A STUDY OF CATALYTIC SYSTEM FOR COTTON FINISHING TREATMENT

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M.Phil
The Hong Kong
Polytechnic University
2015

The Hong Kong Polytechnic University

Institute of Textiles and Clothing

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A thesis submitted in partial fulfilment of

the requirements for the degree of Master of Philosophy

February

2015

Certificate of Originality

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POON CHIN KUEN

Abstract

Cotton is an essential natural textile fibre and plays an important role in our daily life because of its various usages. However, there are some defects of cotton cellulose fabrics which are easily wrinkling after being washed or immersed in water and sensitive to fire causing fatalities. Applying wrinkle-resistant finishing and flame-retardant finishing on cotton cellulose are the major issues studied in this thesis. The formulations of the two functional finishes were modified with addition of metal oxides and varying the curing condition in order to attain the best fabric performance after treatment.

Different combinations of curing temperature and curing time have been studied to investigate the performance of functional finishing. It was found that curing temperature and curing time have significant effect on the wrinkle-resistant performance and the flame-retardant performance. Higher curing temperature and longer curing time resulted in a better performance as there was sufficient energy and duration for the reaction occurred. Moreover, it was confirmed that the addition of titanium dioxide (TiO_2) have positive influence to the fabric functional performance with lower curing temperature. The treatment effectiveness can be enhanced by the addition of metal oxides which can improve the adverse effects of the treatment. The surface morphology was examined by scanning electron microscopy and other advanced analytical techniques that gave the structural information of the treated fabrics. Besides, the role of TiO_2 in the two finishing treatments had been proposed. Finally, as fabric hand is a critical physical property of fabrics, the objective measurement of low stress mechanical properties had been investigated by KES-F in order to evaluate the fabric hand. The fabric hand became worse than the untreated cotton fabrics after functional finishing.

List of Publication

Poon, C. K., & Kan, C. W. (2015). Effects of TiO_2 and curing temperatures on flame retardant finishing of cotton. *Carbohydrate polymers*, 121, 457-467.

C.K. Poon, C.W. Kan, Optimization of wrinkle-resistant finishing with dimethyloldihydroxyethyleneurea (DMDHEU) using titanium dioxide as co-catalyst, Cellulose Chemistry and Technology (Accepted)

C.K. Poon, C.W. Kan, Low stress mechanical properties of cotton fabric treated with titanium dioxide catalysed wrinkle-resistant finishing, Journal of Natural Fibers (Accepted)

C.K. Poon, C.W. Kan, Effect of curing temperature on objective measurement of hand properties of cotton fabrics treated with flame-retardant finishing, Polymer Degradation and Stability (Preparing)

Acknowledgements

I am greatly obliged to my chief-supervisor, Dr. C.W. Kan, Associate professor of Institute of Textiles and Clothing at The Hong Kong Polytechnic University, for his continuous guidance, beneficial advice, sustained interest and encouragement throughout my study and development of my dissertation.

I would like to express my greatest appreciation to all the staff members and technicians in the textile laboratories and Materials Research Centre at The Hong Kong Polytechnic University for their help and guidance in operating the laboratory equipment.

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List of abbreviations

% o.w.f.	percentage of weight of fabric or fibre
2HB	bending moment
2HG	shear stress at 0.5^o
2HG5	shear stress at 5^o
AATCC	American Association of Textile Chemists and Colorists
AGU	anhydroglucose unit
AHP	aluminium hydroxyphosphate
$Al_2O_3 \cdot 3H_2O$	tri-hydrated alumina
APS	3-amino propylethoxysilane
ASTM	American Society for Testing and Materials
ATR	attenuated total reflection
B	bending rigidity
BTCA	1,2,3,4-butanetetracarboxylic acid
C	carbon
CA	citric acid
$CaCO_3$	calcium carbonate
CL	Knittex CHN
CO	carbon monoxide
CO_2	carbon dioxide
DGHP	diguanidine hydrogen phosphate
DHEU	dihydroxyethylene urea
DMU	dimethylol urea
DMDHEU	dimethyloldihydroxyethylene urea
DMeDHEU	N,N-1,1,3-dimethyl-4,5-dihydroxyethylene urea

DP	degree of polymerization
EDX	energy dispersive X-ray analysis
EMT	extensibility
FR	Pyrovatex CP New
FTIR	Fourier Transform Infrared Spectroscopy
G	shear stiffness / shear rigidity
H_2O	water
HMM	hexamethylolmelamine
ISO	International Organization for Standardization
KES-F	Kawabata evaluation system for fabrics
LC	compressional linearity
MA	maleic acid
MDPA	N-Methylol dimethylphosphonopropionamide
MGHP	monoguanidine dihydrogen phosphate
MgO	magnesium hydroxide
MIU	coefficient of friction
Na	sodium
Na_2CO_3	sodium carbonate
O	oxygen
P	phosphorus
PA	phosphoric acid
RC	compressional resilience
RT	tensile resilience
SEM	scanning electron microscopy
SHP	sodium hypophosphite
SMD	geometrical roughness

T_c	combustion temperature
T_M	appearance thickness
T_o	intrinsic thickness
T_p	pyrolysis temperature
TG	thermogravimetric
THPC	tetrakis(hydroxymethyl)phosphonium chloride
Ti	titanium
TiO_2	titanium dioxide
TMM	trimethylolmelamine
UV	ultraviolet
WC	compressional energy
WRA	wrinkle recovery angle
WT	tensile energy or tensile work
XRD	X-ray diffraction
$ZnCO_3 \cdot Zn(OH)_2$	zinc carbonate hydroxide
ZnO	zinc oxide

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Chapter 1: Introduction

1.1. Background of study

Cotton is an essential natural textile fibre and plays an important role in our daily life because of its various usages. Cotton fibre is widely used in apparel, home furnishings and industrial products. It has a major share in the world textile marketing (Price et al., 1997). The annual production of cotton fibre grown in 35 countries has nearly 22 million tons. China, India and the USA are the biggest producers around the world. *Gossypium hirsutum*, one of the cotton species known as upland cottons, provides over 90% of raw cotton fibre. The large usage amount of cotton fibre is due to its numerous advantages such as good absorbent, inexpensive and breathable (Wakelyn et al., 2007). Although there are supreme properties of cotton cellulose, cotton still have some drawbacks. For example, cotton fabrics are easily wrinkling such that poor wrinkle recovery property. Besides, cotton fabric, which is composed of carbohydrate compounds, are easily burnt and susceptible to fire. Therefore, in order to improve the wrinkle recovery ability and flammability problem, cotton fabrics are usually subjected to various treatments in textile industry. Functional finishing of cotton is a common treatment used in many daily applications (Horrocks, 2003; Schindler & Hauser, 2004; Sharpe & Mallinson, 2003).

Finishing refers to the final process carried out after coloration and before the materials made up into garment. The purposes of finishing are to furnish the textile materials suitable for their end uses and to meet the expectations of certain customers. In the finishing process, the cotton fabrics are usually impregnated with functional finishing agents followed by drying and curing at high temperature. Although functional finishing treatment can impart specific properties on the cotton fabrics, the other fabric properties such as tensile strength, tear strength are weakened. Moreover, the exhaust of functional finishing agent may cause some harmful effects to the marine environment and lead to various environmental problems (Connell, 1995; Gutenmann & Lisk, 1975). In addition, formaldehyde, which is known as carcinogenic, is commonly released during curing process and arouses health concerns. Therefore, the modification and improvement of conventional functional finishing, the reduction in the side effects, and the environmental issues are the hot topics that have been widely studied in textile research industry.

In the present study, there is a comprehensive examination on the two specific functional finishes that are wrinkle-resistant finishing and flame-retardant finishing of cotton. The formulations and conditions used in the functional finishing have been modified based on the conventional one. In conventional treatment, a high curing temperature such as 170 ^{o}C above is usually employed (Horrocks, 2003; Lam et al., 2011b; Lam et al., 2011e; Schindler & Hauser, 2004; Sharpe & Mallinson, 2003). In the present study, the all-round performance of the treated fabrics subjected to different combinations of curing temperature and time has been evaluated in order to study the effect of curing conditions on wrinkle-resistant finishing and flame-retardant finishing.

Moreover, the technique of the application of metal oxides as co-catalyst has not matured in the textile industry. There are only limited studies about the addition of metal oxides as co-catalyst in functional finishing. In limited previous studies, addition of metal oxide has been proved to be feasible in enhancement of the performance of functional finishing at conventional curing conditions (Lam et al., 2010a; Lam et al., 2010b; Lam et al., 2011b; Lam et al., 2011e; Wang & Chen, 2005; Yuen et al., 2007). In the present study, TiO_2 is also employed in this research in order to evaluate the effect of TiO_2 on the fabric performance with various combinations of curing temperature and time. Comprehensive experimental data are obtained from various tests and used to evaluate the performance of treated fabrics. Although TiO_2 is found to be feasible in improving the performance of treated fabrics, the role of TiO_2 has not been discussed in details. The role of TiO_2 is proposed and explained more deeply in the present study in order to give more information on the use of metal oxides.

Besides, the information of physically mixing different metal oxides together as catalyst or co-catalyst in the functional finishing has not yet been done. A novel application of mixed metal oxide as co-catalyst is tried in wrinkle-resistant finishing to study the performance of treated fabrics.

1.2. Objectives

The principal objectives of present study are summarized as follows:

1. To explore the possibility of improving and modifying the conventional functional effect of textiles by transition metals and their compound as catalyst
2. To study various parameters such as curing conditions that will affect the catalytic reaction during textile functional finishing
3. To evaluate and compare the performance of treated fabrics after finishing treatments by means of international standard testing methods
4. To characterize the properties of the fabrics subjected to functional finishing through a comprehensive morphological and structural study with the aid of advanced analytical techniques

1.3. Methodology

The subsequent methodologies had been adopted to attain the objectives

1 Literature Review: To consolidate and review the background knowledge and recent development in textile functional finishing especially in two aspects which are wrinkle-resistant finishing and flame-retardant finishing. Gaining further insight into the reaction mechanism between the reagents and materials used as well as the feasibility of the experiments.

2 To study the effects of curing parameters such as curing temperature and curing time on wrinkle-resistant finishing and flame-retardant finishing with designated formulations on cotton fabrics. Optimum conditions were determined based on the performance of the fabrics

3 To study the possible mixed metal oxide catalyst such as coupled ZnO with TiO_2 applied in the wrinkle-resistant finishing

4 To evaluate the effectiveness of the reaction and performance of the fabrics after functional finishing by a series of international evaluation methods. The objective measurement of fabrics hand properties was also evaluated.

5 To characterize the treated fabrics using advance characterization techniques such as scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray spectroscopy (EDX) and Thermogravimetric analysis (TG) to investigate the surface morphology of the treated cotton fabrics and confirm the attachment of metal oxides on the fabrics.

6 To prepare, summarise and write up the thesis.

1.4. Significance of study

1. Using metal oxides as catalyst or co-catalyst in functional finishing will provide extra functions for the fabrics due to the properties of metal oxides. Mixed catalyst system can give multi-functional properties.
2. Successful improvement of catalytic performance by metal oxides can reduce of the production cost, simplify the production process, and achieve a better ecology. In addition, it can maximize the output and minimize the undesirable effects in the finishing. By studying and optimizing curing temperature and curing time for the reaction, energy can be conserved by saving heat energy and time.

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Chapter 2: Literature Review

2.1. Introduction

2.1.1. Cotton fibre

Cotton is a carbohydrate compound. It is mainly composed of cellulose. The chemical formula of cellulose is $C_6H_{10}O_5$. Cotton cellulose is a linear homopolymer structure of β-D-glucopyanose, known as anhydroglucose unit (AGU). Figure 2-1 shows the linear homopolymer structure of cellulose.

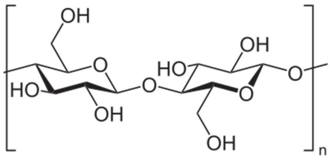


Figure 2-1. Linear homopolymer structure of cellulose

Two monomers, AGUs, are linked together by β-(1, 4)-glucosidic linkage, elimination of one water molecule, to form dimer that is the structural repetitive unit of the cellulose chains. There are a reducing end and a non-reducing end on each chain (Thomas et al., 2013; Wakelyn et al., 2007). The degree of polymerization (DP) of cotton cellulose usually has the number n with over ten thousands which is meant that there are more than ten thousands AGUs linked together. A short cellulose chain is shown in Figure 2-2. Since the chemical structure of cellulose is composed of β-D-glucopyanose, it shows that some reactions are potentially taken place at 2-OH, 3-OH and 6-OH (Wakelyn et al., 2007). The available sites make the cotton can carry out different chemical reactions or textile finishes to give functional properties. Wrinkle-resistant finishing and flame-retardant finishing are two common functional finishes applied on cotton fabric. These two finishes will be deeply discussed in this thesis.

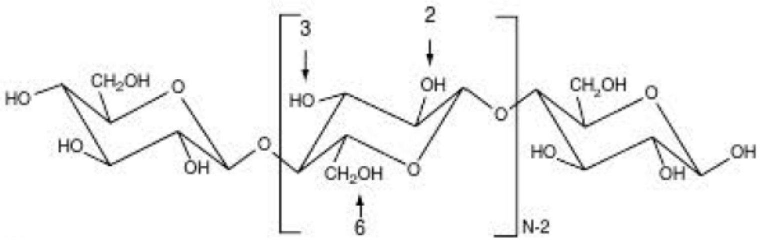


Figure 2-2. The hydroxyl groups that can potentially undergo chemical reactions

Source: M. Lewin, *Handbook of fiber chemistry*. 3rd ed., CRC Press, 2007

2.1.2. Chemical finishing

Finishing can be classified into chemical and mechanical finishing. Chemical finishing will be focused in the study. Chemical finishing is an important component in textile processing industry. It involves the addition of chemicals on the textile materials to attain desired fabric properties in order to satisfy the consumer demands. Apart from satisfying the consumer needs, the objectives of chemical finishing are to decrease production costs, achieve higher quality, and minimize the environmental problem during the process (Holme, 1993; Schindler & Hauser, 2004).

However, chemical finishing is facing some challenges in achieving the objectives. There are several essential factors required in consideration in order to have a proper formulation of chemical finishing. The factors include i) the type of textile being treated; ii) the performance requirements of the finish; iii) the cost to benefit ratio; iv) restrictions imposed on the process according to the availability of machinery, procedure requirements, environmental consideration; and compatibility of different formula components; v) the interaction of the finishing effects (Schindler & Hauser, 2004). It is not easy to handle all parameters to have an acceptable arrangement, especially carrying out various types of finishing in a single bath. Apart from dealing with the finishing bath, the finished fabric should meet some basic requirements for durable finishing. For example (Lewin, 2005; Schindler & Hauser, 2004), the finished fabrics should have high performance for washing and drying cleaning. The important textile qualities such as tear strength, abrasion resistance, appearance and fabric hand should be retained. Medical problems such as skin irritation, sensitising and allergy potential should be avoided. Furthermore, chemical finishing produces large amount of effluent, solid waste or irritating gases such as formaldehyde raising environmental and ecological concerns (Connell, 1995; Schindler & Hauser, 2004). These concerns threaten not only human health but also natural life.

In order to meet the requirements of modern world, achieving a better qualities of finishing and having a more environmentally friendly process, traditional chemistries and manufacturing methods have been continuously studied, changed and modified (Bajaj, 2002; Schindler & Hauser, 2004).

2.2. Wrinkle-resistant treatment

2.2.1. Introduction

Despite numerous advantages of cotton cellulose, there is a main defect of cotton fabrics which is easily wrinkling after being washed or immersed in water. The formation of wrinkle is generally because cotton absorbs moisture readily. A special kind finish is applied on the cotton cellulose in order to overcome the wrinkling problem. It is called wrinkle-resistant finishing. There are some other terms commonly used to describe this kind of finish which are “easy-care” or “durable press”. Wrinkle-resistant finishing is usually applied on cellulose or cellulose blend fabrics. The treatment aims at reducing in swelling and shrinkage, improving wrinkle recovery ability and smoothness of appearance of cotton fabrics. It can also retain the intentional creases and pleats on the cotton fabrics

(Sharpe & Mallinson, 2003; Schindler & Hauser, 2004).

Nevertheless, wrinkle-resistant finishing will generate side effects to cotton fabrics. The treated fabrics suffer from elasticity and flexibility reduction and decrease in abrasion resistance and tear strength. Thus, different kinds of chemicals such as softeners are added into the finishing bath so as to diminish the adverse effects caused during the treatment.

2.2.2. Wrinkle Formation

The wrinkle formation of cotton cellulose is due to rearrangement of free hydroxyl groups between the polymer chains. The hydrogen bonding interactions between the hydroxyl groups are broken and reformed under stressed condition. In the supramolecular structure level of cellulosic fibre, there are amorphous region, intermediate region, and crystalline region. Amorphous region is the region of low order of arrangement which is easily distorted by external force while crystalline regions is the region of high order of arrangement which limits the mobility of the polymer chains (Thomas et al., 2013; Wakelyn et al., 2007). When the fabric is under stressed, some hydrogen bonds at the boundary of crystalline and amorphous region are broken. Then, some hydrogen bonds are newly formed at their new positions preventing from restoring to their original positions. These newly formed hydrogen bonds make the molecule bind in a new configuration and cause the wrinkle formation of the fabrics (Shenai, 1994).

Moreover, the formation of wrinkle is promoted in the presence of moisture. The moisture facilitates the movement internal polymer chains in the amorphous areas and intermediate regions with non-crystalline arrangement. The moisture absorption will disrupt the internal hydrogen bonding between the polymer chains. Once the moisture laden cellulose fibre is stressed, rearrangement of internal polymer chains will be occurred and followed by reformation of hydrogen bonds inside the chains. The bonds form in their new positions and lock in the new configuration inhibiting the movement of cellulose chains. Therefore, a newly formed wrinkle or crease remains on the fabric unless any addition processes like ironing applied (Dehabadi et al., 2013; Sharpe & Mallinson, 2003; Schindler & Hauser, 2004).

2.2.3. General approaches for wrinkle-resistant finishing

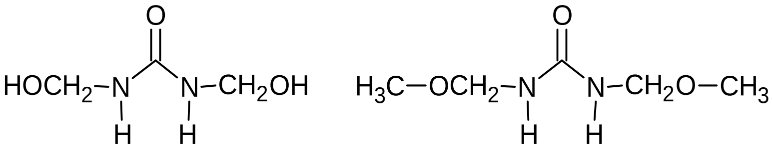
There are two chemical approaches to diminish the wrinkle formation and produce non-swelling fabrics commercially (Schindler & Hauser, 2004). The first one is to hinder the water molecules penetrating the fibres by incorporation of a polymerized finish in the pores of the cotton fibres. The second one is to restrict the movement of polymer chains and inhibit the swelling of cellulosic fibres by reacting multifunctional crosslinking agents with hydroxyl groups. The crosslinking agent links two adjacent cellulose chains by formation of crosslink. Crosslinked polymer chains can lower stress-induced slippage of chain and increase the recovery ability from any deformation. However, wrinkle-resistant finishing by crosslinking method may reduce the extensibility of cellulose fibre since the movement of cellulose chains is restricted. When the external force is applied, the force is concentrated on a particular position and cannot share over many neighbour molecules (Dehabadi et al., 2013; Schindler & Hauser, 2004; Shenai, 1994). Thus, the fabrics become brittle and suffer from loss of abrasion resistance, tensile and tear strength.

2.2.4. Wrinkle-resistant finishing agent

There are mainly two types of crosslinkers which are formaldehyde-based compounds and formaldehyde-free compounds. Formaldehyde-based reagent such as dimethyloldihydroxyethyleneurea (DMDHEU) is widely used in textile industry nowadays due to its popularity and low cost. For the formaldehyde-free compounds, there are mainly polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA) and other polymers.

2.2.4.1. Formaldehyde based crosslinking agent

At the end of 1920s, N-methylol compounds, a formaldehyde-based crosslinker, were firstly introduced as a wrinkle-resistant finishing agent. In the early stage, urea-formaldehyde and melamine-formaldehyde were used. *N,N'* dimethylol urea (DMU) and *N,N'* dimethoxymethyl urea, shown in Figure 2-3, are two examples of urea-formaldehyde type. The reaction between urea and formaldehyde to give DMU is in an equilibrium state so that the high content of free formaldehyde is released using urea-formaldehyde compound. *N,N'* dimethoxymethyl urea is more stable than DMU and derived from the reaction between DMU and methanol. These chemicals are highly reactive in wrinkle-resistant finishing (Cooke et al., 1954; Cooke et al., 1957; Dehabadi et al., 2013; Gagliardi & Gruntfest, 1950; Lineken et al., 1956; Schindler & Hauser, 2004; Sharpe & Mallinson, 2003; Stam et al., 1956).

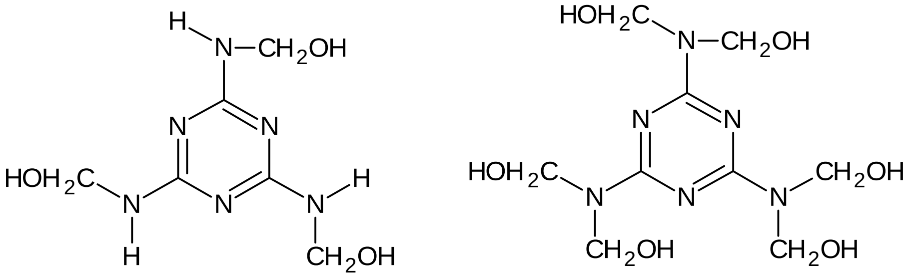


DMU

Dimethoxymethyl urea

Figure 2-3. The chemical structure of urea-formaldehyde of DMU and dimethoxymethyl urea

Melamine-formaldehyde compounds were introduced during 1930s and 1940s (Mustafa, 2012). They have a higher durability to laundering and better stability against hydrolysis compared with urea-formaldehyde. These compounds have good crosslinking efficiency due to the present of three to six N-methylol groups. TMM and HMM are the product of the reaction between melamine and formaldehyde in equilibrium state. The chemical structures of TMM and HMM are shown in Figure 2-4. (Dehabadi et al., 2013; Schindler & Hauser, 2004).



Trimethylol melamine (TMM) Hexamethylol melamine (HMM)

Figure 2-4. The chemical structure of melamine-formaldehyde compound of TMM and HMM

Although urea-formaldehyde and melamine-formaldehyde are effective chemicals in wrinkle-resistant finishing, the treated fabrics will have a relatively high formaldehyde content and free formaldehyde generated during the treatment. Formaldehyde causes many risks. With 1 ppm of formaldehyde in the air will cause pungent odour. It irritates mucous membranes, causes teary eyes, coughing, headache and difficulties in breathing. Moreover, eczema and allergic reactions may occur when skin contacts with textiles that contain a high level of formaldehyde (Dehabadi et al., 2013; Lyapina et al., 2012; Hashem et al., 2009; Sharpe & Mallinson, 2003; Schindler & Hauser, 2004; Wartew, 1983).

The concern of formaldehyde had been drawn attention during 1960s to 1970s encouraging the development of low formaldehyde level crosslinking finishes

(Brotheron et al., 1989; Frick & Harper, 1982; Schindler & Hauser, 2004; Yoon et al., 2003). A new urea compound, DMDHEU, became an important crosslinking agent in 1970s (Holme, 1993). DMDHEU produces less free formaldehyde during finishing. The content is much lower than using urea-formaldehyde and melamine-formaldehyde. DMDHEU gives excellent durability wrinkle-resistant performance with reasonable cost so that it is commonly used these days. In Figure 2-5, 4,5-dihydroxyethylene urea is firstly prepared by urea and glyoxal. Then, 4,5-dihydroxyethylene urea further reacts with formaldehyde to form DMDHEU.

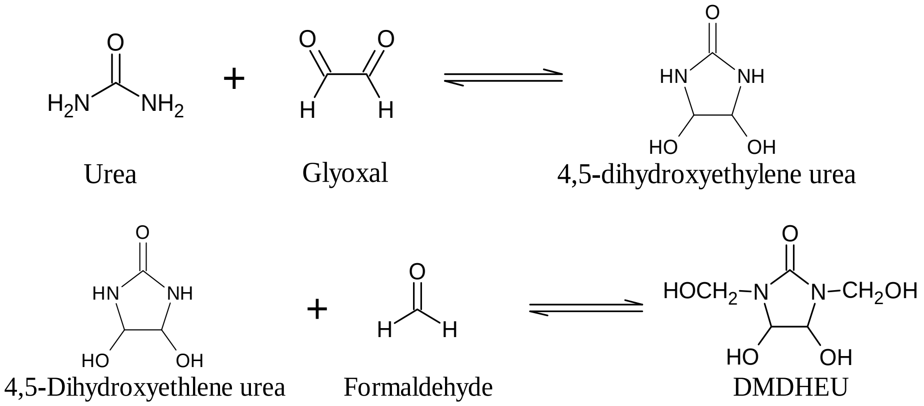


Figure 2-5. Synthesis of DMDHEU through two steps of reaction.

As a wrinkle-resistant agent, DMDHEU reacts with two cellulose chains to form crosslink. The chemical equation is shown in Figure 2-6. The crosslink restricts the movement of cellulose chains when stress is applied preventing it from wrinkle formation. However, the crosslink locks the movement of the molecules lead to the loss of tensile strength and tear strength. It is because the external force from tear stressed can be slightly shared by over many neighbour molecules if there is no crosslink. Sharing of force cannot be done in crosslinked cellulose chains (Dehabadi et al., 2013; Sharpe & Mallinson, 2003; Schindler & Hauser, 2004).

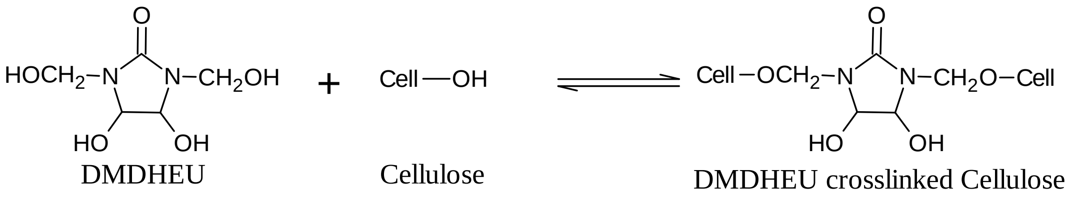


Figure 2-6. Reaction between DMDHEU and cellulose forming DMDHEU crosslinked cellulose

Formaldehyde release is still a problem when using DMDHEU but there are some methods to further reduce the liberation of formaldehyde. It can be done by i) after-washing of cured fabric, ii) addition of formaldehyde acceptors or scavengers such as carbohydrazide in the finishing bath, iii) substitution of part of DMDHEU in the bath by nitroalcohol reactant modifier, and iv) subsequent treatment of the finished fabric according to the fog chamber technique (Bajaj, 2002; Holme, 1993; Petersen & Pai, 1981). Moreover, chemical modification of DMDHEU with alcohol such as methanol to generate etherified DMDHEU can achieve low formaldehyde liberation (Bajaj, 2002; Holme, 1993; Schindler & Hauser, 2004).

2.2.4.2. Non-formaldehyde based crosslinking agent

Since the adverse effects of formaldehyde, formaldehyde-free crosslinking agents have been developed and synthesized to replace the traditional N-methylol compounds by scientists since the late 1980 (Bajaj, 2002; Frick & Harper, 1982; Chen et al., 2005; Holme, 1993; Li et al., 2008; Petersen & Pai, 1981; Schindler & Hauser, 2004). *N*, *N*'-dimethyl-4,5-dihydroxyethylene urea (DMeDHEU) is one of examples of formaldehyde-free compounds. It is a glyoxalurea crosslinking agent derived from the reaction between *N*, *N*'-Dimethyl urea and glyoxal, shown in Figure 2-7. However, DMeDHEU has not been widely used in textile industry because of high cost and far less effective than DMDHEU. It costs about twice as much as DMDHEU to achieve comparable wrinkle-resistant and durable press performance effects to DMDHEU (Frick & Harper, 1981; Frick & Harper, 1982; Gonzales & Benerito, 1965; Holme, 1993; Schindler & Hauser, 2004; Yang et al., 2000).

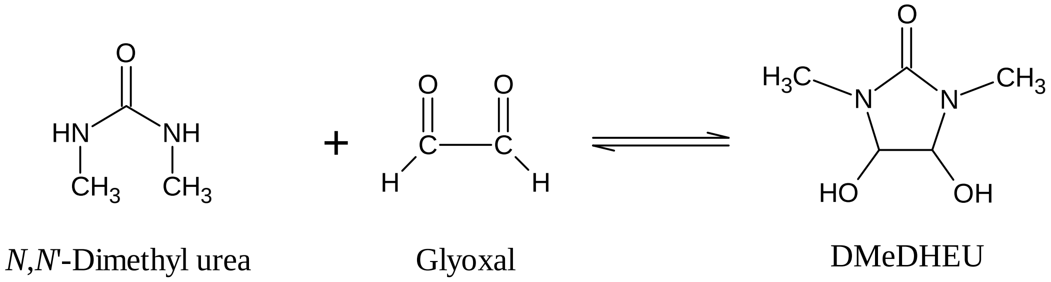
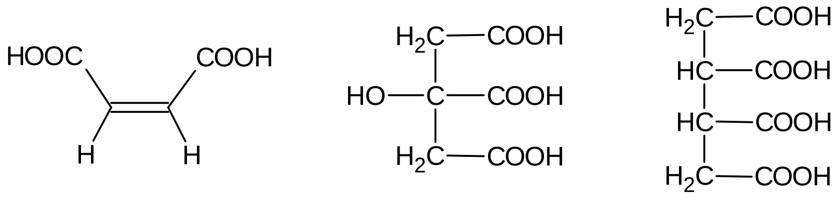


Figure 2-7. Synthesis of DMeDHEU

In addition to DMeDHEU, using polycarboxylic acid as crosslinking agents was documented in 1960s by Rowland et. al. (Rowland et al., 1967). Polycarboxylic acids, such as MA, CA and BTCA, are shown in Figure 2-8. They are formaldehyde-free compounds replacing the traditional crosslinking agents (Schramm & Rinderer, 2006; Welch, 1988; Welch & Andrewes, 1989; Welch et al., 1992; Welch et al., 1994; Yang et al., 1998). BTCA is the most effective formaldehyde-free crosslinking agent among the three examples mentioned above. The effectiveness is assessed by the performance of wrinkle-resistant, duration of curing, laundering durability, retention of fabric whiteness and free from odour (Bajaj, 2002; Dehabadi et al., 2013, Welch, 1988; Welch & Andrewes, 1989). CA causes yellowing due to the formation of unsaturated acids. MA is only bifunctional such that it has just two carboxylic groups per molecule resulting in less effective wrinkle-resistant performance (Dehabadi et al., 2013; Fahmy & Abdel-Halim, 2010).



Maleic acid

Citric acid

BTCA

Figure 2-8. Chemical structure of some carboxylic acids

The reaction of polycarboxylic acids involved two steps. The polycarboxylic acids first form cyclic anhydrides as reactive intermediate by dehydration of two carboxylic acid groups followed by esterifying with cotton cellulose to achieve wrinkle-resistant properties (Dehabadi et al., 2013; Schindler & Hauser, 2004; Yang, 1991; Yang & Wang, 1996). The reaction mechanism is shown in Figure 2-9. The rate of esterification reaction can be accelerated by addition of a proper catalyst such as sodium hypophosphite (SHP). Despite the supreme performance of BTCA for wrinkle-resistant finishing, BTCA is not widely used commercially due to the economical consideration (Dehabadi et al., 2013; Kittinaovarat et al., 2006). It also causes dramatic loss in tensile strength (Fahmy & Abdel-Halim, 2010; Xu & Li, 2000). Moreover, a large amount of SHP, an expensive catalyst, is required in the reaction of BTCA. SHP is a reducing agent that discolours some reactive dyestuff or sulphur dyes (Schindler & Hauser, 2004). Therefore, modification and investigation of conventional formulations, using DMDHEU as main crosslinking agent, is mainly focused in the present study.

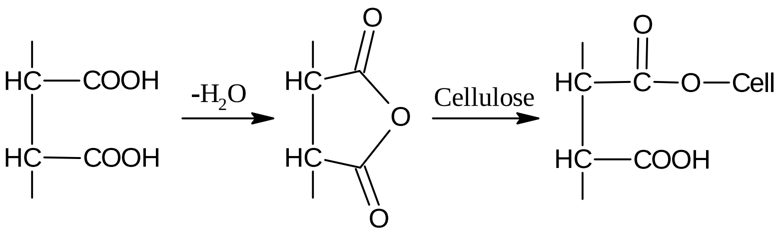


Figure 2-9. Esterification of cellulose with polycarboxylic acids via formation of cyclic anhydrides

2.2.5. Application and evaluation

A successful wrinkle-resistant finishing is achieved by well preparation, using proper application methods and controlling all parameters carefully. The chemical reaction is mainly affected by the drying and curing conditions. The crosslinking agent can be applied to cotton fabrics in a number of ways. Pad-dry-cure procedure is the most common application method for wrinkle-resistant finishing nowadays (Schindler & Hauser, 2004). The fabric is firstly dipped in the solution containing crosslinking agent, catalyst, softener and other components. Secondly, the fabric is then padded using padding mangle to attain a particular wet pick-up under constant environment. The effect of temperature variation is significant in the control of pick-up while cloth speed have little effect to the fabrics (Greenwood & Holme, 2003). Then, the treated fabric is dried before the crosslinking reaction that carries out at curing step. Lastly, the dried fabric is sent to be cured at specific temperature and duration. For the curing step, it is divided into pre-cure and post-cure. Pre-cure refers to the finish is cured promptly after drying, while the fabric is still in an open width configuration. Pre-cure has high process productivity. Post-cure refers to the finish is only dried by the fabrics manufacturer and cured after the garment has been manufactured. Pre-cure finish is suitable for the fabrics and apparel that require wrinkle resistance such as shirting. Post-cure finish produces excellent crease retention and is applicable for the intentional crease retention on trousers and pleated skirts (Bajaj, 2002; Schindler & Hauser, 2004).

Besides, curing can be classified into “dry” curing and “wet” curing. For the dry curing, all water is removed from the fabric prior to the actual crosslinking reaction. For the wet curing, the padded fabrics is wrapped in plastic film and batched under certain conditions for a long time before washing and drying. Wet fixation process allows the resin penetration, deposition, and polymerization inside the fibres. The resin penetrates well within fibres. This makes the uniformity of distribution of crosslinks throughout the fibre structure. Moreover, wet fixation results in improved strength and resilience compared with convention pad-dry-cure procedure (Bertoniere et al., 1974; Hollies & Getchell, 1967a; Hollies, 1967b; Rowland et al., 1971; Rowland et al., 1974; Schindler & Hauser, 2004). As wet-fixation is a time-consuming process, traditional pad-dry-cure procedure is still a major method for the application of wrinkle-resistant finishing.

As mentioned above, wrinkle-resistant finishing suffers from tensile and tear strength loss, it is important to strike a balance among the mechanical properties, hand properties and wrinkle-resistant performance in order to obtain a qualified fabric. A variety of test methods are used to evaluate the characteristics of fabrics treated with wrinkle-resistant finishing (Schindler & Hauser, 2004). For example, AATCC test method 66 is used to determine the wrinkle recovery performance by measuring wrinkle recovery angle of woven fabrics. The larger the recovery angle, the better the wrinkle recovery performance is. AATCC test method 124 is used to assess the appearance of fabric after home launderings and give the durable rating by comparing with standards. The aim of durable press rating of wrinkle-resistant treated fabrics is larger than 3.5. For the mechanical property such as tear strength, it can refer to the standard method ASTM D1424 or BS EN ISO 13937. The tear strength can be obtained by Falling-Pendulum (Elmendorf-Type) apparatus.

2.3. Flame-retardant treatment

2.3.1. Introduction

Flame-retardant finishing is widely applied in our life. It protects consumers from unsafe apparel and the fire fighters require protection from flames as they go about their duties (Schindler & Hauser, 2004). Cotton cellulose is sensitive to fire causing fatalities. The flammability of cotton cellulose mainly depends on the construction and density of the fabric (Yang & Qiu, 2007). When cotton is ignited, cotton cellulose undergoes thermal degradation and then forms combustible volatile compounds such as carbon monoxide which become involved in the propagation of fire (Horrocks, 2001; Kandola et al., 1996; Schindler & Hauser, 2004). In order to solve the problem, there are many successful flame-retardant treatments, formulations and additives were developed in the 1950s – 1980s (Horrocks, 1986; Horrocks et al., 2005). In addition, the flame-retardant finishing has been intensively reviewed by Horrocks and by other authors (Horrocks, 1986; Lewin, 1983). Cellulose has a characteristic structure and chemical composition so that it can interactive with flame-retardant chemicals chemically to equip with flame-retardant property.

A commercially successful flame-retardant textile product must have little or no adverse effects on physical properties of product retaining the aesthetics and physiological properties. The treatment can be done by simple process and inexpensive chemicals. Besides, it should be durable to repeated home launderings, tumble drying and dry cleaning (Oulton, 1995; Schindler & Hauser, 2004).

2.3.2. Background of Combustion

Combustion is an exothermic process. Three basic elements that are needed in combustion process are ignition source, oxygen and fuel. The source of ignition comes from the heat. If anyone element is absent, the substance would not combust (Oulton, 1995; Schindler & Hauser, 2004). Glowing and flaming are two distinct phenomena described the problem of fire in respect of cotton textile. Glowing, a slow combustion under low concentrations of oxygen, is the direct oxidation of solid cellulose or its degradation products while flaming combustion is a complex process involving both solid and gas phases (Price et al., 1997). In order to tackle the fire problem and have effective flame-retardant finishing, the mechanism of combustion is needed to be fully understand. A combustion cycle model for textile material is shown in Fig 2-10. The combustion cycle mainly includes three parts that are pyrolysis, ignition and propagation of the flame, and char formation.

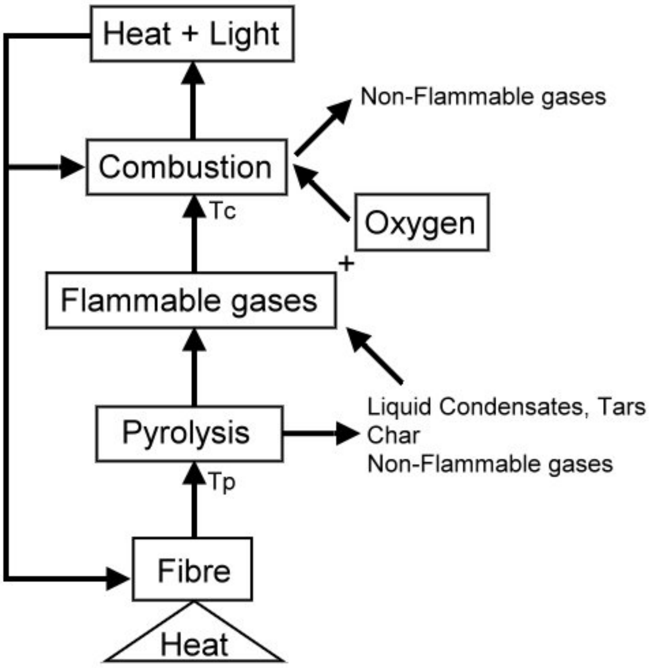


Figure 2-10. Combustion cycle for fibers

Generally speaking, pyrolysis is an endothermic process that absorbs sufficient energy to satisfy dissociation energies of the bond to be broken (Price et al., 2001). It is a thermochemical decomposition of organic materials and usually irreversible. Cellulose pyrolysis is a subject that extensively studied by scientists over the past several decades (Chatterjee & Conrad., 1966; Price et al, 1997; Shafizadeh, 1968; Shafizadeh et al., 1973; Shafizadeh, 1982; Yang et al., 2007; Zhu et al., 2012). The general pathways for pyrolysis of cellulose are mainly divided into two different ways, shown in Figure 2-11. One occurs at lower temperature. Another one takes place at the temperature above 300°C (Shafizadeh, 1982; Zhu et al., 2012).

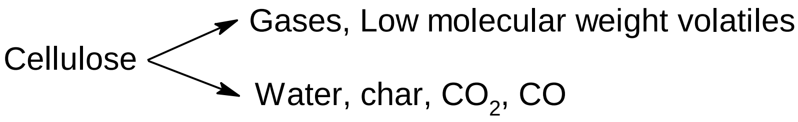


Figure 2-11. Competing pathways for cellulose pyrolysis

Theoretically, pyrolytic degradation of the cellulose molecule may take place through cleavage of the glycosidic groups or dehydration and breakdown of anhydeoglucose units (Shafizadeh, 1968; Shafizadeh et al., 1973). The reaction in the first pathway dominates at the lower temperature (below 300°C). The cellulose pyrolyzes to procedure a wide range of low molecular weight volatiles of aldehydes, ketones and alcohols. These volatiles are highly flammable. Some non-flammable gases such as CO_2, and water vapour also can be found (Oulton, 1995; Schindler & Hauser, 2004; Shafizadeh, 1982). When the energy is sufficient enough, the cellulose is decomposed by an alternative pathways. Rapid cleavage of the glycosidic bond and evaporation of the products occur. At the moment, the cleavage of glycosidic bond can proceed through a homolytic or a heterolytic process (Shafizadeh, 1968; Shafizadeh et al., 1973). The products for the second pathway of pyrolysis contain not only more water vapour, flammable gases, non-flammable gases and solid carbonaceous chars but also tarry pyrolyzates containing levoglucosan, oligosaccharides, other anhydroalucose compounds, and glucose decomposition products (Shafizadeh et al., 1973; Shafizadeh, 1982).

If there are free supply of oxygen and an ignition source, cellulose undergoes completely combustion to form carbon dioxide, water and heat released (Oulton, 1995; Shafizadeh, 1968). This kind of reaction is favoured by lightweight, open and free-hanging materials. Heavily folded tight-woven materials will often smoulder and char by means of dehydration (Oulton, 1995).

When the temperature continuously rises to combustion temperature (T_c) which is higher than the pyrolysis temperature, the flammable gases from pyrolysis combine with oxygen. At this moment, the fibre will be ignited and combustion occurs. The burning process is highly exothermic (Schindler & Hauser, 2004). The heat in the form of radiation, convection and conduction generated from combustion reaction provides additional thermal energy for the fibre to undergo further pyrolysis. Thus, there are more flammable gases produced for combustion. The reaction cycle is repeated and continuous.

Unlimited supply of oxygen sustains the combustion process. Combustion is a series of gas phase free radical reactions occurred. The chain branching step is propagated by extremely reactive H・ and OH・ radicals (Horrocks, 2001). A set of equations of free radical combustion reactions is shown in Figure2-12 (Schindler & Hauser, 2004). In equation (1), hydrogen radical reacts with oxygen to produce OH・ and O・ radicals. Then, the produced O・ radical reacts with the hydrogen gas to yield OH• and H• radicals in equation (2). Equation (3) is the main exothermic reaction which provides most of the energy maintaining the flame.

$$\mathrm{H\cdot + O_2 \rightleftharpoons OH\cdot + O\cdot} \quad \ldots(1)$$

$$\mathrm{O\cdot + H_2 \rightleftharpoons OH\cdot + H\cdot} \quad \ldots(2)$$

$$\mathrm{OH\cdot + CO \rightleftharpoons CO_2 + H\cdot} \quad \ldots(3)$$

Figure 2-12. The free radical combustion reactions

In addition to pyrolysis and combustion process, the formation of carbonaceous chars is another area that needs to be understood. Carbonaceous chars are complex materials, and can be characterized by a numerous number of properties including volume, weight, density, crush, resilience, hardness, toughness, coherence, adherence, permeability, heat conductivity, heat capacity an insulation in addition to structural properties (Lewin, 2005). The cellulosic chars have been analysed (Sekiguchi et al., 1983; Pastorova et al., 1994). When organic polymers are heated, their degradation occurs through the competition between volatilization, crosslinking reaction, as well as those leading to polymer chain unsaturation. The last two can lead to the formation of carbonaceous chars (Horrocks et al., 1996). Char formation in a number of polymers was studied by Van Krevelen (Van Krevelen, 1975). The study shows that the inherent flammability of any polymer reduces as its char-forming tendency increases. The interrelationship between the increased char formation and flame resistance is divided into three parts. 1) Char formation, occurred through crosslinking reaction, will reduce the amount of volatile combustible pyrolysis fragment. 2) Char, which acts as an insulator, separates the polymer from heat of the flame. 3) A charred surface obstructs the outward flow of combustible gases generated from the degradation of underlying unburnt materials (Kandola & Horrocks, 1999). These are the physical actions of the char to improve the flame retardancy. Besides, chemical actions have significant effect as well. It can be done by treating textile materials with flame-retardant chemicals which effectively promote the transformation of the polymer backbone to carbonaceous chars (Horrocks et al., 1996). Therefore, char formation has an important correlation with the flammability of polymer.

2.3.3. Mechanism of flame retardancy

The concept of flame-retardant is to disrupt the combustion cycle for textile substance by altering the mechanism of pyrolysis and combustion physically and chemically. There are several approaches to achieve flame-retardant effect. For example, i) by applying an insulating layer on the fibre that can insulate the fibre from applied heat and oxygen, ii) by producing fuel-poor pyrolytic paths by additives, iii) by forming internal barrier to prevent from evolution of combustible gases, iv) by evolving inert gas to dilute fuel formed in pyrolysis, and v) by dissipation of heat away from flame (Horrocks, 1986; Lewin & Edward, 2001; Schindler & Hauser, 2004). With respect to chemical actions of flame-retardant system, the gas-phase and the condensed-phase proposals have been generally considered as the primary effective mechanism of flame retardancy (Lewin et al., 2001; Schindler & Hauser, 2004).

2.3.3.1. Physical action

Flame-retardant system by physical action can be achieved through cooling, formation of a protective layer, or fuel dilution. Heat sink can be provided on or in the fibre by use of materials such as calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$) and tri-hydrated alumina ($Al_2O_3 \cdot 3H_2O$) that thermally decompose through strongly endothermic reaction. It induces the decrease in temperature by heat consumption so that the fibre cannot reach the pyrolysis temperature and will not combust (Laoutid et al., 2009; Schindler & Hauser, 2004). Moreover, the non-flammable gases such as water vapour, carbon dioxide released during thermal decomposition of those materials diffuse and mix with the oxygen present around the fibre. This helps dilute the fuel and protect it from further combustion.

In addition, some flame-retardant additives such as boric acid and its hydrated salts can lead to the formation of insulating layer around the fibre at the temperature below pyrolysis temperature. The protective layer hinders the transfer of heat, combustible volatile gases and oxygen. The fuel gases are separated from oxygen physically that helps inhibition of combustion (Laoutid et al., 2009; Schindler & Hauser, 2004).

2.3.3.2. Chemical action

For the gas-phase mechanism, the amount of combustible matters remains unchanged but the heat generated in the combustion is lowered with the increase in the amount of flame-retardant agent. There is smaller amount of heat returned to the surface of polymer so that the effect of heat is diminished. Therefore, the pyrolysis is retarded or halted because of the decrease in surface temperature. In order to slow down or stop the combustion, it can be achieved by altering the chain branching reactions (1) and (2) shown in Figure 2-12. Halogen-containing compounds are considered to operate via the gas-phase mechanism. The introduction of halogen-containing compounds yield hydrogen halides that form relatively long lived, less reactive free radicals during combustion shown in Figure 2-13. It can see that hydrogen halides are the actual flame inhibitor altering and competing with the chain branching reactions (1) and (2). Meanwhile, the reactions reduce the heat released effectively and decrease the oxygen content by gas dilution (Lewin et al., 2001; Schindler & Hauser, 2004).

$$\mathrm{MX} \rightleftharpoons \mathrm{M}\bullet + \mathrm{X}\bullet \quad \ldots(4)$$

$$\mathrm{MX} \rightleftharpoons \mathrm{HX} + \mathrm{M}\bullet \quad \ldots(5)$$

$$\mathrm{H}\bullet + \mathrm{HX} \rightleftharpoons \mathrm{H_2} + \mathrm{X}\bullet \quad \ldots(6)$$

$$\mathrm{OH}\bullet + \mathrm{HX} \rightleftharpoons \mathrm{H_2O} + \mathrm{X}\bullet \quad \ldots(7)$$

Figure 2-13. Competing free radical reactions during combustion of halogen containing compound

Apart from gas-phase mechanism, the condensed phase mechanism is another mechanism of flame retardancy. It occurs through the chemical interaction between flame-retardant agent and the polymer. The flame-retardant agent alters the pyrolytic path of the substrate and produces less flammable volatiles by favouring the formation of carbonaceous chars and water and reducing volatile gases usually associated with pyrolysis. The heat released in the combustion will be lowered with an increase in the amount of flame-retardant. This interaction usually occurs at the temperatures lower than those of the pyrolytic decomposition. There are two principal modes of the interaction which are dehydration and cross-linking (Lewin et al., 2001; Schindler & Hauser, 2004). For example, phosphorous-containing flame-retardants operate via the condensed-phase mechanism and are usually applied on cotton cellulose. At the high temperature, the phosphorus-containing compounds break down to phosphoric acids or anhydrides. On one hand, esterification firstly occurs and the phosphorus esters then catalyses the dehydration in order to prevent the formation of levoglucosan. On the other hand, phosphoric acid is able to crosslink with the hydroxyl groups on the cellulose. This alters the pyrolysis to generate less flammable by-products. Water is formed during the reaction (Gaan & Sun, 2007a; Gaan & Sun, 2007b; Lecoeur et al., 2001; Lewin et al., 2001; Schindler & Hauser, 2004). Therefore, the flame-retardant effect via condensed-phase mechanism results the formation of water vapour, reduction in fuel and the protective effect of char.

2.3.4. Classification of flame-retardant agent

There are many kinds of flame-retardant additives such as mineral, halogenated, phosphorus-based, nitrogen-based, silicon-based flame-retardants and nanometric particles (Laoutid et al., 2009). Each type of flame-retardant agent has different mechanism to attain flame-retardant properties. Thus, there are some various ways in the classification of flame-retardant agents. They can be classified by their mode of action in disrupting the combustion process, by the chemical nature of the flame-retardants agent, by durability of the flame-retardant finishing. In this section, the flame-retardant agents and their flame retardancy effects are classified as non-durable, semi-durable and wash durable, based on the durability of the flame-retardant finishing (Hicklin et al., 2009; Ozcan et al., 2006; Perenich, 1994).

2.3.4.1. Non-durable flame-retardant for cellulose

Non-durable flame-retardants are the chemicals that is possible to be removed from the textile by wet processing such as washing and water soaking but usually resist dry cleaning with non-aqueous solvents. As they only provide a temporary protection for the textiles, they are mainly applied on the disposable non-woven goods and cotton mats (Hicklin et al., 2009; Weil & Levchik, 2008; Yang, 2013). Inorganic salts have long been known to provide non-durable flame-retardant treatment for over 200 years. Borax and ammonium salts are firstly proposed as a non-durable flame-retardant in 1820s (Schindler & Hauser, 2004; Shafizadeh & Bradbury, 1979; Yang, 2013). These kinds of compounds are still being used nowadays on cotton cellulose. Borax mixes with boric acid can produce a layer of foam on the top of cotton cellulose acting as a barrier between the flame and the materials (Schindler & Hauser, 2004; Yang, 2013). For the ammonium salts, common examples include ammonium sulphamate, diammonium phosphate and ammonium bromide. The first two examples function as condensed phase flame-retardants. They decompose and release strong acids upon heating to catalyse formation of crosslink and the dehydrating of cellulose to promote the char formation (Schindler & Hauser, 2004; Weil & Levchik, 2008; Yang, 2013). Conversely, ammonium bromide functions as a gas-phase flame-retardant. It decomposes to form hydrogen bromide when being heated. Hydrogen bromide is a component that can interfere the branch chaining reactions to attain flame-retardant property. Ammonium bromide sometimes combines with ammonium phosphates to enhance the flame-retardant effects (Hicklin et al., 2009; Weil & Levchik, 2008). Apart from ammonium bromide, ammonium chloride is another alternative. Although flame-retardants containing bromine are usually more effective, chlorinated flame-retardants are sometime preferred depending upon the cost and other requirements (Mostashari & Mostashari, 2005a).

In addition, there are some other types of non-durable flame-retardants. Diguanidine hydrogen phosphate (DGHP) or monoguanidine dihydrogen phosphate (MGHP) are two inexpensive alternative non-durable flame-retardants for cotton. It can be applied on cotton fabrics individually or in combination with a resin (melamine) or with 3-amino propylethoxysilane (APS) (Vroman et al., 2004). More recently, zinc carbonate hydroxide ($ZnCO_3 \cdot Zn(OH)_2$) formed on cotton fabrics is able to give flame-retardant property to cotton (Mostashari & Zanjanchi, 2005b).

2.3.4.2. Semi-durable flame-retardant for cellulose

Semi-durable flame-retardants are those which can withstand soaking or wetting with water, but do not give consistent durability to repeat washes carried out according to a recognized standard. (Hicklin et al., 2009; Weil & Levchik, 2008). It can be applied on the substrate that will not be frequently washed such as carpets, mattress and drapes (Garba, 1999). Some insoluble salts such as phosphates or borates as well as high degree of polymerization of polyphosphate ions are classified as semi-durable flame-retardant (Kandola et al., 1996; Yang, 2013). Insoluble salts can be applied by the double bath technique where the material is first impregnated with a soluble salt of the flame-retardant chemical in one bath and then transferred to another bath containing a precipitant (Garba, 1999).

Another version of semi-durable treatments is one that reacts onto the cellulosic fabric but lose activity by ion-exchange with alkaline detergents or hard water (Weil & Levchik, 2008). Heating cellulose with phosphoric acid or ammonium phosphates will produce a cellulose phosphate by phosphorylation which has long been known (Isaacs et al., 1974; Weil & Levchik, 2008; Yang, 2013; Zeronian et al., 1980). As cellulose phosphate can hydrolyse under alkaline conditions, phosphoric acid is a semi-durable flame-retardant (Yang, 2013). However, the cotton fabrics treated by such a system will lose tear strength and be yellowing. The problem can be improved by adding urea. After adding urea, the phosphorylation proceeds more gently and tolerably useful flame-retarded cotton fabric can be obtained. When dicyandiamide is used as the co-reactant, there is even less damage or discoloration (Weil & Levchik, 2008; Yang, 2013).

Moreover, aluminium hydroxyphosphate (AHP) is recently studied as a semi-durable flame-retardant. AHP is formed in situ on cotton by the reaction between aluminium sulphate and sodium phosphates which is effective in reducing the flammability. The flammability of treated fabrics is retained after one home laundering cycle. However, the treated fabric become more flammable after combination of one dry-cleaning and one home laundering cycle (Wu & Yang, 2008; Yang, 2013).

2.3.4.3. Durable flame-retardant for cellulose

Durable flame-retardant products have a reasonable laundering durability for apparel use. They can be resistant to a multiple machine washes. Normally, durable flame-retardants are those that can withstand 50 or more laundry cycles. It is majorly applied to workwear, children's sleepwear and bedding (Hicklin et al., 2009; Kandola et al., 1996; Schindler & Hauser, 2004). Nowadays, phosphorous- and nitrogen- containing compounds are the most successful durable flame-retardant agents for cellulose (Schindler & Hauser, 2004). They can react with cellulose to form crosslinked structure with the fibre. Phosphorus compounds strongly affect the pyrolysis process and char formation disrupting the combustion cycle. In combination of nitrogen with phosphorus and halogens has a synergistic effect (Kaur et al., 1986; Tesoro et al., 1969).

Organophosphrous-based compounds are the common chemicals for durable flame-retardant treatment. One of the most important flame-retardant agent is tetrakis(hydroxymethyl)phosphonium chloride (THPC) which has been used since the early 1950s (Hamalainen et al., 1956; Horrocks et al., 1986; Kandola et al., 1996; Reeves et al., 1970; Reid et al., 1956; Weil & Levchik, 1980; Whewell, 1970). In Figure 2-14, THPC, which is a water-soluble stable compound, is prepared from phosphine and formaldehyde in the presence of hydrochloric acid. THPC reacts with urea to form an insoluble structure on cellulose by pad-dry-cure process.

$$\underset{\text{Phosphine}}{PH_3} + \underset{\text{Formaldehyde}}{CH_2O} + HCl \rightleftharpoons \underset{\text{THPC}}{Cl^-P^+(CH_2OH)_4}$$

Figure 2-14. The chemical equation of formation of THPC from phosphine and formaldehyde

Applying 25% THPC and 15% urea resulting in 3.5%-4% final phosphorous add-on is adequate for most fabrics. However, using THPC as flame-retardant finishing agent has some drawbacks. There is formaldehyde released during processing. Moreover, the resultant fabric becomes stiff and the tensile and tear strength are impaired. Therefore, suitable softeners and mechanical finishing techniques are used to produce a commercially acceptable product (Horrocks, 2003; Schindler & Hauser, 2004). Moreover, Proban process is developed to produce finishes with less stiffness and fibre damage (Cole, 1978). The THPC/urea pre-condensate is prepared by the reaction between THPC and then the pre-condensate is padded onto the fabric. The treated cotton fabric is dried and then exposed to ammonia vapours in a special ‘ammonization chamber’ forming a cross-linked polymeric network. Finally, the cotton fabric is finally treated by hydrogen peroxide (H_2O_2) to oxidize the poly(phosphine) to poly(phosphine oxide) for higher stability. The oxidation state of phosphorus is changed from +3 to +5. Proban process, on one hand, gives a more durable flame retardancy that can withstand up to 100 industrial laundering cycles with alkaline detergent due to the absence of hydrolysable links adjacent to phosphorus. One the other hand, a fairly soft hand, good stress-relieving flexibility of the yarn as well as tear strength is maintained due to little damage to cellulose during the treatment (Hicklin et al., 2009; Schindler & Hauser, 2004; Weil & Levchik, 2008; Yang, 2013).

Another popular flame-retardant finishing agent is Pyrovatex CP which is a trade name of N-Methylol dimethylphosphonopropionamide (MDPA) and its structure is shown in Figure 2-15. The application of MDPA has been studied since 1960s (Aenishänslin et al, 1969). MDPA is prepared from the reaction between dimethylphosphite and acrylamide. MDPA is a stable and water-soluble product and sometime contains formaldehyde and odorous volatile impurities. It functions as a condensed phase flame-retardant agent to promote char formation and produce less flammable gases (Weil & Levchik, 2008; Yang, 2013).

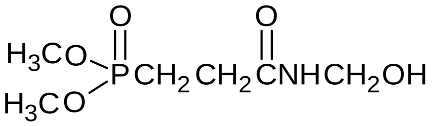


Figure 2-15. The chemical structure of N-Methylol dimethylphosphonopropionamide

MDPA has a methylol group which is able to react with cotton cellulose directly to form linkage under acid-catalysed conditions. It is usually applied together with methylolated melamine resin such as TMM. The presence of TMM not only increases the bonding of MDPA to cotton but also increases the nitrogen content of the product for synergistic effect with phosphorus (Kaur et al., 1986; Kandola et al., 1996; Tesoro et al., 1969; Yang, 2013). The reaction is catalysed by phosphorus acid. Figure 2-16 shows how MDPA and TMM react with cellulose to form crosslink.

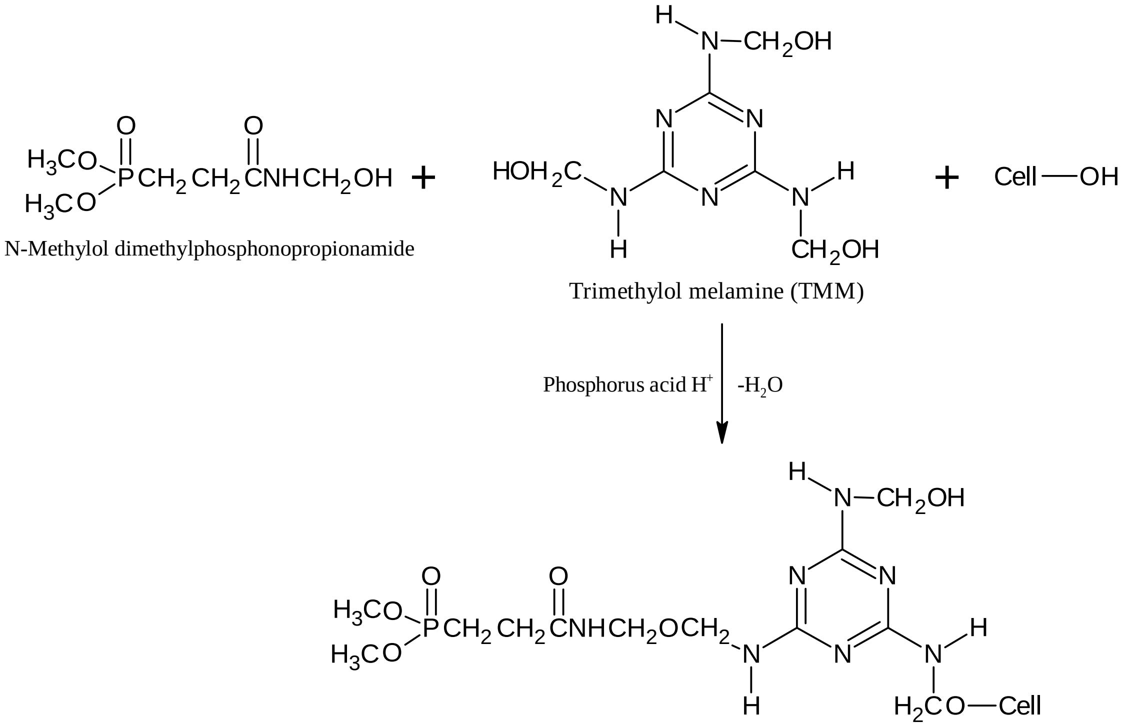


Figure 2-16. Chemistry of the Pyrovatex CP system

However, Pyrovatex CP also has some disadvantages. All residual phosphorus acid catalyst, uncrosslinked phosphonamide and surface crosslinked polymer in the reaction are required to be neutralized and removed by Na_2CO_3 at 40 – 45°C after curing process and washed by warm water afterwards. Otherwise, the remaining acid will cause acid-catalysed depolymerisation of cotton cellulose weakening the fabric strength. This process leads to higher production cost (Schindler & Hauser, 2004; Weil & Levchik, 2008; Yang, 2013). In addition, the treated fabrics suffer from tensile and tear strength loss. Suitable softeners are added to improve the fabric quality. Besides, similar to the process using THPC, gaseous formaldehyde may release during the curing process causing unpleasant smell. Edmunds et al. suggested that an optimized recipe for the finishing could reduce the emission level of formaldehyde (Edmonds & Horrocks, 1997; Horrocks, 2003).

2.3.5. Application and Evaluation of flame-retardant finishing

There are many techniques for imparting durable fire retardant properties to fabrics described in the literature such as pad-dry-cure, exhaust, spray-dry-cure and coat-dry cure (Kandola et al., 1996; Wakelyn & Rearick, 1998). The most common one being used is the pad-dry-cure method. However, using this method may result in poor mechanical strength, moisture regain and fabric stiffness (Siriviriyanun et al., 2008a; Siriviriyanun et al., 2008b). In addition, the thermal curing process of finishing often associates with the problems of energy cost, thermal inertia, inefficiency of conventional ovens, possible release of formaldehyde and acid-catalysed tendering (Horrocks, 1986). Therefore, a suitable recipe to minimize the above problems is essential.

There are five main types of testing method for the major fire properties which are ignitability tests, flame spread tests, limiting oxygen index, heat release tests, and smoke tests (Lu & Hamerton, 2002). The main ignitability tests include vertical and 45^o flammability of the fabrics. The sample is exposed to the standard butane flame with designated time according to different international test standards. The burning time and the char characteristic can be obtained after the test (Schindler & Hauser, 2004). For the limiting oxygen index, it is used to measure the minimum oxygen concentration required to support candle-like downward flame combustion in a flowing mixture of oxygen and nitrogen. (Lu & Hamerton, 2002; McCrum et al., 1997). ASTM D2863 is one of typical international standards. The sample is positioned vertically in a transparent test column and the gases flow upward. The sample is ignited at the top and the oxygen concentration is adjusted until the sample just supports combustion. Besides, thermogravimetric (TG) analysis can be done under either air or nitrogen atmosphere in order to study the char formation and the pyrolysis process.

2.4. Catalyst for Chemical Finishing

2.4.1. Significance of Catalyst in Functional Finishing

Catalyst has been used industrially for a long time. In 1746, catalyst is used in the manufacture of lead chamber sulphuric acid by John Roebuck (Leach, 1983; Lloyd, 2011). Catalysts are essential and play an important role in the chemical industry and industrial research nowadays. They are widely used and applied in different chemical processes (Salem, 2003). There are many famous processes involving catalyst. For example, in food industry, using nickel as catalyst in hydrogenation of fat is one of common applications for the processing of vegetable oils (Wells, 2001). Besides, Haber process, which syntheses of ammonia form nitrogen and hydrogen in the presence of finely divided iron as catalyst, is another famous example (Veldsink et al., 1997). Catalyst provides an alternative pathway with low activation energy for the reaction and is not consumed during the reaction (Leach, 1983). Catalyst will temporarily change in molecular structure, giving a site for substrate. After the reaction, it will be restored to its original structure (Wells, 2001). Catalyst is undoubtedly a re-generable resource because of its characteristic. It is an environmentally and economically friendly substance that helps us a lot in daily applications. The Figure 2-17 is a potential energy diagram of a hypothetical exothermic reaction. It shows that the activation energy is lower for the reaction with catalyst compared to that of without catalyst.

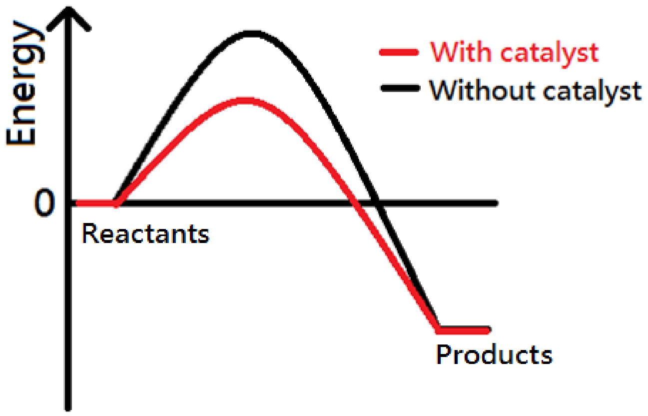


Figure 2-17. Energy diagram showing the effect of catalyst

in a hypothetical exothermic chemical reaction

There are two types of catalysis which are homogeneous catalysis and heterogeneous catalysis. The catalyst is in the same phase as one or more the reactants that is called homogeneous catalysis. And heterogeneous catalysis means that the number of phase present increases in the presence of catalyst (Atkins & Paula, 2006; Wells, 2001).

In order to maximize the functions of catalyst, the conditions should be appropriate and suitable. The catalytic reaction depends on some factors such as the nature of reactant, the concentration of reactant, the surface area of reactant and the reaction temperature. The catalytic reaction generally follows Arrhenius equation which indicates that every 10°C increase results in double the rate. Besides, the surface area of reactants is important in heterogeneous catalysis (Atkins & Paula, 2006; Schindler & Hauser, 2004). The greater the surface area, the higher is the rate of reaction due to greater contact between individual particles. Therefore, nanotechnology becomes more and more popular these years. Nanoparticles are the particles that have at least one dimension with 100 nm or less. Nanoparticles can have a larger surface area and attractive force between nanoparticles and the substrate compared to ordinary particles (Karst & Yang, 2006).

2.4.2. Conventional catalyst for functional finishing

Application of catalyst is also common in textile finishing processes. For example, magnesium chloride or zinc nitrate is used as an acid catalyst generating acidic condition for the reaction of N-methylol reactants such as DMDHEU (Rippon & Evans, 2012; Schindler & Hauser, 2004; Sharpe & Mallinson, 2003). This metal-based catalyst is also called Lewis acid catalyst which acts as an electron pair acceptor. The following equation shows metal ions draws in lone pairs from oxygen.

$$M^{2+} + 2\ H_2O \rightleftharpoons M(OH)_2 + 2\ H^+$$

Although Lewis acid catalyst can provide hydrogen ions for reaction, citric acid or acetic acid is often added to boost the reaction. With appropriate acid catalyst and reaction conditions providing enough activation energy, the reaction occurs. The reaction mechanism of N-methylol compound with cellulose catalyzed by Lewis acid catalyst is shown in Figure 2-18 (Rippon & Evans, 2012; Schindler & Hauser, 2004). Nitrogen protonation or oxygen protonation occurs because of high electronegativity properties. The hydrogen ions from Lewis acid catalyst or organic acid attach on oxygen atom or nitrogen atom. Nitrogen protonation is an undesirable pathway for the reaction due to the generation of amine and formaldehyde. Urea-formaldehyde and melamine-formaldehyde have a higher chance for nitrogen protonation so that there are large amount of formaldehyde released after curing process. However, DMDHEU product favours oxygen protonation owing to steric hindrances from the ethylene bridge interfering with nitrogen protonation. Carbonium ion is formed through oxygen protonation and elimination of water. The carbonium ion is stabilized by resonance with their immonium forms. Finally, the cellulose reacts with the carbonium ion to form crosslinked cellulose. The hydrogen ions are restored. Therefore, catalyst plays an important role for initiation of the reaction.

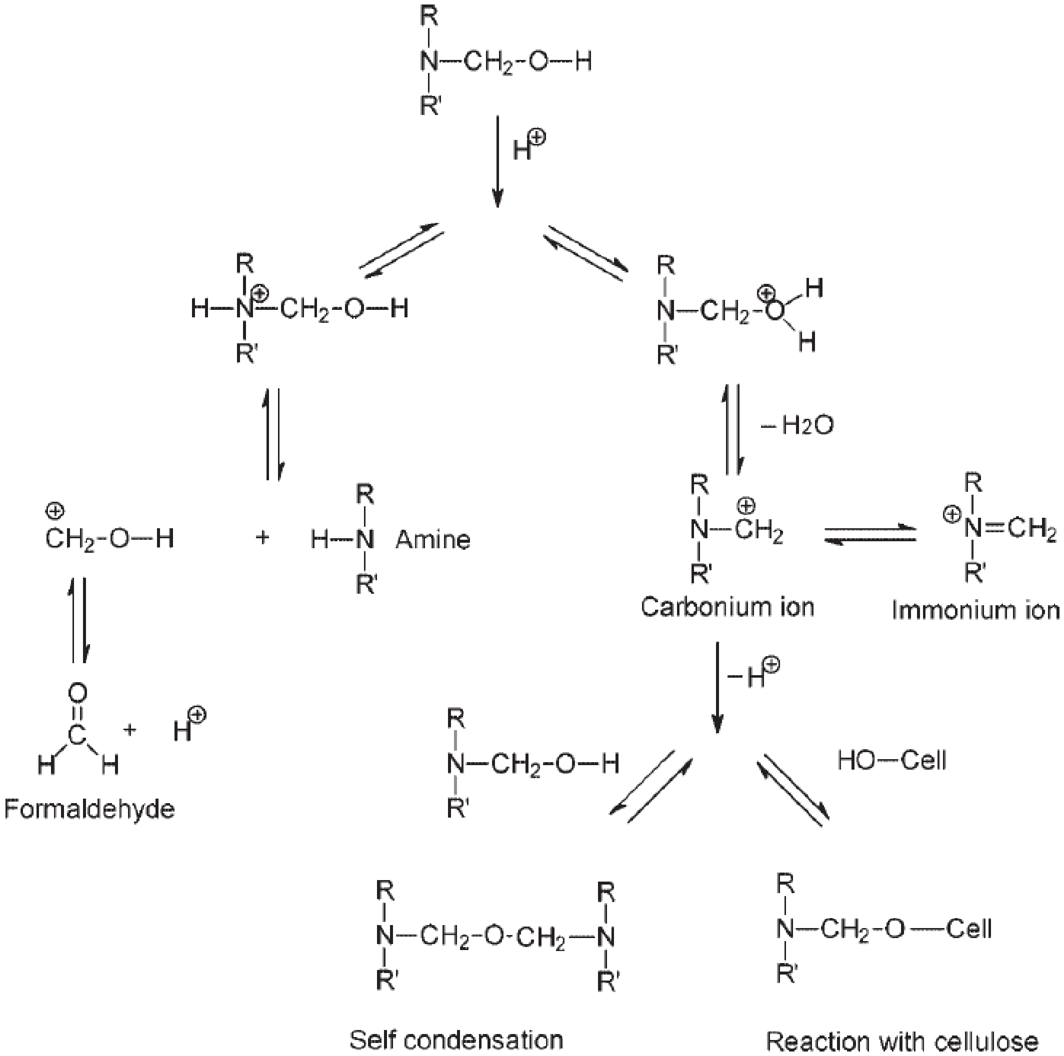


Figure 2-18. Reaction mechanism of N-methylol compunds initiated by Lewis acid catalyst

Source: W.D. Schindler & P.J. Hauser, Chemical finishing of textiles., Woodhead Publinshing Ltd & CRC Press, 2004

In addition to use single catalyst, there are some studies showing that using mixed catalyst system for producing and improving durable press cotton (Chen, 1989; Kullman et al., 1971; Pandey & Raje, 1985; Pandey & Raje, 1987; Reeves & Salleh, 1984). Mixed catalysts composed of magnesium chloride and an organic acid have been used commercially in the production of durable press cotton (Reeves & Salleh, 1984). Pierce & Frick has demonstrated the advantages of using highly active catalysts which are the mixtures of magnesium chloride and an alkoxy or hydroxy-substituted carboxylic acid (Pierce & Frick, 1968; Pierce et al., 1970). Moreover, in the combination of mixed catalyst containing aluminium dichlorhydroxide with magnesium chloride, low energy consumption, low formaldehyde release and high durable press properties can be obtained (Reeves & Salleh, 1984). There are some other catalyst combinations such as hydrated aluminium sulphate with citric acid, glycolic acid or tartaric acid. These combinations show positive effectives to durable press finishing. Therefore, there is still room for improvement of wrinkling resistant finishing in coupling with different catalysts.

Apart from applying catalyst in the wrinkle-resistant finishing, catalyst is also essential for carrying out flame-retardant finishing. For the Pyrovatex CP system, phosphoric acid is commonly used as effective catalyst to initiate the crosslinking reaction (Horrocks, 2003; Schindler & Hauser, 2004). Phosphoric acid facilitates the dehydration process. If another flame-retardant finishing system for cotton based on a hydroxy-functional organophosphorus oligomer (HFPO) is used, NH_4Cl-based catalyst is the optimum catalyst for the HFPO system (Wu & Yang, 2008). Moreover, Cheng & Yang studied the flammability of cotton fleece using the phosphorus-containing maleic acid oligomers (PMAO) with SHP as the catalyst. They found that PMAO can be bound to cotton fleece by esterifying with cotton cellulose in the presence of SHP and reduces the fabric flammability (Cheng & Yang, 2009; Lessan et al., 2011). Therefore, a right catalyst functions well in specific system and is essential.

2.4.3. Catalytic reaction of metal oxide for functional finishing

Recently, many studies proposed that metal oxides such as (nano-) titanium (IV) oxide (TiO_2) or zinc oxide (ZnO) could be used as a heterogeneous catalyst or co-catalyst for the functional finishing (Lam et al., 2010a; Lam et al., 2010b; Lam et al., 2011a; Lam et al., 2011b; Wang & Chen, 2005; Yuen et al., 2007). According to those studies, using the new mixed catalyst system shows that the finishing performance was enhanced and the side effects were minimized. Using metal oxides as a catalyst can give some additional properties for the fabrics. For example, TiO_2 and ZnO have been used separately as flame-retardant agents to impart flame retardancy to cellulosic fabrics. (Fallah et al., 2011a; Fallah et al., 2011b). This shows that metal oxides have additional positive effects on flame-retardant properties. The inclusion of TiO_2 and ZnO in the system can improve mechanical strength and UV-absorption (Lam et al., 2012; Yadav et al., 2006).

Since metal oxides are not soluble in the finishing agents, they act as heterogeneous catalyst. Reaction mechanisms of heterogeneous catalysis involve three steps which are adsorption, reaction and desorption. In the adsorption process, the catalyst provides a surface for the reactants or substrates adsorption. There are two types of adsorption which are physical adsorption and chemical adsorption. For physical adsorption, weakly bound state, reactant is attracted to the surface of a solid catalyst by van der Waals' forces. In contrary, strongly bound state is called chemical adsorption. It is sub-divided into associative adsorption and dissociative adsorption. Associative adsorption means the species stay intact when absorbed whereas dissociative adsorption involves some degree of molecular dissociation (Atkins & Paula, 2006).

M.A. Henderson suggested that titanium (IV) oxide is in favour of dissociative adsorption as $\Delta G < 0$ (Henderson, 2002). The Ti-sites of TiO_2 act as Lewis acids site which can employ an electron lone pair from another molecule in completing the stable group of one of its own atoms. Therefore, in aqueous solution, Ti draws in lone pair electron from oxygen atom of water molecule to satisfy electron demand (Diebold, 2003; Guo et al., 2012; Henderson, 2002; Schaub et al., 2001). Powdered TiO_2 has large surface area so that there are large numbers of active sites. This can achieve an acceptable reaction rates. Because of the dissociative adsorption properties of TiO_2, TiO_2 might assist the catalytic reaction with different finishing agents in functional finishing treatment.

2.5. Development of functional finishing in textile industry

2.5.1. Future trends in functional finishing

The historical and current development and application of wrinkle-resistant finishing and flame-retardant finishing has been discussed in the previous section. As discussed in earlier section 2.1.2, there are several essential factors required in consideration in order to have an optimized formulation for functional finishing. Therefore, in the future development and application of functional finishing, it should focus on three main aspects which are technical, economic and ecological trend (Schindler & Hauser, 2004).

2.5.2. Cost and efficiency

In the commercial application, the most important trend in functional finishing is about the cost and efficiency (Schindler & Hauser, 2004). It is better to minimize the cost for the finishing processes and final products by proper modification and maximize the quality of fabrics produced by improving the fabric properties and reducing the undesirable side effects. The functional finishing can be modified by adding different kinds of chemicals and catalysts to achieve the objectives. In addition, according to Purcell, energy is equal to materials and vice versa. Purcell proposed some strategies for energy saving. Energy can be saved by i) using fewer products; ii) developing more durable and reusable product; iii) using more energy-efficient products; iv) substituting energy-intensive materials; and v) recycle waste products (Kim et al., 1983).

2.5.3. Reduction of undesirable effects and easier application

Every kind of finishing has disadvantages and generates some problems such as the release of formaldehyde or reduction in mechanical strength of fabric. The manufacturers make great effort to minimize the undesirable effects. For example, the loss of strength associated with the crosslinking of cellulose during wrinkle-resistant finishing. The loss of strength can be minimized and improved by using new continuous damp crosslinking process with controlled humidity instead of traditional dry crosslinking process (Schindler & Hauser, 2004). As discussed before, the release of formaldehyde can be minimized by addition of metal oxides as co-catalyst. Development a new catalyst system of medication of functional finishing process can result in a reduction of undesirable effects.

For the easier application, it can be achieved by i) cost reduction through shorter production times and less complicated machinery; ii) less energy and water consumption; iii) easier or less costly process control and automation; and iv) fewer possibilities to make mistakes and less skilled personnel (Schindler & Hauser, 2004).

2.5.4. Better Ecology

Nowadays, there is increasing number of people aware of the environmental problem in the textile industry. A better ecological and economical functional finishing is going to be developed and studied in the future. Textile production, textile use and their disposal are three sectors of ecological importance to textiles. Not many of chemicals used in textile production and processing are highly toxic (Connell, 1995). However, some chemicals such as flame-retardant chemicals and surfactants cause some harmful effects to the marine environment (Connell, 1995; Gutenmann & Lisk, 1975). Phosphorous compounds present in waste water lead to various environmental problems. Besides, large amount of thermal is consumed during textile production. Therefore, ecological improvements are reached by using more careful synthetic routes to finishing products and by less energy consumption (Schindler & Hauser, 2004). Secondly, from the aspect of textile use, the finished textiles especially those in contact with human skin are controlled by strict regulations. For example, the concentration of free formaldehyde and the chemicals containing antimony and halogen is limited. Thirdly, from the aspect of textile disposal, the best solution for the used textiles and the textile waste is recycling (Schindler & Hauser, 2004). Moreover, for the waste generated from functional finishing, a proper treatment to the effluent is required and this can reduce the damage to the environment (Connell, 1995).

2.6. Conclusion

Cotton is an essential natural textile fibre and plays an important role in our daily life because of its various usages. Despite numerous advantages of cotton cellulose, there are two defects of cotton cellulose fabrics which are easily wrinkling after being washed or immersed in water and sensitive to fire causing fatalities. Therefore, wrinkle-resistant finishing and flame-retardant finishing is applied on the cotton cellulose to solve the above problems. They are done by addition of particular chemicals on the cotton cellulose to attain targeted fabric properties. For these two existing finishes, the fabrics generally suffer from the release of formaldehyde, mechanical strength loss and abrasion resistance loss. In order to minimize the adverse effects of the treated fabrics, proper formulations and finishing treatment are needed. Meanwhile, the finishing treatment should not cause any skin irritation, sensitising and allergic problems. Moreover, in order to attain a better environmental process, an appropriate heat treatment is controlled. What is more, additional substances such as metal oxides in finishing process are used as co-catalyst to enhance the performance of chemical finishing and obtain more desirable fabrics. In short, the details of wrinkle-resistant and flame-retardant treatment have been deeply reviewed. Moreover, catalysts are essential in the textile chemical finishing.

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Chapter 3: Experimental Details

3.1. Introduction

This chapter introduces the experimental details including materials, apparatus, test methods and experimental procedures.

3.2. Materials

3.2.1. Cotton specimens

100% semi-bleached plain weave cotton fabric purchased from Lai Tak Enterprise Limited (67 ends/cm, yarn count 34 tex, in warp; 55 picks/cm, yarn count 40 tex, in weft; fabric weight 169 g/m^2) was used for wrinkle-resistant finishing.

100% semi-bleached plain woven cotton fabric purchased from Lai Tak Enterprise Limited (14 ends/cm, yarn count 74 tex, in warp; 14 picks/inch, yarn count 93 tex, in weft; fabric weight 226 g/m^2) was used for flame-retardant finishing.

3.2.1.1. Pre-treatment of the specimens

The fabrics were cut into a size of 30 x 30 cm^2 for the finishing treatment. Before finishing, they were soaked with 30% acetone (ACS grade, supplied by VWR International S.A.S) for 10 minutes in order to remove the oily particles and organic substances attached on the fabrics. The fabrics were then immersed in deionized water for 5 minutes washing excess acetone. The cleaned fabrics were dehydrated by using the Nyborg C290R Hydro-extractor (HERKA CmbH & Co.) for 2 minutes. Finally, the fabrics were dried in a Nyborg T4350 tumble dryer (HERKA GmbH & Co.) at about 60°C for 15 minutes. After preparation, the fabrics were conditioned at temperature of 21±1°C and relative humidity of

65±5% for 24 hours before carrying out any treatment.

3.2.2. Metal oxides used

Titanium dioxide and zinc oxide were two metal oxides used as catalyst or co-catalyst in the study. Titanium dioxide (effective diameter = 444 nm) supplied by Accuchem with purity ≥99.8% was employed while zinc oxide (effective diameter = 1036 nm) was supplied by Sigma-Aldrich with purity of ≥99.0%.

3.2.2.1. Particle size analyzer

The particle size of the metal oxides was measured by the Brookhaven ZetaPlus zeta potential/particle size analyser manufactured by BrookHaven Instrument Corp. It measures particle size distributions by dynamic light scattering. The metal oxides were firstly dispersed in distilled water and filled into a cell. The particle size information can be obtained within a minutes.

3.3. Functional finishing

3.3.1. Wrinkle-resistant finishing

3.3.1.1. Apparatus and chemical

Modified DMDHEU containing magnesium chloride as catalyst was served as the crosslinking agent supplied by DyStar Limited. TiO_2 and ZnO were used as catalyst or co-catalyst. Tween 80, a non-ionic dispersing agent was supplied by Shanghai Lingfeng chemical reagent co. Ltd. All other chemicals used in the study were reagent grade.

The padding process was performed using the Rapid padding machine manufactured by the Labortex Co. Ltd. The speed of the roll was set 10 rpm and the pressure of 1.2 kg/cm^2. The fabrics were padded twice until 75-80% wet pick up.

The drying process was performed in Universal Thermal Oven manufactured by the Memmert GmbH & Co. and the curing process was performed by using Mathis LabDryer curing machine manufactured by the Werner Mathis AG.

3.3.1.2. Experimental Details

One bath pad-dry-cure method was used in carrying out the finishing process. The fabrics were impregnated and padded with the prepared wrinkle-resistant finishing solution until 75-80% wet pick up at room conditions. Then, the samples were dried in oven at 85 °C for 5 minutes followed by curing at four different curing temperatures which were 110 °C, 130 °C, 150 °C and 170 °C for 1, 2 or 3 minutes. There were totally 12 combinations of various curing temperatures and times. Finally, the specimens were conditioned at the temperature of 21±1 °C and relative humidity of 65±5% for 24 hours before performing any tests. The composition of the wrinkle-resistant finishing solutions used for treatments was listed in Table 3-1.

Table 3-1. The composition of the wrinkle-resistant finishing solution

SOLUTION	**DMDHEU**	**Acetic acid**	**TiO_2**	**ZnO**
A	5%	0.1%	0	--
B	5%	0.1%	0.1%	--
C	5%	0.1%	0.2%	--
E	5%	0.1%	0.05%	0.05%
F	5%	0.1%	0.1%	0.1%

Remarks: The reagents were dissolved in 100ml distilled water on weight of volume.

Remarks: TiO_2 and ZnO was dispersed in non-ionic dispersing agent.

3.3.2. Flame-retardant finishing

3.3.2.1. Apparatus and chemical

Pyrovatex CP NEW (FR), which is an organic phosphorus compound and a durable flame-retardant agent, was used in the treatment. A cellulose crosslinking agent used, Knittex CHN (CL), is a melamine resin. Both were provided by Huntsman Limited. Catalyst, 85% phosphoric acid supplied by Sigma-Aldrich Co., was added. Titanium dioxide was served as co-catalyst. Sodium carbonate used for neutralization was supplied by Sigma-Aldrich.

The padding process was performed using the Rapid padding machine manufactured by the Labortex Co. Ltd. The speed of the roll was set 10 rpm and the pressure of 3 kg/cm^2. The fabrics were padded twice until 75-80% wet pick up. The drying process was performed in Universal Thermal Oven manufactured by the Memmert GmbH & Co. and the curing process was performed using Mathis LabDryer curing machine manufactured by the Werner Mathis AG.

3.3.2.2. Experimental Details

One bath pad-dry-cure method was used in carrying out the finishing process. The fabrics were impregnated and padded with the prepared flame-retardant finishing agents until 75-80% wet pick up at room conditions. Then, the samples were dried in oven at 110°C for 5 minutes followed by curing at four different temperatures which were 110°C, 130°C, 150°C and 170°C for 1, 2 or 3 minutes. Half of samples prepared from each condition have been done further treatments. The sample fabrics were neutralized in 30g/L sodium carbonate at 50°C for 30 minutes. Then, the fabrics were rinsed in running warm water at about 50°C. Finally, the specimens were conditioned at the temperature of 21±1°C and relative humidity of 65±5% for 24 hours before performing any tests. The composition of the flame-retardant finishing solution used for treatment was listed in Table 3-2.

Table 3-2. The composition of the flame-retardant finishing solution

SOLUTION	**Pyrovatex CP NEW**	**Knittex CHN**	**85% PA**	**TiO_2**
Z	40%	5%	2.5%	0
X	40%	5%	2.5%	0.2%
Y	40%	5%	2.5%	0.4%

3.4. Physical and mechanical properties of fabrics

The physical and mechanical properties of fabrics had been assessed by various tests and comprehensively evaluated. These included wrinkle recovery test, Elmendorf tear strength test, whiteness of textile, flammability test, and Kawabata evaluation system for fabrics (KES-F). All fabrics were conditioned at the temperature of 21±1°C and relative humidity of 65±5% for 24 hours before performing any tests.

3.4.1. Wrinkle recovery test

The wrinkle recovery angle (WRA) test was performed according to the guideline of AATCC Test Method 66-2008. The wrinkle recovery angles of the fabrics were measured by the wrinkle recovery tester manufactured by Daiei Kagaku Seiki MFG Co., Ltd. Twelve conditioned specimens, including six warp and six weft directions with size 40 x 15 mm, were folded face-to-face and back-to-back. Then, they were compressed with 500g weight for 5 minutes. Then, the compressed specimens were mounted on the specimen holder for another 5 minutes. After 5 minutes, the specimen was recovered to certain extent and record the recovery angle. The WRAs were averaged by sum of all values taken from warp or weft directions which obtained within 3% tolerance level.

3.4.2. Retention of Creases in Fabrics

The retention of pressed-in creases in fabrics after repeated home laundering was assessed according to the guideline of AATCC Test Method 88C-2006. The treated fabrics were subjected to machine wash with 1993 AATCC Standard Reference Detergent. The normal or cotton sturdy mode is used. After washing and drying, three trained observers rated each test specimen independently with designated lighting and viewing arrangement.

3.4.3. Elmendorf tear strength test

The tear properties of fabrics were assessed by Elmendorf tear strength test following the guideline of BS EN ISO 13937. The Elmatear Digital Tear Tester is manufactured by James H. Heal & Co. Ltd., Halifax England. Standard weight with 1600g was mounted on the tester for the measurement. There were ten specimens, including five warp and five weft directions, cut according to the template shown in the standard. The test specimens were clamped centrally and cut a slit using the knife. Then, the pendulum was released and the readings were record. The average value was calculated from all warp and weft measurements.

3.4.4. Whiteness of textile

The whiteness of textiles was measured in accordance with AATCC Test Method 110-2005 in order to show how white the textile appears to an average viewer. Each sample was measured three times using the spectrophotometer of GretagMacbeth Color-Eye 7000A with C standard illuminant and 10^o observer.

3.4.5. Flammability test

Flammability of fabrics was tested in accordance with Standard 16 CFR Part

1610. The test was performed using a 45^o flammability tester for apparel textiles manufactured by the Govmark Organization Inc. A 16mm standardized butane flame length was applied on the specimens for 4 seconds (instead of 1 second to increase the burning chance of a fabric sample during testing) (Lam et al, 2011a; Lam et al., 2011c). The burning time and the char length was measured and recorded. Five specimens were tested and the average burning time was calculated.

3.4.6. Kawabata evaluation system for fabrics (KES-F)

The Kawabata evaluation system for fabric (KES-F) was used for measuring the low-stress mechanical properties of the fabrics. The system assesses the fabric properties including tensile, shearing, bending, compression and surface properties. The configuration of KES-F comprises four testers which are tensile and shear tester (FB1-A instrument of KES-F), compression tester (FB3-A instrument of KES-F), pure bending tester (FB2 instrument of KES-F) and surface tester (FB4-A instrument of KES-F). The description of the parameters is described in Table 3-3 (Kawabata et al., 2002; Kan & Yuen, 2006; Lam et al., 2011c; Lam et al., 2011d; Sun & Stylios, 2012; Lam et al., 2014). The specimens were examined under the standard environmental conditions such that the temperature was controlled at 21±1ºC and the relative humidity was 65±5%. The results were obtained from averaging the sum of six measurements taken along both warp and weft directions except for compression properties. For the compression properties, only three district points with compressed area is 2 cm^2 were measured automatically by the compression tester. This makes no distinction between warp and weft direction. The analytical tolerance was limited to 5%.

Table 3-3. Characteristic of the parameters in KES-F system

Properties	Symbol	Definition	Characteristic	Unit
Tensile energy	WT	Energy used for extending fabric to 490N/m (WR^1 finishing part) or 1960 N/m (FR^2 finishing part) width	WT reflects the ability of a fabric to withstand external stress during extension. A larger value of WT represents a fabric with good tensile strength and toughness.	N/m
Tensile resilience	RT	Percentage energy recovery from tensile deformation	A low value of RT indicates inelastic behaviour. Hence, the fabric is difficult to restore to its initial shape after removing the applied tensile stress.	%
Extensibility	EMT	Percentage of extension at the maximum applied load of 490N/m (WR^1 finishing part) or 1960 N/m (FR^2 finishing part) specimen width	EMT is proportional to the elongation of a fabric under a specific applied stress. The greater the EMT, the larger the elongation of the fabric will be.	%
Remarks: ➢ The tensile properties are usually affected by fabric composition, fabric structure, yarn twist and yarn count. In general, a fabric with higher WT, RT and EMT has a better tensile strength. ➢ ^{1}: Wrinkle-resistant finishing part; ^{2}: Flame-retardant finishing part As the fabrics used for these two treatment are not the same, the parameters has been changed.				
Shear stiffness	G	Average slope of the linear regions of the shear hysteresis curve to ±2.5^{o} shear angle	G refers to the ability of a fabric to resist shear stress. A large G value represents a stiff and paper-like fabric while low G value represents a soft fabric having better drape.	N/m/deg
Shear stress at 0.5^{o}	2HG	Average width of the shear hysteresis loop at ±0.5^{o} shear angle	2HG is the ability of a fabric to recover after applying the shear stress value of 0.5^{o} shear angle.	N/m
Shear stress at 5^{o}	2HG5	Average width of the shear hysteresis loop at ±5^{o} shear angle	2HG5 The ability of a fabric to recover after applying the shear stress value of 5^{o} shear angle	N/m

Remarks:

- G depends on the mobility of cross yarns at the intersection point which is affected by fabric weave, yarn diameter, and the fabric surface characteristic. Moreover, G of the fabric is also related to yarn interaction. The increase in yarn interaction results in higher G.
- If the shear hysteresis (2HG or 2HG5) has a large value, it indicates inelastic behaviour in shearing such that the recovery ability of fabric is unsatisfactory.

Bending rigidity	B	Average slope of the linear regions of the bending hysteresis curve to 1.5 cm^{-1}	B reflects the ability of a fabric to resist the bending moment. A fabric which is capable of resisting to bending motion has a greater value of B.	10^{-4} Nm/m
Bending moment	2HB	Average width of the bending hysteresis loop at 0.5 cm^{-1} curvature	2HB reflects the recovery ability after bending motion at a range of 2.5 cm^{-1} to -2.5cm^{-1}. The greater value of 2HB, the worse the bending recovery ability of the fabric will be.	10^{-2} N/m

Remarks:

- The bending properties are related to the bending resistance of fibres and yarns. Bending properties impose essential effects on both the hand and tailoring performance of a fabric. A fabric with good bending properties should have a low B and 2HB.
- The friction between fibres and yarns will affect the value of B.

Compressional linearity	LC	Linearity of compression-thickness curve	LC reflects the compressibility along with the change in fabric thickness after treatment. A high value of LC causes a hard feeling in compression such that the fabric has high compressional rigidity.	--
Compressional energy	WC	Energy in compressing fabric under 50 gf/cm^2 or 4900 N/m^2	WC shows fluffy feeling of the fabric. The higher WC value, the more fluffy fabric (higher compressibility) is.	Nm/m^2
Compressional resilience	RC	Percentage energy recovery from lateral compression deformation	RC represents the recoverability of a fabric in the thickness after removal of compressional force. A lower value implies inelastic compression property.	%

Remarks:

- A fabric with high LC, WC and RC acquires good compression properties.
- Compressional properties are usually influenced by fabric thickness.

Appearance thickness	T_o	Fabric thickness at 0.5 gf/cm^2 or 490 N/m^2 pressure	T_o represents the surface thickness of fabrics at the pressure of at 0.5 gf/cm^2 or 490 N/m^{2}pressure.	mm
Intrinsic thickness	T_m	Fabric thickness at 5 gf/cm^2 or 4900 N/m^2 pressure	T_m represents fabric intrinsic thickness of fabrics at the pressure of 5 gf/cm^2 or 4900 N/m^{2}pressure.	mm
Coefficient of friction	MIU	Coefficient of friction between the fabric surface and a standard contactor	MIU shows the fabric smoothness, roughness and crispness which is determined by the friction between two surfaces. A lower MIU value corresponds to smaller friction or resistance.	--
Geometrical roughness	SMD	Variation in surface geometry of the fabric	SMD shows the evenness of a fabric surface. A more even fabric surface results in a lower value of SMD	μm

Remarks:

- A fabric with low values of MIU and SMD corresponds to good fabric surface properties.

3.5. Structural properties of fabrics

The structural properties of fabrics had been assessed by various analytical instruments in order to study the chemical compositions, surface morphology and thermal behaviour of cotton specimens after functional finishing. These include scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray analysis (EDX), and thermogravimetric analysis (TG).

3.5.1. Scanning Electron Microscopy (SEM)

SEM was used to investigate the surface morphology of the cotton specimens before and after treatment. Some of specimens were examined by the JEOL JSM-6490 Scanning Electron Microscope with 20kV accelerating voltage and 10µA current under high magnification. Some of specimens were investigated by a Hitachi TM3000 Tabletop Microscope with 15kV accelerating voltage and 1750 mA filament current under high magnification.

3.5.2. Fourier transform infrared spectroscopy (FTIR)

The chemical compositions of the samples were studied by Fourier transform infrared – attenuated total reflection (FTIR-ATR) spectroscopy. The analysis was done by a PerkinElmer Spectrum 100 FTIR spectrophotometer with scanning range from 4000 cm^{-1} to 650 cm^{-1}. The average number of scan was 8.

3.5.3. Energy dispersive X-ray analysis (EDX)

Energy dispersive X-ray analysis (EDX) was performed by JEOL JSM-6490 Scanning Electron Microscope. It was used to collect the elemental information of cotton species. The microscope is equipped with a cathode and magnetic lenses to create and focus a beam of electrons for elemental analysis. The X-ray energy was converted into voltage signals by a detector. The signals were sent to a pulse processor and then to an analyser for data analysis.

3.5.4. Thermogravimetric analysis (TG)

Thermogravimetric analysis was performed by using Mattler-Toledo thermogravimetric analyser to investigate the thermal behaviour of the samples. 5 mg fabric samples were weighed in an alumina crucible. The analysis was performed under oxygen atmosphere with flow rate 50 ml/min. The temperature range for the analysis was 30 - 800 ºC and the heating rate was 10ºC/minute.

3.6. Conclusion

The physical, structural and mechanical properties of fabrics after functional finishing treatment were comprehensively examined and studied by various test methods and advanced analytical techniques. These help us to understand the property changes of the fabrics after treatment in order to determine an optimum formulation and treatment conditions for the functional finishing.

Chapter 4: Wrinkle-resistant finishing of cotton fabric

4.1. Introduction

Cotton fabric has numerous advantages such as good absorbent, inexpensive and breathable (Wakelyn et al., 2007). Despite numerous advantages of cotton cellulose, the most important defect of cotton fabrics is easily wrinkling after being washed or immersed in water. The formation of wrinkle is generally because cotton absorbs moisture readily. A special kind finish is applied on the cellulose in order to overcome the wrinkling problem.

In the present study, the wrinkle-resistant finishing is carried out by using DMDHEU. DMDHEU, as a traditional crosslinking agent, linked two adjacent cellulose chains by formation of crosslink. Crosslinked cellulosic chains can lower stress-induced slippage of the chains and increase the recovery ability from any deformation (Dehabadi et al., 2013; Schindler & Hauser, 2004; Shenai, 1994). DMDHEU gives excellent wrinkle-resistant performance with reasonable cost and it is commonly used these days. However, as the crosslinks lock the movement of the molecules, the tensile strength and tear strength will lose. In conventional wrinkle-resistant finishing, a high temperature around 170 – 190 ^{o}C is usually used during curing process (Sharpe & Mallinson, 2003). The high temperature will cause the degradation of cotton cellulose and lead to the severe loss of tear strength. Thus, the effect of curing temperature and curing time on wrinkle-resistant finishing will be studied. In addition, application of metal oxides for improvement the functional finishing performance was found to be feasible in previous studies (Lam et al., 2010a; Lam et al., 2010b; Wang & Chen, 2005; Yuen et al., 2007). However, the details of varying the curing conditions impacting the performance of the wrinkle recovery property in the presence of metal oxides have not been reported. Different combinations of curing temperature and curing time were comprehensively evaluated in the study. Moreover, generating a mixed catalytic system by two metal oxides and applying in the wrinkle-resistant finishing was done. All treated fabrics were evaluated by a series of international testing methods, instrumental methods and advanced analytical techniques.

4.2. Effect of curing temperature and curing time on wrinkle-resistant finishing using DMDHEU

4.2.1. Wrinkle recovery performance

4.2.1.1. Wrinkle recovery angle

The reported WRAs are an average of WRAs from the warp and weft directions that consist of three trials of face-to-face WRAs and three trials of back-to-back WRAs from each direction. The Figure 4-1 shows wrinkle recovery angles of the fabrics treated in different concentration of TiO_2 and cured at different temperatures and times.

From the Figure 4-1, it is obvious to see that the WRAs increase with the temperature from 130°C to 170°C. There is only slightly change between 110°C and 130°C. The first yellow bar represents the control specimen, which did not have any pre-treatment. The WRA of control specimen is 77.7^{o}. At the curing temperature of 110°C and 130°C, the WRAs obtained are lower than that of control specimen. This phenomenon is because of inactivated crosslinking reaction and the deterioration of cotton cellulose under heat treatment. Obviously, the specimens, which were cured at conventional temperature 170°C, have a significant increase, averagely 10.60% improvement, in WRAs compared with the control specimen. The specimen cured at 150°C for 3 minutes also shows a 2.96% improvement in WRAs. Moreover, the WRAs are affected by the curing time. The longer the curing time, the higher the WRAs are. The specimens with 3 minutes curing time have the largest WRAs because there is more time for the reaction taken place compared with the specimens cured for 1 minute.

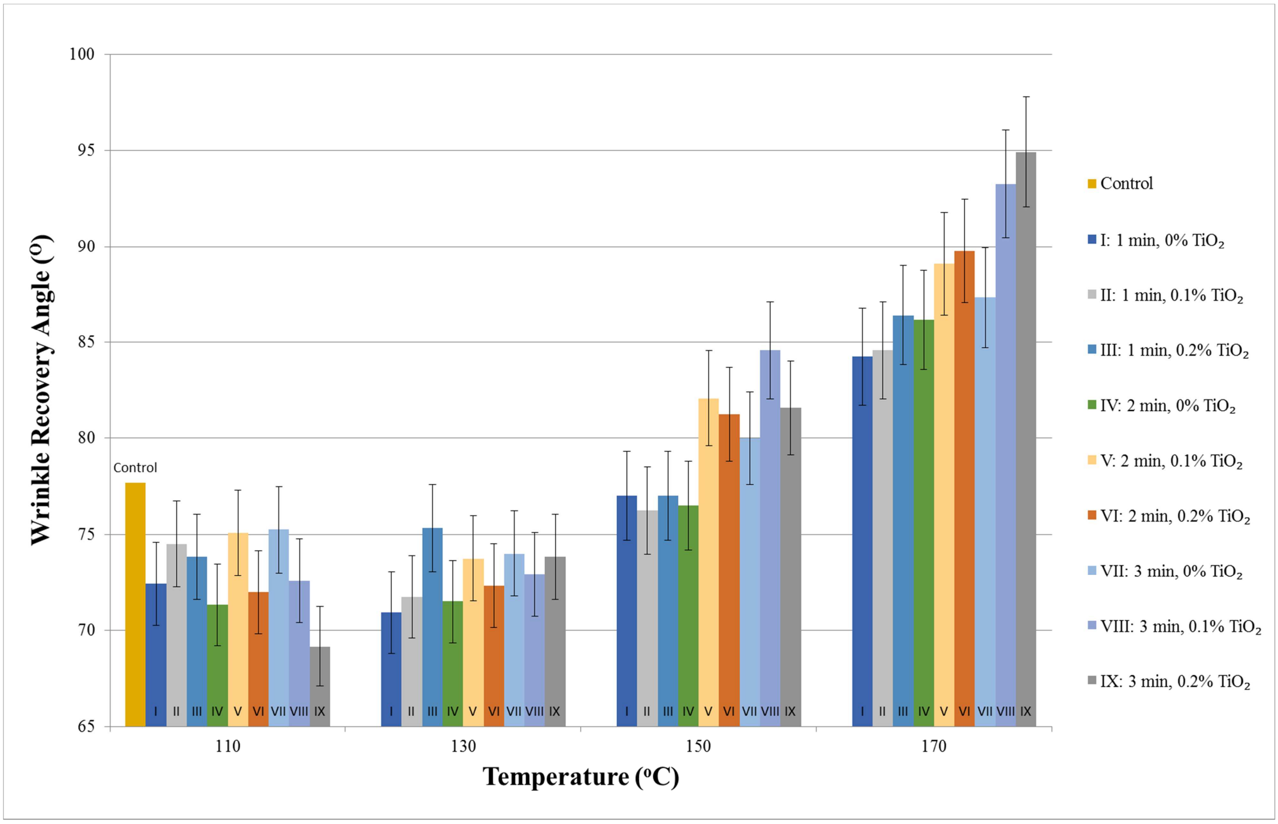

Figure 4-1. Wrinkle recovery angles of the fabrics treated in different concentration of TiO_2 and cured at different temperatures and times

In addition, for the fabrics treated in the presence of 0.1% TiO_2, the WRAs are slightly higher than that of treated in absence of TiO_2. This shows that 0.1% TiO_2 could improve the wrinkle recovery performance which is consistent with the previous studies (Lam et al., 2010a; Lam et al., 2010b; Wang & Chen, 2005; Yuen et al., 2007). In Figure 4-1, the specimens cured at 150°C for 2 and 3 minutes in the presence of 0.1% TiO_2 were recorded 82.1^{o} and 84.6^{o} which show an about 5.6% and 8.9% improvement respectively compared with the WRA of control specimen ($77.7\ ^{o}$). The presence of TiO_2 restricts interfibillar movement within the yarn structure so that wrinkle recovery property is improved (Lam et al., 2010b). The other possible reason is that TiO_2 acts as a Lewis acid catalyst to boost and enhance the reaction effectiveness. Figure 4-1 shows the WRAs with the concentration of TiO_2 further increased to 0.2%. The WRAs measured are similar to that of in the presence of 0.1% TiO_2. It does not help promote WRAs significantly by increasing the concentration of TiO_2 to 0.2%. Thus, an alternative curing condition for the wrinkle-resistant treatment can be achieved by curing the fabric at 150°C for 2 minutes in the presence of 0.1% TiO_2. The curing temperature can be lowered by addition of TiO_2 as a co-catalyst in the wrinkle-resistant solution.

In short, it was found that the higher temperature and longer curing time results in a better wrinkle recovery property. The wrinkle recovery property could be further improved by additional of 0.1% TiO_2.

4.2.1.2. Retention of Creases in Fabrics after Repeated Home Laundering

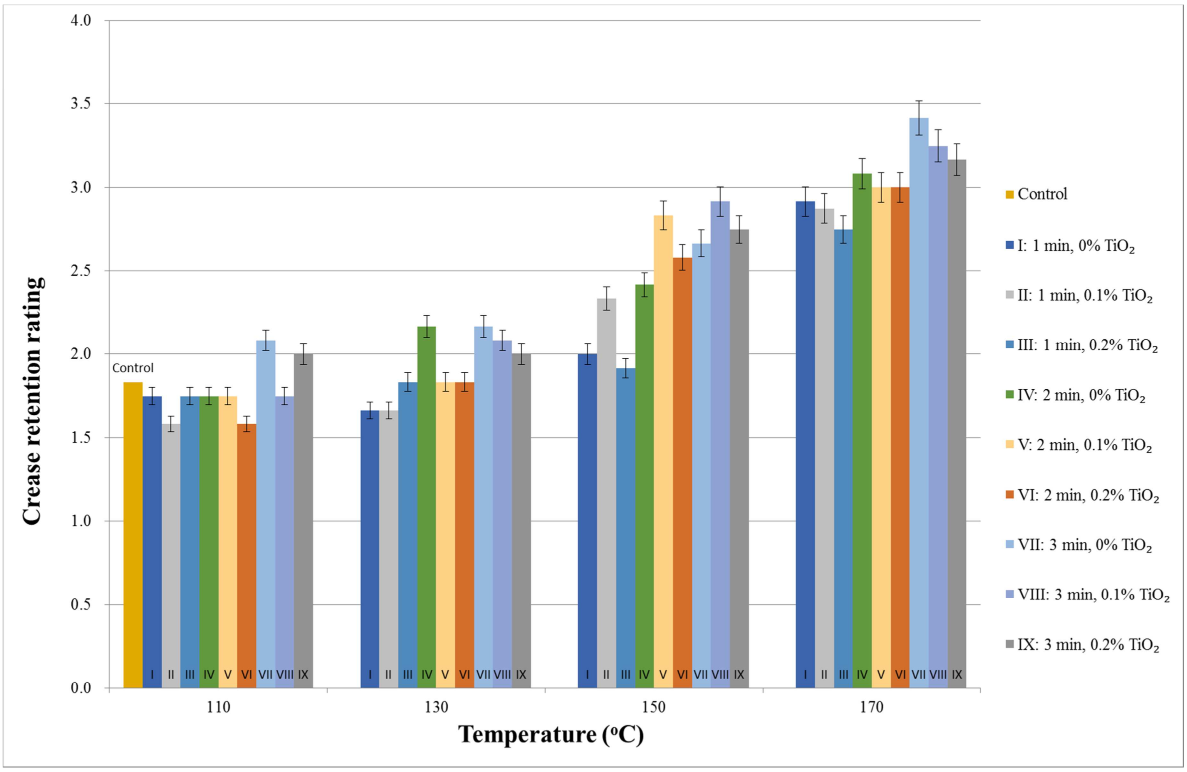

Figure 4-2. Crease retention rating of the fabrics treated in different concentration of TiO_2 and cured at different temperatures and times

The crease retention grade 5 is the best level of crease appearance, i.e. smooth fabric appearance while the crease retention grade 1 represents a very poor level of crease appearance. From the Figure 4-2, the first yellow bar represents the control specimen. The control specimen has a poor level of crease appearance, recorded 1.83. The fabrics cured at 170°C have the best crease appearance with average rating 3.14. These fabrics demonstrate good wrinkle recovery properties. The fabrics cured at 150°C have average crease retention rating 2.36 which has 29% improvement compared with that of control specimen. Based on the results, the crease retention grade is directly proportional to not only the curing temperature but also curing time. The higher the curing temperature and the longer the curing time, the better the crease appearance is. The results of crease retention rating are consistent with the results of WRAs. The higher crease retention rating corresponds to higher WRAs. Therefore, good crease retention rating of the fabrics is with respect to the extensive crosslink formation on the fabrics surface. Inactivated crosslinking reaction at low curing temperature and the deterioration of cotton cellulose under heat treatment cause the poor crease retention rating. Furthermore, the effect of TiO_2 cannot reflect on the crease retention rating because the crease rating is a rough measurement of the fabrics. The rating is assessed by human eyes using a standard lighting and viewing area. There is only a 5-level rating given by the appearance of specimens in comparison with reference standards. The effect of TiO_2 can only be measured through the wrinkle recovery test which is a more accurate and precise test. In short, the crease rating was mainly influenced by the curing temperature and time employed and the presence of TiO_2 did not affect the crease retention rating obviously.

4.2.2. Tear strength

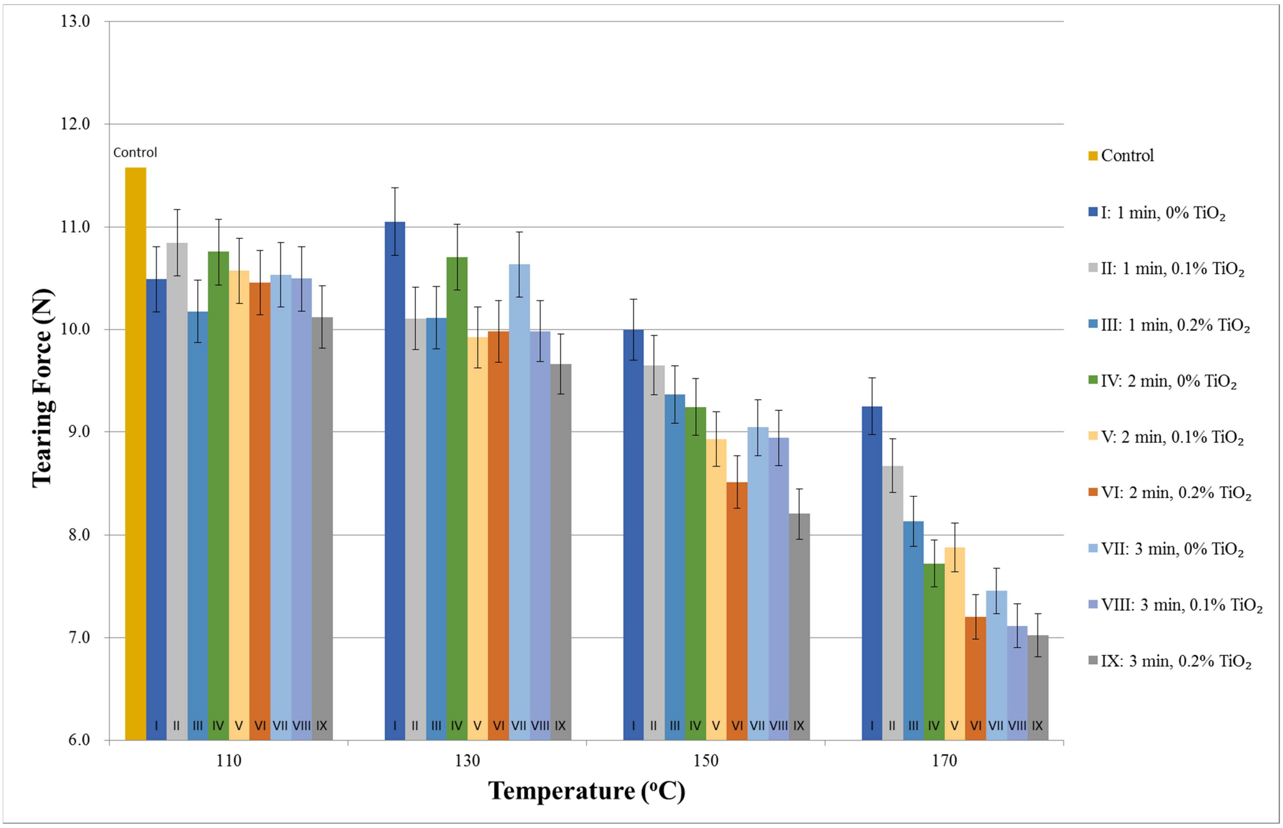

Figure 4-3. Tearing force of the fabrics treated in different concentration of TiO_2 and cured at different temperatures and times

Figure 4-3 demonstrates the tearing force in Newton (N) of the fabrics after wrinkle-resistant finishing. The first yellow bar represents the control specimen, which did not have any pre-treatment, with tearing force 11.6N. The tearing forces of all treated fabrics are lower than that of the control specimen. There is a great drop in tearing force after wrinkle-resistant finishing using DMDHEU as crosslinking agent. The drop of tear strength is because of the formation of crosslink. The crosslinks restrict the movement of cellulose chains and lock the movement of the molecules. The external force from tear stress can no longer be slightly shared by over many neighbour molecules. Therefore, sharing of force cannot be done in crosslinked cellulose chains leading to the drop of tear strength (Schindler & Hauser, 2004; Sharpe & Mallinson, 2003). Another reason for the drop of tear strength is because of the slight acidic medium of the bath (Lam et al., 2010b). The pH of finishing solution is around 3-4. The cotton fibres are tendered and damaged by acid slightly. There is a decreasing trend of the tearing force for curing temperature increased from 110°C to 170°C. The tearing force is lowered 30% at the curing temperature of 170°C while there is only 19% reduction at the curing temperature of 150°C compared with control specimen. Moreover, when the curing time is increased, the lower tearing force will be obtained. The number of crosslinks formed is expected to be greater in higher curing temperature and longer curing time. Thus, at the higher curing temperature and longer curing time, the loss of tear strength is more significant.

Furthermore, the tearing force is slightly further reduced in the presence of TiO_2. About 2% more reduction in tearing force for the fabrics cured at 170°C in the presence of 0.1% TiO_2. Further increase in concentration of TiO_2 to 0.2%, a lower tearing force is obtained. Owing to enhancement of reaction effectiveness by TiO_2, the crosslink formation may be more extensive resulting in the drop of tearing force. Although the TiO_2 particles slightly affect the tearing force, the curing temperature and time used are the major factors that cause the reduction in tearing force.

4.2.3. Optimization of curing conditions for wrinkle-resistant finishing

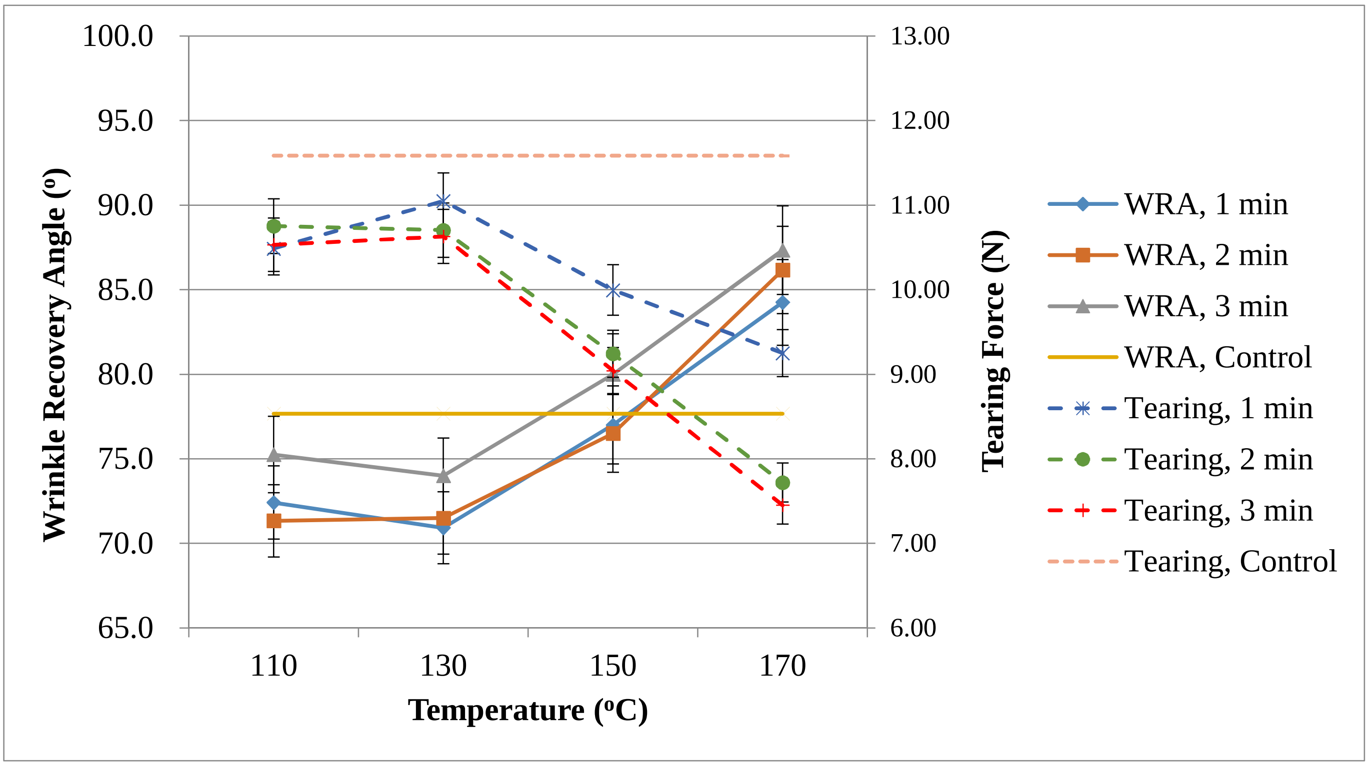

Figure 4-4. Combination of WRAs and tearing forces of the treated fabrics in the absence of TiO_2 with curing different temperatures and curing times

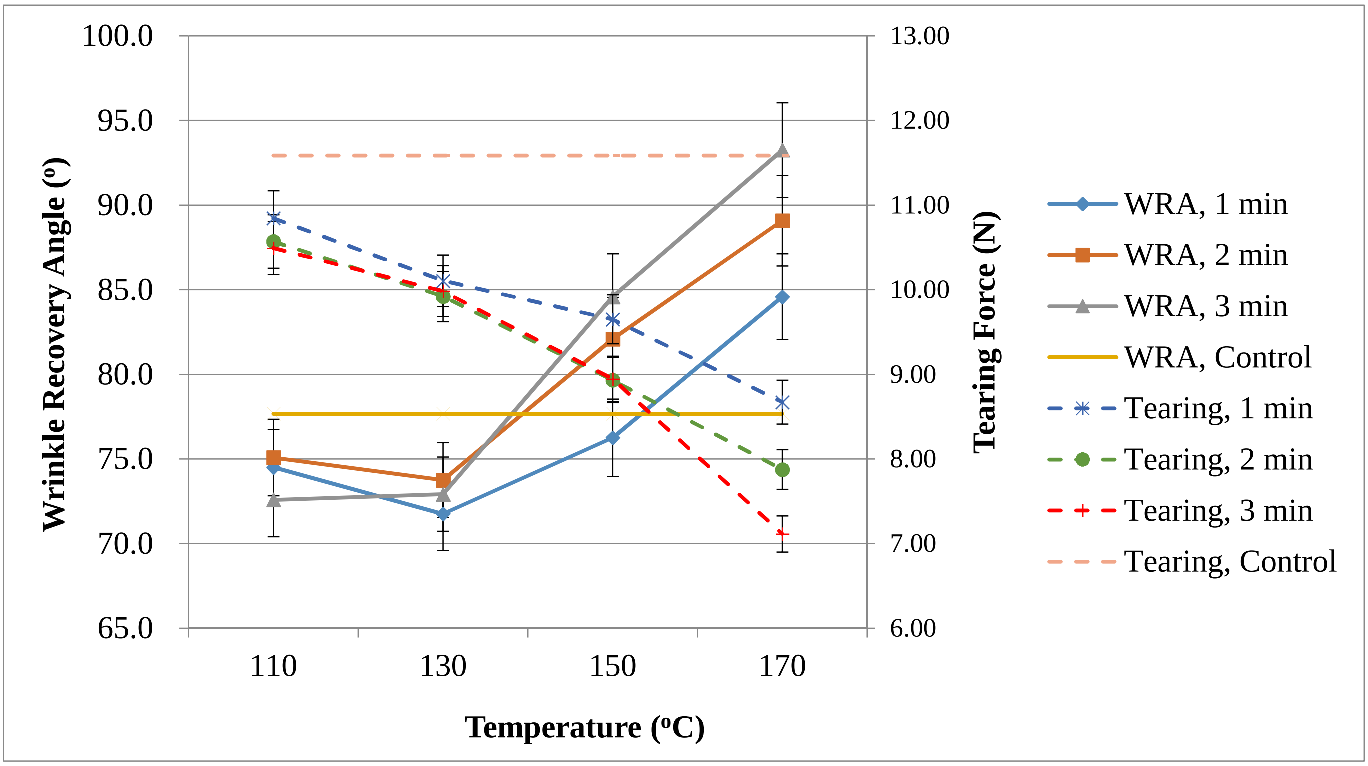

Figure 4-5. Combination of WRAs and tearing forces of the treated fabrics in the presence of 0.1% TiO_2 with different curing temperatures and curing times

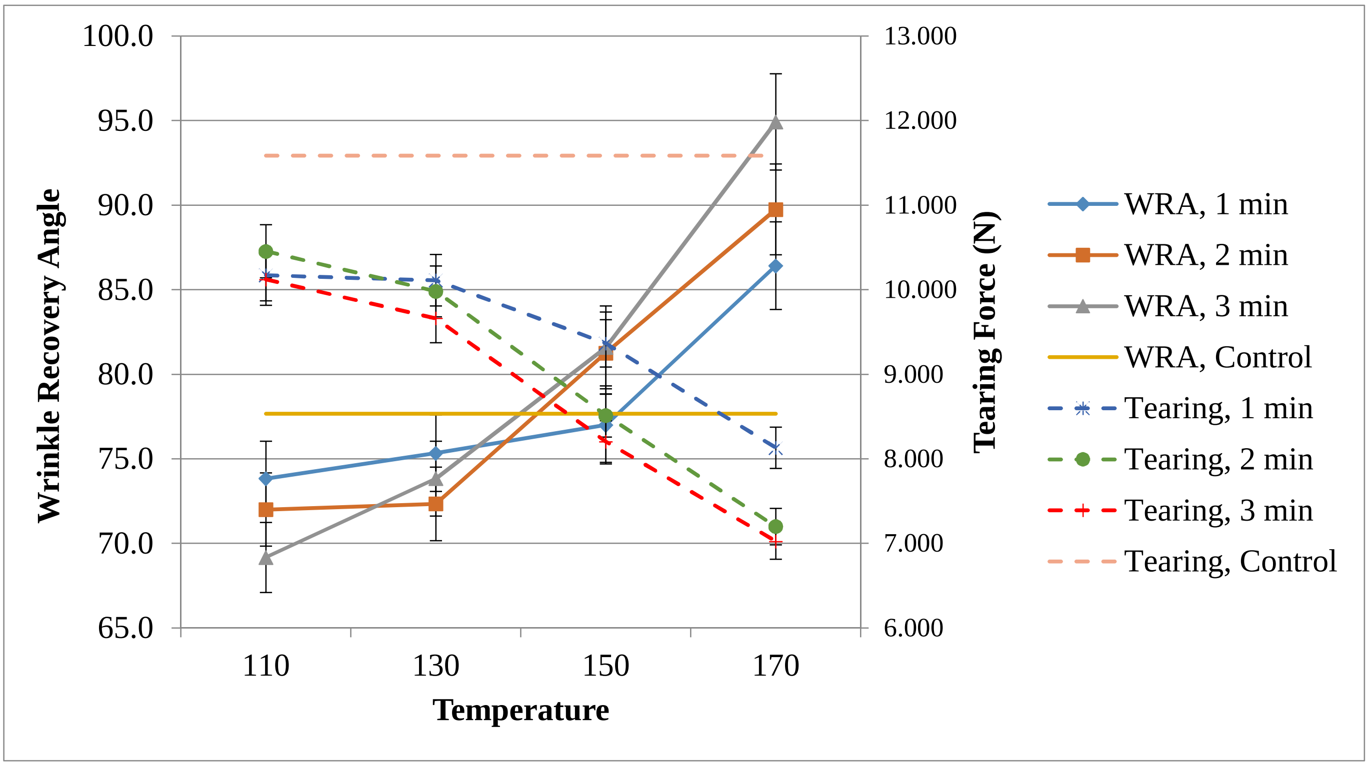

Figure 4-6. Combination of WRAs and tearing forces of the treated fabrics in the presence of 0.2% TiO_2 with different curing temperatures and curing times

In Figure 4-4, 4-5, 4-6, the left y-axis illustrates the wrinkle recovery angle in degree and the right y-axis illustrates the tearing force in Newton. The dash lines are the results of tearing force whereas the solid lines are the results of WRA. The pink dash line represents the tearing force of control specimen while the yellow line represents the WRA of control specimen. The decrease in tearing force after heat curing treatment is unavoidable. The longer curing time and the higher curing temperature used will lower the tear properties. Lowering the curing temperature is a feasible method to reduce the tear strength loss. Meanwhile, in order to obtain a satisfactory wrinkle recovery performance, curing at 150°C above is required. In Figure 4-4 to 4-6, the intersection points of the solid lines and dash lines lie on near 150°C. This is the optimum point by considering the results of WRA and tearing force.

Hence, the optimized conditions concerning the factors of WRA and tear strength can be determined. Maximum improvement of WRA with minimum loss of tear strength is achieved at the optimized conditions. In Figure 4-4, in the absence of TiO_2, the fabric cured at 150°C for 3 minutes was found to be feasible. However, a better result could be obtained by the addition of TiO_2. Therefore, the fabric was recommended to be cured at 150°C for 2 minutes in the presence of 0.1% TiO_2.

4.2.4. Whiteness of textile

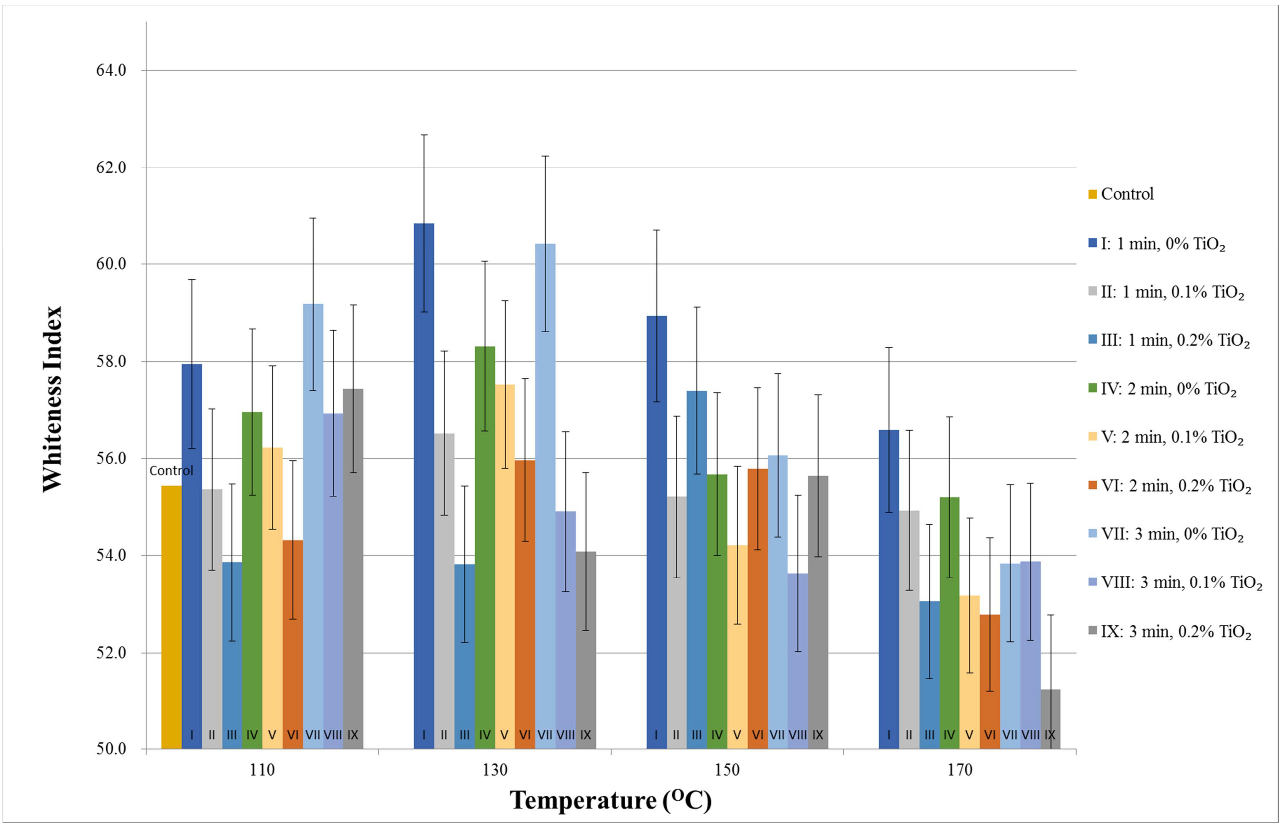

Figure 4-7. Whiteness index of the fabrics treated in different concentration of TiO_2 and cured at different temperatures and times (C standard illuminant and 10^o observer)

The whiteness index of the fabrics is illustrated in Figure 4-7. The whiteness index falls into a range between 50 and 62. There is little colour difference before and after finishing as the whiteness index of the treated fabric is measured within ±10% compared with the control specimen. The graph shows a slight decrease in whiteness when the curing temperature is increased from 110°C to 170°C. The relative low value of whiteness index at high curing temperature is because of thermal degradation of cotton. When the cotton cellulose is heated above 140°C or higher temperature, yellowing will be occurred due to broken down of cellulose. Small carbon substances are formed and the carbonyl content is increased (Schindler & Hauser, 2004; Wakelyn et al., 2003). Therefore, curing at 170°C results in the lowest whiteness for all conditions. From the Figure 4-7, the whiteness index is not improved in the presence of TiO_2. Even though TiO_2 is sometimes used as a pigment, the colour effect of TiO_2 on the fabric is not significant. The effect of TiO_2 on the whiteness index is mainly due to the enhancement of reaction effectiveness. This may lead to more small carbon-containing compounds formed under the heat curing treatment. Thus, the values obtained in the presence of TiO_2 are averagely slightly lower than that of in the absence of TiO_2.

4.2.5. Scanning Electron Microscopy (SEM)

Figure 4-8 and 4-9 show the SEM images of control sample at the magnification of 1000X and 2000X respectively. The spiral structure characteristic is clearly observed and defined. The surface of control cotton fibre is flat with a twisted ribbon-like structure caused by spiralling of cellulose fibrils. The control cotton fabrics have a smooth fibre surface with some wrinkles.

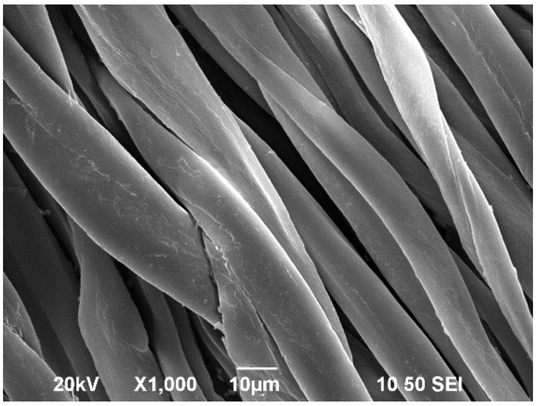

Figure 4-8. SEM image of control sample at 1000X

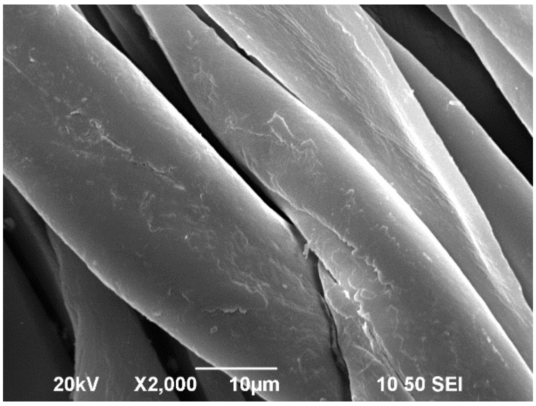

Figure 4-9. SEM image of control sample at 2000X

Figure 4-10 and 4-11 demonstrate the SEM images of DMDHEU crosslinked cotton sample in the absence of TiO_2 at the magnification of 1000X and 2000X respectively. After wrinkle-resistant treatment with DMDHEU, the spiral structure characteristic is still clearly observed and defined. The surface of control cotton fibre has not changed by the crosslinking agent. The extent of smoothness is similar to the control sample. The fibres have not been damaged.

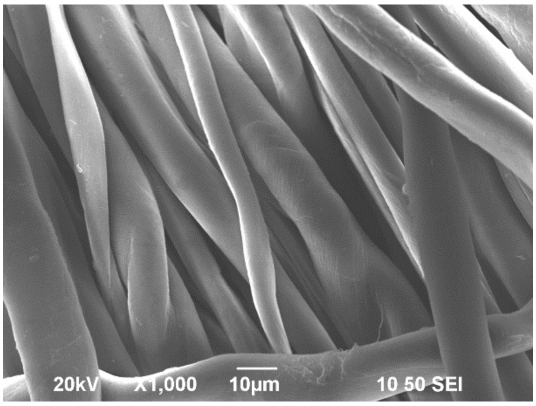

Figure 4-10. SEM image of DMDHEU-treated sample in the absence of TiO_2 at 1000X

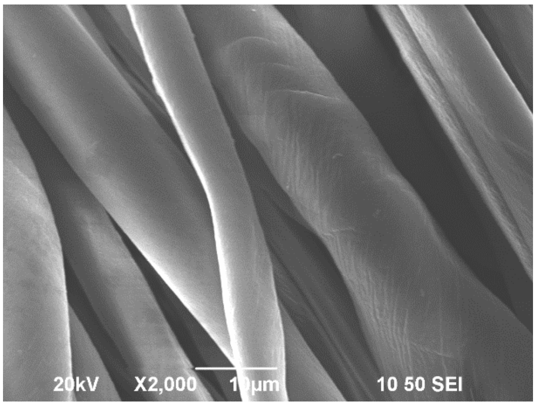

Figure 4-11. SEM image of DMDHEU-treated sample in the absence of TiO_2 at 2000X

Figure 4-12 to 4-15 illustrates the SEM images of DMDHEU crosslinked cotton sample in the presence of 0.1% and 0.2% TiO_2 at the magnification of 1000X and 2000X respectively. Large amount of small particles attaches on the fibre surface and exists in the interval between the fibres. These particles are the evidence of existence of TiO_2. The TiO_2 agglomerates together to form a TiO_2 cluster. Clustered TiO_2 particles deposit on the fibre surface irregularly and with different sizes. The particle sizes of TiO_2 are ranged from 1 – 6 μm in length.

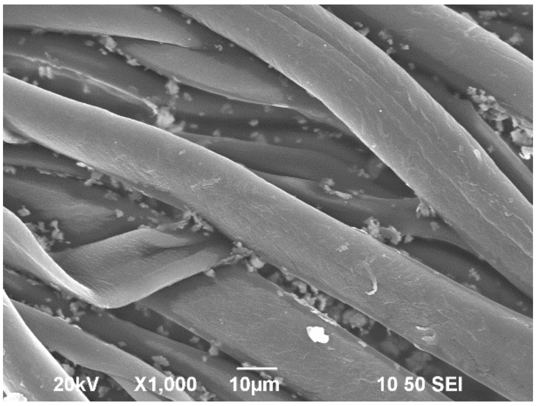

Figure 4-12. SEM image of DMDHEU-treated sample in the presence of 0.1% TiO_2 at 1000X

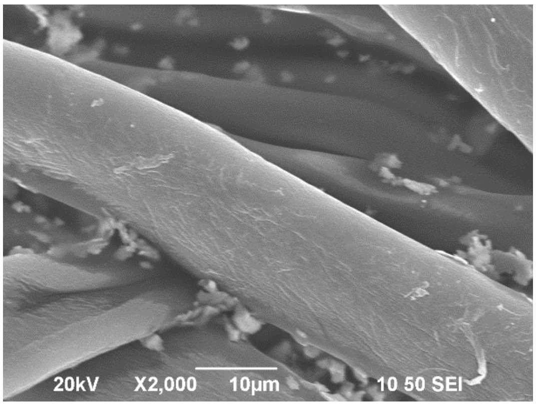

Figure 4-13. SEM image of DMDHEU-treated sample in the presence of 0.1% TiO_2 at 2000X

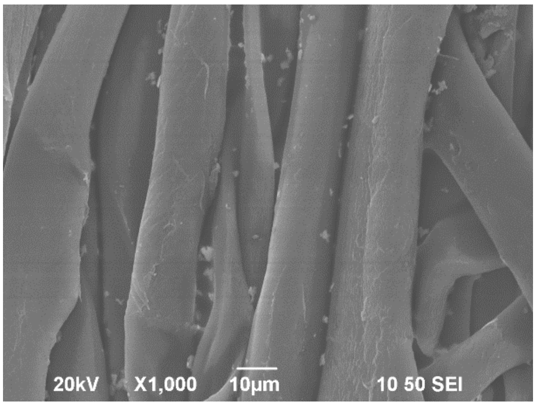

Figure 4-14. SEM image of DMDHEU-treated sample in the presence of 0.2% TiO_2 at 1000X

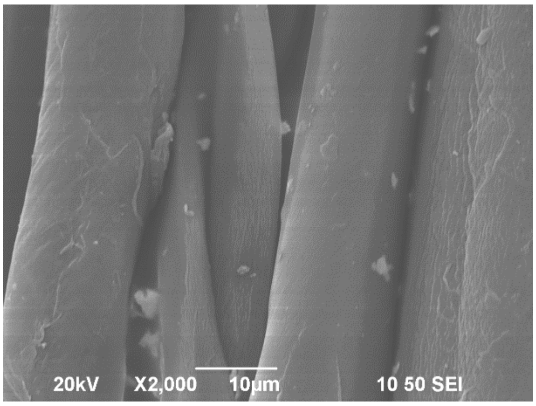

Figure 4-15. SEM image of DMDHEU-treated sample in the presence of 0.2% TiO_2 at 2000X

4.2.6. Confirmation of the presence of DMDHEU by FTIR-ATR

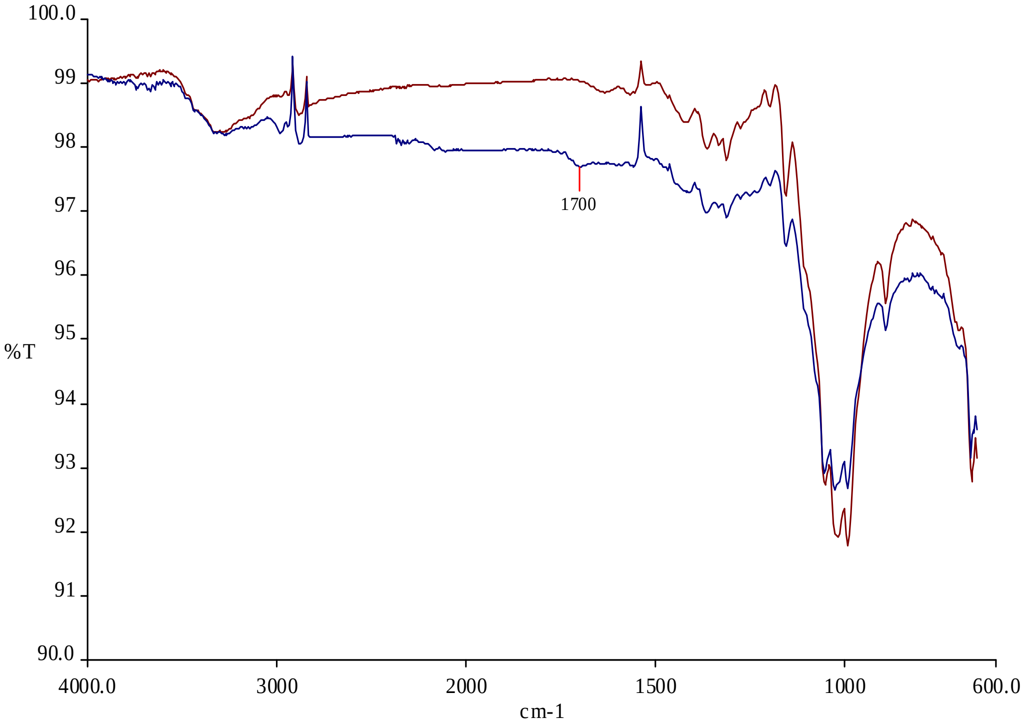

Figure 4-16. FTIR-ATR spectra of a) untreated cotton fabric and b) DMDHEU-treated cotton fabric

FTIR-ATR spectroscopy is a surface-sensitive technique that can characterize the chemical structure of a substrate (Chung et al., 2004; Lam et al., 2011b). In order to confirm the presence of DMDHEU on the cotton fabric after crosslinking reaction, FTIR-ATR analysis has been done on the untreated cotton fabric and the DMDHEU-treated cotton fabric. The FTIR-ATR spectra are shown in Figure 4-16. When the cotton fabric was treated with modified DMDHEU, there is a prominent band appeared near 1700 cm^{-1} which corresponds to the stretching of C=O bond (Kongdee & Bechtold, 2007; Morris et al., 1984; Orhan, 2013). The characteristic peak is absent in the untreated cotton fabric. Therefore, this is strong evidence showing that the modified DMDHEU has been successfully coated onto the cotton surface after crosslinking reaction.

4.3. Effect of mixed metal oxide catalyst on wrinkle-resistant finishing using DMDHEU

4.3.1. Wrinkle recovery performance

4.3.1.1. Wrinkle recovery angle

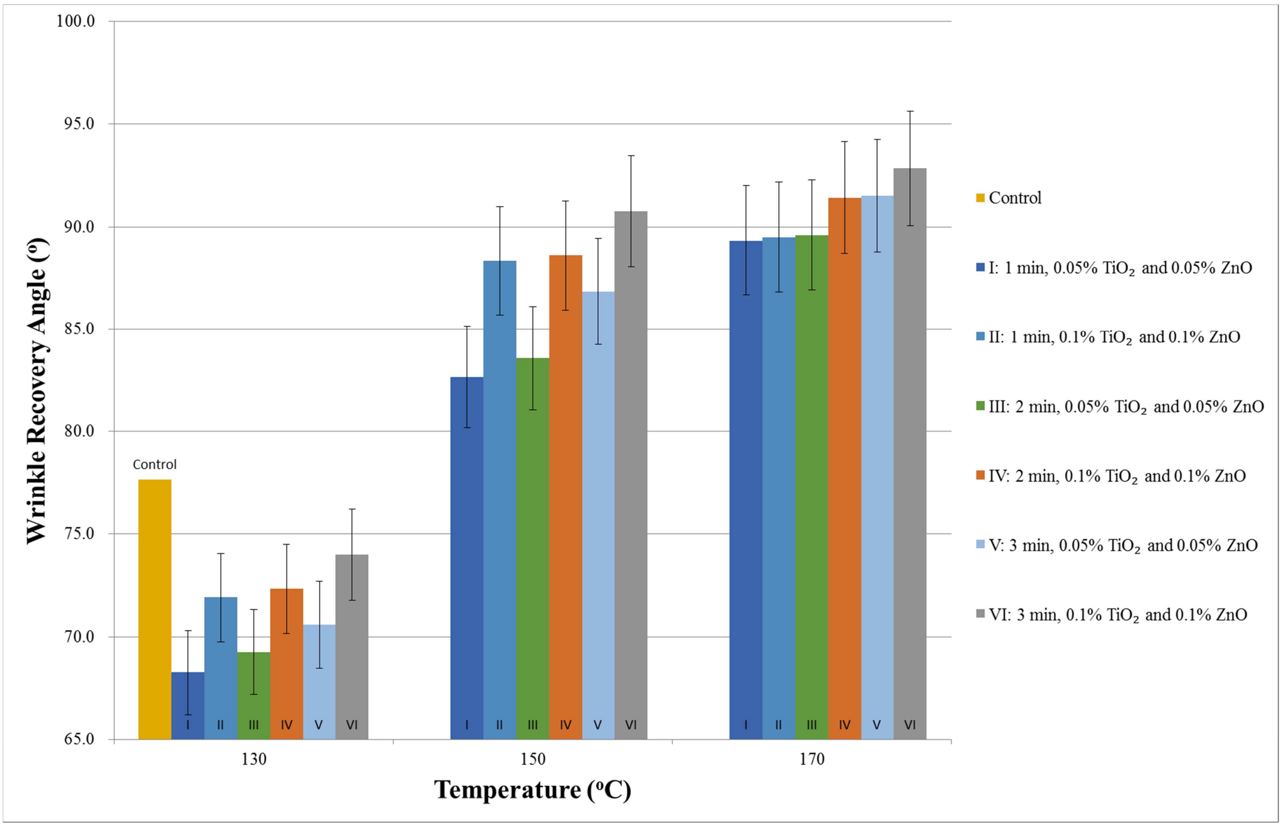

Figure 4-17. Wrinkle recovery angles of the fabrics treated in different concentration of TiO_2 & ZnO and cured at different temperatures and times

In Figure 4-17, a mixed catalytic system 0.05% TiO_2 and 0.05% ZnO was employed in wrinkle-resistant finishing. The first yellow bar shows the control specimen. As the wrinkle-resistant performance of the fabrics cured at 110°C were found to be unsatisfactory in the previous tests demonstrated in section 4.2.1, this condition was no longer applied in the mixed catalytic system. The results show that the performance of wrinkle-resistant treatment at 170°C is still the best. However, by comparing the fabrics cured at 150°C, the WRAs have been improved obviously after addition of mixed metal oxides. The average WRA for the fabrics cured at 150°C in the absence of TiO_2 was found to be 78°. The average WRA is improved to 81° in the presence of 0.1% TiO_2 and further improved to 84° in the presence of 0.05% TiO_2 and 0.05% ZnO. The summary of percentage change of WRAs after wrinkle-resistant finishing with selected types and concentrations of catalyst is listed in Table 4-1. The introduction of ZnO should function like as TiO_2. ZnO should restrict interfibillar movement within the yarn structure in a greater extent since the particle size of ZnO is larger than TiO_2. Therefore, wrinkle recovery property is further improved. Moreover, ZnO is nearly insoluble in water, but it is able to react with hydrogen ion under acidic solution to form salt (Greenwood & Earnshaw, 1998). The excessive hydrogen ions in the finishing solution may be removed by the presence of trace amount of ZnO. This may reduce the damage to the cellulose caused by acidic environment. These may make the promotion of wrinkle recovery properties. The Figure 4-17 shows that increasing the concentration of TiO_2 and ZnO to 0.1%, the WRAs are significantly improved for the fabrics cured at 150°C while the WRAs are slightly promoted for the fabrics cured at 170°C. In short, the wrinkle recovery performance using DMDHEU with TiO_2 and ZnO as co-catalyst was found to obviously increase in WRAs at curing temperature of 150°C.

Table 4-1. A summary of percentage change* in WRAs of selected conditions after wrinkle-resistant finishing

Wrinkle recovery angles with selected conditions				
Control	77.7°	Curing Temperature		
Curing Time (min)		170 °C	150 °C	130 °C
1	In the absence of TiO_2	84.3° 8.4%	77.0° -0.9%	70.9° -8.7%
2		86.2° 10.9%	76.5° -1.5%	71.5° -8.0%
3		87.3° 12.4%	80.0° 3.0%	74.0° -4.8%
1	In the presence of 0.1% TiO_2	84.6° 8.9%	76.3° -1.9%	71.8° -7.7%
2		89.1° 14.7%	82.1° 5.6%	73.8° -5.1%
3		93.3° 20.0%	84.6° 8.9%	72.9° -6.2%
1	In the presence of 0.1% TiO_2 & 0.1% ZnO	89.5° 15.2%	88.3° 13.6%	71.9° -7.5%
2		91.4° 17.6%	88.6° 14.0%	72.3° -6.9%
3		92.8° 19.4%	90.8° 16.9%	74.0° -4.8%

*The percentage changes are reference to the control specimen.

4.3.2. Tear strength

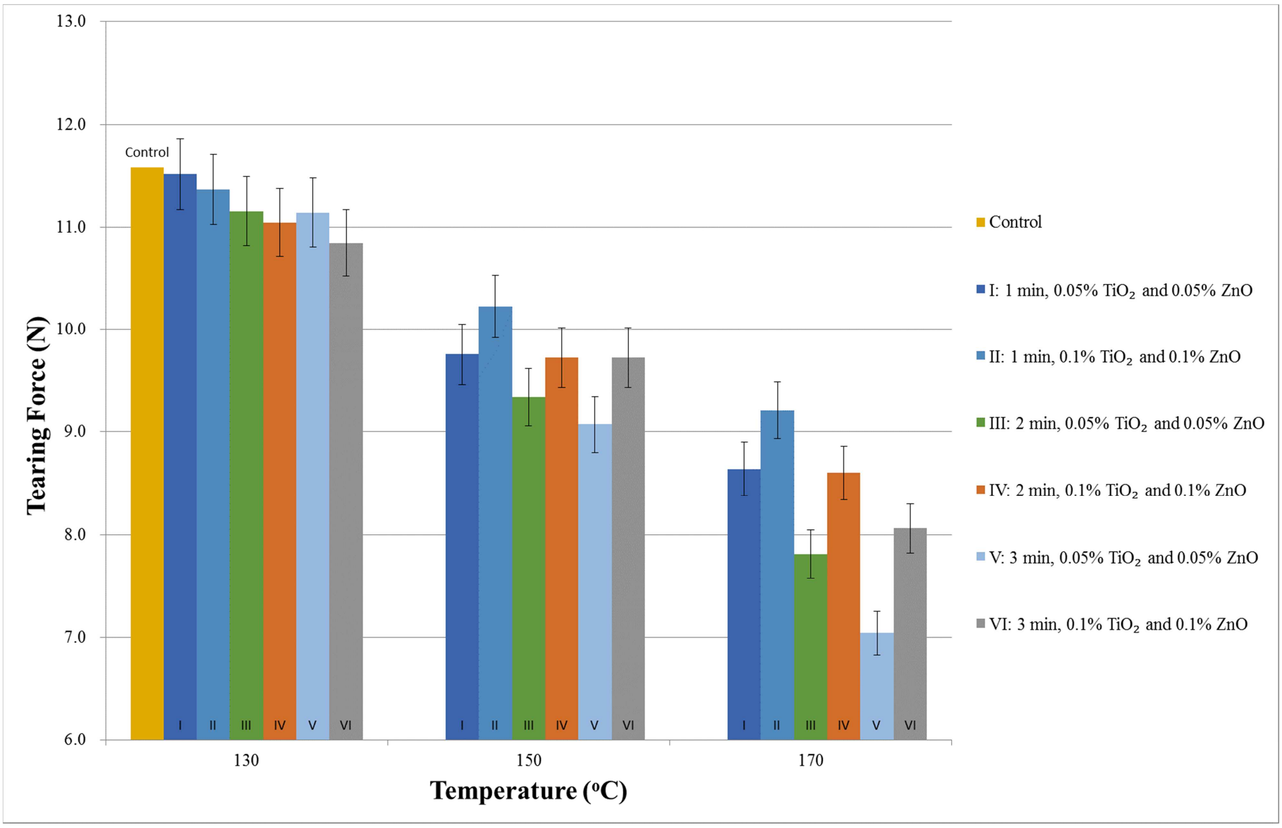

Figure 4-18. Tearing force of the fabrics treated in different concentration of TiO_2 & ZnO and cured at different temperatures and times

In Figure 4-18, the tearing forces of the fabrics after wrinkle-resistant finishing in the presence of TiO_2 and ZnO are shown. The first yellow bar represents the control specimen. The tearing force decreases when the curing temperature is increased. However, compared the Figure 4-18 with Figure 4-3, the loss of tearing force in the presence of 0.1% TiO_2 and ZnO is less than that of in the presence of 0.1% TiO_2. As ZnO particles are relatively larger than TiO_2, the addition of ZnO can increase yarn friction, which resists yarn slippage in a greater extent. The more particles attached on the fabric surfaces or filled between the fibres, the higher the friction to resist yarn slippage will be (Lam et al., 2011a, Lam et al., 2011c). Thus, the loss of tear strength is compensated when the concentration of each metal oxide changed from 0.05% to 0.1%. Table 4-2 has summarized the percentage change of tear strength of selected conditions. The maximum loss of tear strength compared with the control specimen is nearly 40% at 170°C curing temperature for 3 minutes. The loss of tear strength of treated fabrics cured at 150°C is dramatically lowered compared with those cured at 170°C. Therefore, curing carried out at 150°C could retain the tear strength in a great extent.

Table 4-2. A summary of percentage change* in tearing force of selected conditions after wrinkle-resistant finishing

Tearing force table with selected conditions				
Control	11.59	Curing Temperature		
Curing Time (min)		170 °C	150 °C	130 °C
1	In the absence of TiO_2	9.25 -20.2%	10.00 -13.7%	11.05 -4.6%
2		7.72 -33.4%	9.24 -20.2%	10.70 -7.6%
3		7.45 -35.7%	9.04 -21.9%	10.63 -8.2%
1	In the presence of 0.1% TiO_2	8.67 -25.1%	9.65 -16.7%	10.11 -12.8%
2		7.88 -32.0%	8.93 -22.9%	9.92 -14.4%
3		7.11 -38.6%	8.95 -22.8%	9.98 -13.8%
1	In the presence of 0.1% TiO_2 & 0.1% ZnO	9.21 -20.5%	10.22 -11.8%	11.37 -1.9%
2		8.60 -25.8%	9.73 -16.1%	11.04 -4.7%
3		8.06 -30.4%	9.72 -16.1%	10.85 -6.4%

* The percentage changes are reference to the control specimen.

4.3.3. Whiteness of textile

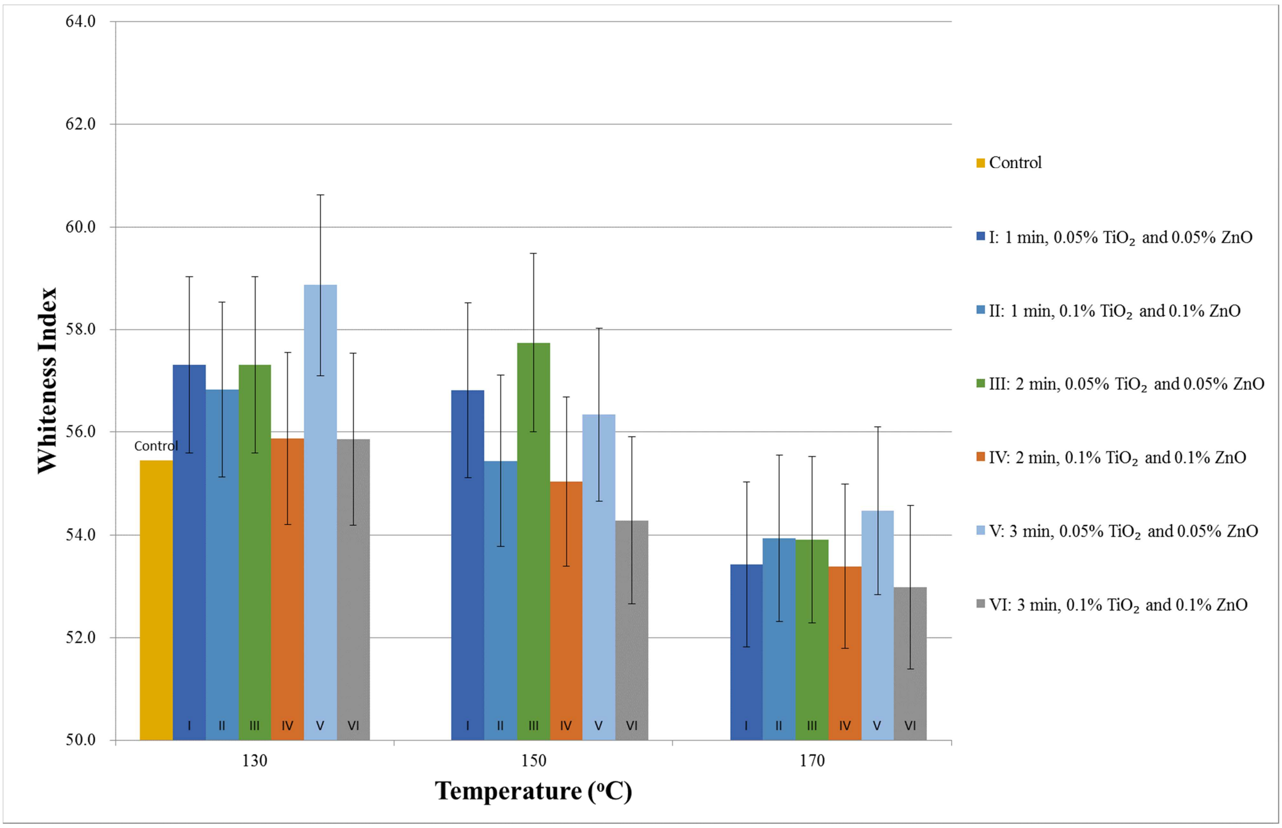

Figure 4-19. Whiteness Index of the fabrics treated in different concentration of TiO_2 & ZnO and cured at different temperatures and times

The whiteness index of the fabrics treated with mixed catalysts is illustrated in Figure 4-19. The whiteness index still falls into a range between 50 and 62. It is clearly to observe that the whiteness decreases when the curing temperature is increased from 130°C to 170°C. As discussed previously, thermal treatment will cause yellowing of cotton cellulose due to thermal degradation. The whiteness indexes of the fabrics treated in the presence of 0.1% TiO_2 and ZnO are lower than that of treated in the presence of 0.05% TiO_2 and ZnO. It may show that the crosslink reaction is more effective in the presence of 0.1% TiO_2 and ZnO as co-catalyst leading to more small carbon-containing compounds formed under the heat curing treatment. It can conclude that the higher the concentration of the mixed metal oxides used, the lower the whiteness index obtained as the reaction effectiveness of crosslinking reaction is enhanced. Moreover, the white solid particles of TiO_2 and ZnO do not have effect on the fabric colour. The whiteness index obtained is very close by comparing with the fabrics treated in the presence of 0.1% TiO_2 and in the presence of 0.05% TiO_2 and ZnO. The colour of fabric should be near the same. In summary, the addition of TiO_2 and ZnO did not cause a large adverse effect to the whiteness of textile.

4.3.4. Scanning Electron Microscopy (SEM)

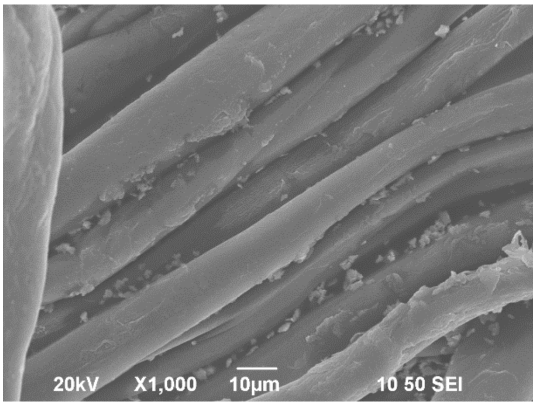

Figure 4-20. SEM image of DMDHEU-treated sample in the presence of 0.05% TiO_2, 0.05% ZnO mixed catalytic system at 1000X

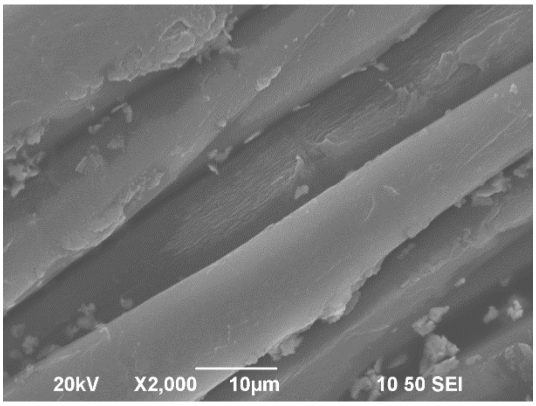

Figure 4-21. SEM image of DMDHEU-treated sample in the presence of 0.05% TiO_2, 0.05% ZnO mixed catalytic system at 2000X

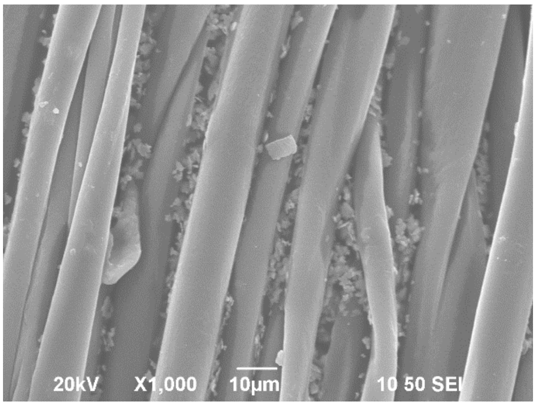

Figure 4-22. SEM image of DMDHEU-treated sample in the presence of 0.1% TiO_2, 0.1% ZnO mixed catalytic system at 1000X

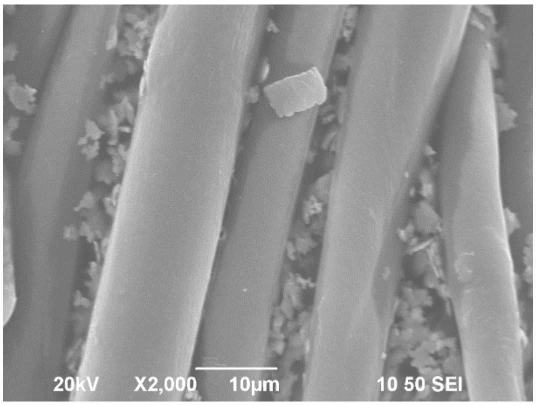

Figure 4-23. SEM image of DMDHEU-treated sample in the presence of 0.1% TiO_2, 0.1% ZnO mixed catalytic system at 2000X

Figure 4-20 to 4-23 demonstrates the SEM images of DMDHEU-treated cotton sample in the presence of 0.05% TiO_2 and ZnO as well as 0.1% TiO_2 and ZnO at the magnification of 1000X and 2000X respectively. From the figures, there are many micro particles attached on the fibres and the interval between the fibres. The particles are irregular in shape and size. The particles in Figure 4-22 are denser then in Figure 4-20 because the concentration of metal oxides is increased. It is difficult to distinguish TiO_2 from ZnO. They might agglomerate each other to form a cluster or there may be some interaction between TiO_2 and ZnO. Meanwhile, the spiral structure characteristic of cotton fibre is not damaged. The control cotton fabrics still have a smooth fibre surface.

4.4. Low stress mechanical properties of DMDHEU-treated fabric

For the KES-F test, tensile, shearing, bending, compressional and surface properties are measured. The definitions and characteristics of the parameters of these properties have been defined and described at Table 3-3 in chapter 3. The results are demonstrated in Table 4-5. Each property will be discussed comprehensively in the following parts. The sample codes are used to express different conditions. “A” refers to the padding solutions without TiO_2. “B” and “C” refer to the padding solutions containing 0.1% and 0.2% TiO_2 respectively. More information about padding solutions is shown in Table 3-1. The first number digit of the code refers to curing time in minute, and the last three-digit refers to curing temperature in degree Celsius.

Table 4-3. Low stress mechanical properties of the wrinkle-resistant-treated fabric as measured by the KES-F system

	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
Sample Code	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (gf/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
Control	13.91	44.14	8.32	1.97	5.03	7.22	0.114	0.140	0.130	6.96	0.380	0.122	45.49	0.560	0.689
A1110	11.85	50.51	7.21	2.21	4.07	8.67	0.099	0.113	0.143	6.56	0.326	0.161	35.74	0.520	0.728
A1130	11.77	51.11	7.30	2.15	3.28	8.08	0.098	0.112	0.140	6.54	0.340	0.165	35.95	0.522	0.719
A1150	11.51	52.74	7.19	1.99	2.89	7.49	0.094	0.099	0.154	6.61	0.349	0.168	35.29	0.527	0.726
A1170	11.76	52.92	7.29	2.07	2.78	7.67	0.095	0.091	0.150	5.91	0.329	0.184	36.66	0.534	0.758
B1110	12.16	48.77	7.35	2.19	4.30	8.64	0.097	0.109	0.148	6.78	0.342	0.169	33.66	0.527	0.738
B1130	11.68	51.17	7.08	2.09	4.13	8.25	0.096	0.109	0.146	6.27	0.342	0.172	35.03	0.529	0.726
B1150	11.54	52.87	7.29	2.03	3.80	7.87	0.095	0.098	0.145	6.74	0.335	0.170	34.58	0.534	0.735
B1170	11.47	53.61	7.26	1.99	2.87	7.60	0.093	0.092	0.150	6.38	0.321	0.189	35.93	0.535	0.765
C1110	12.21	49.07	7.62	2.30	4.71	8.74	0.103	0.123	0.150	6.51	0.331	0.183	34.79	0.530	0.752
C1130	11.87	51.12	7.28	2.18	4.27	8.37	0.103	0.112	0.156	6.64	0.351	0.175	35.34	0.529	0.728
C1150	11.58	53.33	7.17	2.11	4.17	8.35	0.101	0.110	0.155	6.85	0.352	0.183	34.58	0.537	0.752
C1170	11.39	55.26	7.05	2.13	3.25	8.08	0.099	0.096	0.162	6.43	0.323	0.187	36.56	0.536	0.754

Low stress mechanical properties of the wrinkle-resistant-treated fabric as measured by the KES-F system (Cont'd)

Sample Code	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (gf/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
A2110	12.06	49.45	7.36	2.24	4.06	8.69	0.097	0.113	0.151	6.72	0.355	0.149	37.36	0.539	0.708
A2130	11.77	52.52	7.36	2.14	3.01	8.05	0.100	0.118	0.155	6.59	0.368	0.151	38.44	0.539	0.703
A2150	11.70	52.74	7.30	2.00	2.84	7.69	0.097	0.096	0.150	6.87	0.360	0.154	37.67	0.539	0.710
A2170	11.43	54.00	6.95	2.12	3.03	7.86	0.096	0.092	0.146	6.68	0.359	0.153	38.46	0.542	0.713
B2110	11.92	49.06	7.48	2.26	4.37	9.14	0.096	0.106	0.152	6.25	0.368	0.171	35.58	0.545	0.731
B2130	11.50	51.08	7.09	2.17	4.42	8.47	0.100	0.120	0.155	6.75	0.348	0.172	37.62	0.545	0.744
B2150	11.45	54.67	7.20	2.09	3.86	8.14	0.097	0.108	0.145	6.49	0.359	0.171	37.51	0.547	0.731
B2170	11.32	55.24	7.07	2.18	3.27	7.92	0.096	0.098	0.151	6.52	0.346	0.174	38.14	0.540	0.729
C2110	11.53	51.50	7.06	2.34	4.54	9.09	0.103	0.116	0.146	6.25	0.370	0.189	35.13	0.547	0.752
C2130	11.47	51.42	7.04	2.16	4.17	8.45	0.103	0.114	0.147	6.42	0.375	0.183	36.39	0.545	0.741
C2150	11.37	53.89	7.04	2.07	3.76	8.26	0.103	0.113	0.154	6.89	0.376	0.176	36.59	0.549	0.729
C2170	11.03	55.93	6.88	2.09	2.89	7.64	0.103	0.098	0.156	6.60	0.371	0.176	38.78	0.542	0.732

Low stress mechanical properties of the wrinkle-resistant-treated fabric as measured by the KES-F system (Cont'd)

Sample Code	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (gf/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
A3110	12.29	48.23	7.46	2.19	4.05	8.35	0.104	0.115	0.148	6.54	0.336	0.170	34.35	0.519	0.734
A3130	11.50	50.72	7.13	2.07	3.02	8.05	0.101	0.107	0.138	6.12	0.346	0.181	37.15	0.522	0.731
A3150	11.77	52.49	7.36	2.00	2.74	7.82	0.097	0.094	0.150	5.72	0.328	0.187	36.37	0.529	0.739
A3170	11.06	53.19	6.65	2.12	3.15	8.16	0.100	0.099	0.150	5.90	0.335	0.194	36.50	0.534	0.751
B3110	11.79	49.35	7.26	2.20	4.08	8.62	0.099	0.105	0.143	6.15	0.362	0.189	33.33	0.532	0.744
B3130	11.76	52.10	6.95	2.17	4.21	8.46	0.098	0.109	0.146	5.89	0.330	0.187	33.24	0.535	0.751
B3150	11.48	54.24	7.18	2.05	3.77	8.01	0.097	0.106	0.147	6.28	0.343	0.190	34.50	0.540	0.746
B3170	11.32	53.85	7.01	2.15	3.25	8.12	0.098	0.092	0.150	6.62	0.322	0.189	34.26	0.535	0.755
C3110	11.97	50.88	7.30	2.30	4.18	8.66	0.107	0.107	0.146	6.01	0.348	0.192	35.18	0.525	0.745
C3130	11.75	52.23	7.35	2.20	4.00	8.34	0.105	0.110	0.139	6.11	0.332	0.186	35.59	0.529	0.749
C3150	11.48	54.34	7.11	2.15	3.75	8.38	0.098	0.097	0.153	6.34	0.339	0.194	34.26	0.540	0.767
C3170	11.33	55.69	7.15	2.12	3.05	7.90	0.102	0.099	0.154	6.03	0.333	0.198	35.76	0.537	0.749

4.4.1. Tensile properties

WTs of treated samples are significantly lower than that of the control sample shown in Table 4-3. Thus, the treated fabrics suffer from a severe tensile loss after the wrinkle-resistant treatment. During the treatment, DMDHEU reacts with hydroxyl groups on the cellulose chains to form crosslink through etherification. The crosslink restricts the movement of cellulose chains when stress is applied. Stress and stains imposed on the fibres during mechanical deformation are less able to be distributed. This causes the loss of tensile strength. Compared with various curing temperatures, WT decreases moderately upon the change of curing temperature from 110ºC to 170ºC. A higher curing temperature results in better effectiveness in the crosslinking reaction as the crosslinks formed are more extensive. Thus, the lowest WTs are acquired at the curing temperature of 170ºC. Moreover, when the curing time is increased from 1 minute to 3 minutes, the WTs are slightly reduced. Therefore, higher temperature environment and longer curing time give sufficient energy and time to activate and carry out crosslinking reaction. Furthermore, WTs of the samples treated in the presence of TiO_2 are slightly reduced compared with those of the samples treated without TiO_2. The TiO_2 particles theoretically attach on the fabric surface without any chemical bonding. TiO_2 particles should not have a great effect on tensile properties of the treated fabrics (Lam et al., 2011c). However, TiO_2 probably acts as a Lewis acid catalyst to enhance the effectiveness of crosslinking reaction resulting in a lower WT.

In addition to WT, RT is another factor that has been measured and discussed. The untreated control sample possesses the lowest RT value. The gain in RT after treatment is due to the crosslink formation, which improves the recovery ability of the fabric. In addition, an increasing trend of RT with respect to the change in curing temperature from 110 to 170ºC is observed. The observed pattern can be explained by the degree of crosslink formation. At a higher curing temperature, crosslink formation was more extensive. The extensive crosslinks that restrict the movement of cellulose chains help the fabric to regain their original shape after the removal of forces applied. Besides, lengthening the curing time can also gradually improve the RT properties. In addition, the presence of TiO_2 in the treatment slightly enhances the recovery ability at higher curing temperature. The higher concentration of TiO_2, the greater the RT values are. Therefore, the TiO_2 particles not only acted as a co-catalyst in the crosslinking reaction, but also attached on the fabric surface and in-between the fibres and resisted the applied tensile stress.

Apart from WT and RT, EMT is the third parameter about tensile properties. The untreated control sample has the highest value of EMT. The drop of EMT of treated samples is owing to the formation of crosslinks after the wrinkle-resistant finishing. The elongation of the fabrics is limited by the presence of crosslinks. Curing at a high temperature also tenders the cellulosic fibres, causing the drop of EMT (Lam et al., 2011c). The curing time do not show a considerable effect to the EMT. The EMT values fall into a narrow range. Moreover, EMTs of the samples treated in the presence of TiO_2 are comparable with those treated in the absence of TiO_2. Therefore, the effect of TiO_2 to the EMT property is also negligible.

4.4.2. Shearing properties

Shearing rigidity, also known as shear stiffness (G), shear stress at 0.5^o (2HG) and shear stress at 5^o (2HG5) are usually used to assess the shearing properties of a fabric. The experimental results are listed in Table 4-3. The control specimen has the lowest G value among the tested specimen. The increase in G values after the wrinkle-resistant treatment implies stiffer hand feel of fabrics. However, it is unexpected that G values of samples treated at curing temperature of 110 ºC recorded are generally the highest. One possible postulation for such phenomenon is that the unreacted chemicals remains on the fabric surface increased the yarn interaction. The curing temperature of 110 and 130ºC could not provide sufficient energy for activation of the reaction and crosslink formation so that the chemicals remained on the fabric surface and physically altered the shear properties. Another pattern can be observed is that the G values fall gradually with respect to the curing temperature from 110 to 150 ºC and slightly rebound at 170ºC. This shows that curing at 150 ºC is an optimum curing temperature in order to reduce the shear rigidity and keep the fabrics as soft as possible. However, the increase in curing time does not show a great effect to the G. The G values obtained are similar. Moreover, the presence of TiO_2 in the treatment causes a slightly higher G which is meant that the hand feel of fabric become stiffer. The increase in G in the presence of TiO_2 may promote the crosslinking reaction to take place.

Besides, the control sample possesses the highest value of 2HG while the control sample has the lowest value of 2HG5 among the tested specimen. At the 0.5^{o} shear angle, the shear recovery ability is promoted after the wrinkle-resistant treatment. The treated fabrics with lower values of shear hysteresis represent the satisfactory recovery ability. The crosslinks formed between DMDHEU and cellulose restrict the movement of cellulose chains when shear stress is applied. The fabrics restore to its original shape easily. Conversely, at the 5^{o} shear angle, the shear recovery ability becomes worse than the control sample. It is probably due to the permanent distortion of the fabrics. The fabrics may not able to return to its original shape easily resulting in the higher 2GH5. In addition, the fabric recovery ability is highly correlated to the curing temperature used in the treatment. A decreasing trend is observed when the curing temperature is increased from 110 to 170ºC for both 2HG and 2GH5. The presence of TiO_2 in the treatment slightly reduces the fabric recovery ability such that there is little promotion in 2HG and 2GH5 results.

4.4.3. Bending properties

The control sample has the highest B value and 2HB value. This implies that the control sample is resistant to bending but it has poor recovery ability compared with the treated samples. The possible reason for the drop of B of treated samples is due to the dominant effect of thermal curing treatment under acidic condition and the presence of surfactant in the finishing agent. The crosslink formed during the treatment should increase the interaction between fibres and yarns and resulted in an increase of B and 2HB (Sun & Stylios, 2012). However, some reasons cause the drop of B value. The acidic environment causes some irreversible depolymerisation of cellulose fibres. In addition, the surfactant used acts as softener to decrease the friction between inter-fibre and inter-yarn movement (Hassan, 2005; Sun & Stylios, 2012). On the other hand, the treated fabrics possess better recovery ability, i.e. lower B value, because of the presence of crosslinks preventing from distortion. The influence of irreversible depolymerisation as well as the formation of crosslinks is more significant at the curing temperature of 150 and 170ºC. Therefore, the higher the curing temperature, the lower values of B and 2HB are. Thus, the fabrics treated at the temperature of 170ºC without TiO_2 have the lowest B. The change of curing time does not show obvious differences. The curing temperature is the main factor that determines the bending properties of the fabrics. Furthermore, 0.1% TiO_2 also does not show significant effect to the bending properties. However, when the concentration of TiO_2 is raised to 0.2% in the treatment, the result generally reveals the increase in the B and 2HB values especially at the higher curing temperature. This can be explained by the attachment of TiO_2 particles on the fibre surface that increases the interaction between fibres and yarns. The movement of yarns and fibres may be restricted. Thus, B and 2HB values are promoted.

4.4.4. Compressional properties

As the fabric thickness is varied after physical and chemical treatment, the fabric thickness is measured at three distinct points by KES-F system with a pressure of 0.5 gf/cm^2 and 5.0 gf/cm^2, which correspond to appearance thickness (T_o) and intrinsic thickness (T_m). The measured T_o and T_m is shown in Table 4-3. T_o of the treated fabrics without TiO_2 is increased by about 5.5% in average compared with the control sample. The increase is due to the chemical changes on the fibre surface after the treatment. The thickness of fabric, which was cured at temperature of 170^{o}C, usually is the thickest. This shows that the reaction is more favourable at the high temperature. Besides, the presence of TiO_2 adhered on the surface further increases the thickness of the fabrics. Higher concentration of TiO_2 leads to the thicker fabric thickness. Conversely, T_m of the treated fabrics is lowered than that of the control sample. The T_m is reduced about 5%. It can be explained by the fact that the wet treatment done on the fabrics especially involving high temperature drying process decreases the intrinsic thickness of the fabrics (Lam et al., 2011d). T_m of the fabrics treated in the presence of TiO_2 is thickened compared with those treated without TiO_2 particles. In short, the change of curing temperature and curing time only demonstrated a moderate variation to T_o and T_m of the fabrics. However, the presence of TiO_2 on the fabric surface dominated the change of thickness after the treatment.

After analysed the fabric thickness, LC, WC, and RC are discussed. LC is decreased after the treatment. The reduction of LC is caused by the heat treatment which weakens the compressional properties. The fabrics become less rigid after the treatment. The acidic environment causes some irreversible depolymerisation of cellulose which damages the originality of the fibres leading to the drop of LC values (Lam et al., 2011c; Sun & Stylios, 2012). The LC values have limited variation when the curing temperature is rose from 110 to 170ºC. For the fabrics cured at 170°C generally have the a bit lower LC value. Moreover, for the fabrics treated in the presence of TiO_2, the LC values do not show obvious differences to those fabrics treated in the absence of TiO_2. Thus, TiO_2 has no effect on LC values.

On the other hand, the WC values are increased after the treatment. The promotion of WC is owing to the formation of crosslinks between DMDHEU and cellulose fibres which increases the T_o of fabric. The thicker the fabrics, the higher compressional energy is required to reach a given loading (Sun & Stylios, 2012). Thus, an improvement of WC is observed. As the fabric cured at temperature of 170°C is generally thicker mentioned above, the WCs of those fabrics are generally higher. However, the change of curing time does not cause a dramatic variation to the WT. In addition, the WC of the fabrics treated in the presence of TiO_2 has further increased compared with those fabrics treated without TiO_2. TiO_2 attached on the fabrics surface increases the thickness of the fabrics. The higher the concentration of TiO_2 used in the treatment, the thicker the fabrics are, leading to higher WC values.

RC is the last parameter studied in the compressional properties. RC values of fabrics are remarkably reduced after the treatment. The compressional recovering ability of the fabrics loses. This illustrates the less spongy property. The spongy effect of the fabrics is reduced by the attack of acid during the wrinkle-resistant treatment (Sun & Stylios, 2012). The change of curing temperature and curing time show some variations to RC. Moreover, after adding of TiO_2 particles, the RC values are further lowered as the effectiveness of the reaction is enhanced in the presence of TiO_2. This leads to inelastic compression property and cause the lower values of RC.

4.4.5. Surface properties

Hand, comfort, and aesthetic properties of the fabric are influenced by the surface characteristic of fabrics. The results of MIU and SMD are shown in the Table 4-3. The MIU of the control specimen is the lowest while the SMD of the control specimen is the highest among the tested specimens. Wrinkle recovery finishing causes an increase in the MIU values because DMDHEU forms crosslink with cellulose chain in the treatment altering the surface properties. The MIU values of the treated samples ranges from 0.138 to 0.162. Most of MIU measured is around 0.150. The MIU do not show a regular pattern when the curing temperature and curing time are changed. The presence of TiO_2 in the finishing agent also does not cause a significant promotion of the MIU values in the present study. However, it is believed that the presence of TiO_2 will enhanced the friction to a small extent (Lam et al., 2011c; Lam et al., 2011d). It can be explained by the uneven distribution of TiO_2 on the fabrics surface. On the other hand, the lowered SMD shows the treated samples have a more even surface than the control one after chemical modification treatment. The crosslink formation is evenly constructed on the fabric surface. Moreover, there is no obvious influence to SMD values using various curing temperatures and curing times. Besides, the data also shows that TiO_2 particles dispersed on the fabric surface do not cause significant unevenness of the surface. In short, there was no obvious trend for the change of fabric surface properties when the curing temperature was rose from 110 to 170ºC for different curing times. In addition, the addition of TiO_2 particles did not impose significant negative effects to the surface properties.

4.5. Conclusion

A traditional wrinkle-resistant finishing agent, DMDHEU, accompanying different formulations was used in present study. The effect of curing temperature, curing time and metal oxides on wrinkle-resistant finishing had been evaluated. It was found that the properties of the fabrics was significantly affected by the curing condition. Higher curing temperature and longer curing time resulted in a better wrinkle recovery performance but with worse tear strength and causing yellowing of the fabrics. Nevertheless, the addition of TiO_2 in the formulation could improve the wrinkle recovery properties. It was important to strike a balance between the gain of wrinkle recovery performance and the loss of tear strength under high temperature thermal treatment. Therefore, an optimized condition was recommended. The fabric was recommended to be cured at 150°C for 2 minutes in the presence of 0.1% TiO_2. At this curing condition, the improvement of WRA was maximized and the tear strength loss was minimized. Besides, a novel application was investigated in this thesis. If 0.1% TiO_2 and ZnO were used as co-catalyst in the treatment with curing temperature of 150°C and curing time of 1 minute, the wrinkle recovery performance and tear strength can be further improved.

Besides, fabric hand is a critical physical property of fabrics when making the choice of fabrics. Therefore, intensive investigation of low stress mechanical properties helped us to assess and control the apparel fabrics. The objective measurement of low stress mechanical properties had been investigated by KES-F. After the wrinkle-resistant finishing, the change of low stress mechanical properties mainly depended on the formation of crosslink between DMDHEU and cellulose chains, and the acidic medium used in the treatment. This changed the inter-yarn and inter-fibre interaction resulting in different alteration in low stress mechanical properties. There were obvious influences to tensile, shearing and bending properties when the curing temperature changed from 110 to 170 ºC. Surface and compression properties did not show a significant variation. The use of TiO_2 particles in the treatment showed that the performance of the low stress mechanical properties of fabrics was influenced to a certain extent, especially in term of compression properties.

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Chapter 5: Flame-retardant finishing of cotton fabric

5.1. Introduction

In addition to wrinkle-resistant finishing, flame-retardant finishing is another finishing that is widely applied in our life because cotton cellulose is sensitive to fire causing fatalities. Cellulose has a characteristic structure and chemical composition so that it can interactive with flame-retardant chemicals to equip with flame-retardant property.

Pyrovatex CP NEW was used as a durable flame-retardant agent in the present study. It is a fibre reactive organic phosphorus compound. This kind of flame-retardant is operated by condensed phase mechanism to impart flame-retardant properties on cotton fabric. Pyrovatex CP NEW can react with cotton cellulose directly to form linkage under acid-catalysed conditions. A melamine resin called Knittex CHN is usually applied together with the flame-retardant agent which can enhance the performance of flame-retardant properties by increasing the bonding of Pyrovatex CP NEW to cotton and increasing the nitrogen content of the product for synergistic effect with phosphorus (Kaur et al., 1986; Kandola et al., 1996; Tesoro et al., 1969; Yang, 2013). Moreover, the performance of flame-retardant properties can be further improved by addition of metal oxide such as TiO_2 or ZnO as a catalyst or co-catalyst (Lam et al., 2011b; Lam et al., 2011e). However, the details of varying the curing conditions impacting the performance of flame-retardant properties in the presence of metal oxide have not been reported. Conventionally, the curing temperature and curing time are set to be 170℃ for 1 minute (Horrocks, 2003; Lam et al., 2011b; Lam et al., 2011e; Schindler & Hauser, 2004). The curing temperature and curing time were varied in the present study. The performance of the treated fabrics was comprehensively evaluated by a series of international testing methods, instrumental methods and advanced analytical techniques. In addition, half of samples were neutralized with 30g/L sodium carbonate after curing process for comparison.

5.2. Result analysis of flame-retardant finishing using Pyrovatex CP NEW

5.2.1. Fabric flammability analysis

The flammability test results of all samples are summarized in the Table 5.1 to 5.5. Sample codes are used to represent the treated fabrics and abbreviation “DNI” corresponds to “did not ignite”. The samples codes are expressed in the form of five characters. “Z” represents the fabrics treated in the absence of TiO_2. “X” and “Y” represents the fabrics treated in the presence of 0.2% and 0.4% TiO_2 respectively. Then, the first number digit refers to curing time in minute, and the last three digits refer to curing temperature in degree Celsius. For example, X2170 represents the treated fabrics cured at 170ºC for 2 minutes in the presence of 0.2% TiO_2

Table 5-1. Fabric flammability test result of control fabric

Code	No. of Laundering	Burning time (s)	Char Length (cm)	Pass/Fail
Control	--	22.01	Entirely Burned	Fail

Table 5-2. Fabric flammability test result of treated fabrics without laundering

Code	No. of Laundering	Burning time (s)	Char Length (cm)	Pass/Fail	Burning time (s)	Char Length (cm)	Pass/Fail
		No Neutralization			30 min Neutralization		
Z1170[b]	0	DNI	1.03	Pass	DNI	0.78	Pass
Z1150	0	DNI	1.03	Pass	DNI	1.00	Pass
Z1130	0	DNI	0.85	Pass	DNI	1.63	Pass
Z1110	0	DNI	1.03	Pass	38.13	13.00	Fail
Z2170	0	DNI	1.00	Pass	DNI	0.70	Pass
Z2150	0	DNI	0.83	Pass	DNI	0.90	Pass
Z2130	0	DNI	1.05	Pass	DNI	0.85	Pass
Z2110	0	DNI	0.89	Pass	46.18	13.00	Fail
Z3170	0	DNI	0.88	Pass	DNI	0.85	Pass
Z3150	0	DNI	0.85	Pass	DNI	0.70	Pass
Z3130	0	DNI	0.84	Pass	DNI	0.80	Pass
Z3110	0	DNI	0.83	Pass	42.75	13.00	Fail
X1170	0	DNI	0.75	Pass	DNI	0.65	Pass
X1150	0	DNI	0.77	Pass	DNI	0.61	Pass
X1130	0	DNI	0.78	Pass	47.13	9.93	Pass
X1110	0	DNI	0.87	Pass	45.15	13.00	Fail
X2170	0	DNI	0.90	Pass	DNI	0.55	Pass
X2150	0	DNI	0.90	Pass	DNI	0.55	Pass
X2130	0	DNI	0.83	Pass	DNI	0.69	Pass
X2110	0	DNI	0.83	Pass	45.80	13.00	Fail
X3170	0	DNI	0.83	Pass	DNI	0.71	Pass
X3150	0	DNI	0.80	Pass	DNI	0.63	Pass
X3130	0	DNI	0.77	Pass	DNI	0.65	Pass
X3110	0	DNI	0.80	Pass	52.15	11.28	Pass
Y1170	0	DNI	0.98	Pass	DNI	0.71	Pass
Y1150	0	DNI	0.88	Pass	DNI	0.66	Pass
Y1130	0	DNI	0.80	Pass	DNI	0.93	Pass
Y1110	0	DNI	0.85	Pass	42.93	13.00	Fail
Y2170	0	DNI	0.93	Pass	DNI	0.70	Pass
Y2150	0	DNI	0.95	Pass	DNI	0.71	Pass
Y2130	0	DNI	0.73	Pass	DNI	0.75	Pass
Y2110	0	DNI	0.88	Pass	44.25	7.89	Pass
Y3170	0	DNI	0.85	Pass	DNI	0.74	Pass
Y3150	0	DNI	0.83	Pass	DNI	0.65	Pass
Y3130	0	DNI	0.73	Pass	DNI	0.70	Pass
Y3110	0	DNI	0.80	Pass	42.03	10.60	Pass

Table 5-3. Fabric flammability test result of treated fabrics with 1-time laundering

Code	No. of Laundering	Burning time (s)	Char Length (cm)	Pass/Fail	Burning time (s)	Char Length (cm)	Pass/Fail
		No Neutralization			30 min Neutralization		
Z1170[b]	1	DNI	0.73	Pass	DNI	0.80	Pass
Z1150	1	DNI	0.93	Pass	DNI	0.76	Pass
Z1130	1	43.00	10.40	Fail	45.58	11.13	Fail
Z1110	1	42.68	10.75	Fail	37.93	10.20	Fail
Z2170	1	DNI	1.06	Pass	DNI	0.76	Pass
Z2150	1	DNI	1.10	Pass	DNI	0.81	Pass
Z2130	1	DNI	0.95	Pass	DNI	0.55	Pass
Z2110	1	49.98	10.83	Fail	41.73	9.65	Fail
Z3170	1	DNI	1.13	Pass	DNI	0.81	Pass
Z3150	1	DNI	1.18	Pass	DNI	0.84	Pass
Z3130	1	DNI	1.68	Pass	DNI	0.69	Pass
Z3110	1	51.50	10.85	Fail	44.20	8.80	Fail
X1170	1	DNI	0.70	Pass	DNI	0.80	Pass
X1150	1	DNI	0.68	Pass	DNI	0.68	Pass
X1130	1	DNI	0.70	Pass	33.25	7.43	Pass
X1110	1	49.08	10.90	Fail	37.53	10.55	Fail
X2170	1	DNI	0.73	Pass	DNI	0.75	Pass
X2150	1	DNI	0.63	Pass	DNI	0.68	Pass
X2130	1	DNI	0.70	Pass	DNI	0.59	Pass
X2110	1	36.80	6.88	Pass	54.28	11.08	Fail
X3170	1	DNI	0.78	Pass	DNI	0.68	Pass
X3150	1	DNI	0.68	Pass	DNI	0.53	Pass
X3130	1	DNI	0.74	Pass	DNI	0.56	Pass
X3110	1	53.65	10.00	Pass	47.83	11.03	Fail
Y1170	1	DNI	0.75	Pass	DNI	0.70	Pass
Y1150	1	DNI	0.88	Pass	DNI	0.55	Pass
Y1130	1	50.18	11.33	Fail	17.90	3.53	Fail
Y1110	1	46.65	11.25	Fail	37.20	11.30	Fail
Y2170	1	DNI	0.78	Pass	DNI	0.83	Pass
Y2150	1	DNI	0.75	Pass	DNI	0.81	Pass
Y2130	1	DNI	0.95	Pass	DNI	0.53	Pass
Y2110	1	40.30	10.43	Fail	48.90	9.69	Fail
Y3170	1	DNI	0.73	Pass	DNI	0.76	Pass
Y3150	1	DNI	0.75	Pass	DNI	0.68	Pass
Y3130	1	DNI	0.95	Pass	DNI	0.98	Pass
Y3110	1	42.10	10.60	Fail	35.40	10.68	Fail

Table 5-4. Fabric flammability test result of treated fabrics with 3-time laundering

Code	No. of Laundering	Burning time (s)	Char Length (cm)	Pass/Fail	Burning time (s)	Char Length (cm)	Pass/Fail
		No Neutralization			30 min Neutralization		
Z1170[b]	3	39.58	8.43	Pass	DNI	0.78	Pass
Z1150	3	38.63	9.13	Pass	DNI	0.80	Pass
Z1130	3	46.18	11.00	Fail	49.30	10.78	Fail
Z1110	3	45.93	12.25	Fail	37.40	10.45	Fail
Z2170	3	DNI	0.93	Pass	DNI	0.73	Pass
Z2150	3	DNI	0.75	Pass	DNI	0.60	Pass
Z2130	3	45.38	9.00	Pass	DNI	0.83	Pass
Z2110	3	39.88	10.78	Fail	38.73	10.25	Fail
Z3170	3	DNI	0.70	Pass	DNI	0.65	Pass
Z3150	3	DNI	0.71	Pass	DNI	0.73	Pass
Z3130	3	51.23	11.38	Pass	DNI	0.79	Pass
Z3110	3	43.08	9.83	Pass	50.23	11.10	Fail
X1170	3	DNI	0.75	Pass	DNI	0.85	Pass
X1150	3	DNI	0.70	Pass	DNI	0.64	Pass
X1130	3	33.40	5.83	Pass	DNI	1.30	Pass
X1110	3	48.78	11.38	Fail	39.75	10.48	Fail
X2170	3	DNI	0.75	Pass	DNI	0.68	Pass
X2150	3	DNI	0.83	Pass	DNI	0.78	Pass
X2130	3	15.48	2.53	Pass	DNI	0.76	Pass
X2110	3	55.13	11.35	Fail	41.78	10.95	Fail
X3170	3	DNI	0.90	Pass	DNI	0.70	Pass
X3150	3	DNI	0.95	Pass	DNI	0.78	Pass
X3130	3	DNI	1.00	Pass	DNI	0.53	Pass
X3110	3	53.85	11.65	Fail	42.73	10.83	Fail
Y1170	3	DNI	0.83	Pass	DNI	0.74	Pass
Y1150	3	DNI	0.85	Pass	DNI	0.64	Pass
Y1130	3	45.93	11.20	Fail	30.23	5.88	Pass
Y1110	3	43.88	11.43	Fail	38.60	10.50	Fail
Y2170	3	DNI	0.86	Pass	DNI	0.81	Pass
Y2150	3	DNI	0.78	Pass	DNI	0.71	Pass
Y2130	3	DNI	0.70	Pass	DNI	0.84	Pass
Y2110	3	37.43	12.50	Fail	46.88	10.98	Fail
Y3170	3	DNI	0.79	Pass	DNI	0.78	Pass
Y3150	3	DNI	0.65	Pass	DNI	0.65	Pass
Y3130	3	DNI	0.75	Pass	DNI	0.79	Pass
Y3110	3	50.05	11.53	Fail	40.25	10.70	Fail

Table 5-5. Fabric flammability test result of treated fabrics with 5-time laundering

Code	No. of Laundering	Burning time (s)	Char Length (cm)	Pass/Fail	Burning time (s)	Char Length (cm)	Pass/Fail
		No Neutralization			30 min Neutralization		
Z1170[b]	5	54.43	12.28	Fail	DNI	1.13	Pass
Z1150	5	43.70	11.55	Fail	DNI	0.90	Pass
Z1130	5	64.33	11.83	Fail	53.95	11.18	Fail
Z1110	5	42.45	11.10	Fail	42.53	10.03	Fail
Z2170	5	52.10	11.13	Fail	DNI	0.85	Pass
Z2150	5	44.55	11.15	Fail	DNI	0.65	Pass
Z2130	5	47.68	12.35	Fail	DNI	0.93	Pass
Z2110	5	45.15	11.25	Fail	45.65	10.63	Fail
Z3170	5	DNI	0.78	Pass	DNI	0.78	Pass
Z3150	5	45.70	11.95	Fail	DNI	0.73	Pass
Z3130	5	39.33	9.45	Fail	DNI	0.90	Pass
Z3110	5	47.25	11.25	Fail	45.13	10.83	Fail
X1170	5	DNI	0.70	Pass	DNI	0.68	Pass
X1150	5	10.98	2.55	Pass	DNI	0.60	Pass
X1130	5	47.58	11.18	Fail	38.78	7.88	Pass
X1110	5	48.90	11.30	Fail	42.78	9.53	Fail
X2170	5	DNI	1.18	Pass	DNI	0.58	Pass
X2150	5	DNI	0.88	Pass	DNI	0.58	Pass
X2130	5	35.05	7.45	Fail	DNI	0.85	Pass
X2110	5	49.15	11.20	Fail	40.03	12.60	Fail
X3170	5	DNI	0.70	Pass	DNI	0.75	Pass
X3150	5	DNI	1.48	Pass	DNI	0.65	Pass
X3130	5	19.20	4.13	Pass	DNI	0.65	Pass
X3110	5	49.48	11.13	Fail	45.70	11.58	Fail
Y1170	5	DNI	0.70	Pass	DNI	0.78	Pass
Y1150	5	28.28	5.13	Pass	DNI	0.75	Pass
Y1130	5	46.48	11.23	Fail	32.18	5.95	Pass
Y1110	5	43.48	10.80	Fail	43.70	10.83	Fail
Y2170	5	DNI	0.60	Pass	DNI	0.65	Pass
Y2150	5	DNI	0.70	Pass	DNI	0.73	Pass
Y2130	5	49.45	11.05	Fail	DNI	0.78	Pass
Y2110	5	34.23	10.15	Fail	43.83	11.48	Fail
Y3170	5	DNI	0.73	Pass	DNI	0.63	Pass
Y3150	5	DNI	1.10	Pass	DNI	0.60	Pass
Y3130	5	DNI	0.98	Pass	DNI	0.70	Pass
Y3110	5	40.10	10.88	Fail	42.30	10.33	Fail

5.2.1.1. Effect of curing temperature and curing time on the flammability

The tables of fabric flammability test results include two important factors that are burning time and char length. The burning time shows the ease of ignition and the ability to sustain the combustion process. Char length refers to the burn mark on the fabric samples. If the progressive burning of a fabric at a distance of 127 mm is recorded or the flame travels up the specimen and the stop thread is broken, the fabric is assumed to have failed the test. If the flame self-extinguishes when traveling along the fabrics without breaking the stop thread, the fabrics are said to be pass.

The test result of control fabric is shown in Table 5-1. The control fabric was burned vigorously and the burning time was found to be 22.01s. The control fabrics is said to be fail in resistance to the flame. There was no burn mark remained on the fabric surface as the cotton fabric was entirely burned out. Table 5-2 shows the fabric flammability test results of the treated fabric without home laundering. All treated fabrics did not ignite after flame-retardant treatment before neutralization. The flame extinguished right after the removal of ignition source without spreading of the flame. The char lengths, which ranged from 0.7-1.15 cm, left on each fabric. These fabrics are classified as flame-retarded fabric. The char residues are caused by thermal decomposition of fabrics. Equation (1) shows the one of pyrolysis route of cotton which is dehydration process. Dehydration of cellulose occurs and carbonaceous residue is left. This process favours at lower temperature (Lam et al., 2011b; Siriviriyanun et al., 2008b).

$$(C_6H_{10}O_5)x \rightarrow 6x\ C + 5x\ H_2O \qquad (1)$$

As a matter of fact, there is another pyrolysis route which can proceed via the formation of levoglucan which is further broken down to flammable volatiles at higher temperature. In order to prevent from forming levoglucan, phosphorus-based flame-retardant treatment facilitates the dehydration process of cotton at lower temperatures during the thermal decomposition of cotton fabrics. Therefore, promotion of char formation via dehydration process improves flame retardancy of the cotton (Lam et al., 2011a; Siriviriyanun et al., 2008).

When the fabrics were subjected to different times of home laundering, the flame-retardant ability was changed. Nearly all fabrics cured at 110ºC were ignited and allowed propagation of flame. These fabrics are classified as fail in resistance to the flame. From the results shown in Table 5-2 to 5-5, it shows that curing at temperature of 110ºC is not an appropriate temperature for flame-retardant finishing. It is probably because the flame-retardant agent and crosslinking agent can easily be removed after home laundering. The unfixed chemicals on the fabric surface were washed off during laundering process. It is expected that the reaction is not fully activated at low curing temperature resulting in low reaction effectiveness so that the chemicals cannot fix on the fabric surface. When the fabrics were subjected to repeated home laundering, the flame-retardant agent and crosslinking agent fixed on the fabric surface were also lost to a certain extent. This can be observed from the fabrics cured at 130ºC. For those fabrics cured at 130ºC, the flame-retardant ability was good before home laundering and after one time home laundering. When the fabrics were subjected to home laundering for three times, the flame-retardant ability was weakened but still acceptable. Long burn marks were remained on the fabric surface without breaking the stop thread. Further home laundering process caused loss of flame-retardant ability of the fabrics cured at 130ºC illustrated in Table 5.5. The durability of the flame-retardant finishing using curing temperature of 130ºC is not satisfactory.

For the fabrics cured at 150ºC and 170ºC, the flame-retardant ability is generally good. High curing temperature provides enough energy for activation of the reaction. The flame-retardant agent and crosslinking agent form extensive crosslinks on cotton fabric surface. This ensures a good flame-retardant ability. In the Table 5.5, the fabrics cured at 150ºC and 170ºC fail in the test after home laundering for five times unless they are subjected to neutralization post treatment and addition of TiO_2 in the formulation. This shows that neutralization post-treatment and addition of TiO_2 can improve the flame-retardant ability. It will be discussed in following section. In short, the flame-retardant treated fabrics cured at 150 and 170ºC were equipped with relatively good flame-retardant properties. Curing temperature of 150ºC was found to be better because less heat energy is consumed in the finishing process.

Apart from curing temperature, curing time is another factor that influences flame-retardant properties. The burning time is often directly proportional to the curing time shown in Table 5-3. Compared with Z1110, Z2110 and Z3110, the burning times of these fabrics are 42.7s, 50.0s, and 51.5s respectively. The longer burning time represents the propagation of fire is slow and less favourable in burning. The trend can also be observed for those fabrics after neutralization. Moreover, from the Table 5-3 to 5-5, it can generally observe that the passing rate for the fabrics cured for 3 minutes is higher than that of cured for 1 minute. A longer curing time allows more heat energy transfer for the crosslinking reaction providing sufficient reaction time. Therefore, the longer curing time used will result in a better flame-retardant ability of the fabrics.

In summary, high curing temperature and long curing time generally produced a fabric with excellent flame-retardant performance. However, using high curing temperature and long curing time will generate other problems such as tear strength loss and yellowing of the fabrics. Thus, too high curing temperature and too long curing time is not suitable for flame-retardant finishing. More factors affecting the flame-retardant and fabrics properties will be discussed.

5.2.1.2. Effect of neutralization on the flammability

Neutralization is usually done after flame-retardant treatment to remove all residual phosphorus acid catalyst, uncrosslinked phosphonamide and surface crosslinked polymer (Schindler & Hauser, 2004). The neutralization was done by treating with Na_2CO_3 at 40 – 45°C for 30 minutes followed by washing with warm water. In Table 5-2, for the fabrics neutralized for 30 minutes, there are six fabric samples which were cured at 110ºC ignited under flammability test. When the curing temperature was set to 110 ºC, the flame-retardant agent and crosslinking agent were not firmly fixed on the fabric surface and easily washed off during neutralization process and rinsing process after neutralization. The flame retardancy performance is retained for the treated fabrics cured at higher curing temperature after neutralization process.

However, more treated fabrics are qualified as flame resistance after 30 minutes neutralization listed in Table 5-5. This is meant that the flame-retardant ability of the treated fabrics is slightly improved after neutralization process. Therefore, neutralization by Na_2CO_3 has positive effect to the flammability of the fabrics. It can be explained by enhancement in fabric thickness. When cotton fabrics were immersed in the Na_2CO_3 solution, swelling occurred. After neutralization with Na_2CO_3 at 50ºC, the appearance thickness of the fabrics increased averagely about 9.82% reported in Table 5-8 in section 5.4. Song et al. reported that fabric thickness has a positive correlation with protection from flame of a material (Song et al., 2013). Thus, increase in fabric thickness can enhance the inherent flame-retardant properties even though there may be some loss of flame-retardant chemicals during neutralization. Moreover, fabrics density also played a significant role with respect to flammability (Song et al., 2013; Shalev & Barker, 1983). The fabrics became denser due to shrinkage effect of fibres. Sequentially, the fibres have more contact with each other and less air is trapped in the fabrics, resulting in increased conductive heat loss due to increased conductivity (Song et al., 2013). Therefore, the flame-retardant properties of the treated fabrics become superior after neutralization.

In short, on one hand, the aim of neutralization process was to remove all residuals on the fabric surface. At the same time, the flame-retardant chemicals that were not firmly attached on the fabric surface were washed off. This made the fabrics become easily ignited when exposed to flame. On the other hand, neutralization post-treatment was found to be have positive effect to the flammability of the fabrics due to the enhancement in fabric thickness.

5.2.1.3. Effect of titanium dioxide on the flammability

In order to improve the flammability characteristics of the product, TiO_2 was added into the formulation acting as co-catalyst. Adding TiO_2 as a co-catalyst is found to be feasible in improving fabric properties in previous studies (Lam et al., 2011b; Lam et al., 2012). The effect of TiO_2 on the flammability is apparently observed in Table 5-4 and 5-5 when the treated fabrics were subjected up to three and five times home laundering. The number of “do not ignite (DNI)” specimens is significantly increased with the inclusion of TiO_2 as the co-catalyst. There are 7 out of 12 “DNI” specimens for those treated in the presence of 0.2% and 0.4% TiO_2 whereas there are only 4 out of 12 “DNI” specimens for those treated without addition of TiO_2 shown in Table 5-4. Moreover, in Table 5-5, only one fabric treated in the absence of TiO_2 was not ignited. There are five and six “DNI” specimens for those treated in the presence of 0.2% and 0.4% TiO_2 respectively. For the Z2130, X2130 and Y2130 specimens, the burning time of Z2130 specimen was recorded as 45.4 seconds. It was greatly reduced by 65% to 15.5 seconds for X2130 specimen. Further increasing the concentration of TiO_2 to 0.4% prevented Y2130 specimen from ignition. Meanwhile, the char length was reduced by 72% when the concentration of TiO_2 was increased from 0% to 0.2%. According to the wall theory (Jolles and Jolles, 1972), if the concentration of dust presents in the air is high enough, no flame can propagate. Therefore, if there is sufficient amount of TiO_2 impregnated onto the fabric, TiO_2 may inhibit propagation of flame. Moreover, the flame-retardant performance is satisfactory for all specimens cured at 150ºC and 170ºC in the presence of 0.2% and 0.4% TiO_2. However, the improvement of flammability for samples cured at 110ºC in the presence of TiO_2 is not significant. In short, the presence of TiO_2 gave a significant improvement on the flame-retardant properties for the fabrics cured at 130ºC above.

Nevertheless, the effect of TiO_2 on flammability may be less effective after neutralization as the content of TiO_2 remained on the fabrics may be decreased. For the condition X and Y, the flame-retardant ability performance remains unchanged or even improved after neutralization shown in Table 5-4 and Table 5-5. The improvement of flame-retardant ability should be because of the effect of neutralization. There are two factors affecting the flammability based on the discussions. If the fabrics are subjected to neutralization after curing process, the factor affecting flammability is dominant by neutralization effect rather than the presence of TiO_2. Therefore, the effect of TiO_2 on flammability after neutralization becomes less significant.

To summarize, the effects of curing temperature, curing time, concentration of TiO_2 and neutralization effect, the best conditions for imparting effective flame-retardant properties are deduced. Cotton fabrics should be treated with the formulation X (in the presence of 0.2% TiO_2) and cured at 150ºC for 1 minute followed by neutralizing the residues on the fabric surface. Compared with the conventional flame-retardant finishing conditions, a reduction of 20ºC in temperature is achieved at the curing step if 0.2% TiO_2 is added as co-catalyst in the formulation.

5.2.2. Tear strength

After crosslinking treatment, the treated fabrics usually suffer from tear strength loss. Thus, the tear strength of treated fabrics was measured in units of Newton (N). The results are summarised in Table 5-6. The percentage change of non-neutralized specimens is compared with the control specimen while the percentage change of neutralized specimens is compared with the non-neutralized specimens.

The tear strength of control specimen, which did not have any pre-treatment, is 28.01N. The tearing force is significantly lowered after flame-retardant treatment which shows severe tear strength loss. The drop of tear strength is mainly attributed to the strong acidic medium, pH 1-2, in the formulation (Lam et al., 2011a; Lam et al., 2011b). The presence of phosphorus acid causes the low pH value and tenders the fabric strength. The occurrence of acid hydrolysis will result in breaking down of cellulose chains. Moreover, the curing step carrying out at high temperature will cause brittleness in cotton fibres that lowers the tear strength (Lam et al., 2011a; Lam et al., 2011b). In addition, tear strength dropped after the flame-retardant treatment is due to fabric stiffening, generally caused by affording high levels of phosphorus coating on weight of fabrics (Fung & Hardcastle, 2001).

There is a decreasing trend of the tearing force for curing temperature from

110°C to 170°C presented in Figure 5-1. When the curing time is increased, the lower tearing force will be obtained. The number of crosslink formed is expected to be greater and the reaction effectiveness is better in higher curing temperature and longer curing time. Thus, at the higher curing temperature and longer curing time, the loss of tear strength is relatively more significant owing to the extensive crosslink formation.

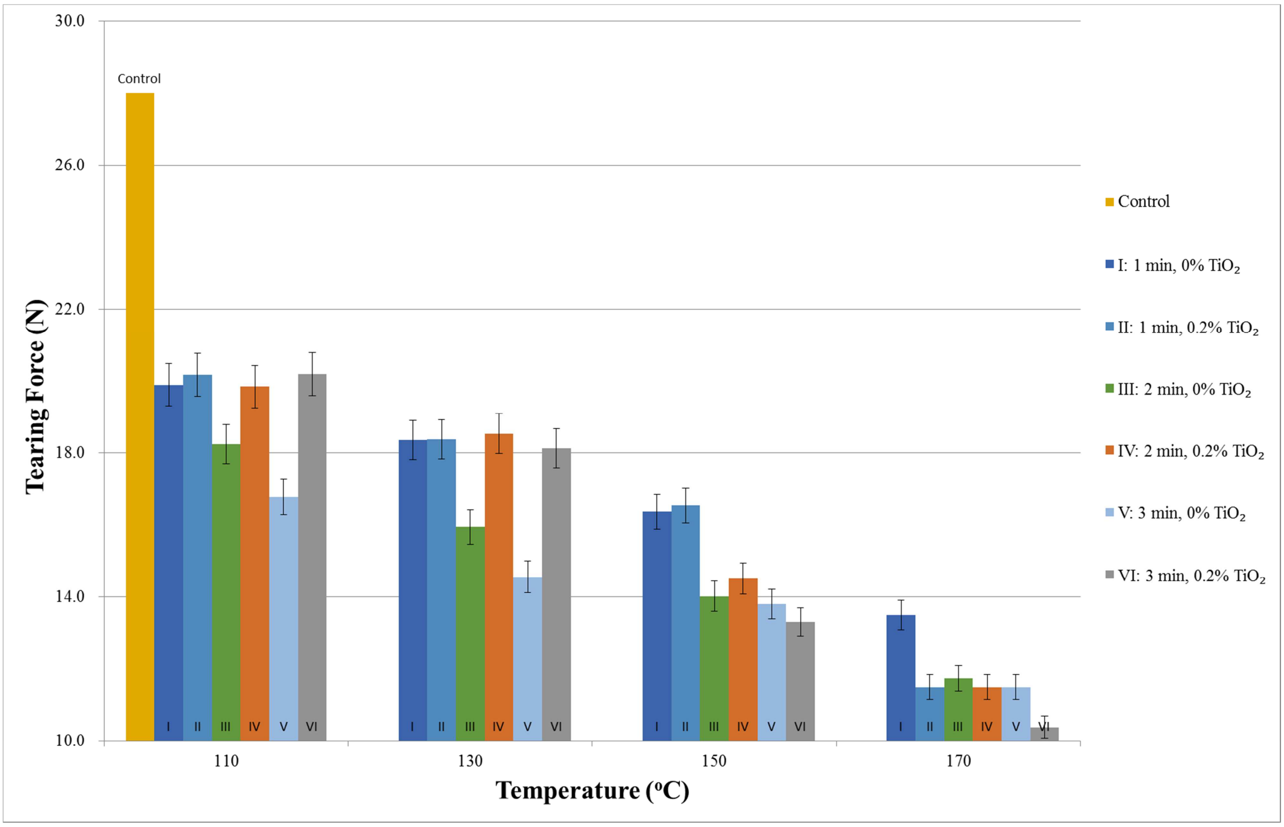

Figure 5-1. Tearing force of the fabrics treated in different concentration of TiO_2 and cured at different temperatures and times

Table 5-6. Tearing force of treated fabrics

Code	Tearing Force (N)	Percentage change [a]	Tearing Force (N)	Percentage change [b]
	No Neutralization		30 min Neutralization	
Control	28.01		--	--
Z1170	13.50	-51.81%	14.25	5.61%
Z1150	16.37	-41.55%	14.12	-13.78%
Z1130	18.36	-34.47%	15.83	-13.78%
Z1110	19.89	-28.98%	17.71	-10.98%
Z2170	11.73	-58.11%	12.33	5.04%
Z2150	14.01	-49.97%	14.86	6.05%
Z2130	15.94	-43.11%	16.22	1.78%
Z2110	18.24	-34.88%	16.07	-11.89%
Z3170	11.49	-58.99%	11.59	0.93%
Z3150	13.80	-50.72%	14.42	4.49%
Z3130	14.56	-48.03%	15.73	8.05%
Z3110	16.78	-40.11%	17.90	6.72%
X1170	11.50	-58.96%	12.03	4.63%
X1150	16.54	-40.95%	12.80	-22.59%
X1130	18.38	-34.39%	14.10	-23.28%
X1110	20.17	-27.99%	16.01	-20.62%
X2170	11.50	-58.96%	11.43	-0.57%
X2150	14.51	-48.18%	12.49	-13.95%
X2130	18.53	-33.85%	13.08	-29.40%
X2110	19.85	-29.15%	14.91	-24.88%
X3170	10.39	-62.92%	10.81	4.12%
X3150	13.30	-52.50%	12.43	-6.58%
X3130	18.13	-35.27%	13.05	-28.03%
X3110	20.19	-27.92%	14.90	-26.22%
Y1170	13.11	-53.19%	13.10	-0.10%
Y1150	15.00	-46.43%	13.30	-11.33%
Y1130	17.48	-37.60%	14.57	-16.67%
Y1110	20.79	-25.77%	14.40	-30.75%
Y2170	12.13	-56.70%	11.46	-5.54%
Y2150	14.93	-46.71%	13.40	-10.25%
Y2130	15.94	-43.09%	14.13	-11.38%
Y2110	19.17	-31.56%	15.34	-19.95%
Y3170	10.87	-61.20%	11.11	2.19%
Y3150	13.46	-51.95%	12.73	-5.42%
Y3130	15.05	-46.28%	13.98	-7.07%
Y3110	19.25	-31.28%	15.04	-21.87%

[a]: % change compared with control; [b]: % change compared with non-neutralized specimens

Moreover, the presence of TiO_2 will influence the tear strength of the fabrics. When the fabrics were treated in the presence of TiO_2 at high curing temperatures of 170ºC, the loss of tear strength was severer than that of treated in the absence of TiO_2. Such discrepancy is probably caused by the promotion of effectiveness of crosslinking reaction by TiO_2. The TiO_2 in the finishing solution enhances the crosslinking reaction as a co-catalyst to improve the crosslinking performance. This make the tear strength become worse. However, at lower curing temperatures of 110ºC to 150ºC, the tearing forces of fabrics treated in the presence of 0.2% TiO_2 were superior to the fabric treated in the absence of TiO_2. At the low curing temperature, the crosslinking reaction is not as effective as that of carrying out at 170ºC. However, TiO_2 particles attached on the surface increase the yarn friction resulting in a better tearing force. Further increase to 0.4% TiO_2 induces a similar result as 0.2% TiO_2. The flame-retardant finishing reduces the tear strength of the fabric unavoidably. Nevertheless, the addition of 0.2% TiO_2 reduces and compensates the loss of tear strength for the fabrics cured at lower temperature such as 150ºC. Thus, TiO_2 helps minimise the side effect of the flame-retardant treatment, i.e. loss in tear strength.

The tearing forces of the treated fabrics after neutralization post-treatment are listed in Table 5-6. Most of the fabrics acquire a worse tearing force after neutralization compared with the non-neutralized one. The neutralization process is carried out at 50ºC. Such temperature and alkali treatment cause further deterioration of tear strength. However, it is interesting to note that the fabric cured at 170ºC has little improvement in tear strength after neutralization process. One postulation for such phenomenon is that the fabrics treated at high temperature is well coated and crosslinked with flame-retardant agent and crosslinking agent. Further chemical treatment does not cause significant change on the tear strength.

5.2.3. Whiteness of Textiles

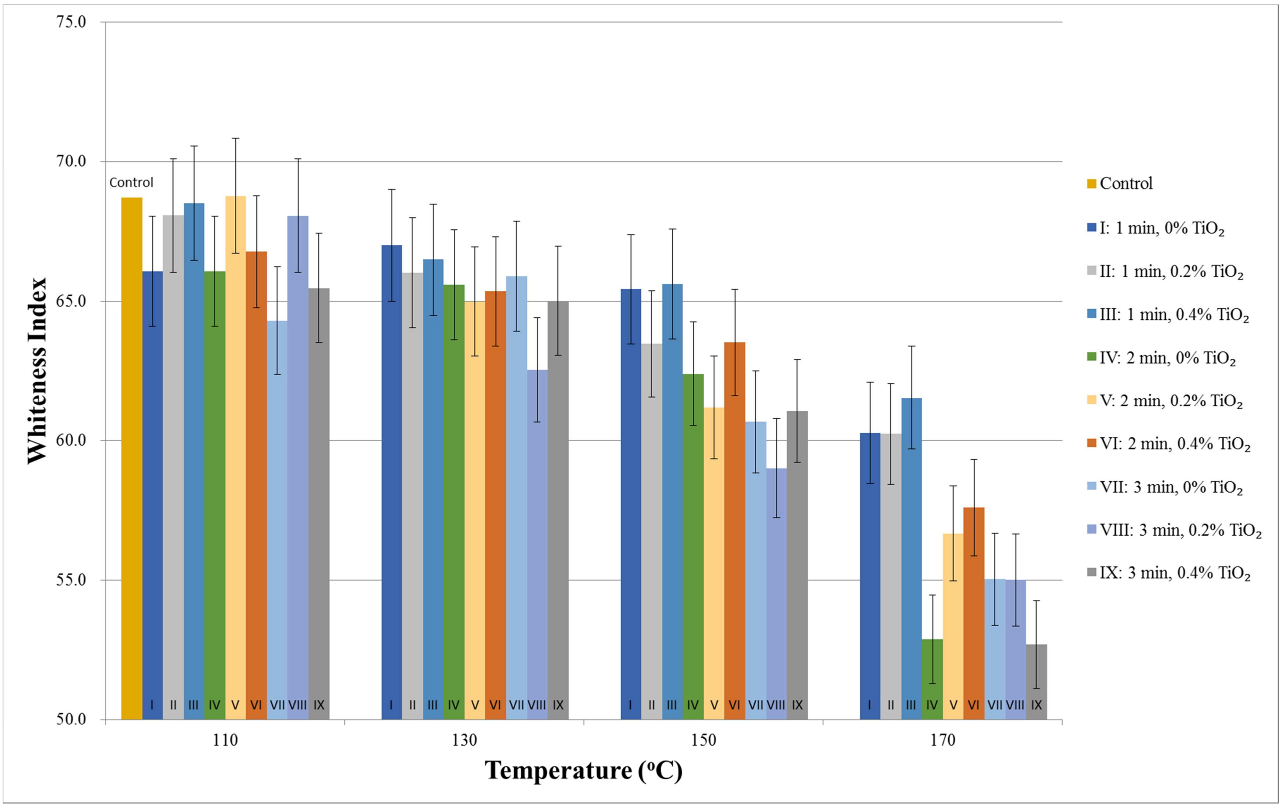

Figure 5-2. Whiteness index of the fabrics treated in different concentration of TiO_2 and cured at different temperatures and times

The whiteness of textile fabric is expressed as whiteness index which refers to the attribute of colour perception by which an object colour being judged to approach the preferred white. The whiteness index of the fabrics after flame-retardant finishing is illustrated in Figure 5-2. The fabrics were treated in the presence of 0%, 0.2% and 0.4% TiO_2 under different conditions respectively. The whiteness index falls into a range between 50 and 70. The first yellow bar represents the control sample without any pre-treatment where the whiteness index is recorded as 69. The whiteness index gradually decreases with the increasing curing temperature from 110°C to 170°C and curing time in both these figures. The fabrics treated at 170 ºC get the lowest whiteness index. The decrease in whiteness index at a high temperature is because of thermal degradation of cotton. When cotton fabric is heated above 140ºC or even higher temperatures, cellulose breaks down into small carbon substances with carbonyl functionalities, resulting in the fabric yellowing (Schindler & Hauser 2004; Horrocks 2003).

Moreover, the fabrics suffer from more serious yellowing for longer thermal treatment. Higher curing temperatures and longer curing time lead to more serious yellowing. Therefore, fabrics treated at the highest curing temperature and the longest curing time resulted in the lowest whiteness index.

The whiteness index remains steady at curing temperature 110°C and 130°C as the reaction at that temperature may not be fully activated and favourable. The highest whiteness indexes are usually recorded at curing temperature 110°C may be due to the presence of TiO_2 causing whitening of the fabrics. However, no significant variation of whiteness was observed, in relation to the concentration of TiO_2 when the curing temperature was increased from 130ºC to 170ºC. Therefore, the use of TiO_2 as co-catalyst did not trigger negative effects to the whiteness of fabrics when compared with conventional flame-retardant treatment, i.e. curing temperature of 170ºC and curing time of 1 minute..

5.2.4. Proposed role of titanium dioxide in the flame-retardant treatment

From the physical aspect, the TiO_2 particles adhered on the fabric surface that can physically retard the propagation of flame according to Wall theory (Jolles and Jolles, 1972), discussed in section 5.2.1.3. The theory mentions that if the concentration of dust presented in the air is high enough, no flame can propagate. Therefore, if there is sufficient amount of TiO_2 impregnated onto the fabric, TiO_2 may inhibit or retard propagation of flame.

From the chemical aspect, TiO_2 is a transition metal that is usually used as catalyst in the reaction. Since the TiO_2 is not at the same phase with the reagent used in the study, the TiO_2 acts as heterogeneous catalyst. Heterogeneous catalysis involves adsorption and desorption during the reaction. As reported by many previous studies (Bahruji et al., 2013; Leon et al., 2014; Nuhu, 2009), the ethanol adsorption and desorption on TiO_2 where TiO_2 acts as catalyst was widely studies. Here proposed that the hydroxyl group on the Pyrovatex CP NEW, melamine resin and cellulose can probably adsorb on the TiO_2 surface in a certain extent. The surface of TiO_2 catalyst is made up of basic site and the acidic site. When the hydroxyl group adsorb on the TiO_2 surface, this may assist the propagation of the reaction. As shown by the Figure 5-3, the reaction intermediates are stabilized by TiO_2. When two molecules combine together, they form an ether linkage and produce the product as demonstrated in the section 2.3.4, Figure 2-16. After desorption, TiO_2 remains unchanged in chemical nature and adheres and remains on the fabrics surface. However, TiO_2 is only a co-catalyst in the reaction system. The proposed mechanism is probably carried out in small extent due to the presence of main catalyst, phosphoric acid. The proposed mechanism is deduce from the ethanol adsorption and desorption properties (Nuhu, 2009) and have not confirmed by any analytical technique.

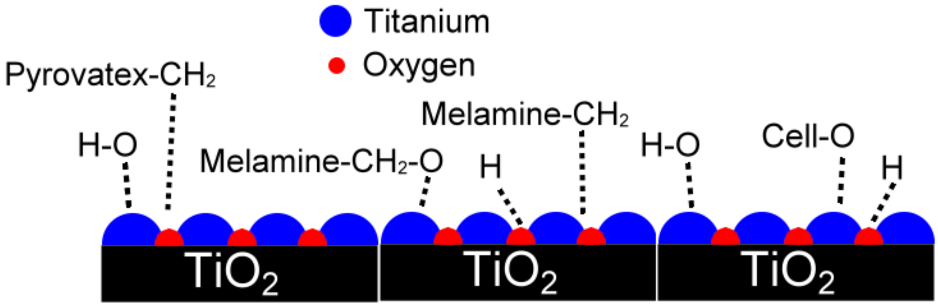

Figure 5-3. Proposed reaction mechanism of flame-retardant treatment

5.3. Structural properties of flame-retardant treated fabrics

5.3.1. Scanning Electron Microscopy (SEM)

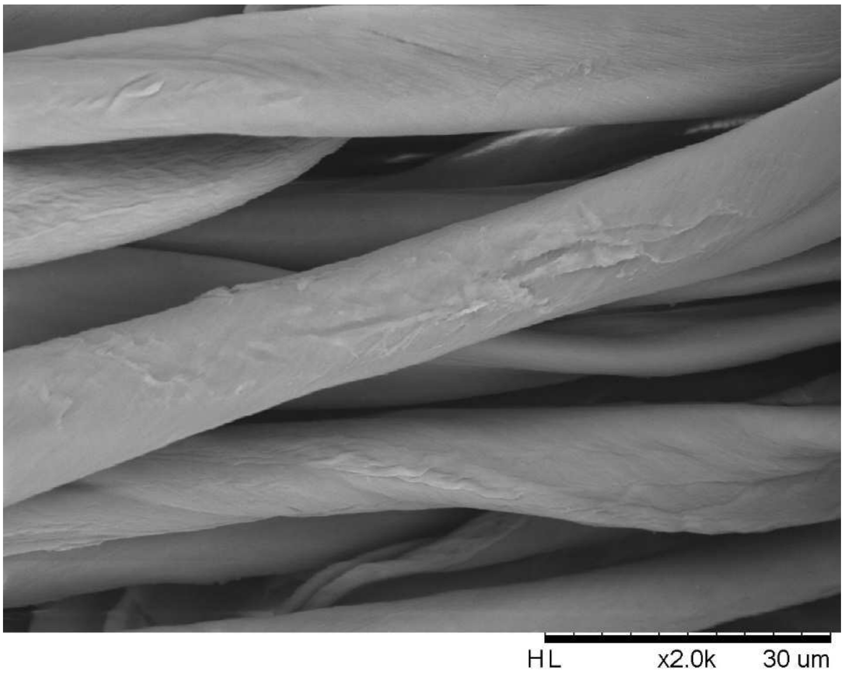

Figure 5-4. SEM images of pure untreated (control) cotton cellulose at a magnification of 2000x

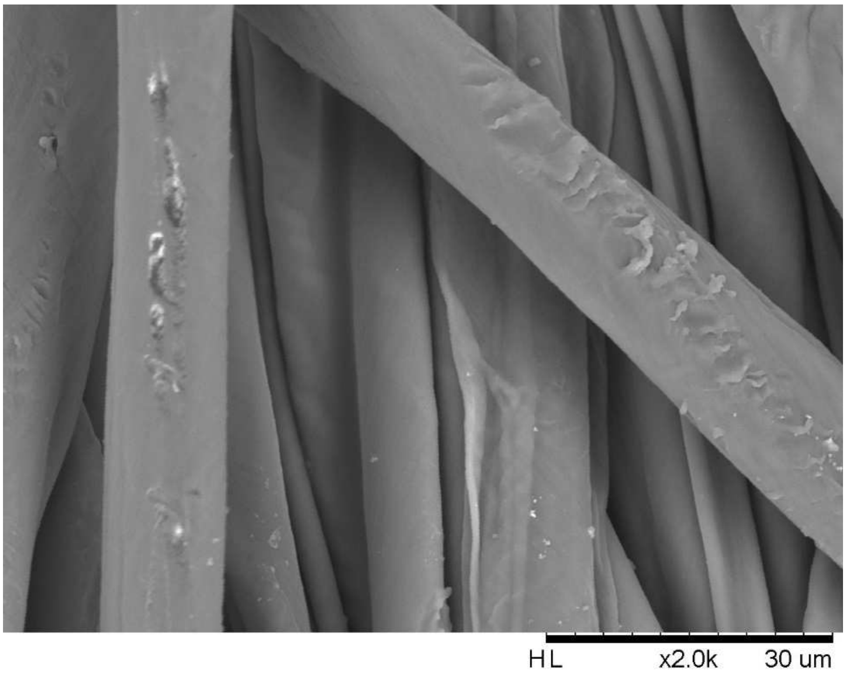

Figure 5-5. SEM images of treated cotton cellulose in the absence of TiO_2 at a magnification of 2000x

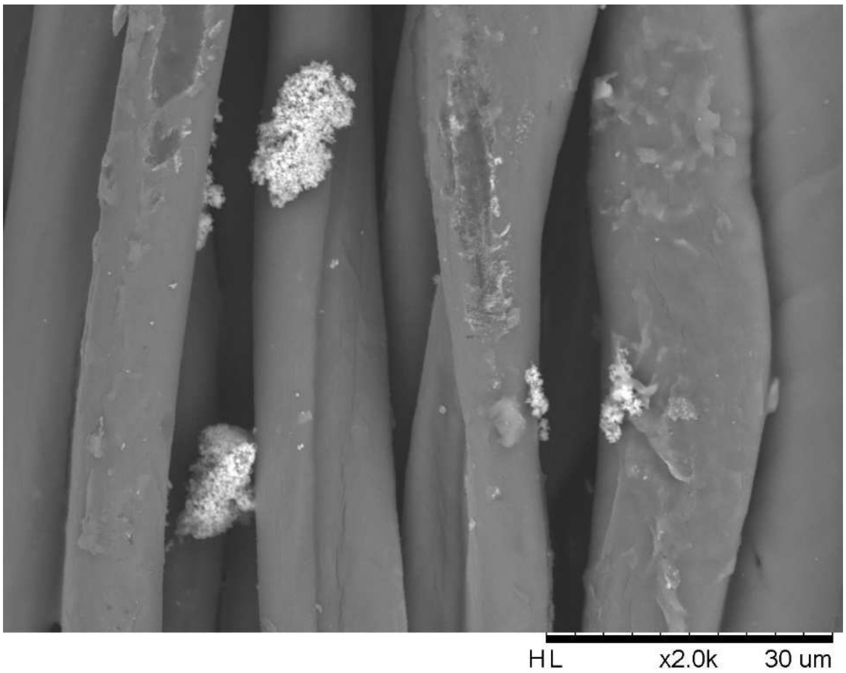

Figure 5-6. SEM images of treated cotton cellulose in the presence of 0.2% TiO_2 at a magnification of 2000x

Figure 5-4 shows the untreated (control) cotton fibre surface at a magnification of 2000x. Some wrinkles can be seen on the smooth fibre surface. The cotton fibres have a twisted ribbon-like structure caused by spiralling of cellulose fibrils. The direction of wrinkles on the fibre indicates the fibrillar directional changes. Moreover, there are natural folds running parallel to the fibre axis. The normal spiral structure is clearly defined.

Figure 5-5 demonstrates the cotton fibre surface after flame-retardant finishing treatment in the absence of TiO_2 at a magnification of 2000x. The treated cotton fibres become rougher than the untreated cotton fibre. Some cracks and damages are observed on the fibre surface which is probably caused by the highly acidic medium of the padding bath in the treatment. The existence of phosphoric acid significantly lowers the pH of the bath to about 1-2. The cotton fibres are damaged through acid hydrolysis of glycosidic linkages resulting in the cracks.

Moreover, Figure 5-6 is the SEM image of cotton fibre surface after flame-retardant finishing treatment in the presence of 0.2% TiO_2 at a magnification of 2000x. Cracks and damage are observed which is consistent with Figure 5-5. In addition, some irregular TiO_2 particles attach on the fibre surface. The irregular shape of the TiO_2 particles is due to formation of clusters. TiO_2 particles are unevenly distributed on the cotton fabrics surface. The particles have diameters of up to 10.5 μm. According to the SEM images of cotton fibres, the structure and characteristics of cotton fibre were found to be influenced by the finishing treatment.

5.3.2. Fourier transform infrared spectroscopy (FTIR)

FTIR-ATR spectroscopy is a surface-sensitive technique that can characterize the chemical structure of a substrate (Chung et al., 2004; Lam et al., 2011b). The analysis has been done on the control sample and the treated samples. Figure 5-7 illustrates the spectrum of control samples. The characteristic peaks and bands of the spectra that associate with cellulose structure of cotton fibre are identified with reference to the previous studies (Chung et al., 2004; Fan et al., 2012; Hartzell-Lawson et al., 2000; Lam et al., 2011b). There are characteristic peaks or bands. Here listed out some major peaks. There are OH stretching centred at 3284 cm^{-1}, CH stretching centred at 2889 cm^{-1}, CH_2 symmetric bending centred at 1419 cm^{-1}, CH wagging centred at 1313 cm^{-1}, C-O-C non-symmetric bridge centred at 1200 cm^{-1}, CO stretching centred at 1027 cm^{-1}, non-symmetric out-of-phase ring stretching centred at 893 cm^{-1}, and OH out-of-phase bending centred at 665 cm^{-1}. The absorbed water molecules vibrated at about 1640 cm^{-1}. When the fabrics were treated with flame-retardant treatment, there were some new characteristic peaks found such as carbonyl bands, CH_2 rocking bands, and CH_3 asymmetric and CH_2 symmetric stretching (Lam et al., 2011b). The spectrum of treated samples with code X1150 is demonstrated in Figure 5-8. A much stronger peak is observed at 1660 cm^{-1}. This peak was dominant by C=O stretching of amide that is present at the flame-retardant agent instead of absorbed water vibration. The non-cyclic secondary amide group (O=C–NH–C) not only had a C=O stretch at 1670 cm^{-1}, but another strong band in the IR spectrum near 1550 cm^{-1} involving the CNH bending and the C–N stretching (El-Bahy 2005; Larkin 2011). Furthermore, for the peaks centred at 826 cm^{-1}, it was contributed by CH_2 rocking band for P-CH_2. The rocking band of –CH_2 is a characteristic strong-medium intensity band for phosphonate structures that have P-CH_2-R groups (Gaan et al., 2007b; Guan et al., 2006; Lam et al., 2011b). However, the vibration of phosphorus bonding (P=O) occurring usually at 1320–1140 cm^{-1} is difficult to identify as a result of overlapping with the characteristic absorption peaks of the primary and secondary OH deformation of cotton (Lam et al., 2011b; Siriviriyanun et al., 2008b). The spectra of other samples treated under different curing conditions were similar to each other. From the evidence provided from the FTIR-ATR spectra, it can show that the flame-retardant agent accompanying with crosslinker was successful adhered on the cellulose surface.

Figure 5-7. The FTIR-ATR spectrum of control sample

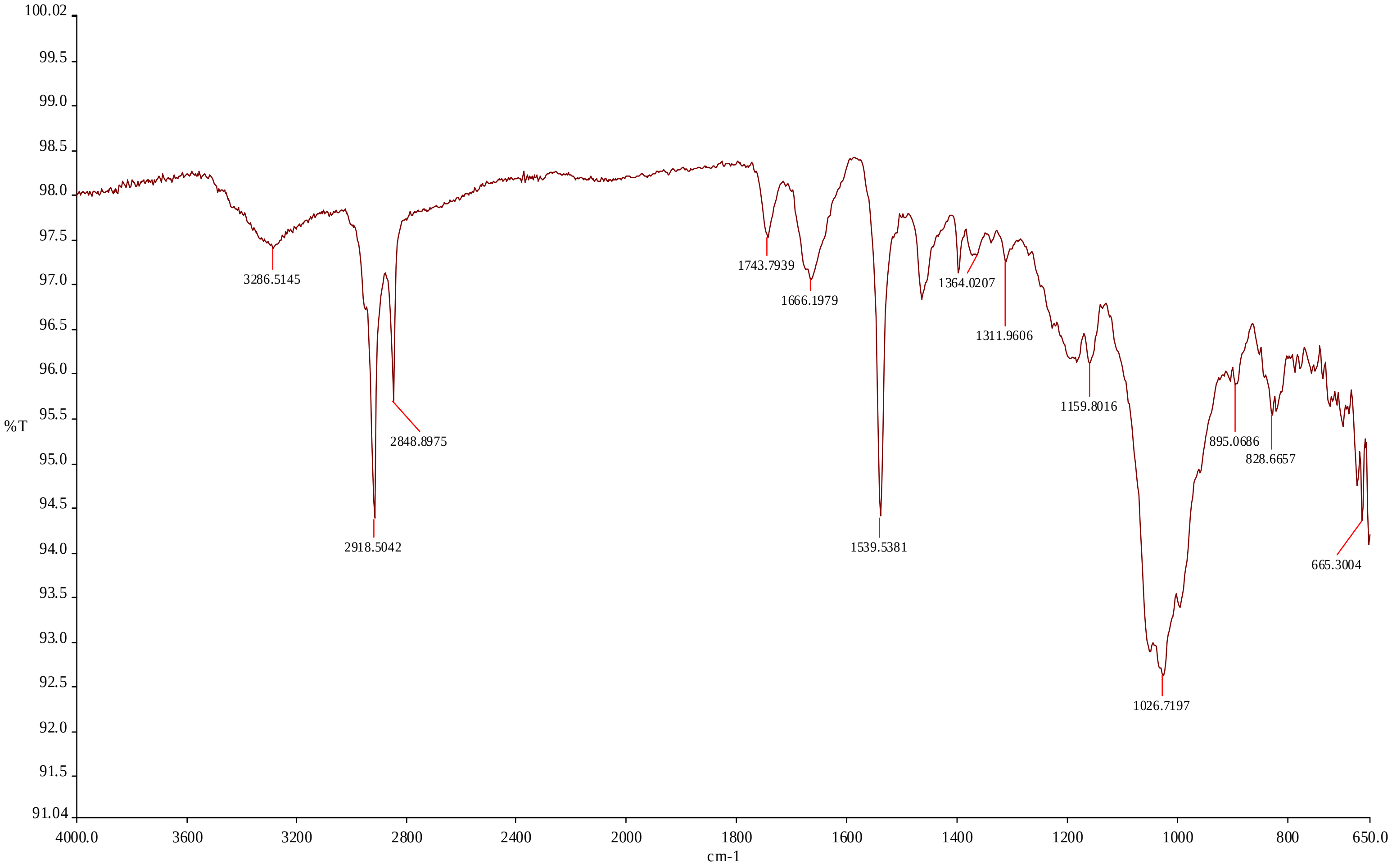

Figure 5-8. The FTIR-ATR spectrum of treated samples with code X1150

5.3.3. Energy dispersive X-ray analysis (EDX)

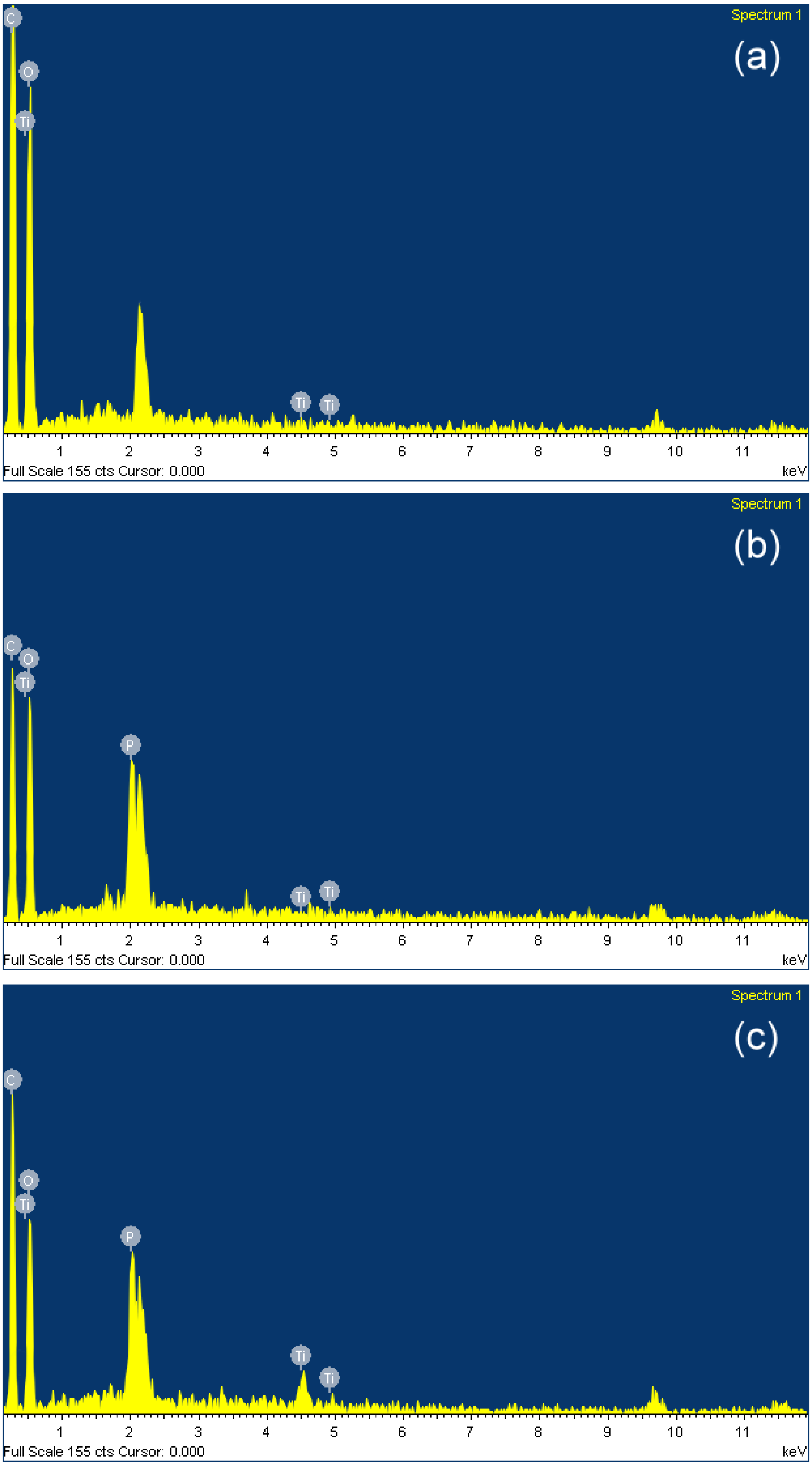

Figure 5-9. EDX spectrum of a) pure untreated (control) cotton cellulose b) treated cotton cellulose in the absence of TiO_2 c) treated cotton cellulose in the presence of 0.2% TiO_2

In order to confirm the TiO_2 particles adhered on the cotton fabrics surface, EDX was used to collect the elemental information of cotton fabrics. Figure 5-9(a), (b) and (c) shows the EDX spectra of pure untreated (control) cotton cellulose, treated cotton cellulose in the absence of TiO_2 and treated cotton cellulose in the presence of 0.2% TiO_2 respectively. The atomic percentages of carbon (C), oxygen (O), phosphorus (P), and titanium (Ti) are shown inTable 5-7. The signal of the cotton species is dominant by C and O as cellulose is a carbohydrate compound. In Figure 5-9(a), (b) and (c), the signal near 2.2 keV is responsible for the gold element as the sample was coated with gold before performing analysis in order to increase the conductivity of the sample. About 2% phosphorus content was successfully added after flame-retardant treatment. In addition, EDX analysis also confirmed that there is TiO_2 particles attached on the cellulose fibrils after treatment.

Table 5-7. The atomic percentage of different elements present in the cotton fabrics

SAMPLE	C (%)	O (%)	P (%)	Ti (%)
Control	54.68	45.32	--	--
Z	53.72	44.19	2.1	--
Y	56.97	40.34	1.88	0.81

5.3.4. Thermogravimetric analysis (TG)

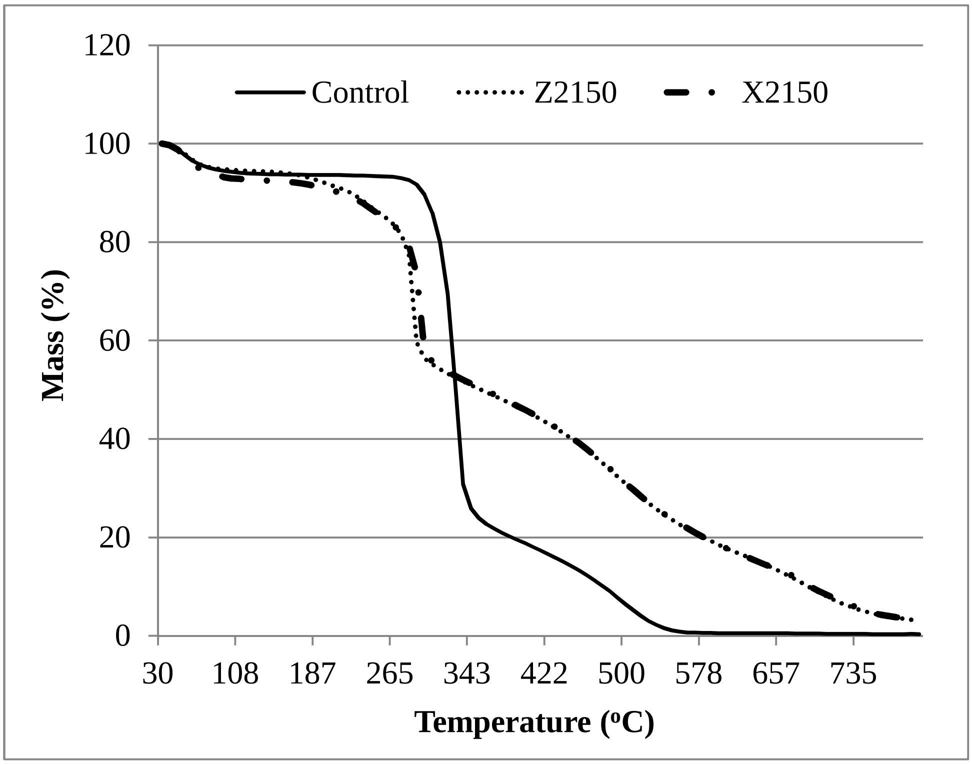

Figure 5-10. TG comparative curves of untreated (control) and treated cellulosic fabric with different flame-retardant formulation

In order to investigate the effect of TiO_2 on flame retardancy, thermogravimetric analysis was performed on selected samples. Thermogravimetric analysis (TG) is used to investigate the thermal decomposition process of polymers by continuously recording the mass changes of a sample of material as a function of a combination of temperature and time. The relative thermal stability, combustion pathway and pyrolysis process were evaluated. In Figure 5-10, the solid line represents the TG curve of the control sample. The dotted line and the dashed line represent treated samples Z2150 and X2150, respectively. The TG curve of the control sample shows three stages of cellulosic pyrolysis, initial, main and char decomposition steps (Fallah et al., 2011a; Zhu et al., 2004). For the control sample, temperature at the initial stage was below

300ºC. The curve is flat with a minimal mass loss. There are changes in physical properties of the cellulose and the damage to cellulose occurred mostly in amorphous region, in the initial stage (Fallah et al., 2011a; Zhu et al., 2004). In the range of 300ºC to 350ºC, the curve drops suddenly, indicating the main pyrolysis stage. The mass loss is significant and rapid. Pyrolysis takes place in crystalline region and the pyrolysis products are mainly produced in this stage. Glucose and all kinds of combustible gases are the main pyrolysis products. Char decomposition stage refers to a temperature beyond 350ºC. In this stage, dehydration and charring reactions compete with the production of non-volatile liquid L-glucose by depolymerisation (Fallah et al., 2011a; Zhu et al., 2004). The latter is more obvious. The mass decreases gradually, due to dehydration and decarboxylation, by release of water and carbon dioxide molecules and production of carbonyl products. The remaining mass was only 0.35% at the end of series of reactions.

For the TG curves of samples Z2150 and X2150, the shape of the curves is similar to that of the control sample with the three stages clearly defined. The treated samples show a lower decomposition temperature and mass loss. These stages happened well below the temperature for thermal degradation of the untreated cellulose (Fallah et al., 2011a). Decomposition temperatures of the treated samples are obviously lower than the control samples. Such difference is a result of the presence of flame-retardant agent. The sudden drop of the mass began at about 280ºC. The differences in decomposition temperature between the treated sample and the control sample is caused by the postponed formation of volatile pyrolysis products when the polymer is subjected to thermal degradation (Fallah et al., 2011a; Zhu et al., 2004). Approximately 3.0 - 3.4% mass remained at the end of the series of reactions. A significantly larger amount of solid residues was produced from the flame-retardant treated samples. This indicates that more charred products were produced after the treatment. TG curves of samples Z2150 and X2150 are highly similar to each other. At the end of the series reactions at 800ºC, the remaining mass of Z2150 was about 3.07% and X2150 was about 3.33% which is higher than that of Z2150 because there was a small amount of TiO_2 still remaining at the end of series of reactions in sample X2150.

5.4. Low stress mechanical properties of Pyrovatex CP NEW-treated fabric

For the KES-F test, tensile, shearing, bending, compressional and surface properties are measured. The definition and characteristic of the parameters of these properties have been defined and described at Table 3-3 in chapter 3. The results of flame-retardant treated fabrics are demonstrated in Table 5-8 and Table 5-9. The sample codes are used to express different conditions. “Z” refers to the padding solutions without TiO_2. “X” and “Y” refer to the padding solutions containing 0.2% and 0.4% TiO_2 respectively. The letter “N” used in Table 5-9 before “Z”, “X” and “Y” represents the fabrics have been neutralized. More information about padding solutions is shown in Table 3-2. The first number digit of the code refers to curing time in minute, and the last three-digit refers to curing temperature in degree Celsius.

Table 5-8. Low stress mechanical properties of the flame-retardant-treated fabric as measured by the KES-F system

	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
Sample Code	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (Nm/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
Control	82.43	48.93	11.80	5.23	4.87	12.58	0.739	0.763	0.139	6.28	0.306	0.121	48.47	0.742	0.900
Z1110	78.84	38.50	11.45	8.73	12.55	33.05	1.05	1.780	0.29	8.62	0.28	0.137	43.18	0.713	0.908
Z1130	78.02	40.88	10.60	10.03	12.66	38.03	1.38	2.089	0.35	9.49	0.26	0.162	44.83	0.715	0.965
Z1150	77.20	46.83	10.29	10.37	13.48	40.56	1.44	2.329	0.33	8.50	0.25	0.158	44.64	0.721	0.975
Z1170	76.38	47.78	9.59	12.50	15.33	43.80	1.55	2.483	0.28	7.96	0.31	0.170	46.37	0.726	0.949
X1110	79.27	39.46	10.25	12.10	24.26	47.18	1.37	2.268	0.30	8.75	0.27	0.116	45.57	0.710	0.884
X1130	76.22	44.88	9.26	12.47	22.98	50.33	1.73	2.710	0.37	8.94	0.26	0.133	47.79	0.703	0.905
X1150	81.12	51.90	9.16	14.85	23.06	58.75	2.21	3.567	0.25	7.23	0.29	0.158	50.40	0.706	0.921
X1170	74.70	58.48	8.01	17.33	25.34	71.44	3.19	4.004	0.28	7.70	0.29	0.162	52.74	0.719	0.946
Y1110	80.69	42.92	11.01	8.68	11.95	33.67	1.40	2.079	0.41	9.29	0.26	0.150	44.05	0.711	0.947
Y1130	77.97	44.61	10.41	10.67	13.77	38.58	1.69	2.478	0.42	8.19	0.24	0.161	45.06	0.713	0.981
Y1150	81.50	49.80	10.54	11.05	10.81	40.92	2.06	2.559	0.37	8.43	0.29	0.177	45.88	0.710	0.958
Y1170	75.51	50.18	9.18	11.01	10.95	39.31	2.18	3.004	0.32	8.25	0.26	0.179	47.40	0.720	0.996

Low stress mechanical properties of the flame-retardant-treated fabric as measured by the KES-F system (Cont'd)

Sample Code	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (Nm/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
Z2110	82.86	37.51	11.56	8.24	12.39	34.73	1.58	1.867	0.33	9.11	0.30	0.143	42.83	0.705	0.895
Z2130	79.00	40.16	10.98	10.12	13.80	37.54	1.76	2.339	0.36	9.15	0.25	0.150	43.32	0.710	0.947
Z2150	80.58	52.46	10.14	12.24	15.26	45.08	1.85	2.401	0.31	8.72	0.24	0.161	44.80	0.721	0.988
Z2170	73.06	53.38	9.38	13.02	15.90	49.11	1.73	2.526	0.28	8.19	0.27	0.159	45.26	0.731	0.968
X2110	80.74	43.32	9.84	14.64	26.34	53.36	1.81	2.605	0.33	8.93	0.29	0.111	46.67	0.700	0.855
X2130	78.18	50.67	9.24	13.94	25.15	56.05	2.14	3.340	0.32	8.02	0.25	0.126	46.97	0.706	0.905
X2150	80.30	56.49	9.18	15.13	25.48	62.28	2.72	3.596	0.26	8.45	0.27	0.137	48.77	0.707	0.908
X2170	75.57	58.89	7.91	18.42	29.24	70.70	3.35	4.160	0.30	7.38	0.28	0.144	51.25	0.715	0.918
Y2110	77.10	41.96	10.14	9.96	13.77	37.02	1.52	2.133	0.45	8.30	0.27	0.157	45.72	0.715	0.952
Y2130	82.81	41.73	10.72	11.30	13.12	41.98	2.07	2.500	0.40	7.84	0.28	0.175	46.36	0.713	0.966
Y2150	77.85	51.40	9.84	11.82	11.08	42.01	2.19	2.898	0.34	7.98	0.27	0.185	48.09	0.716	0.992
Y2170	73.34	55.33	9.00	12.40	11.57	43.72	2.29	3.140	0.31	7.65	0.26	0.185	49.73	0.728	1.015

Low stress mechanical properties of the flame-retardant-treated fabric as measured by the KES-F system (Cont'd)

	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
Sample Code	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (Nm/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
Z3110	81.51	40.26	11.56	8.81	13.20	33.35	1.67	2.187	0.35	8.19	0.29	0.155	44.67	0.706	0.923
Z3130	80.96	42.75	11.19	9.88	13.76	38.28	1.89	2.394	0.35	9.02	0.24	0.157	45.43	0.703	0.962
Z3150	78.24	43.65	10.12	11.68	14.95	46.49	1.95	2.674	0.32	8.86	0.26	0.171	45.23	0.715	0.980
Z3170	77.80	42.15	9.46	13.07	15.93	49.89	2.01	2.826	0.29	8.27	0.30	0.196	47.87	0.729	0.988
X3110	78.34	44.74	9.58	12.47	23.22	51.64	1.86	2.933	0.35	8.36	0.27	0.131	45.15	0.715	0.909
X3130	81.83	52.91	9.68	14.36	23.63	58.36	2.53	3.316	0.33	7.79	0.29	0.150	47.92	0.711	0.919
X3150	81.67	57.86	9.38	16.79	8.40	46.18	2.87	3.974	0.28	7.73	0.24	0.157	51.54	0.706	0.968
X3170	75.30	60.18	7.96	21.48	30.54	76.47	3.37	4.179	0.27	8.47	0.29	0.170	53.17	0.710	0.942
Y3110	77.48	42.47	10.04	9.98	13.23	36.42	1.65	2.192	0.43	8.94	0.28	0.158	47.13	0.715	0.945
Y3130	78.18	50.98	9.77	12.08	13.69	43.88	2.13	2.936	0.40	9.01	0.28	0.188	49.37	0.712	0.983
Y3150	80.25	50.35	10.22	11.83	11.08	42.17	2.16	2.920	0.33	8.40	0.28	0.189	50.48	0.711	0.981
Y3170	74.92	55.82	9.12	12.13	10.18	43.07	2.78	3.540	0.29	8.46	0.29	0.207	51.11	0.726	1.013

Table 5-9. Low stress mechanical properties of the flame-retardant-treated fabric as measured by the KES-F system (Neutralized for 30 minutes)

Sample Code	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (Nm/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
NZ1110	81.72	40.33	12.09	3.72	2.64	12.58	1.08	1.156	0.16	7.36	0.27	0.234	44.23	0.735	1.090
NZ1130	79.49	40.21	12.12	3.54	2.61	12.44	1.23	1.413	0.17	7.73	0.30	0.216	46.98	0.731	1.027
NZ1150	79.49	42.52	11.91	4.10	2.92	14.73	1.45	1.284	0.17	8.53	0.27	0.218	47.20	0.710	1.048
NZ1170	76.30	42.31	11.24	3.92	4.21	15.73	1.72	1.681	0.15	8.21	0.28	0.235	38.86	0.719	1.069
NX1110	78.13	39.79	11.46	5.51	6.38	16.65	1.69	1.535	0.17	7.31	0.28	0.247	45.93	0.729	1.085
NX1130	78.18	43.40	11.16	5.87	6.97	18.21	1.68	1.822	0.18	8.46	0.28	0.231	44.58	0.708	1.045
NX1150	76.06	46.37	10.74	5.35	5.58	16.25	1.93	2.031	0.16	6.65	0.29	0.238	46.17	0.723	1.061
NX1170	74.81	45.78	10.32	6.44	6.72	21.70	2.30	2.133	0.16	8.56	0.30	0.198	47.61	0.728	0.996
NY1110	85.37	42.01	12.72	6.49	11.98	22.62	0.87	0.823	0.15	7.73	0.26	0.230	42.82	0.711	1.068
NY1130	79.48	43.85	11.49	6.54	11.49	22.60	1.06	0.935	0.17	8.22	0.30	0.186	45.93	0.726	0.981
NY1150	75.96	46.97	11.23	7.07	13.88	25.21	1.21	1.165	0.17	7.70	0.32	0.164	45.45	0.705	0.915
NY1170	75.58	48.77	10.84	7.26	11.87	27.14	1.55	1.439	0.16	7.10	0.28	0.168	45.70	0.720	0.970

Low stress mechanical properties of the flame-retardant-treated fabric as measured by the KES-F system (Neutralized for 30 minutes) (Cont’d)

	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
Sample Code	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (Nm/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
NZ2110	80.74	42.43	11.56	3.50	2.78	11.90	1.08	1.194	0.15	6.80	0.29	0.236	45.74	0.731	1.066
NZ2130	78.83	41.17	11.91	3.72	2.64	13.04	1.24	1.265	0.16	8.04	0.29	0.240	44.85	0.728	1.064
NZ2150	78.51	43.42	11.62	3.98	3.87	15.71	1.53	1.310	0.17	6.99	0.28	0.229	45.98	0.715	1.048
NZ2170	75.62	45.41	11.26	4.71	4.63	19.35	1.53	1.614	0.15	8.17	0.30	0.238	46.50	0.732	1.053
NX2110	83.63	41.83	12.25	5.68	6.78	17.13	1.75	1.764	0.17	7.54	0.27	0.240	42.90	0.715	1.074
NX2130	77.91	44.41	11.22	5.48	7.35	16.49	1.85	1.777	0.18	7.07	0.28	0.264	43.73	0.723	1.110
NX2150	79.11	45.36	10.95	6.11	8.25	20.58	2.05	2.188	0.16	7.10	0.28	0.261	44.06	0.716	1.095
NX2170	74.97	46.60	10.11	6.28	6.21	20.88	2.33	2.284	0.17	7.33	0.29	0.251	45.74	0.720	1.073
NY2110	78.67	41.03	12.36	6.36	12.28	22.16	1.11	1.177	0.15	7.19	0.30	0.218	42.68	0.711	1.011
NY2130	76.93	42.47	11.18	6.52	10.97	23.22	1.22	1.168	0.17	8.61	0.30	0.196	43.44	0.708	0.980
NY2150	75.19	46.71	10.89	6.89	13.50	25.92	1.41	1.237	0.17	6.51	0.29	0.215	43.75	0.718	1.024
NY2170	74.40	46.40	10.54	7.00	9.91	26.19	1.59	1.461	0.16	8.49	0.30	0.203	45.03	0.728	1.008

Low stress mechanical properties of the flame-retardant-treated fabric as measured by the KES-F system (Neutralized for 30 minutes) (Cont’d)

Sample Code	Tensile properties			Shear properties			Bending properties		Surface properties		Compressional properties				
	WT (N/m)	RT (%)	EMT (%)	G (N/m/deg)	2HG (N/m)	2HG5 (N/m)	B (x 10^{-4} Nm/m)	2HB (x 10^{-2} N/m)	MIU	SMD	LC	WC (Nm/cm^2)	RC (%)	T_M (mm)	T_0 (mm)
NZ3110	78.84	41.84	12.00	3.50	3.00	11.98	1.05	1.109	0.16	7.06	0.30	0.211	44.92	0.732	1.022
NZ3130	79.16	42.55	11.71	3.54	2.64	12.01	1.43	1.303	0.17	7.52	0.27	0.212	45.99	0.724	1.051
NZ3150	74.92	42.13	11.31	4.13	4.38	15.91	1.54	1.561	0.15	7.19	0.27	0.291	41.43	0.721	1.159
NZ3170	75.24	45.71	10.59	4.28	4.79	18.08	1.64	1.872	0.15	8.59	0.27	0.204	43.07	0.740	1.047
NX3110	77.58	42.70	11.48	5.39	6.54	15.87	1.73	1.696	0.18	6.17	0.27	0.233	43.56	0.739	1.098
NX3130	79.11	44.78	11.09	5.96	7.02	18.62	1.77	1.834	0.18	7.11	0.29	0.236	44.09	0.713	1.042
NX3150	79.33	43.68	11.16	6.35	7.95	21.59	2.07	2.294	0.17	7.45	0.30	0.270	45.17	0.721	1.089
NX3170	72.96	49.29	9.82	7.02	7.38	24.42	2.29	2.556	0.16	7.35	0.27	0.201	46.61	0.718	1.027
NY3110	76.54	42.44	10.97	6.73	10.81	23.63	1.26	1.214	0.16	8.83	0.28	0.208	43.95	0.723	1.029
NY3130	73.50	42.15	11.28	6.75	11.92	24.12	1.31	1.232	0.17	8.13	0.28	0.190	45.12	0.723	1.001
NY3150	72.75	46.63	10.81	7.08	14.02	26.00	1.58	1.657	0.17	8.32	0.30	0.194	43.88	0.708	0.973
NY3170	68.73	49.96	9.44	7.49	12.41	27.63	1.68	1.698	0.16	7.55	0.29	0.204	43.13	0.721	1.009

5.4.1. Tensile properties

Tensile energy (WT), tensile resilience (RT) and extensibility (EMT) are three parameters used to assess the tensile properties of a fabric. The definition and physical meaning of these parameters has been discussed in Chapter 3.

The control specimen acquires a relatively high WT. WTs decrease averagely about 8.8% after curing at temperature of 170°C. The main reason for the drop of tensile strength is because of the highly acidic conditions i.e. pH 1-2 (Lam et al., 2001b; Lam et al., 2014). Phosphorus acid served as catalyst in the flame-retardant treatment. The cotton fibres are tendered and damaged by acid-catalysed depolymerisation resulting in breaking down the cellulose chains. Moreover, the crosslinking agent in the flame-retardant system may reduce the tensile strength of the crosslinked fabrics (Kang et al., 1998; Yang et al., 2005). In Table 5-8, the fabrics cured at lower temperature have larger WT values which imply that the fabrics acquire a better tensile strength. The acidic and thermal damage to the cotton cellulose is less serious at the lower curing temperature. Besides, the crosslink formation is not effective at low curing temperature. A moderate decreasing trend can be observed when the curing temperature is increased from 110°C to 170°C. Furthermore, the presence of TiO_2 particles does not affect WT in a large extent. Therefore, WT is mainly affected by the curing temperature rather than the concentration of TiO_2 particles.

RT is another parameter associated with the tensile properties. The untreated control specimen possesses the moderate RT value. RT values of the fabrics treated at the curing temperature of 110°C and 130°C are significantly lower than that of control specimen. At the low curing temperature, the reaction of flame-retardant treatment is not completely activated. The low pH value cause severe damage to the cotton cellulose by acid-catalysed depolymerisation (Lam et al., 2011e; Kang et al., 1998). The cotton fibres are destroyed and triggered to inelastic behaviour. The fabric cannot restore to its initial shape after removing the applied tensile stress. When the curing temperature is increased to 150°C and 170°C, RT is remarkably improved compared with that of control specimen. The sufficient crosslinks formed during the treatment restrict the movement of the cellulose chains. This makes the fabrics become more elastic. In addition, in the presence of 0.2% TiO_2, RT values are superior to other conditions. One postulation for the phenomenon is that a suitable concentration of TiO_2 particles as co-catalyst improves the reaction effectiveness significantly. The TiO_2 particles may not only act as co-catalyst, but also attach on the fabric surface and in-between the fibres and withstand the applied tensile stress. However, the effect is not applicable in the presence of 0.4% TiO_2. Too high concentration of TiO_2 may block the reaction in the flame-retardant treatment leading less extensive crosslink formation.

In addition, the untreated control specimen obtains the highest value of EMT. The EMT of treated samples decreases when the curing temperature is increased from 110°C to 170°C. The reduction in EMT is owing to the formation of crosslinks after the flame-retardant treatment. The crosslinks limit and inhibit the elongation of the fabrics. The fabrics that have higher RT values result in lower EMTs. Therefore, EMT of the fabrics treated in the presence of 0.2% TiO_2 are the lowest among all tested specimens because they have largest RT values which is meant that the fabrics are more elastic. The addition of TiO_2 further limits and inhibits the elongation of the fabrics. Thus, low value of percentage extension is resulted.

Furthermore, half of treated fabrics have been neutralized after curing process. The WT values do not have a large variation compared with the non-neutralized fabrics. However, RT of the treated fabrics after neutralization post treatment decreases about 8.1% averagely. It is probably attributed to the neutralization process carried out at 50ºC which further weakens the strength of the fabrics. This results in worse tensile resilience properties. Conversely, the EMT of the fabrics increases about 13.8% after neutralization. As mentioned above, a lower RT results in a better EMT of the fabrics. Therefore, the fabrics become more extensible due to the weakening of cotton fibre.

5.4.2. Shearing properties

From Table 5-8, it shows the control specimen has the lowest G, 2HG and 2HG5. G, 2HG and 2HG5 are significantly increased after flame-retardant treatment such that the hand feel of the fabrics becomes stiff. Besides, the treated fabrics have unsatisfactory recovery ability. The shear stresses are found to be directly proportional to the shear rigidity. The greater the value of shear stress, the worse the recovery ability of fabric and stiffer the fabric will be. The crosslinking reaction may lead to the formation of brittle polymer layers even though the mobility of cellulose macromolecules is limited (Lam et al., 2011c). These changes are mainly caused by the acid-catalysed depolymerisation and crosslinking of cellulose (Lam et al., 2011c; Kang et al., 1998; Yang et al., 2000). Moreover, the low pH reaction condition contributes to the stiffer fabrics. G, 2HG and 2HG5 values generally increase with increasing temperature from 110°C to 170°C. The fabrics cured at high temperature acquire the worst shearing properties.

Furthermore, G, 2HG and 2HG5 are further promoted after flame-retardant treatment in the presence of 0.2% TiO_2 particles. An adequate amount of TiO_2 employed in the treatment can enhance the reaction effectiveness. This causes stiffer fabric and worse recovery ability. At the same time, the presence of 0.2% TiO_2 promotes the shear rigidity. Meanwhile, TiO_2 particles do not help improve the recovery ability after applying shear stresses such that the values of 2HG and

2HG5 increase after treatment. However, excessive amount of TiO_2 employed does not have an obvious influence to the shear rigidity and shear stress.

After neutralization, the G, 2HG and 2HG5 are significant decreased. Neutralization removes all residual phosphorus acid catalyst, uncrosslinked phosphonamide, surface crosslinked polymer and the loosely held TiO_2 particles on fabric surface. This helps minimize the rigid effect so that the neutralized fabrics are less resistant to shear stress (Lam et al., 2014). As the surface residuals are removed, the fabrics become softer after neutralization such that better recovery ability can be restored.

5.4.3. Bending properties

The control specimen has the lowest B and 2HB which implies that the control specimen is less resistance to bending and has better recovery ability. The fabric hand is soft. The values of B and 2HB are remarkably promoted after flame-retardant treatment. The situation is similar to the shearing properties. The treated fabrics become stiff. The promotion of B is because of the formation of crosslinks. The crosslinks formed during the treatment should increase the interaction between fibres and yarns leading to an increase of B and 2HB (Sun & Stylios, 2012). The B and 2HB values increase when the curing temperature is increased from 110°C to 170°C. Extensive crosslink formation and better reaction effectiveness at the high curing temperature correspond to the trend of the results. On one hand, the existence of crosslink will enhance the B values. On the other hand, the crosslinking reaction may lead to the formation of brittle polymer layers (Lam et al., 2011c). This makes the fabrics with poor bending recovery ability such that a higher value of 2HB is obtained.

Moreover, the B and 2HB values obtained after the treatment in the presence of 0.2% TiO_2 are further promoted. The presence of TiO_2 undoubtedly increases the interaction between fibres and yarns on the fabric surface that makes the fabric restricts from bending motion. Besides, TiO_2 also serves as co-catalyst to enhance the crosslinking reaction effectiveness. The crosslinking reaction may lead to more brittle polymer layers. Thus, the fabrics are resistance to bend but with poor recovery ability towards bending. The B and 2HB values of the fabric treated in the presence of 0.4% TiO_2 is slightly promoted compared with that of treated in the absence of TiO_2. Further increase the concentration of TiO_2 from 0.2% to 0.4% reserves the result to give a lower B and 2HB. Excessive TiO_2 particles may block the reaction lowering the reaction effectiveness. However, it is evident that TiO_2 remains on the surface should have some effects on bending properties by increasing the interaction between fibres and yarns.

Furthermore, the B and 2HB are also remarkably lowered after neutralization process. As discussed in shearing part, neutralization helps minimize the rigid effect so that the bending rigidity is also lowered. Generally, bending motion deforms a fabric perpendicularly to the longitudinal axis of the fabric. The fuzzy or tangled surface fibrils appear after neutralization pull outward. The natural fibre crimp provides an elastic characteristic to restore the fibres into original shape that makes the lowered 2HB (Lam et al., 2014).

5.4.4. Compressional properties

First of all, appearance thickness (T_o) and intrinsic thickness (T_m) represents the fabric thickness at the pressure of 490 N/m^2 and 4900 N/m^2 respectively. The thickness of the fabrics is averagely thickened about 5.43% after flame-retardant treatment compared with the control specimen. The increase in thickness is as a result of the formation of crosslinks and phosphorus add-ons on the fabric surface.

Moreover, the fabrics may exhibit shrinkage upon wet treatment (Lam et al., 2011a) which lead to the change in fabric density. This causes the increase in thickness. In addition, the appearance thickness is also affected by the presence of 0.4% TiO_2 particles. The use of 0.2% TiO_2 does not influence the fabric thickness. The thickness measured is even thinner than that of in the absence of TiO_2. When the pressure is exerted on the fabrics surface, the treated fabrics have a lower intrinsic thickness than the control specimen. It can explain by the fact that the wet treatment done on the fabrics, especially involving high temperature drying process, decreases the intrinsic thickness of the fabrics (Lam et al., 2011d). The intrinsic thickness does not vary vigorously when the curing temperature is increased from 110°C to 170°C and the inclusion of TiO_2 in the flame-retardant treatment. The results lie between around 0.70 mm and 0.73 mm.

From the Table 5-8, it shows that LC is lowered after flame-retardant treatment. The control specimen has the highest LC value. Lower LC values are found for the fabric curing at high temperature. Heat curing process, which weakens the compressional properties, may lead to the reduction of LC. Besides, the highly acidic medium used causes some irreversible depolymerisation of cellulose which damages the originality of the fibres resulting in the drop of LC values (Lam et al., 2011a; Sun & Stylios, 2012). The presence of TiO_2 does not show an obvious effect to the LC parameter. On the other hand, WC is increased after flame-retardant treatment. This parameter correlates with the appearance thickness of the fabrics. For the thicker samples, higher compressional energy is required to reach a given loading (Sun & Stylios, 2012). For the fabrics treated in the presence of 0.4%, they have the highest appearance thickness. Meanwhile, the WC of those fabrics is also the highest. The high WC can also be explained by surface raising of cotton fabric providing a high compressibility structure after treatment. In addition to LC and WC, RC is the third parameter associated with compressional properties. The RC values are reduced after the treatment because the spongy effect of the fabrics is reduced by the attack of strong acid during the treatment. However, the RC values gradually increase with increasing curing temperature such that the compressional recoverability is improved. At the high curing temperature, the extensive crosslinks formation and the add-ons on the fabric surface help improve the compressional recoverability of the fabrics. Moreover, in the presence of TiO_2, the RC values are further improved. As the existence of TiO_2 particles on the fabric surface, the RC values less reduced. TiO_2 has strong compressive strength that can withstand a relatively high pressure. Thus, TiO_2 particles can compensate the side effect of treatment and enhance compressional recoverability of the fabrics.

Compared the neutralized fabrics with the non-neutralization fabrics, the appearance thickness has been thicken 9.47% while the intrinsic thickness remains nearly the same. Neutralization develops tangled fibrils during wet processing and it swells the fibres causing fabric shrinkage (Lau et al., 2002; Lam et al., 2014). Swelling of fibres makes the fabrics appearance thickness become thicker. However, the intrinsic thickness measured under pressure shows the thickness remain steady. Besides, LC and WC are increased after neutralization which reveals the presence of surface fibrils. This is meant that the fabric is more compressible and more energy is required to compress the treated fabrics due to the increase in fabric thickness. However, the slightly decrease in RC values may be owing to the second chemical treatment done on the fabrics reducing the spongy effect.

5.4.5. Surface properties

The results of MIU and SMD are illustrated in Table 5-7. The control specimen has the lowest MIU and SMD which is meant that the control fabric surface has small friction and even surface. The MIU and SMD are significantly increased after flame-retardant treatment. The newly formed crosslinks and the attack of strong phosphorus acid cause the rougher fabric surface. Besides, the fabric surface becomes uneven after treatment. The MIU and SMD have a decreasing trend when the curing temperature is increased from 110°C to 170°C. The friction of the fabric cured at low temperature is generally higher than that of cured at high temperature. One possible postulation for such a phenomenon is that the unreacted chemicals remained on the surface at the low curing temperature. This also leads to the unevenness of the fabric surface resulting in a higher value of SMD. Therefore, the flame-retardant treatment changes the surface morphology. When 0.4% TiO_2 is employed in the flame-retardant treatment, the surface of the fabric has the greatest friction. The excessive TiO_2 particles may agglomerate together to form TiO_2 cluster with different size that affects the surface properties. The agglomeration is due to the surface attraction between the huge amounts of small particles. The enhancement in MIU values highly depends on the degree of agglomeration of particles (Lam et al., 2014). In addition, the TiO_2 particles may be distributed evenly on the fabric surface that gives a lower value of SMD.

Furthermore, the MIU and SMD are decreased by neutralization process. The dropped in MIU values may be indicative of development of tangled fibrils after neutralization (Lam et al., 2014). Also, the removal of the residuals and some of titanium dioxide on the fabric surface decrease the surface friction leading a diminished MIU. A slightly decrease in SMD values shows the development of tangled fibrils is random and in different extent.

5.5. Conclusion

In the present study, Pyrovatex CP NEW was used as a durable flame-retardant agent. The flame-retardant agent was combined with crosslinking agent to enhance the flame-retardant performance. The use of TiO_2 in the formulation is a relatively novel method. The effect of curing temperature, curing time and metal oxides on flame-retardant finishing had been evaluated. Different curing condition and concentration of TiO_2 employed in the treatment would affect the flame-retardant performance. The fabrics cured at higher temperature and longer time had a better flame-retardant ability and could withstand multiple times of home laundering. However, these fabrics generally suffered from tear strength loss. Therefore, a lower curing temperature was recommended to be applied in flame-retardant finishing in order to minimize the tear strength loss. Combining with the effects of curing temperature, curing time, concentration of TiO_2 and neutralization effect, the best conditions for imparting effective flame-retardant properties were deduced. Cotton fabrics should be treated with the formulation X (in the presence of 0.2% TiO_2) and cured at 150ºC for 1 minute followed by neutralizing the residues on the fabric surface. Compared with the conventional flame-retardant finishing conditions, a reduction of 20ºC in temperature was achieved at the curing step if 0.2% TiO_2 was added as co-catalyst in the formulation. Moreover, the structural properties of the fabrics had also been examined. SEM and EDX proved the presence of TiO_2 appeared on the fabric surface. FTIR and TG characterized the properties changes after flame-retardant treatment.

In addition, the fabric hand was strongly altered after flame-retardant treatment resulting in stiffer hand, tensile loss, brittle polymer layers, less spongy fabric. These changes were mainly contributed by the formation of crosslinks after treatment, acid-catalysed depolymerisation in the strong acidic medium and the presence of co-catalyst TiO_2. These would affect the inter-yarn and inter-fibre interaction so that the low stress mechanical properties were altered. Moreover, the choice of curing temperature obviously influenced the outcome hand properties of the fabrics. Using high curing temperature usually caused poor hand properties of the fabrics. Furthermore, the addition of TiO_2 in the treatment not only enhanced the reaction effectiveness but also had some positive influences with respect to compressional recovery ability and tensile properties. Lastly, the neutralization process would further weaken the fibres resulting in worse tensile resilience properties but better tensile extensibility. The shear properties and bending properties had been improved due to minimization of the rigid effect. The fabrics had better compressibility because of increase in fabric thickness and the neutralization altered the surface properties.

Chapter 6: Conclusion and Recommendations

6.1. Summary of the study

Two textile functional finishes which are wrinkle-resistant finishing and flame-retardant finishing have been comprehensively and systematically studied, examined and evaluated in present thesis. An encyclopedic knowledge was introduced in the literature review in Chapter 2. Detail background knowledge and the recent developments of these two textile functional finishes can be obtained. In Chapter 3, the experimental details in present study including materials, apparatus, test methods and experimental procedure of two textile functional finishes was introduced. After the experimental section, the results and discussions of these two functional finished were shown and analysed in Chapter 4 and 5. In Chpater 4, the wrinkle-resistant finishing was carried out by using DMDHEU. Different curing temperature and curing time combinations were comprehensively evaluated in the study. Five formulations were examined. It showed that addition of metal oxides serving as co-catalyst could enhance the wrinkle-resistant performance to a certain extent. The hand feel of the fabrics after treatment was also evaluated. Besides, in Chapter 5, Pyrovatex CP NEW was used as a durable flame-retardant agent. Similarly, different curing temperature and curing time combinations were comprehensively evaluated in the study. Titanium dioxide was also employed in the formulations to enhance the flame-retardant performance. Moreover, the structural and mechanical properties were also evaluated. Lastly, the role of TiO_2 in the flame-retardant treatment was proposed. Optimized conditions were recommended for these two finishing in order to attain the best reaction effectiveness and obtain a good fabric performance.

6.2. Conclusion

The major results and the findings of the present study are summarised in the following paragraphs. It was found that the curing temperature and curing time significantly influenced the wrinkle-resistant performance and the flame-retardant performance. Higher curing temperature and longer curing time resulted in a better performance as there was sufficient energy and time for the reaction occurred. At reaction temperature, DMDHEU linked two adjacent cellulose chains by formation of crosslink. Crosslinked cellulosic chains could lower stress-induced slippage of chain and increase the recovery ability from any deformation. Meanwhile, Pyrovatex CP NEW and Knittex CHN reacted with cotton cellulose to form linkage under acid-catalysed conditions. At lower curing temperature and shorter curing time, the reaction might not be activated resulting in poor functional performance. Therefore, the curing temperature and time was an important factor affecting the fabric performance. However, at the high curing temperature and long curing time, the tear strength loss was unavoidable. It was important to strike a balance between the gain of fabric functional performance and the loss of tear strength under high temperature thermal treatment. On the other hand, the addition of TiO_2 was confirmed to have positive influences to the fabric functional performance. The reaction effectiveness could be enhanced by the existence of metal oxides without obvious adverse effects to the fabrics. For wrinkle-resistant finishing part, a reaction condition was recommended by concerning the wrinkle-resistant performance, the tear strength loss and the effect of TiO_2 on the performance. The fabric cured 150°C for 2 minutes in the presence of 0.1% TiO_2 (Formulation B) was found to be good and satisfactory. A mixed catalyst system was primarily introduced in this thesis. It was found that 0.1% TiO_2 and ZnO were used as co-catalyst in the treatment with curing temperature of 150°C and curing time of 1 minute, the wrinkle recovery performance and tear strength could even be further improved. In addition, for flame-retardant finishing part, combining with the effects of curing temperature, curing time, concentration of TiO_2 and neutralization effect, a reaction condition was recommended. The cotton fabric should be treated with the formulation X (in the presence of 0.2% TiO_2) and cured at 150ºC for 1 minute followed by neutralizing the residues on the fabric surface. It could see that the recommended conditions for both finishing treatment were 150ºC. A temperature reduction was achieved compared with conventional treatment. Such temperature reduction could minimize the loss of tear strength, the yellowing caused by heat treatment and save energy.

It was proposed that TiO_2 acted as Lewis acid in wrinkle-resistant treatment. The Ti-sites of TiO_2 acted as Lewis acids sites which could employ an electron lone pair from another molecule. For the flame-retardant treatment, it was proposed that hydroxyl group on the Pyrovatex CP NEW, melamine resin and cellulose could probably adsorb on the TiO_2 surface in assisting the propagation of the reaction.

Moreover, the fabrics generally suffered from yellowing at high temperature due to the thermal degradation of cotton cellulose. The cotton fabric and the treated fabrics were also examined by SEM. The SEM images showed a smooth and normal spiral structure. The DMDHEU-treated fabric showed similar extent of smoothness to the control sample while some cracks and damages were observed on the flame-retardant-treated fibre surface. More various structural analysis had been done on flame flame-retardant-treated fabrics. For the FTIR, some characteristic peaks were identified. For example, a much stronger peak was observed at 826, 1660, 1670 and 1550 cm^{-1}. These vibration peaks observed in the spectrum were the best evidence for the flame-retardant-treated fabrics. Moreover, EDX analysis collected the elemental information of cotton fabrics. This showed and confirmed the TiO_2 particles adhered on the cotton fabrics surface. Furthermore, thermogravimetric analysis (TG) was used to investigate the thermal decomposition process of the treated fabrics. The treated samples showed a lower decomposition temperature and mass loss. Besides, a large amount of solid residues was produced after analysis. These were the evidence of the presence of flame-retardant agent. In addition, the presence of TiO_2 could be deduced from remaining mass after analysis.

Last but not least, fabric hand is a critical physical property of fabrics when making the choice of fabrics. Therefore, intensive investigation of low stress mechanical properties helped us to assess and control the apparel fabrics. The objective measurement of low stress mechanical properties had been investigated by KES-F. The low stress mechanical properties was significantly changed after two functional finishes. These changes were mainly contributed by the formation of crosslinks after treatment, the acidic medium in the treatment and the presence of co-catalyst TiO_2. Moreover, varying the curing temperature and curing time resulted in different mechanical properties of fabrics. The two functional finishing carrying out high curing temperature usually caused poor hand properties of the fabrics. For the flame-retardant-treated fabrics, the neutralization process would further weaken the fibres resulting in worse tensile properties but improve the other four mechanical properties.

6.3. Recommendation

A study of catalytic system for wrinkle-resistant and flame-retardant finishing has been comprehensively studied and evaluated. Although the objectives of this study have been achieved, there is plenty of room for improvement, modification and further investigation of the present study in order to develop a much better technique and fabric performance for textile industrial application.

The formaldehyde release has not been determined in this study. Although DMDHEU produces less free formaldehyde during finishing, formaldehyde release is still a problem when using DMDHEU. It is suggested that the concentration of formaldehyde release of the treated fabrics should be measured. It can study the relationship between the curing temperature and the concentration of formaldehyde release. Moreover, the effect of metal oxides on the release of the formaldehyde is another interesting area.

Besides, TiO_2 is the main metal oxide used in the present study. The effect of coupling ZnO with TiO_2 on the wrinkle-resistant performance is primarily studied. However, there are wide ranges of transition metals and their metal oxides can be tried in the later studies. For example, the study of anti-bacterial ability can be examined if silver oxide (Ag_2O) is added on the fabrics. Apart from using the micro-size of metal oxides, nano-size of metal oxides can also be employed in future studies as the nanotechnology become more popular nowadays.

Moreover, the fabrics obtained from the present study do not have a satisfactory fabric hand. This is a critical problem found after functional finishing. Thus, in the future, softener or other chemicals should be added in order to improve the fabric hand. Some more physical test can also be done on the treated fabrics such as air permeability test and moisture permeability test. These two measurements also help assess the fabrics comfort.

Furthermore, the mechanism of TiO_2 in the functional finishing still lacks of sufficient supportive information. It is worth to know about the reaction mechanism between the metal oxide, functional finishing agent and cotton cellulose. This helps us to design and modify the treatment in future studies. In order to investigate the role of titanium dioxide, some more advanced techniques such as in-situ spectroscopy technique can be used to monitor the reaction intermediate and the propagation of the reaction.

Most importantly, finishing cannot be isolated in textile wet processing. Textile wet processing includes pre-treatment, colouration and finishing. The coloration process is a complex chemical reaction between the dye and the fabrics. The finishing is usually carried out right after textile colouration process. The effect of metal oxides on the dyed fabric has not been studied in details. Thus, in order to determine a proper formulation, it is important to consider other parameters in order to maintain the quality of the final product after coloration and finishing.

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