed with 0.5 mol/L sodium hydroxide solution at room temperature for 30 min and stirred to neutralize the acetic acid adequately, and then the fabrics were washed with de-ionized water sufficiently and dried. And then, the fabrics treated with the same coating process were chlorinated in beaker with stirring at room temperature with 0.8, 1.0 and 1.2 % of sodium hypochlorite solution over 10, 20, 40 and 60 min respectively, to transform some of the amino groups on the finished fabrics into N-halamines and impart antimicrobial properties to cotton fabrics. After chlorination, to ensure there was no free chlorine, these fabrics were washed with de-ionized water until the water did not change to blue; this was tested with KI/starch solution. After antibacterial finishing, the cotton fabrics were dried and stored under standard conditions of 20±2ºC temperature and 65±2% relative humidity for at least 24 prior to further evaluation.

3.6 Evaluation of cotton fabrics

3.6.1 Fourier Transform Infrared Spectroscopy with Attenuated Total Reflection Mode (FTIR-ATR)

FTIR-ATR spectrometer, Spectrum 100 was used to detect the chemical composition 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 was calculated to remove the noise in the FTIR-ATR spectroscopy data.

3.6.2 The active chlorine content of the fabric

The active chlorine content on fabric was measured by colorimetric method. In this study, 0.1 g of 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 mixture was 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. The same amount of unchlorinated cotton fabric was treated under the same conditions as control.

Active chlorine content on the chlorinated sample was calculated according to the absorbance tested by UV spectrophotometer Lambda 18. Firstly, the absorbance of sodium hypochlorite was tested under spectrum ranging from 400nm to 700nm, and the wavelength of maximum absorption (λ_{max}) was found out. 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} was 427.60 nm.

3.6.3 Regenerability

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

3.6.4 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 six months at 20 ± 2 ºC and 65 ± 2% relative humidity, their active chlorine content was tested again.

3.6.5 Antibacterial test

Antibacterial activity of samples was tested referring to AATCC Test Method 147-2011. Staphylococcus aureus (ATCC 6538) was used as the model bacteria (Gouda & Ibrahim, 2008; Mohammadkhodaei, Mokhtari, & Nouri, 2010; Sathianarayanan, Bhat, Kokate, & Walunj, 2010; Scholz, Nocke, Hollstein, & Weissbach, 2005; Sun & Xu, 1999). The bacteria were inoculated in a blood agar plate and incubated at 37 ºC 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. Then, the suspension was diluted to 100-fold. After that, the diluted suspension was inoculated on new sterile blood agar plates using the Autoplate 4000 microprocessor-controlled Spiral Platter (Advanced Instruments, Inc.) and fresh prepared samples (20×20 mm) were placed on the seeded agar surfaces. After standing for 5-10 min, these plates were placed in the aerobic incubator and incubated at 37 ºC for 48 h. Finally, clear zones were observed to evaluate the antibacterial activity of samples.

3.6.6 Scanning Electron Microscope (SEM)

JEOL Model JSM-6490 SEM was used for observation of the surface morphological change. Magnification of the image was set at 4000x.

3.6.7 Tearing strength

Elmatear Digital Tear Tester (James H. Heal & CO. LTD. Halifax England) was used to test tearing strength of fabric according to ASTM D1424-09. Maximal capacity of testing machine used in this test was 32N.

3.6.8 Weight change

The weight of all test specimens with the size of 200mm×100mm was measured by the AG204 DeltaRange Electronic Balance (METTLER TOLEDO) before and after treatment. 40 samples were measured to obtain the averaged result for the treatment. Positive change implied a gain in the weight while negative change indicated a weight loss of the substrate. The percentage change of fabric weight was calculated by Equation 3.3:

$$\text{Weight Change (\%)} = \frac{W-W_0}{W_0} \times 100\% \quad \text{. . . . . Equation 3.3}$$

Where: W (g) is weight of the substrate after treatment; W_0 (g) is initial weight of the substrate.

3.7 Conclusion

Several finishing processes were used to regenerable antimicrobial finishing of cotton fabrics. And physical, chemical, mechanical and biological properties of regenerable antimicrobial cotton fabrics were investigated through numerous evaluation methods. By means of these comprehensive analyses, an applicable regenerable antimicrobial finishing process could be obtained and cotton fabrics with regenerable antimicrobial properties would be developed.

CHAPTER 4 NITROGEN PLASMA TREATMENT OF COTTON FABRIC

4.1 Introduction

Textiles made from cotton fibers are breathable, absorbent and comfortable to wear due to the porous hydrophilic structure. Since the structure is such that it retains water and oxygen easily, it provides a suitable environment for the growth of microorganisms. This makes cotton textiles susceptible to bacteria (Shahidi et al., 2007; Zhou & Kan, 2014b; Zhou & Kan, 2015). Therefore it is essential to enable cotton fabrics with antibacterial property, particularly in view of the growing emphasis upon health and hygiene nowadays.

Conventional antibacterial finishing involves numerous chemicals which may be harmful to environment. Environmental protection is an issue the textile industry has to address. Plasma technology relieves the problem to some extent because plasma is a dry process for surface modification. The application principle of plasma is that the feed gas is converted into active particles by electrical energy applied from plasma reactor. These active particles impinge on the surface of the fabric and rupture the chemical bonds, forming free radicals on the surface. These free radicals react with oxygen and water in surroundings to form oxidation surface and these radicals also polymerize with other chemicals to introduce various functional groups onto the material surface (Abidi & Hequet, 2004; Inagaki, 1984; Inagaki, 2000; Kuo et al., 2010; Narushima et al., 2007; Poll et al., 2001; Virk et al., 2004; Zhou & Kan, 2014b).

The final treatment effect mostly depends on the nature of gases used (Kan et al., 1998; T. Yasuda et al., 1984). For example, nitrogen plasma introduces several N-containing groups on the material surface, including $–NH_2$, -NH, =NH, $CONH_2$ and C≡N (Shahidi et al., 2010; Silva et al., 2008; Zhou & Kan, 2014b). Plasma treatment changes only the uppermost atomic layers of material surface and bulk of the properties remain unaffected (Bhat & Benjamin, 1999; Poll et al., 2001).

Recently, regenerable antibacterial textiles have gained much popularity. These fabrics are finished with N-halamines, chemicals containing amine, amide and amide halamine bonds which have the capability of rapidly and totally inactivating a wide spectrum of micro-organisms (Y. Sun & Sun, 2001a; Y. Sun & Sun, 2001b; Y. Sun & Sun, 2001c; Y. Sun & Sun, 2002). Chlorine in N-halamine is consumed in the process of inactivation of the bacteria and it can be regenerated with sodium hypochlorite. In order to protect the environment and improve production efficiency, N-halamine structure was introduced on the surface of cotton fabric with nitrogen plasma treatment directly, and then investigated its antibacterial property.

4.2 Optimization of nitrogen plasma treatment for cotton fabric

Orthogonal analysis is a convenient method to optimize experiments containing several variables or factors. It is easy to obtain the optimum conditions and the importance of different factors in experiments through orthogonal experiments. The mean clear width of sample against *S. aureus* (ATCC 6538) from sample to bacteria is used to evaluate antibacterial effect of sample illustrated in Figure 4.1 (Gouda &

Ibrahim, 2008; Mohammadkhodaei et al., 2010; Sathianarayanan et al., 2010; Scholz et al., 2005; Sun & Xu, 1999). The clear width matches with the antibacterial activity. The mean clear widths of the samples against *S. aureus* obtained from the nine specimens generated by the OATS technique and the result of orthogonal analysis, where T_{mn} refers to the sum of the evaluation indexes of all levels (n, n=I, II, III) in each factor (m, m=A, B, C), such that T_{AI}=1.329+1.285+1.300+1.400=5.314 is the sum of level I of factor A; T_{CII}=1.285+1.307+1.471+1.399=5.462 is the sum of level II of factor C; and K_{mn} implies the mean value of T_{mn}, such that $K_{AI}=T_{AI}/4$=5.314/4=1.329 is the mean value of T_{AI}; $K_{CII}=T_{CII}/4$=5.462/4=1.366 is the mean value of T_{CII} are shown in Table 4.1. In addition, T is the sum of the evaluation indexes, w_i, which is an evaluating indicator for antimicrobial activity of cotton fabrics evaluated by AATCC Test Method 147-2011; and the range of factors in each column, R=Max(K_j)-Min(K_j), indicates the function of the corresponding factor (Chuanwen, Feng, Yuguo, & Shuyun, 2010). The larger value of R means the greater impact of the level of the factor on the experimental index. Therefore, the impact of every factor on the final treatment effect can be distinguished clearly on the comprehensive condition that every factor changes. The results of orthogonal analysis for four parameters used in the finishing process are shown in Table 4.1and the order of importance of these factors is $R_A > R_C > R_B > R_D$. That is, discharge power of APP has the greatest impact on the experimental result, and concentration of sodium hypochlorite has a comparatively less impact, next factor in the order is moving speed of fabric, and the last one is time of chlorination (Chuanwen et al., 2010; Kan et al., 2011). The best level is suggested by orthogonal analysis based on the mean value of the testing factors. Thus, the optimum process for DMH coating

is $A_{III}B_{I}C_{IV}D_{IV}$, that is, discharge power of APP = 120W, moving speed of fabric = 4.5×10^{-3}m/s, concentration of sodium hypochlorite =1.4% and time of chlorination = 60min. When cotton fabric is treated under the optimum conditions and the mean clear width against *S. aureus* is 1.839 mm, which is wider than the mean clear width of the other nine specimens in Table 4.1. Therefore, the optimum conditions were verified. The samples are used for further evaluation in regeneration ability, FTIR-ATR and SEM.

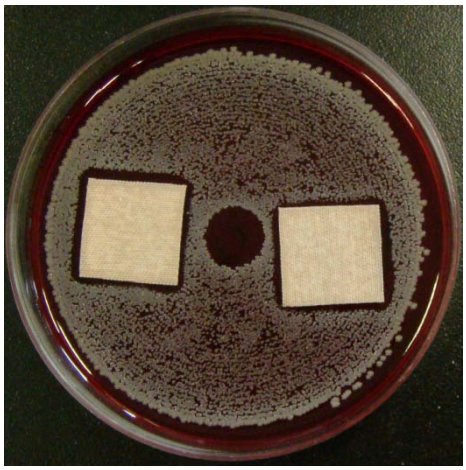

Figure 4.1 Example of antibacterial test

Table 4.1 Orthogonal table for optimizing the antibacterial property of cotton fabric treated with plasma[a]

Test run	Parameters				Results
	Discharge power of APP (W) A	Moving speed of fabric ($\times 10^{-3}$ m/s) B	Concentration of sodium hypochlorite (%) C	Time of chlorination (min) D	Mean Clear Width against *S. aureus* (mm) w_i
1	Ⅰ	Ⅰ	Ⅰ	Ⅰ	1.329
2	Ⅰ	Ⅱ	Ⅱ	Ⅱ	1.285
3	Ⅰ	Ⅲ	Ⅲ	Ⅲ	1.300
4	Ⅰ	Ⅳ	Ⅳ	Ⅳ	1.400
5	Ⅱ	Ⅰ	Ⅱ	Ⅲ	1.307
6	Ⅱ	Ⅱ	Ⅰ	Ⅳ	1.336
7	Ⅱ	Ⅲ	Ⅳ	Ⅰ	1.314
8	Ⅱ	Ⅳ	Ⅲ	Ⅱ	1.195
9	Ⅲ	Ⅰ	Ⅲ	Ⅳ	1.667
10	Ⅲ	Ⅱ	Ⅳ	Ⅲ	1.806
11	Ⅲ	Ⅲ	Ⅰ	Ⅱ	1.567
12	Ⅲ	Ⅳ	Ⅱ	Ⅰ	1.471
13	Ⅳ	Ⅰ	Ⅳ	Ⅱ	1.667
14	Ⅳ	Ⅱ	Ⅲ	Ⅰ	1.163
15	Ⅳ	Ⅲ	Ⅱ	Ⅳ	1.399
16	Ⅳ	Ⅳ	Ⅰ	Ⅲ	1.263
T_{mI}	5.314	**5.970**	5.495	5.277	$T_{mn}=\sum_{i=1}^{9} w_i$
T_{mII}	5.152	5.590	5.462	5.714	
T_{mIII}	**6.511**	5.580	5.325	5.676	$K_{mn}=\frac{1}{3}T_{mn}=\frac{1}{3}\sum_{i=1}^{9} w_i$
T_{mVI}	5.492	5.329	**6.187**	**5.802**	
K_{mI}	1.329	1.492	1.374	1.319	
K_{mII}	1.288	1.398	1.366	1.419	
K_{mIII}	1.628	1.395	1.331	1.451	$R = \mathrm{Max}(K_{mI}, K_{mII}, K_{mIII}) - \mathrm{Min}(K_{mI}, K_{mII}, K_{mIII})$
K_{mVI}	1.373	1.332	1.547	1.451	
R	*1.359*	*0.641*	*0.862*	*0.525*	

[a]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.

As shown in Figure 4.2, the mean clear width of samples against *S. aureus* fluctuates with the increase of discharge power. When the discharge power is 120W, the mean clear width is greater than under other discharge powers. And the value of mean clear width fluctuates around 1.33±0.05 mm when the discharge power is 60, 90 or 150W.

The reason is that a higher discharge power is more effective in substrate surface breakage providing more active particles to form N-containing groups, leading to enhancement of antibacterial activity of samples. However, high discharge power of plasma transfers high temperature energy to the material surface resulting in over-drying and hardening, which affects the reaction of free radicals with molecules on material surface (Wong et al., 1999; Yasuda et al., 1984). Therefore, when discharge power is higher than 120W, the antibacterial activity of samples reduces.

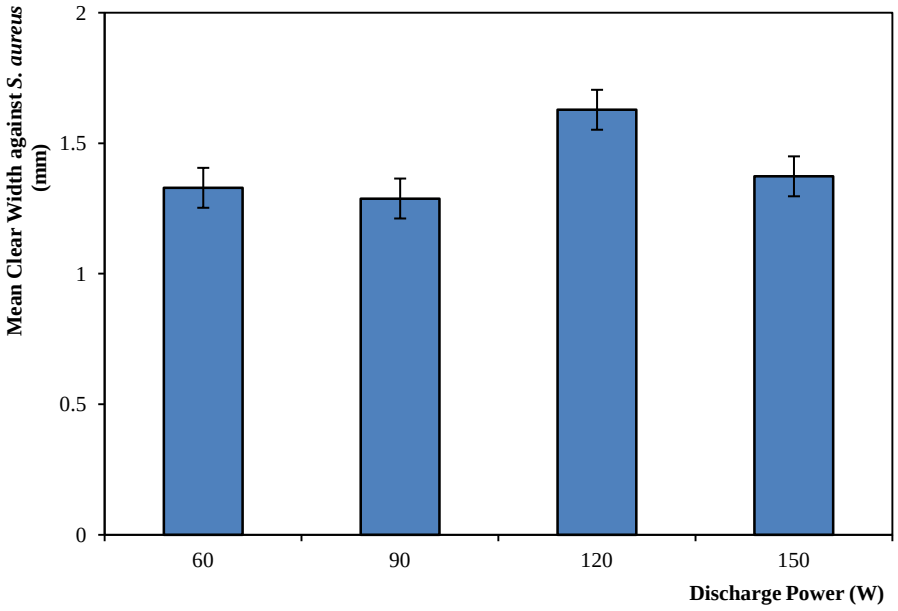

Figure 4.2 Effect of discharge power of APP on antibacterial property of cotton fabric treated with plasma.

As shown in Figure 4.3, the mean clear width of the sample against *S. aureus* decreases with the increase of moving speed of fabric. That is because interaction time between fabric per unit area and plasma decreases with the increase of moving speed of fabric. Short plasma exposure of the sample reduces density of free radicals generated by plasma. Then molecules have fewer opportunities to react with these free radicals and

fewer new functional groups are formed on the material surface.

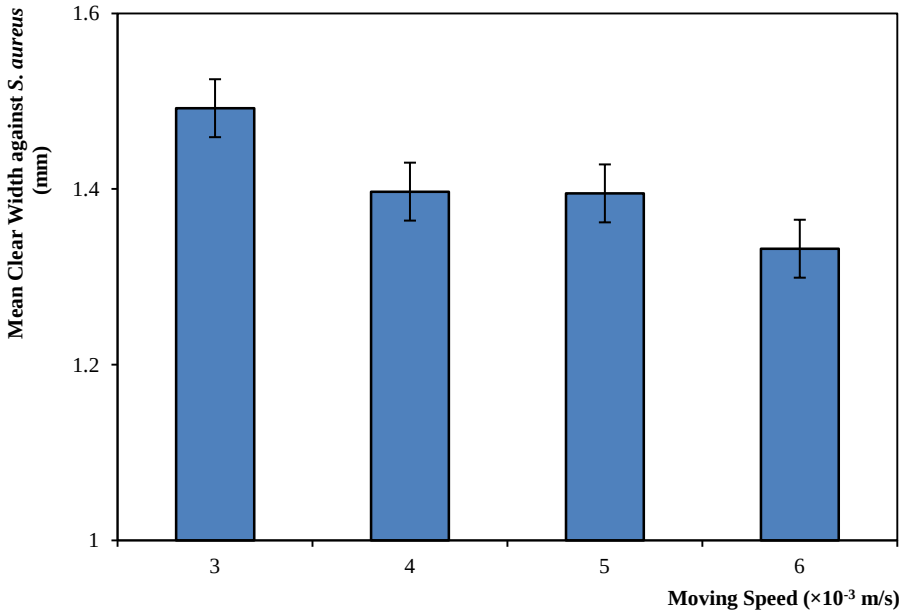

Figure 4.3 Effect of moving speed of fabric on antibacterial property of cotton fabric treated with plasma.

As shown in Figure 4.4, the mean clear width of sample against *S. aureus* decreases as concentration of sodium hypochlorite increases up to 1.2%; after concentration exceeds 1.2% mean clear width of sample against *S. aureus* increases with the increase of concentration. That is because sodium hypochlorite with high concentration has strong oxidizing power (Yu, Ma, & Wu, 2012). With the increase of concentration sodium hypochlorite can oxidize functional groups on material surface, which reduces its chlorination efficiency to N-containing groups. However, when the concentration of sodium hypochlorite is higher than 1.2%, chlorine in sodium is enough for both chlorination of N-containing groups and oxidation of other groups. Thus, the antibacterial activity becomes inactive at first and then increases with the increase of concentration of sodium hypochlorite.

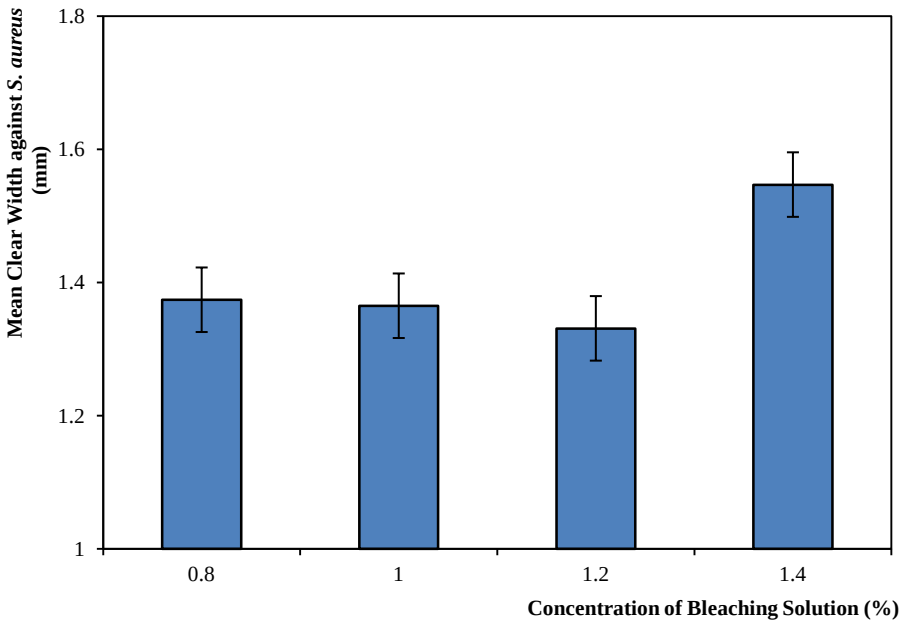

Figure 4.4 Effect of concentration of sodium hypochlorite on antibacterial property of cotton fabric treated with plasma.

The mean clear width of samples against *S. aureus* shown in Figure 4.5 increases significantly with extension of chlorination time up to 30 min, beyond which the mean clear width remains approximately stable, although there is a little increase when chlorination time is 60 min. That is caused by quantitative limitations of N-containing groups on material surface. When fabric is chlorinated for 30 min, chlorine on fabric is nearly saturated. Thus, when chlorination time is longer than 30 min, antibacterial activity is nearly constant. Considering the time cost, the chlorination time should be 30 min. However, given the amount of chlorine on fabric and environment, the chlorination time should be 60 min.

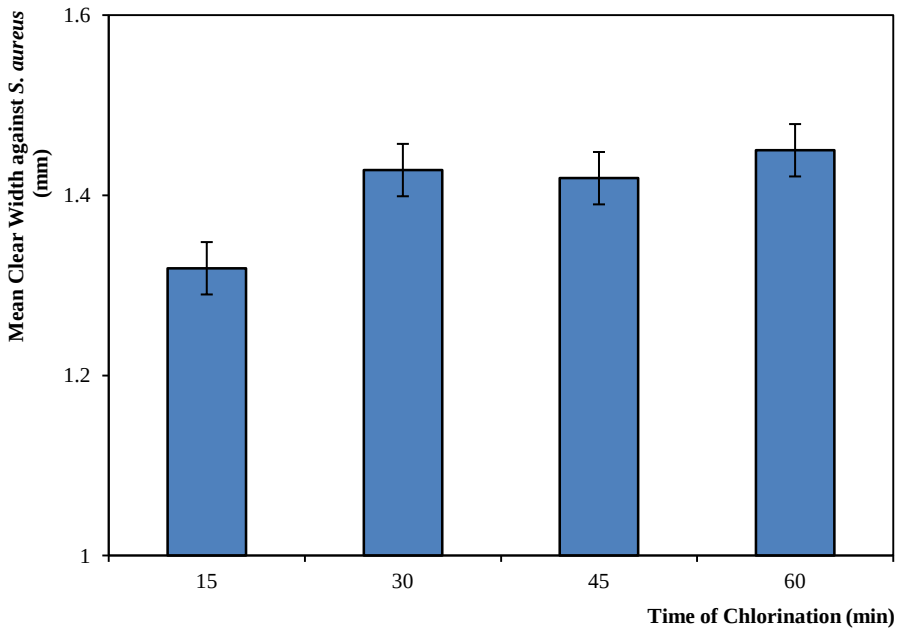

Figure 4.5 Effect of time of chlorination on antibacterial property of cotton fabric treated with plasma.

4.3 Evaluation

4.3.1 Relationship between antibacterial property and concentration of chlorine on cotton fabric

The relationship between antimicrobial activity and concentration of chlorine on cotton fabric is shown in Figure 4.6; it is seen that the mean clearance width against *S. aureus* becomes wider with increase of concentration of chlorine on cotton fabric treated with nitrogen plasma, which appears to be a linear relationship, and the fitting linear equation is $y = 0.2039x + 0.3571$ and decisive coefficient $R^2 = 0.9614$. That is because the antimicrobial principle of the cotton fabric treated with nitrogen plasma is that chlorine is used to kill microorganisms. When the content of chlorine increases, more bacteria can be killed. Therefore, the effective method to improve the antimicrobial activity of cotton fabric is to increase the amount of chlorine on cotton

fabric.

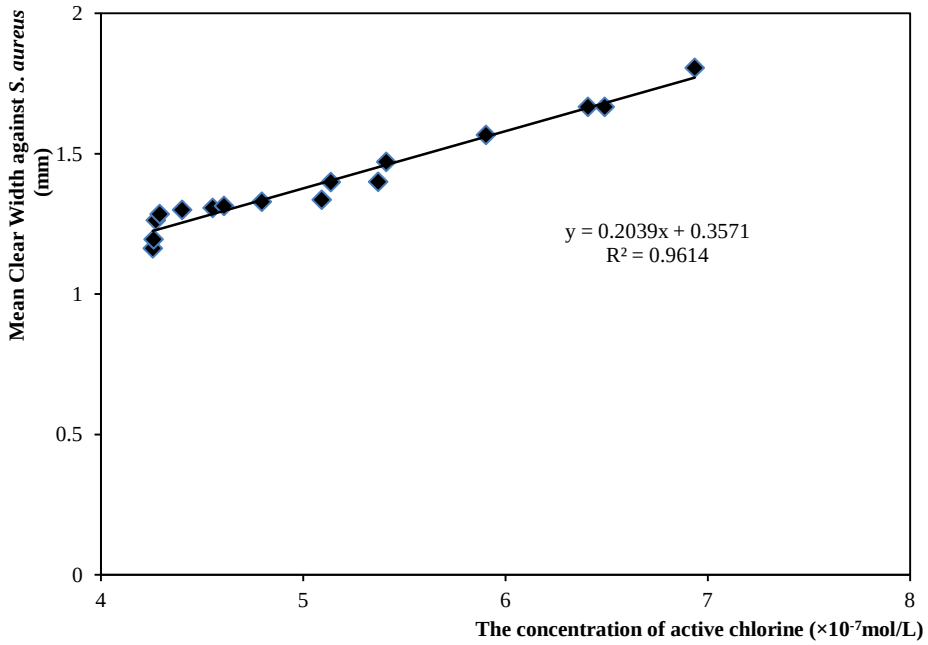

Figure 4.6 Relationship between antimicrobial property and concentration of chlorine on cotton fabric.

4.3.2 FTIR

The FTIR-ATR spectra were employed to characterize the variation of substrate surface after plasma treatment. The second derivative FTIR-ATR spectrum of untreated cotton fabric (Figure 4.7a), cotton fabric treated with plasma (Figure 4.7b), cotton fabric treated with plasma followed with chlorination (Figure 4.7c) is shown in Figure 4.7.

Compared with Figure 4.7a, absorbance peak at around 1550 cm^{-1} represents the deformation of N-H and absorbance peak in 1750 cm^{-1} region is assigned to the stretching vibration of C=O of carboxyl group in Figures 4.7 (b) and 4.7 (c) (Hui, Guan, & Hou, 2005). This demonstrates that particles N_2^+, N_2 (excited), N, N^+ and

electrons generated in nitrogen plasma treatment introduce nitrogen-containing groups on cotton fabrics and oxidize the primary hydroxyl group to carboxyl group (Zhou & Kan, 2015).

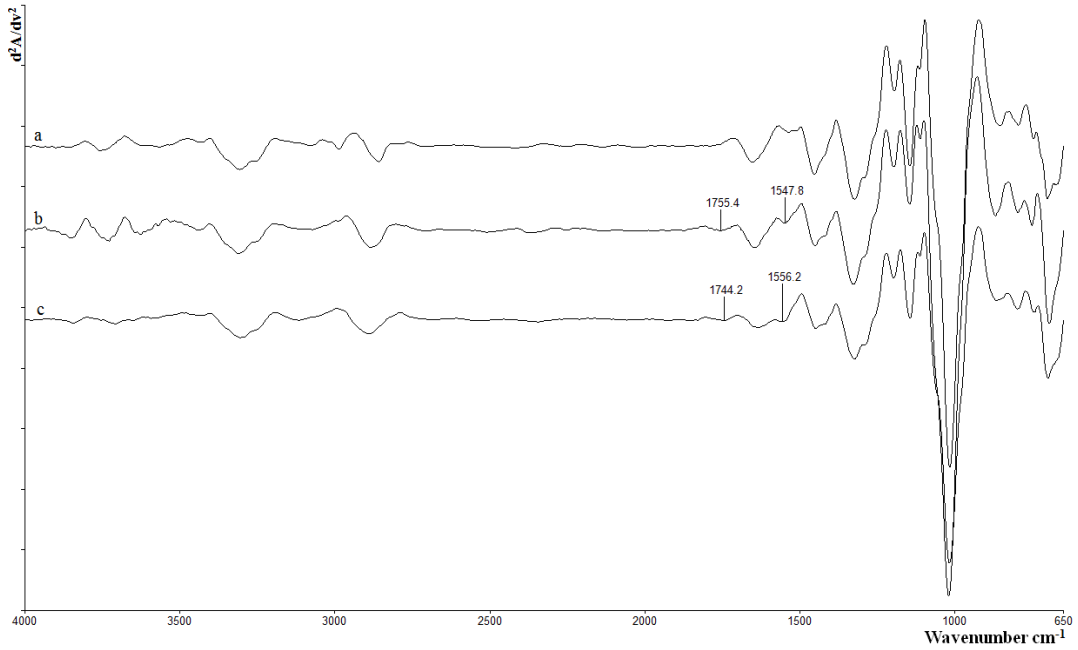

Figure 4.7 Second derivative FTIR spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric treated with plasma followed with chlorination.

In order to eliminate the effect of environmental factors, spectral subtraction was employed to process the second derivative FTIR-ATR spectrum data (Figure 4.8), that is, untreated cotton fabric was subtracted from cotton fabric treated with plasma (Figure 4.8a) and cotton fabric treated with plasma followed with chlorination (Figure 4.8b). It is observed that absorbance still peaks at around 1550 cm^{-1} and 1750 cm^{-1} which represent N-H deformation and C=O stretching vibration, respectively. Accordingly, nitrogen plasma treatment introduces N-containing group and carboxyl group on the surface of cotton fabric.

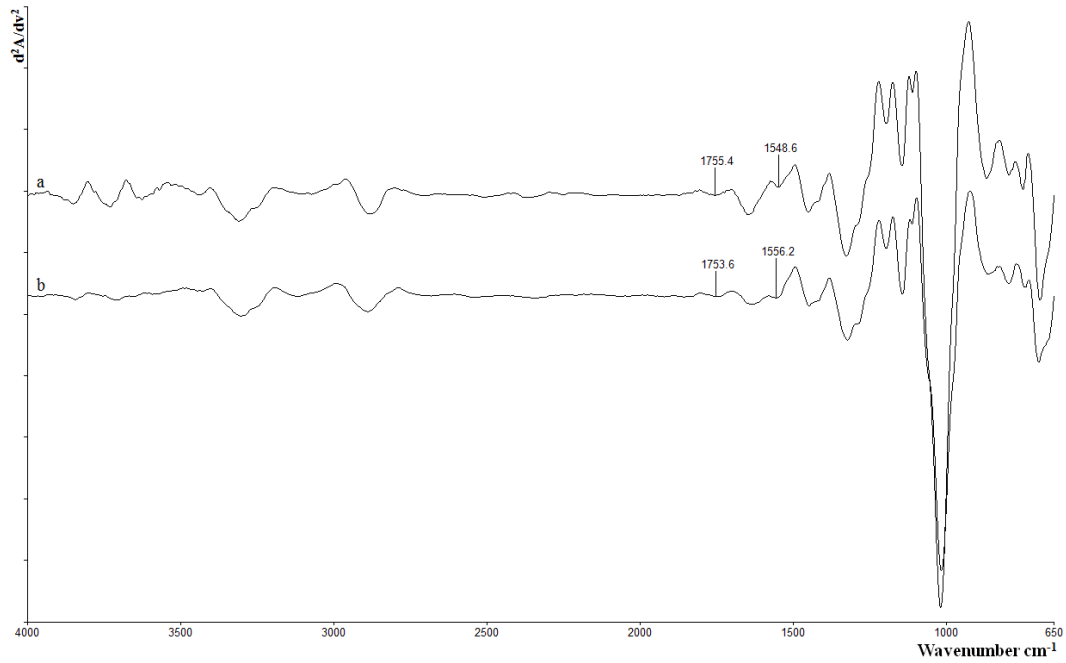

Figure 4.8 Spectral subtraction of second derivative FTIR spectrum of (a) cotton fabric treated with plasma - untreated cotton fabric, (b) cotton fabric treated with plasma followed with chlorination - untreated cotton fabric.

4.3.3 Regenerability

Regenerability is extremely important for antimicrobial textiles. It extends service life of antimicrobial textiles. The content of active chlorine on fabric before washing (BW), after washing (AW) and after rechlorination (AW+CH) is shown in Figure 4.9.

Compared with concentration of chlorine on fabric before washing (Figure 4.9), it is found that concentration of chlorine on fabric decreases slightly after laundering. However, concentration of chlorine on cotton fabric after rechlorination is approximately the same as before washing. That is because cotton fabric and N-containing groups introduced by nitrogen plasma are connected by chemical bonds, which are stable. Therefore, antibacterial activity of cotton fabric finished by nitrogen

plasma treatment is stable and regenerable.

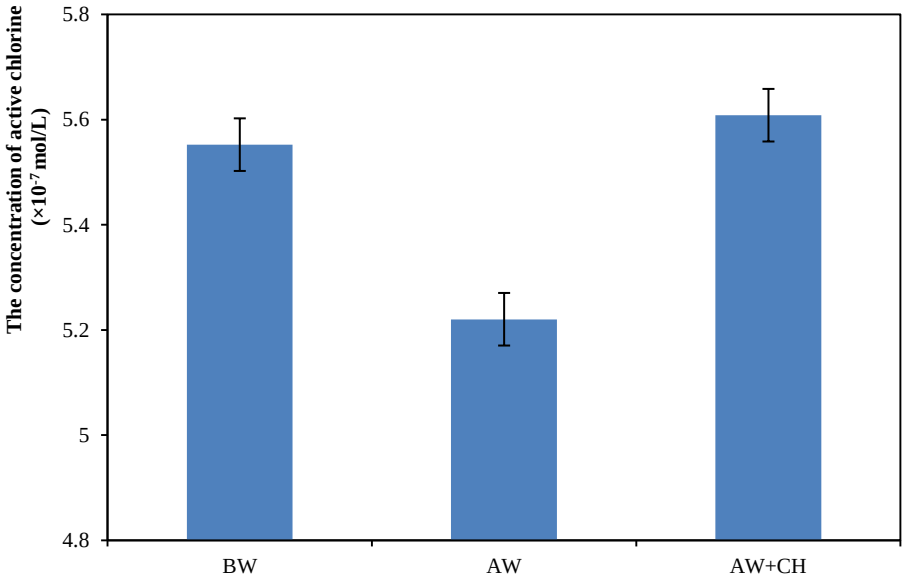

Figure 4.9 Regenerability of cotton fabric with plasma treatment.

4.3.4 SEM

SEM was used to evaluate the variation of fiber surface before and after plasma treatment. Based on Figure 4.10, it is found that the surface of the untreated fibers is smoother than cotton fibers with plasma treatment (Figure 4.10a and 4.10b). This is due to the etching effect caused by interaction of plasma particles with the fiber surface forming micro-cracks on plasma treated fibers. Thus, fiber surface becomes rougher after plasma treatment (Shahidi et al., 2010; Tourrette et al., 2009). This is helpful for adhesion of chemicals to the material surface. Meanwhile, these micro-cracks result in the increase of surface area providing more place for the adhesion of chemicals.

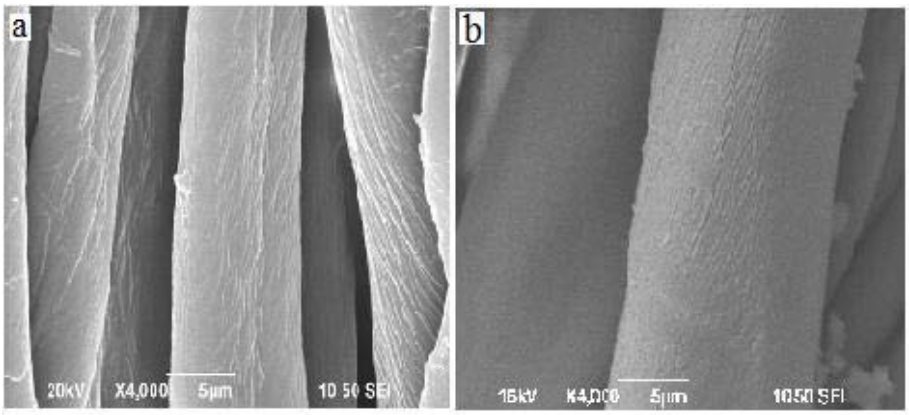

Figure 4.10 SEM image of (a) untreated cotton fabric, (b) cotton fabric treated with plasma treatment

4.3.5 Tearing strength

The tearing strength of cotton fabrics with and without plasma treatment is shown in Table 4.2. Due to plasma treatment, tearing strength of cotton fabrics decreases about 10% in both warp and weft directions (Table 4.2). That is because etching effect of plasma treatment increases the surface friction and roughness which restrict the sliding action of yarn during tearing. Therefore, the tearing strength decreases after plasma treatment (Cheng et al., 2010; Kan, Chan, & Yuen, 2004). Although the tearing strength of cotton fabrics declines after plasma treatment, it still satisfies the basic requirements of textiles (Zeng, 2012). Therefore, plasma treatment in this antibacterial finishing has no significant effect on the tearing strength of cotton fabrics.

Table 4.2 The tearing strength of the cotton fabric in both warp and weft directions.

Sample	Untreated	Plasma treated
Tearing strength in warp direction (N)	14.35	12.92
Tearing strength in weft direction (N)	9.05	8.23

4.4 Effect of flow rate of N_2 on antimicrobial activity of cotton fabric

Based on optimal finishing process, the effect of flow rate of N_2 on antimicrobial activity of fabric is shown in Table 4.3. According to Table 4.3, mean clear width of fabric against *S. aureus* increases with the increase of nitrogen flow rate. The reason is that more active particles generated in plasma generator with the increase of nitrogen flow rate, and then fabric has more opportunities to react with these active particles. This results in the formation of functional groups containing nitrogen which inhibit microorganisms. Therefore, it is a practical way to increase the flow rate of nitrogen to enhance the content of functional groups to substrate.

Table 4.3 Effect of flow rate of N_2 on antimicrobial activity of cotton fabric

Flow rate of N_2 (LPM)	Mean Clear Width against *S. aureus* (mm)
0.2	1.266
0.3	1.384
0.4	1.535

4.5 Effect of plasma treatment on weight of fabric

Weight change is evaluated to observe the effect of plasma treatment on the properties of cotton fabrics. The effects of discharge power, nitrogen flow rate on weight change of fabrics and moving speed of fabrics are studied as shown in Figure 4.11, Figure 4.12 and Figure 4.13, respectively.

As shown in Figure 4.11, weight loss increases with the increase of discharge power. That is mainly caused by the etching effect of plasma treatment (Wong et al., 1999;

Yoon, Lim, Tahara, & Takagishi, 1996), that is, species generated in plasma generator possess active energy, which collide with material surfaces to destroy its microstructure resulting in the weight loss of material. Therefore, much higher discharge power for plasma treatment is not always better in view of the bulk property of cotton fabric.

From Figure 4.12, it is found that the weight loss decrease with the increase of nitrogen flow rate. That is because the etching effect of plasma is accompanied with plasma polymerization of active particles generated in plasma generator, that is, the flow rate of helium in this research remains unchanged, and active particles containing nitrogen in the N_2/He mixed plasma react with the material surface forming new groups, which partly recoups weight loss of fabrics caused by the etching effect of helium plasma (Kale & Desai, 2011; Yasuda et al., 1984). This also proves that antimicrobial activity become strong with the increase of flow rate of nitrogen and etching effect of plasma treatment is more significant than plasma polymerization. Consequently, although high flow rate of nitrogen can compensate for the weight loss of fabrics by introducing functional groups, it must be set depending on the instructions of plasma machine.

According to Figure 4.13, it can be seen that weight loss decreases with the increase of moving speed of fabrics. That is because, with the increase of moving speed of fabrics, plasma species have less time to contact with fabric and less plasma species interact with fabric surfaces. That is why antimicrobial activity decreases with the increase of moving speed of fabrics. Thus, long duration of plasma treatment results in weight loss of fabrics significantly.

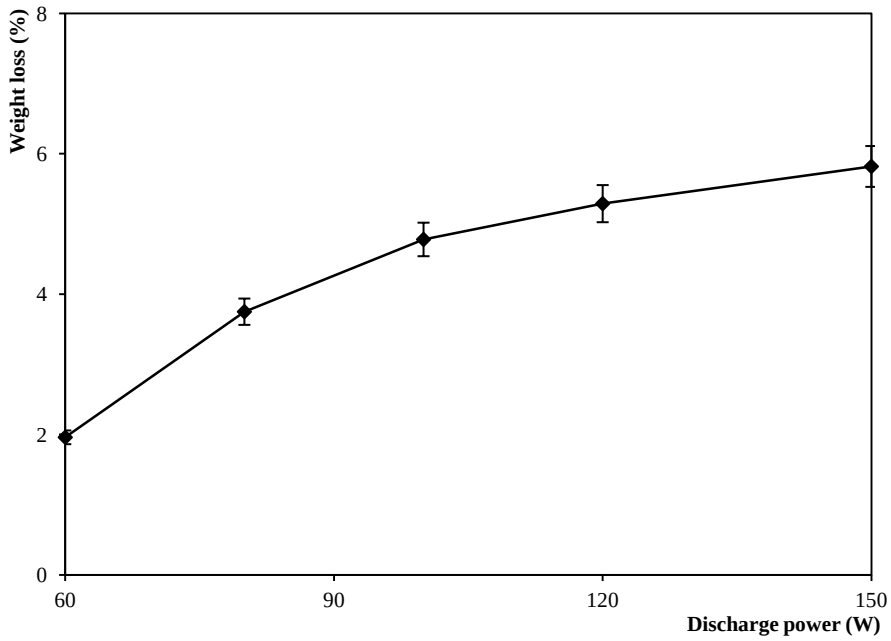

Figure 4.11 Effect of discharge power on weight loss of fabrics

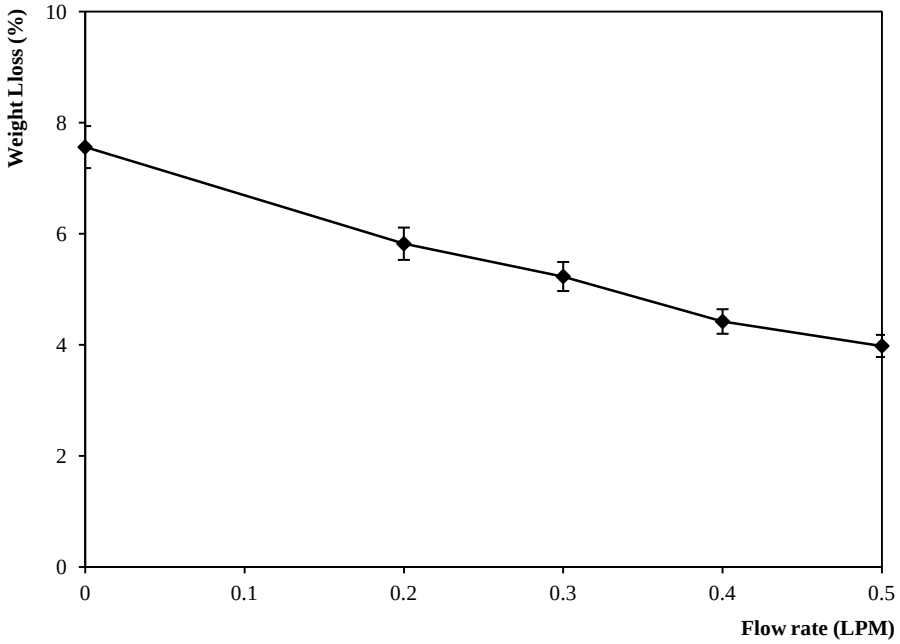

Figure 4.12 Effect of nitrogen flow rate on weight loss of fabric

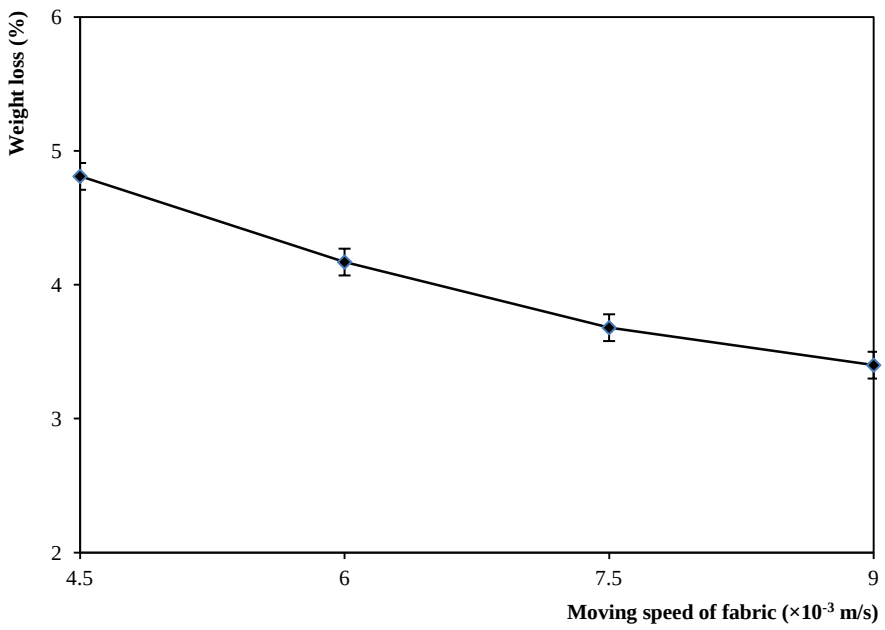

Figure 4.13 Effect of moving speed of fabrics on weight loss of fabrics

4.6 Conclusion

Nitrogen plasma can introduce nitrogen-containing group onto the surface of cotton fabrics. After chlorination with sodium hypochlorite, the cotton fabrics are antimicrobial and can inhibit the bacteria, *S. aureus*, effectively. And the antimicrobial activity can be recharged.

The optimum conditions for the finishing process for antimicrobial property in this research are discharge power of APP = 120W, moving speed of fabric = 4.5×10^{-3}m/s, concentration of sodium hypochlorite =1.4% and time of chlorination = 60min. This study finds the relationship of the mean clear width of fabric against *S. aureus* under varying parameters for the antibacterial finishing process, including discharge power of APP, moving speed of fabric, concentration of sodium hypochlorite and time of chlorination. When discharge power of APP is 120 W, the mean clear width of fabric

against *S. aureus* is wider than that under other discharge powers. When the moving speed of fabric is increased, the mean clear width of fabric against *S. aureus* decreases. The mean clear width of fabric keeps stable when the concentration of sodium hypochlorite is lower than 1.2% but it increases significantly when the concentration is higher than 1.2%. And the mean clear width against *S. aureus* increases rapidly when the chlorination time is shorter than 30 min, and then it is nearly stable. In this study, chlorine is used to inhibit bacteria. Therefore, the antimicrobial activity is proportional to the concentration of chlorine on the finished cotton fabric.

Except the effect of plasma treatment on the antimicrobial activity of cotton fabrics, the effect of the parameters of plasma treatment, discharge power, moving speed of fabrics and flow rate of nitrogen on weight loss of fabrics is also measured to demonstrate the effect of plasma treatment on the antimicrobial activity of cotton fabrics. And the evaluation of the tearing strength shows that nitrogen/helium mixed plasma treatment will not affect its usability of cotton fabric.

CHAPTER 5 ANTIMICROBIAL FINISHING OF COTTON FABRIC WITH 5, 5-DIMETHYLHYDANTOIN (DMH)

5.1 Introduction

Due to the nature of cotton fabric infected by microbe easily, a number of chemicals are used to impart antimicrobial properties to textiles, such as chitosan, phenols, organic and inorganic acids and salts, aromatic diamidines, biguanides, aldehydes, heavy metal derivatives, alcohols, anilides and miscellaneous preservatives (Afeltra, Dannaoui, Meis, Rodriguez-Tudela, & Verweij, 2002; Braun & Sun, 2004; Chung et al., 1998; Gao & Cranston, 2008; Lim & Hudson, 2004; Seong, Kim, & Ko, 1999; Simoncic & Tomsic, 2010; Ureyen, Gurkan, Namligoz, Armakan, & Dogan, 2010; Zhu & Sun, 2004). Antimicrobial property of cotton fabrics finished with these chemicals, however, is not regenerable.

In order to enable cotton fabrics with regenerable antimicrobial ability, cotton fabrics was finished with synthetic chemicals with N-halamine structure. 5,5 - dimethylhydantoin (DMH) is the simplest cyclic finishing agent for regenerable antimicrobial finishing. DMH was used as a disinfectant from 1979 onwards in US (X. Wang & Wang, 2000). In later years, DMH was used for antimicrobial finishing in the textile industry. Numerous finishing agents based on DMH for antimicrobial finishing have been developed to improve the antimicrobial effect of cotton fabrics finished with DMH derivates, for example, 3-allyl-5,5-dimethylhydantoin (ADMH) (Y. Sun &

Sun, 2001b), 3-(4'-vinylbenzyl)-5,5-dimethylhydantoin (VBDMH) (Ren et al., 2008), 3-glycidyl-5,5-dialkylhydantoins (GH's) (Liang et al., 2007), dimethylol-5,5-dimethylhydantoin (DMDMH) (Qian & Sun, 2004), 3-(2,3-dihydroxypropyl)-5,5-dimethylimidazolidine-2,4-dione (Ren et al., 2009) etc. These antimicrobial agents can be finished onto cotton fabrics with the help of other auxiliaries, such as cationic surfactant cetylmethylammonium bromide (CTAB), initiator ammonium cerium (IV) nitrate (ACN), cross-linking agent 1,2,3,4-butanetetracarboxylic acid (BTCA), etc (Ren et al., 2008; Ren et al., 2009; Y. Sun & Sun, 2001b). Cotton fabrics finished with these finishing agents possess excellent antimicrobial activities. However, these finishing processes involve various auxiliaries, which is not good for environment. Therefore, an alternative method, plasma treatment can be used to regenerable antimicrobial finishing of cotton fabrics. Compared with traditional chemical treatments, plasma processing adds value to textiles in an environmentally friendly way. When the working gases are reactive gas, plasma treatment introduces functional groups on the surface on textiles which can react with chemicals and connect fabrics with chemicals (Huh et al., 2001; Parvinzadeh Gashti, Hegemann, Stir, & Hulliger, 2014; Parvinzadeh & Ebrahimi, 2011a; Parvinzadeh & Ebrahimi, 2011b; Zhou & Kan, 2014b).

Compared with the derivatives of DMH, DMH is obtained more easily and inexpensive. Therefore, DMH is coated onto cotton fabrics with the aid of plasma treatment, and the plasma treatment parameters are the optimum conditions of antimicrobial finishing for cotton obtained from Chapter 4, that is, discharge power

of APP is120W, flow rate of nitrogen is 0.4 LPM, moving speed of fabric is 4.5×10^{-3}m/s. Antimicrobial principle of DMH is shown in Figure 5.1. In order to investigate the effect of plasma treatment on the antimicrobial activity of coated fabrics, plasma treatment is applied at different stages of the pad-dry-cure finishing processes, i.e. (i) plasma-pad-dry-cure (Section 5.3); (ii) pad-plasma-dry-cure (Section 5.4) and (iii) pad-dry-plasma-cure (Section 5.5). And in order to observe the function of plasma treatment in the antimicrobial finishing processes, DMH is also coated onto cotton fabric through pad-dry-cure process. Orthogonal array testing strategy (OATS) is used to optimize the treatment conditions for obtaining the best antimicrobial and other properties of cotton fabrics coated with DMH.

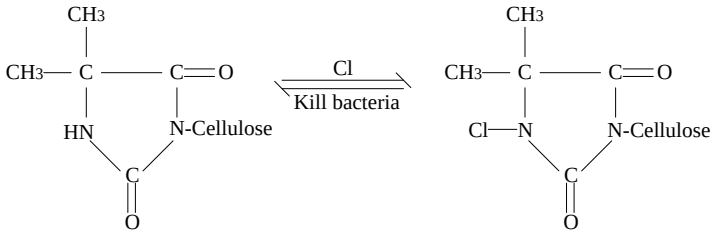

Figure 5.1 Antimicrobial principle of DMH on cotton fabrics

5.2 Optimization of DMH antimicrobial finishing for cotton fabric through pad-dry-cure process

5.2.1 Optimum Condition Analysis

OATS is an efficient and economical technique for analyzing variables or factors involved in experiments. It is a simple and convenient way to find out the optimum conditions and the importance of different factors in experiments. Mean clear width of sample against *S. aureus* (ATCC 6538) from the sample was used to evaluate

antimicrobial activity of sample. A wider mean clear width means the antimicrobial property is more effective. The mean clear width of the bacteria against *S. aureus* obtained from the nine specimens generated by the OATS technique and the result of orthogonal analysis, where T_{mn} refers to the sum of the evaluation indexes of all levels (n, n=I, II, III) in each factor (m, m=A, B, C), such that T_{AI}=1.795+1.792+1.032=4.619 is the sum of level I of factor A; T_{CII}=1.792+1.346+1.373=4.511 is the sum of level II of factor C; and K_{mn} implies the mean value of T_{mn}, such that $K_{AI}=T_{AI}/3$=4.619/3=1.540 is the mean value of T_{AI}; $K_{CII}=T_{CII}/3$=4.511/3=1.504 is the mean value of T_{CII} are shown in Table 5.1. In addition, T is the sum of the evaluation indexes, w_i, which is an evaluating indicator for antimicrobial activity of cotton fabrics evaluated by AATCC Test Method 147-2011; and the range of factors in each column, R=Max(K_j)-Min(K_j), indicates the function of the corresponding factor (Chuanwen et al., 2010). The larger value of R means the greater impact of the level of the factor on the experimental index. Therefore, the impact of every factor on the final treatment effect can be distinguished clearly on the comprehensive condition that every factor changes.

The results of orthogonal analysis for four parameters used in the finishing process are shown in Table 5.1and the order of importance of these factors is $R_D > R_A > R_C > R_B$. That is, duration of chlorination has the greatest impact on the experimental result, and concentration of DMH has a comparatively less impact, next factor in the order is concentration of bleaching solution, and the last one is temperature of curing (Chuanwen et al., 2010; Kan et al., 2011). The best level is suggested by orthogonal analysis based on the mean value of the testing factors. Thus, the optimum process for DMH coating is $A_IB_IC_{II}D_I$, that is, concentration of DMH = 2%, temperature of curing = 120ºC, concentration of bleaching solution 1% and time of chlorination 20min. Fabric prepared based on the optimum condition shows mean clear width against *S.*

aureus of 1.802 mm which is wider than the mean clear width in the other nine specimens (Table 5.1). The optimum condition is verified and is used for cotton fabric coated with DMH for further evaluation in regenerability, FTIR-ATR and SEM.

Table 5.1 Orthogonal table for optimizing the antimicrobial property of cotton fabric coated with DMH[b]

Test run	Parameters				Results
	Concentration of DMH (%) A	Temperature of curing (ºC) B	Concentration of bleaching solution (%) C	Time of chlorination (min) D	Mean clear width against *S. aureus* (mm) wi
1	Ⅰ	Ⅰ	Ⅰ	Ⅰ	1.795
2	Ⅰ	Ⅱ	Ⅱ	Ⅱ	1.792
3	Ⅰ	Ⅲ	Ⅲ	Ⅲ	1.032
4	Ⅱ	Ⅰ	Ⅱ	Ⅲ	1.346
5	Ⅱ	Ⅱ	Ⅲ	Ⅰ	1.465
6	Ⅱ	Ⅲ	Ⅰ	Ⅱ	1.334
7	Ⅲ	Ⅰ	Ⅲ	Ⅱ	1.225
8	Ⅲ	Ⅱ	Ⅰ	Ⅲ	0.788
9	Ⅲ	Ⅲ	Ⅱ	Ⅰ	1.373
T_{mI}	**4.619**	**4.366**	3.917	**4.633**	$T_{mn}=\Sigma_{i=1}^{9} w_i$
T_{mII}	4.145	4.045	**4.511**	4.351	
T_{mIII}	3.386	3.739	3.722	3.133	$K_{mn}=\frac{1}{3}T_{mn}=\frac{1}{3}\Sigma_{i=1}^{9} w_i$
K_{mI}	**1.540**	**1.455**	1.306	**1.544**	
K_{mII}	1.382	1.348	**1.504**	1.450	
K_{mIII}	1.129	1.246	1.241	1.055	
R	*0.411*	*0.209*	*0.263*	*0.489*	$R = \mathrm{Max}(K_{mI}, K_{mII}, K_{mIII}) - \mathrm{Min}(K_{mI}, K_{mII}, K_{mIII})$

[b]Figure in **Bold** exhibits the greatest value among all the values shown in the levels of different variables used while the *Italic* shows the level of importance if each variable.

As concentration of DMH increases (Figure 5.2), the mean clear width against *S. aureus* decreases, that is, antimicrobial activity of cotton fabric coated with DMH decreases. This is because molecules of DMH aggregate easily with the increase of concentration of DMH, which reduces the coating of DMH on the fabric. On the contrary, molecules of DMH disperse easily in the diluted solution and molecules of DMH can adhere to the fabric stably and evenly.

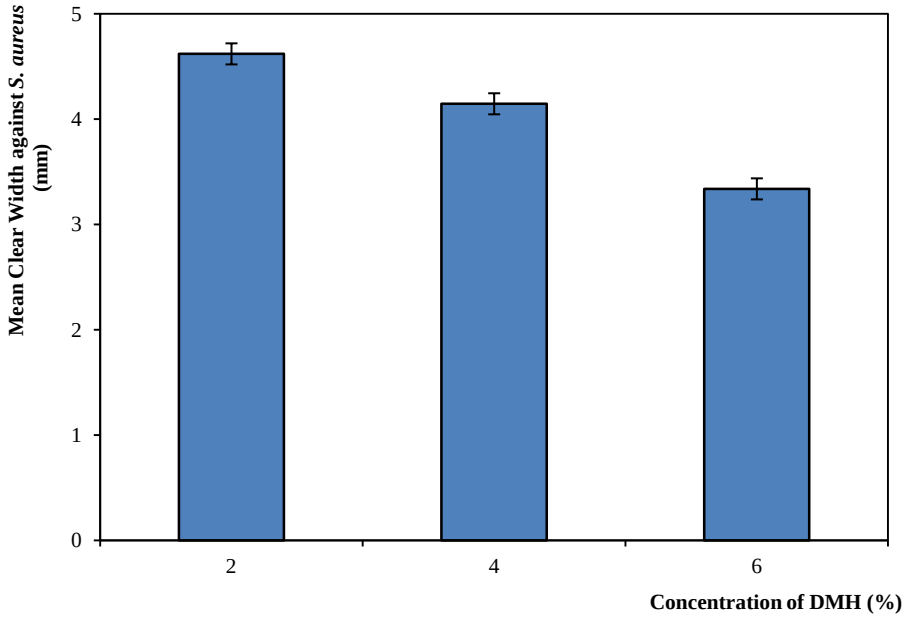

Figure 5.2 Effect of concentration of DMH on antimicrobial property of cotton fabric

As curing temperature increases, the mean clear width against *S. aureus* decreases (Figure 5.3), that is, antimicrobial activity decreases with increase of the curing temperature. Since the melting point of DMH is about 175ºC, there is a risk of DMH getting detached from the fabric surface at high curing temperatures, which may lead to poor fixation of DMH, meaning it may dissolve again in water during the subsequent finishing process. Finally, the quantity of DMH and chlorine decreases with the increase of the curing temperature and then the antimicrobial effect decreases.

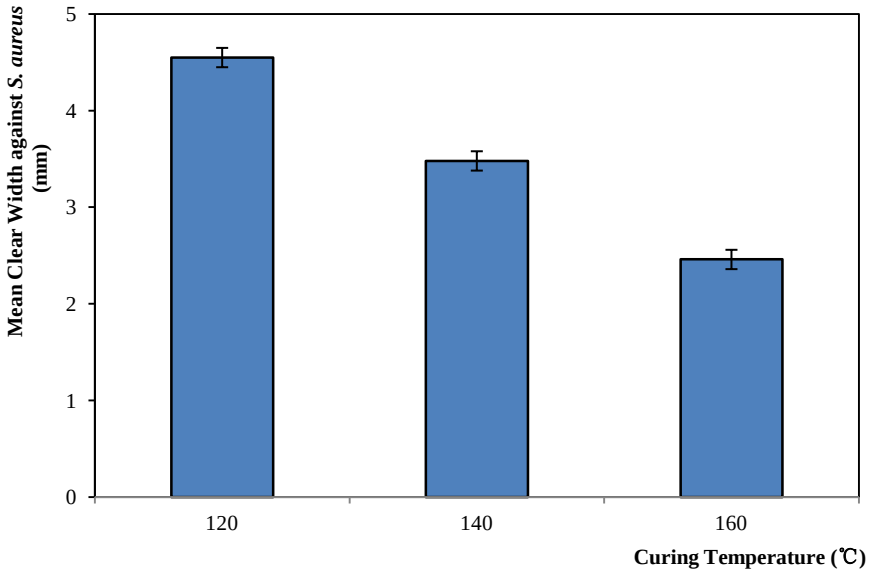

Figure 5.3 Effect of curing temperature on antimicrobial property of cotton fabric.

When concentration of bleaching solution is 1%, mean clear width against *S. aureus* is the widest (Figure 5.4). Generally speaking, the higher the concentration of bleaching solution is, more of chlorine would be expected to interact with the DMH in the cotton. However, this assumption does not verify the outcome when concentration of bleaching solution is 1.2%. This may be due to the strong oxidizing ability of chlorine solution which is believed to be able to damage functional moieties on fabrics and these damages correspond to the occurrence of decreased antimicrobial efficacy of treated fabrics. Thus, 1% is the most active and stable concentration of chlorine in bleaching solution for increasing the chance of interaction between chlorine and DMH on cotton fabric.

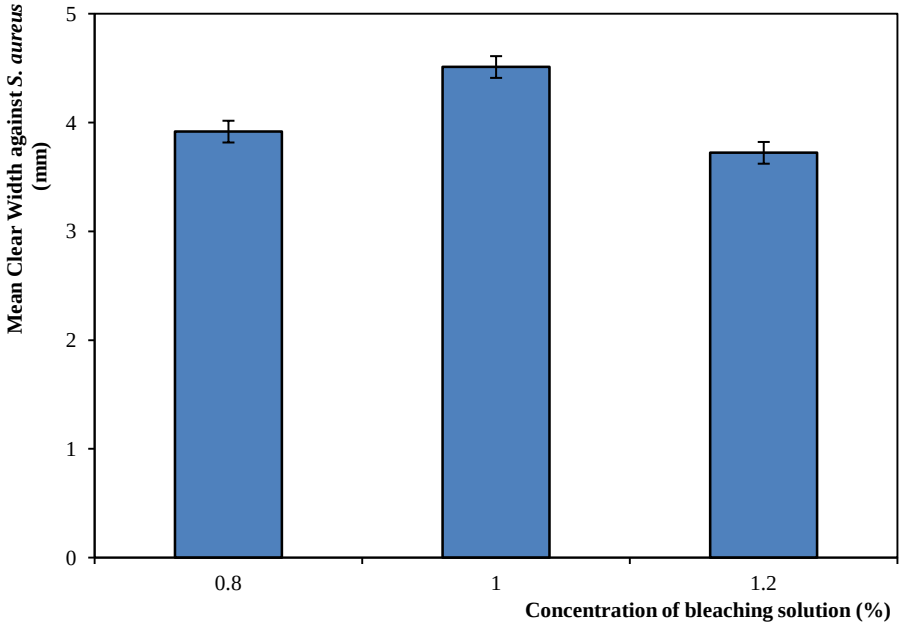

Figure 5.4 Effect of concentration of bleaching solution on antimicrobial property of cotton fabric.

When the time of chlorination increases, the mean clear width against *S. aureus* decreases (Figure 5.5). The reason is that DMH is coated onto cotton fabric without any other binding agents and DMH easily dissolves into water when the fabric is chlorinated. Thus, with extension of the time of chlorination, some DMH may dissolve again into the chlorination solution, leading to reduction in antimicrobial activity.

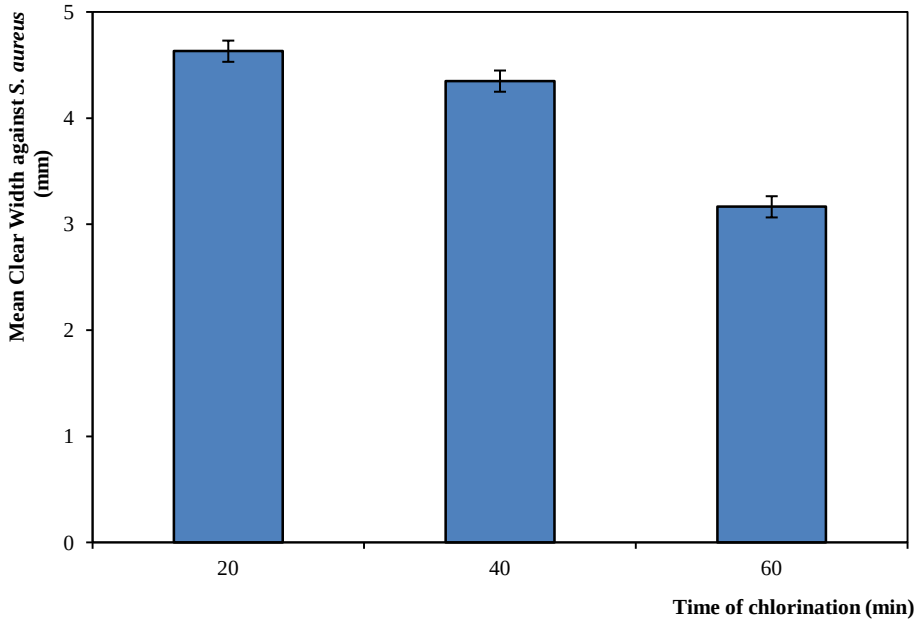

Figure 5.5 Effect of time of chlorination on antimicrobial property of cotton fabric.

5.2.2 Relationship between Antimicrobial Property and Concentration of Chlorine in Cotton

The relationship between antimicrobial property and concentration of chlorine in cotton fabric is shown in Figure 5.6; the mean clear width becomes wider with increase of concentration of chlorine. A linear relationship with a fitting linear equation is $y = 0.3403x - 0.396$ and decisive coefficient $R^2 = 0.8615$ was noted. This relationship implies that when the quantity of chlorine increases, more bacteria can be killed. Therefore, the antimicrobial principle based on N-halamine type treatment is confirmed in this study.

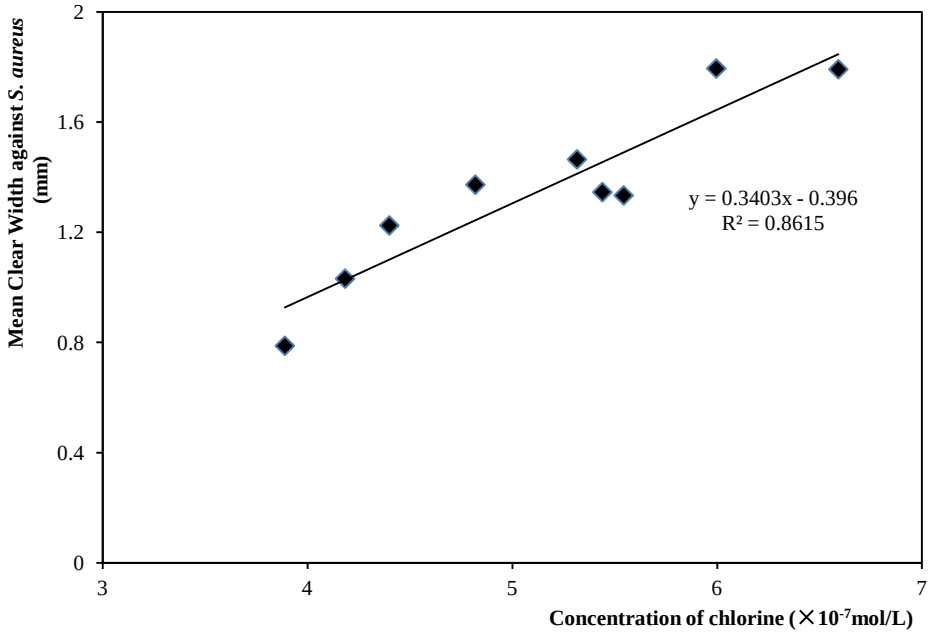

Figure 5.6 Relationship between antimicrobial property and the concentration of chlorine in cotton fabric.

5.2.3 Regenerability

Regenerability is an important property for antimicrobial textiles. Regenerable antimicrobial textiles have long service life and are environmentally friendly. The regenerability of cotton fabric coated with DMH under optimum conditions (i.e. concentration of DMH = 2%, curing temperature = 120 ºC, concentration of bleaching solution=1% and time of chlorination = 20min.) is shown in Figure 5.7.

Based on Figure 5.7, it is found that concentration of chlorine in cotton fabric after washing (AW) is lower than before washing (BW). However, after re-chlorination, concentration of chlorine increases again. Therefore, chlorine in cotton fabric coated with DMH can be recharged and it can be said that antimicrobial property of cotton fabric coated with DMH is regenerable. Moreover, it is also seen from Figure 5.7 that concentration of chlorine after washing and rechlorination (AW+CH) is lower than that in cotton fabric coated with DMH before washing (BW). That is because

solubility of DMH is high in water. The DMH on cotton fabric dissolves in water easily, even during chlorination, which reduces the amount of DMH on cotton fabric and results in lower concentration of chlorine in cotton fabric coated with DMH.

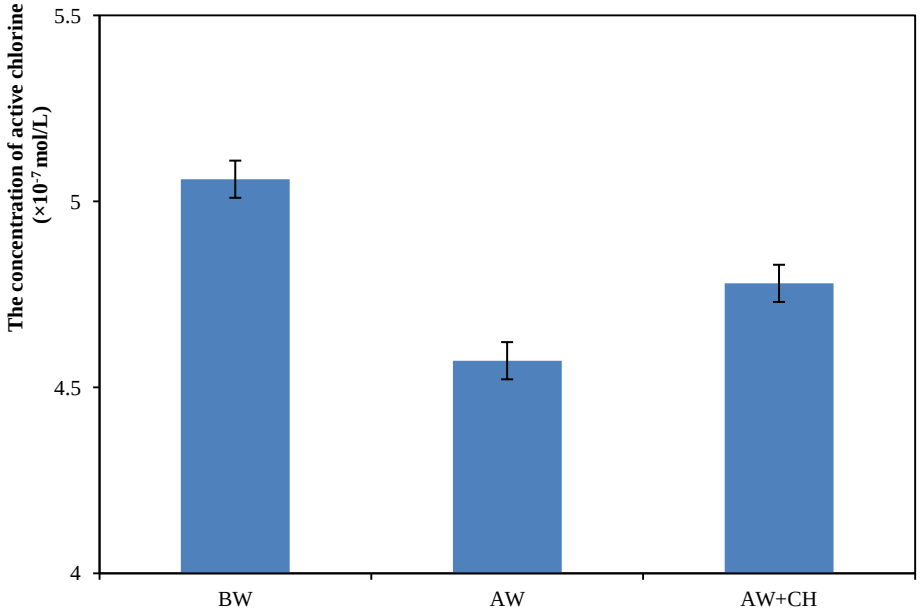

Figure 5.7 Regenerability of cotton fabric coated with DMH.

5.2.4 FTIR-ATR

FTIR-ATR is used to evaluate whether there is DMH on cotton fabric coated with DMH. The characteristic absorbance band of DMH is amide II and C=O stretching of hydantoin ring. The FTIR-ATR spectrum of untreated cotton fabric (Figure 5.8a), cotton fabric coated with DMH before washing (Figure 5.8b) and cotton fabric coated with DMH after washing (Figure 5.8c) is shown in Figure 5.8. According to the spectra in Figures 5.8b and 5.8c, the peaks at around 1550 cm^{-1} are standing for N-H (amine II) deformation. The absorbance bands in the 1758 cm^{-1} region (Figures 5.8b and 5.8c) are attributable to the stretching vibrations of C=O (El-Newehy et al., 2011; Kocer et al., 2008; Kocer et al., 2011; Sun et al., 2012; L. Wang et al., 2006). These three kinds of absorbance peaks are not found in Figure 5.8a. Therefore, it is

concluded that DMH is coated onto cotton fabric. Compare absorbance peaks at same region, it is found that absorbance peaks at around 1550 cm^{-1} and 1758 cm^{-1} in Figure 5.8b are higher than those in Figure 5.8c. According to Beer–Lambert law, concentration of DMH on samples with higher absorbance peaks is much higher. This demonstrates that some DMH on cotton fabrics dissolves into water after washing, thereby reducing the concentration. As a consequence, though DMH can be coated onto cotton fabric, the coating of DMH on cotton fabric needs to be strengthened.

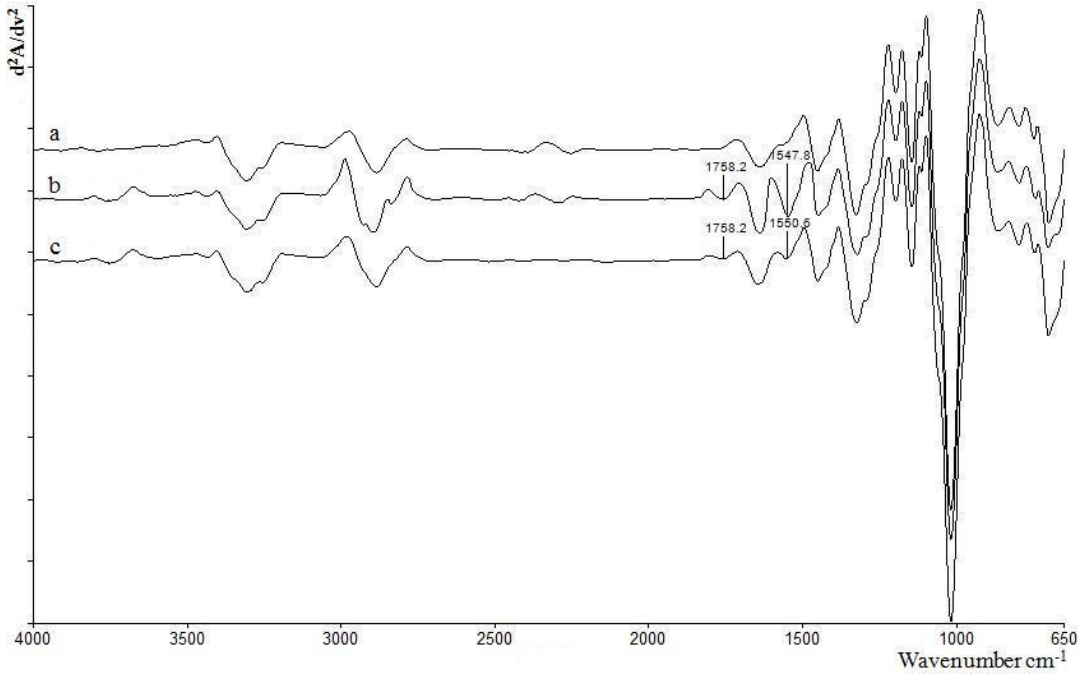

Figure 5.8 Second **derivative FTIR spectrum of (a) untreated cotton fabric; (b) cotton fabric coated with DMH before washing; and (c) cotton fabric coated with DMH after washing.**

5.2.5 SEM

SEM is used to evaluate the morphological properties of the surface of cotton fabric coated with DMH. SEM image of untreated cotton fabric (Figure 5.9a) and cotton fabric coated with DMH through “pad-dry-cure” method under optimum conditions obtained in this study (Figure 5.9b) is shown in Figure 5.9. According to Figure 5.9, it

is found that the surface of cotton fabric without treatment is even and smooth, while the surface of cotton fabric coated with DMH is uneven. There are linear structures in Figure 5.9b which shows accumulation of DMH on cotton fabric. Therefore, it is concluded that the fabric is coated with DMH.

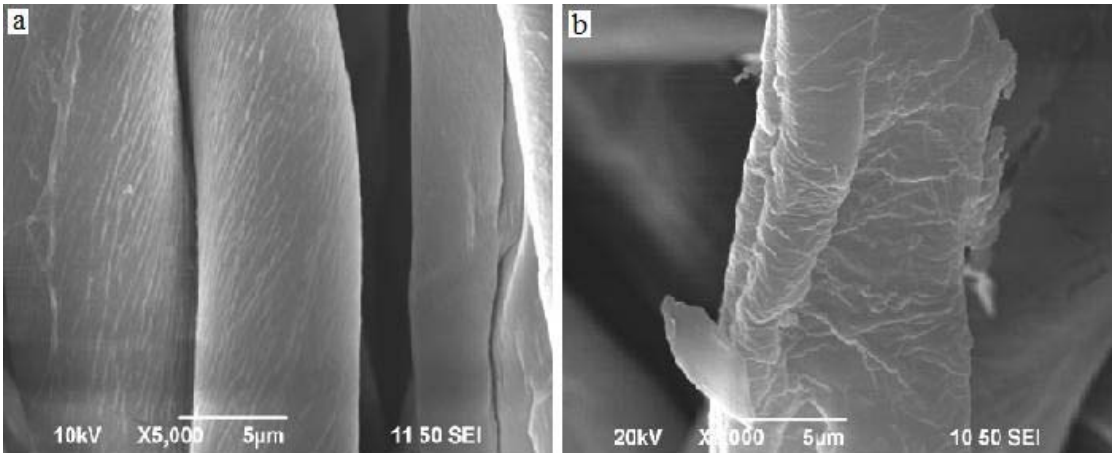

Figure 5.9 SEM images of (a) untreated cotton fabric; and (b) cotton fabric coated with DMH through "pad-dry-cure" method

5.3 Optimization of DMH antimicrobial finishing for plasma pre-treated cotton fabric (plasma-pad-dry-cure)

5.3.1 Optimum condition analysis

Orthogonal analysis is efficient and economical for experiments with variables or factors. It is a convenient means to identify the optimum conditions and the importance of different factors in experiments. Plasma pre-treated cotton fabrics coated with DMH were studied through OATS. Mean width of the clear zone of the sample against *S. aureus* (ATCC 6538) was used as the measure of antimicrobial activity on the sample; a wider clear zone means more antimicrobial activity. The mean clear width of the bacteria against *S. aureus* obtained from the nine specimens generated by OATS and the result of orthogonal analysis, where T_{mn} refers to the sum

of the evaluation indexes of all levels (n, n=I, II, III) in each factor (m, m=A, B, C), such that T_{AI}=1.232+1.708+1.3953=4.335 is the sum of level I of factor A; T_{CII}=1.708+0.887+1.804=3.679 is the sum of level II of factor C; and K_{mn} implies the mean value of T_{mn}, such that $K_{AI}=T_{AI}/3=4.335/3=1.445$ is the mean value of T_{AI}; $K_{CII}=T_{CII}/3=3.679/3=1.226$ is the mean value of T_{CII} are shown in Table 5.2. In addition, T is the sum of the evaluation indexes, w_i, which is an evaluating indicator for antimicrobial activity of cotton fabrics evaluated by AATCC Test Method 147-2011; and the range of factors in each column, R=Max(K_j)-Min(K_j), indicates the function of the corresponding factor (Chuanwen et al., 2010). The larger value of R means the greater impact of the level of the factor on the experimental index. Therefore, the impact of every factor on the final treatment effect can be distinguished clearly on the comprehensive condition that every factor changes.

The results of orthogonal analysis for four parameters used in the finishing process are shown in Table 5.2 and the order of importance of these factors is $R_B > R_A > R_D > R_C$. That is, temperature of curing has the greatest impact on the experimental result, and concentration of DMH has a comparatively less impact, next factor in the order is duration of chlorination, and the last one is concentration of bleaching solution (Chuanwen et al., 2010; Kan et al., 2011). The best level is suggested by orthogonal analysis based on the mean value of the testing factors. Thus, the optimum process for DMH coating is $A_IB_{II}C_ID_{II}$, that is, concentration of DMH = 2%, temperature of curing = 140 ºC, concentration of bleaching solution 0.8% and time of chlorination 40min. Fabric finished under the optimum condition shows mean clear width against *S. aureus* of 1.773 mm which is wider than the mean clear width in the other nine specimens (Table 5.2). This sample will be used to further evaluations.

Table 5.2 Results of orthogonal analysis for optimizing the antimicrobial property of cotton fabric coated with DMH[c]

Test run	Parameters				Results
	Concentration of DMH (%) A	Temperature of curing (ºC) B	Concentration of bleaching solution (%) C	Time of chlorination (min) D	Mean clear width against *S. aureus* (mm) w_i
1	I	I	I	I	1.232
2	I	II	II	II	1.708
3	I	III	III	III	1.395
4	II	I	II	III	0.887
5	II	II	III	I	1.679
6	II	III	I	II	1.473
7	III	I	III	II	0.945
8	III	II	I	III	1.359
9	III	III	II	I	1.084
T_{mI}	**4.335**	3.064	**4.064**	3.995	$T_{mn}=\sum_{i=1}^{9} w_i$
T_{mII}	4.039	**4.746**	3.679	**4.126**	
T_{mIII}	3.388	3.952	4.019	3.641	$K_{mn}=\frac{1}{3}T_{mn}=\frac{1}{3}\sum_{i=1}^{9} w_i$
K_{mI}	**1.445**	1.021	**1.355**	1.332	
K_{mII}	1.346	**1.582**	1.226	**1.375**	
K_{mIII}	1.129	1.317	1.340	1.214	$R = \mathrm{Max}(K_{mI}, K_{mII}, K_{mIII}) - \mathrm{Min}(K_{mI}, K_{mII}, K_{mIII})$
R	*0.316*	*0.561*	*0.129*	*0.161*	

[c] Figures in bold denote the highest value among all values shown in the levels of different parameters used while figures in italics show the level of importance of each parameter.

The mean clear width against *S. aureus* decreases with increase of concentration of DMH (Figure 5.10), implying antimicrobial activity decreases with increase of concentration of DMH. Before DMH was applied onto the surface of fabric, the fabric was pretreated with plasma. This treatment introduces many functional groups to the fabric surface including N-H group and carboxyl group (Zhou & Kan, 2015). When DMH is applied to the fabric, N-H group in DMH will react with carboxyl group on fabric. However, with the increase of the concentration of DMH, carboxyl groups are consumed by DMH at some point. And then, the redundant DMH molecules will agglomerate with DMH reacted with carboxyl groups because of hydrogen bonding and intermolecular force (Girard, 1984). These DMH will consume some chlorine during chlorination and impede the chlorination of DMH reacted with carboxyl groups.

When washing, these redundant DMH dissolve in water. Therefore, antimicrobial activity decreases with the increase of concentration of DMH. Conversely, molecules of DMH disperse easily in the diluted solution and can adhere to the fabric stably and evenly.

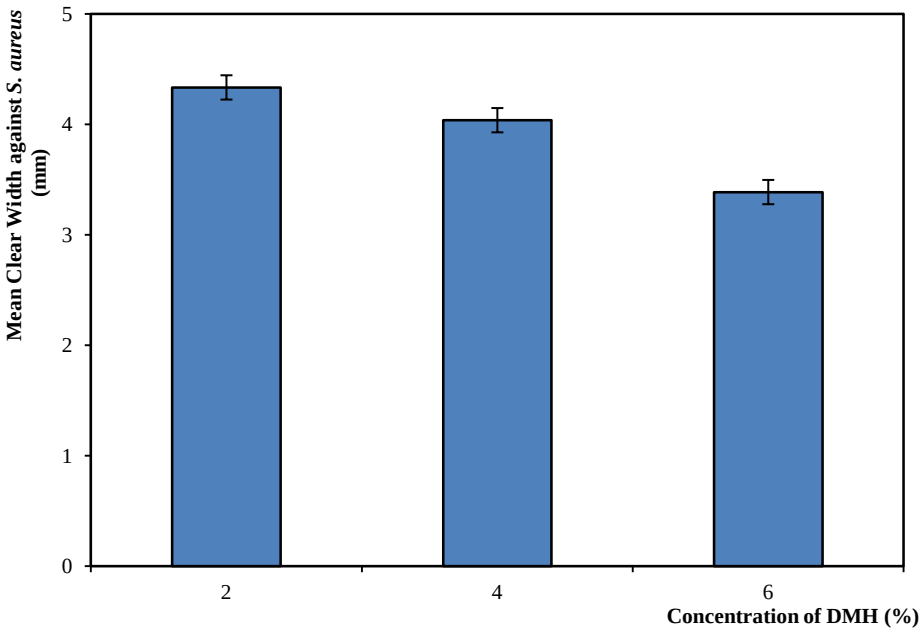

Figure 5.10 Effect of concentration of DMH on antimicrobial property of cotton fabric coated with DMH.

Until curing temperature is below 140 ºC, the mean clear width against *S. aureus* increases with increase of curing temperature (Figure 5.11). However, after curing temperature exceeds 140 ºC, the mean clear width against *S. aureus* decreases when curing temperature increases further (Figure 5.11), that is, antimicrobial activity decreases. That is because the melting point of DMH is about 175 ºC and it is possible that DMH molecules detach from the fabric surface at high curing temperature and dissolve again in water during the subsequent finishing process. This results in the content of DMH and chlorine decreasing with increase of the curing temperature (beyond 140 ºC).

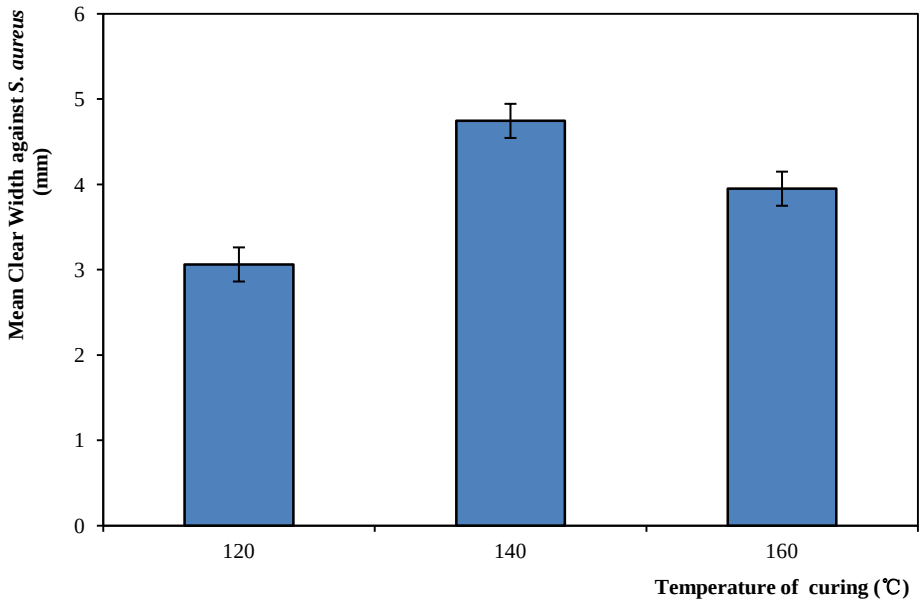

Figure 5.11 Effect of temperature of curing on antimicrobial property of cotton fabric coated with DMH.

As shown in Figure 5.12, until concentration of bleaching solution is lower than 1%, the mean clear width against *S. aureus* decreases with the increase of concentration of bleaching solution but when concentration exceeds 1%, it increases with increase of concentration. Generally speaking, higher concentration of bleaching solution provides more chlorine to interact with the DMH. However, this assumption does not verify the outcome in Figure 5.12. This may be attributable to the strong oxidizing ability of chlorine, which is capable of damaging functional moieties on fabrics; these damages correspond to the occurrence of decreased antimicrobial efficacy of treated fabrics. Chlorine in bleaching solution replaces hydrogen in N-containing groups in DMH first and then the redundant chlorine damages functional moieties on fabrics because of the strong oxidizing ability of the chlorine solution. After that, chlorine may react with N-containing groups introduced by plasma treatment because N_2 plasma can functionalize the substrate with N-containing groups such as $–NH_2$, -NH, =NH, $CONH_2$ or C≡N (Silva et al., 2008). This also can be verified in FTIR part in this

study. That is why the mean clear width is the smallest when concentration of the bleaching solution is 1% and it is nearly the same when concentration of the bleaching solution is 0.8% to 1.2%.

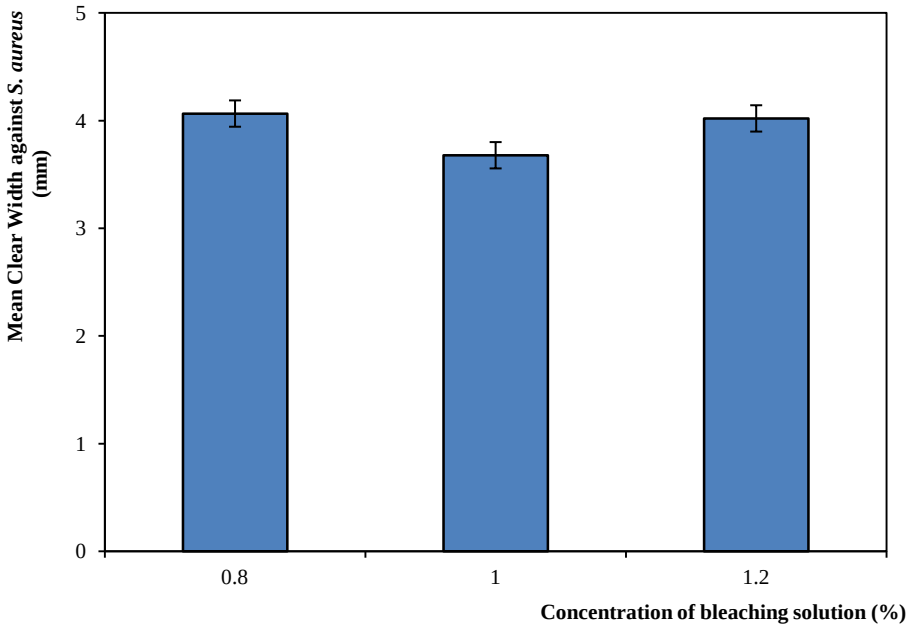

Figure 5.12 Effect of concentration of bleaching solution on antimicrobial property of cotton fabric coated with DMH.

As shown in Figure 5.13, the width of the clear zone fluctuates with the duration of chlorination slightly; it becomes larger as the duration increases from 20 to 40 min. However, it decreases after 40 min because DMH dissolves into the bleaching solution. Therefore, the optimum bleaching time is 40 min.

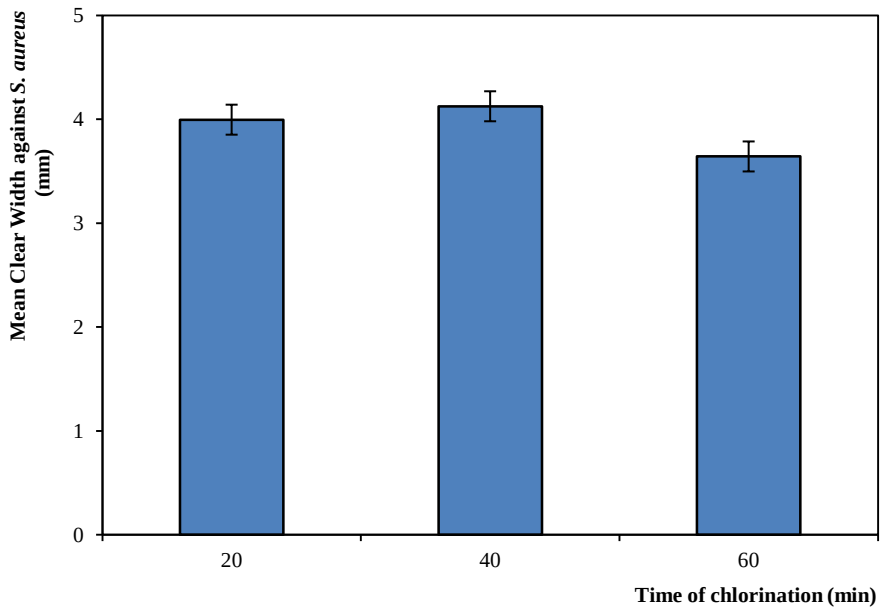

Figure 5.13 Effect of time of chlorination on antimicrobial property of cotton fabric coated with DMH.

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

The relationship between antimicrobial property and concentration of chlorine on cotton fabric is shown in Figure 5.14; the mean clear width against *S. aureus* becomes wider with increase of concentration of chlorine, which appears to be a linear relationship, and the fitting linear equation is y = 0.2948x + 0.0003 and decisive coefficient R^2 = 0.9534. That is because chlorine is used to kill microorganisms. When the quantity of chlorine increases, more bacteria can be killed. Therefore, the effective way to improve the antimicrobial property of cotton fabric is to increase the amount of chlorine on the fabric.

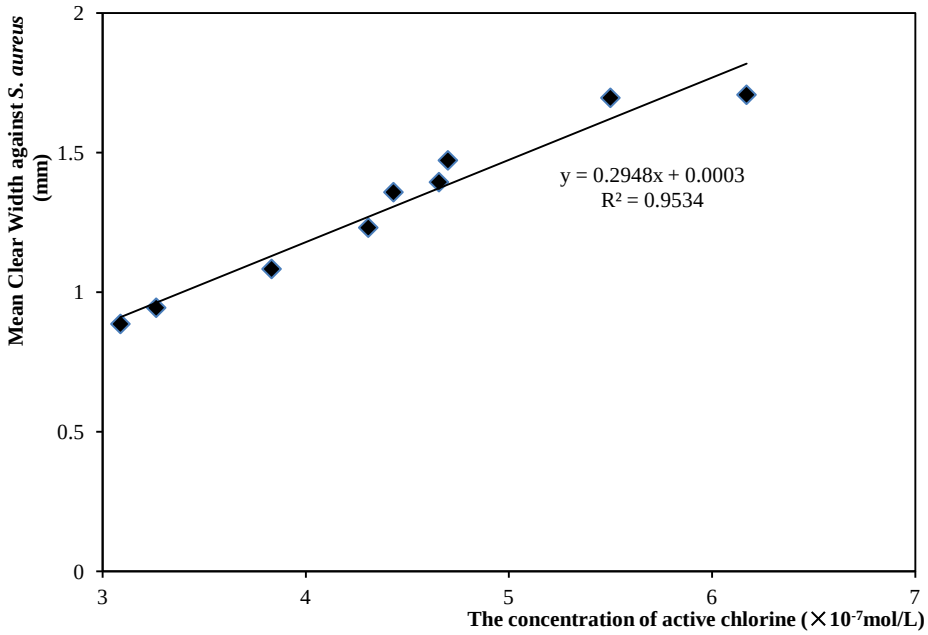

Figure 5.14 Relationship between antimicrobial property and the concentration of chlorine on cotton fabric.

5.3.3 SEM

SEM is used to evaluate physical characteristics of surfaces of substrates. Untreated cotton fabric, and untreated cotton fabric and plasma pretreated cotton fabric coated with DMH with same finishing process parameters are studied with SEM in this study. SEM image of untreated cotton fabric (Figure 5.15a), cotton fabric coated with DMH (CD, i.e. pad-dry-cure) (Figure 5.15b) and plasma pretreated cotton fabric coated with DMH (CPD, i.e. plasma -pad-dry-cure) (Figure 5.15c) is shown in Figure 5.15.

As shown in Figure 5.15, the surface of the untreated fibers is smoother than cotton fibers coated with DMH. According to Figure 5.15, it is also observed that fibers after coating with DMH are not smooth anymore (Figure 5.15b and 5.15c). DMH content on the surface of the fabric treated with plasma (Figure 5.15c) is more than that on fabric without plasma treatment (Figure 5.15b); more of DMH can be coated onto cotton fabrics after plasma treatment because of the grooves and cracks formed by the

etching effect (Karahan & Özdoğan, 2008).

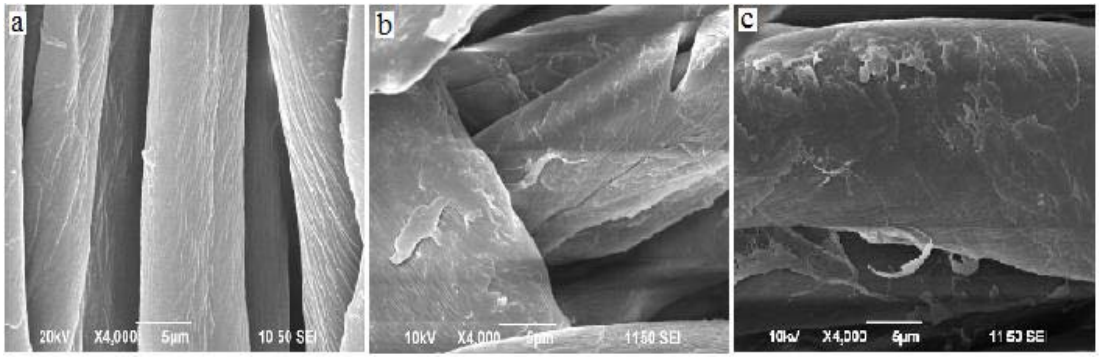

Figure 5.15 SEM image of (a) untreated cotton fabric, (b) cotton fabric coated with DMH through "pad-dry-cure" method (CD), (c) plasma pretreated cotton fabric coated with DMH through 'pad-dry-cure' method (CPD).

5.3.4 FTIR

FTIR is used to evaluate the quantum of DMH present on the cotton fabric. The characteristic absorbance band of DMH is amide II and C=O stretching of hydantoin ring. The second derivative FTIR-ATR spectrum of untreated cotton fabric (Figure 5.16a), cotton fabric with plasma treatment (Figure 5.16b), cotton fabric coated with DMH after plasma treatment (Figure 5.16c) and cotton fabric coated with DMH without plasma treatment (Figure 5.16d) is shown in Figure 5.16.

Compared with Figure 5.16a, the peaks at around 1549 cm^{-1} are assigned to N-H (amine II) deformation (Figure 5.16b, 5.16c and 5.16d). The absorbance bands in the 1758 cm^{-1} region in Figure 5.16b, 5.16c and 5.16d represent the stretching vibrations of C=O (El-Newehy et al., 2011; Kocer et al., 2008; Kocer et al., 2011; Sun et al., 2012; Wang et al., 2006). Reactive particles, such as N_2^+, N_2 (excited), N, N^+ and electrons generated in N_2 plasma introduce nitrogen-containing groups on cotton fabrics and oxidizethe primary hydroxyl group to carboxyl group which can react with amide groups on hydantoin ring (Liu, Nishi, Tokura, & Sakairi, 2001; Zhou & Kan, 2015).

Meanwhile, it is found that the absorbance peak of N-H (amine II) deformation in Figure 5.16c is much higher than that in Figure 5.16d, which means the content of DMH on the sample with plasma treatment is higher than that on the sample without plasma treatment according to Beer–Lambert law (Zhou & Kan, 2015). The reason is that N-H groups on plasma treated fabrics includes N-H groups introduced by plasma treatment and one N-H group in every DMH molecular, because DMH coated onto cotton fabric consumes one N-H group in every DMH to react with carboxyl group on fabric. Consequently, plasma pretreated fabrics with higher content of N-H groups is coated with more quantity of DMH. Therefore, functionalization of N_2 plasma treatment introduces N-containing groups into cotton fabric and the etching effect of plasma treatment results in higher DMH content on cotton fabric (Silva et al., 2008).

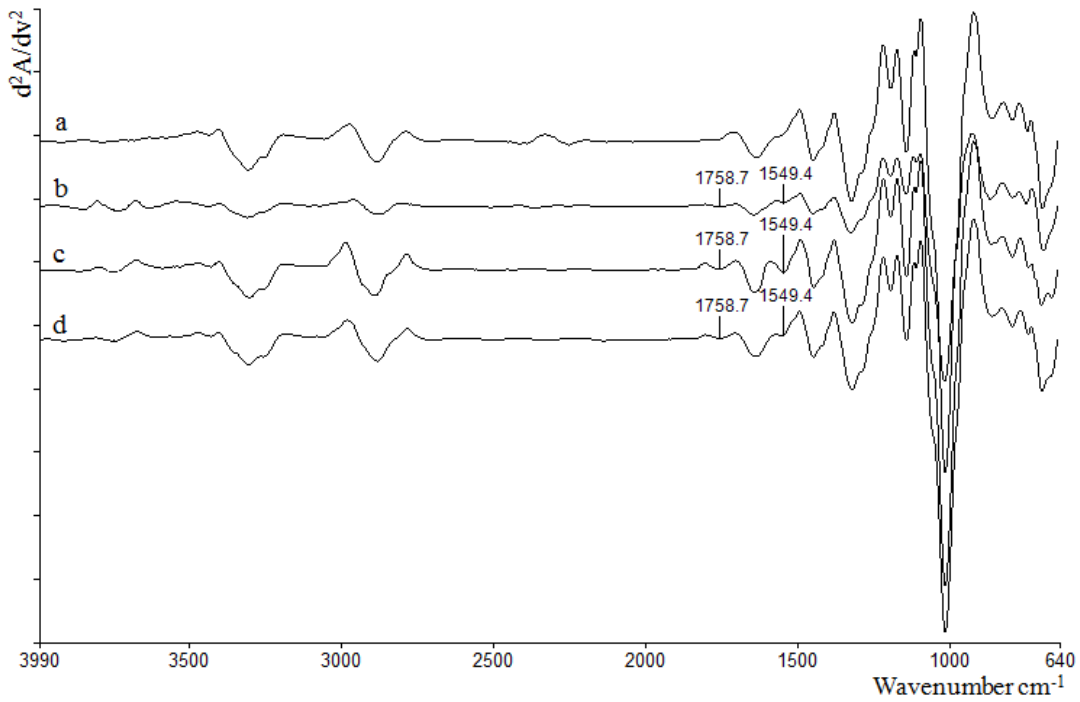

Figure 5.16 Second derivative FTIR spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric treated with plasma, and then coated with DMH through 'pad-dry-cure' method (CPD), (d) cotton fabric coated with DMH through 'pad-dry-cure' method (CD).

5.3.5 Regenerability

Regenerability is an important property for antimicrobial textiles since it implies a longer lifespan and it is environment-friendly. Figure 5.17 compares the regenerability of fabric with plasma pretreatment (CPD) and without plasma treatment (CD) through the content of chlorine on fabrics.

Concentration of chlorine on fabric with plasma treatment is always higher than on fabric without plasma treatment (Figure 5.17), before and after washing, as well as after re-chlorination. Therefore, plasma treatment increases the chlorine content on the fabric. The reason is that plasma treatment etches the surface of the material, producing many grooves. The uneven surface makes the coating easier and enhances adhesion of DMH. Meanwhile, because of the grooves and cracks, surface area of the fabric increases and more DMH can be coated (Karahan & Özdoğan, 2008). In addition, N_2 plasma used in this experiment can functionalize the substrate with carboxyl group and N-containing groups, such as $–NH_2$, -NH, =NH, $CONH_2$ or C≡N (Silva et al., 2008). These N-containing groups also increase the content of chlorine on cotton fabric. And carboxyl group react with DMH leading to good washing fastness. These N-H groups introduced by plasma have long work life. Therefore, it is concluded that the antimicrobial property of cotton fabric coated with DMH with plasma treatment is regenerable and the regenerability is improved by plasma treatment.

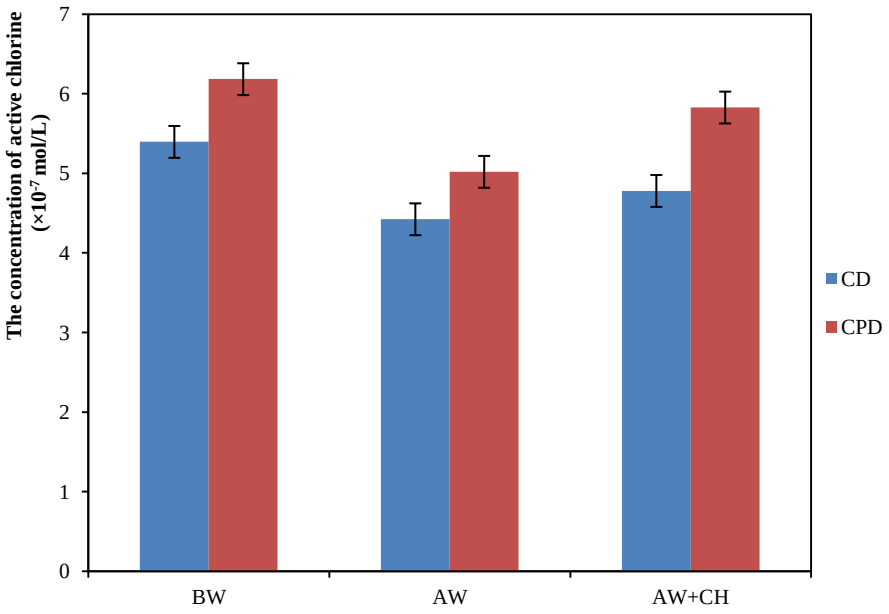

Figure 5.17 Regenerability of cotton fabric coated with DMH.

5.4 Optimization of DMH antimicrobial finishing of cotton fabrics with plasma treatment after padding in pad-dry-cure process (pad-plasma-dry-cure)

5.4.1 Optimum condition analysis

OATS is also used to optimize antimicrobial finishing experiments of cotton fabrics with plasma treatment after padding in the pad-dry-cure process. The optimum condition and the importance of different factors in experiments are obtained easily through orthogonal experiments. The mean clear width of sample against *S. aureus* (ATCC 6538) from sample is used for evaluating antimicrobial activity of sample. The wider clear width means the antimicrobial activity is more active. The mean clear width of the bacteria against *S. aureus* obtained from the nine specimens generated by OATS and the result of orthogonal analysis, where T_{mn} refers to the sum of the evaluation indexes of all levels (n, n=I, II, III) in each factor (m, m=A, B, C), such that

T_{AI}=1.487+1.101+0.610=3.198 is the sum of level I of factor A; T_{CII}=1.101+1.245+0.955=3.301 is the sum of level II of factor C; and K_{mn} implies the mean value of T_{mn}, such that $K_{AI}=T_{AI}/3=3.198/3=1.066$ is the mean value of T_{AI}; $K_{CII}=T_{CII}/3=3.301/3=1.100$ is the mean value of T_{CII} are shown in Table 5.3. In addition, T is the sum of the evaluation indexes, w_i, which is an evaluating indicator for antimicrobial activity of cotton fabrics evaluated by AATCC Test Method 147-2011; and the range of factors in each column, R=Max(K_j)-Min(K_j), indicates the function of the corresponding factor (Chuanwen et al., 2010). The larger value of R means the greater impact of the level of the factor on the experimental index. Therefore, the impact of every factor on the final treatment effect can be distinguished clearly on the comprehensive condition that every factor changes.

The results of orthogonal analysis for four parameters used in the finishing process are shown in Table 5.3 and the order of importance of these factors is $R_B > R_C > R_A > R_D$. That is, temperature of curing has the greatest impact on the experimental result, and concentration of bleaching solution has a comparatively less impact, next factor in the order is concentration of DMH, and the last one is duration of chlorination (Chuanwen et al., 2010; Kan et al., 2011). The best level is suggested by orthogonal analysis based on the mean value of the testing factors. Thus, the optimum process for DMH coating is $A_{II}B_{II}C_ID_I$, that is, concentration of DMH = 4%, temperature of curing = 140 ºC, concentration of bleaching solution 0.8% and time of chlorination 20min. Fabric finished under the optimum condition shows mean clear width against *S. aureus* of 1.773 mm which is wider than the mean clear width in the other nine specimens (Table 5.3). Then this optimum condition is used for cotton fabric coated with DMH for further evaluation.

Table 5.3 Orthogonal table for optimizing the antimicrobial property of cotton fabric coated with DMH[d]

Test run	Parameters				Results
	Concentration of DMH (%) A	Temperature of curing (ºC) B	Concentration of bleaching solution (%) C	Time of chlorination (min) D	Mean clear width against *S. aureus* (mm) w_i
1	I	I	I	I	1.487
2	I	II	II	II	1.101
3	I	III	III	III	0.610
4	II	I	II	III	1.245
5	II	II	III	I	1.597
6	II	III	I	II	1.364
7	III	I	III	II	1.439
8	III	II	I	III	1.711
9	III	III	II	I	0.955
T_{mI}	3.198	4.171	**4.562**	**4.039**	$T_{mn}=\sum_{i=1}^{9} w_i$
T_{mII}	**4.206**	**4.409**	3.301	3.904	
T_{mIII}	4.105	2.929	3.646	3.566	$K_{mn}=\frac{1}{3}T_{mn}=\frac{1}{3}\sum_{i=1}^{9} w_i$
K_{mI}	1.066	1.390	**1.521**	**1.346**	
K_{mII}	**1.402**	**1.470**	1.100	1.301	
K_{mIII}	1.368	0.976	1.215	1.189	$R = \mathrm{Max}(K_{mI}, K_{mII}, K_{mIII}) - \mathrm{Min}(K_{mI}, K_{mII}, K_{mIII})$
R	*0.336*	*0.494*	*0.421*	*0.157*	

[d] Figure in Bold exhibits the greatest value among all the values shown in the levels of different variables used while the Italic shows the level of importance if each variable.

As shown in Figure 5.18, the mean clear width of sample against *S. aureus* increases with the increase of the concentration of DMH at the beginning. However, when the concentration of DMH is up to 4%, the mean clear width against *S. aureus* changes slightly and it nearly remains stable. The reason is that molecules of DMH aggregate easily with the increase of concentration of DMH, which reduces the coating of DMH on the fabric. On the contrary, molecules of DMH disperse easily in the diluted solution and molecules of DMH can adhere to the fabric stably and evenly. When the concentration of DMH is up to 4%, the fabric is saturated with DMH, DMH begins to aggregate. Therefore, the optimum concentration of DMH coated onto cotton fabric is 4% in this study.

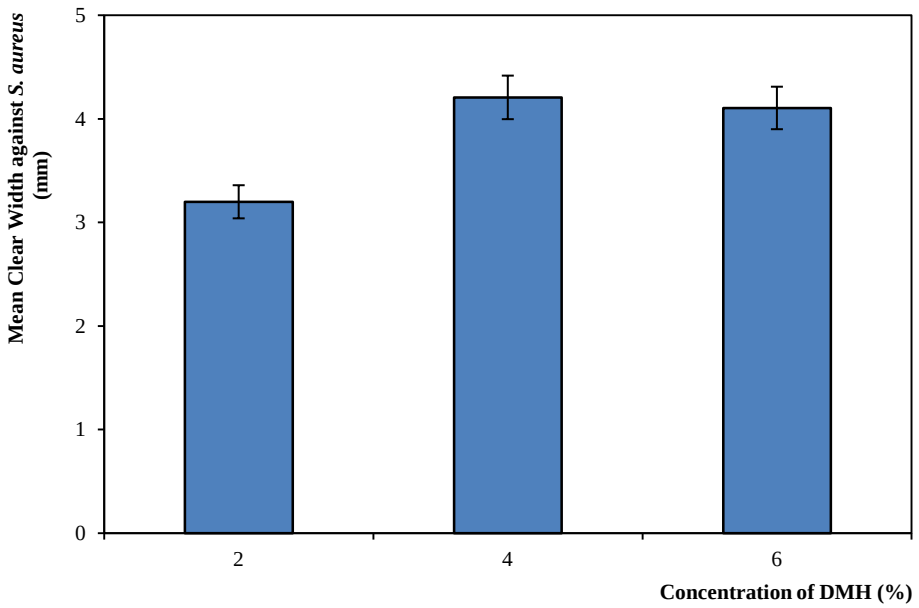

Figure 5.18 Effect of concentration of DMH on antimicrobial property of cotton fabric coated with DMH

When curing temperature is lower than 140 ºC, the mean clear width against *S. aureus* increases with the increase of curing temperature in Figure 5.19, that is, antimicrobial activity increases with increase of the curing temperature. However, as curing temperature is higher than 140 ºC, the mean clear width against *S. aureus* decreases with the increase of curing temperature in Figure 5.19, that is, antimicrobial activity decreases. It is because the melting point of DMH is around 175 ºC, it is easier for DMH getting detached from the fabric surface at high curing temperatures, which may result in poor fixation of DMH, meaning it may dissolve again in water during the subsequent finishing process. Finally, the content of DMH and chlorine decreases with the increase of the curing temperature and the antimicrobial activity decreases (Zhou & Kan, 2014a).

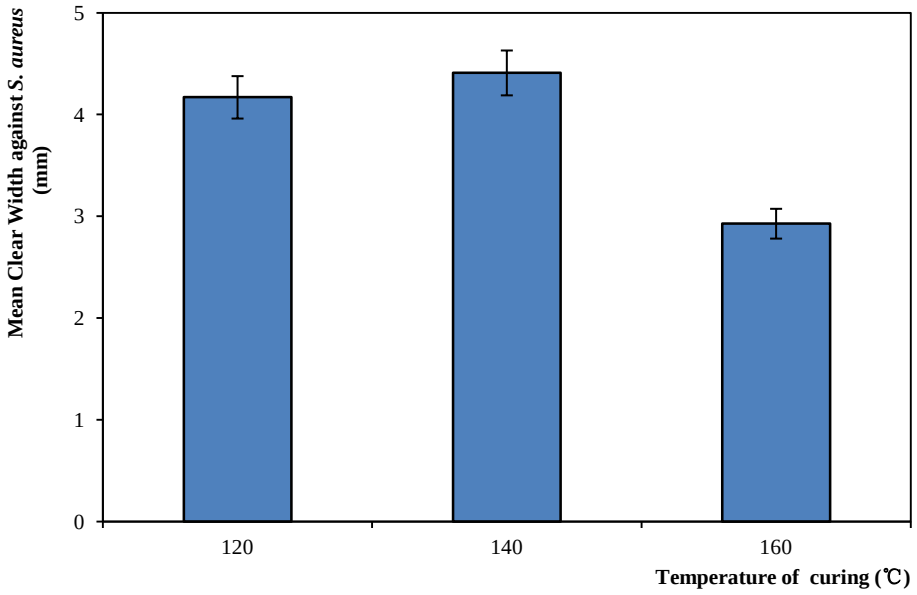

Figure 5.19 Effect of temperature of curing on antimicrobial property of cotton fabric coated with DMH

As shown in Figure 5.20, when concentration of bleaching solution is lower than 1%, the mean clear width against *S. aureus* decreases with the increase of concentration of bleaching solution. While the concentration of bleaching solution is higher than 1%, the mean clear width against *S. aureus* increases with the increase of concentration of bleaching solution. Generally speaking, the higher concentration of bleaching solution provides more chlorine to interact with the DMH in the cotton fabric. However, this assumption does not verify the outcome in Figure 5.20. This may results from the strong oxidizing ability of chlorine solution which is considered to be capable of damage functional moieties on fabrics and 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 in DMH which are not stable after chlorination; and others are introduced into cotton fabric by N_2 plasma treatment, because N_2 plasma can functionalize the substrate with N-containing group, such as $–NH_2$, -NH, =NH, $CONH_2$ or C≡N (Silva et al., 2008). During chlorination,

chlorine in bleaching solution replaces hydrogen in N-containing groups in DMH firstly due to steric hinerance (anonymity, 2015a; anonymity, 2015b). Then, 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 plasma treatment. That is why the mean clear width against *S. aureus* is smallest when the concentration of bleaching solution is 1% and the mean clear width against *S. aureus* is nearly same when the concentration of bleaching solution is 0.8% and 1.2%.

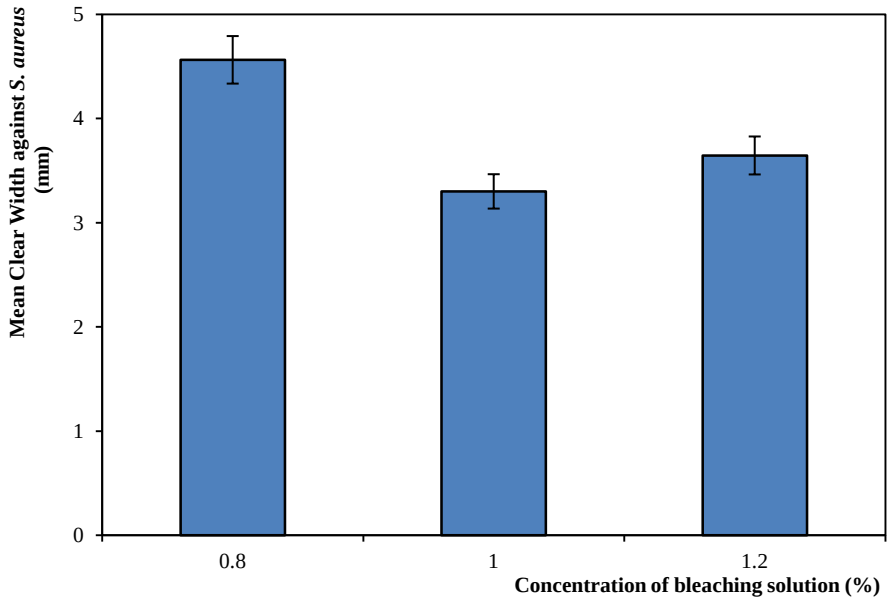

Figure 5.20 Effect of concentration of bleaching solution on antimicrobial property of cotton fabric coated with DMH

As shown in Figure 5.21, the mean clearance distance against *S. aureus* decreases with the extension of the time of chlorination. The reason is that DMH is coated onto cotton fabric without any other binding agents and DMH is easy to dissolve into water. Thus, some chlorine will dissolve in bleaching solution during chlorination. With the extension of the time of chlorination, more DMH is dissolved into water.

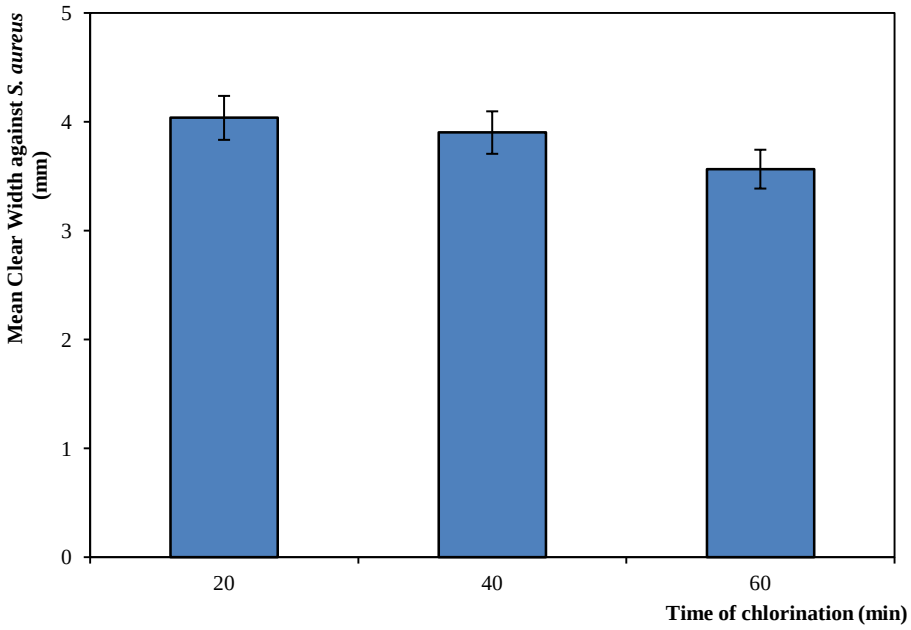

Figure 5.21 Effect of time of chlorination on antimicrobial property of cotton fabric coated with DMH

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

The relationship between antimicrobial property and the concentration of chlorine on cotton fabric is shown in Figure 5.22. From Figure 5.22, it is seen that the mean clearance distance against *S. aureus* become wide with the increase of the concentration of chlorine on cotton fabric coated with DMH, which appears a linear relationship, and the fitting linear equation is y = 0.3069x - 0.882 and decisive coefficient R^2 = 0.8688. That is because the antimicrobial principle of the cotton fabric coated with DMH is that chlorine is used to kill microorganism. When the quantity of chlorine increases, more bacteria can be killed. Therefore, the effective method to improve the antimicrobial property of cotton fabric is to increase the amount of chlorine on cotton fabric.

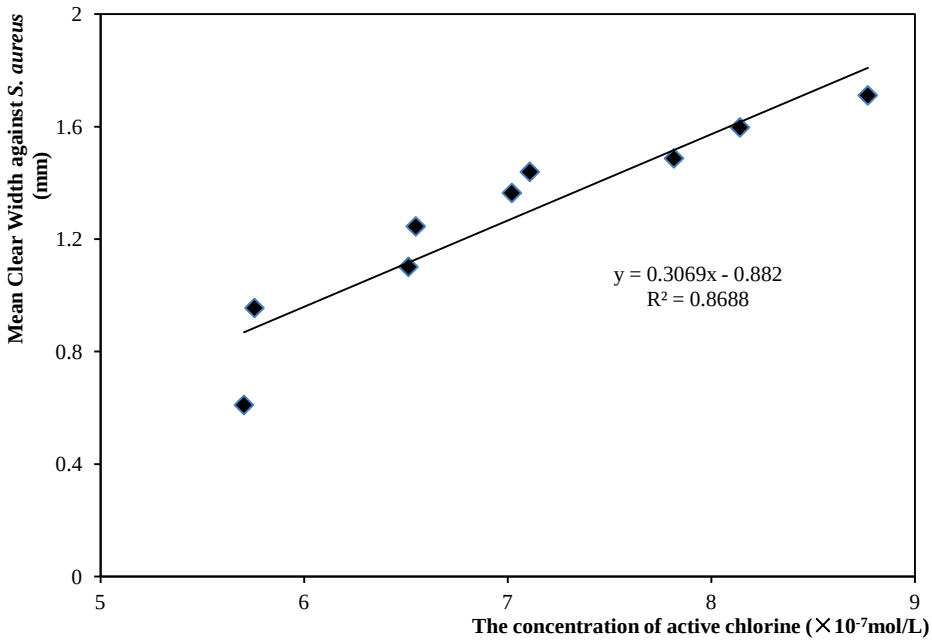

Figure 5.22 Relationship between antimicrobial property and the concentration of chlorine on cotton fabric

5.4.3 Regenerability

Regenerability is extremely important for antimicrobial textiles. It extends service life of antimicrobial textiles. Figure 5.23 compares the regenerability of cotton fabric coated with DMH with the aid of plasma treatment (coded as CWPD) and without plasma treatment (coded as CD).

According to Figure 5.23, the concentration of chlorine on cotton fabric with plasma treatment is almost same as that on fabric without plasma treatment before washing and after. However, the concentration of chlorine on fabric with plasma treatment is higher than that on fabric without plasma treatment after re-chlorination. Therefore, plasma treatment increases the adhesion of DMH on cotton fabric as well as the content of chlorine on cotton fabric. The reason is that plasma treatment etches the surface of material leading to many cracks on the surfaces of material. The uneven surface of material makes the coating of the material easier, which enhances the

adhesion of DMH on cotton fabric (Karahan & Özdoğan, 2008). In addition, N_2 plasma used in this experiment can functionalize the substrate with N-containing group, such as $–NH_2$, -NH, =NH, $CONH_2$ or C≡N (Silva et al., 2008), which also increases the content of chlorine on cotton fabric. Meanwhile, N_2 plasma treatment provides carboxyl groups on the surface of cotton fabric and these carboxyl groups can react with amide groups on hydantoin ring in DMH to form new amide group, which increase the adhesion of DMH on the surface of cotton fabric (Zhou & Kan, 2015). Therefore, it is concluded that the antimicrobial property of cotton fabric coated with DMH with plasma treatment is regenerable and the regenerability is improved by plasma treatment compared with cotton fabric coated with DMH without plasma treatment.

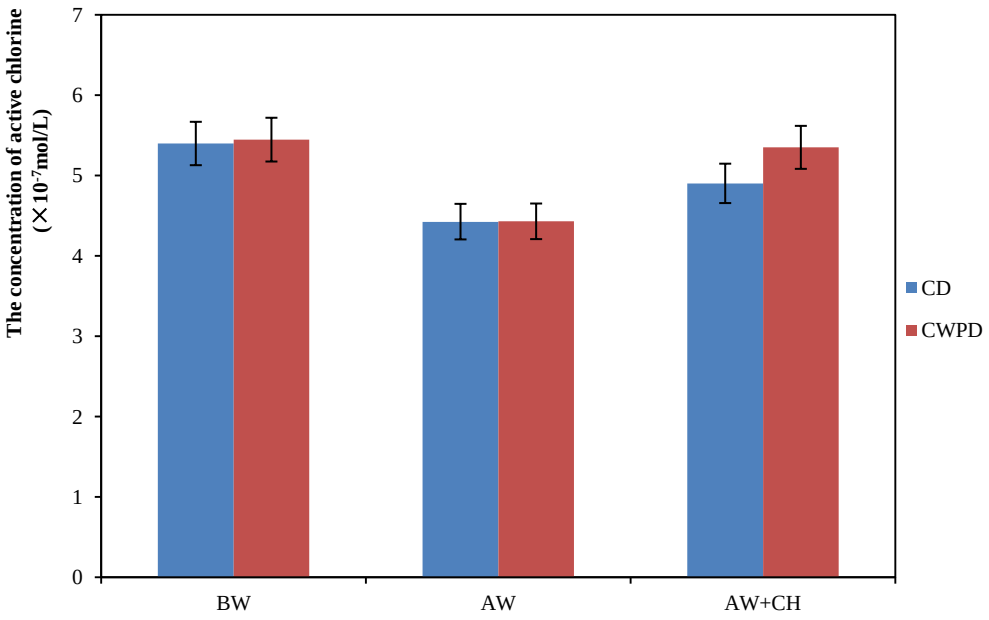

Figure 5.23 Regenerability of cotton fabric coated with DMH

5.4.4 FTIR-ATR

FTIR-ATR is used to determine the existing and the 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 N_2 plasma treatment will be determined. The second derivative FTIR-ATR spectrum of untreatd cotton fabric (Figure 5.24a), cotton fabric treated with plasma (Figure 5.24b), cotton fabric coated with DMH with the aid of plasma (Figure 5.24c) and cotton fabric coated with DMH without plasma treatment (Figure 5.24d) is shown in Figure 5.24.

Compared with Figure 5.24a, the peaks at around 1547 cm^{-1} are assigned to N-H (amine II) deformation in Figure 5.24b, 5.24c and 5.24d. The absorbance peak at 1768 cm^{-1} is attributable to the stretching vibrations of C=O of carboxyl group which can react with amide groups on hydantoin ring (Zhou & Kan, 2015). Absorbance bands in the 1754 cm^{-1} region of Figure 5.24c and 5.24d represent the stretching vibrations of C=O (El-Newehy et al., 2011; Kocer et al., 2008; Kocer et al., 2011; Sun et al., 2012; Wang et al., 2006). Meanwhile, it is found that the absorbance peak of C=O in Figure 5.24c is higher than that in Figure 5.24d, which means the content of DMH on sample with plasma treatment is higher than that on sample without plasma treatment. Therefore, the functionalization of N_2 plasma treatment introduces N-containing groups into cotton fabric and the etching effect of plasma treatment improves the content of DMH on cotton fabric (Silva et al., 2008).

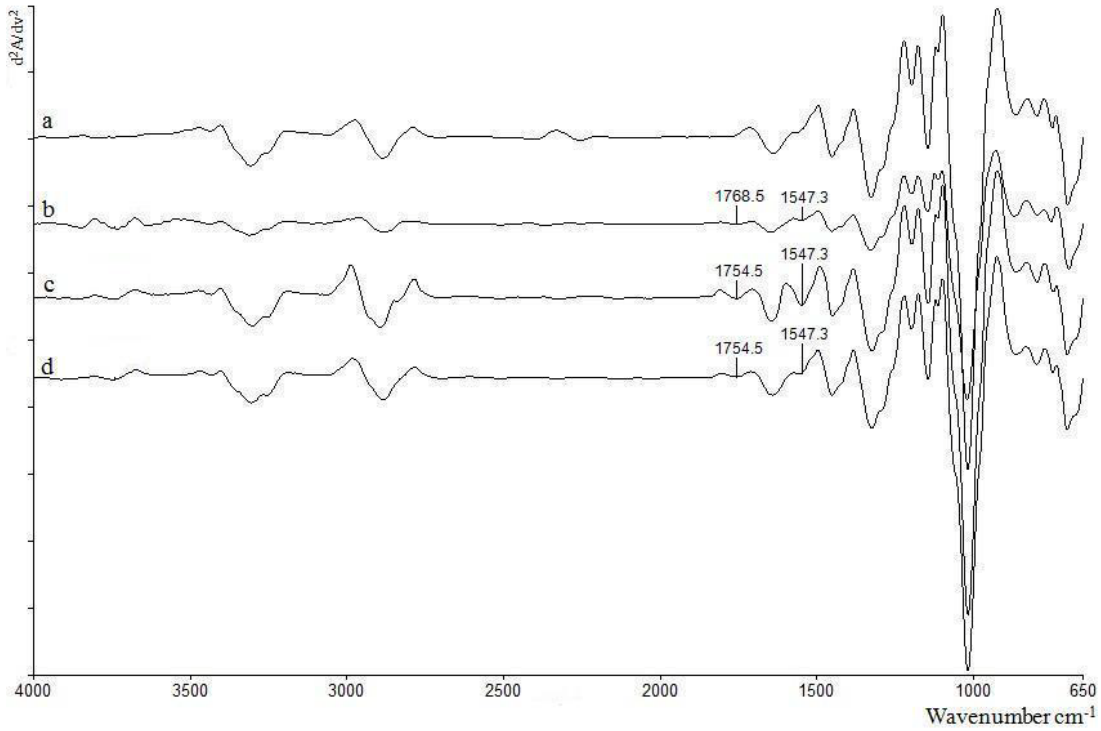

Figure 5.24 Second derivative FTIR spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric coated with DMH through 'pad-dry-cure' method with the aid of plasma (CWPD), (d) cotton fabric coated with DMH through 'pad-dry-cure' method (CD)

5.4.5 SEM

SEM is employed to observe the variation of the physical characteristics of the modified substrates' surface. SEM image of untreated cotton fabric (Figure 5.25a), cotton fabric coated with DMH through "pad-dry-cure" method (CD) (Figure 5.25b) and cotton fabric coated with DMH through 'pad-plasma-dry-cure' method (CWPD) (Figure 5.25c) is shown in Figure 5.25.

As shown in Figure 5.25, the surface of cotton fibers is smooth and even before coating, while the surface of cotton fibers coated with DMH is not smooth and even anymore. Compared Figure 5.25b and 5.25c, it is found that DMH on the surface of fibers treated with plasma in Figure 5.25c is more than that on the surface of fibers

without plasma treatment in Figure 5.25b. Therefore, DMH can be coated onto cotton fabrics, and the distribution of DMH on the surface of cotton fibers is improved by plasma treatment. That is because the groves and cracks formed by the etching effect of plasma treatment make the adhesion of DMH onto the surface of cotton fabrics easy (Karahan & Özdoğan, 2008).

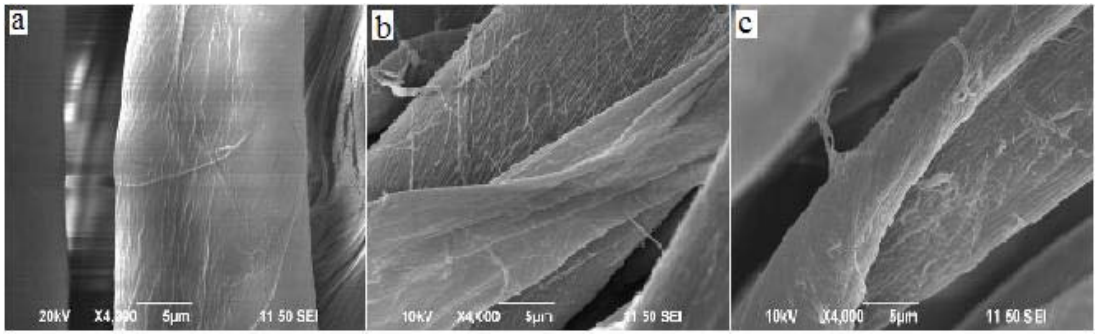

Figure 5.25 SEM image of (a) untreated cotton fabric, (b) cotton fabric coated with DMH through "pad-dry-cure" method (CD), (c) coated with DMH through 'pad-dry-cure' method with the aid of plasma (CWPD).

5.5 Optimization of DMH antimicrobial finishing of cotton fabric with plasma treatment after drying in pad-dry-cure process (pad-dry-plasma-cure)

5.5.1 Optimum condition analysis

OATS is used for optimizing antimicrobial finishing experiments of cotton fabrics with plasma treatment after drying in pad-dry-cure process. The optimum condition and the importance of different factors in experiments are obtained easily through orthogonal experiments. The mean clear width of sample against *S. aureus* (ATCC 6538) from sample is used for evaluating antimicrobial activity of sample. The wider clear width means the antimicrobial activity is more active. The mean clear width of the bacteria against *S. aureus* obtained from the nine specimens generated by OATS

technique and the result of orthogonal analysis, where T_{mn} refers to the sum of the evaluation indexes of all levels (n, n=I, II, III) in each factor (m, m=A, B, C), such that T_{AI}=1.156+1.090+1.611=3.857 is the sum of level I of factor A; T_{CII}=1.090+1.062+1.258=3.410 is the sum of level II of factor C; and K_{mn} implies the mean value of T_{mn}, such that $K_{AI}=T_{AI}/3$=3.857/3=1.286 is the mean value of T_{AI}; $K_{CII}=T_{CII}/3$=3.410/3=1.137 is the mean value of T_{CII} are shown in Table 5.4. In addition, T is the sum of the evaluation indexes, w_i, which is an evaluating indicator for antimicrobial activity of cotton fabrics evaluated by AATCC Test Method 147-2011; and the range of factors in each column, R=Max(K_j)-Min(K_j), indicates the function of the corresponding factor (Chuanwen et al., 2010). The larger value of R means the greater impact of the level of the factor on the experimental index. Therefore, the impact of every factor on the final treatment effect can be distinguished clearly on the comprehensive condition that every factor changes.

The results of orthogonal analysis for four parameters used in the finishing process are shown in Table 5.4 and the order of importance of these factors is $R_A > R_C > R_D > R_B$. That is, temperature of curing has the greatest impact on the experimental result, and concentration of bleaching solution has a comparatively less impact, next factor in the order is concentration of DMH, and the last one is duration of chlorination (Chuanwen et al., 2010; Kan et al., 2011). The best level is suggested by orthogonal analysis based on the mean value of the testing factors. Thus, the optimum process for DMH coating is $A_{III}B_{II}C_{III}D_{III}$, that is, concentration of DMH = 6%, temperature of curing = 140 ºC, concentration of bleaching solution 1.2% and time of chlorination 60min. Fabric finished under the optimum condition shows mean clear width against *S. aureus* of 1.798 mm which is wider than the mean clear width in the other nine specimens (Table 5.4). The optimum condition was verified. And the samples were used for further

evaluation in terms regenerability, FTIR-ATR and SEM.

Table 5.4 Orthogonal table for optimizing the antibacterial property of cotton fabric coated with DMH [e]

Test run	Parameters				Results
	Concentration of DMH (%) A	Temperature of curing (ºC) B	Concentration of bleaching solution (%) C	Time of chlorination (min) D	Mean clear width against *S. aureus* (mm) w_i
1	I	I	I	I	1.156
2	I	II	II	II	1.090
3	I	III	III	III	1.611
4	II	I	II	III	1.062
5	II	II	III	I	1.338
6	II	III	I	II	0.879
7	III	I	III	II	1.468
8	III	II	I	III	1.601
9	III	III	II	I	1.258
T_{mI}	3.857	3.686	3.636	3.752	$T_{mn}=\Sigma_{i=1}^{9} w_i$
T_{mII}	3.279	**4.029**	3.410	3.437	
T_{mIII}	**4.327**	3.748	**4.417**	**4.274**	$K_{mn}=\frac{1}{3}T_{mn}=\frac{1}{3}\Sigma_{i=1}^{9} w_i$
K_{mI}	1.286	1.229	1.212	1.251	
K_{mII}	1.093	**1.343**	1.137	1.146	
K_{mIII}	**1.442**	1.249	**1.472**	**1.425**	$R = \mathrm{Max}(K_{mI}, K_{mII}, K_{mIII}) - \mathrm{Min}(K_{mI}, K_{mII}, K_{mIII})$
R	*0.349*	*0.114*	*0.335*	*0.279*	

[e] Figures in bold exhibit the highest value among all values of different variables used while italics show the level of importance of each variable.

Effect of concentration of DMH on antibacterial property is shown in Figure 5.26; mean clear width against *S. aureus* decreases with the increase of concentration of DMH when the concentration of DMH is lower than 4%, while it increases when concentration of DMH increases beyond 4%. The reason is that the molecules of DMH aggregate with the increase of concentration of DMH solution, which affects the distribution and adhesion of DMH on fabric resulting in the decrease of mean clear width against *S. aureus* with the increase of concentration of DMH. However, when the concentration of DMH is high enough, the aggregated DMH can cover more area of fabric and more DMH can be coated on the fabric. That is why mean clear width

against *S. aureus* increases with until concentration of DMH increases to 6%.

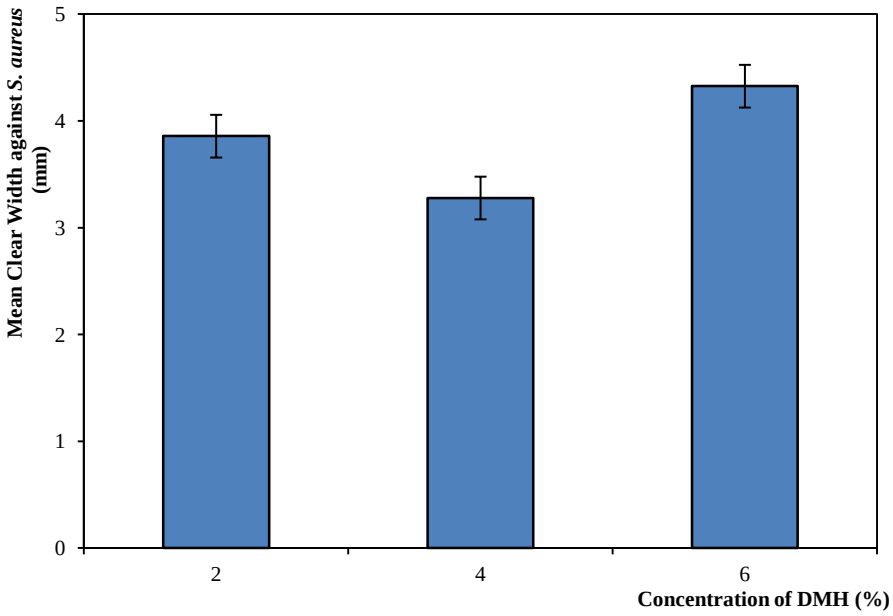

Figure 5.26 Effect of concentration of DMH on antibacterial property of cotton fabric coated with DMH.

As shown in Figure 5.27, the mean clear width against *S. aureus* increases with the increase of curing temperature until it reaches 140 ºC but it decreases with the increase of curing temperature beyond 140 ºC (Figure 5.27). The reason is that the melting point of DMH is around 175ºC and DMH getting detached from the fabric surface at high curing temperatures can result in poor fixation of DMH on fabric; it gets dissolved in water easily during the following finishing process. Finally, the DMH content on the fabric and chlorine decrease with the increase of the curing temperature and the antimicrobial activity decreases.

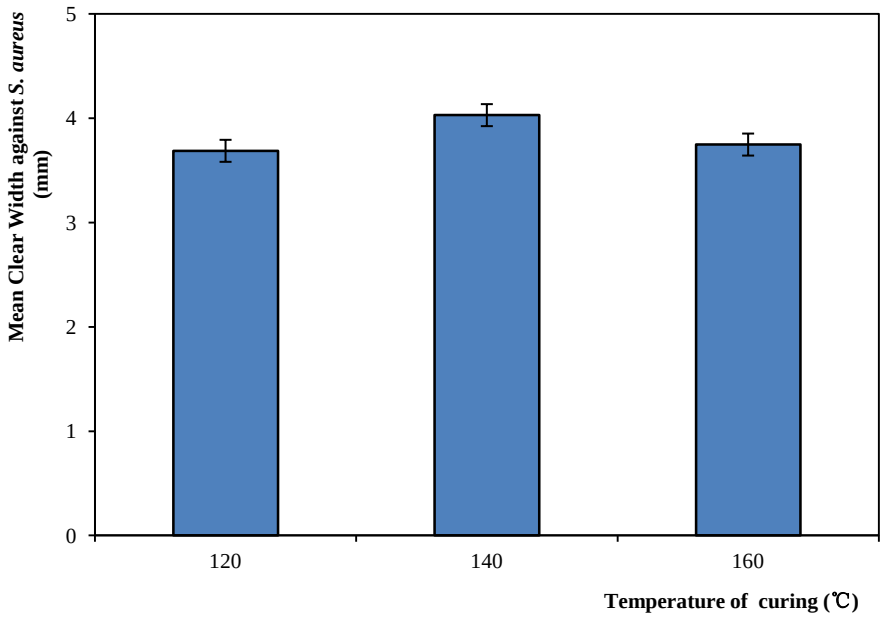

Figure 5.27 Effect of temperature of curing on antibacterial property of cotton fabric coated with DMH.

As shown in Figure 5.28, when concentration of bleaching solution is lower than 1%, the mean clear width against *S. aureus* decreases with the increase of concentration of bleaching solution. However, when concentration exceeds 1%, the mean clear width against *S. aureus* increases with further increase of concentration of bleaching solution. Generally speaking, the higher concentration of bleaching solution provides more chlorine to interact with the DMH in the cotton fabric and then the concentration of chlorine on fabric increases with increase of concentration of bleaching solution. However, this assumption does not verify the outcome depicted in Figure 5.28. This may be because of the strong oxidizing ability of chlorine in sodium hypochlorite solution, which is considered to be capable of damaging functional moieties on fabrics. These damages correspond to the occurrence of decreased antimicrobial efficacy of treated fabrics. The N-containing groups come from two sources: DMH and N_2 plasma (Silva et al., 2008). N-containing groups in DMH are chlorinated easily due to the effect of steric hindrance of functional groups in cellulose molecules. After

chlorination, chlorine in N-containing groups in DMH reduces the stability of hydantoin ring, which is destroyed easily by chlorine. With the increase of concentration of bleaching solution, the redundant chlorine has the chance to react with N-containing groups introduced by N_2 plasma. That is why the mean clear width against *S. aureus* decreases with the increase of concentration of bleaching solution when the concentration of bleaching solution is lower than 1% and it increases with the increase of concentration of bleaching solution after the concentration exceeds 1%.

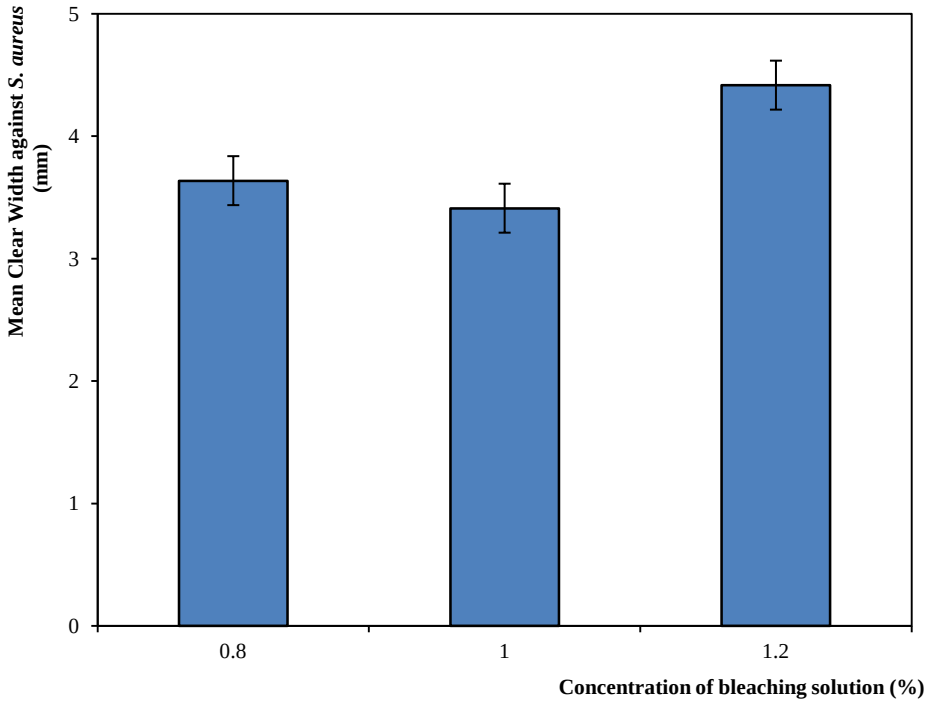

Figure 5.28 Effect of concentration of bleaching solution on antibacterial property of cotton fabric coated with DMH.

As shown in Figure 5.29, mean clear width of finished cotton fabric against *S. aureus* decreases with the increase of chlorination time until time of chlorination reaches 40 min but after it exceeds 40 min, mean clear width against *S. aureus* starts increasing. The reason is that sources of N-containing groups on cotton fabric are DMH and nitrogen plasma treatment. At the beginning of chlorination, N-containing groups in DMH get chlorinated by sodium hypochlorite due to the steric hindrance of vicinal

chemical groups of N-containing groups introduced by nitrogen plasma on cotton fabrics (Kocer et al., 2008; Qian & Sun, 2003). However, N-Cl structure in DMH is not stable. N-Cl bonds are hydrolyzed (reverse reaction, Figure 5.1) with the extension of chlorination time (Sun & Worley, 2005). The functional groups in DMH are potentially destroyed by the strong oxidizing ability of sodium hypochlorite. Meanwhile, N-containing groups introduced by plasma on cotton fabric are transferred into the N-halamine structure with the extension of chlorination time. Therefore, the mean clear width of cotton fabric against *S. aureus* increases after the initial decrease.

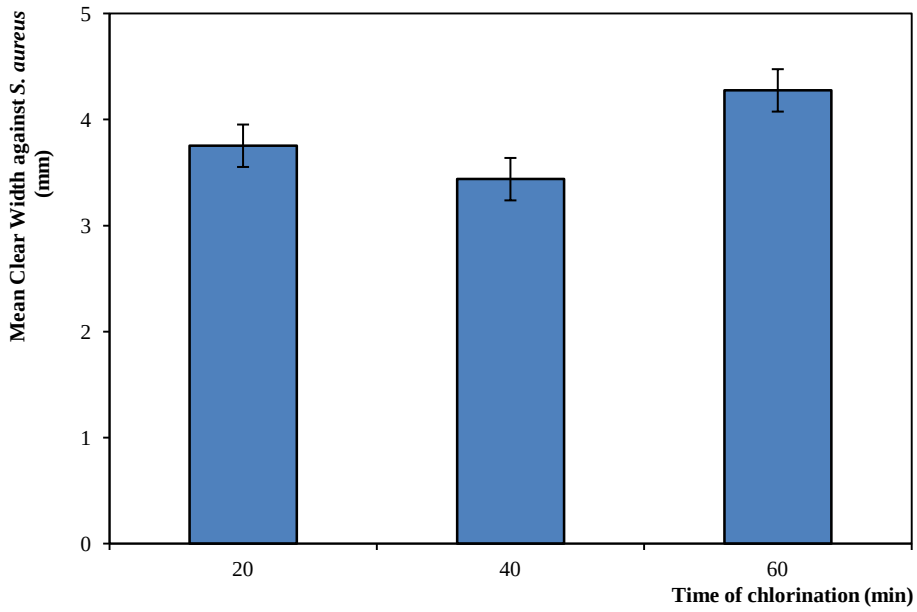

Figure 5.29 Effect of time of chlorination on antibacterial property of cotton fabric coated with DMH.

5.5.2 Relationship between antibacterial property and concentration of chlorine on cotton fabric

The relationship between antimicrobial properties and concentration of chlorine on cotton fabric is shown in Figure 5.30; the mean clear distance against *S. aureus* becomes wider with the increase of concentration of chlorine on cotton fabric coated

with DMH, which appears to be a linear relationship, and the fitting linear equation is y = 0.1957x + 0.5112 and decisive coefficient R^2 = 0.8626. That is because the antimicrobial principle is that chlorine is used to kill microorganism. When the quantity of chlorine increases, more bacteria can be killed. Therefore, the effective method to improve the antimicrobial property of cotton fabric is to increase the amount of chlorine on cotton fabric.

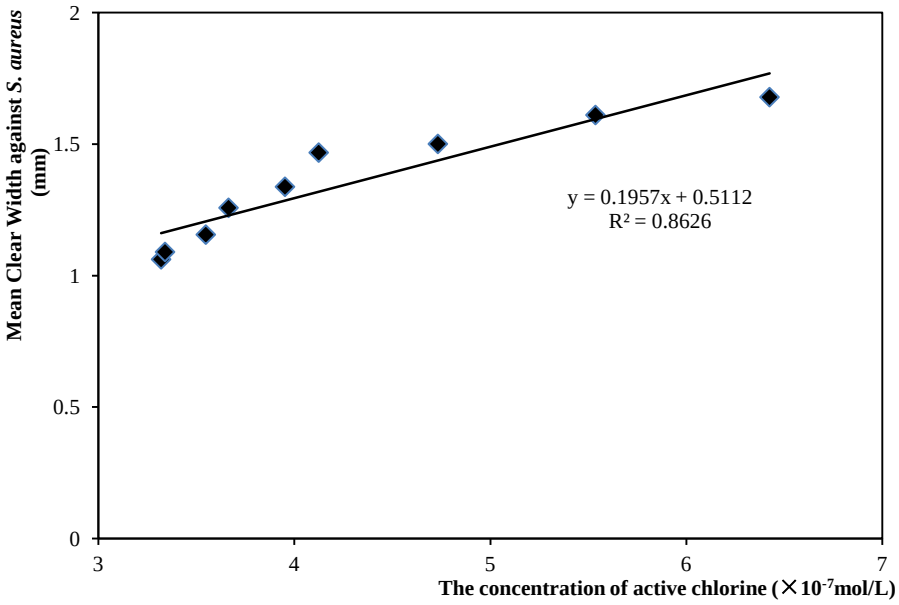

Figure 5.30 Relationship between antimicrobial property and concentration of chlorine on cotton fabric.

5.5.3 Regenerability

Regenerability makes antimicrobial textiles environmentally friendly. Meanwhile, it prolongs service life of antimicrobial textiles. Figure 5.31 compares the regenerability of cotton fabric with plasma treatment (CDPD) and without plasma treatment (CD).

In Figure 5.31, concentration of chlorine on fabric with plasma treatment is always higher than on fabric without plasma treatment under all conditions. According to Figure 5.31, the concentration of chlorine on cotton fabric with plasma treatment after re-chlorination is approximately the same as that before washing. However,

concentration of chlorine on fabric without plasma treatment decreases after washing and re-chlorination, compared with that before washing. It is also found that the concentration of chlorine on fabric with plasma treatment after washing decreases slightly when compared with that without plasma treatment after washing. Therefore, plasma treatment increases the content of chlorine on cotton fabric. The reason is that plasma treatment etches the surface of material leading to many cracks on the surface of the material. The uneven surface of material makes the coating of the material easier, which enhances the adhesion of DMH on cotton fabric (Karahan & Özdoğan, 2008). In addition, N_2 plasma used in this experiment can functionalize the substrate with N-containing groups, such as $–NH_2$, -NH, =NH, $CONH_2$ or C≡N (Silva et al., 2008), which also increases the content of chlorine on cotton fabric. Therefore, it is concluded that the antimicrobial properties of cotton fabric coated with DMH with plasma treatment are regenerable and the regenerability is improved by plasma treatment.

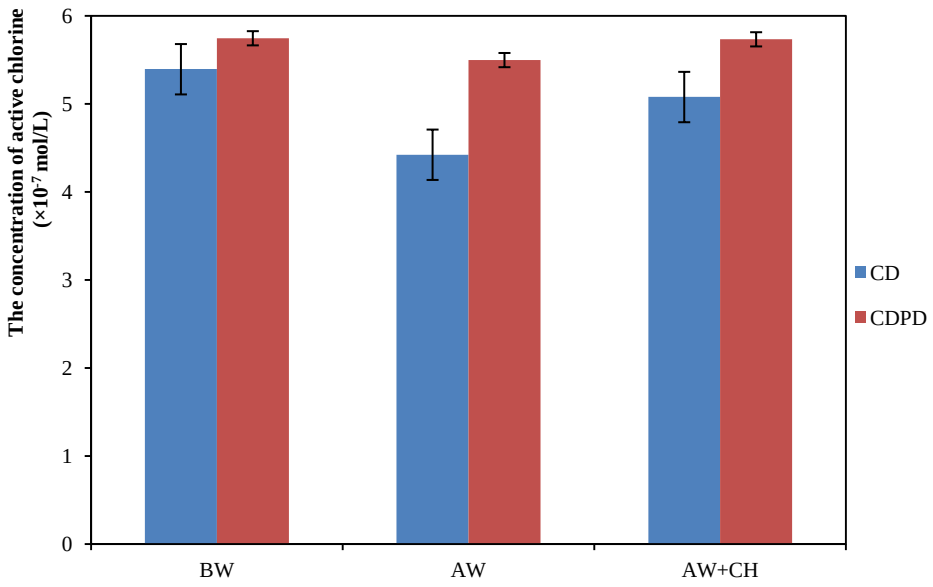

Figure 5.31 Regenerability of cotton fabric coated with DMH.

5.5.4 FTIR-ATR

FTIR-ATR is used to determine the existence and the 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 N_2 plasma treatment are determined. The second derivative FTIR-ATR spectrum of untreated cotton fabric (Figure 5.32a), cotton fabric treated with plasma (Figure 5.32b), cotton fabric coated with DMH with plasma treatment (Figure 5.32c) and cotton fabric coated with DMH without plasma treatment (Figure 5.32d) is shown in Figure 5.32.

Compared with Figure 5.32a, the peaks at around 1550 cm^{-1} are assigned to N-H (amine II) deformation in Figure 5.32b, 5.32c and 5.32d. And the absorbance bands in the 1755 cm^{-1} region of Figure 5.32b, 5.32c and 5.32d represent the stretching vibrations of C=O (El-Newehy et al., 2011; Kocer et al., 2008; Kocer et al., 2011; Sun et al., 2012; Wang et al., 2006). Absorbance peak of C=O in Figure 5.32b belongs to stretching vibration of carboxyl group formed through oxidation of hydroxyl group in cotton fabric by particles in N_2 plasma (Hui et al., 2005). Absorbance peaks of C=O in Figure 5.32d are derived from DMH. And Absorbance peaks of C=O in Figure 5.32c include stretching vibration of carboxyl group and amide. Therefore, the absorbance peak of C=O in Figure 5.32c is higher than that in Figures 5.32b and 5.32d, which means the content of C=O in Figure 5.32c is higher than that in Figures 5.32b and 5.32d, according to the Beer–Lambert law. Moreover, etching effect of plasma treatment can improve the content of DMH on cotton fabric (Silva et al., 2008). Accordingly, N_2 plasma treatment improves the antibacterial effect of cotton fabric coated with DMH.

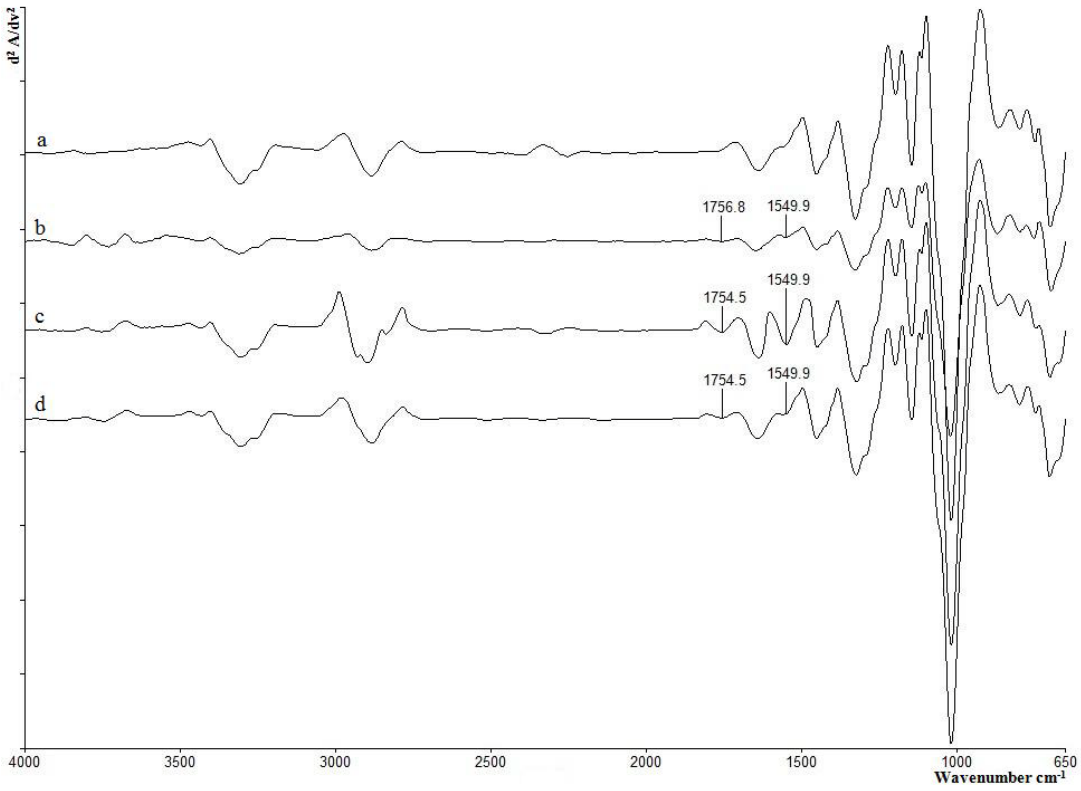

Figure 5.32 Second derivative FTIR spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric coated with DMH through 'pad-dry-cure' method with plasma treatment (CDPD), (d) cotton fabric coated with DMH through 'pad-dry-cure' method (CD).

5.5.5 SEM

SEM is employed to observe the variations of physical characteristics of surface of the modified substrates. SEM image of untreated cotton fabric (Figure 5.33a), cotton fabric coated with DMH through "pad-dry-cure" method (CD) (Figure 5.33b) and cotton fabric coated with DMH through 'pad- dry- plasma-cure' method (CDPD) (Figure 5.33c) is shown in Figure 5.33.

As shown in Figure 5.33, the surface of cotton fibers is smooth even before coating, while the surface of cotton fibers coated with DMH is not smooth. Compared with the distribution of DMH on fabric without plasma treatment (Figure 5.33b), DMH is more

evenly distributed on the surface of fibers treated with plasma (Figure 5.33c). Thus, distribution of DMH coated onto cotton fabrics is improved by plasma treatment. That is because the grooves and cracks formed by the etching effect of plasma treatment provide space for DMH to adhere on the surface of cotton fabrics (Karahan & Özdoğan, 2008).

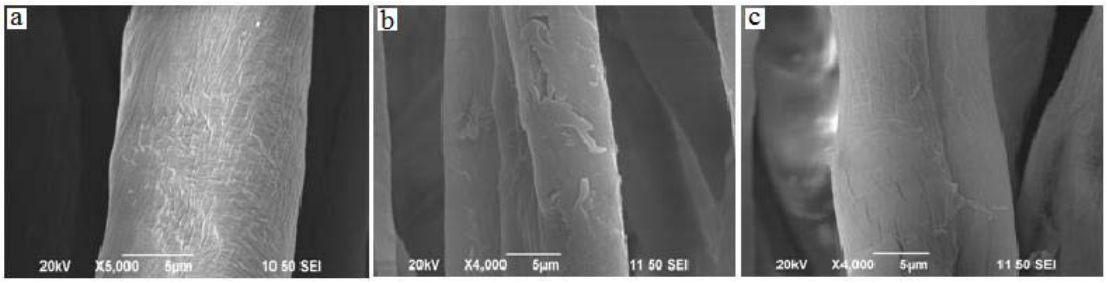

Figure 5.33 SEM image of (a) untreated cotton fabric, (b) cotton fabric coated with DMH through "pad-dry-cure" method (CD), (c) coated with DMH through 'pad-dry-cure' method with plasma treatment (CDPD).

5.6 Comparison of antimicrobial cotton finished with DMH with plasma treatment at different stage

In order to study the different function of plasma treatment in different finishing processes and obtain optimum finishing process for cotton fabric with regenerable antimicrobial property, properties of cotton fabrics finished with four different finishing processes mentioned above under same process parameters are compared.

5.6.1 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. The effect of bleaching time on concentration of active chlorine on coated fabrics (same concentration of bleaching solution) is shown in Figure 5.34

when plasma treatment was applied in different stages of the DMH finishing process. According to Figure 5.34, it can be seen that the impacts of bleaching time on concentration of active chlorine on fabrics with and without plasma treatment are different, when concentration of sodium hypochlorite is 0.8%. When bleaching time is less than 40 min, concentration of chlorine on cotton fabrics with plasma treatment is higher than that on cotton fabrics without plasma treatment under same finishing conditions. While bleaching time is 60 min, concentration of chlorine on cotton fabrics with plasma treatment before padding (CPD) or after drying (CDPD) is higher than that on cotton fabrics finished by the other two finishing processes (CD and CWPD). Compared the concentration of chlorine on cotton fabrics with plasma treatment chlorinated within 40 min, it is found that the values of chlorine on the fabrics are around 8×10^{-7} mol/L. When bleaching time is up to 60 min, concentrations of chlorine on cotton fabrics with plasma treatment after padding (CWPD) decrease obviously compared with that on cotton fabrics with plasma treatment before padding (CPD) or after drying (CDPD). It is also found that chlorine on cotton fabrics with plasma treatment after drying (CDPD) is more stable than that on cotton fabric with plasma treatment before padding (CPD) with the extension of bleaching time. Therefore, the optimal chlorination time is less than 40 min for cotton fabrics coated with DMH to transfer the amino groups into N-halamine structures. It can be seen that plasma treatment enhances concentration of active chlorine on cotton fabrics, that is to say, plasma treatment increases the adhesion of DMH and N_2 plasma treatment introduces nitrogen groups onto the surface of cotton fabrics, because the etching effect of plasma

treatment makes the surface of fibers uneven which provides more surface area for DMH coating. Meanwhile, N_2 plasma can functionalize the substrate with N-containing groups, such as $–NH_2$, -NH or $CONH_2$ (Silva et al., 2008; Wagner, Fairbrother, & Reniers, 2003). Among these three antibacterial finishing processes with plasma treatment (CPD, CWPD and CDPD), the adhesion of fabrics treated by plasma after drying, i.e. CDPD is improved more significantly than the other two processes (CPD and CWPD). The reason may be that H_2O in cotton fabric of plasma treatment reacts with active free radicals generated by plasma, which weakens the action of plasma to adhesion of DMH (Sanchis, Calvo, Fenollar, Garcia, & Balart, 2008). Adhesion of DMH on cotton fabrics with CDPD process is better than that with CPD process is because both cotton fabrics and DMH are treated by plasma, and these numerous free radicals interlock DMH with fabrics at the same time (Sanchis et al., 2008).

The effects of concentration of bleach solution on concentration of active chlorine are shown in Figure 5.35, when chlorination time is 40 min. In general, concentration of active chlorine on fabric increases with concentration of bleach solution (Figure 5.35). The concentration of active chlorine on fabrics treated with plasma after drying (CDPD) is higher than that on fabrics finished with the other two processes (CPD and CWPD). This proves that plasma treatment can enhance the adhesion of DMH especially in dry condition, that is, dry condition is more suitable for plasma treatment to work. 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 being coated onto cotton fabrics (Sanchis et al., 2008).

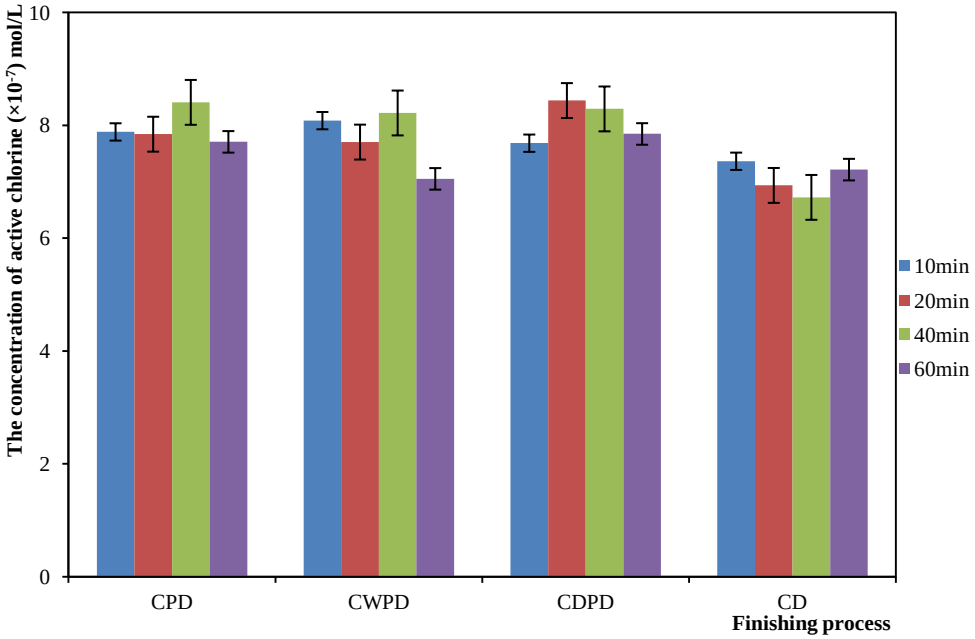

Figure 5.34 The effect of bleaching time on concentration of active chlorine on fabrics

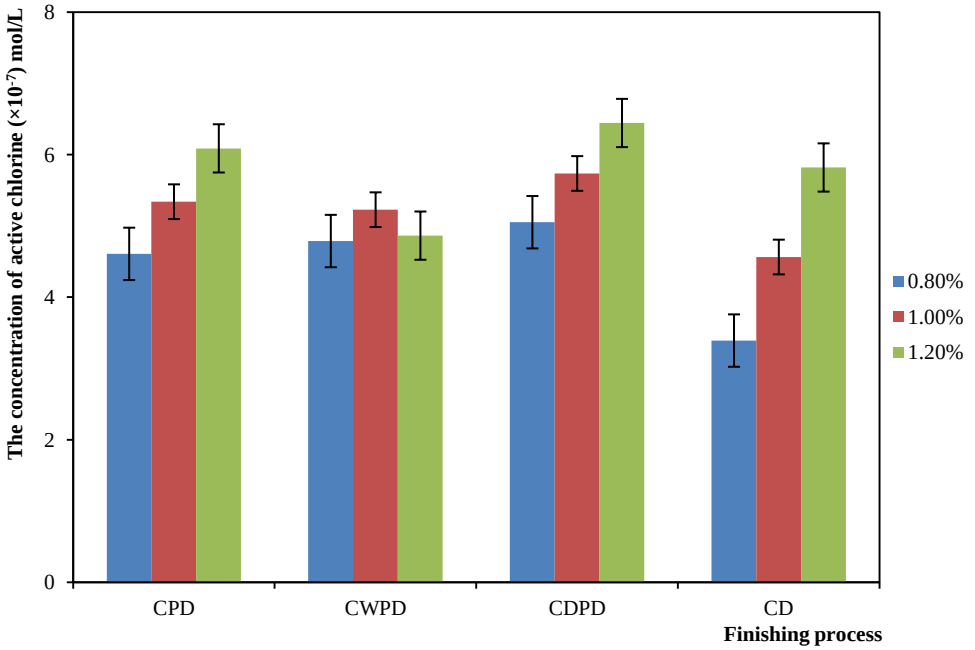

Figure 5.35 The effect of the concentration of bleaching solution on the concentration of active chlorine on the fabrics

5.6.2 FTIR-ATR

The FTIR-ATR spectra are employed to characterize DMH coated on the surface of cotton fabrics followed by chlorination. The characteristic absorbance band of DMH is amide and C=O stretching of hydantoin ring. The second derivative FTIR-ATR spectrum of untreated cotton fabric (Figure 5.36a), cotton fabric treated with plasma (Figure 5.36b), cotton fabric coated with DMH through 'pad-dry-cure' method (Figure 5.36c, CD), cotton fabric treated with plasma, and then coated with DMH through 'pad-dry-cure' method (Figure 5.36d, CPD), cotton fabric padded with DMH, treated with plasma, dried and cured (Figure 5.36e, CWPD), cotton fabric padded with DMH, dried, treated with plasma and cured (Figure 5.36f, CDPD) are shown in Figure 5.36. Compared with Figure 5.36a, the peak at around 1557 cm^{-1} is assigned to N-H deformation and the absorbance bands in 1768 cm^{-1} region represents the stretching vibrations of C=O of carboxyl group in the spectra in Figure 5.36b (Hui et al., 2005). After plasma treatment, there are N-H group and C=O group, which means particles N_2^+, N_2 (excited), N, and N^+ generated in nitrogen plasma treatment introduce nitrogen-containing groups on cotton fabrics and oxidize the primary hydroxyl group to carboxyl group which can react with amide groups on hydantoin ring. And the peaks at around 1549 cm^{-1} are assigned to N-H deformation and the absorbance bands in the 1757cm^{-1} region represent the stretching vibrations of C=O in the spectra in Figure 5.36c, 5.36d, 5.36e and 5.36f (El-Newehy et al., 2011; Kocer et al., 2008; Kocer et al., 2011; Sun et al., 2012; Wang et al., 2006). These demonstrate that DMH is coated on to fabrics. However, hydantoin ring in DMH has two carbonyls which should show two

absorbance bands in the FTIR-ATR spectrum. In order to observe absorbance bands in the FTIR-ATR spectrum more clearly, spectral subtraction was employed to process the second derivative FTIR-ATR spectrum data shown in Figure 5.37, that is, untreated cotton fabric was subtracted from DMH coated cotton fabrics. It is found that absorbance band at 1643 cm^{-1} is still shown after spectral subtraction in Figure 5.37, which is attributed to stretching vibrations of another C=O and overlapped with absorbance peaks of H_2O in original spectrum. In the FTIR-ATR spectrum, absorbance peaks of C=O in hydantoin ring move to lower wavenumber, which is because the mesomeric effect of the nitrogen lone pair is more important than the inductive effect of the nitrogen in amides, especially after the hydrogen in amide is replaced by chlorine (Hartwell, Richards, & Thompson, 1948). In differential spectrum, it is also found that stretching vibrations of N-H at 3304cm^{-1} overlapped with associated O-H stretching vibration in original spectrum moves to higher wavenumber resulting by the inductive effect of chlorine introduced by chlorination in hydantoin ring. And the absorbance peaks of carbonyls and amide in Figure 5.37b, 5.37c and 5.37d are higher than that in Figure 5.37a. According to Beer–Lambert law, concentration of DMH on samples with higher absorbance peaks is much higher. Therefore, plasma treatment enhances the adhesion of DMH on cotton fabrics.

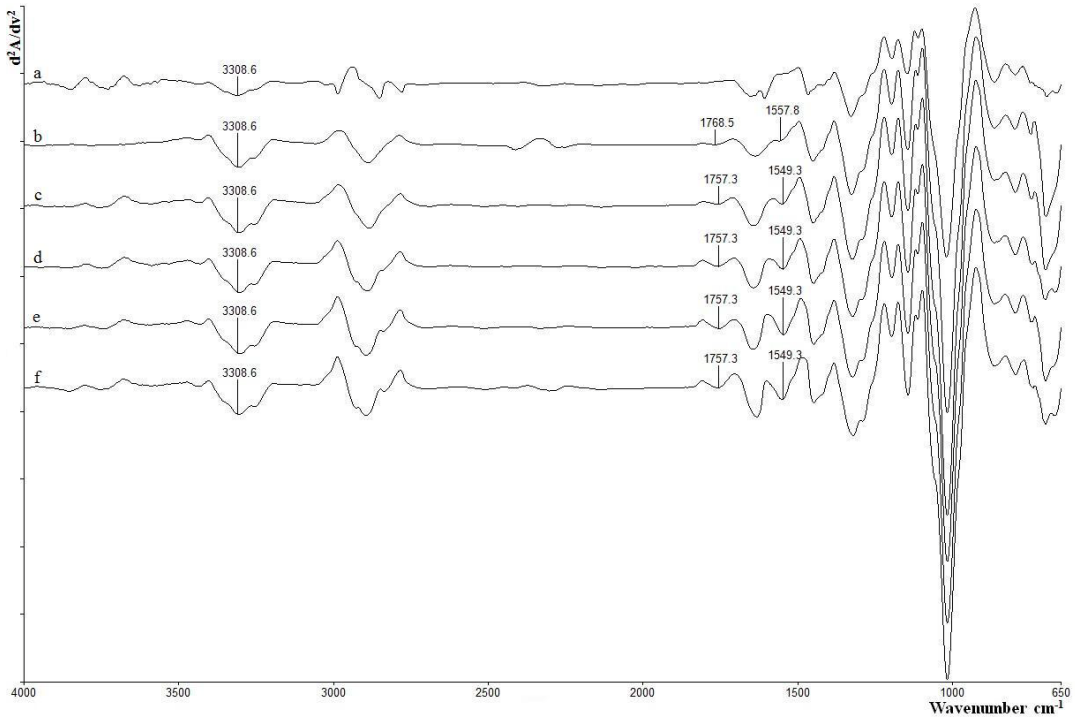

Figure 5.36 Second derivative FTIR spectrum of (a) untreated cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric coated with DMH through 'pad-dry-cure' method (CD), (d) cotton fabric treated with plasma, and then coated with DMH through 'pad-dry-cure' method (CPD), (e) cotton fabric padded with DMH, treated with plasma, dried and cured (CWPD), (f) cotton fabric padded with DMH, dried, treated with plasma and cured (CDPD).

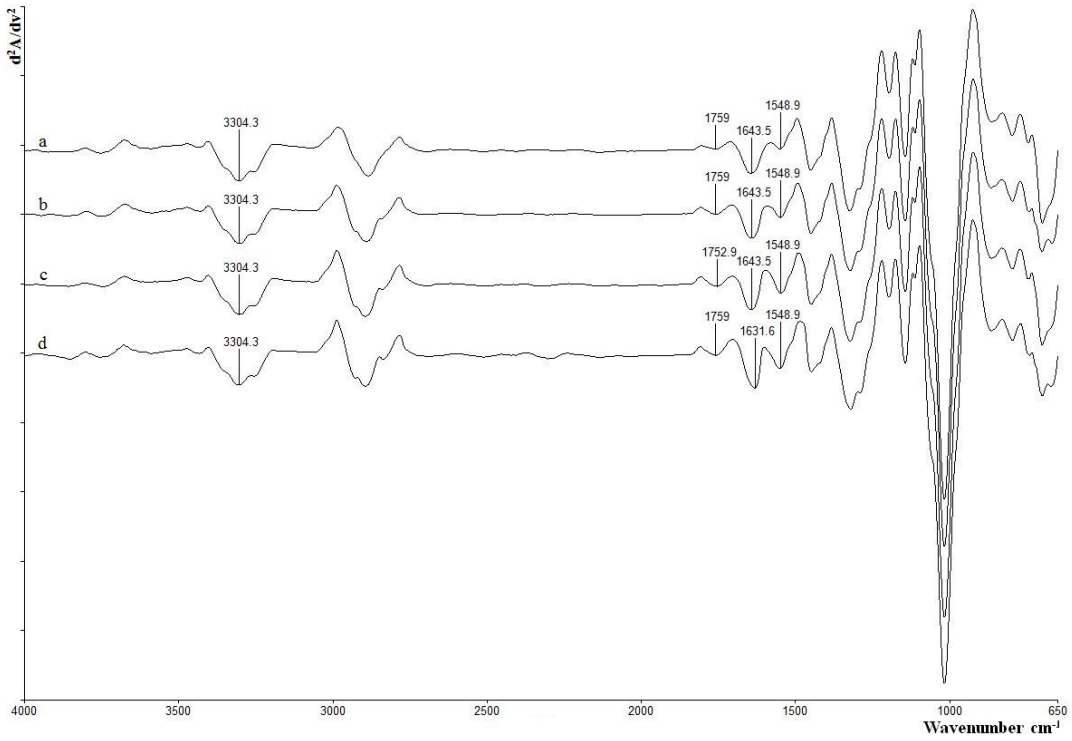

Figure 5.37 Spectral subtraction of second derivative FTIR spectrum of (a) cotton fabric coated DMH with 'pad-dry-cure' method(CD) – untreated cotton fabric, (b) cotton fabric treated with plasma firstly, and then coated DMH with 'pad-dry-cure' method(CPD) - untreated cotton fabric, (c) cotton fabric padded with DMH, treated with plasma, dried and cured(CWPD) –untreated cotton fabric, (d) cotton fabric padded with DMH, dried, treated with plasma(CDPD) –untreated cotton fabric.

5.6.3 Morphological properties

SEM is used to analyze coated fabrics' surface morphological properties to observe the effect of plasma-based DMH grafting on cotton fabric. SEM images of untreated cotton fabric (Figure 5.38a), cotton fabric grafted with DMH through 'pad-dry-cure' method (Figure 5.38b, CD), cotton fabric treated with plasma firstly, and then coated with DMH through 'pad-dry-cure' method (Figure 5.38c, CPD), cotton fabric padded with DMH, and then treated with plasma, dried and cured (Figure 5.38d, CWPD),

cotton fabric padded with DMH, dried, treated with plasma and cured (Figure 5.38e, CDPD) is shown in Figure 5.38. Surface of fibers in untreated cotton fabric is even and smooth (Figure 5.38a), while cotton fibers coated with DMH are not smooth (Figure 5.38b, 5.38c, 5.38d and 5.38e). It also can be observed that the surfaces of fibers coated with DMH without plasma treatment (CD) in Figure 5.38b and with plasma treatment after padding (CWPD) in Figure 5.38d have more line-shape structures than those with plasma treatment before padding (CPD) in Figure 5.38c and with plasma treatment after drying (CDPD) in Figure 5.38e. That is to say, surfaces of fibers with plasma treatment in dry condition (CPD and CDPD) in Figure 5.38c and 5.38e are more even than those without plasma treatment (CD) in Figure 5.38c and with plasma treatment in wet condition (CWPD) in Figure 5.38e. This is because the functions of plasma treatment also include etching the surface of materials, besides functionalizing the surface of matrixes. After etching, there are many cracks on the surfaces of materials, which are not even anymore, which makes the coating of the materials easier. Meanwhile, because of the cracks, surface area of fibres is increased, and more DMH can be coated onto the fabrics (Karahan & Özdoğan, 2008). Moreover, etching can remove the micro line-shape structure on the surface of materials, which makes it even (Karahan & Özdoğan, 2008). Because most of the particles generated during plasma treatment are greatly unstable and have a high tendency to react, these free radicals in the humid environment may react with the H_2O present in fabrics, which affects the effects of plasma treatment on cotton fabrics (Sanchis et al., 2008). As a consequence, cotton fabrics coated with DMH with plasma treatment have uniform

appearance, especially in dry condition (CPD and CDPD). Therefore, it can be concluded that dry conditions are beneficial for the appearance of substance with functional finish with the aid of plasma treatment.

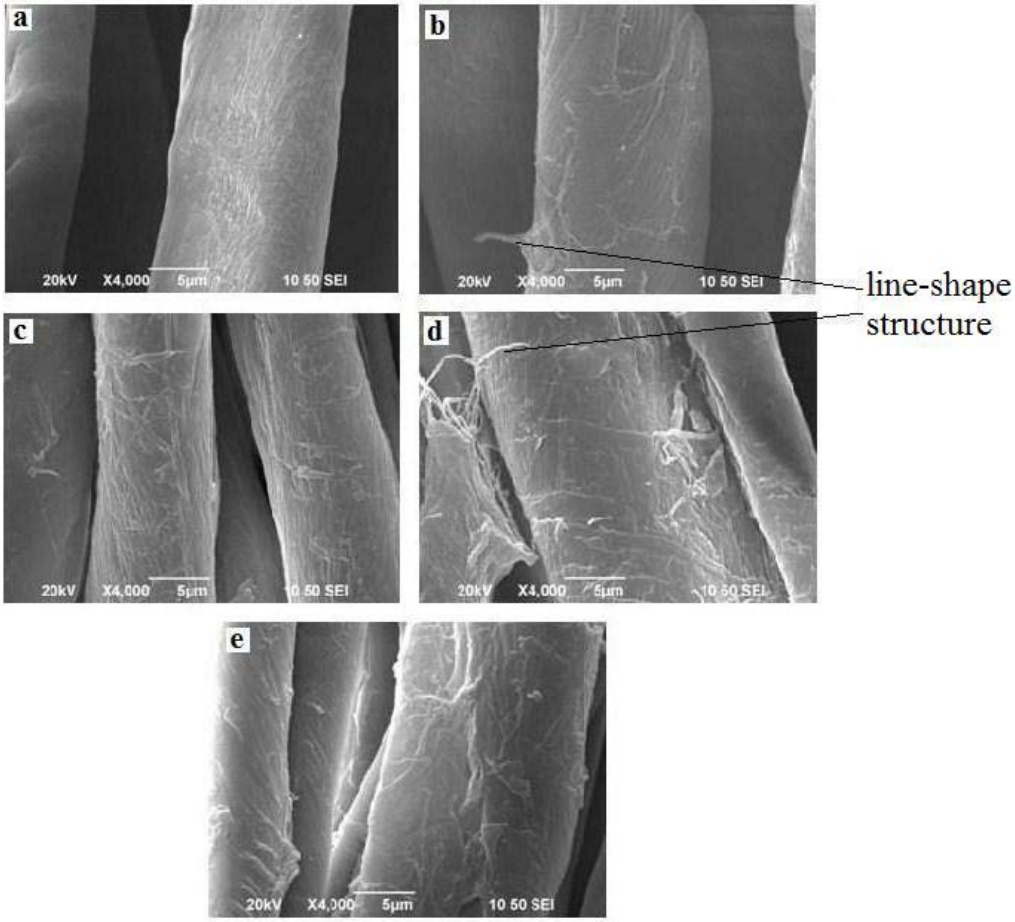

Figure 5.38 SEM image of (a) untreated cotton fabric, (b) cotton fabric grafted with DMH through 'pad-dry-cure' method (CD), (c) cotton fabric treated with plasma firstly, and then coated with DMH through 'pad-dry-cure' method (CPD), (d) cotton fabric padded with DMH, and then treated with plasma, dried and cured (CWPD), (e) cotton fabric padded with DMH, dried, treated with plasma and cured (CDPD).

5.6.4 Regenerability and durability

The regenerability and durability are very important for antibacterial textiles. Antibacterial textiles with good regenerability and storage stability have long useful life. Figure 5.39 and 5.40 show the regenerability and storage stability, respectively, of

cotton fabrics coated with DMH with the aid of plasma treatment.

It can be seen in Figure 5.39 that almost all samples coated with DMH with the aid of plasma treatment can be regenerable after washing because active chlorine concentration of these fabrics decreases after washing while active chlorine concentration increases after they are re-chlorinated. However, active chlorine concentration on cotton fabrics after they are re-chlorinated is a little lower than before washing. Regenerability of cotton fabrics coated with DMH without plasma treatment (CD) is not very good. The active chlorine concentration decreases after washing, even after re-chlorination. That is because the adhesion of DMH on cotton fabrics is not very good; DMH on cotton fabrics easily dissolves into water, even in bleaching solution. Regenerable effect on cotton fabrics treated with plasma after padding (CWPD) is better than others (CPD and CDPD). Regardless of what the concentration of bleaching solution is, the difference between concentration of active chlorine on cotton fabrics treated with plasma after padding (CWPD) before washing and after re-chlorination is smaller than that on the cotton fabrics treated with the other two kinds of processes (CPD and CDPD). That may be because of the existence of moisture in the working environment which reacts with unstable particles generated by plasma when the fabrics are treated with plasma after padding (Sanchis et al., 2008). Therefore, it can be concluded that plasma treatment is helpful for improving regenerability of cotton fabrics coated with DMH and plasma treatment after padding (CWPD) can enhance the adhesion of DMH on cotton fabrics which increases the durability of antibacterial effect of cotton fabrics coated with DMH.

In Figure 5.40, it can be seen that active chlorine concentration on fabrics coated with DMH decreases around 15% after storage for six months in darkness because microorganism during the storage consumes the chlorine on cotton fabrics. Compared with fabrics without plasma treatment, concentration of active chlorine on nearly all samples with plasma treatment is much higher. Among these samples with plasma treatment, concentrations of active chlorine on fabrics treated with plasma after drying (CDPD) is always higher than the other two finishing processes (CPD and CWPD), irrespective of concentration of the bleaching solution. The first reason is that N_2 plasma treatment introduces the nitrogen functional groups on cotton fabrics, which can increase the content of chlorine on cotton fabrics (Silva et al., 2008; Wagner et al., 2003). The second reason is that the unstable particles generated during the plasma treatment react to form free radicals, and the interlocking of these free radicals enhances stability of N-halamine structures on the fabrics (Sanchis et al., 2008). Consequently, plasma treatment after drying (CDPD) can increase the content of nitrogen functional groups and strengthen the stability of N-halamine structures on cotton fabrics as well.

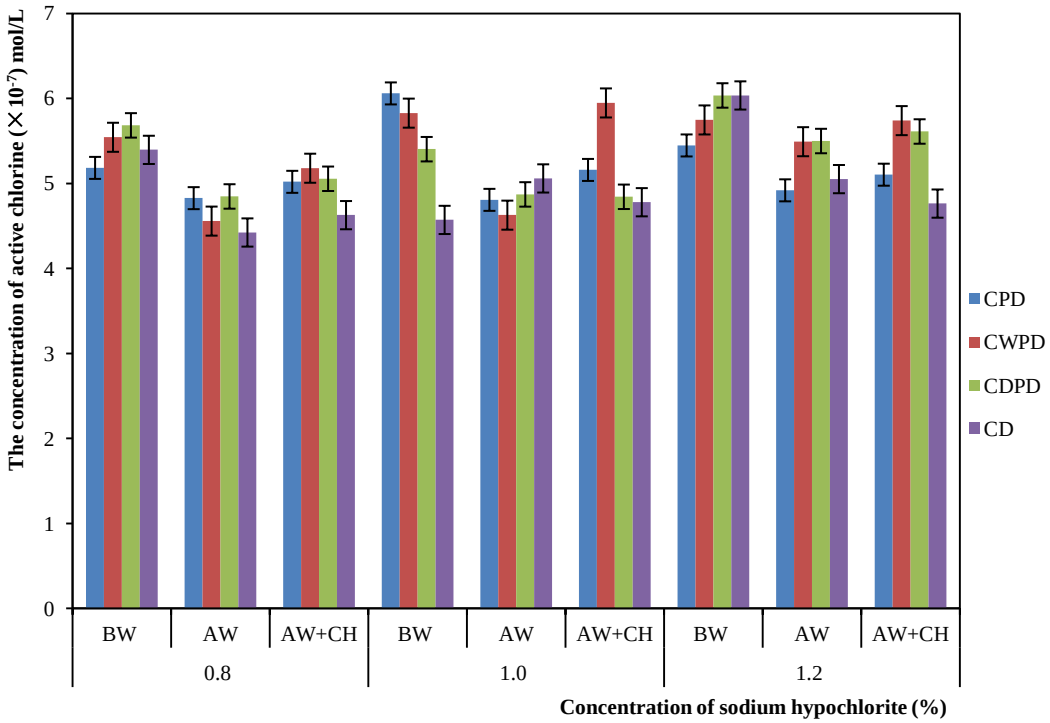

Figure 5.39 The regenerability of cotton fabric coated with DMH and plasma treatment

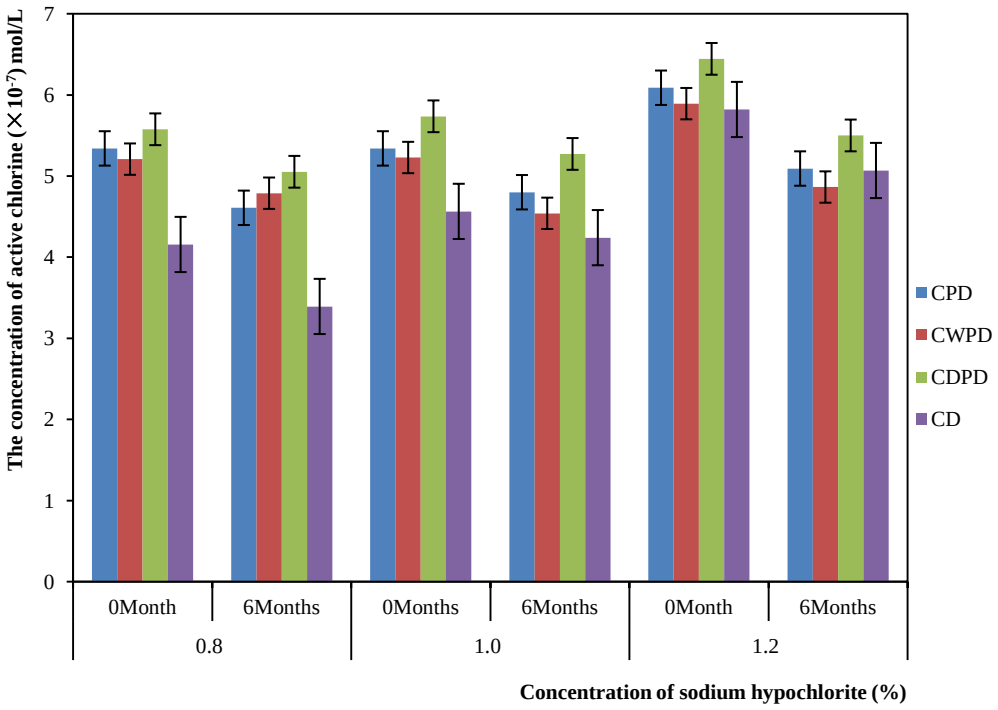

Figure 5.40 The duration of antimicrobial effect of cotton fabric coated with DMH and plasma treatment

5.6.5 Antimicrobial activity

In this part, the effect of concentration of DMH and content of sodium hypochlorite on antibacterial activity of samples is studied. 4% of DMH solution is coated onto the surface of cotton fabrics. 0.8%, 1% and 1.2% of sodium hypochlorite solution are used to chlorinate the DMH coated cotton fabrics. The growth of microorganism underneath the tested specimen was observed and the width of the clear zone was measured. The antibacterial efficacy data are presented in Table 5.5.

No growth of *S. aureus* (ATCC 6538) underneath the tested specimen was 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 5.5, it can be seen that the clear zone of samples widens with the increase of concentration of sodium hypochlorite. Also, clear zone of samples with plasma treatment is wider than that without plasma treatment (CD). And the clear zone of samples with plasma treatment after padding and drying (CDPD) is much wider than the other two kinds of samples with plasma treatment (CPD and CWPD). Therefore, it can be concluded that plasma treatment following padding and drying (CDPD) is the best antibacterial finishing process for cotton fabrics coated with DMH among all of finishing processes (CD, CPD and CWPD) examined in this study.

Table 5.5 The mean clearance distance of the bacteria obtained from the specimens

Treatment process	Concentration of sodium hypochlorite (%)	Mean Clear Width against *S. aureus* (mm)
Untreated fabric	0.0	0.000
CPD	0.8	0.887
	1.0	1.252
	1.2	1.473
CDPD	0.8	1.478
	1.0	1.561
	1.2	1.679
CWPD	0.8	0.885
	1.0	1.364
	1.2	1.607
CD	0.8	0.638
	1.0	1.052
	1.2	1.434

5.7 Conclusion

Cotton fabrics finished with DMH with different finishing processes followed by chlorination with sodium hypochlorite provide different effective antimicrobial functions against bacteria, *S. aureus* (ATCC 6538).

The optimum condition of the antimicrobial finishing process for cotton fabric coated with DMH through pad-dry-cure method is concentration of DMH = 2%, curing temperature = 120 ºC, concentration of bleaching solution = 1% and time of chlorination = 20 min. The findings show that concentration of DMH, curing temperature and the time of chlorination have an inversely proportional relationship with the mean clear width against *S. aureus*, i.e. antimicrobial activity. While the relationship between concentration of bleaching solution and antimicrobial activity is

not linear, that is, when concentration of bleaching solution is lower than 1%, the mean clear width against *S. aureus* increases with increase of concentration and when concentration of bleaching solution is higher than 1%, the mean clear width against *S. aureus* decreases with increase of concentration.

The optimum condition of the antimicrobial finishing process for cotton fabric coated with DMH through pad-dry-cure method with plasma pretreatment (plasma-pad-dry-cure) in this research is concentration of DMH = 2%, temperature of curing = 140 ºC, concentration of bleaching solution = 0.8% and duration of chlorination = 40min. The findings show that concentration of DMH is inversely proportional to the mean clear width against *S. aureus*, i.e. antimicrobial activity; the relationship between temperature of curing and the antimicrobial activity is not a linear relationship; antimicrobial activity of the fabric becomes active with the increase of curing temperature from 120ºC to 140ºC but weakens when the temperature rises beyond 140ºC, to 160ºC; and both the duration of chlorination and concentration of the bleaching solution have a slight effect on the antimicrobial activity.

The optimum condition of the antimicrobial finishing process for cotton fabrics coated with DMH through pad-dry-cure method with plasma treatment after padding (plasma-pad-dry-cure) in this research is concentration of DMH = 4%, curing temperature = 140 ºC, concentration of bleaching solution = 0.8% and time of chlorination = 20min. The findings show that only time of chlorination in these four factors has an inversely proportional relationship with the mean clear width against *S. aureus*, i.e. antimicrobial activity. However, the relations of concentration of DMH, curing temperature and concentration of bleaching solution to the mean clear width

against *S. aureus* are not liner. These relations are: as concentration of DMH is lower than 4%, the mean clear width against *S. aureus* increases with the increase of concentration of DMH and as concentration of DMH is higher than 4%, the mean clear width against *S. aureus* decreases with the increase of concentration of DMH; when curing temperature is lower than 140 ºC, the mean clear width against *S. aureus* increases with the increase of curing temperature and when curing temperature is higher than 140 ºC, the mean clear width against *S. aureus* decreases with the increase of curing temperature; and the mean clear width against *S. aureus* decreases with the increase of concentration of bleaching solution, when concentration of bleaching solution is lower than 1%, while the mean clear width against *S. aureus* increases with the increase of concentration of bleaching solution, when concentration of bleaching solution is higher than 1%.

The optimum condition of the antimicrobial finishing process for cotton fabrics coated with DMH through pad-dry-cure method with plasma treatment after drying, as identified in this research, is concentration of DMH = 6%, curing temperature = 140 ºC, concentration of bleaching solution = 1.2% and time of chlorination = 60min. The findings show that the relations of these four factors to the mean clear width against *S. aureus*, i.e. antimicrobial activity, are not linear. These relations are: as concentration of DMH is lower than 4%, the mean clear width against *S. aureus* decreases with the increase of concentration of DMH and as concentration of DMH exceeds 4%, the mean clear width against *S. aureus* increases with the increase of concentration of DMH; when curing temperature is lower than 140 ºC, the mean clear width against *S. aureus* increases with the increase of curing temperature and when curing temperature is higher than 140ºC, the mean clear width against *S. aureus* decreases with the increase of curing temperature; the mean clear width against *S. aureus* decreases with

the increase of concentration of bleaching solution until concentration of bleaching solution is lower than 1%, while it increases with the increase of concentration of bleaching solution after concentration increases beyond 1%; and when chlorination time is less than 40 min, the mean clear width against *S. aureus* decreases with the increase of chlorination temperature but when chlorination time is longer than 40 min, the mean clear width against *S. aureus* increases with the increase of chlorination temperature.

In this study, chlorine is used to inhibit bacteria. Therefore, the antimicrobial activity is proportional to the concentration of chlorine on the finished cotton fabric.

The evaluations of cotton fabric coated with DMH followed by chlorination show the antimicrobial activity can be regenerable. With the help of plasma treatment, durability of antimicrobial cotton fabrics coated with DMH is improved, because the introduction of nitrogen-containing group onto the surface of cotton fabrics by nitrogen plasma enhances the antimicrobial activity. Compared with traditional pad-dry-cure process, there is no crosslinker in these processes in the study. Because N_2 plasma treatment provides carboxyl groups on the surface of cotton fabric and these carboxyl groups can react with amide groups on hydantoin ring in DMH to form new amide group. The absorbance peak of amide is same as the absorbance peak of amide on hydantoin ring. This is environmentally friendly. And the distribution, the content and the adhesion of DMH on cotton fabrics are improved by plasma treatment. It is found that pad-dry-plasma-cure finishing process shows more helpfulness on the antimicrobial finishing of cotton fabrics finished with DMH.

CHAPTER 6 ANTIMICROBIAL FINISHING COTTON FABRIC WITH CHITOSAN

6.1 Introduction

Healthcare related textiles have started receiving much attention because of increased hygiene concerns and the increasingly felt need for antimicrobial treatment of cotton fabric. Researchers have focused on antimicrobial polymers and textiles in the past few decades due to the growing concern about contact transmissions of infectious diseases and personal protection from undesirable effects. Consequently, durable and regenerable antimicrobial materials based on N-halamine structure have been developed, which are optimal for antimicrobial application and environmental safety (Huang & Sun, 2003; Liu & Sun, 2006).

N-halamines, regenerable antibacterial agents, refer to compounds that contain amine, amide and imide halamine bonds which have the capability of rapid and total inactivation of a wide spectrum of micro-organisms (Y. Sun & Sun, 2001a; Y. Sun & Sun, 2001b; Y. Sun & Sun, 2001c; Y. Sun & Sun, 2002; Y. Sun & Sun, 2004). Most of N-halamine antimicrobial agents are synthesized from other chemicals which are not safer than the antimicrobial agents modified from natural chemicals. The most typical natural antimicrobial agent is chitosan, which is inexpensive, hypoallergenic, non-toxic, biocompatible and biodegradable. It has been used in many different areas as an antimicrobial agent, such as food industry, medical industry and textile industry (Abdou, Elkholy, Elsabee, & Mohamed, 2008; El-Tahlawy, El-Bendary, Elhendawy, & Hudson, 2005; Kim, Choi, & Yoon, 1998; Lim & Hudson, 2004; Tavaria et al., 2012). The mechanism of its inhibitory activity towards microorganisms is that the positive amino groups in chitosan bind tightly with the anionic components of cell

surfaces. Therefore, chitosan and lots of its derivatives have been studied to improve the potency of the antimicrobial effect (Kan, Yuen, & Tsoi, 2011). For example, chitosan was attached on cotton fabrics with different crosslinking agents (Abdou et al., 2008; El-Tahlawy et al., 2005). Chitosan derivatives, such as N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC) and O-acrylamidomethyl-N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (NMAHTCC), are synthetized and applied to cotton fabrics to increase the durability of antimicrobial finishing (Kim et al., 1998; Lim & Hudson, 2004). Compared with these modified chitosan derivatives, chitosan with N-halamine structures has provided relatively more exciting results. Cao and Sun (2008) found that upon chlorine bleach treatment, some of the amino groups in chitosan can be transformed into N-halamine structures and the antimicrobial functions of N-halamine-based chitosan against both gram-negative and gram-positive bacteria are potentially durable and regenerable (Cao & Sun, 2008).

Plasma techniques have been demonstrated to be a suitable tool to assist the generation of the specific modification, which can activate the surface of fabric and improve the absorption of chemicals (Kan et al., 2011; Lam, Kan, & Yuen, 2011a; Lam, Kan, & Yuen, 2011b). Compared with chemical treatments, plasma processing adds value to traditional textiles in an environmentally friendly way and does not affect the bulk characteristics of textiles. When the working gases are reactive gas, plasma pretreatment introduces some groups on the surface on textiles which can be used as catalysts to increase the reactivity of substance toward chemicals (Huh et al., 2001; Parvinzadeh Gashti et al., 2014; Parvinzadeh & Ebrahimi, 2011a; Parvinzadeh & Ebrahimi, 2011b). In this study, with the aid of plasma, chitosan was coated onto the surface of cotton fabric and then the N-halamine structure was introduced into

chitosan (Figure 6.1). Plasma was applied at a different stage of antimicrobial finishing process which results in different antimicrobial effects on cotton fabric.

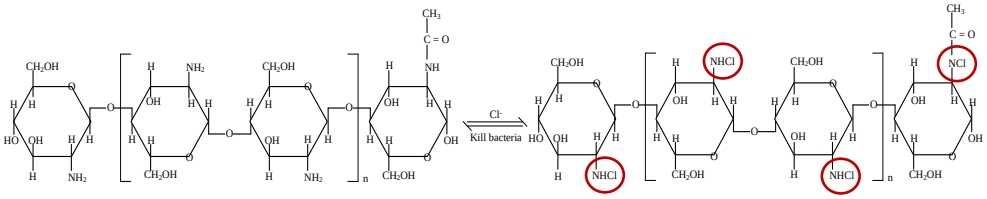

Figure 6.1 The reversible redox reaction of chitosan with halamine structures (red cycle shows the N-halamine structure).

6.2 Comparison of optimal processes of chitosan antibacterial finishing for cotton fabric with plasma treatment at different stage

6.2.1 The effect of chlorination conditions on concentration of active chlorine on cotton fabric

Plasma treatment affects the amount of chitosan coated on cotton fabrics. The amount of chitosan on fabric can be estimated by testing the concentration of active chlorine on the fabric and the concentration of chitosan solution is 4% for finishing. The effect of chlorination time on concentration of active chlorine on chitosan coated fabrics under the same concentration of sodium hypochlorite is shown in Figure 6.2 when plasma treatment was applied in different stages of the chitosan finishing process. According to Figure 6.2, when concentration of sodium hypochlorite is 1.0%, treating fabrics with plasma after drying is an efficient method to improve the coating of chitosan (CDPC sample). It seems that N_2 as reactive gas in the mixture of nitrogen and helium plasma treatment can trigger the reaction between cotton fabric and chitosan in dry conditions, which increases the coating of chitosan. Alternately, it is convenient for N_2 as reactive gas in the mixture of nitrogen and helium plasma

treatment to introduce amine, amide or imide into cotton and chitosan in that conditions which can enhance the amount of chlorine in the chitosan coated fabrics, because N_2 plasma can functionalize the substrate with N-containing group, such as $–NH_2$, -NH, =NH, $CONH_2$ or C≡N (Silva et al., 2008). The effect of chlorination time on the coating rate is also shown in Figure 6.2. It is found that concentration of active chlorine reduces with the increase of chlorination time under the same concentration of sodium hypochlorite when fabrics are treated with plasma before 'pad-dry-cure' process and fabrics are not treated with plasma in the finishing process. When plasma treatment is carried out during the 'pad-dry-cure' process, concentration of active chlorine does not reduce with the variation of chlorination time. That is to say, plasma treatment during the 'pad-dry-cure' process can improve the coating of chitosan on the fabrics.

The effect of concentration of sodium hypochlorite on concentration of active chlorine on chitosan coated fabrics is shown in Figure 6.3 under chlorination time of 10 min. when plasma treatment was applied in different stages of the chitosan finishing process. As can be seen from Figure 6.3, plasma treatment after padding and drying can increase the number of nitrogen groups because concentration of active chlorine in these fabrics is denser than in any other fabrics. The results in Figure 6.3 also demonstrate that concentration of sodium hypochlorite does not have obvious effects on concentration of active chlorine. But, when the concentration of sodium hypochlorite is 1%, the concentration of chlorine on fabric is slightly higher than that on fabrics chlorinated with 0.8% and 1.2% sodium hypochlorite solution. It will be better to chlorinate the chitosan coated fabrics with 1% sodium hypochlorite.

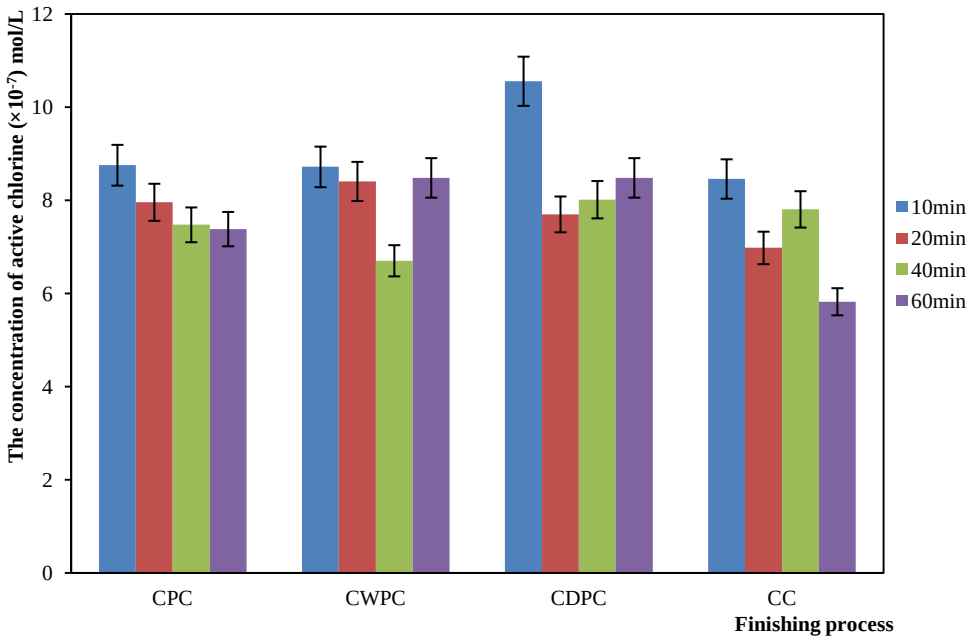

Figure 6.2 The effect of chlorination time on concentration of active chlorine on cotton fabrics

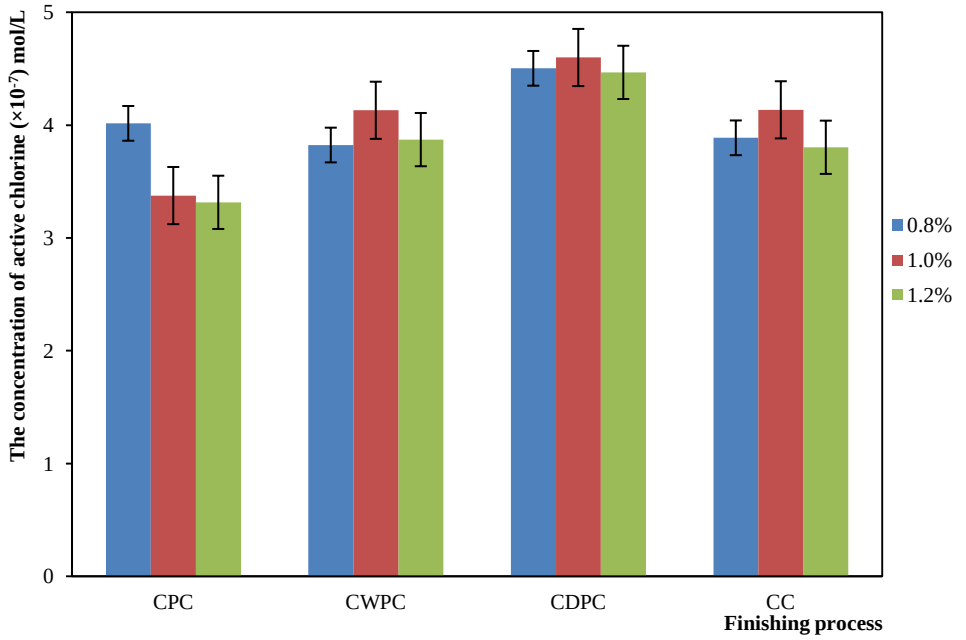

Figure 6.3 The effect of the concentration of sodium hypochlorite on the concentration of active chlorine on the fabrics

6.2.2 FTIR-ATR

To confirm the variation of fabric surface after coating, chitosan coated fabrics after

chlorination were characterized by FTIR-ATR spectroscopy and the concentration of chitosan solution is 4% for finishing. The characteristic absorbance band of chitosan is amide I, C=O stretching and amide II. The absorbance band of N-H appears at 1640-1550 cm^{-1} normally, depending on the groups it connects, while the C=O stretching vibration usually shows absorbance band between 1680$cm^{-1}$and 1630cm^{-1} (Yuen et al., 2012).

The FTIR-ATR spectra of pure cotton fabric (Figure 6.4a, pure cotton fabric), cotton fabric treated with plasma (Figure 6.4b, cotton fabric treated with plasma), cotton fabric coated with chitosan through 'pad-dry-cure' method (Figure 6.4c, CC), fabric treated with plasma first and then coated with chitosan through 'pad-dry-cure' method (Figure 6.4d, CPC), cotton fabric padded with chitosan, treated with plasma, dried and cured (Figure 6.4e, CWPC) and cotton fabric padded with chitosan, dried, treated with plasma and cured (Figure 6.4f, CDPC) is shown in Figure 6.4. The peak 1548 cm^{-1} corresponds to N-H bending vibration in curves c, d, e and f and the C=O stretching vibration corresponds to the region at 1760cm^{-1}. These two absorbance values are out of their normal range because chlorine replaces the hydrogen in -NH-C=O during chlorination. The absorbance peaks appear in the region of 2900 cm^{-1}, revealing the existence of CH_2. After chitosan coated finishing, the absorbance value is increased that is because the concentration of CH_2 grows bigger. Therefore, it can say that chitosan was coated onto cotton fabrics.

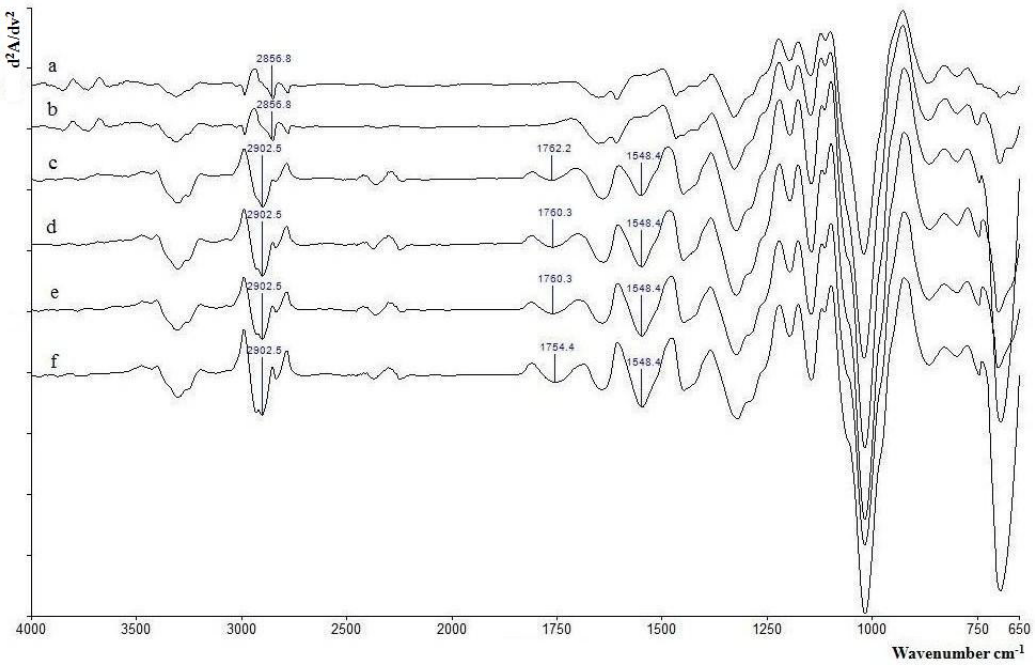

Figure 6.4 FTIR spectrum of (a) pure cotton fabric, (b) cotton fabric treated with plasma, (c) cotton fabric coated with chitosan through 'pad-dry-cure' method (CC), (d) cotton fabric treated with plasma, and then coated with chitosan through 'pad-dry-cure' method (CPC), (e) cotton fabric padded with chitosan, treated with plasma, dried and cured (CWPC), (f) cotton fabric padded with chitosan, dried, treated with plasma and cured (CDPC).

In order to investigate the effect of plasma treatment in detail, the pure cotton spectrum was subtracted from the plasma treated cotton fabric and the chitosan coated cotton fabric was subtracted from chitosan coated cotton fabrics with plasma treatment in three different processes (Figure 6.5). According to Figure 6.5a, the absorbance peak at 1642 cm^{-1} reveals the existence of amide group, which proves N_2 plasma treatment adds amide groups onto cotton fabric. This absorbance band overlaps with the absorbance peak of H_2O in the original spectrum in Figure 6.4. Bands at 2247 cm^{-1} in Figure 6.5 are assigned to the C≡N stretching vibration, because N_2 plasma treatment can functionalize the substrate with C≡N. These absorbance peaks overlap with the absorbance bands of carbon dioxide in the original absorbance spectrum in Figure 6.4. Comparing the peaks at 1548 cm^{-1} (N-H bending vibration), 1739 cm^{-1} (C=O

stretching vibration) and 2938 cm^{-1} (CH_2 stretching vibration) in Figures 6.5b, 6.5c and 6.5d, respectively, it is found that peaks in Figure 6.5b are bigger than those in Figures 6.5c and 6.5d, which once again demonstrates that it is an effective means to improve coating rate of chitosan on cotton fabric with plasma treatment after drying in the coating process.

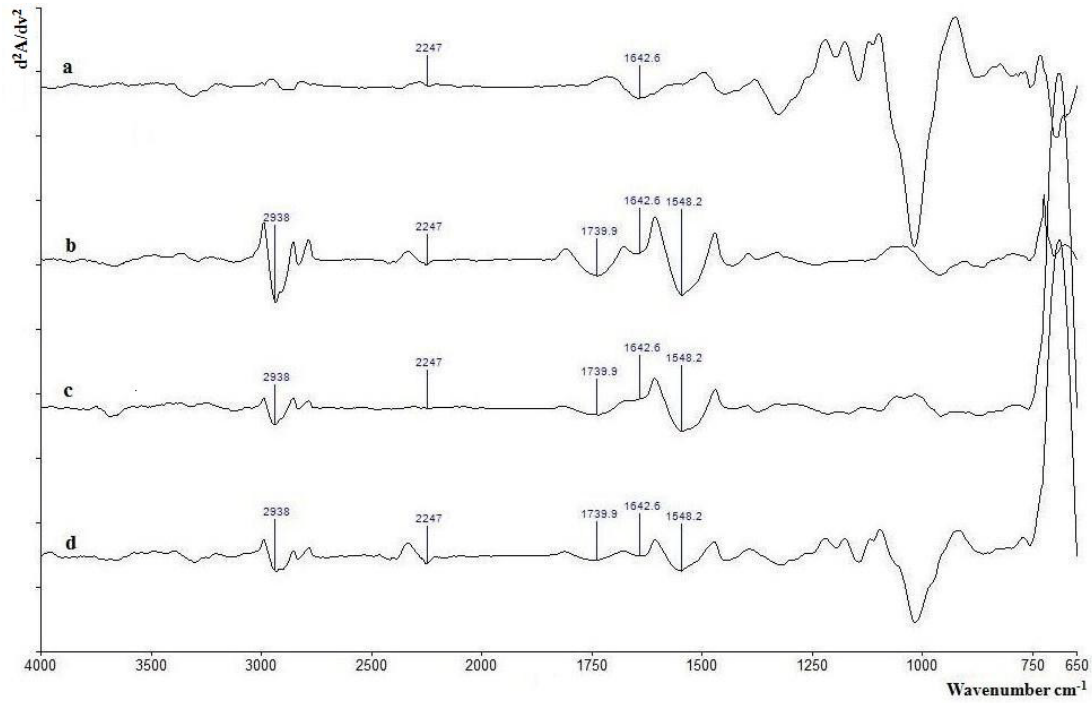

Figure 6.5 Spectral subtraction of (a) cotton fabric treated with plasma – pure cotton fabric, (b) cotton fabric padded with chitosan, dried, treated with plasma(CDPC) – cotton fabric coated chitosan with 'pad-dry-cure' method(CC), (c) cotton fabric padded with chitosan, treated with plasma, dried and cured(CWPC) – cotton fabric coated chitosan with 'pad-dry-cure' method(CC), (d) cotton fabric treated with plasma firstly, and then coated chitosan with 'pad-dry-cure' method(CPC) - cotton fabric coated chitosan with 'pad-dry-cure' method(CC).

6.2.3 Morphological properties

In order to investigate the effect of plasma-based chitosan coating on cotton fabric, SEM is used to analyze these chitosan coated fabrics' surface morphological

properties and the concentration of chitosan solution is 4% used for finishing. SEM images of chitosan coated fabrics are shown in Figure 6.6 which shows the surfaces of fibers in pure cotton fabric are even and smooth (Figure 6.6a) while cotton fibers coated with chitosan are not smooth in Figures 6.6b, 6.6c, 6.6d and 6.6e. When the differences between images of cotton fabrics coated with chitosan are compared, it can be seen that the distribution of chitosan on fabric treated with plasma before padding (Figure 6.6c) and fabric treated with plasma after padding and drying (Figure 6.6e) is more even, while chitosan on cotton fabric without plasma treatment (Figure 6.6b) and fabric with plasma treatment after padding and before drying (Figure 6.6d) tends to have crosslinking structure on the fibre surface. The reason is that plasma treatment can not only functionalize the surface of matrixes, but also etch the surface of materials. After etching, there are many cracks on the surfaces of materials, which are not even anymore, which makes the coating of the materials easier. Because of the presence of the cracks, surface area of fibers is increased and more chitosan can be coated onto the fabrics. However, it seems that humid conditions affect the effect of plasma treatment, so chitosan on fabrics treated with plasma after padding is distributed unevenly. This is because most of the particles generated during plasma treatment are greatly unstable and have a high tendency to react. These free radicals in the humid environment may react with the H_2O present in fabrics, which affects the effects of plasma treatment on cotton fabrics (Sanchis et al., 2008). Therefore, it can be concluded that dry condition is more suitable for plasma treatment to work.

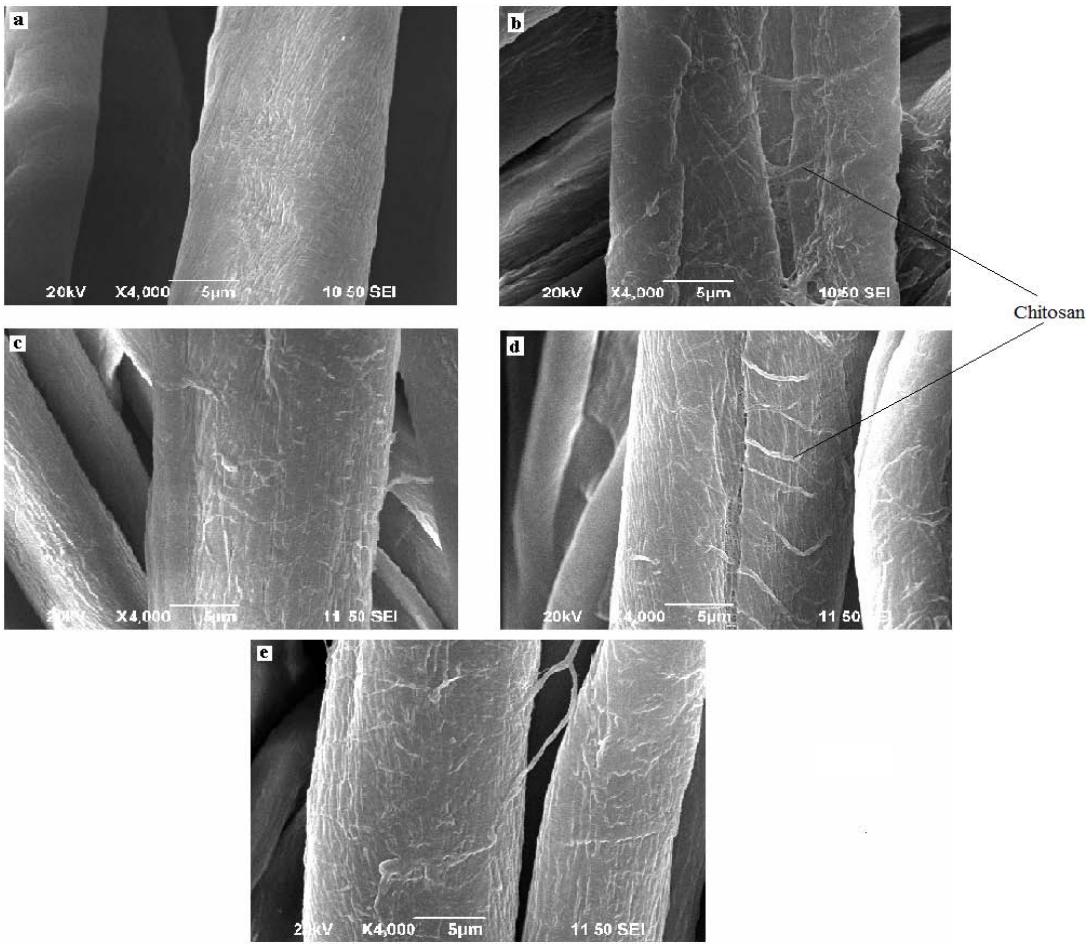

Figure 6.6 SEM image of (a) pure cotton fabric, (b) cotton fabric coated with chitosan through 'pad-dry-cure' method (CC), (c) cotton fabric treated with plasma firstly, and then coated with chitosan through 'pad-dry-cure' method (CPC), (d) cotton fabric padded with chitosan, and then treated with plasma, dried and cured (CWPC), (e) cotton fabric padded with chitosan, dried, treated with plasma and cured (CDPC).

6.2.4 Regenerability and durability

The regenerability and durability are important properties of antimicrobial materials to be worn in daily life. The regenerability of cotton fabrics coated with chitosan with the aid of plasma treatment is shown in Figure 6.7 and the stability of these cotton fabrics is shown in Figure 6.8, and the concentration of chitosan solution is 4% for finishing.

According to Figure 6.7, concentration of active chlorine on fabrics reduces slightly

after washing. The active chlorine content on fabrics, however, regains after these fabrics are chlorinated with sodium hypochlorite solution. Concentration of active chlorine on fabrics does not change significantly before washing and after re-chlorinating with sodium hypochlorite. When the concentration of active chlorine on samples bleached for different durations was compared, it seems that the difference between concentration of active chlorine before washing and after re-chlorination decreases with the increase of chlorination time. When chlorination time is set to 20 min, the concentration of active chlorine after re-chlorinating is approximately that before washing. That is because with the extension of duration of bleaching, there is higher probability of chlorine replacing the hydrogen in N-containing group until it is saturated. Compared with fabrics without plasma treatment, it is found that the concentration of chlorine on fabrics with plasma treatment is high, whether it is before washing, after washing or after re-chloination. The nitrogen plasma treatment increases the content of chlorine on fabric as well as the regenerability of antimicrobial fabrics. Therefore, it can be concluded that the coating of chitosan on cotton fabrics is resistant to laundering and antimicrobial properties of cotton fabric coated with chitosan is regenerable.

As shown in Figure 6.8, almost the entire active chlorine on samples stays at 4×10^{-7} mol/L after six months storage. During these six months, the quantity of chlorine on all samples was reduced. That is because microorganisms in the storage condition consume the chlorine on cotton fabrics. When samples were treated with plasma before padding (CPC) or after padding and before drying (CWPC), the amount of chlorine decreases 45% approximately when chlorination time is 10min, 20min and 40min. When plasma treatment was carried out after drying (CDPC), the amount of chlorine reduces more than 55% when chlorination time is 10min, 20min and 40min.

However, when samples were bleached for 60 min, the amount of residual active chlorine on all samples was up to 75%. The reason is that when the chlorination time is shorter than 60 min, the fibers do not swell very well and, therefore, chlorine on the chlorinated chitosan can kill bacteria easily, while the fibers swell adequately on bleaching for 60 min., which makes chitosan stay in the cracks of fibers and after drying, it is difficult for chlorine to react with bacteria and kill them. Hence, the chlorination time should not be too long, which is not beneficial. It is also found that the concentration of chlorine on sample coated without plasma treatment is always lower than that on the cotton fabric coated with assist of plasma treatment. This is because nitrogen plasma treatment increases coating yield on fabric and introduces N-containing groups which can inhibit the growth of microbial after chlorination. That is to say, the nitrogen plasma treatment enhances the antimicrobial activity of antimicrobial cotton fabric. Meanwhile, compared with fabric without plasma treatment, chlorine on fabrics with plasma treatment is still active to kill microbial.

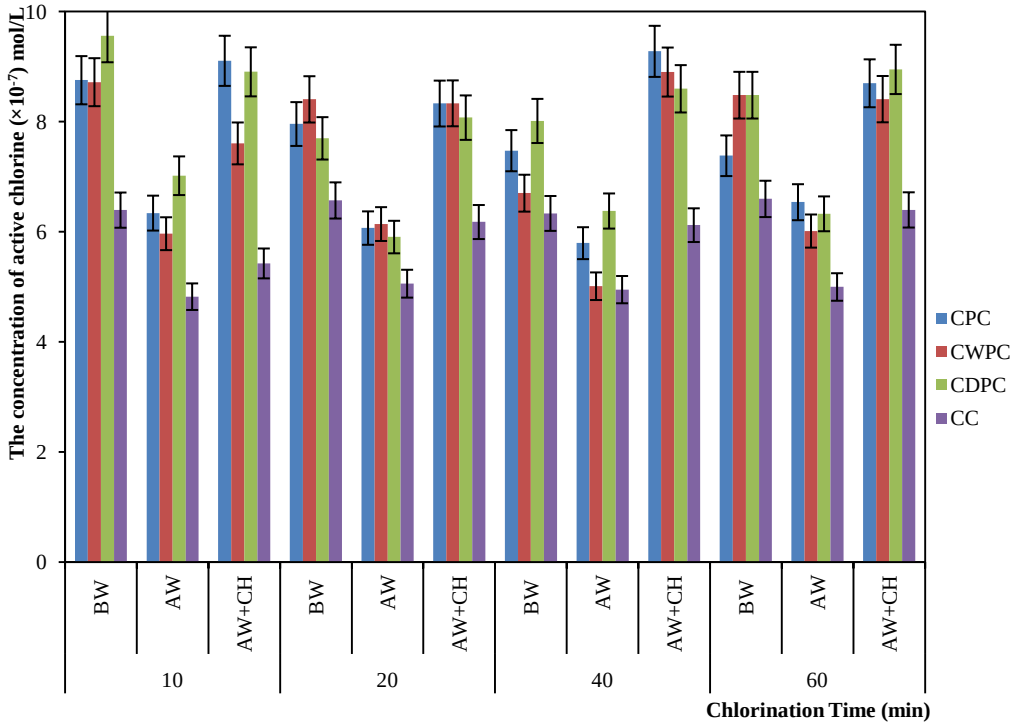

Figure 6.7 The regenerability of cotton fabric coated with chitosan and plasma treatment

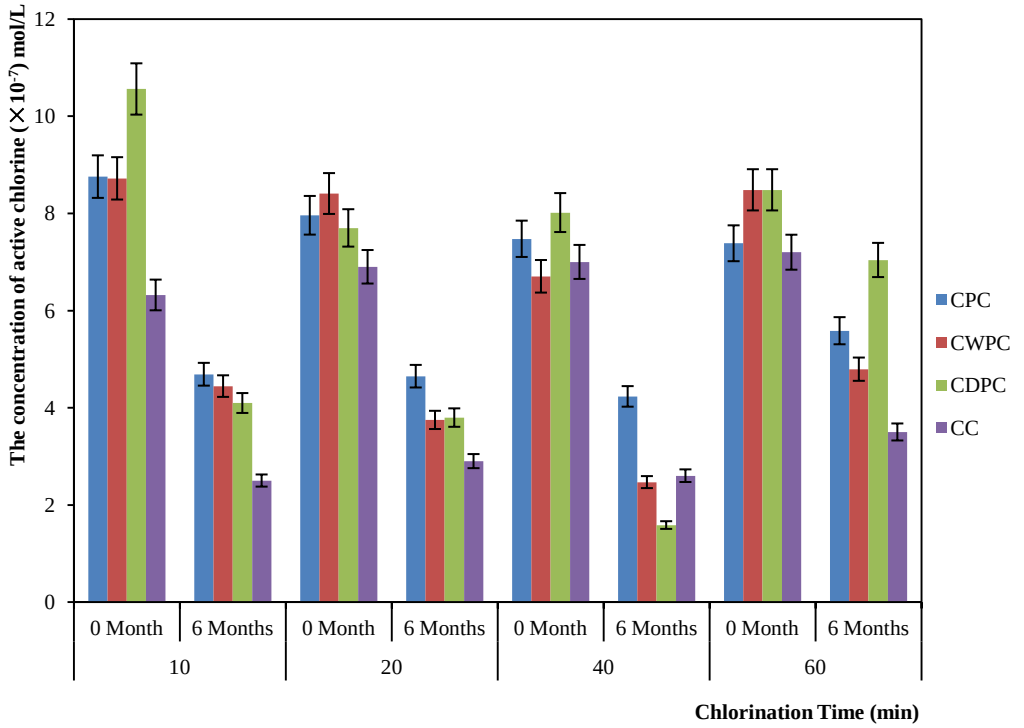

Figure 6.8 The duration of antimicrobial effect of cotton fabric coated with chitosan and plasma treatment

6.2.5 Antimicrobial activity

In this part, the effect of concentration of chitosan and the content of sodium hypochlorite on antimicrobial activity of samples was studied. 4% of chitosan solution was coated onto the surface of cotton fabrics. 0.8%, 1% and 1.2% of sodium hypochlorite solution were used to chlorinate the chitosan coated cotton fabrics. The growth of microorganism, *S. aureus* (ATCC 6538), underneath the tested specimen and the width of the clear zone were observed.

The growth of *S. aureus* (ATCC 6538) underneath the tested specimen was not observed except in the sample without chitosan coating. That is to say, cotton fabrics coated with chitosan can inhibit the growth of *S. aureus* (ATCC 6538) effectively. However, the mean clear zones of samples against *S. aureus* (ATCC6538) are not significant, even it is unable to measure them accurately. The reason may be chlorine is not easy to dissociate from the chitosan molecular due to the high bond energy of N-Cl in chitosan.

6.3 Conclusion

Durable and regenerable antibacterial functions can be chemically imparted onto cotton fabrics by coating with chitosan, followed by chlorine bleaching. The durable and regenerable antibacterial properties can be improved by N_2 plasma treatment, especially plasma treatment following padding and drying, which can be proved by concentration of chlorine on chitosan coated fabrics, SEM and FTIR. The new system provides potent, durable and regenerable antimicrobial functions against bacteria, *S. aureus* (ATCC 6538). Considering all properties of fabric coated with chitosan, the better chlorination time in these four finishing processes is 20 min, the better concentration of sodium hypochlorite for plasma-pad-dry-cure finishing processes

(CPC) is 0.8% and for the other finishing processes (CDPC, CWPC and CC) is 1%, while keeping the concentration of chitosan solution was 4%, fabrics were dried at 90 ºC for 5min and cured at 140 ºC for 10min.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

This section provides a major results and findings coving physical, chemical and antimicrobial properties of cotton fabrics after subjecting to antimicrobial finishing. This thesis attempted to present a comprehensive and systematic study of the regenerable antimicrobial finishing for cotton fabrics with the assist of plasma treatment. It explored the feasibility of imparting regenerable antimicrobial finishing of cotton fabrics by means of plasma treatment and combination of plasma treatment and wet chemical processes.

In Chapter 4, the attainment of antimicrobial cotton fabrics finished with nitrogen plasma was analyzed. It was confirmed that nitrogen plasma introduces N-containing groups and imparts antimicrobial property to cotton fabrics. The antimicrobial property was regenerable and durable. In order to enhance antimicrobial activity, plasma treatment combined with wet chemical finishing for cotton fabric was investigated in Chapter 5 and Chapter 6. With plasma treatment, antimicrobial agents, DMH and chitosan, could be bound with cotton fabrics without crosslinkers and other auxiliaries. When comparing with plasma-pad-dry-cure process and pad-plasma-dry-cure process, it was found that pad-dry-plasma-cure finishing process was feasible by evaluation the antimicrobial activity of samples. Moreover, according to the discussion in these two chapters, antimicrobial activity of fabrics finished with

DMH was much stronger than that finished with chitosan. The reason was that bond energy of N-Cl in chitosan was stronger than that in DMH due to inductive effect in molecular, which result in dissociation of chlorine in chitosan is not easy.

In addition, a series of evaluation methods were adopted to determine the variation of structure and properties of cotton fabrics brought by the functional treatments in Chapter 4, Chapter 5 and Chapter 6. Meanwhile, these evaluations also proved the feasibility of plasma treatment used to regenerable antimicrobial finishing.

7.1.1 Study of plasma-based antimicrobial finishing for cotton fabrics

Nowadays, cotton fabrics are still recognized as paramount textiles because of their advantages. However, their main drawback is that they are easily attacked by microorganisms. Antimicrobial finishing for cotton fabrics must satisfy the safe requirement of individuals and environment. It is proved that nitrogen plasma treatment process is environmentally friendly and introduce nitrogen-containing group as well as imparts antimicrobial property to cotton fabrics. Based on orthogonal analysis, when the flow rate of nitrogen keep unchanged, the optimal antimicrobial finishing process with plasma treatment was achieved as follows: discharge power of APP = 120W, moving speed of fabric = 4.5×10^{-3}m/s, concentration of sodium hypochlorite =1.4% and time of chlorination = 60 min. The FTIR spectrum of sample treated with optimal plasma finishing process shows plasma treatment introduces N-containing groups and carboxyl groups on the fabric surfaces. N-containing groups

after chlorination with sodium hypochlorite make cotton fabrics antimicrobial. Carboxyl groups can react with other finishing agents. This provides convenience for other functional finishing. The test of concentration of active chlorine on finished fabrics is to prove the presence of antimicrobial functional groups as well as the regenerability and duration of antimicrobial activity. The SEM image demonstrated that plasma treatment results in the formation of micro-cracks on the material surface, which increased the roughness of material surface and enhance the adhesion of chemicals to the surface of fabrics. The decrease of tearing strength after plasma treatment also showed the increases of the surface friction and roughness of fabrics. Moreover, the effect of flow rate of nitrogen on antimicrobial was also studied, and the result was that high flow rate of nitrogen enhances the antimicrobial activity of cotton fabric. In addition, the effect of parameters of plasma treatment on the variation of weight of fabrics was investigated. With the increase of discharge power and the extension of duration of plasma treatment, the weight loss of fabrics increased. However, with the increase of flow rate of nitrogen, the weight loss decreased. This explained the differences of the interaction of N_2 plasma particles and He plasma particles with the surface of cotton fabrics, that is, both of these two kinds of plasma particles have etching effect on the material, but only nitrogen plasma particles can react with the material surface chemically.

7.1.2 Study of combination of plasma treatment with pad-dry-cure antimicrobial finishing for cotton fabrics

This section mainly study the antimicrobial effect of cotton fabrics finished with the

combination of plasma treatment with pad-dry-cure finishing processes, i.e. plasma-pad-dry-cure, pad-plasma-dry-cure and pad-dry-plasma-cure. In this study, chitosan and DMH were treated onto cotton fabrics with the assist of plasma treatment. The FTIR spectra of these two chemicals showed the existence of their characteristic functional group, which indicated both chitosan and DMH are coated onto cotton fabrics. Both of these two chemicals have amino groups which can react with carboxyl groups on fabrics introduced by nitrogen plasma treatment. According to SEM test, it was found that the surfaces of fibers had numerous line-shape crosslinking structures which make the surface not smooth. This kind of structures is more on the fibers with plasma treatment than that without plasma treatment, especially on the fibers treated with pad-dry-plasma-cure finishing process. The evaluation of regenerability and duration of antimicrobial activity by means of the concentration of active chlorine on fabrics also proved plasma treatment after drying increase the content of chemicals significantly compared with other finishing processes. Meanwhile, it was found that water in pad-plasma-dry-cure finishing process had influences on the finishing effect, that is, it resulted in the distribution of chitosan unevenly and it enhance the adhesion of DMH on materials. For the antimicrobial activity, cotton fabrics finished with DMH can inhibit the growth of bacteria on the fabrics and around the fabrics simultaneously, while fabrics with chitosan only kill the bacteria on the fabrics. In the study, finishing processes did not involve other crosslinker or auxiliaries, which is safe for manufacturer, user and environment.

According to antimicrobial results, the optimal finishing processes for cotton fabrics

finished with DMH were achieved based on orthogonal analysis. For pad-dry-cure finishing processes, concentration of DMH was 2%, temperature of curing was 120ºC, concentration of bleaching solution was 1% and time of chlorination was 20 min. For plasma-pad-dry-cure finishing processes, concentration of DMH was 2%, temperature of curing was 140ºC, concentration of bleaching solution was 0.8% and time of chlorination was 40 min. For pad-plasma-dry-cure finishing process, concentration of DMH was 4%, temperature of curing was 140ºC, concentration of bleaching solution was 0.8% and time of chlorination was 20 min. For pad-dry-plasma -cure finishing process, concentration of DMH was 6%, temperature of curing was 140ºC, concentration of bleaching solution was 1.2% and time of chlorination was 60 min.

In addition, fabrics with chitosan only could inhibit the bacteria on the fabrics. Thus, its finishing parameters could not be optimized through OATS by comparing the antimicrobial results. Considering all properties of fabric coated with chitosan, the better chlorination time in these four finishing processes is 60 min, the better concentration of sodium hypochlorite for plasma-pad-dry-cure finishing processes (CPC) is 0.8% and for the other finishing processes (CDPC, CWPC and CC) is 1%, while keeping the concentration of chitosan solution was 4%, fabrics were dried at 90 ºC for 5min and cured at 140 ºC for 10min.

7.2 Recommendations for future work

Although the objectives have been achieved in the study, it is recognized that more research works in the area of regenerable antimicrobial finishing of cotton fabrics

should be conducted in the future to produce safer and more effectiveness antimicrobial cotton textiles.

7.2.1 Plasma-based antimicrobial finishing for textiles

In the present work, cotton fabrics were treated with nitrogen plasma to introduce antimicrobial activity. Although these samples can inhibit the growth of bacteria, the stronger antimicrobial activity is better. Other plasma can be used to accelerate the formation of N-containing groups. As an example, the adding of hydrogen plasma to nitrogen plasma can promote the formation of NH groups on the substrates. Fabrics with more NH groups posses more effective antimicrobial activity. However, atmospheric pressure plasma generator is not suitable for the antimicrobial finishing after the adding of hydrogen plasma, because hydrogen is easy to burn and explode in the presence of oxygen at ambient temperature and pressure. Consequently, vacuum plasma treatment systems should be provided for the hydrogen/nitrogen plasma treatment.

7.2.2 Combination of plasma treatment with other functional finishing of textiles

There are multitudes of regenerable antimicrobial agents mentioned in Chapter 2, and they may cause fewer problems on fabric quality, health risk and environment. Further study is highly recommended to seek antimicrobial agents which are more effective and compatible with other finishing processes so as to get a multi-functional type of cotton fabrics.

In this research, the physical and chemical variations caused by plasma treatment and chemical finishing were mainly studied by the FTIR and SEM techniques as well as tearing strength. In the future work, it is proposed to use X-ray photoelectron spectroscopy (XPS) to detect the variation of chemical elements quantitatively. This characterization technique provides a more precise result of the variation of chemical elements on the surface of materials. Fabric handle should also be measured, which is a favorable way to judge the comfort of cotton fabrics in use. Finally but not least, cytotoxicity test is highly recommended to be done in order to ensure the safety of finished fabrics when contact with human.

REFERENCES

Abdou, E. S., Elkholy, S. S., Elsabee, M. Z., & Mohamed, E. (2008). Improved antimicrobial activity of polypropylene and cotton nonwoven fabrics by surface treatment and modification with chitosan. *Journal of Applied Polymer Science, 108*(4), 2290-2296.

Abidi, N., & Hequet, E. (2004). Cotton fabric graft copolymerization using microwave plasma. I. universal attenuated total reflectance–FTIR study. *Journal of Applied Polymer Science, 93*(1), 145-154.

Abidi, N., & Hequet, E. (2005). Cotton fabric graft copolymerization using microwave plasma. II. physical properties. *Journal of Applied Polymer Science, 98*(2), 896-902.

Abidi, N., Hequet, E., & Cabrales, L. (2010). Changes in sugar composition and cellulose content during the secondary cell wall biogenesis in cotton fibers. *Cellulose, 17*(1), 153-160.

Afeltra, J., Dannaoui, E., Meis, J. F., Rodriguez-Tudela, J. L., & Verweij, P. E. (2002). In vitro synergistic interaction between amphotericin B and pentamidine against scedosporium prolificans. *Antimicrobial Agents and Chemotherapy, 46*(10), 3323-3326.

Anonymity. (27,7,2015a). Illustrated glossary of organic chemistry. Retrieved from http://www.chem.ucla.edu/harding/IGOC/S/steric_hindrance.html

Anonymity. (15,2,2015). Mode of action — antimicrobial resistance learning site for veterinary students. Available: http://amrls.cvm.msu.edu/pharmacology/antimicrobials/mode-of-action.

Anonymity. (10,9,2013). Plasma technology – What is plasma?. Available: http://www.plasmatreat.com/plasma-technology/what-is-plasma.html.

Anonymity. (27,7,2015b). Steric effects. Retrieved from https://en.wikipedia.org/wiki/Steric_effects

Attia, S. (2002). Review on sol-gel derived coatings: Process, techniques and optical applications. *Journal of Materials Science & Technology*, *18*(3), 211-218.

Badrossamay, M. R., & Sun, G. (2008). Acyclic halamine polypropylene polymer: Effect of monomer structure on grafting efficiency, stability and biocidal activities. *Reactive and Functional Polymers*, *68*(12), 1636-1645.

Badrossamay, M. R., & Sun, G. (2009). Durable and rechargeable biocidal polypropylene polymers and fibers prepared by using reactive extrusion. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, *89*(1), 93-101.

Balazs, D., Triandafillu, K., Sardella, E., Iacoviello, G., Favia, P., d'Agostino, R., Harms, H., & Mathieu, H. (2005). PE-CVD modification of medical-grade PVC to inhibit bacterial adhesion: PEO-like and nanocomposite ag/PEO-like coatings. *Plasma Processes and Polymers*, , 351-372.

Beck, A. J., Jones, F. R., & Short, R. D. (1996). Plasma copolymerization as a route to the fabrication of new surfaces with controlled amounts of specific chemical functionality. *Polymer*, *37*(24), 5537-5539.

Beck, A. J., Whittle, J. D., Bullett, N. A., Eves, P., Mac Neil, S., McArthur, S. L., & Shard, A. G. (2005). Plasma co-polymerisation of two strongly interacting monomers: Acrylic acid and allylamine. *Plasma Processes and Polymers*, *2*(8), 641-649.

Belin, R. (1976). 33—The effect of corona treatment on the cohesion between fibres and on their wettability. *Journal of the Textile Institute*, *67*(7-8), 249-252.

Bhat, N., & Benjamin, Y. (1999). Surface resistivity behavior of plasma treated and plasma grafted cotton and polyester fabrics. *Textile Research Journal, 69*(1), 38-42.

Blackburn, R. S., Harvey, A., Kettle, L. L., Manian, A. P., Payne, J. D., & Russell, S. J. (2007). Sorption of chlorhexidine on cellulose: Mechanism of binding and molecular recognition. *The Journal of Physical Chemistry B, 111*(30), 8775-8784.

Blackburn, R. S., Harvey, A., Kettle, L. L., Payne, J. D., & Russell, S. J. (2006). Sorption of poly (hexamethylenebiguanide) on cellulose: Mechanism of binding and molecular recognition. *Langmuir, 22*(13), 5636-5644.

Braun, M., & Sun, Y. (2004). Antimicrobial polymers containing melamine derivatives. I. preparation and characterization of chloromelamine-based cellulose. *Journal of Polymer Science Part A: Polymer Chemistry, 42*(15), 3818-3827.

Buyle, G. (2009). Nanoscale finishing of textiles via plasma treatment. *Materials Science and Technology, 24*(1), 46-51.

Byarugaba, D. K. (2010). Mechanisms of antimicrobial resistance. *Antimicrobial resistance in developing countries* (pp. 15-26) Springer.

Cao, Z., & Sun, Y. (2008). N-halamine-based chitosan: Preparation, characterization, and antimicrobial function. *Journal of Biomedical Materials Research Part A, 85*(1), 99-107.

Cao, Z., & Sun, Y. (2009). Chitosan-based rechargeable long-term antimicrobial and biofilm-controlling systems. *Journal of Biomedical Materials Research Part A, 89*(4), 960-967.

Capelli, C. C. (1990). *Metal-based antimicrobial coating* Google Patents.

Cerkez, I., Kocer, H. B., Worley, S., Broughton, R., & Huang, T. (2012). N-halamine copolymers for biocidal coatings. *Reactive and Functional Polymers, 72*, 673-679.

Chadeau, E., Oulahal, N., Dubost, L., Favergeon, F., & Degraeve, P. (2010). Anti-listeria innocua activity of silver functionalised textile prepared with plasma technology. *Food Control, 21*(4), 505-512.

Chang, Y., Tu, P., Wu, M., Hsueh, T., & Hsu, S. (2008). A study on chitosan modification of polyester fabrics by atmospheric pressure plasma and its antibacterial effects. *Fibers and Polymers, 9*(3), 307-311.

Chen, C., Chen, J., & Yao, W. (2009). Argon-plasma treatment for improving the physical properties of crosslinked cotton fabrics with dimethyloldihydroxyethyleneurea-acrylic acid. *Textile Research Journal, 80*(8), 675-682.

Chen, K., Hung, T., Wu, H., Wu, J., Lin, M., & Feng, C. (2010). Preparation of thermosensitive gold nanoparticles by plasma pretreatment and UV grafted polymerization. *Thin Solid Films, 518*(24), 7557-7562.

Chen, S., Chen, S., Jiang, S., Xiong, M., Luo, J., Tang, J., & Ge, Z. (2011). Environmentally friendly antibacterial cotton textiles finished with siloxane sulfopropylbetaine. *ACS Applied Materials & Interfaces, 3*(4), 1154-1162.

Chen, Y., & Han, Q. (2011). Designing N-halamine based antibacterial surface on polymers: Fabrication, characterization, and biocidal functions. *Applied Surface Science, 257*(14), 6034-6039.

Chen, Z., Luo, J., & Sun, Y. (2007). Biocidal efficacy, biofilm-controlling function, and controlled release effect of chloromelamine-based bioresponsive fibrous materials. *Biomaterials, 28*(9), 1597-1609.

Chen, Z., & Sun, Y. (2005). Antimicrobial polymers containing melamine derivatives. II. biocidal polymers derived from 2-vinyl-4, 6-diamino-1, 3, 5-triazine. *Journal of Polymer Science Part A: Polymer Chemistry, 43*(18), 4089-4098.

Cheng, S.Y., Yuen, C.W.M., Kan, C.W., Cheuk, K.K.C., Daoud, W.A., Lam, P.L., & Tsoi, W.Y.I. (2010). Influence of atmospheric pressure plasma treatment on various fibrous materials: Performance properties and surface adhesion analysis. *Vacuum, 84*(12), 1466-1470.

Chen-Yu, J. H., Eberhardt, D. M., & Kincade, D. H. (2007). Antibacterial and laundering properties of AMS and PHMB as finishing agents on fabric for health care workers' uniforms. *Clothing and Textiles Research Journal, 25*(3), 258-272.

Chuanwen, C., Feng, S., Yuguo, L., & Shuyun, W. (2010). Orthogonal analysis for perovskite structure microwave dielectric ceramic thin films fabricated by the RF magnetron-sputtering method. *Journal of Materials Science: Materials in Electronics, 21*(4), 349-354.

Chung, Y., Lee, K., & Kim, J. (1998). Durable press and antimicrobial finishing of cotton fabrics with a citric acid and chitosan treatment. *Textile Research Journal, 68*(10), 772-775.

Crowther, J. M., & Badyal, J. P. S. (1998). Non-Isothermal plasma metallization of Polymer-Supported gold (III) complexes. *Advanced Materials, 10*(5), 407-411.

Dastjerdi, R., Montazer, M., & Shahsavan, S. (2009). A new method to stabilize nanoparticles on textile surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 345*(1), 202-210.

Daw, R., Candan, S., Beck, A. J., Devlin, A. J., Brook, I. M., MacNeil, S., Dawson, R., & Short, R. D. (1998). Plasma copolymer surfaces of acrylic acid/1, 7

octadiene: Surface characterisation and the attachment of ROS 17/2.8 osteoblast-like cells. *Biomaterials, 19*(19), 1717-1725.

Delgado, K., Quijada, R., Palma, R., & Palza, H. (2011). Polypropylene with embedded copper metal or copper oxide nanoparticles as a novel plastic antimicrobial agent. *Letters in Applied Microbiology, 53*(1), 50-54.

Denadai, A. M., Teixeira, K. I., Santoro, M. M., Pimenta, A. M., Cortés, M. E., & Sinisterra, R. D. (2007). Supramolecular self-assembly of β-cyclodextrin: An effective carrier of the antimicrobial agent chlorhexidine. *Carbohydrate Research, 342*(15), 2286-2296.

Eknoian, M., Putman, J., & Worley, S. (1998). Monomeric and polymeric N-halamine disinfectants. *Industrial & Engineering Chemistry Research, 37*(7), 2873-2877.

El-Newehy, M. H., Al-Deyab, S. S., Kenawy, E., & Abdel-Megeed, A. (2011). Nanospider technology for the production of nylon-6 nanofibers for biomedical applications. *Journal of Nanomaterials, 2011*, 9.

El-Tahlawy, K. F., El-Bendary, M. A., Elhendawy, A. G., & Hudson, S. M. (2005). The antimicrobial activity of cotton fabrics treated with different crosslinking agents and chitosan. *Carbohydrate Polymers, 60*(4), 421-430.

Favia, P., Vulpio, M., Marino, R., d'Agostino, R., Mota, R. P., & Catalano, M. (2000). Plasma-deposition of ag-containing polyethyleneoxide-like coatings. *Plasmas and Polymers, 5*(1), 1-14.

Fouda, M. M. (2012). *Antibacterial modification of textiles using nanotechnology*. InTech Open Access Publisher, 2012, pp. 47-72.

Foulkes, D. (1973). Some toxicological observations on chlorhexidine. *Journal of Periodontal Research, 8*(s12), 55-60.

Gao, Y., & Cranston, R. (2008). Recent advances in antimicrobial treatments of textiles. *Textile Research Journal, 78*(1), 60-72.

Gilbert, P., & Moore, L. (2005). Cationic antiseptics: Diversity of action under a common epithet. *Journal of Applied Microbiology, 99*(4), 703-715.

Girard, T. A. (1984). *Agglomerated halo-hydantoins* Google Patents.

Gomes, A., Mano, J., Queiroz, J., & Gouveia, I. (2010). Assessement of bacteria-textile interactions using scanning electron microscopy: A study on LbL chitosan/alginate coated cotton. *Microscopy: Science, Technology, Applications and Education,* , 286-292.

Gorjanc, M., Bukošek, V., Gorenšek, M., & Vesel, A. (2010). The influence of water vapor plasma treatment on specific properties of bleached and mercerized cotton fabric. *Textile Research Journal, 80*(6), 557-567.

Gouda, M., & Ibrahim, N. (2008). New approach for improving antibacterial functions of cotton fabric. *Journal of Industrial Textiles, 37*(4), 327-339.

Gregorski, K., & Pavlath, A. (1980). Fabric modification using the Plasmod1 the effect of extensive treatment in nitrogen and oxygen plasmas at low pressure. *Textile Research Journal, 50*(1), 42-46.

Hartwell, E., Richards, R., & Thompson, H. (1948). The vibration frequency of the carbonyl linkage. *Journal of the Chemical Society*, 1436-1441.

Hebeish, A., El-Naggar, M., Fouda, M. M., Ramadan, M., Al-Deyab, S. S., & El-Rafie, M. (2011). Highly effective antibacterial textiles containing green synthesized silver nanoparticles. *Carbohydrate Polymers, 86*(2), 936-940.

Hegemann, D., Amberg, M., Ritter, A., & Heuberger, M. (2009). Recent developments in ag metallised textiles using plasma sputtering. *Materials Science and Technology, 24*(1), 41-45.

Hegemann, D. (2006). Plasma polymerization and its applications in textiles. *Indian Journal of Fibre and Textile Research, 31*(1), 99.

Hegemann, D., Brunner, H., & Oehr, C. (2003). Plasma treatment of polymers for surface and adhesion improvement. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 208*, 281-286.

Hegemann, D., Hossain, M. M., Körner, E., & Balazs, D. J. (2007). Macroscopic description of plasma polymerization. *Plasma Processes and Polymers, 4*(3), 229-238.

Hesse, A., Thomas, H., & Höcker, H. (1995). Zero-AOX shrinkproofing treatment for wool top and fabric part I: Glow discharge treatment. *Textile Research Journal, 65*(6), 355-361.

Hofer, D. (2006). Antimicrobial textiles - evaluation of their effectiveness and safety. *Current Problems in Dermatology, 33*, 42-50. doi:93935 [pii]

Hossain, M. M., Hegemann, D., Fortunato, G., Herrmann, A. S., & Heuberger, M. (2007). Plasma deposition of permanent superhydrophilic a‐C: H: N films on textiles. *Plasma Processes and Polymers, 4*(4), 471-481.

Huang, L. K., & Sun, G. (2003). Durable and oxygen bleach rechargeable antimicrobial cellulose: Sodium perborate as an activating and recharging agent. *Industrial & Engineering Chemistry Research, 42*(22), 5417-5422.

Huh, M. W., Kang, I., Lee, D. H., Kim, W. S., Lee, D. H., Park, L. S., Min, K. E., & Seo, K. H. (2001). Surface characterization and antibacterial activity of chitosan‐

grafted poly (ethylene terephthalate) prepared by plasma glow discharge. *Journal of Applied Polymer Science, 81*(11), 2769-2778.

Hui, R., Guan, C., & Hou Dongyan. (2005). Study on IR characteristics of carboxylic acid and their salts. *Journal of Anshan Teachers College, 3*(1), 95-98.

Ilic, V., Šaponjić, Z., Vodnik, V., Lazović, S., Dimitrijevic, S., Jovancic, P., Nedeljkovic, J., & Radetic, M. (2010). Bactericidal efficiency of silver nanoparticles deposited onto radio frequency plasma pretreated polyester fabrics. *Industrial & Engineering Chemistry Research, 49*(16), 7287-7293.

Inagaki, N. (1984). Preparation of quaternary nitrogen-containing plasma films and their application to moisture sensors. *Thin Solid Films, 118*(2), 225-230.

Inagaki, N. (2000). Surface modification of polymeric materials by remote plasma. *Macromolecular Symposia, , 159*(1) 151-162.

Jia, B., Mei, Y., Cheng, L., Zhou, J., & Zhang, L. (2012). Preparation of copper nanoparticles coated cellulose films with antibacterial properties through one-step reduction. *ACS Applied Materials & Interfaces, 4*(6), 2897-2902.

Kale, K. H., & Desai, A. (2011). Atmospheric pressure plasma treatment of textiles using non-polymerizing gases. *Indian Journal of Fibre & Textile Research, 36*(3), 289-299.

Kan, C. W. (2007). Evaluating antistatic performance of plasma-treated polyester. *Fibers and Polymers, 8*(6), 629-634.

Kan, C. W., Chan, K., & Yuen, C. W. M. (2004). A study of the oxygen plasma treatment on the serviceability of a wool fabric. *Fibers and Polymers, 5*(3), 213-218.

Kan, C. W., Chan, K., Yuen, C. W. M., & Miao, M. H. (1998). Surface properties of low-temperature plasma treated wool fabrics. *Journal of Materials Processing Technology, 83*(1), 180-184.

Kan, C. W., Yuen, C. W. M., & Tsoi, W. Y. (2011). Using atmospheric pressure plasma for enhancing the deposition of printing paste on cotton fabric for digital ink-jet printing. *Cellulose, 18*(3), 827-839.

Kan, C. W., Yuen, C. W. M., & Wong, W. Y. (2011). Optimizing color fading effect of cotton denim fabric by enzyme treatment. *Journal of Applied Polymer Science, 120*(6), 3596-3603.

Karahan, H., & Özdoğan, E. (2008). Improvements of surface functionality of cotton fibers by atmospheric plasma treatment. *Fibers and Polymers, 9*(1), 21-26.

Kawabata, A., & Taylor, J. A. (2004). Effect of reactive dyes upon the uptake and antibacterial action of poly (hexamethylene biguanide) on cotton. part 1: Effect of bis (monochlorotriazinyl) dyes. *Coloration Technology, 120*(5), 213-219.

Kawabata, A., & Taylor, J. A. (2007). The effect of reactive dyes upon the uptake and antibacterial efficacy of poly (hexamethylene biguanide) on cotton. part 3: Reduction in the antibacterial efficacy of poly (hexamethylene biguanide) on cotton, dyed with bis (monochlorotriazinyl) reactive dyes. *Carbohydrate Polymers, 67*(3), 375-389.

Kenawy, E., & Abdel‐Fattah, Y. R. (2002). Antimicrobial properties of modified and electrospun poly (vinyl phenol). *Macromolecular Bioscience, 2*(6), 261-266.

Kim, Y. H., & Sun, G. (2001). Durable antimicrobial finishing of nylon fabrics with acid dyes and a quaternary ammonium salt. *Textile Research Journal, 71*(4), 318-323.

Kim, Y. H., Choi, H., & Yoon, J. H. (1998). Synthesis of a quaternary ammonium derivative of chitosan and its application to a cotton antimicrobial finish. *Textile Research Journal, 68*(6), 428-434.

Kim, Y. H., Nam, C. W., Choi, J. W., & Jang, J. (2003). Durable antimicrobial treatment of cotton fabrics using N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride and polycarboxylic acids. *Journal of Applied Polymer Science, 88*(6), 1567-1572.

Kiwi, J., & Pulgarin, C. (2010). Innovative self-cleaning and bactericide textiles. *Catalysis Today, 151*(1), 2-7.

Kocer, H. B., Akdag, A., Ren, X., Broughton, R., Worley, S., & Huang, T. (2008). Effect of alkyl derivatization on several properties of N-halamine antimicrobial siloxane coatings. *Industrial & Engineering Chemistry Research, 47*(20), 7558-7563.

Kocer, H. B., Worley, S., Broughton, R., & Huang, T. (2011). A novel N-halamine acrylamide monomer and its copolymers for antimicrobial coatings. *Reactive and Functional Polymers, 71*(5), 561-568.

Koprowska, J., Ziaja, J., & Janukiewicz, J. (2008). Plasma metallization textiles as shields for electromagnetic fields. *Electromagnetic Compatibility-EMC Europe, 2008 International Symposium On,* 1-4.

Kou, L., Liang, J., Ren, X., Kocer, H. B., Worley, S., Broughton, R., & Huang, T. (2009). Novel N-halamine silanes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 345*(1), 88-94.

Kral, M., Ogino, A., Narushima, K., Inagaki, N., Yamashita, M., & Nagatsu, M. (2007). Low-temperature nitrogen introduction onto polyurethane surface using

surface-wave excited N_2/H_2 plasma. *Japanese Journal of Applied Physics, 46*, 7470.

Krebs, F. C., Miller, S. R., Ferguson, M. L., Labib, M., Rando, R. F., & Wigdahl, B. (2005). Polybiguanides, particularly polyethylene hexamethylene biguanide, have activity against human immunodeficiency virus type 1. *Biomedicine & Pharmacotherapy, 59*(8), 438-445.

Kuo, Y., Chang, K., Hung, T., Chen, K., & Inagaki, N. (2010). Atmospheric-pressure plasma treatment on polystyrene for the photo-induced grafting polymerization of N-isopropylacrylamide. *Thin Solid Films, 518*(24), 7568-7573.

Lam, Y. L., Kan, C. W., & Yuen, C. M. W. (2011a). Effect of zinc oxide on flame retardant finishing of plasma pre-treated cotton fabric. *Cellulose, 18*(1), 151-165.

Lam, Y. L., Kan, C. W., & Yuen, C. M. W. (2011b). Physical and chemical analysis of plasma-treated cotton fabric subjected to wrinkle-resistant finishing. *Cellulose, 18*(2), 493-503.

Lee, H., Yeo, S., & Jeong, S. (2003). Antibacterial effect of nanosized silver colloidal solution on textile fabrics. *Journal of Materials Science, 38*(10), 2199-2204.

Li, R., Hu, P., Ren, X., Worley, S., & Huang, T. (2012). Antimicrobial N-halamine modified chitosan films. *Carbohydrate Polymers, 92*(1), 534-539.

Li, Y., & Worley, S. (2001). Biocidal copolymers of N-haloacryloxymnethylhydantoin. *Journal of Bioactive and Compatible Polymers, 16*(6), 493-506.

Liang, J., Chen, Y., Barnes, K., Wu, R., Worley, S., & Huang, T. (2006). N-halamine/quat siloxane copolymers for use in biocidal coatings. *Biomaterials, 27*(11), 2495-2501.

Liang, J., Owens, J., Huang, T., & Worley, S. (2006). Biocidal hydantoinylsiloxane polymers. IV. n‐halamine siloxane‐functionalized silica gel. *Journal of Applied Polymer Science, 101*(5), 3448-3454.

Liang, J., Wu, R., Huang, T., & Worley, S. (2005). Polymerization of a hydantoinylsiloxane on particles of silicon dioxide to produce a biocidal sand. *Journal of Applied Polymer Science, 97*(3), 1161-1166.

Liang, J., Wu, R., Wang, J., Barnes, K., Worley, S., Cho, U., Lee, J., Broughton, R., & Huang, T. (2007a). N-halamine biocidal coatings. *Journal of Industrial Microbiology & Biotechnology, 34*(2), 157-163.

Liang, J., Barnes, K., Akdag, A., Worley, S. D., Lee, J., Broughton, R. M., & Huang, T. (2007b). Improved antimicrobial siloxane. *Industrial & Engineering Chemistry Research, 46*(7), 1861-1866.

Liang, J., Chen, Y., Ren, X., Wu, R., Barnes, K., Worley, S., Broughton, R., Cho, U., Kocer, H., & Huang, T. (2007). Fabric treated with antimicrobial N-halamine epoxides. *Industrial & Engineering Chemistry Research, 46*(20), 6425-6429.

Lim, S., & Hudson, S. M. (2003). Review of chitosan and its derivatives as antimicrobial agents and their uses as textile chemicals. *Journal of Macromolecular Science, Part C: Polymer Reviews, 43*(2), 223-269.

Lim, S., & Hudson, S. M. (2004). Application of a fiber-reactive chitosan derivative to cotton fabric as an antimicrobial textile finish. *Carbohydrate Polymers, 56*(2), 227-234.

Liu, S., & Sun, G. (2006). Durable and regenerable biocidal polymers: Acyclic N-halamine cotton cellulose. *Industrial & Engineering Chemistry Research, 45*(19), 6477-6482.

Liu, X., Nishi, N., Tokura, S., & Sakairi, N. (2001). Chitosan coated cotton fiber: Preparation and physical properties. *Carbohydrate Polymers, 44*(3), 233-238.

Luo, J., & Sun, Y. (2008). Acyclic N-halamine coated kevlar fabric materials: Preparation and biocidal functions. *Industrial & Engineering Chemistry Research, 47*(15), 5291-5297.

Luo, S., & Van Ooij, W. J. (2002). Surface modification of textile fibers for improvement of adhesion to polymeric matrices: A review. *Journal of Adhesion Science and Technology, 16*(13), 1715-1735.

Lv, W., Luo, J., Deng, Y., & Sun, Y. (2013). Biomaterials immobilized with chitosan for rechargeable antimicrobial drug delivery. *Journal of Biomedical Materials Research Part A, 101*(2), 447-455.

Lymberis, A., & Olsson, S. (2003). Intelligent biomedical clothing for personal health and disease management: State of the art and future vision. *Telemedicine Journal and E-Health, 9*(4), 379-386.

Ma, M., Sun, Y., & Sun, G. (2003). Antimicrobial cationic dyes: Part 1: Synthesis and characterization. *Dyes and Pigments, 58*(1), 27-35.

Mahltig, B., Fiedler, D., & Böttcher, H. (2004). Antimicrobial sol–gel coatings. *Journal of Sol-Gel Science and Technology, 32*(1-3), 219-222.

Mahltig, B., Haufe, H., & Böttcher, H. (2005). Functionalisation of textiles by inorganic sol–gel coatings. *Journal of Materials Chemistry, 15*(41), 4385-4398.

McCord, M., Hwang, Y., Hauser, P., Qiu, Y., Cuomo, J., Hankins, O., Bourham M., & Canup, L. (2002). Modifying nylon and polypropylene fabrics with atmospheric pressure plasmas. *Textile Research Journal, 72*(6), 491-498.

Mohammadkhodaei, Z., Mokhtari, J., & Nouri, M. (2010). Novel anti‐bacterial acid dyes derived from naphthalimide: Synthesis, characterisation and evaluation of their technical properties on nylon 6. *Coloration Technology, 126*(2), 81-85.

Morent, R., De Geyter, N., Leys, C., Gengembre, L., & Payen, E. (2007). Surface modification of non-woven textiles using a dielectric barrier discharge operating in air, helium and argon at medium pressure. *Textile Research Journal, 77*(7), 471-488.

Morita, S., & Park, S. H. (1992). Plasma polymerization model in gas-flow type reactor. *Applied Surface Science, 60*, 338-341.

Narushima, K., Fukuoka, M., Kawai, H., Inagaki, N., Isono, Y., & Islam, M. R. (2007). Amination and oxidation reactions on polyethylene surfaces by ammonia plasma treatment. *Japanese Journal of Applied Physics, 46*, 7855.

Neeta, L. L., Ramakrishnan, R., Li, B., Subramanian, S., Barhate, R., Liu, Y., & Seeram, R. (2007). Fabrication of nanofibers with antimicrobial functionality used as filters: Protection against bacterial contaminants. *Biotechnology and Bioengineering, 97*(6), 1357-1365.

Noeske, M., Degenhardt, J., Strudthoff, S., & Lommatzsch, U. (2004). Plasma jet treatment of five polymers at atmospheric pressure: Surface modifications and the relevance for adhesion. *International Journal of Adhesion and Adhesives, 24*(2), 171-177.

Nostro, P. L., Fratoni, L., & Baglioni, P. (2002). Modification of a cellulosic fabric with β-cyclodextrin for textile finishing applications. *Journal of Inclusion Phenomena and Macrocyclic Chemistry, 44*(1-4), 423-427.

Orhan, M., Kut, D., & Gunesoglu, C. (2007). Use of triclosan as antibacterial agent in textiles. *Indian Journal of Fibre & Textile Research, 32*, 114-118.

Orhan, M., Kut, D., & Gunesoglu, C. (2009). Improving the antibacterial activity of cotton fabrics finished with triclosan by the use of 1, 2, 3, 4 - butanetetracarboxylic acid and citric acid. *Journal of Applied Polymer Science, 111*(3), 1344-1352.

Parvinzadeh Gashti, M., Hegemann, D., Stir, M., & Hulliger, J. (2014). Thin film plasma functionalization of polyethylene terephthalate to induce bone-like hydroxyapatite nanocrystals. *Plasma Processes and Polymers, 11*(1), 37-43.

Parvinzadeh, M., & Ebrahimi, I. (2011a). Atmospheric air-plasma treatment of polyester fiber to improve the performance of nanoemulsion silicone. *Applied Surface Science, 257*(9), 4062-4068.

Parvinzadeh, M., & Ebrahimi, I. (2011b). Influence of atmospheric-air plasma on the coating of a nonionic lubricating agent on polyester fiber. *Radiation Effects & Defects in Solids, 166*(6), 408-416.

Perelshtein, I., Applerot, G., Perkas, N., Wehrschuetz-Sigl, E., Hasmann, A., Guebitz, G., & Gedanken, A. (2009). CuO–cotton nanocomposite: Formation, morphology, and antibacterial activity. *Surface and Coatings Technology, 204*(1), 54-57.

Perucca, M., & Benveniste, G. (2006). LCA comparative analysis of textile applications for oleophobic and hydrophobic properties. Available: http://www.davidlu.net/LCA_oleophobic_PET_public.pdf?G=736&ln=jp.

Pinho, E., Magalhães, L., Henriques, M., & Oliveira, R. (2011). Antimicrobial activity assessment of textiles: Standard methods comparison. *Annals of Microbiology, 61*(3), 493-498.

Poll, H., Schladitz, U., & Schreiter, S. (2001). Penetration of plasma effects into textile structures. *Surface and Coatings Technology, 142*, 489-493.

Qian, L., Guan, Y., Ziaee, Z., He, B., Zheng, A., & Xiao, H. (2009). Rendering cellulose fibers antimicrobial using cationic β-cyclodextrin-based polymers included with antibiotics. *Cellulose, 16*(2), 309-317.

Qian, L., & Sun, G. (2003). Durable and regenerable antimicrobial textiles: Synthesis and applications of 3 - methylol - 2, 2, 5, 5 - tetramethyl - imidazolidin - 4 - one (MTMIO). *Journal of Applied Polymer Science, 89*(9), 2418-2425.

Qian, L., & Sun, G. (2004). Durable and regenerable antimicrobial textiles: Improving efficacy and durability of biocidal functions. *Journal of Applied Polymer Science, 91*(4), 2588-2593.

Rabea, E. I., Badawy, M. E., Stevens, C. V., Smagghe, G., & Steurbaut, W. (2003). Chitosan as antimicrobial agent: Applications and mode of action. *Biomacromolecules, 4*(6), 1457-1465.

Ren, X., Kocer, H. B., Worley, S., Broughton, R., & Huang, T. (2009). Rechargeable biocidal cellulose: Synthesis and application of 3-(2, 3-dihydroxypropyl)-5, 5-dimethylimidazolidine-2, 4-dione. *Carbohydrate Polymers, 75*(4), 683-687.

Ren, X., Kou, L., Kocer, H. B., Zhu, C., Worley, S., Broughton, R., & Huang, T. (2008). Antimicrobial coating of an N-halamine biocidal monomer on cotton fibers via admicellar polymerization. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 317*(1), 711-716.

Rigby, A., Anand, S., & Horrocks, A. (1997). Textile materials for medical and healthcare applications. *Journal of the Textile Institute, 88*(3), 83-93.

Rutscher, A., & Wagner, H. (1993). Chemical quasi-equilibria: A new concept in the description of reactive plasmas. *Plasma Sources Science and Technology, 2*(4), 279-288.

Sanchis, M., Calvo, O., Fenollar, O., Garcia, D., & Balart, R. (2008). Characterization of the surface changes and the aging effects of low-pressure nitrogen plasma treatment in a polyurethane film. *Polymer Testing, 27*(1), 75-83.

Sathianarayanan, M., Bhat, N., Kokate, S., & Walunj, V. (2010). Antibacterial finish for cotton fabric from herbal products. *Indian Journal of Fibre & Textile Research, 35*(1), 50.

Satyamurthy, P., Jain, P., Balasubramanya, R. H., & Vigneshwaran, N. (2011). Preparation and characterization of cellulose nanowhiskers from cotton fibres by controlled microbial hydrolysis. *Carbohydrate Polymers, 83*(1), 122-129.

Sayed, A. Z., & El‐Gaby, M. S. (2001). Synthesis of novel dyestuffs containing sulphonamido moieties and their application on wool and polyamide fibres. *Coloration Technology, 117*(5), 293-297.

Scholz, J., Nocke, G., Hollstein, F., & Weissbach, A. (2005). Investigations on fabrics coated with precious metals using the magnetron sputter technique with regard to their anti-microbial properties. *Surface and Coatings Technology, 192*(2), 252-256.

Seong, H., Kim, J., & Ko, S. (1999). Preparing chito-oligosaccharides as antimicrobial agents for cotton. *Textile Research Journal, 69*(7), 483-488.

Shahidi, S., Rashidi, A., Ghoranneviss, M., Anvari, A., Rahimi, M., Moghaddam, M. B., & Wiener, J. (2010). Investigation of metal absorption and antibacterial activity on cotton fabric modified by low temperature plasma. *Cellulose, 17*(3), 627-634.

Shahidi, S., Ghoranneviss, M., Moazzenchi, B., Rashidi, A., & Mirjalili, M. (2007). Investigation of antibacterial activity on cotton fabrics with cold plasma in the presence of a magnetic field. *Plasma Processes and Polymers, 4*(S1), S1098-S1103.

Shahidi, S., & Wiener, J. (2012). *Antibacterial agents in textile industry* InTech Open Access Publisher.

Shishoo, R. (2007). *Plasma technologies for textiles*. Boca Raton Boston New York Washington, DC: Cambridge : Woodhead Pub.

Silva, S. S., Luna, S. M., Gomes, M. E., Benesch, J., Pashkuleva, I., Mano, J. F., & Reis, R. L. (2008). Plasma surface modification of chitosan membranes: Characterization and preliminary cell response studies. *Macromolecular Bioscience, 8*(6), 568-576.

Simoncic, B., & Tomsic, B. (2010). Structures of novel antimicrobial agents for textiles-a review. *Textile Research Journal, 80*(16), 1721-1737.

Singh, R., Jain, A., Panwar, S., Gupta, D., & Khare, S. (2005). Antimicrobial activity of some natural dyes. *Dyes and Pigments, 66*(2), 99-102.

Son, Y., Kim, B., Ravikumar, K., & Lee, S. (2006). Imparting durable antimicrobial properties to cotton fabrics using quaternary ammonium salts through 4-aminobenzenesulfonic acid-chloro-triazine adduct. *European Polymer Journal, 42*(11), 3059-3067.

Sparavigna, A. (2008). Plasma treatment advantages for textiles. *arXiv Preprint arXiv:0801.3727*,

Stoimenov, P. K., Klinger, R. L., Marchin, G. L., & Klabunde, K. J. (2002). Metal oxide nanoparticles as bactericidal agents. *Langmuir, 18*(17), 6679-6686.

Sun, D., & Stylios, G. (2004). Effect of low temperature plasma treatment on the scouring and dyeing of natural fabrics. *Textile Research Journal, 74*(9), 751-756.

Sun, D., & Stylios, G. (2006). Fabric surface properties affected by low temperature plasma treatment. *Journal of Materials Processing Technology, 173*(2), 172-177.

Sun, G., Chen, T., & Worley, S. (1996). A novel biocidal styrenetriazinedione polymer. *Polymer, 37*(16), 3753-3756.

Sun, G., & Worley, S. D. (2005). Chemistry of durable and regenerable biocidal textiles. *Journal of Chemical Education, 82*(1), 60.

Sun, G., & Xu, X. (1999). *Durable and regenerable microbiocidal textiles* Google Patents.

Sun, G., Xu, X., Bickett, J. R., & Williams, J. F. (2001). Durable and regenerable antibacterial finishing of fabrics with a new hydantoin derivative. *Industrial & Engineering Chemistry Research, 40*(4), 1016-1021.

Sun, J., Yao, L., Gao, Z., Peng, S., Wang, C., & Qiu, Y. (2010). Surface modification of PET films by atmospheric pressure plasma-induced acrylic acid inverse emulsion graft polymerization. *Surface and Coatings Technology, 204*(24), 4101-4106.

Sun, X., Cao, Z., Porteous, N., & Sun, Y. (2012). An N-halamine-based rechargeable antimicrobial and biofilm controlling polyurethane. *Acta Biomaterialia, 8*(4), 1498-1506.

Sun, Y., Chen, T., Worley, S., & Sun, G. (2001). Novel refreshable N-halamine polymeric biocides containing imidazolidin-4-one derivatives. *Journal of Polymer Science Part A: Polymer Chemistry, 39*(18), 3073-3084.

Sun, Y., Chen, Z., & Braun, M. (2005). Preparation and physical and antimicrobial properties of a cellulose-supported chloromelamine derivative. *Industrial & Engineering Chemistry Research, 44*(21), 7916-7920.

Sun, Y., & Sun, G. (2001a). Novel regenerable N-halamine polymeric biocides. I. synthesis, characterization, and antibacterial activity of hydantoin-containing polymers. *Journal of Applied Polymer Science, 80*(13), 2460-2467.

Sun, Y., & Sun, G. (2001b). Novel regenerable N-halamine polymeric biocides. II. grafting hydantoin-containing monomers onto cotton cellulose. *Journal of Applied Polymer Science, 81*(3), 617-624.

Sun, Y., & Sun, G. (2001c). Novel regenerable N-halamine polymeric biocides. III. grafting hydantoin-containing monomers onto synthetic fabrics. *Journal of Applied Polymer Science, 81*(6), 1517-1525.

Sun, Y., & Sun, G. (2002). Durable and regenerable antimicrobial textile materials prepared by a continuous grafting process. *Journal of Applied Polymer Science, 84*(8), 1592-1599.

Sun, Y., & Sun, G. (2004). Novel refreshable N-halamine polymeric biocides: N-chlorination of aromatic polyamides. *Industrial & Engineering Chemistry Research, 43*(17), 5015-5020.

Švorčík, V., Kotál, V., Slepička, P., Bláhová, O., Špírková, M., Sajdl, P., & Hnatowicz, V. (2006). Modification of surface properties of polyethylene by ar plasma discharge. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 244*(2), 365-372.

Tan, K., & Obendorf, S. K. (2007). Fabrication and evaluation of electrospun nanofibrous antimicrobial nylon 6 membranes. *Journal of Membrane Science, 305*(1), 287-298.

Tavaria, F., Soares, J., Reis, I., Paulo, M., Malcata, F., & Pintado, M. (2012). Chitosan: Antimicrobial action upon staphylococci after impregnation onto cotton fabric. *Journal of Applied Microbiology, 112*(5), 1034-1041.

Tendero, C., Tixier, C., Tristant, P., Desmaison, J., & Leprince, P. (2006). Atmospheric pressure plasmas: A review. *Spectrochimica Acta Part B: Atomic Spectroscopy, 61*(1), 2-30.

Tenover, F. C. (2006). Mechanisms of antimicrobial resistance in bacteria. *The American Journal of Medicine, 119*(6), S3-S10.

Thanh, N. V. K., & Phong, N. T. P. (2009). Investigation of antibacterial activity of cotton fabric incorporating nano silver colloid. *Journal of Physics: Conference Series, 187*(1), 1-7. doi:10.1088/1742-6596/187/1/012072

Tourrette, A., De Geyter, N., Jocic, D., Morent, R., Warmoeskerken, M. M., & Leys, C. (2009). Incorporation of poly (N-isopropylacrylamide)/chitosan microgel onto plasma functionalized cotton fibre surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 352*(1), 126-135.

Ureyen, M. E., Gurkan, P., Namligoz, E. S., Armakan, D. M., & Dogan, A. (2010). Antibacterial and physical properties of knitted cotton fabrics treated with antibacterial finishes. *AATCC Review, 10*(1), 48.

van Ooij, W. J., Luo, S., & Datta, S. (1999). Surface modification of textile fibers and cords by plasma polymerization. *Plasmas and Polymers, 4*(1), 33-55.

Virk, R. K., Ramaswamy, G. N., Bourham, M., & Bures, B. L. (2004). Plasma and antimicrobial treatment of nonwoven fabrics for surgical gowns. *Textile Research Journal, 74*(12), 1073-1079.

Vohrer, U., Müller, M., & Oehr, C. (1998). Glow-discharge treatment for the modification of textiles. *Surface and Coatings Technology, 98*(1), 1128-1131.

Wagner, A., Fairbrother, D., & Reniers, F. (2003). A comparison of PE surfaces modified by plasma generated neutral nitrogen species and nitrogen ions. *Plasmas and Polymers, 8*(2), 119-134.

Wang, L., Xie, J., Gu, L., & Sun, G. (2006). Preparation of antimicrobial polyacrylonitrile fibers: Blending with polyacrylonitrile-co-3-allyl-5, 5-dimethylhydantoin. *Polymer Bulletin, 56*(2-3), 247-256.

Wang, X., & Wang, Y. (2000). Synthesis and application of 5, 5- dimethylhydantion. *Shandong Chemical Industry, 4*(29), 19-21.

Wang, X., Du, Y., Fan, L., Liu, H., & Hu, Y. (2005). Chitosan-metal complexes as antimicrobial agent: Synthesis, characterization and structure-activity study. *Polymer Bulletin, 55*(1-2), 105-113.

Wei, Q., Liu, Y., Hou, D., & Huang, F. (2007). Dynamic wetting behavior of plasma treated PET fibers. *Journal of Materials Processing Technology, 194*(1), 89-92.

Windler, L., Height, M., & Nowack, B. (2013). Comparative evaluation of antimicrobials for textile applications. *Environment International, 53*, 62-73.

Wong, K., Tao, X., Yuen, C., & Yeung, K. (1999). Low temperature plasma treatment of linen. *Textile Research Journal, 69*(11), 846-855.

Worley, S., Chen, Y., Wang, J., Wu, R., Cho, U., Broughton, R., Kim, J., Wei, C., Williams, J., & Chen, J. (2005). Novel N-halamine siloxane monomers and polymers for preparing biocidal coatings. *Surface Coatings International Part B: Coatings Transactions, 88*(2), 93-99.

Worley, S., Eknoian, M., & Li, Y. (1999). *Monomeric and polymeric surface active biocidal N-halo-oxazolidinones* WO Patent 1,999,029,678.

Yasuda, H. K. (2005). Some important aspects of plasma polymerization. *Plasma Processes and Polymers, 2*(4), 293-304.

Yasuda, T., Gazicki, M., & Yasuda, H. (1984). Effects on glow discharges on fibers and fabrics. *Journal of Applied Polymer Science*, (38), 201-214.

Yazdankhah, S. P., Scheie, A. A., Høiby, E. A., Lunestad, B., Heir, E., Fotland, T. Ø, Naterstad, K., & Kruse, H. (2006). Triclosan and antimicrobial resistance in bacteria: An overview. *Microbial Drug Resistance, 12*(2), 83-90.

Ye, W., Leung, M. F., Xin, J., Kwong, T. L., Lee, D. K. L., & Li, P. (2005). Novel core-shell particles with poly (n-butyl acrylate) cores and chitosan shells as an antibacterial coating for textiles. *Polymer, 46*(23), 10538-10543.

Ye, W., Xin, J. H., Li, P., Lee, K. D., & Kwong, T. (2006). Durable antibacterial finish on cotton fabric by using chitosan‐based polymeric core‐shell particles. *Journal of Applied Polymer Science, 102*(2), 1787-1793.

Yen, M., Chen, J., Hong, P., & Chen, C. (2006). Pore structures and anti-bacterial properties of cotton fabrics treated with DMDHEU-AA by plasma processes. *Textile Research Journal, 76*(3), 208-215.

Yeo, S. Y., Lee, H. J., & Jeong, S. H. (2003). Preparation of nanocomposite fibers for permanent antibacterial effect. *Journal of Materials Science, 38*(10), 2143-2147.

Yildiz, O., Cerkez, I., Kocer, H. B., Worley, S., Broughton, R., & Huang, T. (2012). N‐(hydroxymethyl) acrylamide as a multifunctional finish to cotton and a tether for grafting methacrylamide for biocidal coatings. *Journal of Applied Polymer Science,*

Yoon, N. S., Lim, Y. J., Tahara, M., & Takagishi, T. (1996). Mechanical and dyeing properties of wool and cotton fabrics treated with low temperature plasma and enzymes. *Textile Research Journal, 66*(5), 329-336.

Yu, F., Ma, J., & Wu, Y. (2012). Adsorption of toluene, ethylbenzene and xylene isomers on multi-walled carbon nanotubes oxidized by different concentration of NaOCl. *Frontiers of Environmental Science & Engineering, 6*(3), 320-329.

Yuen, C. W. M., Yip, J., Liu, L., Cheuk, K., Kan, C. W., Cheung, H. C., & Cheng, S. Y. (2012). Chitosan microcapsules loaded with either miconazole nitrate or

clotrimazole, prepared via emulsion technique. *Carbohydrate Polymers, 89*(3), 795-801.

Zeng, L. (2012). *Essence of test in textile trade* Chemical Industry Press.

Zhang, J., France, P., Radomyselskiy, A., Datta, S., Zhao, J., & van Ooij, W. (2003). Hydrophobic cotton fabric coated by a thin nanoparticulate plasma film. *Journal of Applied Polymer Science, 88*(6), 1473-1481.

Zhou, C. E., & Kan, C. W. (2014a). Optimizing rechargeable antimicrobial performance of cotton fabric coated with 5, 5-dimethylhydantoin (DMH). *Cellulose, 22*, 879-886.

Zhou, C. E., & Kan, C. W. (2014b). Plasma-assisted regenerable chitosan antimicrobial finishing for cotton. *Cellulose, 21*, 2951-2962.

Zhou, C. E., & Kan, C. W. (2015). Plasma-enhanced regenerable 5, 5-dimethylhydantoin (DMH) antibacterial finishing for cotton fabric. *Applied Surface Science, 328*, 410-417.

Zhu, P., & Sun, G. (2004). Antimicrobial finishing of wool fabrics using quaternary ammonium salts. *Journal of Applied Polymer Science, 93*(3), 1037-1041.

Ziaja, J., Koprowska, J., & Janukiewicz, J. (2008). Using plasma metallisation for manufacture of textile screens against electromagnetic fields. *Fibres & Textiles in Eastern Europe, 16*(5), 64-66.