INVESTIGATION OF ATMOSPHERIC PRESSURE PLASMA TREATMENT FOR COTTON FABRICS PREPARATION

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Investigation of Atmospheric Pressure Plasma Treatment for Cotton Fabrics Preparation

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CERTIFICATE OF ORIGINALITY

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Abstract

This thesis is concerned with a study on the effects of atmospheric pressure plasma treatment on cotton fabric preparation. Cotton is the most widely used natural fiber in clothing today and is well known for its good softness and moisture absorption properties. To obtain a functional cotton fabric, the grey cotton fabric is going through a series of wet chemical preparation treatments, such as desizing, scouring and bleaching. Although the performances of the cotton fabric can be enhanced after treated with conventional wet treatments, a large amount of water, chemicals and energy are incurred in the processes. Moreover, with increasing concerns about the environment, a more effective and environmentally friendly cotton pretreatment process is essential in order to minimize the chemical wastes and associated disposal problems.

In this study, four types of cotton woven fabrics and two types of cotton knitted fabrics were used. Both woven and knitted cotton fabrics were treated with atmospheric pressure plasma under different output powers and oxygen flow rates, in order to determine how these different combinations of plasma processing parameters influenced the chemical and physical properties of the treated fabrics towards different evaluation tests. For comparison purposes, the cotton fabrics have been treated with conventional wet chemical pretreatment processes and the evaluation tests were based on the aim of wet chemical pretreatment.

A series of physical and mechanical tests have been carried out to evaluate the performances of the conventional and plasma treated cotton fabrics. The results revealed that there was desirable improvement on the wettability of the plasma

treated cotton woven and knitted fabrics, which even had an outstanding result than those fabrics treated with conventional desizing and/or scouring process. The reduction on fabric weight after plasma treatment revealed that plasma treatment can help to remove starch sizes and/or impurities. Characterization techniques and analytical instruments such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) have been used for investigating the property changes of untreated and treated fabrics. The studies on the cotton surface and chemical characteristics help to offer a better understanding of how the reaction mechanism occurs between plasma treatment on cotton fabrics and wet processing agents, and also give an entire comparison between conventional wet processing and plasma treatment. The conventional treated and plasma treated fabrics also have been dyed with two different colors to observe the dyeability changes.

List of publications

Invited seminar

1. Lam, C.F., Kan, C.W., Ng, S.P. and Chan, C.K. 9 July, 2012, 'Investigation of atmospheric pressure plasma treatment for cotton fabrics preparation and finishing', Ming Chi University of Science and Technology, Taiwan, pp 47.

2. Lam, C.F., Kan, C.W., Ng, S.P. and Chan, C.K. 10 July, 2012, 'Investigation of atmospheric pressure plasma treatment for cotton fabrics preparation and finishing', Tatung University, Taiwan, pp 47.

Conference paper

1. Lam, C.F., Kan, C.W., Ng, S.P. and Chan, C.K. 2-5 October, 2012, 'Desizing starch-based sizing material from cotton grey fabric using atmospheric pressure plasma', *Book of Abstracts of The Asia Pacific Conference on Plasma Science and Technology (11th APCPST) and 25th Symposium on Plasma Science for Materials (25th SPSM),* Kyoto University, ROHM Plaza, Kyoto, Japan, pp. 4-7.

2. Lam, C.F., Kan, C.W., Ng, S.P. and Chan, C.K. 14-18 April, 2013, 'Helium/oxygen atmospheric pressure plasma jet treatment on cotton fabric preparation', *Proceedings of International Journal of Arts & Sciences Semi-Annual Conference,* Austria Trend Hotel, Ananas, Vienna, Austria (CD-ROM Format).

<u>Journal</u>

1. Lam, C.F., Kan, C.W., Ng, S.P. and Chan, C.K. and Yuen, C.W.M. January 2013, ‘Plasma treatment in cotton desizing’, *Textiles Asia*, vol. 44, no. 1, pp. 17-19.

2. Kan, C.W., Lam, C.F., Chan, C.K. and Ng, S.P. ‘Using atmospheric pressure plasma treatment for treating grey cotton fabric’, *Carbohydrate Polymers* (accepted for publication) **(SCI)**.

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Chapter 1 Introduction

1.1 Background

Cotton fabric is widely used in textile and clothing nowadays. Approximately 25 million tonnes of cotton are produced in the world every year (International Year of Natural Fibers, 2009) and cotton has more than 34% market share in the world textile fiber consumption in recent decades (Plastina, 2009). As a massive amount of water, chemicals and energy are incurred in the preparation process of cotton materials, the handling of waste water and associated chemical disposal is costly and the side effects arouse from chemical wastes would influence the environment. Cost efficiency and environment protection are emphasized in this generation, as a result the textile industry is seeking for a more cost saving and environmentally friendly cotton preparation process as an alternative of the conventional wet chemical process.

Preparation process is one of the most important procedures during the manufacturing of cotton material in textile industry. Pretreatment of raw cotton is a basic and crucial process as the natural impurities and the residual oils which appear on the fiber surface after manufacturing will affect the performances of the finished goods. The chemical pretreatment process of cotton material generally consists of desizing, scouring and bleaching which are the essential parts to remove all or most of the impurities away and thus satisfactory or qualified semi-products can be supplied for subsequent processes such as dyeing and further finishing. For the cotton woven fabric, sizing materials are applied on the cotton warp yarns before weaving and have to be removed in the desizing process. After desizing, the sizing materials, dirt and parts of the impurities will be removed. Several types of sizing materials can be used in the cotton warp yarn sizing. Starch is the most commonly used sizing materials in the textile industry as it is cheap, easy to apply and remove from the cotton warp yarn. Scouring and bleaching processes help to remove the residual impurities, and improve the whiteness and appearance of cotton material. Although the conventional chemical wet treatment is useful for preparing the cotton material for subsequent processes, the existence problems of large amount usage of water and chemicals have to be alleviated and there are still many rooms for improving and modifying the physical and chemical properties of cotton fiber in the preparation stage. It is believed that the fewer steps involved in the whole material handling process, the more costs can be saved. Moreover, the combination of both physical and chemical treatments will be a trend for future textile processing to achieve desired fabric properties in a more flexible way.

Plasma treatment is a new method for textile material modification in both physical and chemical properties in these few decades. The application of plasma treatment on textile materials has been proved to be successful in altering the material performances without affecting its bulk properties (Malek and Holme, 2003; Tendero et al., 2006; Karahan et al., 2009; Bhat et al., 2011b; Ratnapandian et al., 2011). Moreover, as plasma treatment is a totally dry process, single step and without much chemical usage, which is a convenience and cost efficient treatment, increasing attentions have been drawn on analyzing and developing this novel technology. Apart from the mentioned advantages, plasma treatment also has been considered as a potential alternative to the conventional chemical wet treatment

(Cai and Qiu, 2006; Peng et al., 2009).

The results given by conventional wet chemical treated and plasma treated cotton fabrics is worth to be compared and analyzed so as to minimize the problems caused by waste water and associated chemical disposal. However, studies that focus on cotton fabric treated by plasma treatment for preparation purpose have so far been scanty. Few works had been done in this area and most of the existing papers have been published regarding the application of atmospheric pressure plasma treatment in desizing PVA on cotton woven fabric (Cai et al., 2003; Matthews et al., 2005; Peng et al., 2009), not in desizing starch. Furthermore, little attentions have been given to the wettability and dyeability changes of the plasma desized woven and plasma treated knitted fabrics as compared with the conventional desized, scoured and/or bleached processes. And hardly any study has been conducted in the effect of plasma treatment on cotton knitted grey fabric.

Therefore, the aims of this study are to investigate the efficiency of plasma desizing and/or impurities removal on cotton woven and knitted fabrics with different fabric structures and to analyze how does the plasma treatment affect the performances of the cotton woven and knitted fabrics when compare with conventional wet treatment.

1.2 Objectives

This study concerns with an investigation on the effects of atmospheric pressure plasma treatment on cotton woven and knitted fabrics. The objectives are summarized as follows:

1. To investigate the changes in physical and chemical properties of cotton woven and knitted fabrics experimentally after atmospheric pressure plasma treatment.
2. To obtain a comprehensive morphological and chemical composition study of conventional and plasma treated woven and knitted fabrics instrumentally.
3. To examine the effects on dyeability of plasma treated woven and knitted fabrics.
4. To study how the plasma conditions (gas flow rate and output power) of plasma treatment affect the performances of cotton woven and knitted fabrics.
5. To compare the results of plasma treated fabrics with the fabrics treated with conventional wet chemical preparation treatment.

1.3 Methodology

The following methodologies have been adopted to achieve the objectives:

1. A comprehensive literature review will be conducted in order to obtain the background knowledge and recent development in the relevant areas.
2. International standards will be adopted for evaluation and comparison.
3. The wetting and wicking behavior of the plasma treated woven and knitted fabrics will be evaluated.
4. A series of mechanical testing, characterization techniques and analytical instruments such as scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) will be applied to acquire a comprehensive evaluation of the conventional and plasma treated cotton woven and knitted fabrics' features.

5. The cotton woven and knitted fabrics will be treated with conventional wet chemical treatment for comparison purposes and the starch sized cotton woven fabric will be plasma treated in order to evaluate the effectiveness of plasma desizing.

1.4 Scope of thesis

The thesis comprises of 7 chapters which are outlined as follows:

Chapter 1 introduces the background information, objectives, methodology and scope of this thesis.

Chapter 2 summarizes the literature review that gives a brief introduction of cotton material and the conventional chemical wet treatment. The types of plasma, principle, plasma technology applications and effect of plasma treatment will also be discussed. Comparisons between conventional wet chemical treatment and plasma treatment will also be made.

Chapter 3 describes the details of plasma treatment and the experimental procedures which applied to evaluate and compare the effectiveness between plasma treatment and conventional wet treatment.

Chapter 4 determines the influences of physical properties changed by the plasma treatment with several evaluations, including weight loss measurement, wettability and yellowness values. Results will be compared with those conventional desized, scoured and bleached fabrics.

Chapter 5 analyzes the surface and chemicals changes of the conventional treated and plasma treated fabrics by characterization techniques.

Chapter 6 studies the dyeability changes of the plasma treated fabrics and results will be compared with conventional desized, scoured and bleached fabrics.

Chapter 7 summaries the findings and major results of the present work, draws general conclusion and proposes recommendations for future research work.

Chapter 2 Literature review

2.1 Introduction

Cotton is the most widely used natural fiber in clothing today and around 25 tonnes of cotton are produced in the world every year (International Year of Natural Fibers, 2009) and cotton has more than 34% market share in the world textile fiber consumption in recent decades (Plastina, 2009). The procedures involved in manufacturing the cotton materials are complicated, in which pretreatment process is one of the most important processes for preparing the cotton materials for further treatments.

The impurities of natural cotton fibers include the natural matters, such as natural oil, waxes, pectin and coloring matters, etc.; the impurities from manufacturing and/or transformation environment, such as stain of machine oil and dust; and some purposely added impurities, such as sizing materials on warp yarns (Kalantzi et al., 2008; Wang et al., 2013). As most of the impurities are hard to be removed simply by water alone, various types of chemicals and reagents are necessary to aid the removal of impurities on cotton substrate. To remove all or most of the impurities and chemical residuals from the previous processes and to prepare the cotton fabric ready for further wet chemical treatments such as dyeing and finishing, the preparation process is essential. The conventional chemical pretreatment process of cotton fabric usually consists of various steps, generally includes desizing, scouring and bleaching. Although the performances of the cotton fabric can be enhanced after conventional chemical wet treatment, a large amount of water, chemicals and energy are consumed. Associated costs are thus incurred in processing the waste water with high chemical oxygen demand (COD) and biological oxygen demand (BOD) values, and disposed chemicals which would give rise to the environmental problems. The textiles made with natural fibers with pretreatment, including cotton and cotton based fabrics, have attracted increasing environmental concerns (Kalantzi et al., 2008; Traore and Buschle-Diller, 2000; Wang et al., 2007b; Wang et al., 2013; Traore and Buschle-Diller, 2000; Tian et al., 2011). As a result, a more effective, cost efficient and environmentally friendly cotton preparation process is desirable as an alternative of the conventional chemical wet treatment.

Plasma treatment is well known for its capability for altering the substrate surface physiochemically without affecting the bulk properties (Malek and Holme, 2003; Tendero et al., 2006; Karahan et al., 2009; Inbakumar et al., 2010; Bhat et al., 2011b; Rashidi et al., 2004; Wakida et al., 1993; Yuan et al., 1992), thus plasma treatment has been widely applied in the textile industry. Moreover, as plasma treatment is a totally dry, single step process and less chemical is needed, which has been considered as having enormous potential as an alternate technology to the conventional textile wet processing in terms of cost saving, water saving and eco-friendliness (Goto et al., 1992; Cai and Qiu, 2006; Cai et al., 2003; Peng et al., 2009; Wang et al., 2013; Nasadil and Benešovský, 2008). Moreover, the fact that plasma treatment can change the polymer solubility behavior has been proven by many researchers (Matthews et al., 2005; Bae et al., 2006; Li and Qiu, 2012), so more attentions have been put on studying the influences of plasma treatment on desizing and cleaning. The effectiveness of plasma desizing and the performance comparisons between the plasma treated fabrics and the convetional wet treated fabrics are worth to be analyzed, so as to minimize the environmental problems caused by waste water, associated chemical disposal and to reduce energy and chemicals consumption.

In cotton sizing, polyvinyl alcohol (PVA) is one of the most frequently used sizing agents for cotton warp yarns, providing impressive tensile strength and excellent film forming properties (Peng et al., 2009; Jang and Lee, 2004; Cai and Qiu, 2006; Cai et al., 2003), but PVA size is difficult to be removed and is a environmentally unfriendly material if proper waste water recycling or releasing process does not carry out. Starch is another commonly used cotton sizing agent because of its lower price and easier to be removed in desizing process when compare with synthesis sizes.

Many research have been done on PVA desizing by atmospheric pressure plasma treatment on cotton woven fabrics (Cai et al., 2003; Beliakova et al, 2004; Cai and Qiu, 2006; Peng et al., 2009; Ma et al., 2009) and proven that plasma technology is able to desize PVA on cotton woven grey fabric (Cai and Qiu, 2006; Matthews et al., 2005; Peng et al., 2009, Kan and Yuen, 2012), however, there are only few previous works concerning on starch desizing by such treatment on cotton woven grey fabrics. As a result, a study of the effects on starch desizing on cotton woven grey fabric by atmospheric pressure plasma treatment and the comparisons on desizing efficiency between conventional wet treatment and plasma treatment will be carried out. Moreover, little papers have been reported about the effects on impurities removal of cotton knitted grey fabrics by atmospheric pressure plasma treatment, so the plasma treated cotton knitted grey fabric will be analyzed and compared with conventional preparation treatment.

With an aim to ensure the experimental and analytical works can run feasibly and smoothly throughout the whole thesis, and to enrich the knowledge of the related field, a thorough and intensive understanding of the fundamental knowledge about the conventional preparation methods, plasma treatment and materials used are essential in this research. In order to fulfill the above aims, this chapter begins with a review of the literature on existing information about the materials used and techniques applied in this study, followed by a discussion of the background and properties of cotton fiber. In addition, in an attempt to explore the possibility of modifying the applied techniques, the relevant knowledge of plasma treatment are also reviewed in this chapter.

2.2 Materials

2.2.1 Cotton

Cotton is one of the most important textile materials and the most widely used natural fiber cloth in clothing today, which is a natural vegetable cellulosic fiber obtained from the mature capsule of cotton plant. The fibers are mostly spun into yarns or threads which are used to make soft and breathable textile. Cotton is a versatile material, which is suitable for many types of clothing and can be used to make a wide range of outer and under garments.

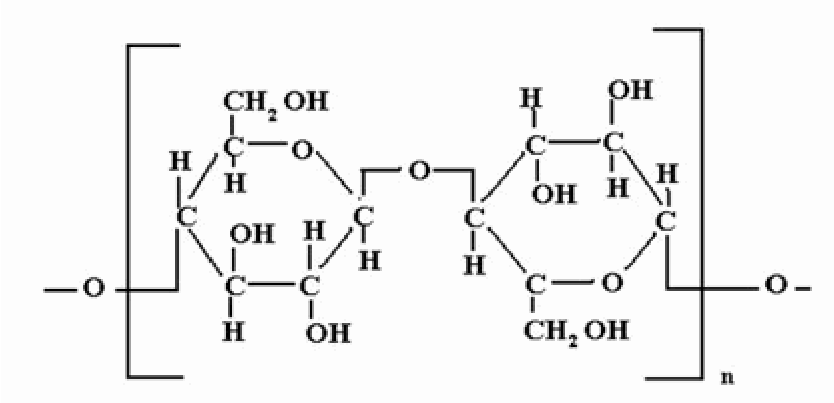

Figure 2.1 Molecular structure of cotton (University of Missouri, 2008)

Cotton is mainly composed of cellulose which is a homopolysaccharide of D-glucoses linked by β-1, 4 glycosidic bonds. From the molecular structure of cotton illustrated in Figure 2.1, there is a large amount of polar hydroxyl groups present in glucose units offering hydrophilicity to the fibers. Cotton fiber contains polymer chains in both amorphous and crystalline forms, which contain within the microfibrils are held together by the extensive intermolecular and intramolecular hydrogen bonding forming by the hydroxyl groups. Moreover, favorable fiber surface reactivity with respect to various wetting agents and chemical finishing is given by the hydroxyl groups. Cotton possesses excellent wettability and wickability, nevertheless, the high moisture content provided by the highly hydrated ions could lower the fabric resistibility to microorganisms. In addition, cotton has excellent resistance to alkali but can be attacked by hot dilute or concentrated acid solution, and also will be degraded by oxidation, hydrolysis, visible and ultraviolet light, especially under high temperature around 250-397^{o}C and high humidity.

Each cotton fiber composes of concentric layers, consisting of a cuticle, primary wall, secondary wall and a lumen as illustrated in Figure 2.2. There are variously sized pores or capillary spaces between the variously sized fibrils, that complex porous structure provides cotton with favorable wickability and unique absorbing capacity.

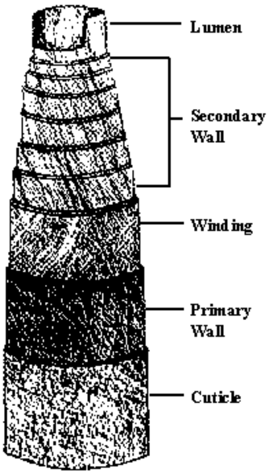

Figure 2.2 Structure of a cotton fiber (Worsham, 2012)

The non-cellulose components of cotton are pectin, waxes and proteins, etc. which can be found in the cuticle layer and the outermost layer (primary wall) of the cotton fiber. Those non-cellulose components are regarded as hydrophobic impurities which would affect the fabric absorbency of finishing solutions and dyes. The weight of each component in cotton fiber is shown in Table 2.1.

Table 2.1 Components of cotton

Weight	Components
80-90%	Cellulose
6-8%	Water
4-6%	Hemicelluloses and pectins
1-1.8%	Ash
0.5-1%	Waxes and fats
0-1.5%	Proteins

After scouring and bleaching, all or most of these hydrophobic impurities can be removed and then the fiber can become 99% cellulose.

2.3 Conventional preparation methods

2.3.1 Desizing methods

Sizing agents play an important role in weaving process as it helps to increase the weaving efficiency for cotton woven fabric. Warp yarns are sized before weaving to increase the yarn strength and reduce yarn hairiness, thus the friction between yarns and the chance for yarn damage during weaving can be greatly reduced. Sizing materials have to be removed through desizing process prior to further chemical and finishing processes, such as scouring, bleaching and dyeing, as the fabric absorbency of chemicals and dye solutions would be affected if fabric contains sizing material.

The efficiency in removing size is depended on the viscosity of size in solution, the ease of dissolution of size film on yarn, the amount of size applied, fabric construction and the method of desizing. Starch and polyvinyl alcohol (PVA) are the most commonly used sizing materials in the textile industry.

The major advantage given by PVA size is its high tensile strength, which minimizes the yarn breakage and ensures good weaving performance. The general way to remove PVA size is using hot water with detergent around 88-93^{o}C. However, PVA size is environmentally unfriendly if proper recycle or releasing process does not carry out, and also high energy cost is incurred in the waste water reusing or releasing process. In addition, completely removal of PVA size is difficult because PVA can gel and redeposit on the fabric tenaciously (Cai et al., 2003; Peng et al., 2009; Cai and Qiu, 2006). For a more eco-friendly purpose and convenient way, starch is commonly used as sizing agent in industrial application. There are several commonly used methods to remove starch size, including oxidative desizing and enzymatic desizing.

2.3.1.1 Oxidative desizing

Oxidative desizing includes the use of hydrogen peroxide, chlorites, hypochlorites, bromites, perborates or persulphates. Although oxidative desizing can give supplementary clean effect and is effective for tapioca starch, fiber damage is unavoidable as aggressive chemicals are in used. For example, hot water washing is required after using hypochlorite in order to ensure that the chlorinated residues do not retained by cotton. Adequate washing is needed after desizing with hypochlorite as the ether bonds and hydroxyl groups of cotton will be attacked and C-H bonds will be cleaved by hypochlorite. This activity is affected by pH, thus the pH of the desizing bath must be under control to maintain the stability (Dickinson, 1987; Tanveer, 2007).

2.3.1.2 Enzymatic desizing

Three main steps are involved in enzymatic desizing, including application of enzyme, digestion of starch and removal of the digestion products. The common components in an enzymatic desizing bath are amylase enzyme, pH stabilizer, chelating agents, salt and surfactants. Alpha amylase is commonly used for cotton enzymatic desizing, which can be obtained from bacteria or animal pancreases and is useful for removing starch. The ability of enzyme is highly dependent on the treating environment. When using enzyme in desizing, the pH and temperature of the water bath should be well controlled in order to enhance the efficiency of enzyme desizing as enzyme is only active within a specific range of pH, thus pH stabilizer is needed. Chelating agents are used to sequester calcium or combined heavy metals which may be injurious to the enzyme and the effectiveness of the chelating agents must be tested before use. The temperature stability of enzyme and fabric wettability can be enhanced by salts and surfactants respectively (Tanveer, 2007).

Theoretically, desizing starch size with amylase enzyme not only causes no damage to fiber as amylase is specified in hydrolyzing and reducing the molecular weight of amylase and amylopectin molecules in starch, but also provides considerable advantages in improving fabric surface luster, hand feel and wettabilitty (Wang et al., 2008). Although the chemical structures of cellulose and starch are similar (see Figure 2.3), amylase will only break down the starch without affecting the cotton cellulose. Nevertheless, if the desizing parameters and process have not been precisely controlled, a certain degree of damage would be caused to fabric.

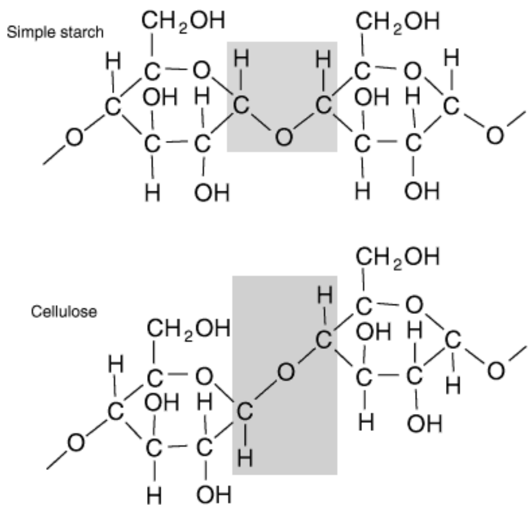

Figure 2.3 Chemical structures of starch and cellulose

Although the chance of fiber damage caused by enzyme is low, no aggressive chemical is used in enzyme desizing and which can be applied in a wide variety of application processes, 100% size removal is difficult to achieve as the removal effectiveness is largely depended on the desizing process parameters such as temperature, pH and desizing time (Tanveer, 2007). Moreover, the additional cleaning effect towards other impurities is low, some oily and fatty impurities such as cotton wax are still remained on cotton fiber even after going through enzymatic desizing process (Sun and Stylios, 2004). Thus, adequate amount of water is needed for removing the residual enzymes and chemicals on fabric surface to ensure there is no residual affecting the effect of subsequent processes.

Among those desizing methods, enzymatic desizing is found to be the most effective method in removing starch sizes and the damage toward fiber is the lowest. However, adequate amount of water is still needed for removing residual enzymes and chemicals which present on fabric surface to ensure there is no residual would affect the subsequent processes.

2.3.2 Scouring

The scouring and bleaching processes are applied to both cotton woven and knitted fabrics. Scouring process is applied to remove most of the natural impurities, for example seed fragments, oils, fats, waxes or greases and natural coloring matters, for improving the wettability, dyeability and cleanliness of fabric, in order to enhance the whole quality and serviceability of the final product. Oily and fatty matters are removed by saponification with hot sodium hydroxide solution; while those unsaponifiable materials such as waxed and dirt are removed by emulsification with surfactants. Most impurities can be removed by scouring process, which normally results in about 5-7% weight loss in cotton goods. Scouring does not remove all natural coloring matters, so bleaching process is needed after scouring.

2.3.3 Bleaching

The fabric is bleached after scouring process so as to further remove the natural coloring matters and impurities, thus the fabric whiteness will be enhanced and the fabric is being well prepared for subsequent processes. Oxidizing agents are usually used in bleaching to oxidize the color impurities to colorless compounds. However, oxidizing agents can also oxidize cotton fibers leading to reduction in fiber strength. The bleaching conditions, such as temperature, pH and treatment duration, must therefore be carefully controlled in order to maximize the destruction of color impurities but minimize the fiber degradation. The common bleaching agents used are hydrogen peroxide, sodium hypochlorite and sodium chlorite.

2.4 Background of plasma treatment

2.4.1 Introduction

Continuous development of textile wet processing has been carried out in an attempt to improve the quality of final products, however, but the conventional wet processing still operated with limitations. With the increasing concerns in environment, a more effective and environmentally friendly wet processing technique is needed. The advantages of a dry processing or physical technique are surpassed chemical wet processing.

As cotton fibers have large surface-to-volume ratios, the surface structure of the fibers often responsible for the many end use properties, which will affect the processing behaviors of the fibers and the performances of the textile material during manufacturing processes. Moreover, as cotton fiber has its inherent limitations, such as problems of wrinkle and shrinkage, low dye uptake and microbial degradation, these limitations have to be overcome in order to enhance the value of finished cotton product. The value of the textile materials can be uplifted after modified the surface by inducing various desired properties or functionalities, the surface modification techniques therefore become an important part in the textile industry. Plasma treatment is one of the surface modification techniques that has been applied on cotton fibers in these recent years and the effects of surface modification on cotton by plasma treatment have been evidenced by many research papers (Karahan et al., 2009; Patiño et al., 2011; Tian et al., 2011; Sun et al., 2011; Sun and Qiu, 2012; Buyle, 2009; Chan et al., 1996; Malek and Holme, 2003; Özdogan et al., 2002).

2.4.2 Fundamentals of plasma

Plasma is regarded as “the fourth state of matter”. Plasma is a fully or partially ionized gas of which a fraction of its constituents are no longer electrically natural, containing equal numbers of positive ions and electrons, free radicals, metastables, photons and natural species from ultraviolet to visible electromagnetic radiation, depending on the degree of ionization as shown in Fig 2.4. Plasma is created by exciting a gas or vapor in electromagnetic or electric fields.

The atmospheric plasmas used in this study are generated from electrical energy. Energy is transmitted by the electric field to the gas electrons, which are the most mobile charged species. This electronic energy is then be transmitted to the neutral species by collisions which follow the probabilistic laws and can be divided in two types:

1. Elastic collisions: the internal energy of the neutral species do not changed but their kinetic energy is slightly rose.
2. Inelastic collisions: the electronic structure of the neutral species is modified by collisions when the electronic energy is high enough. As a result, the excited species or ions are created if the collisions are energetic enough.

The constituents of plasma are responsible for the surface modification of the substrate, especially metastables. Unlike other excited species, metastables have a long decay lifetime and are capable to transfer energy to other species (Braithwaite, 2000; Tendero. 2006).

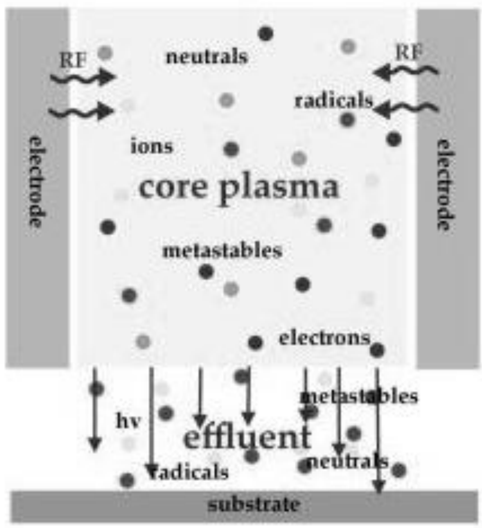

Figure 2.4 Schematic diagram of plasma constituents in an atmospheric pressure plasma jet (Niemi et al, 2007)

The modification degree of the substrate is depending on the penetration power of plasma. The particles in plasma can react with a polymer in the outermost atomic layers. Surface modification of the substrate can be induced by plasma confining to about 1-10μm depth without altering its bulk properties. Energetic photons such as vacuum ultraviolet (VUV) is able to penetrate deeper into the subsurface, even into the bulk region (Hollander et al., 1999). The penetration power of different plasma constituents is shown in Figure 2.5.

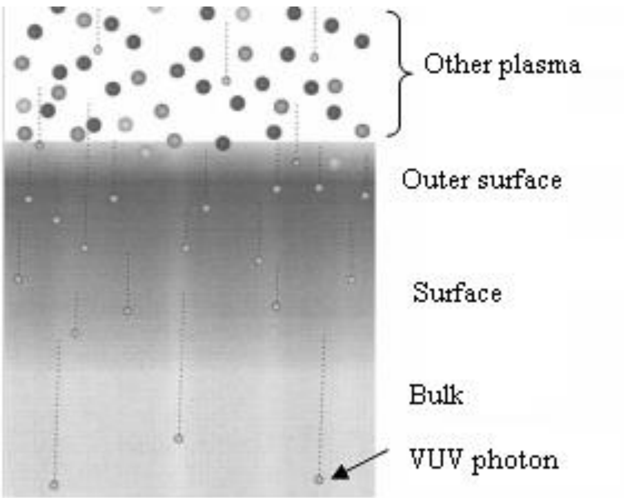

Figure 2.5 Penetration power of different plasma constituents
(Holländer et al., 1999)

Plasma is generated when gas is exposed to an electromagnetic field, which can be generated under atmospheric pressure or in a closed vessel under reduced pressure. The selection of the type of energy supplied, amount of energy transferred to the plasma and the gases used to generate plasma will determine the properties of the plasma, in terms of electronic density or temperature. The categories of plasmas are distinguished by the electronic density and temperature. Also, the desired surface chemistry can be obtained by different combinations of gases, such as oxygen/helium, argon/oxygen and nitrogen/tetrafluoromethane. Both generated plasmas can be used for surface cleaning, surface activation, surface etching cross-linking, chain scission oxidation and/or grafting by mainly breaking the polymer chains through the interaction between active plasma species and polymeric surfaces, inducing new functional groups and altering morphological properties (Inbakumar et al., 2010; Wróbel et al., 1978; Riccardi et al., 2003; D'Agostino et al., 1991; Yuan et al., 1992).

Plasma is classified into two main categories: local thermodynamic (or thermal) equilibrium plasmas (LTE) and non-local thermodynamic equilibrium plasmas (non-LTE). Table 2.2 describes the main characteristics of LTE and non-LTE.

Table 2.2 Classification of plasmas (Tendero et al., 2006)

	LTE plasmas	Non-LTE plasmas
Current name	Thermal plasmas	Cold plasmas
Properties	*$T_e \approx T_i \approx T_n$	*$T_e > T_i \approx T_n$
Electron density	High	Low
Type of collisions	Heavy particles are being heated by elastic collisions	Heavy particles are slightly heated by a few elastic collisions

*T_e= electron temperature, T_i= ion temperature, T_n= neutral temperature

2.4.3 Atmospheric pressure versus reduced pressure

There are two types of low temperature plasmas which are usually used on the treatment of textiles, namely vacuum (low pressure) plasma and atmospheric pressure plasma. Low temperature plasma used in low pressure has been investigated and used for textiles surface modifications in the past few decades. The advantages offered by the low pressure plasma, such as uniform glow, low breakdown voltages, high concentration of reactive species and high concentration of active species non-thermal plasma can be generated, have been proven by several researchers (Long et al., 2008; Luciu et al., 2008; Inakumar et al., 2010). Despite textile surface modification can be done by low pressure plasma with several advantages, limitations are still exited.

Operating with vacuum systems are time, place and energy consuming, and material properties (thickness and size) are highly dependent on the size of the device, thus the size of the object that can be treated is limited by the size of the vacuum chamber (Schütze et al., 1998; Karahan et al., 2009). Also, a vacuum chamber and the necessary vacuum pumps are required, load locks and robotic assemblies must be used to shuttle materials in and out of vacuum, which mean that the investment cost for such a piece of equipment can be very high (Schütze et al., 1998). The machine productivity is limited as the vacuum/low pressure conditions have to be created and sustained during processing. Therefore, the vacuum plasma not only imparts additional costs to the system but also limits the size and the amount of products.

On the other hand, the atmospheric pressure plasma has overcome the disadvantages of vacuum operation, as the atmospheric pressure plasma treatment is operated under atmospheric conditions and no vacuum system is required, with lower investment and maintenance costs and the operation processes are easier. Moreover, the low pressure plasma cannot fulfill the requirement of continuous textile processing in a batch process, but atmospheric pressure plasma can be applied on-line in production, which thus enables continuous processing of fabric rolls. As a result, the atmospheric pressure plasma treatment is considered as more suitable for textile surface modification. The atmospheric pressure plasma treatment has emerged as a novel technique for textile applications and evolved to fulfill the needs of textile industry (Senthilkumar et al., 2008; Kale and Desai, 2011).

The comparisons between the characteristics of plasma operated in vacuum pressure and atmospheric pressure are summarized in Table 2.3, and the comparisons between vacuum plasma treatment and atmospheric pressure plasma treatment are shown in Table 2.4. Table 2.5 shows the comparisons between atmospheric pressure plasma, vacuum pressure plasma and conventional wet processing systems.

Table 2.3 Summary of the characteristics of plasma operated in different pressures

	Vacuum (low) pressure	Atmospheric pressure
Operation	Batch	Batch/ continuous
Capital and maintenance costs	High	Relatively low
Lifetime of active species	Long	Short
Mean free path length	Long	Short
Breakage voltage V_b	Similar	

Table 2.4 Comparison between vacuum plasma and atmospheric pressure plasma systems (Shenton and Stevens, 2001)

	Vacuum (low pressure) plasma treatment	Atmospheric pressure plasma treatment
Cost of machinery set up	High. Vacuum chambers are required, thereby increasing the operation cost.	Relatively low. Plasma eliminates the need for harsh chemicals or inefficient vacuum chambers.
Complexity of operation	Complicated procedures for loading the sample into the chamber, pump down the pressure, run the process, vent the system to air and upload the sample.	Relatively easy. The sample treating time is short, usually only few seconds are needed to obtain the desired effects. Large amount of product can be produced in a short time by rapidly scanning the sample surface by the tool.
Possibility of integration	Difficult to integrate into other process equipment.	Easily integrated with the existing textile processing set up.
Surface modification capabilities	Similar	

Table 2.5 Comparison between atmospheric pressure plasma, vacuum pressure plasma and conventional wet processing systems

System feature	Atmospheric pressure plasma	Vacuum pressure plasma	Conventional wet processing
Technological process	Treatment time is short, single continuous process	Complicated procedures for loading the sample into the chamber and long pumping time for vacuum before actual treatment	Multiple steps process
Operating temperature	Low	Low	High temperature in the pad-dry-cure process
Types of reaction gas	Noble gases, air, oxygen, helium, etc.	Noble gases, air, oxygen, helium, etc.	None
Functionalities	Depending on the reaction gas, ease for tailor-making the functionalities	Depending on the reaction gas, ease for tailor-making the functionalities	Depending on chemicals used for desired functions
Cost	No material consumption and environmental cost	No material consumption and environmental cost	High material consumption and environment costs
Productivity	Single step and continuous	Single steps and batchwise	Multiple steps
Qualities	Very thin layer surface treatment without damaging the interior structure of the material	Very thin layer surface treatment without damaging the interior structure of the material	Penetrate into the interior structure of the material which may cause damaging effect
Durability	Good	Good	Good
Safety	Good	Good	Good
Environmental impact	Very low, no unreacted chemical waste	Very low, no unreacted chemical waste	High, pollution due to unreacted chemical waste

Table 2.5 shows that the advantages given by atmospheric pressure plasma treatment surmount vacuum pressure plasma treatment and conventional chemical wet processing.

2.4.4 Different atmospheric pressure plasma sources

The capability to modify textile material surface by atmospheric pressure plasma treatment has been proven in these few decades. The atmospheric pressure plasma treatment can enhance the surface reactivity of the textile substrates, such as improvement in wettability, dyeability, adhesion and hydrophobicity and other finishing processes without affecting the fabric bulk properties (Temmerman and Leys, 2005; Wang and Qiu, 2007a; Samanta et al., 2009; Sun and Qiu, 2012; Cai and Qiu, 2006; Karahan and Özdoğan, 2008; Patiño et al., 2011; Kostić et al., 2008; Wang et al., 2008).

The main classification of atmospheric pressure plasmas is mainly divided into three classes: corona discharge, dielectric barrier discharge (DBD) and glow discharge. Corona discharge is a non-LTE discharge with low current density and can only be operated under atmospheric pressure. The plasma volume created by corona discharge is very small, so the size of the treated substrate is restricted. The size of the surface treatment can be increased by replacing the cathode wire by a planer electrode, but a non-homogeneous treatment will be occurred on the material surface. To overcome the shortages of corona discharge, a dielectric barrier discharge was developed. As the treatment carried out by DBD and glow discharge are relatively homogeneous and can be operated under both vacuum and atmospheric pressure, they are usually applied in textile industry for uniform surface modification. There is a variety of DBD and glow discharge sources including atmospheric pressure glow discharge (APGD) (Meade et al., 2008; Samanta et al., 2009), atmospheric pressure plasma jet (APPJ) (Selwyn et al., 1999-2000 ; Wang and Qiu, 2007a; Wang and Qiu, 2007b) and atmospheric pressure non-equilibrium plasma (APNEP) (Shenton et al., 2001, Shenton et al., 2002), etc.. The atmospheric device used in this research is atmospheric pressure plasma jet (APPJ).

APPJ is a capacitively coupled device which utilizes an inductively coupled electrode design and produces a stable discharge at atmospheric pressure with 13.56 MHz radio frequency. The free electrons are accelerated by the RF field and enter into collisions with the molecules of the background gas. Various reactive species are produced by the inelastic collisions and exit the nozzle at high velocity (Laroussi, 2002). The architecture and configuration of APPJ are shown in Figure 2.6 and 2.7 respectively.

The inclusion of helium gas as the seed gas is important as helium will dissociate other atoms/molecules such as oxygen, resulting in stabilizing the APPJ plasma and ionization of the mixed molecules:

$$He^m + O_2 \rightarrow He + O^* + O^+ + e$$

$$He^+ + O_2 \rightarrow He^+ + O + O^*$$

$$He^+ + O_2 \rightarrow He + O^+ + O^*$$

(Kan and Yuen, 2006).

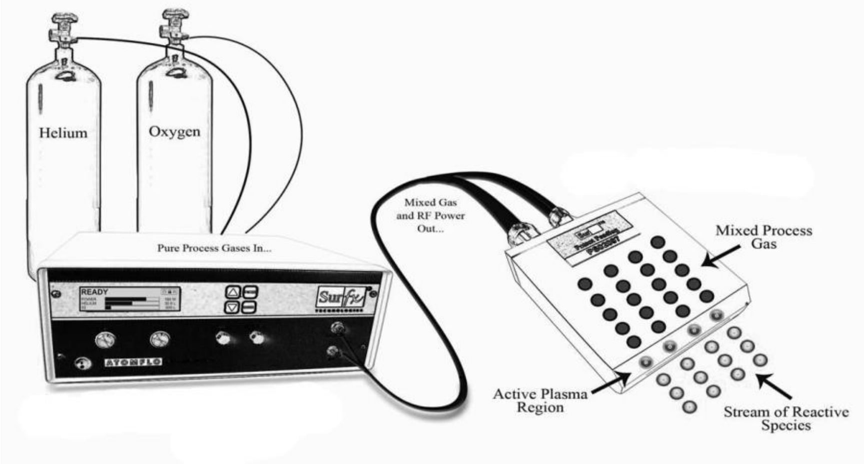

Figure 2.6 Architecture of APPJ (Surfx Tech., US)

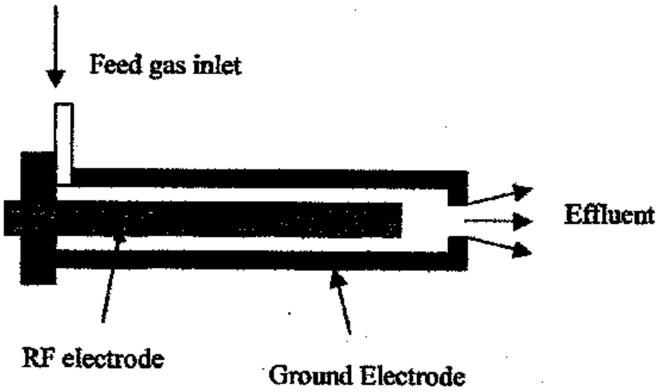

Figure 2.7 Configuration of the APPJ (Herrmann, 1999)

2.4.5 Atmospheric pressure plasma technology applications

The atmospheric pressure plasma treatment can be used in different stages of textile production, such as sliver level, yarn level, woven, nonwoven and knitted, etc., and treat on entire garments is also possible (Buyle, 2009). Moreover, atmospheric pressure plasma treatment can be used for obtaining desire effects on the treated material. Table 2.6 shows some of the typical applications of the plasma technology and the related effects obtained on the plasma treated substrate.

Table 2.6 Atmospheric pressure plasma applications and their effects on substrate (Saravanan and Nalankilli, 2008)

Process	Nature of process	Effects obtained
Alteration of surface energy	Alters chemical nature of surface by active species, embed or remove charges	Wettability, wickability, printability, dyeability, washability
Alteration of adhesive properties	Surface energy is increased by plasma active species. Adhesion results from combination of mechanical, chemical, electrostatic, permeation, micro-profile contributions	Painting of surfaces without volatile organic chemicals (VOC), composite structures, medical applications
Alteration of electrical characteristics	Increases surface conductivity, embeds or imparts electrostatic charges and deposits on the surface	Antistatic finish, charging and discharging action in photocopying, filtration, charge embedding in nonwovens
Alteration of surface finish	Results in microscopic physical damage, removal of absorbed monolayers, inducing chemical reactions	Adhesion of liquids/adhesives, etching, scratch resistance, altering optical characteristics
Altering bulk properties	Changes occur due to changes in surface energy and/or cohesive properties in microscopic scale	Modification of tensile and compressive strength, elasticity, density, hand
Removal of microorganism	Environmental stresses, physical/chemical disruptions	Sterilization, disinfection, cleaning and antisepsis

2.4.6 Advantages and disadvantages of atmospheric pressure plasma treatment

The following advantages can be reached by using the technique:

1. Plasma treatment is an environmental friendly technique because of the low energy and water consumption, few or even no chemical is required and no waste disposal problem and disposal cost incurred.
2. The process is fully controllable as all parameters are controlled by the unit and quality control is possible by print-out and data-logging.
3. Plasma treatment is an effective treatment as the processing time is short and the surface of all polymers, irrespective of their structure and chemical reactivity, can be modified by the excited species in the gas plasma.

4. As the atmospheric pressure plasma treatment is operated under a relatively low temperature than the vacuum plasma treatment, no substrate damage or bulk property changes occurred.
5. Different processes running in the same unit are possible.
6. The substrate geometries are not restricted, no matter small or large, simple or complex, parts or textiles are both possible for treated by atmospheric pressure plasma.

Apart from the above merits of atmospheric pressure plasma treatment, there are some demerits that make the plasma treatment cannot be fully commercialized in the textile industry yet. The disadvantages of plasma treatment are listed in the followings (Chan et al., 1996):

1. The processing parameters are highly system dependent. Optimal parameters may differ from system to system, therefore modification of the system is needed before actual usage.
2. Plasma parameters are rather complex and difficult to control; many factors influence the interaction between the plasma and the substrate surface, such as machine output power, treatment time, gas flow rate and jet to substrate distance.
3. The amount of the specific functional groups that formed on the substrate surface is hard to control.

2.5 Plasma processing versus conventional wet processing

As the conventional chemical pretreatment process is time, chemicals and energy consuming, many shorter and cleaner pretreatment processes have been developed in order to fulfill the environmental requirements, such as low temperature pretreatments (Abdel-Halim and Al-Deyab, 2011; Moeshed, 2011), one-step pretreatments process (Phatthalung et al., 2012; Shafie et al., 2009) and enzymatic desizing combined with ultrasonic technology (Wang et al., 2012), etc.. Among all these newly developed pretreatment processes, the low temperature plasma treatment has its own advantages over those improved wet chemical treatments due to its waterless and dry surface modification process.

The non-LTE plasmas are known as low temperature plasmas, which have received increasing attentions and can be viewed as a potential alternate technology for the textile wet processing, due to its completely dry process which is more economical and ecological. Enormous amounts of water, chemicals and energy are required in the conventional wet processing which would give rise to pollution problems and sequential effluent treatments are required. The plasma surface modification techniques using in textile processing can be used as a stand-alone process or as a pretreatment for improving the efficiency in the next process (Bhat et al., 2011b). Moreover, low temperature plasma treatment is a versatile treatment which is compatible with different gases or precursors in a system. As the bulk gas temperature is near ambient temperature, thermal degradation on materials can be avoided. Moreover, the excited heavy particles, electrons and ultra-photons, etc. have higher energies than covalent and other bonds, which can initiate various chemical reactions (Li et al., 1997; Vallon et al., 1997; Wertheimer et al., 1999) and cause etching effect on the substrate surface by physical bombardments and chemical modifications (Anand et al., 1981; Yuan et al., 1992; Li et al., 1997; Vallon et al., 1997). Thus, low temperature plasma treatment is helpful for improving the surface properties of the substrate by inducing functional groups, increasing surface roughness and removing impurities, etc. without affecting its bulk properties. Because of the effects given by the low temperature plasma, it have been applied on a diversity of textile materials in the past few decades (Höcker, 2002; Morent et al., 2008; Kale and Desai, 2011) and the plasma treated textile materials can be used in different applications as a diversity of surface functionalities can be incorporated by the plasma treatment.

As the shortcomings of the conventional wet chemical processing have been surmounted by the low temperature plasma treatment, the low temperature plasma processing can be seen as a potential alternative in the coming future. Table 2.7 shows the comparisons of the advantages given by the low temperature plasma processing over conventional wet chemical processing.

Table 2.7 Comparison of the advantages offered by plasma processing over conventional wet chemical processing

Manufacturing operation	Conventional wet chemical processing	Plasma processing
Handling and storage of bulk chemicals	Yes	No
Preparation of chemicals and baths	Yes	No
Water usage	Heavy	None or very low
Raw materials consumption	High	Relatively low
Drying and curing operations	Yes	No
Number of process steps incurred	Multiple	Single
Energy consumption	High	Very low
Sequential effluent treatments	Yes	No
Environmentally costly	Yes	No
Equipment footprint	Large	Small
Manufacturing versatility from single kit	Limited to single or few process options	Depending on kit, can be highly flexible with wide range of available processes
Innovation potential	Moderate	Very high

2.5.1 Application of plasma treatment on desizing

Previous research works have been done to analyze the effectiveness of plasma desizing.

Cai et al. (Cai et al., 2003) compared air/helium (air/He) and air/oxygen/helium (air/O_2/He) atmospheric plasmas for desizing PVA, and air/O_2/He atmospheric plasma was found to have a greater effect on PVA desizing. The swelling, dissolving and dispersing of PVA were enhanced by plasma treatment, so some of the PVA sizes were removed and the effectiveness of PVA removal by subsequent washing was significantly facilitated.

Cai and Qiu (Cai and Qiu, 2006) investigated the effects of air/O_2/ He on desizing

PVA on cotton fabric and results were compared with that of conventional hydrogen peroxide (H_2O_2) desizing. Argon/ O_2 (Ar/O_2) plasmas were employed in the study of Peng et al. (Peng et al., 2009). The studies of Cai and Qiu and Peng et al. both found that the oxygen based functional groups such as C-O, C=O and C=C-OR/O=C-OH were increased by the plasma treatment, which implied that the length of the PVA molecular chains were shorten and further oxidized by plasma exposure. The plasma desizing efficacy was similar with the conventional H_2O_2 desizing (Cai and Qiu, 2006) and fiber surfaces were as clean as unsized fibers (Peng et al., 2009). Moreover, microcracks were developed on the fiber surface after plasma treatment. The increase in hydrophilic groups and roughness by oxygen plasmas resulted in enhancement in wettability and the results were even better than the conventional desizing and scouring.

Matthews et al. (Matthews et al., 2005) used PVA films to investigate the effects that given by plasma desizing. Atmospheric pressure plasma was employed to desize the PVA films with helium/oxygen (He/O_2) and helium/carbon tetrafluoride (He/CF_4) plasmas. The weight loss of the PVA film was found to be increased with increasing plasma treatment time until saturation. And because of the chain scission by plasma exposure, the molecular weight of the PVA chains was reduced with increasing treatment durations.

Kan and Yuen (Kan and Yuen, 2012) had investigated the optimum conditions for atmospheric pressure plasma desizing on starch by using He/O_2 plasma followed by an enzymatic color fading process. The level of importance of the plasma processing parameters based on the orthogonal array testing strategy (OATS) was in the order: jet distance> ignition power> oxygen concentration> treatment time.

Shorter jet to substrate distance and higher ignition power were found to be more effective in starch desizing. The adequate amount of oxygen concentration and treatment time were depended on the combination of plasma parameters. Moreover, the lightness of the plasma treated cotton fabrics was higher than the enzyme treated fabrics because of the removal of protruding fiber on fabric surface by the etching process during plasma treatment. The performances of the plasma desized cotton fabrics were significantly enhanced and comparable with conventional enzyme desized cotton fabrics.

Beside cellulose materials, glass fibers (Tomasino et al., 1995; Morent et al., 2008) and ceramic fibers (Wei et al., 2003) also have been used to analyze the size removal efficiency by treating with different low temperature plasmas.

2.6 Conclusion

The textile industry is searching for innovative surface modification techniques to improve the product quality, as well as the requisition for environmentally friendly preparation and finishing processes are being higher than the past few decades. The atmospheric pressure plasma treatment has been revealed as an prospective choice as a pretreatment technique for the textile processing, which can be used to simplify the preparation process of the cotton fabric. The waterless atmospheric pressure plasma treatment has enormous potential to surmount the shortcomings of wet chemical processing by reducing the usage of water, chemicals and energy. Distinct properties of this plasma technique have been stated in the previous sections.

The fundamental knowledge about the structure and properties of the materials, conventional wet treatment and plasma treatment used in this research has been reviewed prior to the application of techniques. The details of experiment procedures of plasma treatment, the experiments done to evaluate the physical and structural properties changes and the result comparisons between conventional wet processing and atmospheric pressure plasma treatment will be illustrated in the following chapters.

Chapter 3 Research methodology

3.1 Introduction

The popularity of using plasma treatment as a textile surface modification method has been increased, not only for the use in finishing process, but also in preparation process. Plasma treatment is an eco-friendly surface modification technique which has been proposed for the sizing, desizing or scouring process of cellulosic materials, viewing as an alternative of the conventional wet processing in the textile industry (Goto et al., 1992; Vladimirtseva et al., 1995; Peng et al., 2009; Sun et al., 2011; Sun & Qiu, 2012). Plasma modification on textile surface has great potential for improving or even replacing the older, multi-process, chemical and energy consuming preparation technologies.

To evaluate the effectiveness of cotton desizing by atmospheric pressure plasma treatment, the cotton samples were conventional and plasma treated separately, then the results obtained from these treatments were compared and analyzed. Also, simulated starch sizing was applied on the bleached woven fabrics, following by plasma treatment for evaluating the plasma desizing effectiveness on starch size. These empirical studies would help to evaluate the practical application and industrial realization in textile industry.

In order to find out the optimum condition for plasma desizing, the cotton fabrics were treated with atmospheric pressure plasma under various treatment conditions, i.e. different oxygen flow rates and output powers. Tests such as topography by scanning electron microscopy for observing the fiber surface changes and wettability tests were carried out to evaluate the physical and chemical property changes of conventional treated and plasma treated fabrics. Moreover, the yellowness values were obtained by measuring the conventional and plasma treated fabrics through the spectrophotometer. Studies of the dyeability of the conventional treated and plasma treated fabrics were also carried out.

3.2 Materials

Four types of woven grey 100% cotton fabrics and two types of knitted grey 100% cotton fabrics were used in this study. The specifications of the cotton woven fabrics and knitted fabrics are shown in Table 3.1 and Table 3.3 respectively; and the SEM fabric surface images and notation diagrams of woven and knitted fabrics are shown in Table 3.2 and 3.4 respectively.

Table 3.1 Fabric specifications of woven fabrics

Weave	Weight (g/m^2)	Fabric count	Fabric thickness (mm)	Yarn twist (turns per inch)		Yarn density	
				Warp	Weft	Warp ends per inch	Weft picks per inch
Poplin	288	32s x 32s	0.27	17	18	90	80
Poplin	263	40s x 40s	0.28	15	18	135	68
2/1 twill	271	40s x 40s	0.29	17	19	132	69
2/2 twill	233	32s x 32s	0.34	12	17	79	69

Table 3.2 SEM fabric surface images, weave and notation diagrams of woven fabrics

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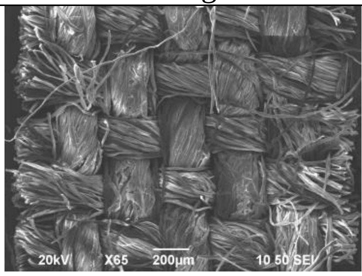
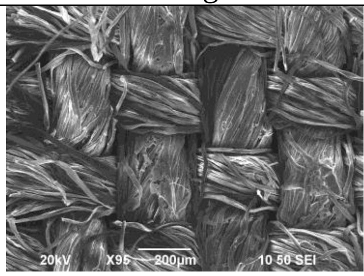
<tr><td rowspan="4">Poplin 32s</td><td>
</td><td>
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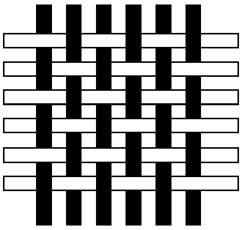
<tr><td rowspan="2"></td><td rowspan="2"><table>
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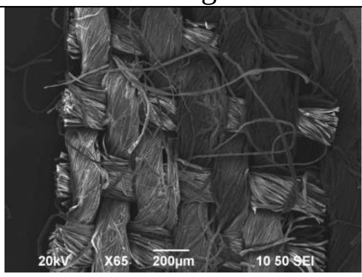
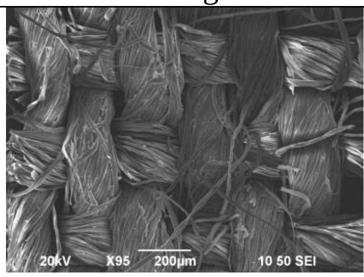
<tr><td>
</td><td>
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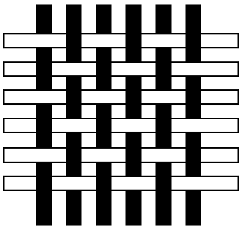
<tr><td></td><td><table>
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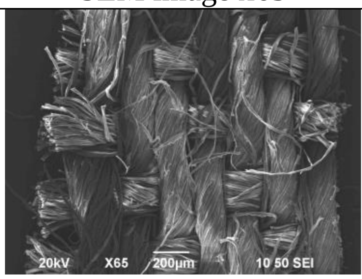
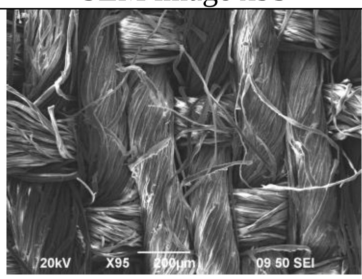
<tr><td>
</td><td>
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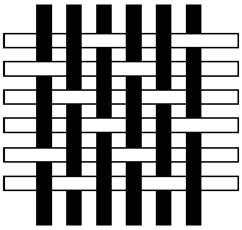
<tr><td></td><td>
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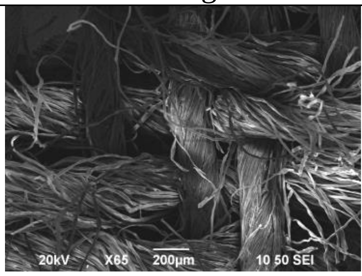
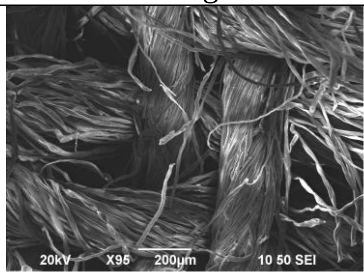
<tr><td>
</td><td>
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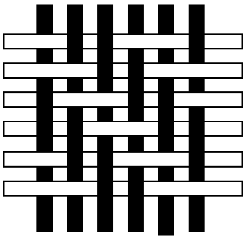
<tr><td></td><td>
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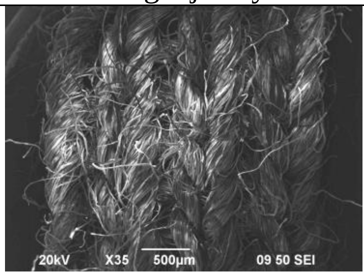
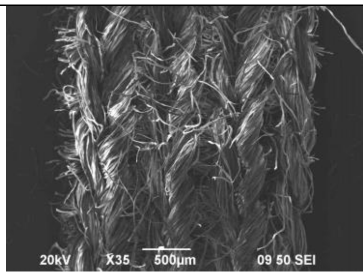
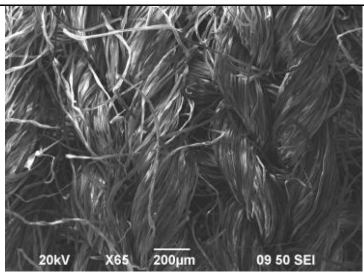
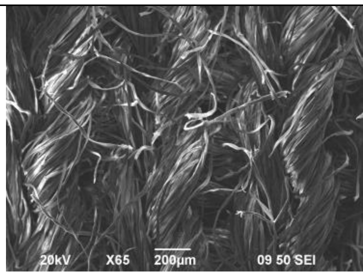
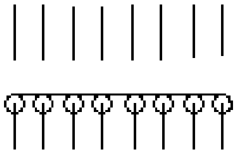
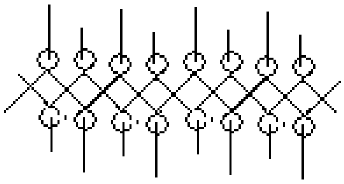
Table 3.3 Fabric specifications of knitted fabrics

Weave	Weight (g/m^2)	Fabric count	Fabric thickness (mm)	Yarn density	
				Wales per inch	Courses per inch
Single jersey	255	30s	0.46	48	31
Interlock	385	32s	0.72	42	35

Table 3.4 SEM fabric surface images and notation diagrams of knitted fabrics

	Single jersey	Interlock
SEM image x35		
SEM image x65		
Yarn path diagram		

3.3 Simulated starch sizing on woven fabric

As the pick-up and the type of sizing material used in the industrial made woven fabrics are not disclosed, the simulated starch sizing on the bleached woven fabrics was conducted in order to evaluate the starch desizing effectiveness of plasma treatment. The well desized, scoured and bleached woven cotton fabric samples were two-dipped-two-nipped in a sizing bath containing 10% starch with the same 100% pick-up ratio. The padded samples were dried in an oven at 95-100℃.

3.4 Conventional preparation process

In the cotton fabric preparation process, a variety of steps are involved. The purpose of the preparation process is to remove all the natural impurities and chemical residuals from the previous process and to prepare the fabric ready for dyeing and finishing. In this study, the woven and knitted cotton fabrics had been gone through several conventional preparation processes for comparisons and analyses. The steps for treating cotton woven and knitted fabrics are shown in Figure 3.1.

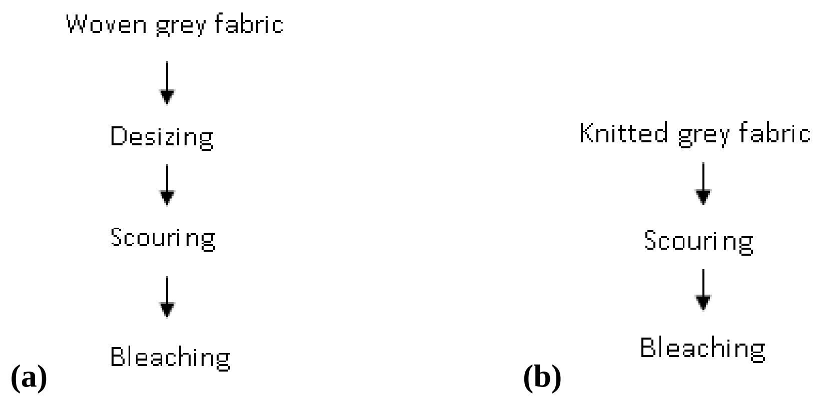


Figure 3.1 Conventional Preparation processes of (a) cotton woven and (b) cotton knitted fabrics

The fabrics used in desizing, scouring, bleaching, simulated starch sizing processes and plasma treatment were both cut into 15cm x 15cm, conditioned under the standard atmosphere of $20\pm2^{o}C$ and $65\pm2\%$ relative humidity for 24 ± 1 hours before and after each process. The total volume of the water bath per 1g fabric was 50ml in the wet processing treatments.

3.4.1 Cotton desizing for woven fabric

Table 3.5 Recipe of cotton desizing

Liquor-to-goods ratio	50:1
Bactosol PHC. HC (liquid)	5g/L
Sandozin NI (10%)	0.2g/L

The recipe for desizing the cotton woven grey fabric is shown in Table 3.5. Bactosol PHC. HC (liquid) was used as the reagent for desizing starch based and starch size mixtures. Bactosol PHC. HC, Sandozin NI, water and woven fabric were added together into the conical flask, and put in the water bath for 60 minutes at 70^{o}C. The pH of the water bath was around 6.5-7.5. The desized fabric sample was washed with water at 30 ^{o}C for 5 minutes and then dried in atmospheric environment.

3.4.2 Cotton scouring

Table 3.6 Recipe of cotton scouring

Liquor-to-goods ratio	50:1
Sodium hydroxide (liquid)(10%)	30g/L
Non-ionic detergent (10%)	2g/L
Sodium silicate (10%)	2g/L
Neutralize: sulphuric acid (0.5%)	5g/L

Table 3.6 shows the scouring recipe for both cotton woven and knitted fabrics. Sodium hydroxide, non-ionic detergent, sodium silicate, water and fabric were added together into the conical flask, and put in the water bath for 60 minutes at 100^{o}C. After scouring, the fabric sample was washed with 0.5% sulphuric acid for neutralization. Then the sample was washed with water at 30^{o}C for 5 mintues and completely dried in atmospheric environment.

3.4.3 Cotton bleaching

Table 3.7 Recipe of cotton bleaching

Liquor-to-goods ratio	50:1
Hydrogen peroxide (30%)	17.5g/L
Sandozin NI (10%)	1g/L
Sodium hydroxide (liquid) (10%)	5g/L
Sodium silicate (10%)	10g/L
Magnesium sulfate (10%)	5g/L

The bleaching recipe of cotton woven and knitted fabrics is shown in Table 3.7. Hydrogen peroxide, Sandozin NI, sodium hydroxide, sodium silicate, magnesium sulfate, water and fabric sample were added together into the conical flask, and put in the water bath for 60 minutes at 90^{o}C. Sodium hydroxide was added for adjusting the water bath pH to 11. The bleached sample was washed with water at 30 ^{o}C for 5 minutes and then dried in atmospheric environment.

3.5 Atmospheric pressure plasma treatment

Plasma treatment of the cotton fabrics was carried out on an atmospheric pressure plasma jet (APPJ) apparatus, Atomflo 200-Series manufactured by Surfx Technologies (California, USA) with one inch linear-beam head connected to the gases supply. Helium and oxygen were used as carrier and reactive gases respectively. Table 3.8 shows the purity of helium and oxygen used for the treatment and the schematic diagram of the plasma treatment used in this study is illustrated in Figure 3.2.

Table 3.8 Purity of gases used

Gas	Purity
Helium	≥ 99.995%
Oxygen	≥ 99.7%

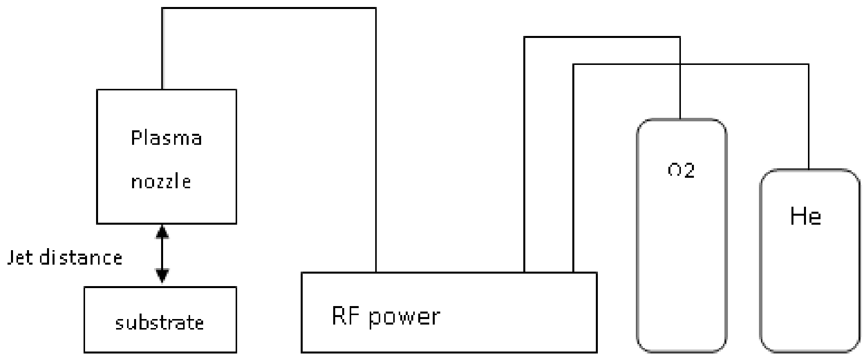


Figure 3.2 Schematic diagram of He-O_2 plasma treatment of cotton fabrics

The cotton fabric was cut into 15cm x 15cm and then stored in the standard testing conditions (20±2^{o}C, 65±2% R.H.) for 24±1 hours. After weighting, the fabric was mounted on a square aluminum frame, which was placed under the nozzle of plasma jet, for plasma treatment. The treatment was carried out by using a rectangular nozzle which covers an active area of 1 x 25mm^2 and mounted vertically above the substrate. The nozzle directs a powerful plasma beam which is generated by a radio-frequency of 13.56MHz onto a sample and scan over the sample surface. The treatment was operated with oxygen flow rate of 0.2L/m, 0.3L/m, 0.4L/m and output power of 140W, 150W and 160W for both woven and knitted fabrics. The helium flow rate and treatment time were kept at 30L/min and 1mm/s respectively during the plasma treatment. The nozzle to substrate distance of woven fabric was 2mm and 3mm for knitted fabric. Those parameters are summarized in Table 3.9. When one parameter changed, the other parameters were held constant.

Table 3.9 Parameters used in plasma treatment

Parameters	Values		
Helium flow rate (L/min)	30		
Oxygen flow rate (L/min)	0.2	0.3	0.4
Treatment time (mm/s)	1		
Output power (W)	140	150	160
Nozzle-to-substrate distance (mm)	2 (woven) / 3 (knitted)		

Experiments for the six types of cotton woven and knitted fabrics were taken with the numbering of different parameters used in the plasma treatment. The numbering of data and parameters are summarized in Table 3.10.

Table 3.10 Numbering of parameters in groups

	Power (W)	Oxygen flow rate (L/m)
1.	140	0.2
2.	140	0.3
3.	140	0.4
4.	150	0.2
5.	150	0.3
6.	150	0.4
7.	160	0.2
8.	160	0.3
9.	160	0.4

Due to the interaction between the plasma active species and the activated surface, the plasma treated samples were subjected to the standard condition ($20 \pm 2^{o}C$, $65 \pm 2\%$ R.H.) for 24 ± 1 hours before the evaluation tests.

3.6 Iodine test

Iodine test was used as a preliminary test for observing the effectiveness of enzyme desizing and plasma desizing. The grey, enzyme desized and plasma treated woven fabrics were subjected to the iodine test before other evaluation tests. The iodine solution was prepared according to AATCC Test Method 103-2004. Five drops of iodine solution were placed randomly on the sample surface, and the color produced on the fabric sample indicated the degree of desizing, which was observed and recorded after 10 minutes.

Table 3.11 Degree of desizing

Indicator	Degree of desizing
Dark blue	Presence of unaffected starch
Light blue	Slight residual starch
Yellowish brown	Starch decomposed to water soluble dextrine
Yellow	Complete absence of starch

3.7 Weight loss measurement

To quantify the degree of enzyme desizing and plasma desizing, the grey, enzyme and plasma treated fabrics were weighted to determine the percent size removed and the difference in weight between those fabrics which were calaulated based on the weight loss measurement (Gao et al., 2009). The fabrics were weighted before (W_0) and after (W_1) each treatment for comparison, and recorded as the average of 3 measurements. The present weight change was calculated by using the following equation:

$$\text{Weight loss (\%)} = \frac{W_0 - W_1}{W_0} \times 100$$

3.8 Washing after plasma treatment

In order to know more about the efficiency of plasma desizing, the fabrics were subjected to wet condition after plasma treated. Different types of woven grey fabrics were plasma treated with the same parameters, i.e. 150W output and 0.4L/m oxygen flow rate, for better comparison. The plasma treated fabrics and the grey fabrics were put in the water bath for 15 minutes at 70^{o}C for hot washing and 30^{o}C for cold washing. The weights of the washed fabrics were recorded and compared.

3.9 Scouring after plasma treatment

Usually long period of treatment time and high temperature are involved in the conventional scouring process, which is a time and energy consuming process. For analyzing the efficiency of plasma desizing and the effect of plasma treatment on scouring of cotton fabrics, conventional scouring process was operated after plasma treatment with shorter treatment time and lower temperature. For both cotton woven and knitted fabrics, the grey fabrics were treated with the same plasma parameters, i.e. 150W output power and 0.4L/m oxygen flow rate, for better comparison and then scoured with sodium hydroxide, non-ionic detergent and sodium silicate (same scouring recipe as listed on Table 3.6) for 60 minutes at 100^{o}C and 45 minutes with different temperatures at 100^{o}C, 80 ^{o}C or 65 ^{o}C, and then the scoured fabrics were weighted after drying. The fabric weights of the plasma treated and scoured fabrics were recorded for comparisons.

3.10 Yellowness (ASTM E313)

The yellowness of the fabric was measured before and after each conventional wet process and plasma treatment. The changes of yellowness of the treated samples were quantified by the CIE yellowness index by using the reflectance spectrophotometer Datacolor 650. CIE illuminant D65 and 10^{o} standard observer were used and the yellowness values of the plasma treated fabrics were compared with grey, enzyme desized and scoured fabrics.

3.11 Wettability

Wetting is important for cellulosic fiber as the degree of comfort is greatly affected by the moisture absorbency. Wettabilty is valuable for the fiber surface characterization, liquid transportation and the interaction of fiber with liquids and surfactants (Merkel, 1991; Miller, 1985).

Wetting and wicking are two related processes as a liquid should wet the fibers before wicking into a fabric. Wicking simply means the capillary movement of moisture within fabric structure. In general, wicking takes place when a liquid travels along the surface of the fiber but is not absorbed into the fiber. Physically, wicking is the spontaneous flow of a liquid in a porous substrate, driven by capillary forces. Since wicking can only occur when fibers assembled with capillary spaces between them are wetted by a liquid, wetting is a prerequisite for wicking (Kissa, 1996).

Based on the relative amount of liquid involved and the way of the liquid-fabric contact, the wicking processes can be divided into two groups:

1. Wicking from an infinite liquid reservoir (immersion, transplanar wicking and longitudinal wicking)
2. Wicking from a finite (limited) reservoir (a single drop wicking into a fabric)

Wettability describes the initial behavior of a fabric, yarn or fiber in contact with liquid (Sharabaty et al., 2008) whereas wickiability of a fabric is determined by the properties of the liquid, liquid-fabric surface interactions and geometric configurations of the pore structure in the fabric. The surface wetting behavior can be altered by the changes in fiber chemical compositions (Hsieh et al., 1996).

The wetting behavior of the liquid over the substrate surface is a complex issue, which is affected by the surface morphology, surface roughness and the chemical composition of the substrate. The wettability of the grey cotton fabric is poor due to the natural impurities and/or sizing agents present on the fiber surface. Apart from the traditional wet chemical processing, plasma treatment is one of the alternatives available to clean the fiber surfaces so as to decrease the tension between fiber and liquid, thus improve the wetting properties. The plasma treatment can change the physical and chemical structures of the fiber surface by etching away the fiber surface, not only with the corresponding changes in fiber diameter and surface roughness, but also introducing polar groups onto the fiber surfaces (Benerito et al., 1981; Goto et al., 1992; Höcker, 2002; Kan and Yuen, 2006). The wettability and surface geometry of the fabric is determined by the degree of etching. The changes of the wetting and wicking properties of the fabric will be expected after plasma treatment.

3.11.1 Drop test (simulated AATCC 79-2010)

The wettability of textile material can be indicated by the wet spot area which is formed by a liquid drop (Kissa, 1981). The drop test of the cotton woven and knitted fabrics was operated by simulating AATCC Test Method 79-2010. The wetted areas were recorded by using dye solution in order to quantify the surface wettability of the grey, conventional treated and plasma treated woven and knitted fabrics (Wardman and Abarabbo, 2010). The size of each fabric specimen was cut into 5cm x 5cm and Methyl Blue dye was used as the aqueous solution. The drop volume of the dye was fixed at 20 μm approximately by using an autopipet and the drop height was fixed at 5cm for each turn. The fabric sample was placed on top of a plastic film in order to avoid the dye droplet being absorbed by other substrates.

The dispersion size of the dye droplet was defined as the area within the liquid boundary after completely dried on the fabric and it was measured by graph paper in mm^2. Measurement was taken when the specular reflection of the dye droplet was disappeared or the measurement will be terminated when excess the time limit 10 minutes. Three measurements were taken on each side of the test specimen and then averaged. The set up of the drop test is shown in Figure 3.3.

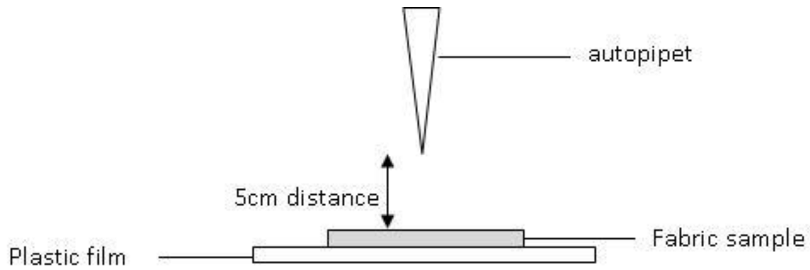


Figure 3.3 Set up of drop test

3.11.2 Longitudinal wicking test (simulated AATCC 197-2011)

Wicking is occurred from an infinite liquid reservoir by the longitudinal wicking test in which the fabric is partially immersed in a large volume of liquid for wetting the fabric. The rate of vertical capillary rise of samples was measured by simulating AATCC Test Method 197-2011. The vertical capillary action behavior of the woven fabrics has been compared by measuring the capillary height as a function of time. Knitted fabrics have not been subjected to this wicking test as knitted fabric will curl during the process and the wicking height is hard to be measured precisely.

The untreated, conventional treated and plasma treated fabrics were both cut into a 20mm x 90mm fabric strips in warp and weft direction respectively. For indicating the water rise level clearly, graduated scale (5mm interval) was marked on the fabric strip surface by a water-soluble pen. Then each fabric strip was being clamped vertically and its edge was immersed in the same volume (500ml) of deionized water. The height of the water uptake is measured by a millimeter ruler which assembled along the fabric strip and then recorded at each 5 minutes interval. The experiment was terminated when the water uptake point had reached at 90mm or reached the time limit of 30 minutes. Triplicate samples were carried out to ensure repeatability. The set up of the wicking test is shown in Figure 3.4.

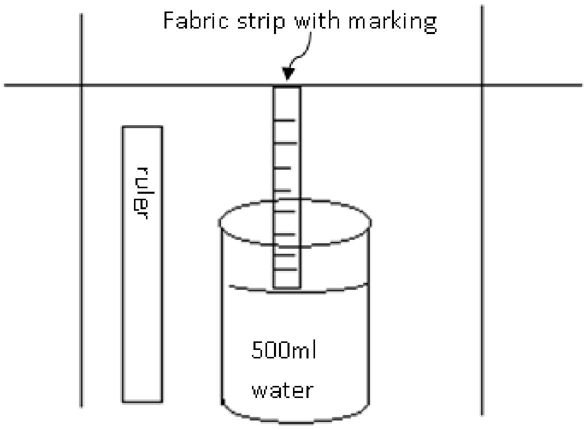


Figure 3.4 Set up of longitudinal wicking test

The wicking rates of the warp and weft fabric strips were also calculated for comparison between different plasma parameters. The wicking height measured at 30 minutes was used for assessing the wicking rate.

$$\text{Wicking rate } (mm/s^{0.5}) = \frac{\text{wicking height at 30 mins}}{1800s^{0.5}}$$

3.12 Characterization

3.12.1 Scanning electron microscopy (SEM)

The surface morphological images of cotton woven and knitted fabric were examined using a scanning electron microscopy (SEM, model JSM-6490, JEOL Ltd., Japan). The samples were coated with a thin layer of gold to induce conductivity before SEM observation. Images of the samples were captured at 3000X magnification to reveal the surface morphological changes caused by the conventional and plasma treatment.

3.12.2 Fourier transform infrared spectroscopy (FTIR-ATR)

The analysis was performed by Perkin Elmer spectrophotometer (Spectrum 100, Perkin Elmer Ltd.) equipped with a total internal reflectance (ATR) accessory which was used to analyze the surface chemical composition of the fabric. ZnSe was used as the ATR crystal. The scanning range was 650-4000cm^{-1} with an average of 64 scans of each fabric and the resolution was 4cm^{-1}.

3.12.3 X-ray photoelectron spectrometer (XPS)

The surface chemical composition of the conventional treated and plasma treated fabrics were analyzed by the XPS model Sengyang SKL-12 electron spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer. X-ray source was a twin-anode (Mg/Al) source from VG (type XR3E2). Non-monochromatic Mg Kα radiation (1253.6 eV) at a current of 15 mA and 10 kV were used. The base pressure within the XPS chamber was 2 x 10^{-9} Mbar. Photo emitted electrons were collected at a take-off angle of 45 degree. The peak positions relative to hydrocarbon were calibrated at 285eV, so the relative intensities of C_{1s} (285eV) and O_{1s} (533eV) peaks could be determined.

3.13 Dyeing

Reactive dyes are usually used for dyeing cellulose fibers as they have very high fastness to wet treatment, dry cleaning and rubbing due to covalent bond is formed between fiber and dye molecule. Moreover, reactive dyes also have a complete color range, especially possess exceptional brilliant of shade; and easy to apply, especially in exhaust dyeing. In order to have an in-depth analysis on desizing and/or scouring cotton grey fabric by plasma treatment, dyeing was carried out with two reactive dyes.

The grey, conventional enzyme desized, scoured and bleached fabrics, and the plasma treated fabrics were cut into 2g each and dyed with two different vinyl sulphone reactive dyes in one depth, Remazol Brilliant Blue R (CI Reactive Blue 19) and Remazol Black B (CI Reactive Black 5), which were obtained from DyStar. These two reactive dyes were used in this study as they are commonly used in commercial purpose and have well-known chemical structure. The details of the dyes are shown in Table 3.12.

Table 3.12 Details of dyes used

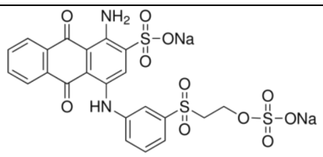
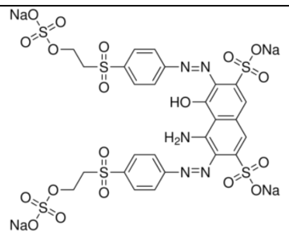
Dye name	Remazol Brilliant Blue R	Remazol Black B
Dye type	Vinyl sulphone – Monofunctional	Vinyl sulphone – Bifunctional
Empirical formula (hill notation)	$C_{22}H_{16}N_2Na_2O_{11}S_3$	$C_{26}H_{21}N_5Na_4O_{19}S6$
Chemical structure	 (Sigma-Aldrich Co., 2013a)	 (Sigma-Aldrich Co., 2013b)

Table 3.13 Dyeing parameters

Liquor-to-goods ratio	50:1
Dye concentration (% owf)	1.0
Glauber's salt (g/l)	40
Soda ash (g/l)	10
1^{st} alkali addition	1/3 amount of soda ash
2^{nd} alkali addition	2/3 amount of soda ash

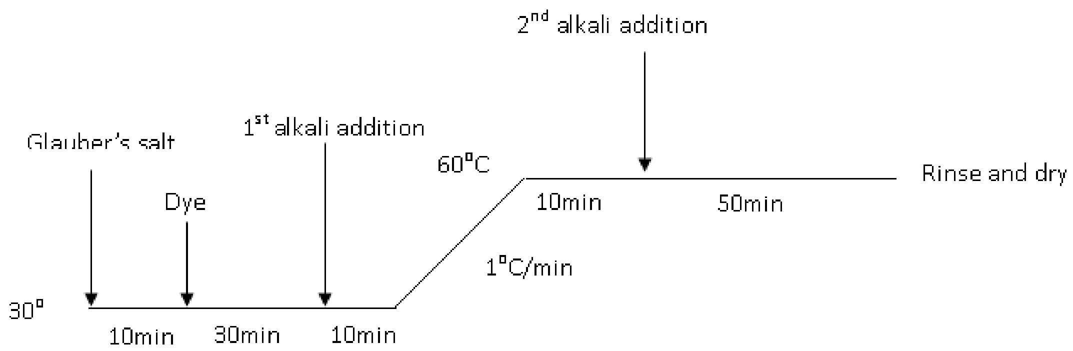


Figure 3.5 Dyeing procedures

The dyeing parameters and the dyeing procedures are shown in Table 3.13 and Figure 3.5 respectively. Glauber's salt (sodium sulphate for exhaustion), water and fabric samples were added together into the conical flask, and then put in the water bath with gently shaking for 10 minutes at 30°C. Dyes were added after 10 minutes. After 30 minutes, the first alkali (sodium carbonate for fixation) was added. 10 minutes later, the temperature was raised from 30°C to 60°C at a rate of 1°C/min. When the dyeing temperature reached 60°C, holding for 10 minutes and then the second alkali was added. Leaving the dye bathes dyed for 50 minutes with gently shaking. After dyeing, the fabric samples were washed with 1% non-ionic detergent at 90°C with gently shaking for 15 minutes to remove the unfixed and hydrolysed reactive dyes. Then the washed fabric samples were completely dried in an oven at 90°C. The fabric samples were conditioned in a standard atmosphere ((20±°C, 65±2% R.H.) for 24 hours before dyeing and prior further evaluations.

To investigate the dyeability of the fabrics affected by plasma treatment, the reflectance spectrophotometer Datacolor 650 was used to assess the color difference between the untreated, conventional treated and plasma treated fabrics. CIE illuminant D65 and 10^{o} standard observer were used. The wavelength interval used was 10nm. The reflectance values (R), relative color strength (K/S) and CIE L*a*b* of the dyed fabrics were measured and compared.

In order to know more about the dyeability of the plasma treated fabrics, a computer color matching system was used. The basis of computer color matching is largely built upon the theory postulated by Kubelka and Munk which describes the scattering and absorption of radiant energy in a turbid medium in terms of reflectance, defining the quantities of radiant energy absorption and scattering by the coefficients of K and S respectively. This theory is called Kubelka-Munk Function:

$$K/S = (1-R)^2 / 2R$$

Where K is the coefficient of absorption, depending on the concentration of the colorant; S is the coefficient of scattering, causing by the dyed substrate; and R is the absolute reflectance factor of the colored sample. The higher the K/S value, the better the color yield will be.

The CIE L* (lightness) a* (redness and greenness) b* (yellowness and blueness) values are used to quantitively determine the colour lightness and the color-opponent dimensions.

In addition, for knowing more about the effects of plasma treatment on the fabric dyeing performance when compare with grey and conventional treated fabrics, the unlevelness of the dyed fabrics were assessed by an objective method with using relatice unlevelness index (RUI) (Chong et al., 1992).

Four different locations on the dyed fabrics were randomly selected and measured over the visible spectrum (λ=400-700nm) at internals of 10nm by using the spectrophotometer Datacolor 650 with CIE illuminant D65 and 10^o standard observer. The relative unlevelness index was obtained by the following equation:

$$\mathrm{RUI} = \sum_{\lambda=400}^{700} C_\lambda V_\lambda = \sum_{\lambda=400}^{700} (S_\lambda / \bar{R}) V_\lambda$$

In which, C_λ is the coefficient of variation of reflectance values measured for each wavelength; V_λ is the coefficients of variation of reflectance by photopic relative luminous efficiency function; S_λ is the standard deviation of reflectance values measured at a specific wavelength; $\bar{R}$ is the mean of the reflectance values measured for each wavelength.

The degree of levelness of the dyed fabric can be described by the suggested interpretation of RUI values (Chong et al., 1992) as shown in Table 3.14.

Table 3.14 Suggested interpretation of RUI values

RUI	Visual appearance of levelness
<0.2	Excellent levelness (unlevelness not detectable)
0.2-0.49	Good levelness (noticeable unlevelness under close examination)
0.5-1.0	Poor levelness (apparent unlevelness)
>1.0	Bad levelness (conspicuous unlevelness)

3.14 Conclusion

The details of materials used in this study, plasma parameters employed for the plasma treatment and methods applied for evaluating the conventional and plasma treated fabrics have been reviewed and explained in this chapter.

The changes in the fabric physical properties, including weight loss, wettability and yellowness values, after conventional and plasma treated will be analyzed and compared in next chapter.

Chapter 4 Physical properties

4.1 Introduction

The low temperature plasma has been used as an effective mean to modify the fiber surface in order to obtain the desirable results, which has attracted considerable attentions and has been proposed for the desizing process and also for the scouring process of cellulosic materials (Cai et al., 2003; Bhat et al., 2011a; Goto et al., 1992; Vladimirtseva et al., 1995, Sun and Stylios, 2004; Kan and Yuen, 2012; Ma et al., 2009; Matthews et al., 2005; Peng et al, 2009). The fiber surface layer can be altered by mean of plasma treatment and the alternation effects are depended on the machine power, gas type, gas power, gas flow rate, treatment time and fiber structure. The alternations by plasma treatment have been evidenced and grouped into three categories, namely surface wetting, surface chemical composition and surface morphology (Yan and Guo, 1989).

The physical properties of the atmospheric pressure plasma treated woven and knitted fabrics were investigated through several physical evaluations and the results were compared with the conventional treated fabrics, in order to evaluate the efficiency of plasma desizing and scouring.

The weight differences between the grey, enzyme desized and plasma desized woven fabrics were compared. The wettability of the plasma treated cotton fabrics were measured by drop test (simulated AATCC 79-2010) (for woven and knitted fabrics) and longitudinal wicking test (simulated AATCC 197-2011) (for woven fabrics), which were applied to investigate the hydrophilicity of the grey, conventional treated and plasma treated cotton fabrics. The plasma treated fabrics also subjected to further wet process by washing with different temperatures and scouring with different times and temperatures for analyzing the effects of plasma treatment. In below evaluations, a same plasma condition, i.e. 150W output power and 0.4L/m oxygen flow rate, was used on different fabric types for getting a better comparison result.

4.2 Woven fabrics

4.2.1 Iodine test

The iodine test was applied on the industrial sized woven fabrics and simulated starch sized woven fabrics before and after enzyme and plasma desizing. The results of the enzyme desized fabrics both show a light brown color and a yellowish brown color is appeared on the plasma desized fabrics. By observing the color change of the iodine solution, the sizing materials on the fabric were mostly removed by the enzyme desizing and plasma treatment gives aid to hydrolyzing the sizing materials.

4.2.2Weight loss measurement

The fabrics were weighted before and after treatments for comparison. The weight loss after treatment reveals the amount of impurities, including sizes, which have been removed from the fiber surface.

4.2.2.1 Simulated starch sizing

Table 4.1 Weight of simulated starch sized, enzyme desized and plasma desized woven fabrics

Fabric type	Weight (g)			Difference in weight (g)	Weight loss percentage (%)
	Simulated starch sized	Enzyme desized	*Plasma desized		
Poplin 32s	2.94	2.76		0.18	6.12
	3.02		2.86	0.16	5.30
Poplin 40s	2.73	2.50		0.23	8.42
	2.82		2.68	0.14	4.96
2/1 twill	2.76	2.60		0.16	5.80
	2.90		2.75	0.15	5.17
2/2 twill	2.43	2.22		0.21	8.64
	2.53		2.40	0.13	5.14

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Raw cotton fibers not only compose of celluloses, but also contain non-cellulosic materials, such as pectin, wax, oil and dust particles on the fiber surface. The conventional wet treatment aids in removing the impurities which present on the fiber surface; plasma treatment also aids in removing the surface contaminants by etching the fiber surface and inducing the chemical changes in fiber (Cai and Qiu, 2006; D'Agostino et al., 1991; Ḧocker, 2002; Inbakumar et al., 2010; Navaneetha Patiño et al., 2011; Bhat et al., 2011a). The removal of these impurities by the wet treatment and plasma treatment can be determined by fabric weight loss.

From Table 4.1, the simulated starch sizing results show that a fabric weight loss after plasma treatment is obtained, and the decreased weight reveals the amount of impurities, including starch sizes, which have been removed by the plasmas. Plasma treatment is a dry surface etching process which occurred by removing a thin layer on the fiber surface directly as well as by the indirect interaction between ions and the molecules of the material. The excited and energetic plasmas are able to attack and break down the sizing materials and other impurities on the fiber surface effectively by physical and/or chemical etching due to the chain scission and oxidation theoretically. Moreover, the etched sizing materials and the impurities are readily to be ablated by the plasma flow during the treatment, or even go in the form of gas vaporization (Wang et al., 2013), thus result in fabric weight loss. The results indicate that the oxygen plasmas do play a role on removing the additional impurities (sizing materials, including starch size) and natural impurities on fiber surface. The etching phenomenon and the removal of impurities by plasmas can further be supported by SEM observation in Chapter 5.

Generally speaking, the weight loss percentage of plasma desized fabric is lower than enzyme desized fabric, which is account for the differences in treatment conditions. Plasma treatment is a waterless surface modification technique, only the surface yarns treated with plasma will be affected; but enzyme desizing is a wet treatment process, every yarn is being immersed in the desizing bath during the process, thus the inner layer of the fabric can also be affected and the starch sizes on the fiber surface can be all or mostly removed.

4.2.2.2 Conventional enzyme desizing and plasma desizing on woven fabrics

Table 4.2 Weight before and after conventional enzyme desizing of woven fabrics

Fabric type	Weight (g)		Difference in weight (g)	Weight loss percentage (%)
	Before enzyme desizing	After enzyme desizing		
Poplin 32s	3.27	2.88	0.39	11.93
Poplin 40s	3.10	2.72	0.38	12.26
2/1 twill	2.99	2.67	0.32	10.70
2/2 twill	2.65	2.35	0.30	11.32

Table 4.3 Weight of poplin 32s before and after plasma desizing under different parameters

Power (W)	Oxygen flow rate (L/m)	Weight (g)		Difference in weight (g)	Weight loss percentage (%)
		Before plasma desizing	After plasma desizing		
140	0.2	3.25	3.15	0.10	3.08
140	0.3	3.33	3.22	0.11	3.30
140	0.4	3.26	3.14	0.12	3.68
150	0.2	3.26	3.16	0.10	3.07
150	0.3	3.37	3.27	0.10	2.97
150	0.4	3.27	3.15	0.13	3.98
160	0.2	3.31	3.21	0.10	3.02
160	0.3	3.30	3.22	0.08	2.42
160	0.4	3.30	3.21	0.09	2.73

Table 4.4 Weight of poplin 40s before and after plasma desizing under different parameters

Power (W)	Oxygen flow rate (L/m)	Weight (g)		Difference in weight (g)	Weight loss percentage (%)
		Before plasma desizing	After plasma desizing		
140	0.2	3.07	2.97	0.09	3.03
140	0.3	3.11	3.00	0.11	3.40
140	0.4	3.09	2.96	0.12	3.93
150	0.2	3.08	2.98	0.10	3.25
150	0.3	3.06	2.98	0.08	2.57
150	0.4	3.05	2.94	0.11	3.63
160	0.2	3.07	2.95	0.11	3.73
160	0.3	3.05	2.92	0.13	4.14
160	0.4	3.08	2.96	0.11	3.70

Table 4.5 Weight of 2/1 twill before and after plasma desizing under different parameters

Power (W)	Oxygen flow rate (L/m)	Weight (g)		Difference in weight (g)	Weight loss percentage (%)
		Before plasma desizing	After plasma desizing		
140	0.2	2.97	2.89	0.08	2.82
140	0.3	2.94	2.86	0.07	2.49
140	0.4	2.95	2.87	0.08	2.74
150	0.2	2.95	2.86	0.09	3.14
150	0.3	2.96	2.88	0.08	2.69
150	0.4	2.95	2.86	0.09	3.06
160	0.2	2.98	2.87	0.11	3.55
160	0.3	2.97	2.85	0.12	4.05
160	0.4	2.97	2.87	0.10	3.36

Table 4.6 Weight of 2/2 twill before and after plasma desizing under different parameters

Power (W)	Oxygen flow rate (L/m)	Weight (g)		Difference in weight (g)	Weight loss percentage (%)
		Before plasma desizing	After plasma desizing		
140	0.2	2.62	2.53	0.09	3.33
140	0.3	2.65	2.53	0.12	4.51
140	0.4	2.58	2.47	0.11	4.23
150	0.2	2.65	2.55	0.10	3.95
150	0.3	2.65	2.55	0.10	3.89
150	0.4	2.66	2.53	0.13	4.90
160	0.2	2.67	2.52	0.15	5.62
160	0.3	2.58	2.45	0.13	5.04
160	0.4	2.69	2.55	0.13	4.97

The woven grey fabrics were plasma treated with different parameters and the weight loss after plasma direct treatment was recorded and compared with enzyme desized fabric. The weight loss percentages of the enzyme desized fabrics are shown in Table 4.2 and plasma treated fabrics are shown from Table 4.3 to 4.6 according to the fabric type. The reason for the higher weight loss percentage of fabrics treated with conventional enzyme desizing than treated with plasma desizing is due to different desizing conditions. Plasma treatment is a waterless surface modification technique, only the surface yarns treated with plasma will be affected; but enzyme desizing is a wet treatment process, every yarn is being immersed in the enzymatic desizing bath during the process, thus the inner layer of the fabric can also be affected and the starch sizes on the fiber surface can be all or mostly removed. From Table 4.3 to 4.6, the reductions in the weights of the plasma treated cotton woven fabrics are due to the removal of impurities, including sizing materials, by plasma etching. When compare among different sets of plasma parameters within the same type of fabric, the results in the weight loss percentage of the woven grey fabrics after plasma treatment are similar, suggesting a higher discharge power and/or higher gas flow rate may not give greater benefit for the direct removal of size film and impurities.

To determine the optimum plasma parameters from the results of plasma desizing, poplin 32s fabric treated with 150W output power and 0.4L/m flow rate; poplin 40s fabric and 2/1 twill fabric treated with 160W output power and 0.3L/m flow rate; and 2/2 twill fabric treated with 160W output power and 0.2L/m flow rate give the highest weight loss percentage among other set of treatment parameters when compare with the same type of fabric. From the above observations, the fabrics treated with a higher output power (150W or 160W) give a higher weight loss than fabrics treated with lower output power (140W) among the same type of woven fabric. Among the four types of woven fabrics, 2/2 twill fabrics generally give the highest weight loss percentage after plasma treatment, which may due to the looser structure of 2/2 twill fabric, i.e. fewer yarn twist and lower yarn density. With larger inter-yarn spaces, plasma species would be easier to contact with the surface of those under-layer fibers, thus greater desizing efficiency can be obtained.

Although plasma treatment only affects the surface yarns, the results given by the plasma treated fabrics are comparable with the enzyme desized fabrics. The weights of the starch sized fabrics and the industrial sized fabrics are both decreased after plasma treatment, which suggest that plasma treatment gives aid to the removal of sizing materials, including starch size.

4.2.2.3 Washing after plasma treatment

The weight differences between the plasma treated fabrics before and after washing were calculated and compared. The results of the plasma treated woven fabrics washed with cold and hot water are shown in Table 4.7 and Table 4.8 respectively.

Table 4.7 Plasma treated woven fabric with cold (30^{o}C) washing

Fabric type	*After plasma treatment (g)	After cold washing (g)	Weight difference (g)	Weight loss percentage (%)
Poplin 32s	3.14	3.10	0.04	0.67
Poplin 40s	2.87	2.80	0.07	2.41
2/1 twill	2.95	2.86	0.09	4.31
2/2 twill	2.53	2.45	0.08	3.12

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Table 4.8 Plasma treated woven fabric with hot (70^{o}C) washing

Fabric type	*After plasma treatment (g)	After hot washing (g)	Weight difference (g)	Weight loss percentage (%)
Poplin 32s	3.11	2.98	0.13	4.44
Poplin 40s	2.86	2.68	0.19	6.99
2/1 twill	2.94	2.80	0.14	2.98
2/2 twill	2.57	2.43	0.14	5.68

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Plasma treatment is a dry surface etching process. The sizing materials and other impurities are being etched and broken into small fragments by plasmas, which surface changes can be observed from the SEM images (see Chapter 5). The etched size particles and other impurities may still leave on the fiber surface after plasma treatment as direct removal of impurities may not occur, but those impurities on the fiber surface can be loosen by the bombardment of electrons and ions, which thus can be readily to be hydrolyzed or dissolved in subsequent wet process. As a result, in order to know more about the desizing efficiency of the plasma treatment, the plasma treated fabrics were subjected to wet process by washing with different water temperatures.

The fabric weights of the plasma treated woven fabrics are all decreased after both cold and hot washing, suggesting plasma treatment may be effective in etching and breaking the sizing materials and other impurities into smaller sizes, thus the solubility of the etched particles of sizes and other impurities is increased, which can be easily dissolved and removed in subsequent wet process. The plasma treated fabrics that washed with hot water (70^{o}C) give a larger difference in weight than the one washed with cold water (30 ^{o}C), revealing higher temperature is more efficient in hydrolyzing and dissolving the sizing particles and impurities.

4.2.2.4 Scouring after plasma treatment

The differences in weights between the plasma treated and scoured woven fabrics are calculated and listed in Table 4.9 to 4.12 according to the fabric type.

Table 4.9 Difference in weight between plasma treated and scoured poplin 32s fabric

Grey (g)	*After plasma treatment (g)	Scouring duration	Scouring temperature	Scoured (g)	Difference in weight (g)	Weight loss percentage (%)
3.33	---	60 min	100 ^{o}C	2.88	0.45	13.51
3.36	3.24	60 min	100 ^{o}C	2.93	0.43	12.80
3.37	3.22	45 min	100 ^{o}C	2.92	0.45	13.26
3.39	3.25	45 min	80^{o}C	3.01	0.38	11.23
3.33	3.22	45 min	65^{o}C	3.04	0.30	8.85

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Table 4.10 Difference in weight between plasma treated and scoured poplin 40s fabric

Grey (g)	After plasma treatment (g)	Scouring duration	Scouring temperature	Scoured (g)	Difference in weight (g)	Weight loss percentage (%)
3.10	---	60 min	100 ^{o}C	2.66	0.44	14.19
3.15	3.01	60 min	100 ^{o}C	2.71	0.44	13.97
3.18	3.05	45 min	100 ^{o}C	2.74	0.44	13.90
3.13	3.00	45 min	80^{o}C	2.74	0.39	12.41
3.13	3.01	45 min	65^{o}C	2.80	0.33	10.65

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Table 4.11 Difference in weight between plasma treated and scoured 2/1 twill fabric

Grey (g)	After plasma treatment (g)	Scouring duration	Scouring temperature	Scoured (g)	Difference in weight (g)	Weight loss percentage (%)
3.02	---	60 min	100 ^{o}C	2.61	0.41	13.58
2.95	2.84	60 min	100 ^{o}C	2.56	0.39	13.22
2.97	2.84	45 min	100 ^{o}C	2.57	0.40	13.61
3.00	2.86	45 min	80^{o}C	2.63	0.37	12.38
2.96	2.85	45 min	65^{o}C	2.63	0.33	11.02

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Table 4.12 Difference in weight between plasma treated and scoured 2/2 twill fabric

Grey (g)	After plasma treatment (g)	Scouring duration	Scouring temperature	Scoured (g)	Difference in weight (g)	Weight loss percentage (%)
2.65	---	60 min	100 ^{o}C	2.27	0.38	14.34
2.68	2.53	60 min	100 ^{o}C	2.30	0.38	14.18
2.69	2.56	45 min	100 ^{o}C	2.31	0.38	14.13
2.66	2.53	45 min	80^{o}C	2.31	0.36	13.37
2.66	2.54	45 min	65^{o}C	2.35	0.32	11.90

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

The grey woven fabrics were scoured with normal conventional scouring process and scoured with different scouring parameters after plasma treatment. When comparing the fabric weight loss percentages between the scoured fabrics, similar results are obtained from the plasma treated fabrics scoured with 45 minutes and 60 minutes at 100^{o}C among the same type of woven fabrics, indicating plasma treatment could help to shorten the scouring duration for at least 25% than normal scouring process. Moreover, the fabrics treated with the same scouring duration (45 minutes) but with different temperatures (100^{o}C and 80^{o}C) show a similar weight loss percentage, which reveal that lower scouring temperature could be applied in the scouring process after plasma treated by at least 20% when compare with normal scouring temperature. The results reveal that the time and energy consumption for the scouring process can be greatly reduced after plasma treated, as the hydrophilicity of the fabric surface and the activities of the scouring chemicals are enhanced by plasma pre-treatment.

Plasma treatment can uplift the scouring efficiency because the hydrophilicity of the cotton grey fabric has been enhanced by oxygen plasmas, which can be observed from the results of wettability tests in the following section 4.2.4 and FTIR-ATR results in Chapter 5. Moreover, the enhancement in impurity removal efficiency in the scouring process after plasma treatment is due to the sizes and impurities have been broken into small particles by plasmas, which can be swelled, hydrolyzed or dissolved in further wet chemical medium more easily.

The results from Table 4.9 to 4.12 prove that the plasma previous treatment is useful for improving the pretreatment efficiency of cotton grey fabrics, and also a chemical and energy saving scouring process can be achieved.

4.2.3 Yellowness (ASTM E313)

The yellowness values of the fabrics treated with different plasma parameters had been compared with the grey, enzyme desized and scoured fabrics. The results are shown in Figure 4.1 to 4.4 according to the fabric type. The higher the yellowness value, the yellower the fabric will be.

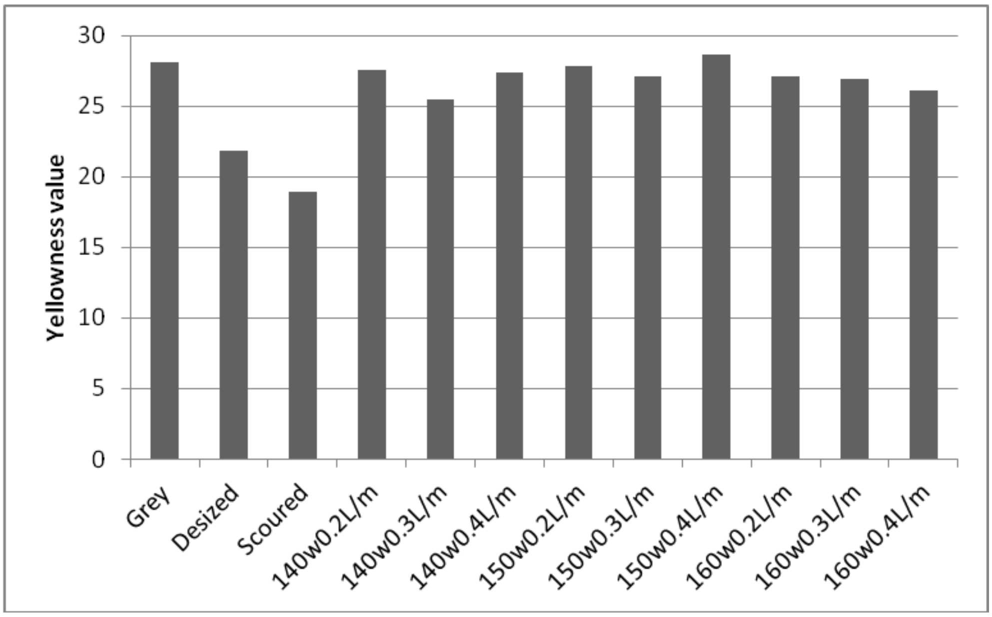


Figure 4.1 Yellowness values of poplin 32s woven fabric

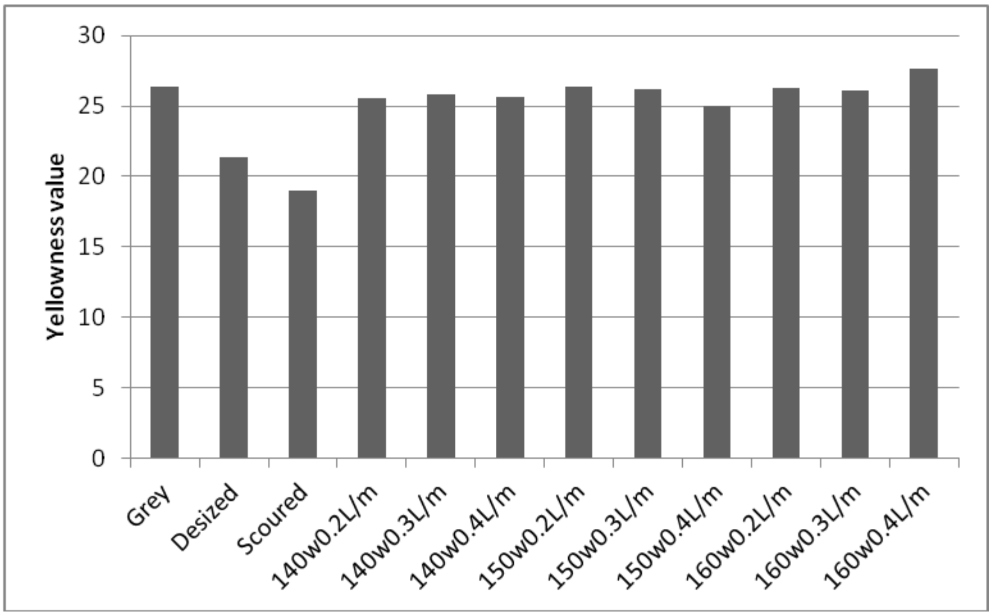


Figure 4.2 Yellowness values of poplin 40s woven fabric

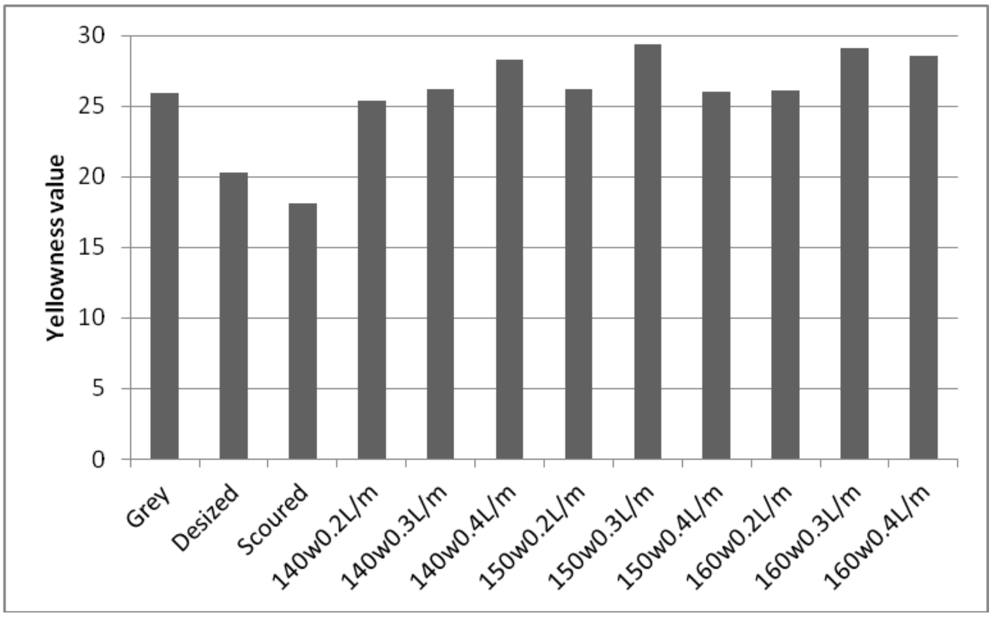


Figure 4.3 Yellowness values of 2/1 twill woven fabric

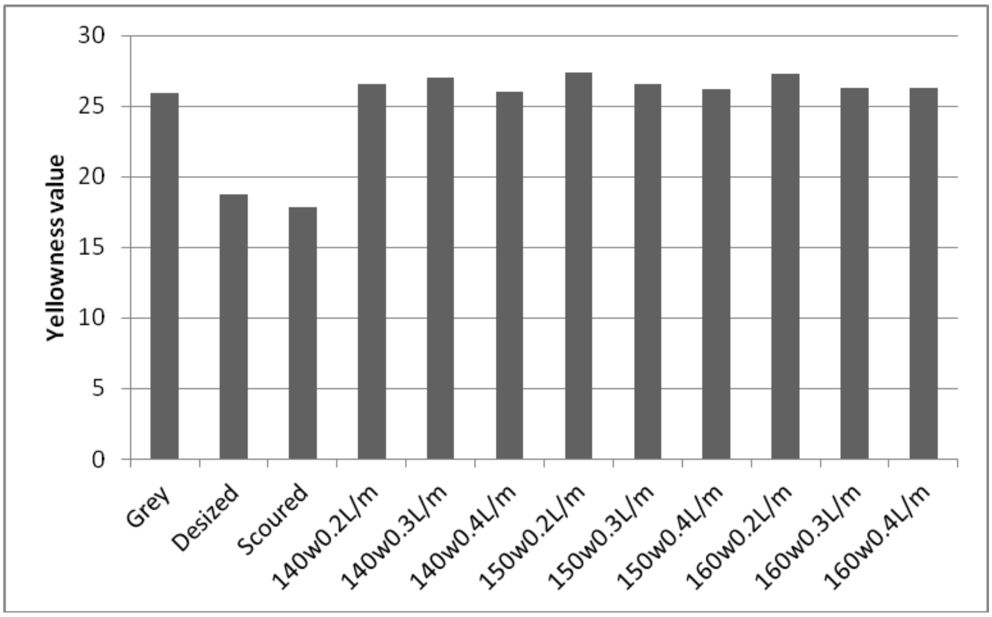


Figure 4.4 Yellowness values of 2/2 twill woven fabric

From Figure 4.1 to 4.4, the results both show that the yellowness values of the plasma treated fabrics are similar with the grey fabrics in general. Most of the yellowness values of the 32s and 40s poplin fabrics are even decreased after plasma treatment, which may due to the balanced structure of the poplin fabrics. A balanced structure can let the active plasma species evenly distribute on the fiber surface, so the natural yellowing matters and size film on the fiber surface can be ablated effectively by plasmas. The reduction in yellowness values reveals that plasma treatment not only does not cause fabric color to be yellower, but also helps to increase the fabric whiteness on poplin fabrics. This explanation is supported by the weight loss values of the plasma treated fabrics as discussed in section 4.2.2.2. The colors of the 2/2 twill fabrics are all became slightly yellower after treated with different plasma parameters, which may due to the loser fabric structure of 2/2 twill fabric. 2/2 twill fabric has a lower yarn density than the other three types of woven fabric structures, which provides larger fabric surface area to contact with the plasma active species, causing greater thermal oxidation effect during plasma treatment (Kan et al., 2011; Kan and Yuen, 2012).

4.2.4 Wettability

The wettabiliy of the conventional treated and plasma treated cotton woven fabrics were measured by the drop test and the longitudinal wicking test. The drop test results of poplin 32s, poplin 40s, 2/1 twill and 2/2 twill fabrics are shown in Figure 4.5 to 4.8 respectively. From Figure 4.9 to 4.16 show the wicking results and wicking rates of poplin 32s, poplin 40s, 2/1 twill and 2/2 twill fabrics respectively.

4.2.4.1 Drop test (simulated AATCC 79-2010)

The results of the drop test are illustrated in Fig.4.5 to 4.8, according to the structure of cotton fabric. The results are shown according to the treatments with face and back sides on x-axis, and the dispersion size in mm^2 of the dye droplet is shown on y-axis. Due to the poor wetting nature of the woven grey fabrics which cannot be wetted by the dye droplet within the time limit, no record is shown on the following graphs.

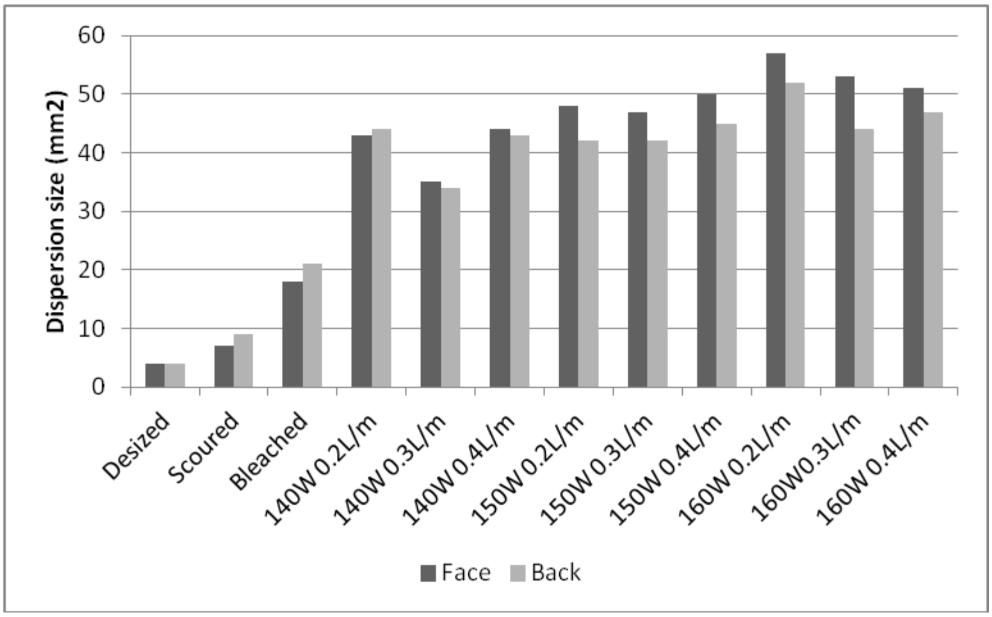


Figure 4.5 Drop test result of poplin 32s woven fabric

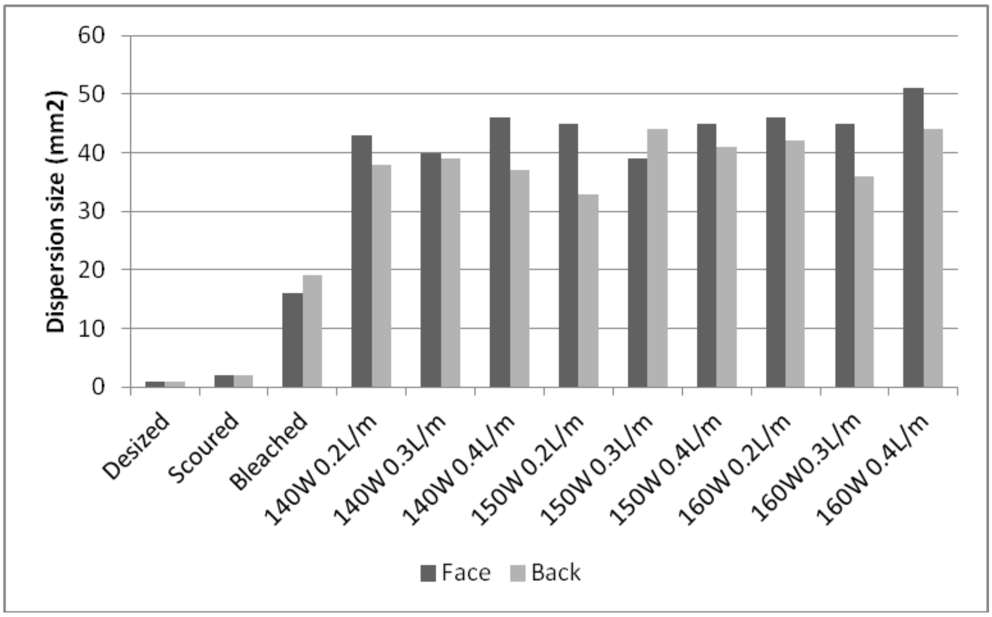


Figure 4.6 Drop test result of poplin 40s woven fabric

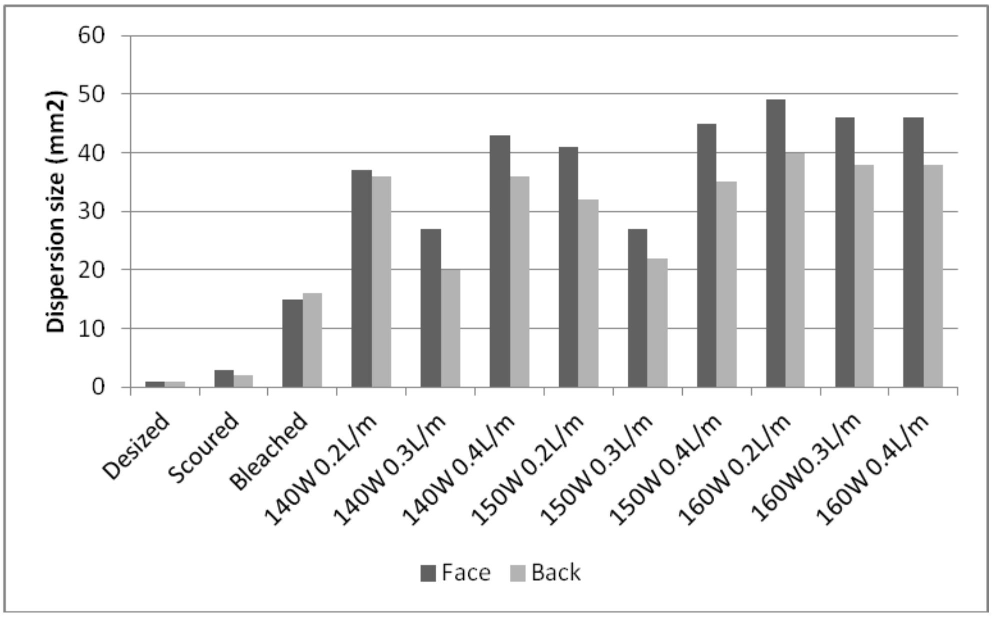


Figure 4.7 Drop test result of 2/1 twill woven fabric

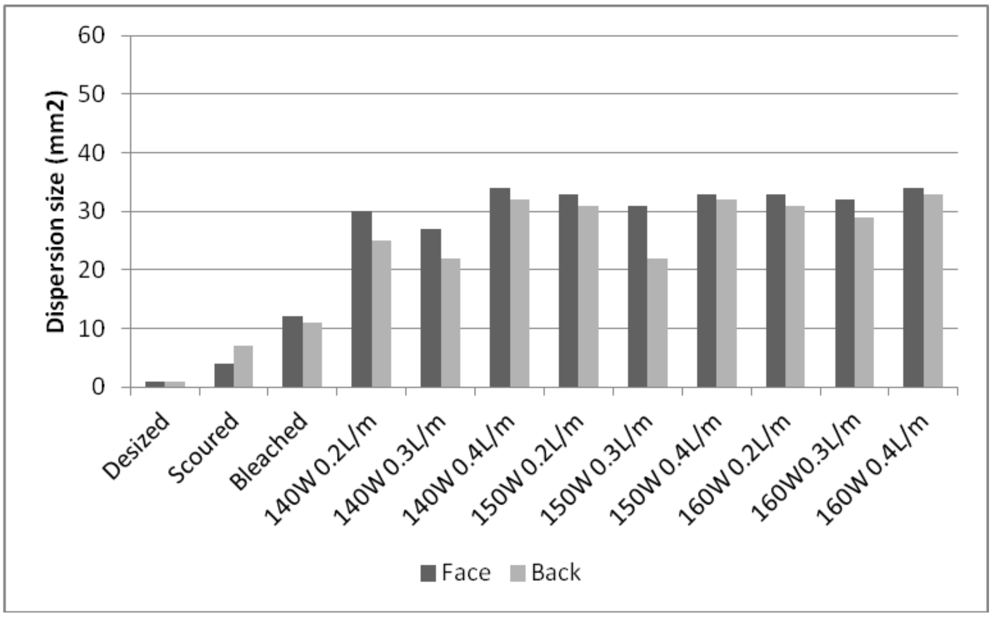


Figure 4.8 Drop test result of woven 2/2 twill fabric

From the drop test results (Figure 4.5 to 4.8), four types of woven fabrics both show that there is a dramatic improvement in the wettability after plasma treated when compare with the results of conventional treated fabrics, which dye dispersion sizes are even two times larger than the bleached cotton fabric. The dramatic enhancement in wettability of the grey fabrics is mainly due to the introduction of polar functional groups and direct bombardment on the fiber surface by active plasma species, which phenomenon can be observed from the FTIR and XPS results in Chapter 5. As the wettability of fabric can be used as an indicator for observing the desizing and scouring efficiency for impurities removal after treatments, the enhancement on wettability of plasma treated fabrics suggests that plasma treatment gives aid to remove sizing material and some of the impurities on the fiber surface. Although the size removal efficiency of plasma desizing is lower than enzyme desizing in terms of weight loss (see section 4.2.2.2), the plasma treated woven fabrics have given an impressive result in terms of wettability.

To determine the optimum plasma parameters from the drop test results, poplin 32s fabric and 2/1 twill fabric treated with 160W output power and 0.2L/m flow rate; poplin 40s fabric and 2/2 twill fabric treated with 160W output power and 0.4L/m flow rate give the largest dispersion size on both fabric face and back side among other set of treatment parameters when compare with the same type of fabric. From the above observations, 160W output power gives a better result in drop test than the other two powers among the same type of woven fabric.

4.2.4.2 Longitudinal wicking test (simulated AATCC 197-2011)

The results of the wicking test have been grouped according to the type of fabric and the direction of the fabric treated. The wicking results of poplin 32s, poplin 40s, 2/1 twill and 2/2 twill fabrics are shown in Figure 4.9, 4.11, 4.13 and 4.15 respectively. The results are illustrated in graphs, in which x-axis represents the treatment time in minutes and y-axis represents the wicking height in mm. The rise in the water height was measured with the interval of every 5 minutes, and 30 minutes was considered as the end time of the assessment. For the grey, desized and/or scoured fabrics, as the fabric strips cannot be wetted within the 30 minutes time limit, no result can be presented in the following graphs. The wicking rates of those fabrics are shown in Figure 4.10, 4.12, 4.14 and 4.16 according to the fabric type.

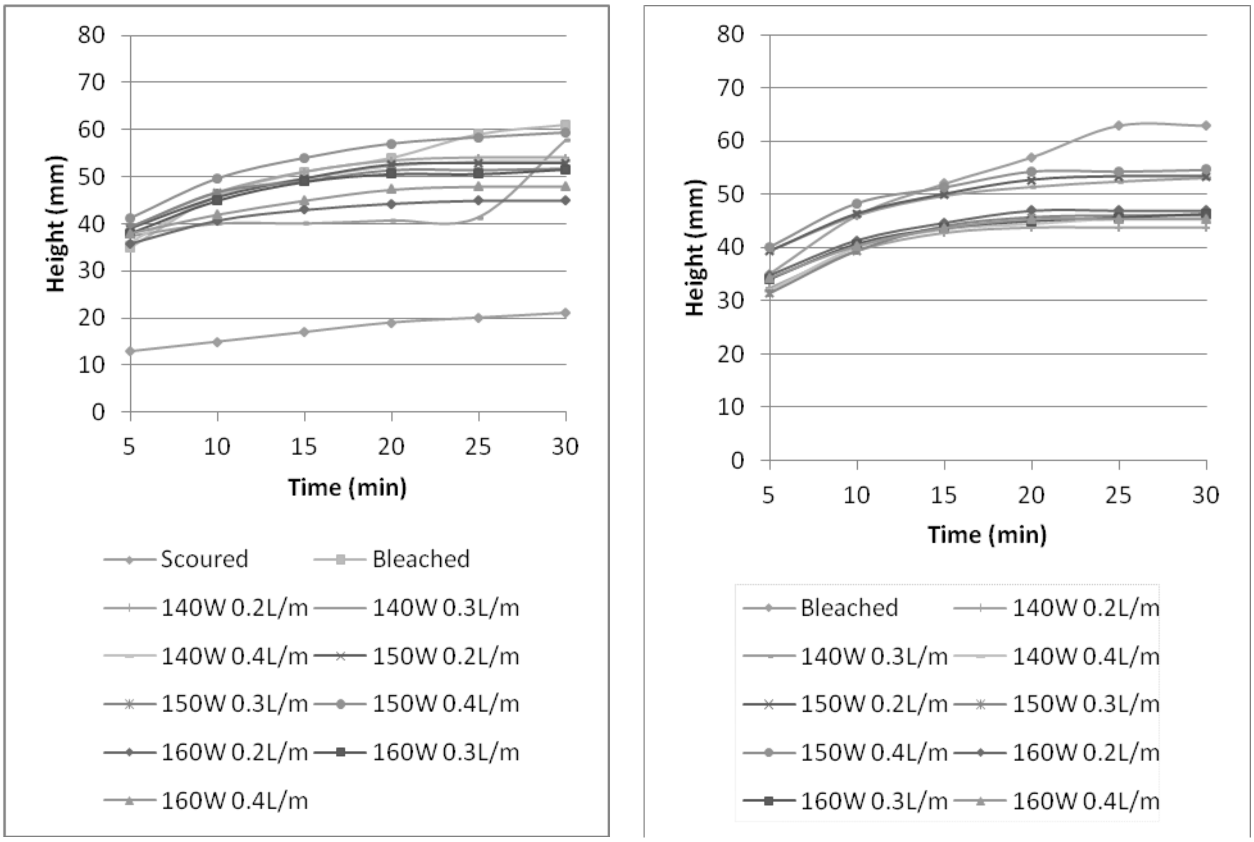


Figure 4.9 Wicking results of poplin 32s fabric warp direction (left) and weft direction (right)

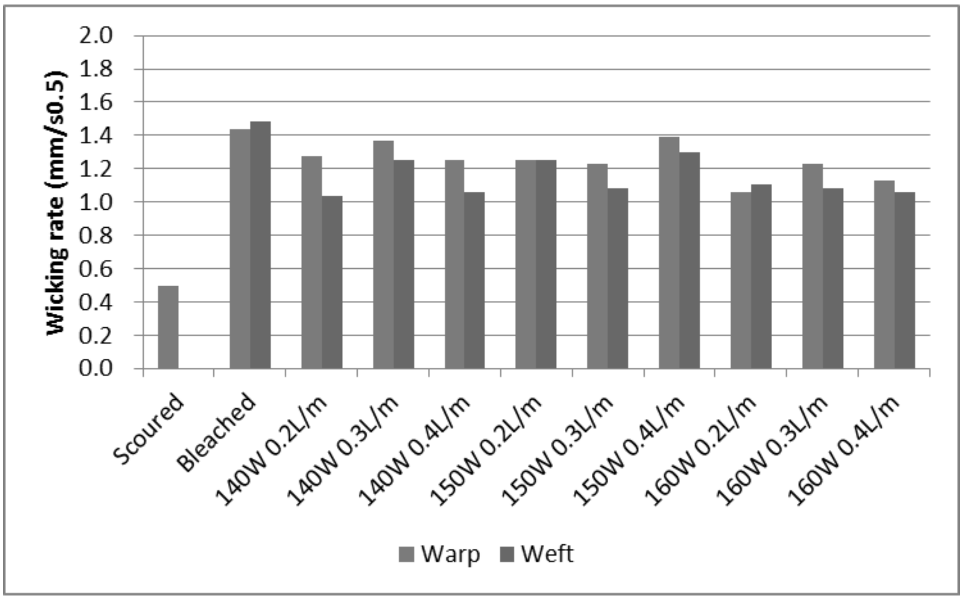
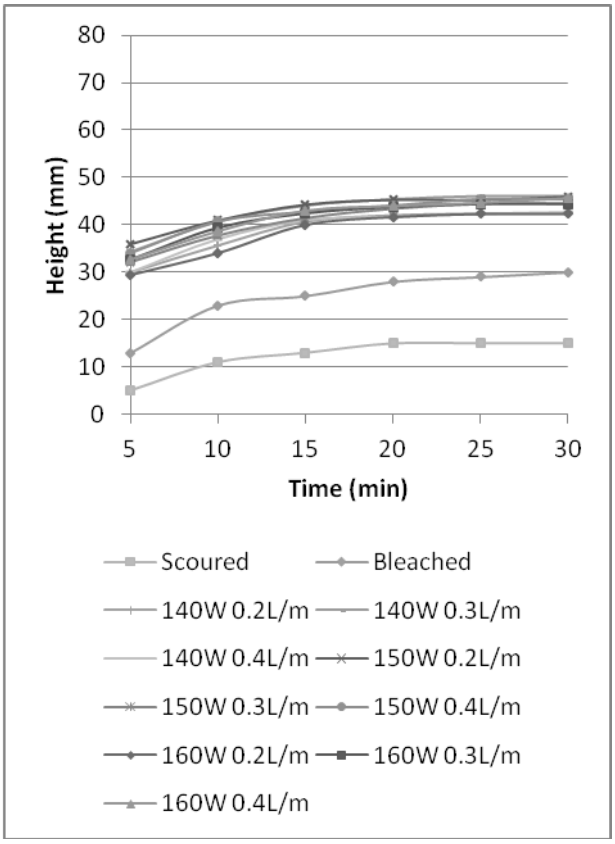


Figure 4.10 Wicking rate of poplin 32s fabric



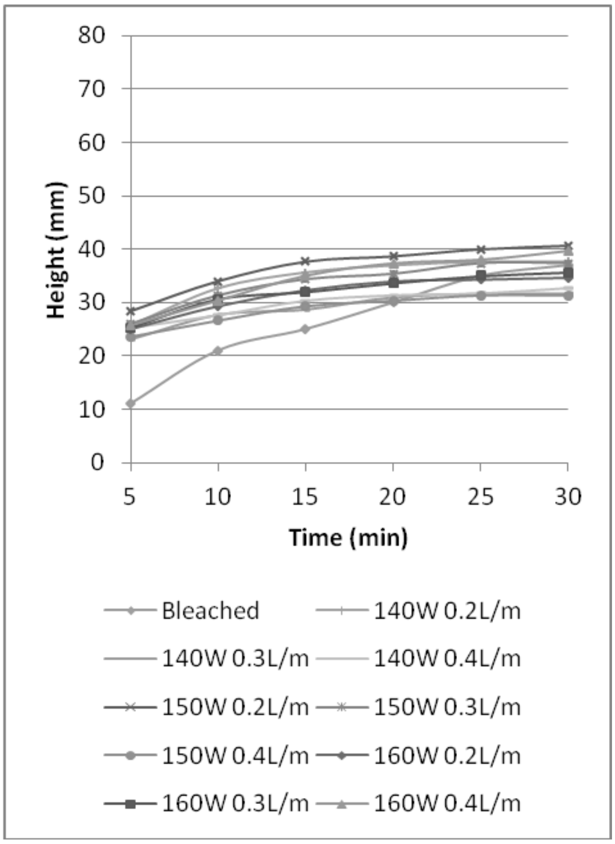


Figure 4.11 Wicking results of poplin 40s fabric warp direction (left) and weft direction (right)

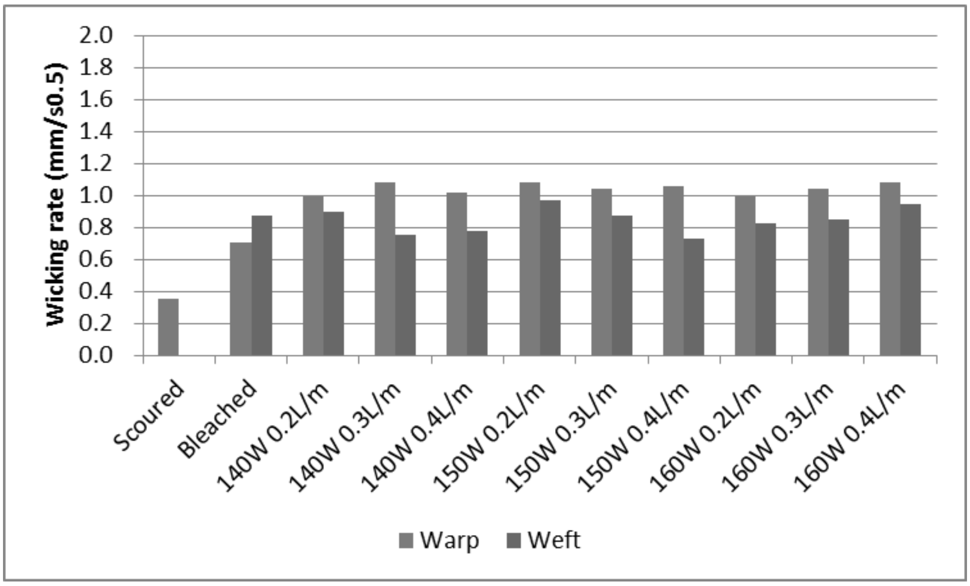
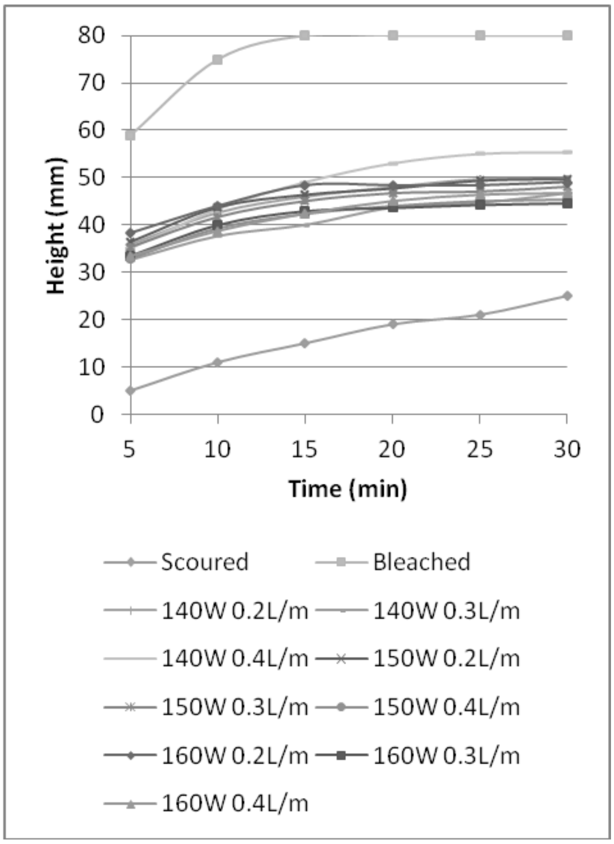


Figure 4.12 Wicking rate of poplin 40s fabric



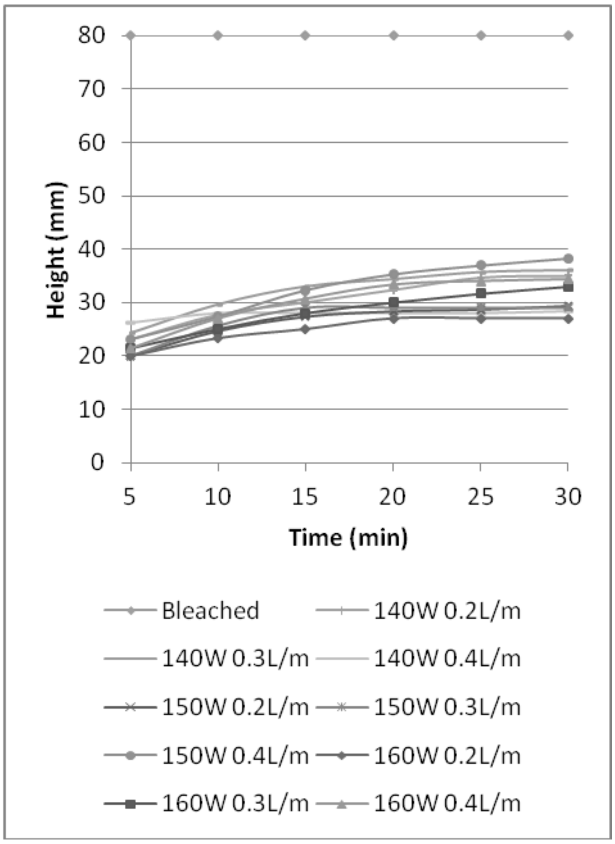


Figure 4.13 Wicking results of 2/1 twill fabric warp direction (left) and weft direction (right)

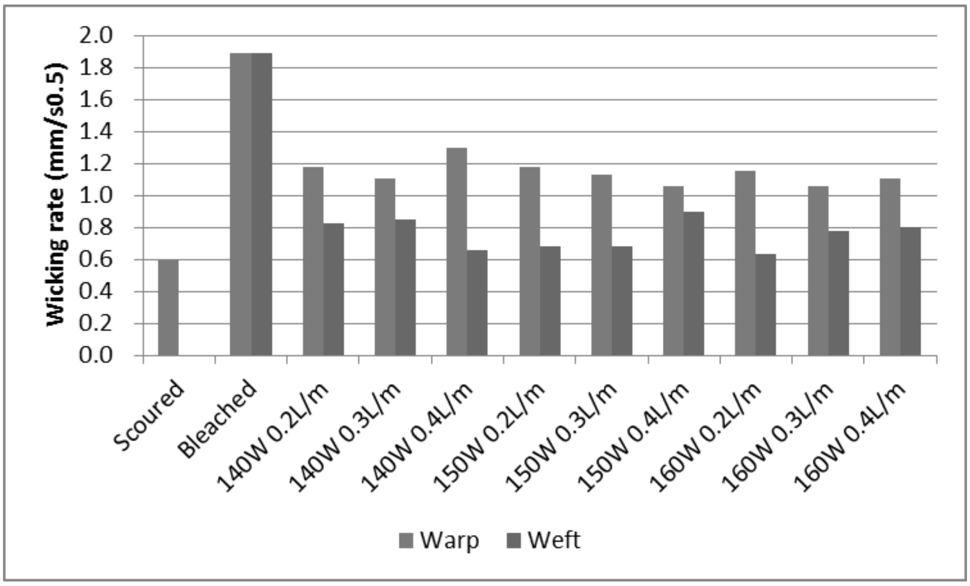


Figure 4.14 Wicking rate of 2/1 twill fabric

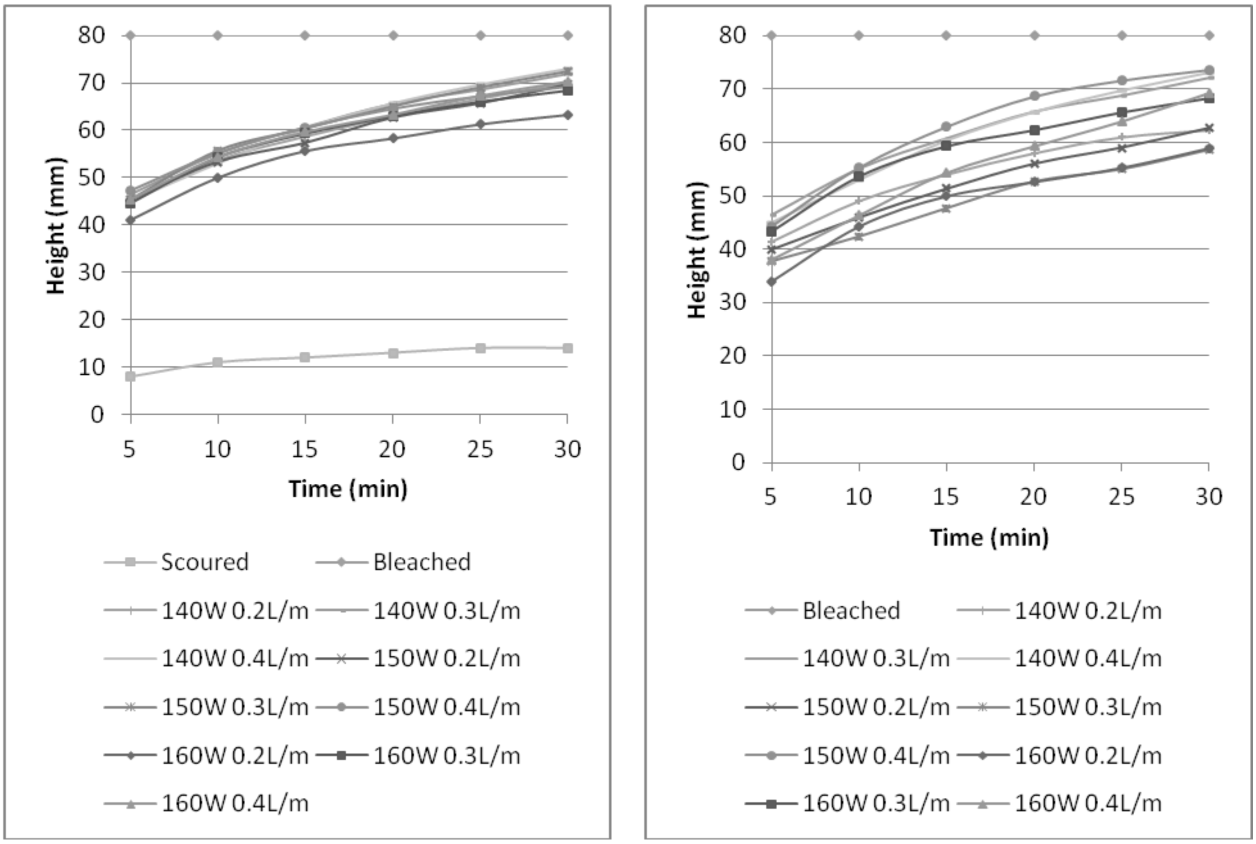


Figure 4.15 Wicking results of 2/2 twill fabric warp direction (left) and weft direction (right)

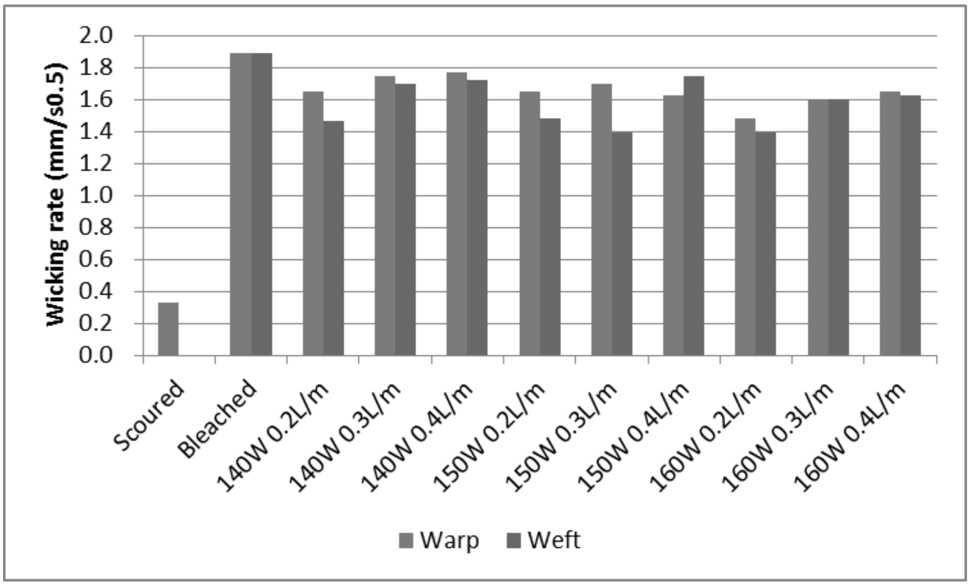


Figure 4.16 Wicking rate of 2/2 twill fabric

The wickability of the grey, conventional treated and plasma treated woven fabrics were assessed by using longitudinal wicking test, and the results were measured in terms of the wicking height and wicking rate. Wicking does not occur on the grey and conventional desized and/or scoured fabrics within the time limit, which may because of the presentation of the significant amount of non-cellulosic components present on the surface, therefore no result of those fabrics can be presented on the corresponding graphs. Generally speaking, the wickability of the grey fabrics is dramatically enhanced by the plasma treatment. The wickability enhancement is due to the physical changes on fiber surface which the sizing materials have been broken into small particles and the effective pore size may be increased by the plasma etching effect and adversely reduced the capillary pressure; and also because of the chemical changes induced by the formation of polar groups on fabric surface (Navaneetha Pandiyaraj and Selvarajan, 2008; Bhat et al., 2011; Inbakumar et al., 2010; Sun and Stylios, 2004; Wong wt al., 2001). The changed surface properties of the plasma treated fabrics result in increased wicking rate and which is even higher than the scoured fabrics. The physical and chemicals changes on the plasma treated fabric surface are confirmed and discussed later in the following chapter (see Chapter 5).

In summary, from the study of the above graphs in the wetting and wicking tests, the poplin 32s, poplin 40s, 2/1 twill and 2/2 twill woven fabrics both show that the fabric wettability and wickability are greatly improved after plasma treatment, especially when compared with the fabrics treated with conventional desizing and scouring processes. The results of the wettability and wickability changes, the effects of plasma treatment when compare with conventional treatment and the comparisons between different fabric structures are further explained in the followings.

Effect of plasma discharge intensity

The output powers of the plasma discharge are varied from 140W to 160W in this study. In general, 160W output power gives a more significant result in the wetting improvement than the other two output powers among the four types of woven fabrics.

The output power is also known as the ignition power, which is a direct control of plasma power in the plasma discharge. The hydrophilisation of the cotton grey fabric can be enhanced with increasing ignition power as a higher power is capable to produce more active species, resulting in a higher concentration of He and O active species present in plasma and thus a more intense bombardment of active plasma species can be occurred. Theoretically, a higher oxygen flow rate with higher oxygen concentration should be able to incorporate more polar functionalities on the fabric surface, thus the hydrophilicity of the fabric surface would be enhanced by the polar groups induced. However, the results from the drop test and wicking test do not show a linear relationship between the oxygen flow rate and the improvement in the wettability of fabric. This phenomenon may be attributed to the dilution of active species in plasma. The increase in gas flow rate beyond optimum value would increase the gas molecules/atoms per unit volume, thus the chances for the charged species to recombine would be greater at higher flow rates, causing quenching effect in the resultant plasma. Different optimum gas flow rates may actually be found under different ignition powers, so addition investigations are needed for understanding the relation between ignition power and optimum gas flow rate (Kale and Palakar, 2011).

Effect of plasma treatment vs conventional wet processing

From the results of the drop test among the four types of cotton woven fabrics, both show that the values of the dye drop dispersion sizes of the plasma treated fabrics are larger than the conventional treated fabrics, no matter after desizing, scouring or bleaching process. The purpose of the preparation process of cotton grey fabric is to remove the natural impurities and sizing agents on the fibers and to prepare the fabric for further coloration and finishing processes. Although the weight loss of cotton grey fabric after plasma desizing is less than after conventional desizing, the plasma treated fabrics have given a more impressive result in wettability improvement.

The reduction in fabric weight after plasma treatment and the dramatic improvement in wettability evidence that plasma treatment does play a role in removing the sizes from the cotton fiber surface.

Comparison of different fabric structures

When compare the drop test results of poplin and twill fabrics (Figure 4.5 to 4.8), poplin fabrics give a more significant increase in the dispersion size of dye droplet. The main reason for the better result obtained by poplin fabrics is due to the fabric structure. The thickness values of the 32s and 40s poplin fabrics are lower than 2/1 and 2/2 twill fabrics. Moreover, the drop spreading rate is primarily influenced by the liquid migration from yarn to yarn. Poplin fabric is plain weave and thus has a balanced and more compact structure, the migration rate of liquid between yarns therefore is faster; but the structures of 2/1 twill and 2/2 twill fabrics are looser and unbalanced for the 2/1 twill fabric, as the inter-yarn spaces are larger, the liquid migration rate would be lowered by distances. Overall, 32s poplin fabric gives a better result among the four types of woven fabrics in the drop test as it has the most balanced fabric structure, having similar amount of yarn twist values and yarn density in warp and weft yarns. A more balanced structure may help to improve the liquid spreading rate.

To determine the wickability of fiber is a more complex issue than the wettability, as liquid should wet the fibers before wicking into fabric and the important factors determining the wickability of fabrics are the wicking rates of yarns, spaces between threads, and the migration rates of liquid from longitudinal to transverse threads and again from transverse threads back to longitudinal threads (Minor and Schwartz, 1960; Shamal, 2009; Hsieh et al., 1996). From the wicking results of the four woven fabric types (Figure 4.9 To 4.16), both show that the wickability of warp yarns is better than the weft yarns, as higher wicking heights and wicking rates are obtained. The reasons for the differences in wicking results between warp and weft yarns are because of the differences in yarn count, yarn twist and yarn density. From the fabric specifications shown on Table 3.1, the warp yarns of the four types of woven fabrics have fewer yarn twists than the weft yarns. With fewer yarn twists, the radius of the capillary is larger and the yarns are more open to absorb liquid, thus result in a faster wicking rate; the capillary radius of the higher twisted yarns is smaller, making the wicking path more tortuous, thus result in a slower wicking rate. Moreover, the wicking rate is also affected by the migration rate of liquid between longitudinal yarns and transverse yarns. The migration of liquid from longitudinal yarns to transverse occurs only when there is enough liquid available on the surface of the longitudinal yarns (Shamal, 2009), which will occurs easier with twist-less yarns.

Among four types of woven fabrics in wicking results, 2/2 twill fabric gives the most impressive result on both warp and weft directions, in which the wicking rates of the plasma treated warp and weft fabric strips are the highest when compared with other woven fabric types. 2/2 twill fabric has a faster wicking rate than other three types of woven fabrics because it has a faster migration rate between liquid and fabric surface. Having fewer yarn twists in both warp and weft directions, the migration of liquid from longitudinal yarns to transverse yarns can be faster, the liquid stored in the transverse yarns is thus readily available for transferring back to the longitudinal yarns.

The reason for the wicking results of poplin fabric with 32 yarn count better than 40 yarn count and twill fabric with 2/2 structure better than 2/1 structure is because of larger thread spacing. The yarn density of poplin 40s fabric and 2/1 twill fabric is higher than the poplin 32s fabric and 2/2 twill fabric respectively. A higher yarn density means the yarns are packed closer with each other. The close packing of yarns will reduce the capillary radius and thus the wicking rate. Moreover, time is required for the liquid to fill up the inter-yarn spaces as the inter-yarn spaces are filled after all the surrounding yarns are being filled and saturated, hence more time is needed to transfer the liquid when the density of yarns is high. With decreasing yarn density or increasing thread spacing, the inter–yarn spaces can act as liquid reservoirs, thus a better wicking property can be achieved.

4.3 Knitted fabrics

4.3.1 Weight loss measurement

4.3.1.1 Plasma treatment

The knitted fabrics were weighted before and after plasma treatment for comparison. The results of single jersey and interlock fabrics are shown in Table 4.13 and 4.14 respectively.

Table 4.13 Weight of single jersey before and after plasma treatment under different parameters

Power (W)	Oxygen flow rate (L/m)	Weight (g)		Difference in weight (g)	Weight loss percentage (%)
		Before plasma treatment	After plasma treatment		
140	0.20	2.95	2.84	0.11	3.73
140	0.30	3.01	2.90	0.11	3.65
140	0.40	3.01	2.90	0.11	3.65
150	0.20	2.99	2.88	0.11	3.68
150	0.30	3.03	2.91	0.12	3.96
150	0.40	3.00	2.87	0.13	4.33
160	0.20	3.01	2.91	0.10	3.32
160	0.30	3.03	2.94	0.09	2.97
160	0.40	3.05	2.90	0.15	4.92

Table 4.14 Weight of interlock before and after plasma treatment under different parameters

Power (W)	Oxygen flow rate (L/m)	Weight (g)		Difference in weight (g)	Weight loss percentage (%)
		Before plasma treatment	After plasma treatment		
140	0.20	4.17	4.06	0.11	2.64
140	0.30	4.24	4.12	0.12	2.83
140	0.40	4.28	4.17	0.11	2.57
150	0.20	4.19	4.07	0.12	2.86
150	0.30	4.21	4.08	0.13	3.09
150	0.40	4.26	4.12	0.14	3.29
160	0.20	4.19	4.08	0.11	2.63
160	0.30	4.25	4.13	0.12	2.82
160	0.40	4.15	4.01	0.14	3.37

The cotton knitted grey fabrics were treated with different plasma parameters to determine how the plasma treatment affects the grey fabrics by observing the fabric weight loss. From the weight loss measurement results of the knitted fabrics, the weights of the single jersey and interlock fabrics are both decreased after plasma treatment under different plasma parameters. The decrease in fabric weight reveals that the wax, pectin and/or impurities on the fiber surface have been removed by plasmas. As plasma is a dry surface etching process, the impurities on the fiber surface can be broken into smaller particles and able to be ablated by the plasma flow or vaporized into gas during the treatment. To determine the optimum plasma parameters, single jersey and interlock fabric treated with 160W output power and 0.4L/m flow rate give the highest weight loss percentage among other set of treatment parameters when compare with the same type of fabric, revealing a higher output power and higher flow rate may be more effective in removing the impurities on knitted fabric surface. The removal of the hydrophobic substances on the knitted fiber surface can be further observed from the wetting results in the following section 4.3.3 and SEM images in Chapter 5.

4.3.1.2 Washing after plasma treatment

The knitted grey fabrics were washed with cold (30^{o}C) and hot (70 ^{o}C) water after plasma treatment, the weight before and after washing were calculated and compared.

Table 4.15 Plasma treated knitted fabric with cold (30^{o}C) washing

Fabric type	*After plasma treatment (g)	After cold washing (g)	Weight difference (g)	Weight loss percentage (%)
Single jersey	2.86	2.79	0.07	2.45
Interlock	4.03	3.89	0.14	3.47

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Table 4.16 Plasma treated knitted fabric with hot (70^{o}C) washing

Fabric type	*After plasma treatment (g)	After hot washing (g)	Weight difference (g)	Weight loss percentage (%)
Single jersey	2.89	2.80	0.09	3.11
Interlock	4.06	3.91	0.15	3.69

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Table 4.15 and 4.16 show the weights of the plasma treated knitted fabrics after cold and hot water washing respectively. The weights of the plasma treated knitted fabrics are decreased after washing, which reveal that the plasma active species give aid to remove the surface impurities by etching and breaking them into small fragments, and thus the solubility of those loosed impurities is increased, which can be hydrolyzed or dissolved in subsequent wet process easier. The weight loss percentages of the hot water washed knitted fabrics are greater than by cold washing, revealing a higher temperature could help to hydrolyze and dissolve the impurities more effectively.

4.3.1.3 Scouring after plasma treatment

Table 4.17 Difference in weight between plasma treated and scoured single jersey fabric

Grey (g)	*After plasma treatment (g)	Scouring duration	Scouring temperature	Scoured (g)	Difference in weight (g)	Weight loss percentage (%)
3.03	---	60 min	100 ^oC	2.78	0.25	8.25
2.96	2.83	60 min	100 ^oC	2.72	0.24	8.48
2.92	2.80	45 min	100 ^oC	2.70	0.22	7.76
2.98	2.85	45 min	80^oC	2.77	0.21	7.38
2.98	2.86	45 min	65^oC	2.79	0.19	6.71

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

Table 4.18 Difference in weight between plasma treated and scoured interlock fabric

Grey (g)	After plasma treatment (g)	Scouring duration	Scouring temperature	Scoured (g)	Difference in weight (g)	Weight loss percentage (%)
4.27	---	60 min	100 ^oC	3.96	0.31	7.26
4.35	4.19	60 min	100 ^oC	4.05	0.30	7.16
4.35	4.17	45 min	100 ^oC	4.05	0.30	7.29
4.37	4.19	45 min	80^oC	4.08	0.30	7.12
4.41	4.22	45 min	65^oC	4.12	0.29	6.82

*The fabrics were treated with 150W output power and 0.4L/m oxygen flow rate.

The plasma treated knitted fabrics were scoured with different temperatures and times in order to observe the effectiveness of plasma treatment. From Table 4.17 and 4.18, the results of single jersey and interlock fabrics both show that the weight loss percentages of the plasma treated fabrics scoured with normal scouring parameters and scoured with 45 minutes at 100^{o}C are comparable with the grey fabric scoured with normal scouring parameters. The similar differences in weight loss percentages of those scoured fabrics reveal that shorter scouring duration can be applied after plasma treatment; evidencing plasma treatment is useful to help in time and energy saving during scouring process of cotton knitted fabrics. The efficiency of scouring has been enhanced after plasma treatment is because the impurities on the fiber surface have been broken down into tiny pieces by plasma etching, which thus become more readily to be swelled, dissolved and removed by the employment of chemicals and reagents.

4.3.2 Yellowness (ASTM E313)

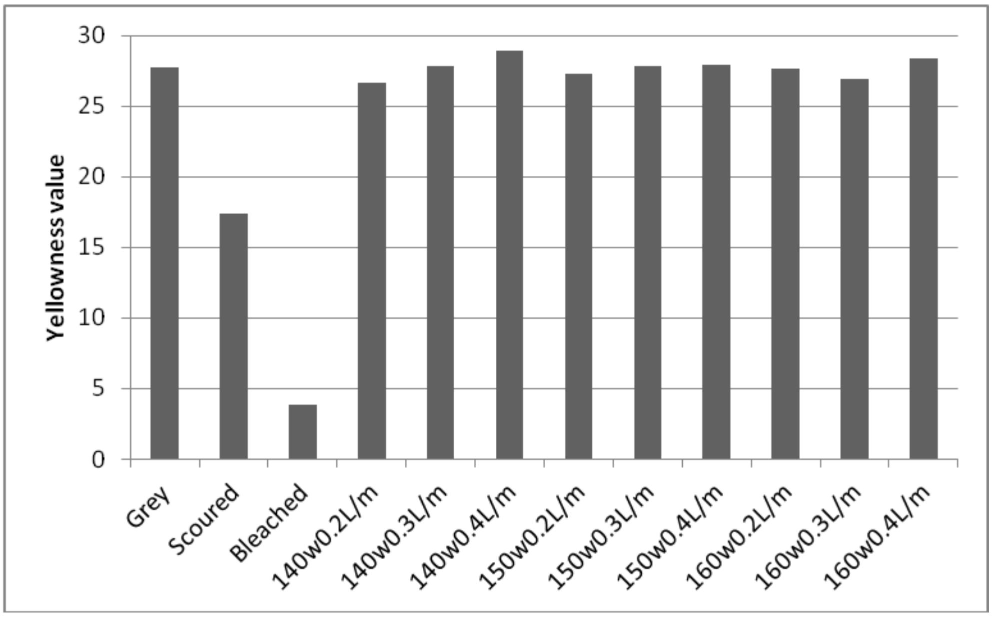


Figure 4.17 Yellowness values of single jersey knitted fabric

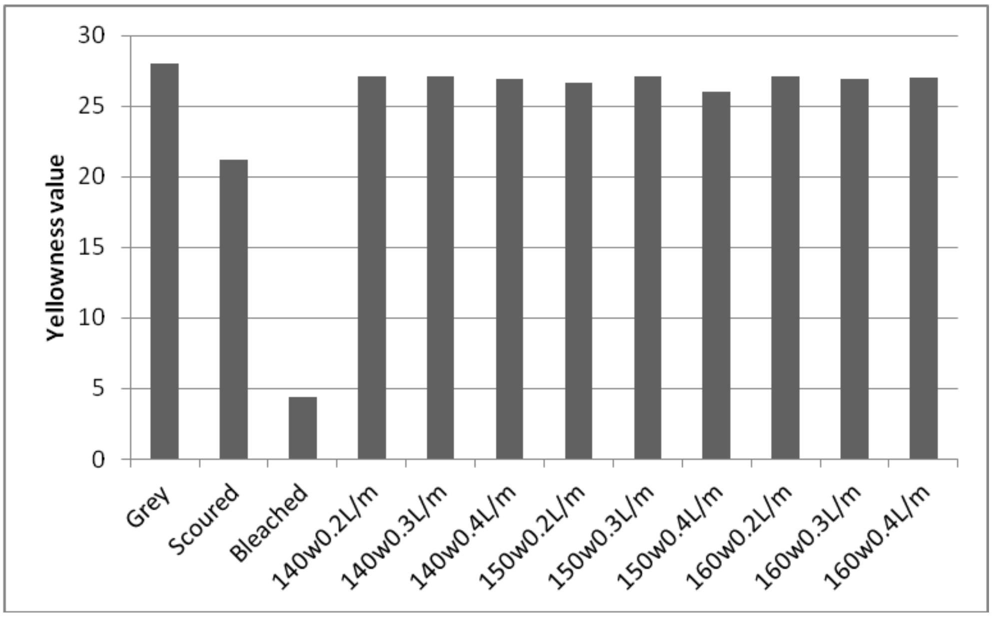


Figure 4.18 Yellowness values of interlock knitted fabric

The higher the yellowness value, the yellower the fabric color will be. From the result of the single jersey fabrics in Figure 4.17, the yellowness values of the plasma treated single jersey fabrics give a similar value with the grey fabric in general. The single jersey fabrics treated with 0.4L/m oxygen flow rate give a slightly higher yellowness value than the grey fabrics. Although plasma treatment is helpful in removing the sizing materials and impurities, it may induce a certain degree of yellowness due to the thermal oxidation effect on the fiber surface (Kan et al., 2011; Kan and Yuen, 2012). Moreover, as the grey cotton knitted fabric contains yellowish color naturally, the yellowish color is still remained even after plasma treatment. From Figure 4.18, the yellowness values of all plasma treated interlock fabrics are lower than the grey fabric, which reveal that plasma treatment may help to improve the fabric yellowness due to the removal of yellow coloring impurities on fiber surface of interlock fabric.

4.3.3 Wettability- Drop test (simulated AATCC 79-2010)

Figure 4.19 and 4.20 show the drop test results of single jersey and interlock knitted fabrics respectively.

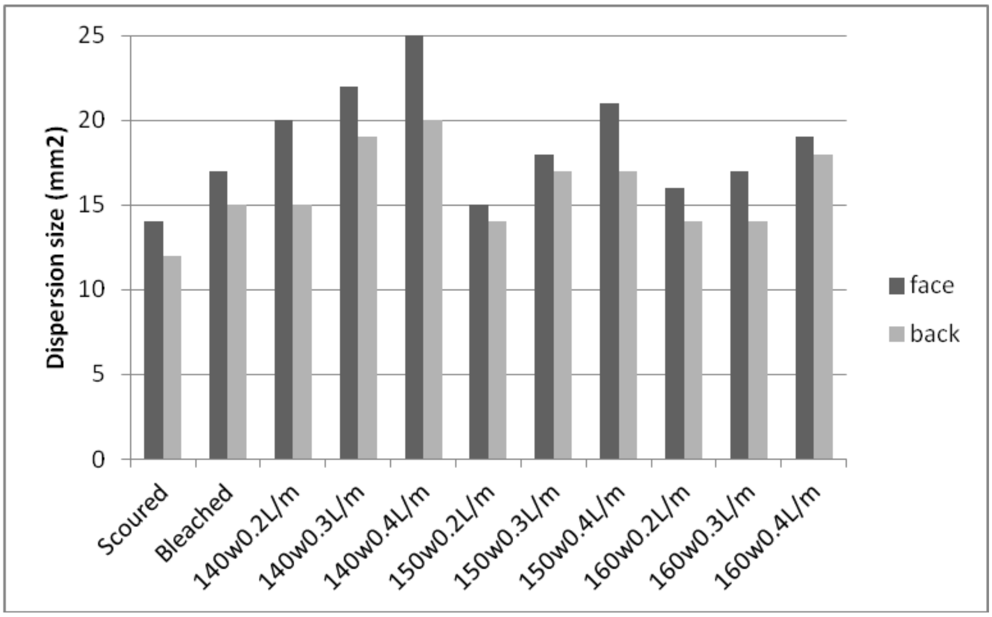


Figure 4.19 Drop test result of single jersey knitted fabric

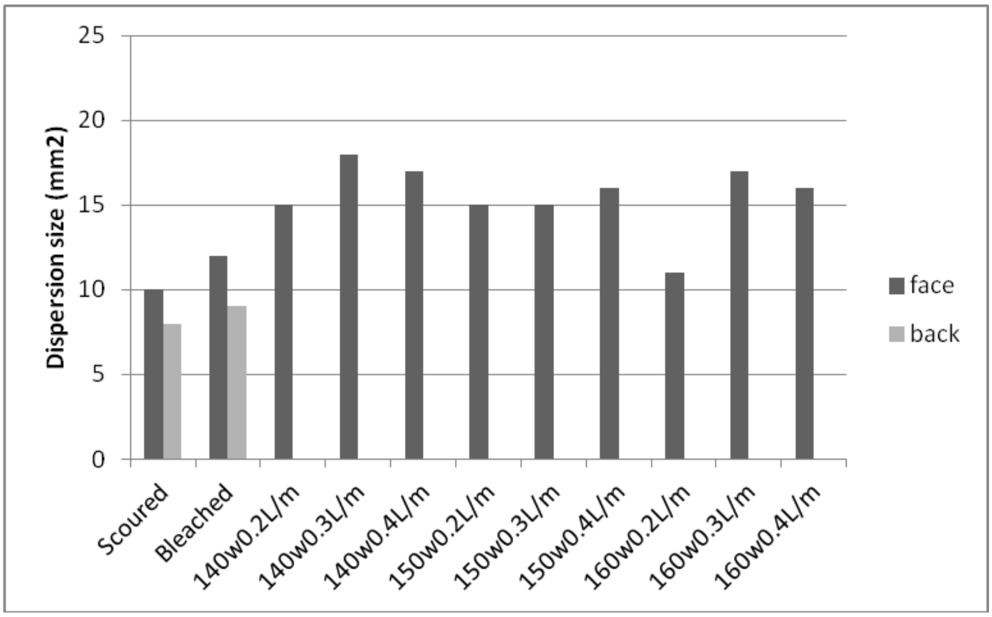


Figure 4.20 Drop test result of interlock knitted fabric

The grey fabrics of the single jersey and interlock knitted fabrics and the back side of plasma treated interlock fabrics cannot be wetted by the dye solution within the time limit, thus no record can be presented in the corresponding figure. From the results of single jersey fabrics, the wettability of the plasma treated fabrics is greatly enhanced when compare with the grey fabric and even have a better result than the scoured fabric, especially for the fabric face side treated with 140W output power. The fabric face side shows a better wetting result than the back side.

For the interlock fabrics, the plasma treated fabric face sides show an obvious enhancement on fabric wettability when compare with the grey and scoured fabrics. In general, those interlock fabrics treated with 140W output power give a better wettability result. The back side of the plasma treated interlock fabric cannot be wetted by the dye solution may because of the fabric structure. Although plasma treatment only affects the fabric surface due to the penetration power of plasma species theoretically, the fabric back side may also be affected by the plasma species. However, interlock fabric is too thick for the plasma species pass through from one side to another side, so the fabric back side cannot be affected and wetted.

To determine the optimum plasma parameters from the drop test results, single jersey treated with 140W output power and 0.4L/m flow rate and interlock fabric treated with 140W output power and 0.3L/m flow rate give the largest dispersion size on fabric face among other set of treatment parameters when compare with the same type of fabric.

4.4 Conclusion

The weight loss, yellowness and wetttability of the plasma treated woven and knitted fabrics have been measured and analyzed in this chapter, and the results also have been compared with the conventional treated fabrics. The plasma treatment increases the solubility of starch sizes and impurities followed by washing with water alone or scouring. Weight loss occurs on the plasma treated fabrics, revealing plasma treatment give aid to the removal of sizing materials and impurities. The hydrophilicity of the grey cotton woven and knitted fabrics is found to be greatly enhanced after plasma treated. A cleaner production of cotton or cotton involved textile materials can be obtained by using plasma pre-treatment with less water, chemicals and energy consumptions.

As plasma treatment not only affects the physical properties of the treated substrate, but also induces a certain degree of chemical modifications on the fiber surface, the surface morphological and chemical changes of the plasma treated fabrics will be studied and compared with the conventional treated fabrics in next chapter.

Chapter 5 Surface and chemical characterizations

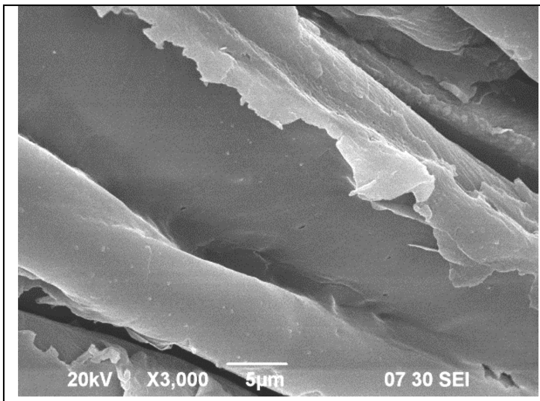
5.1 Introduction

From the previous chapter, the results of the wettability tests showed that the hydrophility of the grey cotton fabrics was greatly improved after plasma treatment. The increase in hydrophilicity of the plasma treated fabric not only attributed to the physical modification by plasma etching, but also due to the chemical changes induced by the interaction between the plasma active species and fabric surface. In order to have a more in-depth analyze on how the plasma treatment can give aid to the pretreatment process, the surface and chemical changes of the conventional and plasma treated woven and knitted fabrics were characterized by using scanning electron microscope (SEM), fourier transfer infrared spectroscopy (FTIR-ATR) and x-ray photoelectron spectroscopy (XPS).

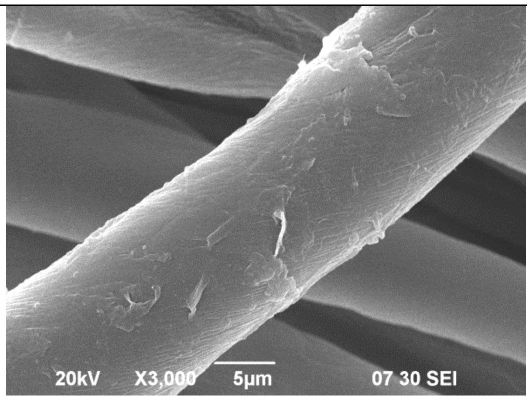
5.2 Woven fabrics

5.2.1 Scanning electron microscope (SEM)

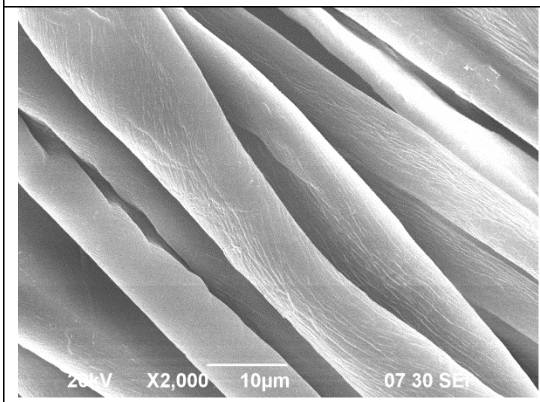
The results of the SEM photographs of woven fabrics are shown according to the type of fabric. Figure 5.1, 5.3, 5.5 and 5.7 show the SEM photographs of the grey, conventional desized, scoured and bleached woven fibers. Figure 5.2, 5.4, 5.6 and 5.8 show the images of fibers treated with different plasma parameters, simulated starch sized, simulated starch sized fabric treated with enzyme desizing and simulated starch sized fabric treated with plasma desizing.



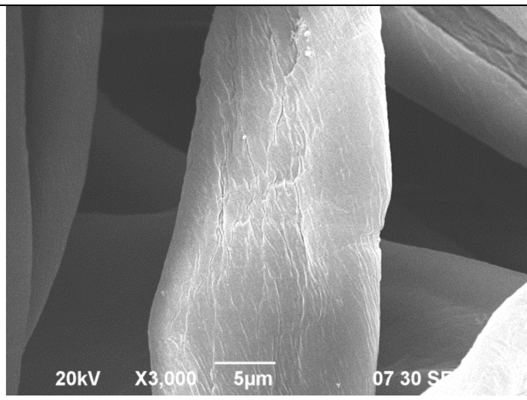
(a) Grey



(b) Desized

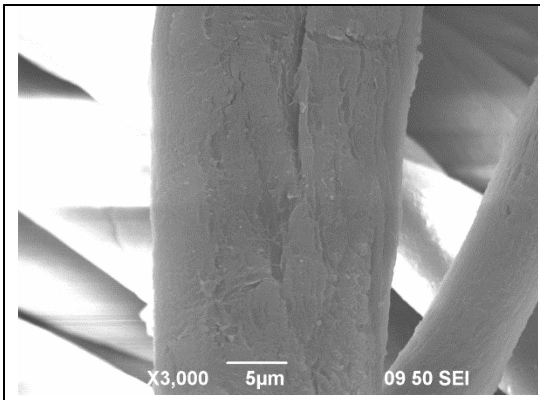


(c) Scoured

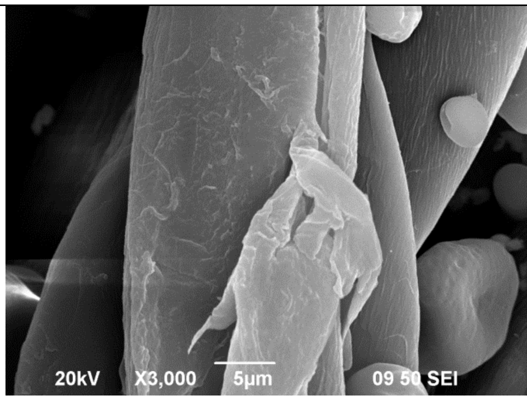


(d) Bleached

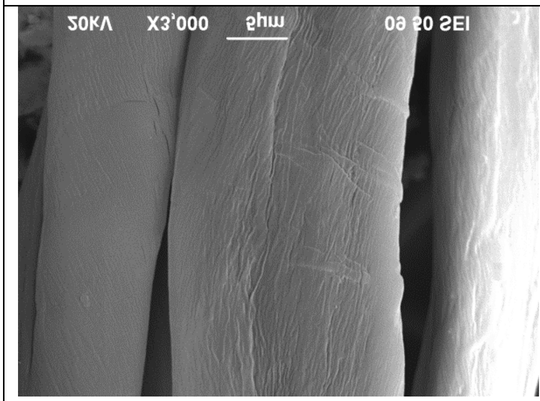
Figure 5.1 SEM photographs of poplin 32s woven fabric (a) grey (b) enzyme desized (c) scoured (d) bleached



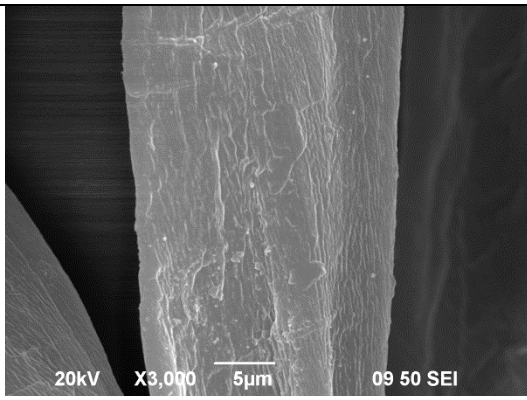
(a) 160W 0.2L/m



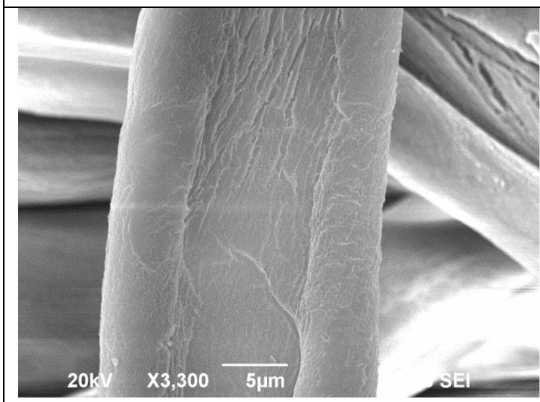
(d) Bleached and simulated starch sized



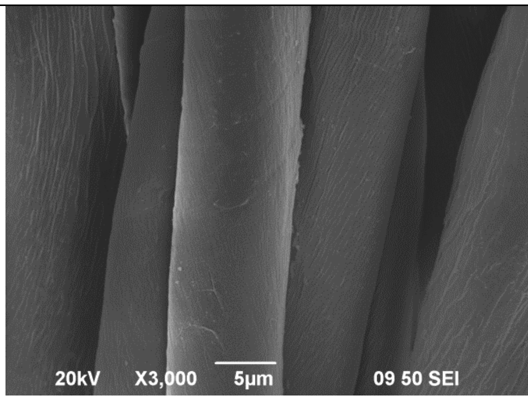
(b) 160W 0.3L/m



(e) Bleached and simulated starch sized and enzyme desized

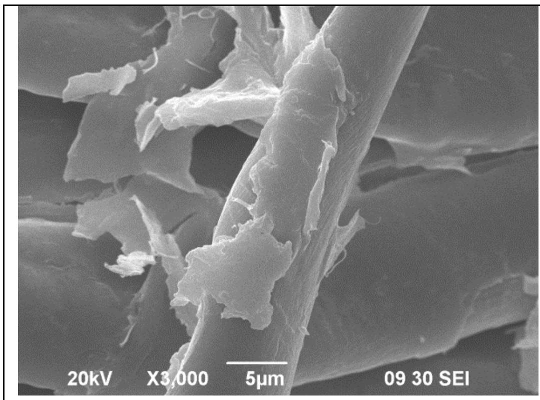


(c) 160W 0.4L/m

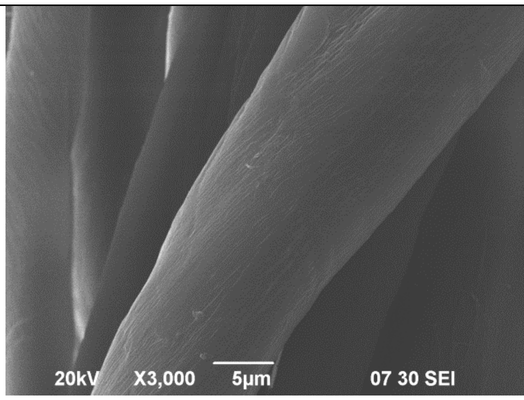


(f) Bleached and simulated starch sized and plasma desized

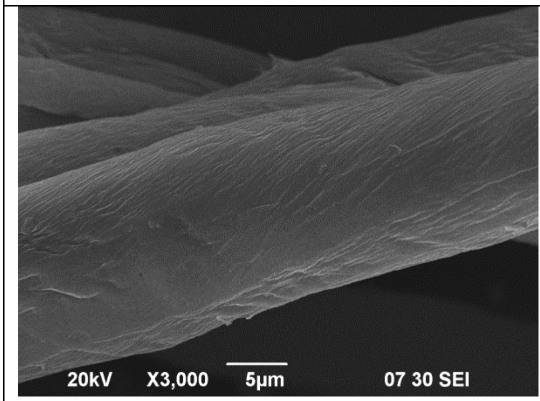
Figure 5.2 SEM photographs of poplin 32s woven fabric, plasma treated with (a) 160W 0.2L/m (b) 160W 0.3L/m (c) 160W 0.4L/m; (d) bleached and simulated starch sized (e) bleached and simulated starch sized and enzyme desized (f) bleached and simulated starch sized and plasma desized



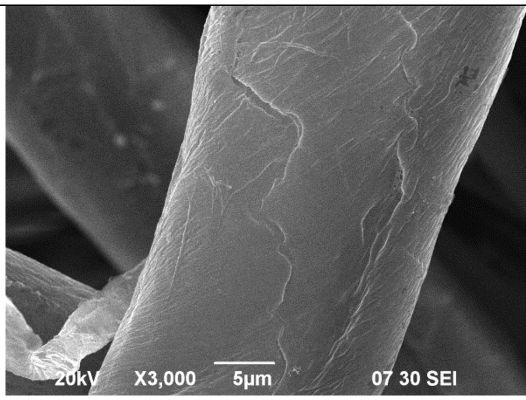
(a) Grey



(b) Desized

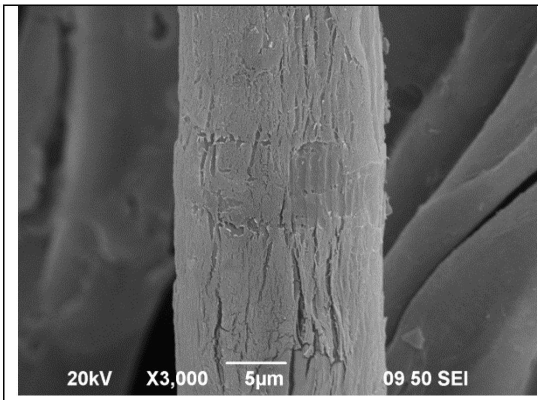


(c) Scoured

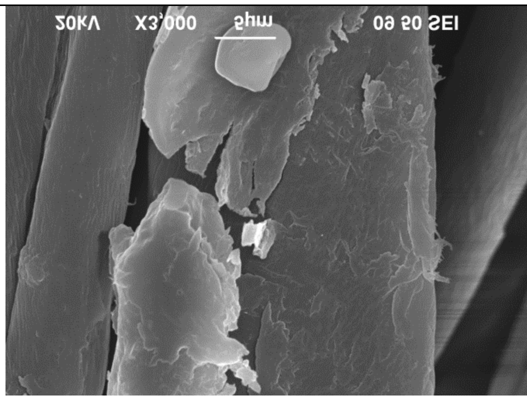


(d) Bleached

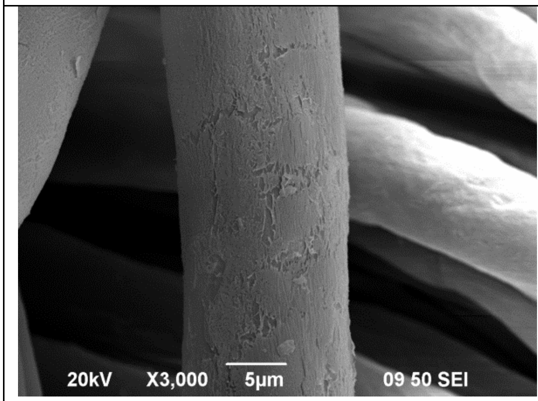
Figure 5.3 SEM photographs of poplin 40s woven fabric (a) grey (b) enzyme desized (c) scoured (d) bleached



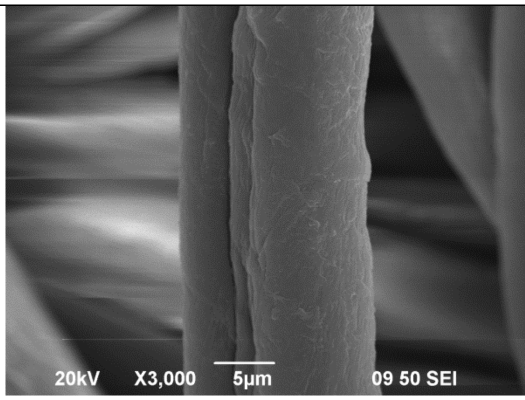
(a) 160W 0.2L/m



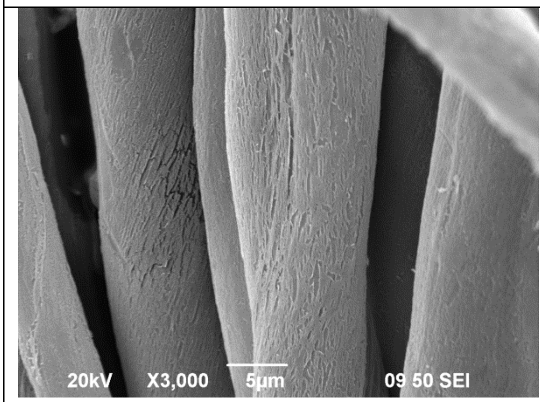
(d) Bleached and simulated starch sized



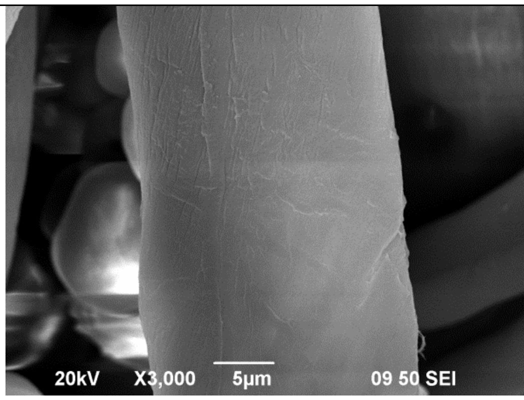
(b) 160W 0.3L/m



(e) Bleached and simulated starch sized and enzyme desized

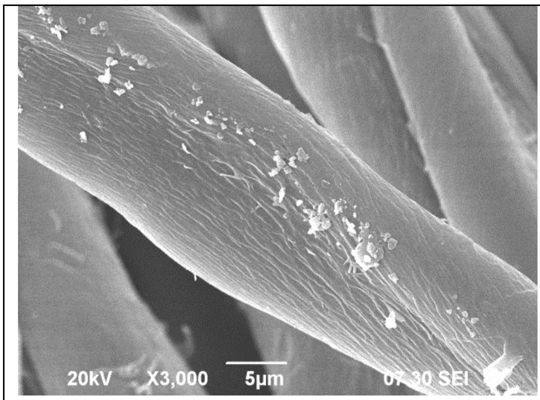


(c) 160W 0.4L/m

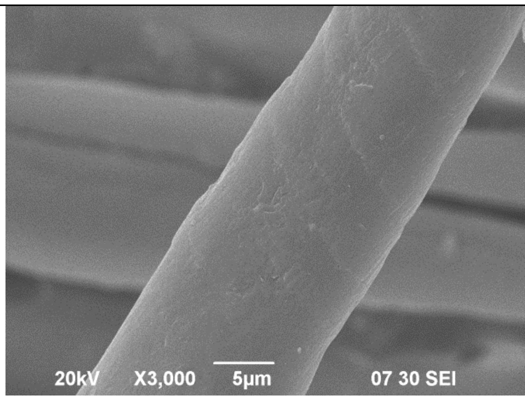


(f) Bleached and simulated starch sized and plasma desized

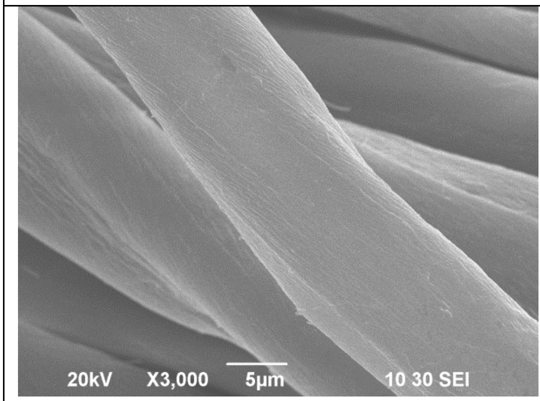
Figure 5.4 SEM photographs of poplin 40s woven fabric, plasma treated with (a) 160W 0.2L/m (b) 160W 0.3L/m (c) 160W 0.4L/m; (d) bleached and simulated starch sized (e) bleached and simulated starch sized and enzyme desized (f) bleached and simulated starch sized and plasma desized.



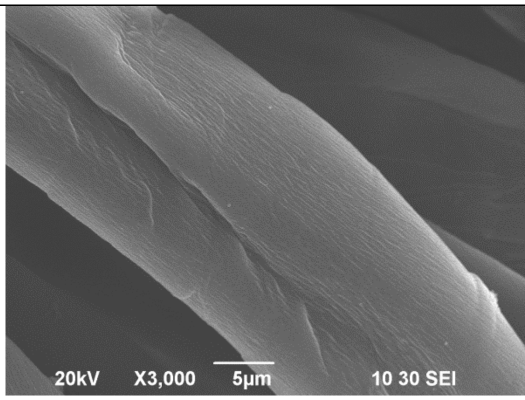
(a) Grey



(b) Desized

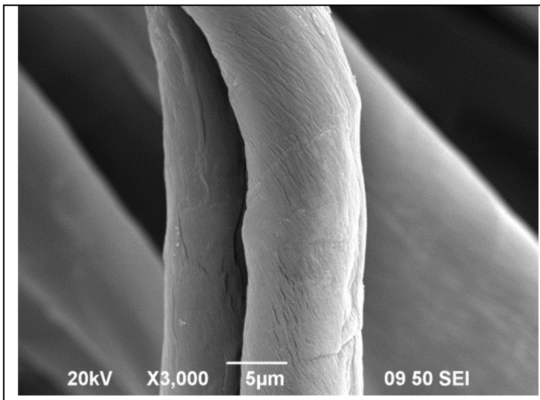


(c) Scoured

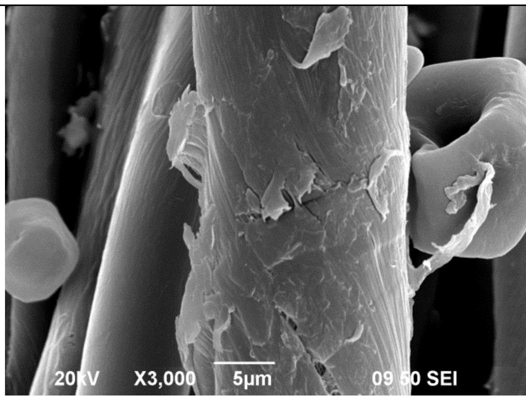


(d) Bleached

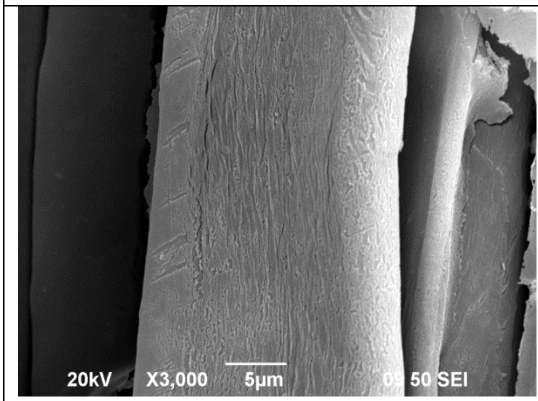
Figure 5.5 SEM photographs of 2/1 twill woven fabric (a) grey (b) enzyme desized (c) scoured (d) bleached



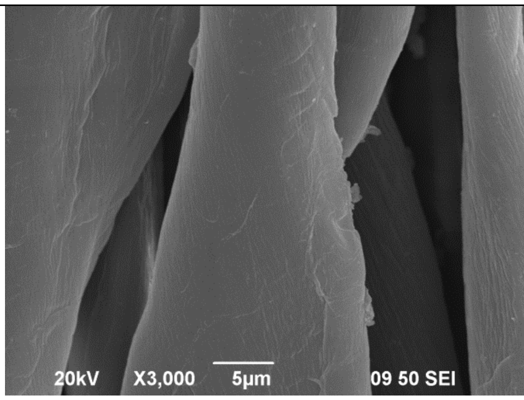
(a) 160W 0.2L/m



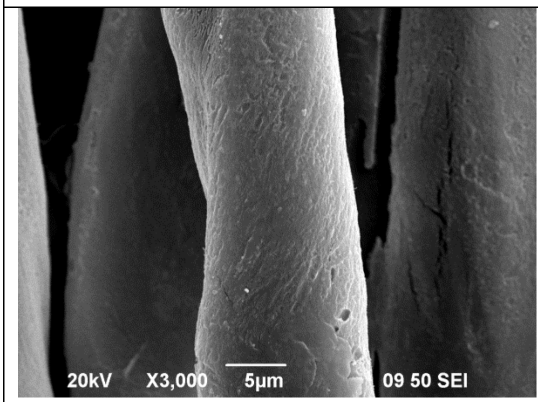
(d) Bleached and simulated starch sized



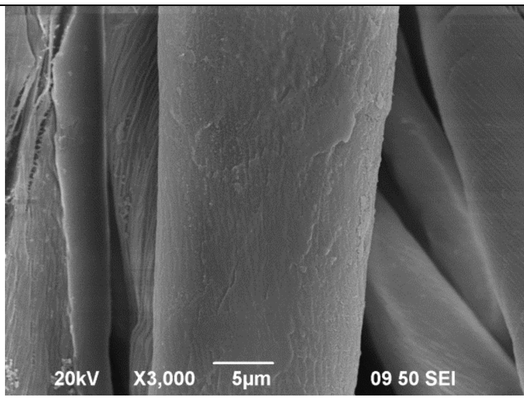
(b) 160W 0.3L/m



(e) Bleached and simulated starch sized and enzyme desized

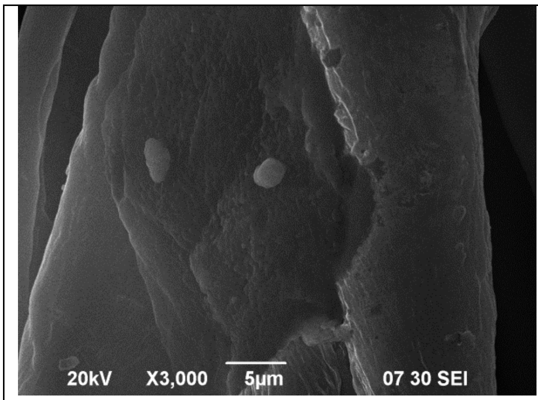


(c) 160W 0.4L/m

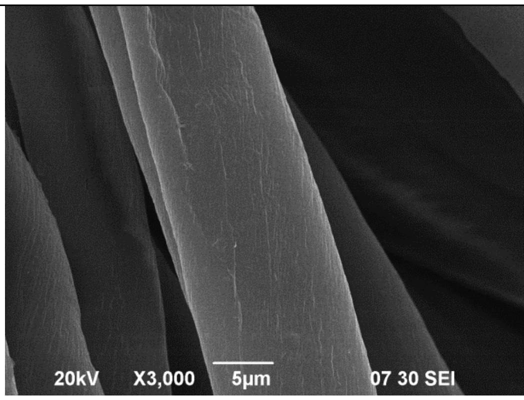


(f) Bleached and simulated starch sized and plasma desized

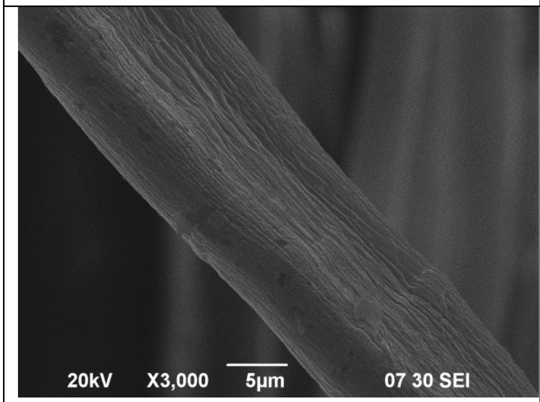
Figure 5.6 SEM photographs of 2/1 twill woven fabric, plasma treated with (a) 160W 0.2L/m (b) 160W 0.3L/m (c) 160W 0.4L/m; (d) bleached and simulated starch sized (e) bleached and simulated starch sized and enzyme desized (f) bleached and simulated starch sized and plasma desized.



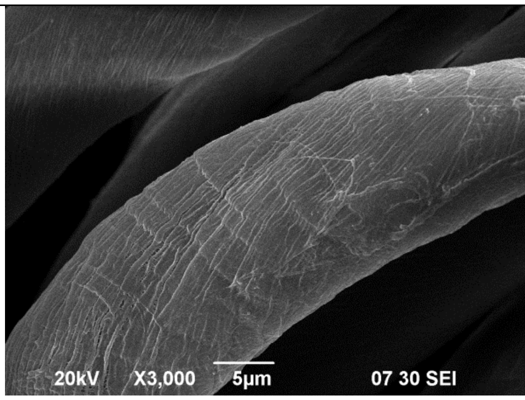
(a) Grey



(b) Desized

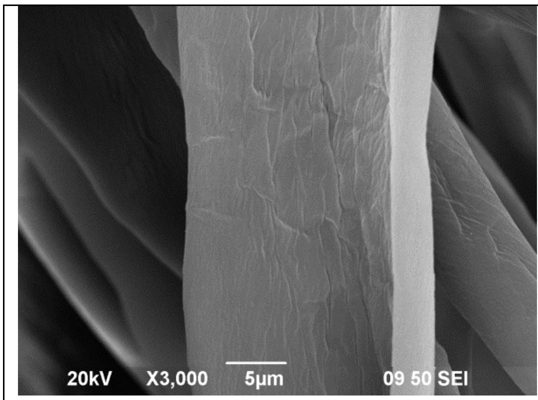


(c) Scoured

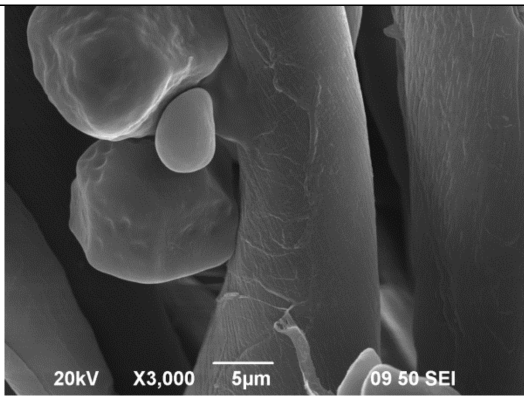


(d) Bleached

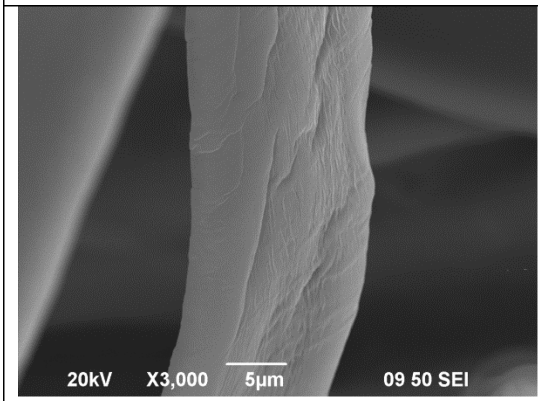
Figure 5.7 SEM photographs of 2/2 twill woven fabric (a) grey (b) desized (c) scoured (d) bleached



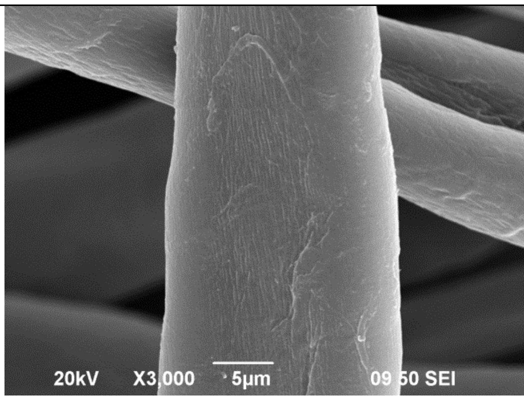
(a) 160W 0.2L/m



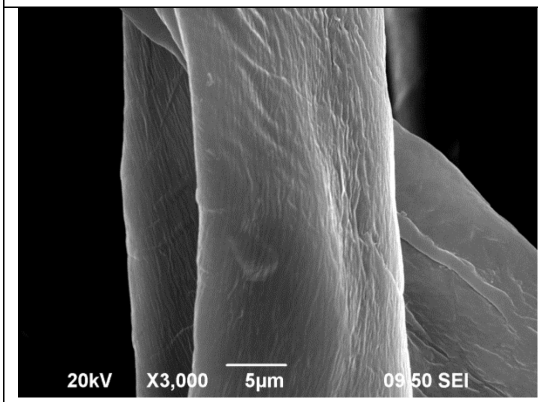
(d) Bleached and simulated starch sized



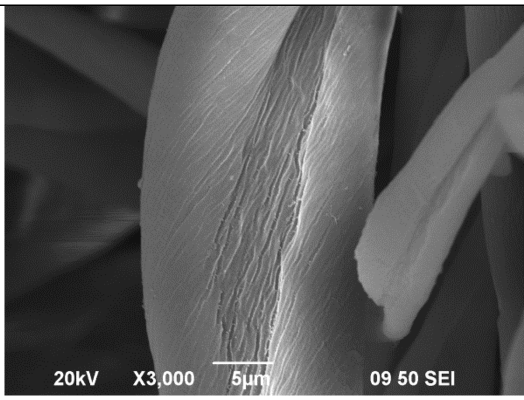
(b) 160W 0.3L/m



(e) Bleached and simulated starch sized and enzyme desized



(c) 160W 0.4L/m



(f) Bleached and simulated starch sized and plasma desized

Figure 5.8 SEM photographs of 2/2 twill woven fabric, plasma treated with (a) 160W 0.2L/m (b) 160W 0.3L/m (c) 160W 0.4L/m ; (d) bleached and simulated starch sized (e) bleached and simulated starch sized and enzyme desized (f) bleached and simulated starch sized and plasma desized

Effects of conventional treatment

Figure 5.1, 5.3, 5.5 and 5.7 show the photographs of those conventional treated woven fabrics obtained from SEM, sizing agents can be clearly observed from the fiber surface of the grey fabric. After conventional desizing process, the amount of sizing agents is obviously decreased and the fiber surface is cleaner after scouring and bleaching processes.

Effects of plasma desizing

Figure 5.2, 5.4, 5.6 and 5.8 show the fiber surface characteristics of those woven grey fabrics after plasma treated under the same output power but with different oxygen flow rates, simulated starch sized bleached fabrics with enzyme desized and plasma desized. Both four types of woven fabrics show a similar SEM result. From the images of the plasma desized grey fabrics (a-c), the sizes are apparently removed and broken into fragments after plasma treatment. Moreover, some voids and microcracks can be observed from the plasma treated fiber surface. The appearance of starch fragments, voids and microcracks reveals that etching occurs on the fiber surface. The starch fragments are formed by oxidation as the starch molecular chains are being cut into shorter lengths by oxygen plasmas during and after the plasma treatment. The development of the voids and microcracks is because of the direct bombardment on the fiber surface by the active species in the plasma after the removal of sizes on the fiber surface. The surface characteristics of the fibers are similar under different oxygen flow rates.

SEM images indicate that there is a significant surface change on the cotton fibers after plasma treatment. The plasma ablation helps to remove some of the sizes, and the etching effect affects the surface smoothness and the performance of fabrics. The property changes of plasma treated fiber due to the etching effect can be observed from the wettability test in Chapter 4. As the surface area of the fiber is significantly increased by the appearance of voids and microcracks, the results in wettability of the plasma treated fabrics are greatly improved when compared with the conventional desized fabrics, no matter on poplin or twill fabrics.

Enzyme desizing vs plasma desizing

The bleached cotton fabrics are simulated starch sized and treated with conventional enzyme desizing and plasma desizing. From Figure 5.2, 5.4, 5.6 and 5.8, similar results are obtained from the four types of cotton woven fabrics. The starch sizes can be seen clearly on the simulated starch sized bleached fiber (d). The amount of starch sizes are found to be significantly reduced after enzyme desized (e) and plasma desized (f). The plasma desized starch sized fabric gives a similar surface characteristic with the enzyme desized fabric, which means plasma treatment is effective in desizing starch size on fiber surface and the result is comparable with the enzyme desizing treatment.

5.2.2 Fourier transfer infrared spectroscopy (FTIR-ATR)

For evaluating the capability of plasma desizing on each type of fabric, several sets of treatment comparisons are made. As the four types of cotton woven fabrics were treated with the same treatment conditions and processes, the FTIR-ATR results would be similar. The fabric treated with 150W output power and 0.4L/m oxygen flow rate is used as the model for analyzing and comparing with different treatments. The important absorption peaks of the bonds of cotton are shown in Table 5.1.

Table 5.1 Absorption peaks of bonds

Bond	Absorption peak (cm^{-1})
O-H stretch	3400-3200
C-H	3000-2850
C=O	1657-1605, 1760-1690
C-O	1320-1000

Figure 5.9, 5.12, 5.15 and 5.18 show the FTIR-ATR spectra of enzyme desized, scoured and bleached fabrics. Figure 5.10, 5.13, 5.16 and 5.19 show the FTIR-ATR spectra of grey and plasma treated woven fabric under 150W output power and 0.4L/m oxygen flow rate according to the fabric type. The spectra of bleached, simulated starch sized fabric treated with enzyme treatment and simulated starch sized fabric treated with plasma treatment are shown in Figure 5.11, 5.14, 5.17 and 5.20 according to fabric type.

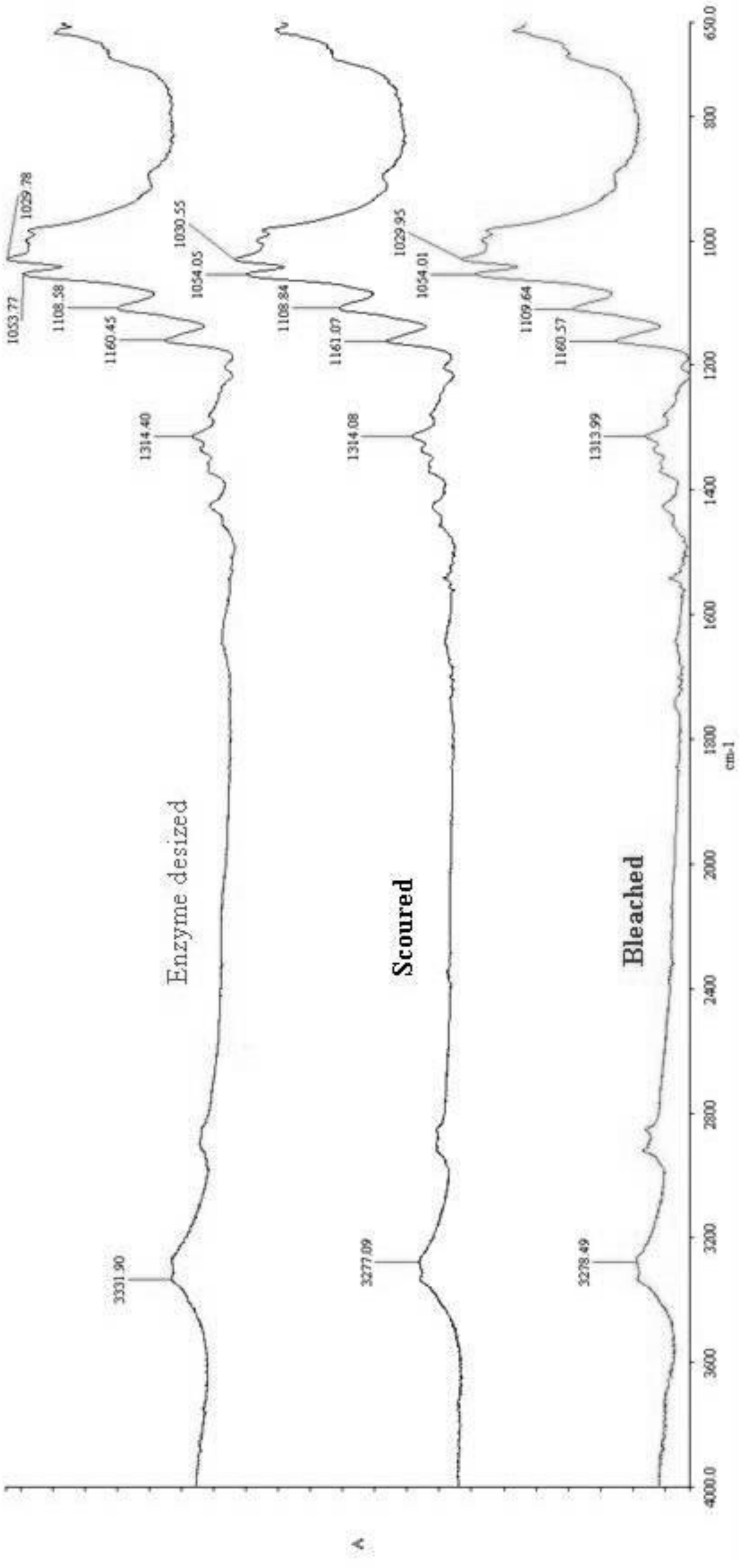


Figure 5.9 FTIR-ATR spectra of enzyme desized, scoured and bleached poplin 32s woven fabric

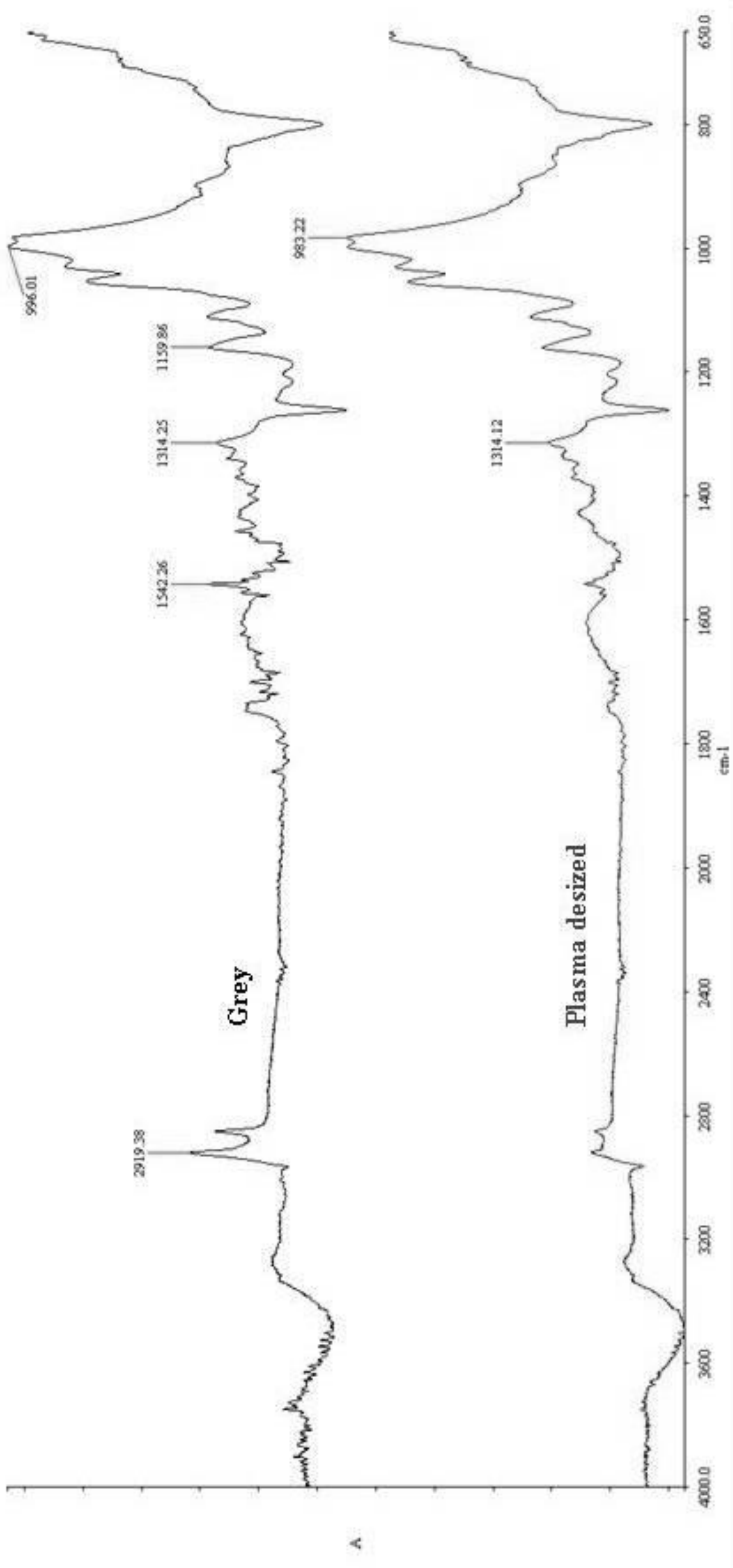


Figure 5.10 FTIR-ATR spectra of poplin 32s grey and plasma treated woven fabric under 150W power and 0.4L/m oxygen flow rate

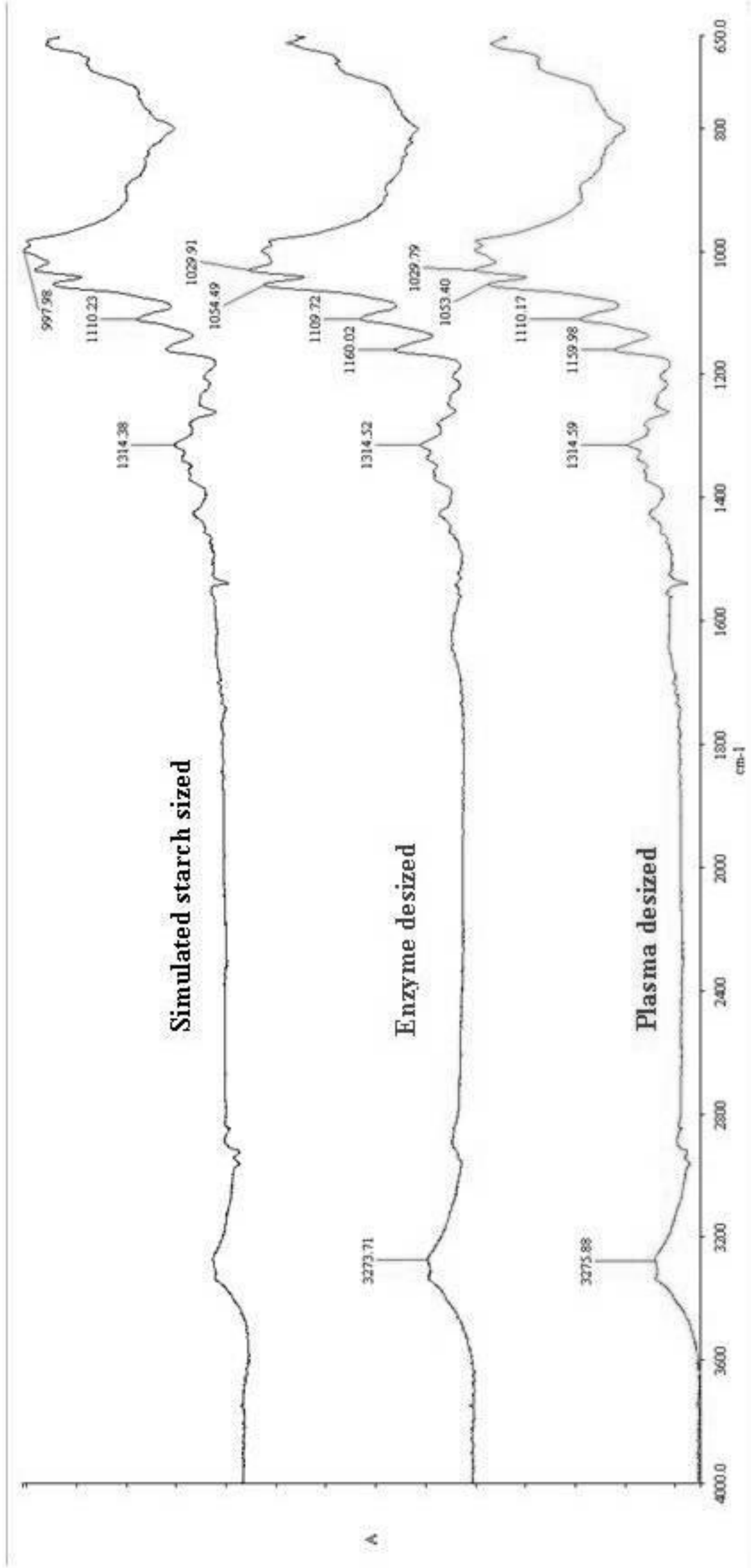


Figure 5.11 FTIR-ATR spectra of simulated starch sized, enzyme desized and plasma desized(150W power and 0.4L/m oxygen flow rate) poplin 32s woven fabric

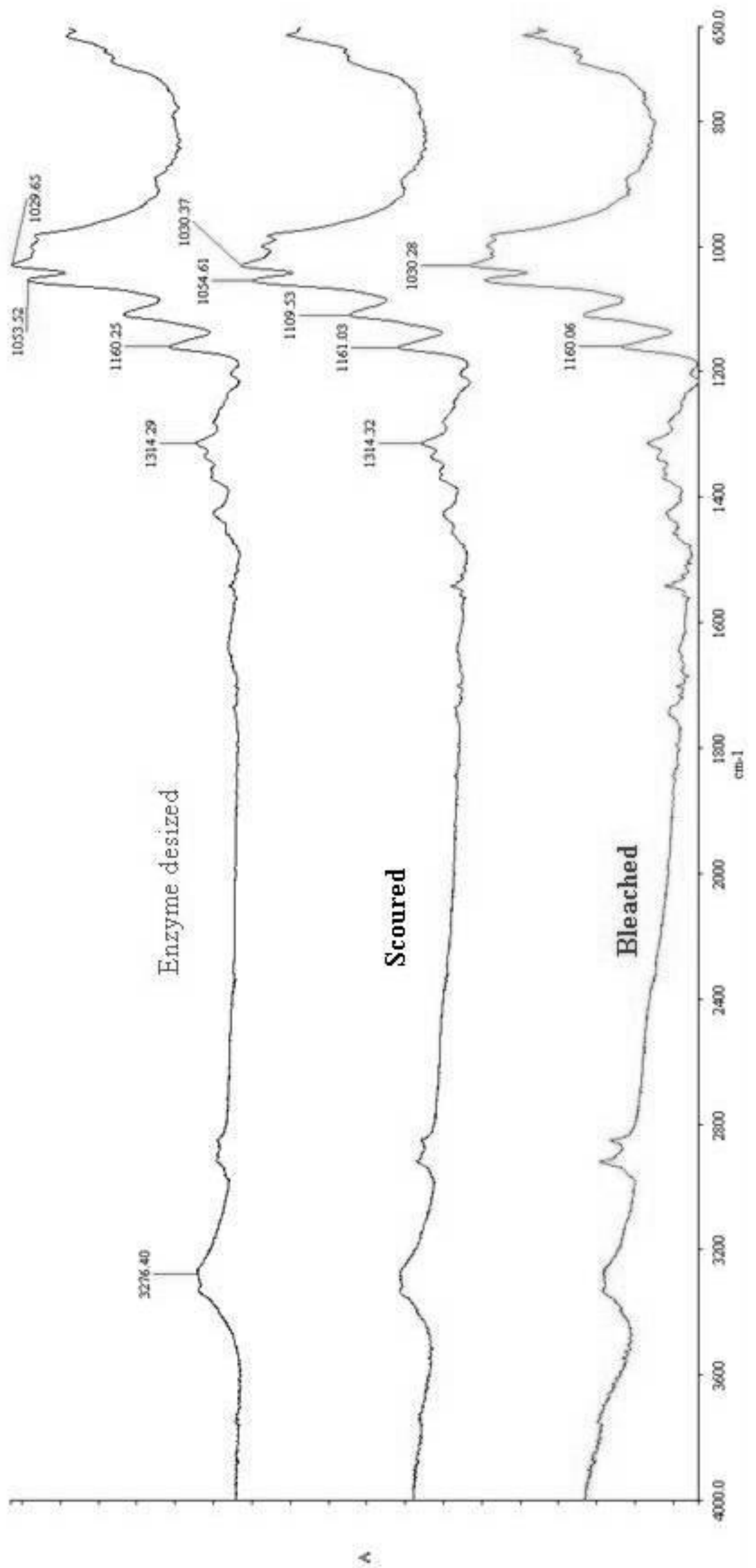


Figure 5.12 FTIR-ATR spectra of enzyme desized, scoured and bleached poplin 40s woven fabric

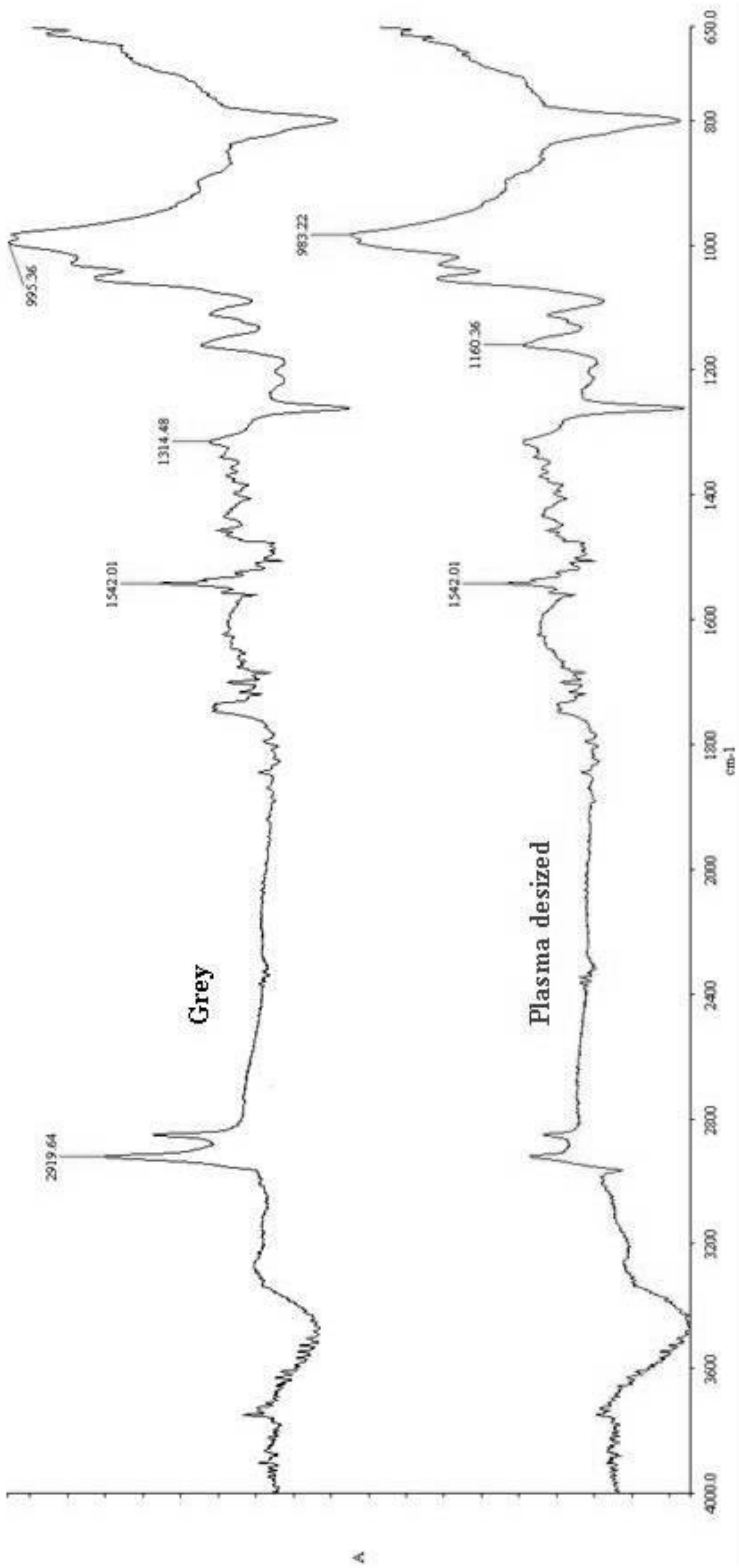


Figure 5.13 FTIR-ATR spectra of poplin 40s grey and plasma treated woven fabric under 150W power and 0.4L/m oxygen flow rate

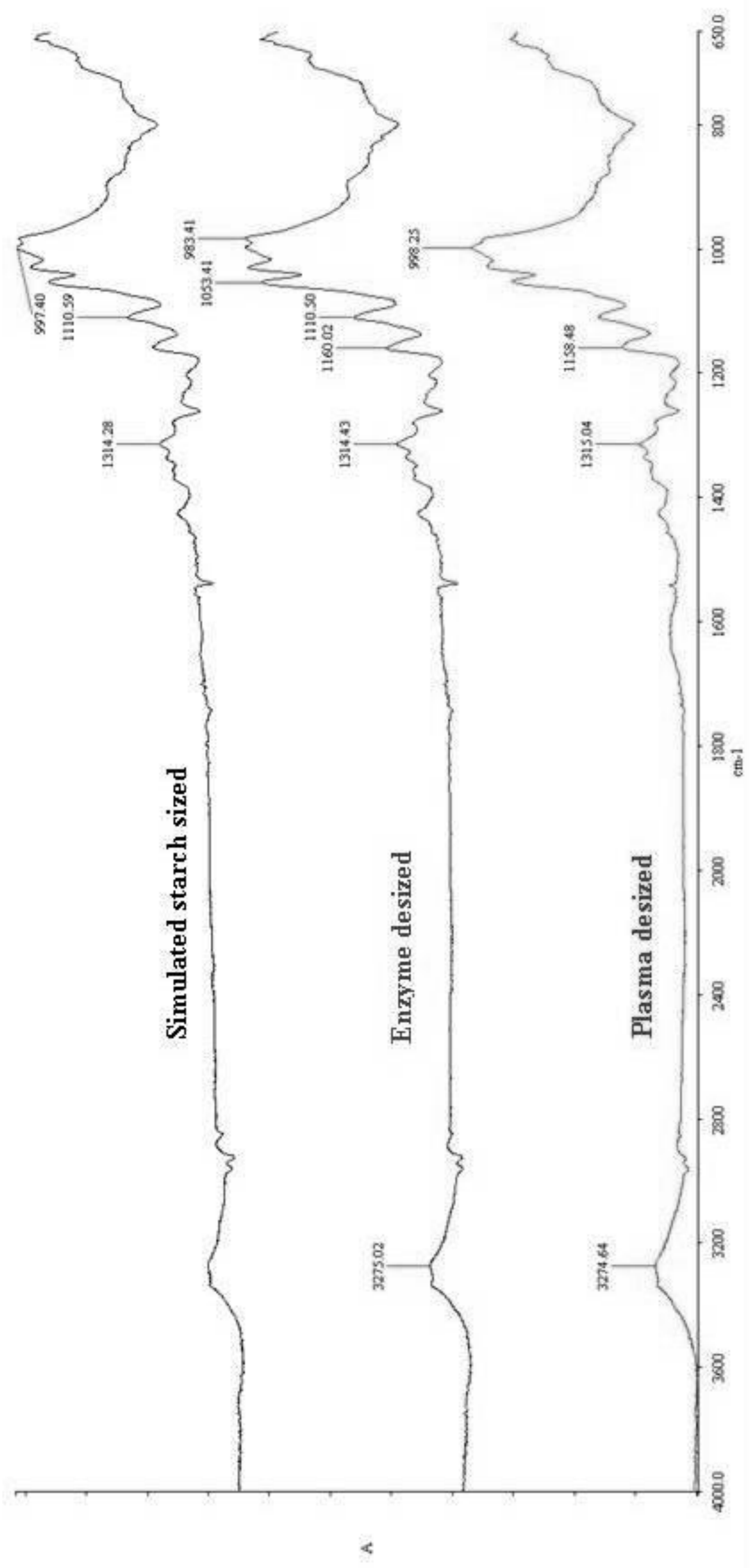
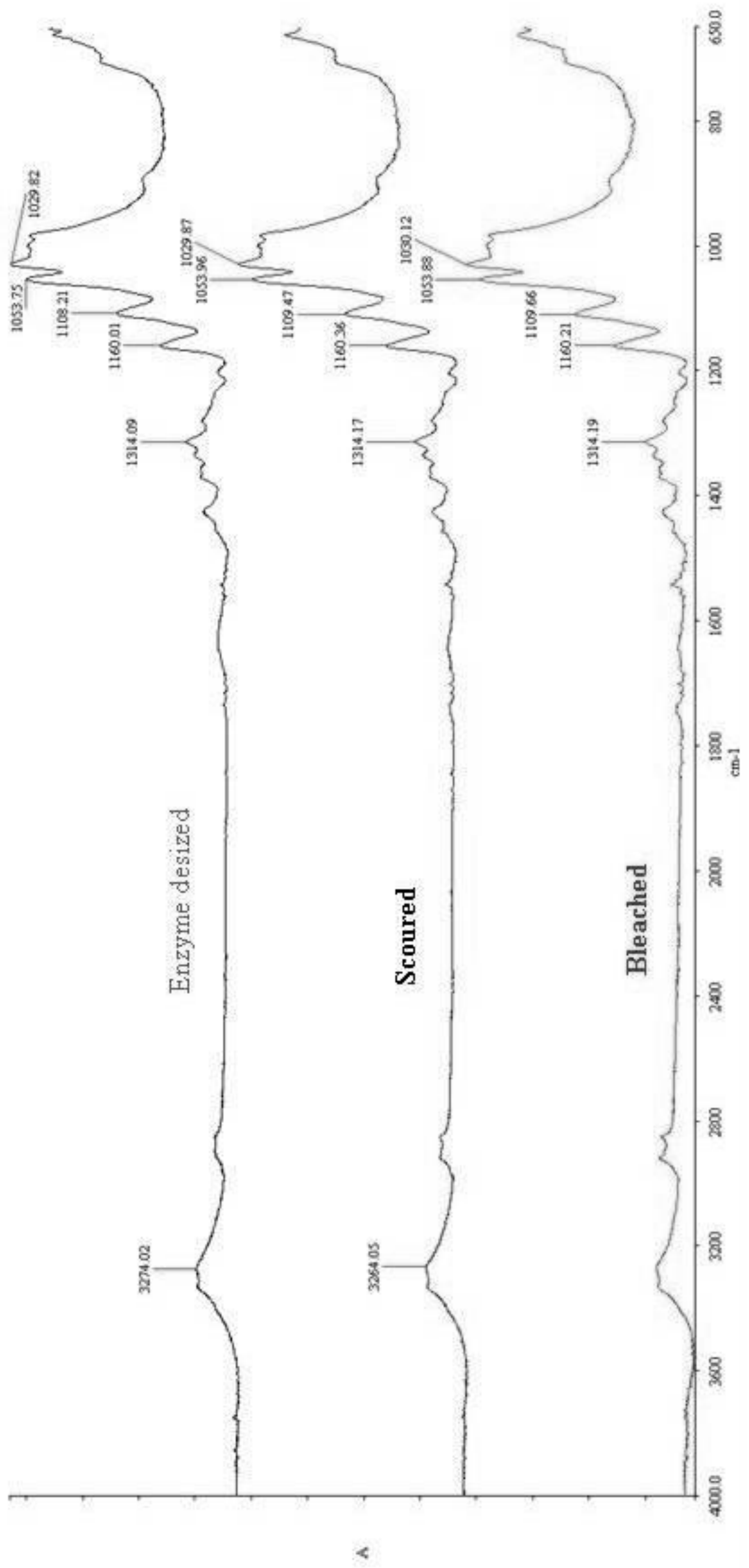


Figure 5.14 FTIR-ATR spectra of simulated starch sized, enzyme desized and plasma desized(150W power and 0.4L/m oxygen flow rate) poplin 40s woven fabric

Figure 5.15 FTIR-ATR spectra of enzyme desized, scoured and bleached 2/1 twill woven fabric



5.15 FTIR-ATR spectra of enzyme desized, scoured and bleached 2/1 twill woven fabric

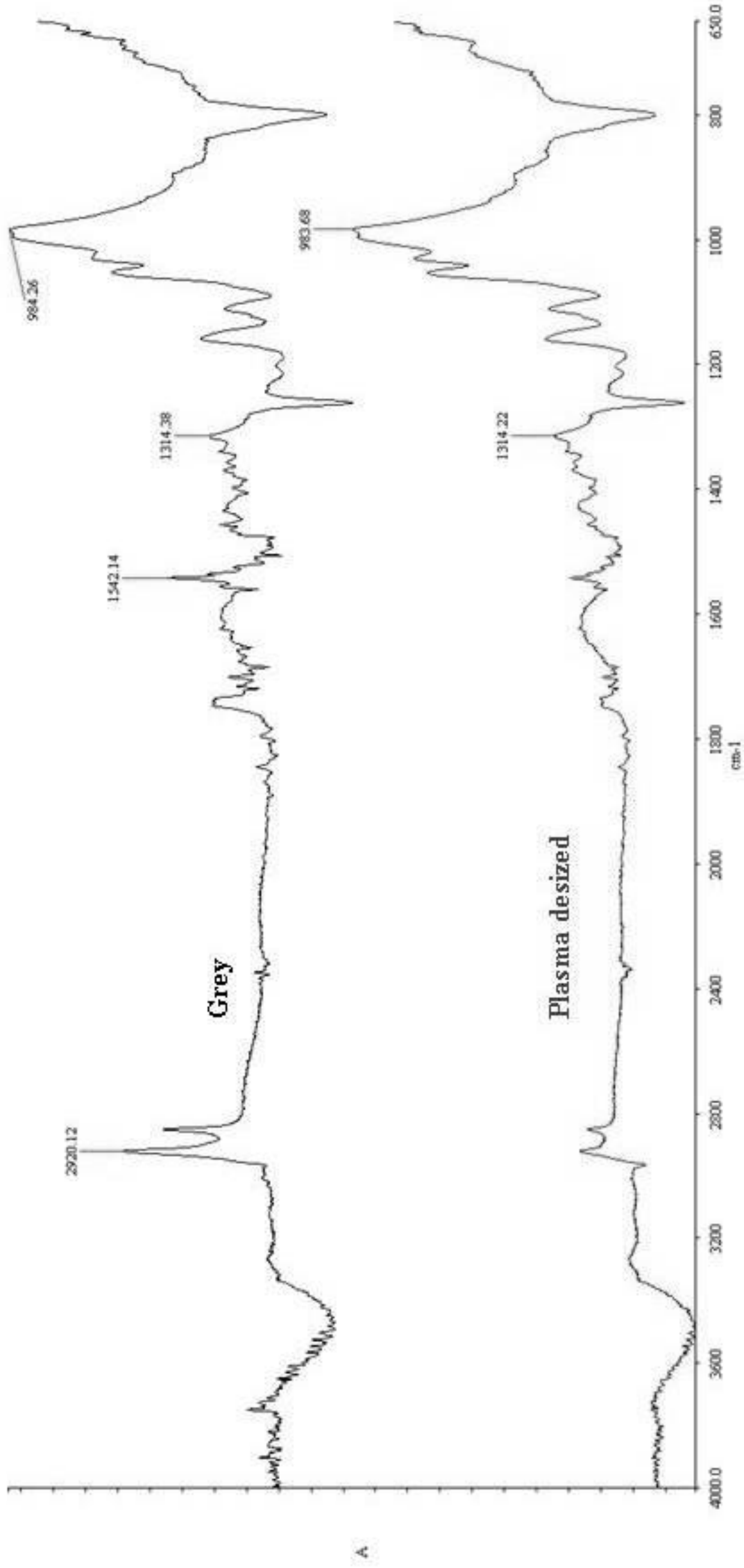


Figure 5.16 FTIR-ATR spectra of 2/1 twill grey and plasma treated woven fabric under 150W power and 0.4L/m oxygen flow rate

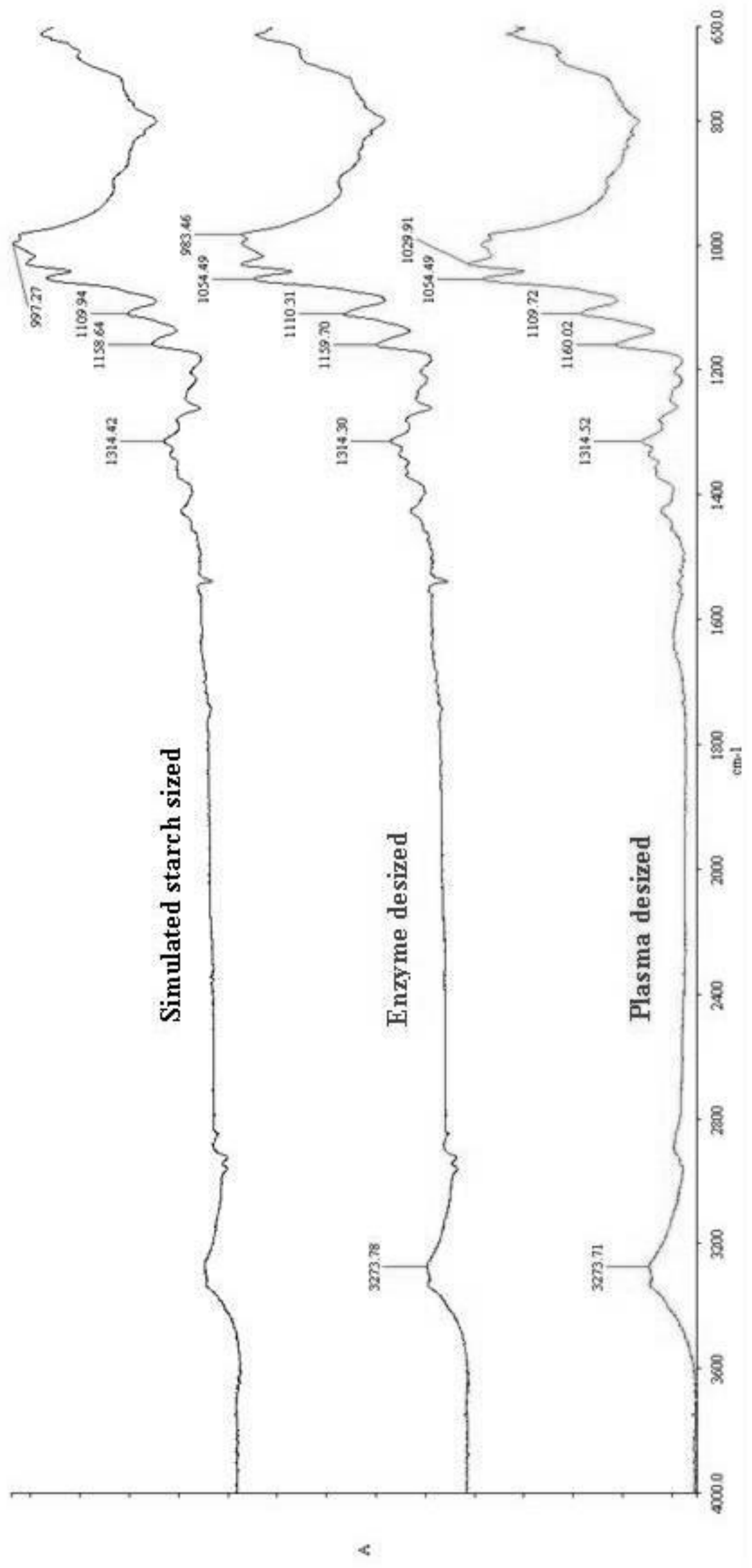


Figure 5.17 FTIR-ATR spectra of simulated starch sized, enzyme desized and plasma desized (150W power and 0.4L/m oxygen flow rate) 2/1 twill woven fabric
Figure 5.18 FTIR-ATR spectra of enzyme desized, scoured and bleached 2/2 twill woven fabric

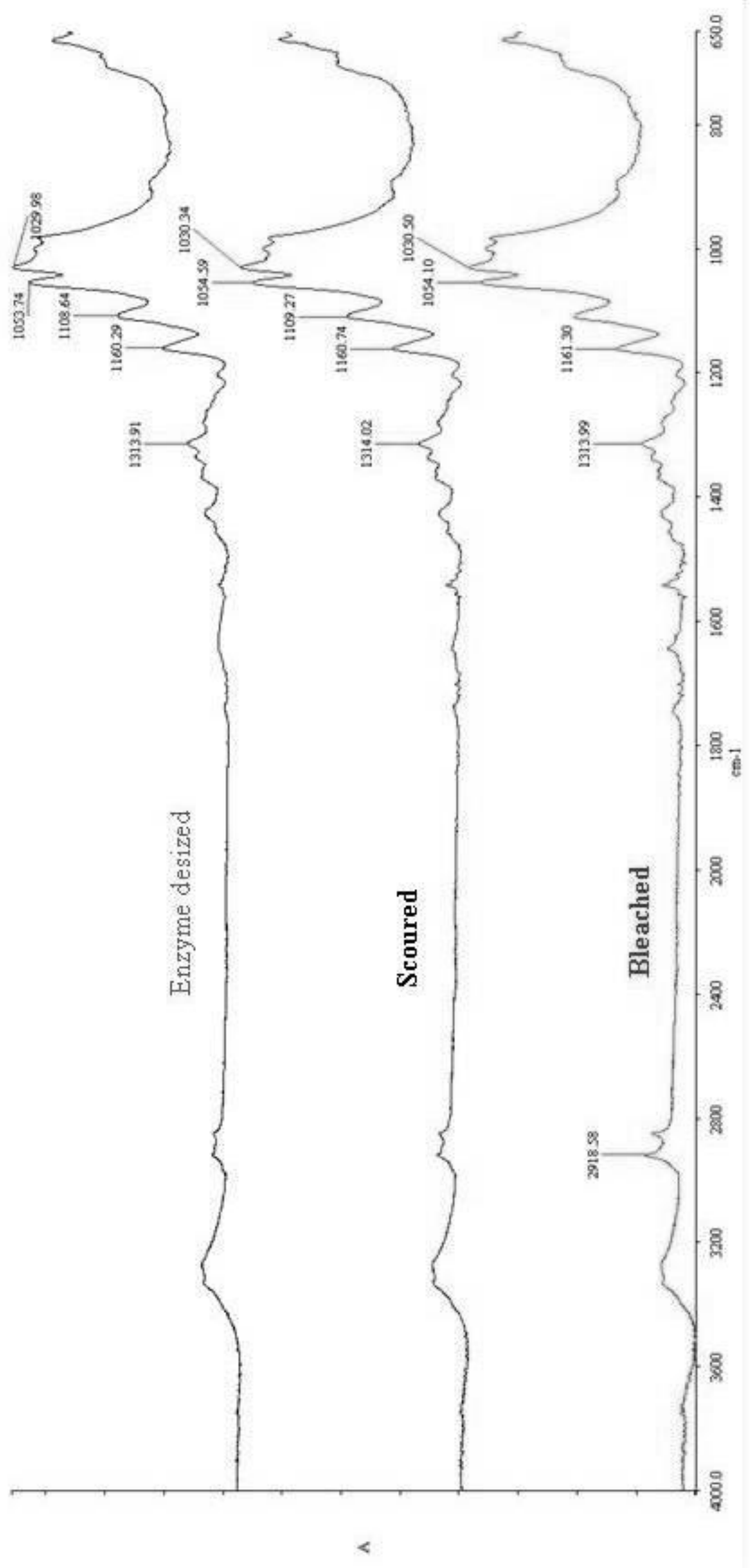


Figure 5.18 FTIR-ATR spectra of enzyme desized, scoured and bleached 2/2 twill woven fabric

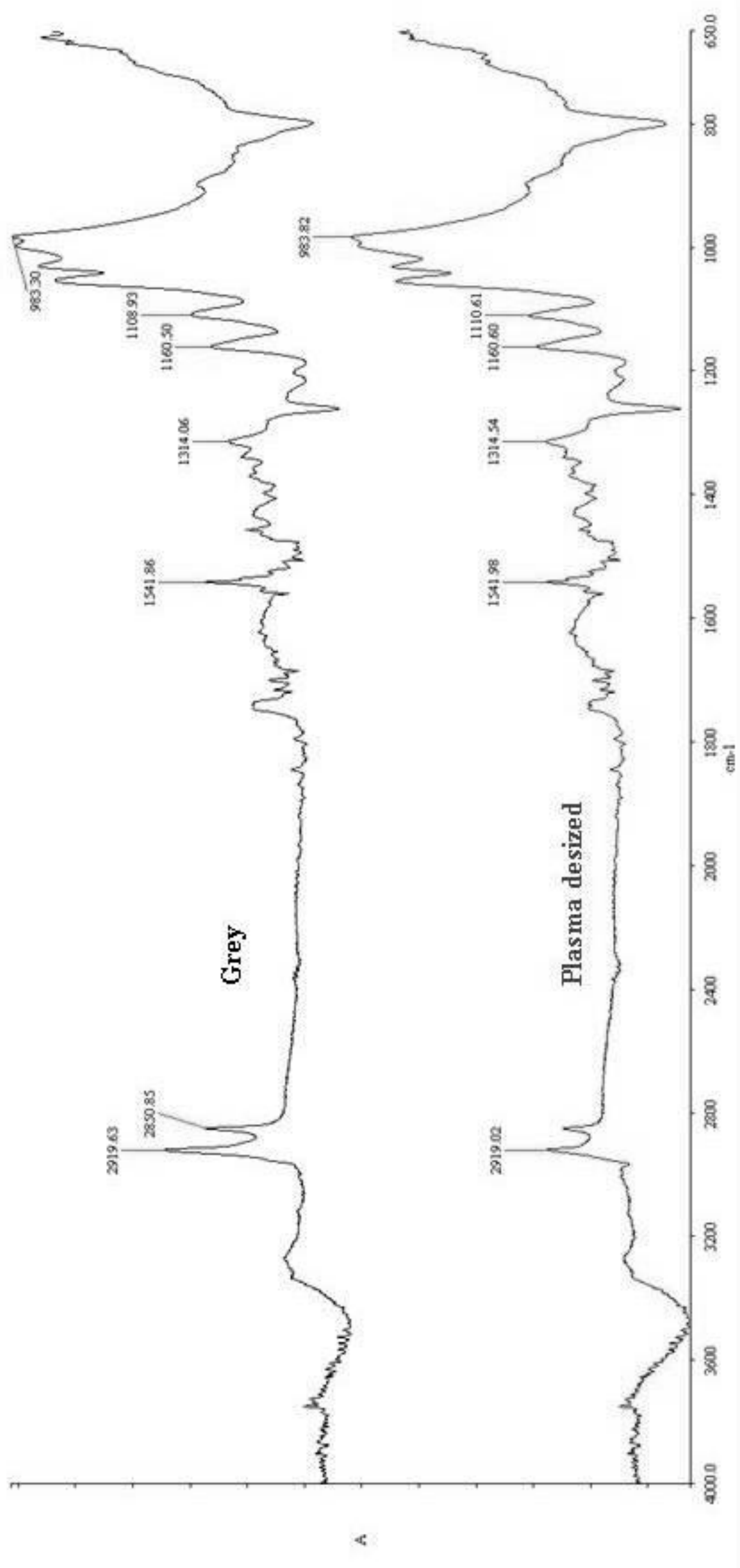


Figure 5.19 FTIR-ATR spectra of 2/2 twill grey and plasma treated woven fabric under 150W power and 0.4L/m oxygen flow rate

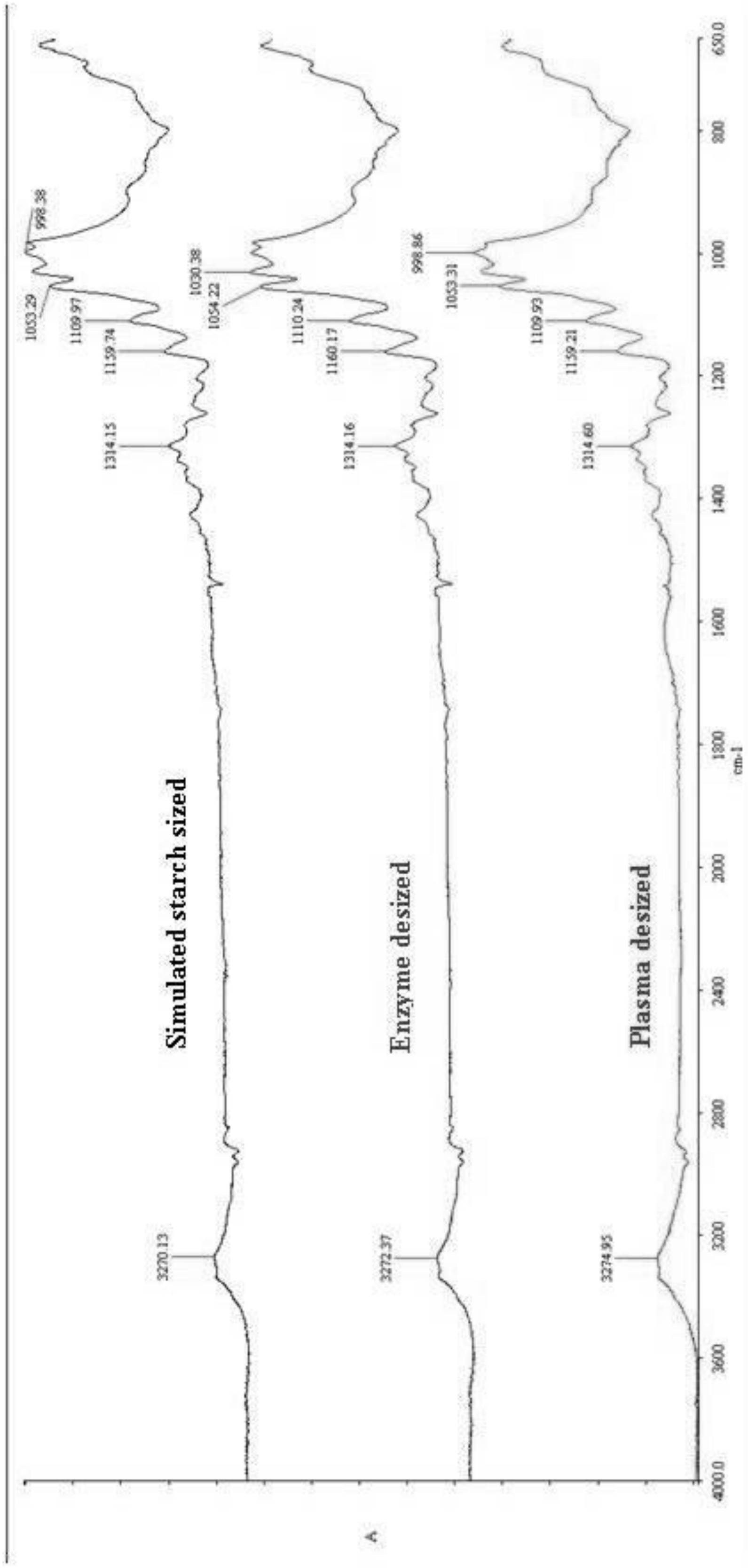


Figure 5.20 FTIR-ATR spectra of simulated starch sized, enzyme desized and plasma desized (150W power and 0.4L/m oxygen flow rate) 2/2 twill woven fabric

The FTIR-ATR spectra of the woven fabrics show characteristic cellulose peaks around 1200-1000cm^{-1}. From the FTIR-ATR spectra of different types of woven fabrics, both give a similar result under same type of treatment. Generally speaking, when comparing between the grey and plasma treated fabric, the peaks in the regions 3400-3200cm^{-1} are reduced after plasma treatment, indicating the polymeric hydroxyl groups that related to the sizing material are removed by plasmas. The absorption peaks in the range of 1657-1605cm^{-1} and 1320-1000 cm^{-1} represent the C=O stretch and C-O stretch respectively. The values of the C=O and C-O stretch are decreased after plasma treatment, which may due to the hydrolyzation of ester groups in pectin and/or wax of the grey fabric into carboxyl groups (Wang et al., 2007a).

The FTIR-ATR results between the simulated starch sized fabric, enzyme desized and plasma desized starch sized cotton fabrics are displayed in Figure 5.11, 5.14, 5.17 and 5.20 according to the fabric type. The peaks of O-H groups (3400-3200cm^{-1}) are decreased after enzyme and plasma treatment, revealing the starch size and some of the impurities related to polymeric hydroxyl groups have been removed. The intensities of the absorption peaks at the ranges of 1760-1690cm^{-1} (representing C=O stretching in COOH group) of the plasma treated fabric are higher than the enzyme treated fabric, which may due to the introduction of polar groups on the fiber surface by oxygen plasmas. The hydrophilicity of the plasma treated cotton fabric is thus enhanced significantly and even has a better result than the enzyme desized fabric (Cai and Qiu, 2006; Ma et al., 2009; Sun et al., 2011; Saravanan and Nalankilli, 2008), which enhancement has been evidenced in the previous chapter (see Chapter 4). The increase in the carbonyl group may because of the formation of –COOH on the fabric surface which may attribute to the dehydrogenation at C_6 carbon and oxidation of primary alcohol (Vaideki et al., 2009; Nithya et al., 2011). For the enzyme desized fabric, the increase in C=O bonds may due to the oxidation of C_1/C_4 carbon on the fabric surface after enzyme hydrolysis, causing the formation of –COOH group (Nithya et al., 2011).

From the FTIR-ATR results of the woven fabrics, the enhancement in hydrophilicity is attributed to the chemical modification of the fabric surface by plasma treatment.

5.2.3 X-ray phtoelectron spectroscopy (XPS)

The oxygen plasma is known to be effective in modifying and improving the fabric hydrophilicity by inducing polar functional groups, such as –CO-, -C=O and –COOH (Goto et al., 1992; Kubota and Funder, 1994). Thus the XPS was applied for analyzing the changes in chemical compositions (carbon and oxygen) after each conventional treatment and plasma treatment. Table 5.2 shows the surface elemental analysis and atomic ratios of woven fabrics.

Table 5.2 Surface elemental analysis and atomic ratios of woven fabrics

Element concentration (%)								
	C_{1s}				O_{1s}			
Fabric sample	Poplin 32s	Poplin 40s	2/1 twill	2/2 twill	Poplin 32s	Poplin 40s	2/1 twill	2/2 twill
Grey	0.64	0.62	0.69	0.71	0.36	0.38	0.31	0.29
Desized	0.64	0.62	0.66	0.65	0.36	0.38	0.34	0.35
Scoured	0.58	0.57	0.57	0.60	0.42	0.43	0.43	0.40
Bleached	0.47	0.52	0.42	0.33	0.53	0.48	0.58	0.67
Plasma*	0.47	0.56	0.56	0.40	0.53	0.44	0.44	0.60

Atomic ratio (O_{1s}/C_{1s})				
Fabric sample	Poplin 32s	Poplin 40s	2/1 twill	2/2 twill
Grey	0.56	0.62	0.45	0.40
Desized	0.57	0.62	0.51	0.53
Scoured	0.72	0.75	0.75	0.67
Bleached	1.12	0.93	1.37	1.99
Plasma*	1.13	0.77	0.78	1.48

*Fabric plasma treated with 150W output power and 0.4L/m oxygen flow rate

Table 5.2 shows the elemental compositions of the grey, conventional treated and plasma treated fabrics. Similar results are shown among different types of woven fabrics. The concentration of C_{1s} is decreased and O_{1s} is increased after each conventional preparation process, revealing some of the carbon bonds present on the fabric surface have been broken or removed during each chemical wet treatment. For the plasma treated grey fabrics, the reduction in C_{1s} and increase in O_{1s} may be attributed to the formation of carbon radicals by abstracting hydrogen atoms from polymer chains, then the combination of carbon radicals and the oxygen atoms generated in plasma gas might be occurred by means of electron impact dissociation (Kan and Yuen, 2012; Wang and Qiu, 2007a). As a result, the oxygen-containing groups such as C=O, -C=O, O-C-O and O-C=O are formed on the fiber surface (Morent et al., 2008; Wong et al., 2000; Inbakumar et al., 2010). From the comparisons within the same type of woven fabrics, the carbon content of the plasma treated grey fabric is lower than the grey fabric, and even lower than the enzyme desized and scoured fabrics, suggesting some of the non-cellulosic components, including sizing materials and natural impurities, have been removed by the plasma active species through etching effect on the fiber surface physically. The etching effect occurs on the fiber surface can be evidenced from the SEM images in the previous section (5.2.1). The surface impurities on fiber have been broken into small pieces and/or removed during the etching process, thus the inner fiber surface is exposed and newly generated functional groups are induced on the fiber surface by the plasma species (Kan and Yuen, 2012; Morent et al., 2008; Wong et al., 1999; Inbakumar et al., 2010). Thus, the oxygen content of the plasma treated fabrics are increased and higher than the grey, enzyme desized and scoured fabrics as shown in Table 5.2.

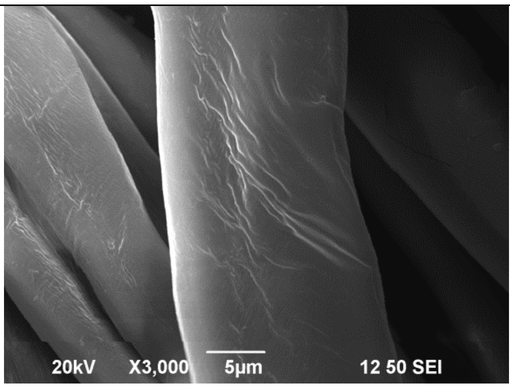
The atomic ratio (O_{1s}/C_{1s}) reflects the degree of surface modification. The O_{1s}/C_{1s} ratios of the woven fabrics are increased after plasma treatment, as the surface elemental compositions have been changed by the plasma species physically and chemically. The reduction in C_{1s}, increase in O_{1s} and increase in O_{1s}/C_{1s} ratios of the plasma treated woven fabrics result in the drastic enhancement in fabric hydrophilicity, and even has a better wettability performance than the grey, enzyme desized and scoured fabrics (see chapter 4).

The results of the XPS confirm the introduction of polar groups and removal of sizing materials by oxygen plasmas.

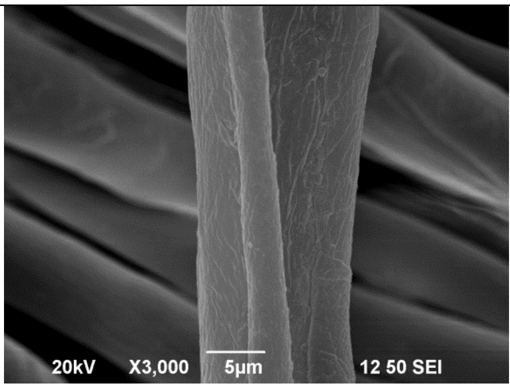
5.3 Knitted fabrics

5.3.1 Scanning electron microscope (SEM)

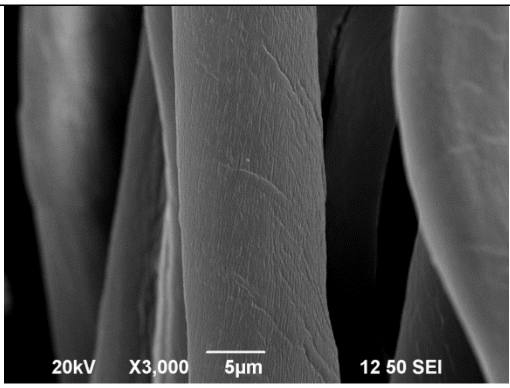
The results of the SEM photographs of knitted fabrics are shown according to the type of fabric. Figure 5.21 and 5.22 show the SEM photographs of the grey, scoured and bleached and fiber treated with different plasma parameters of single jersey and interlock knitted fabrics respectively.



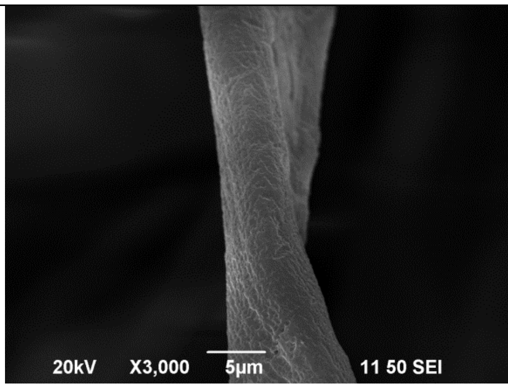
(a) Grey



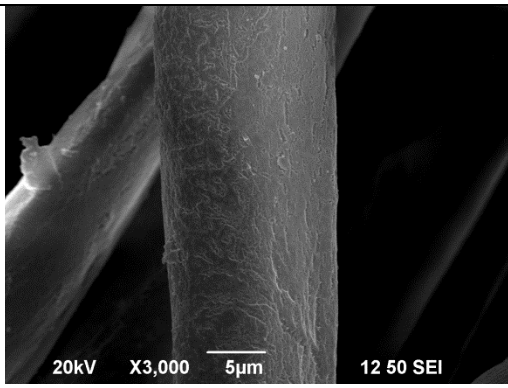
(b) Scoured



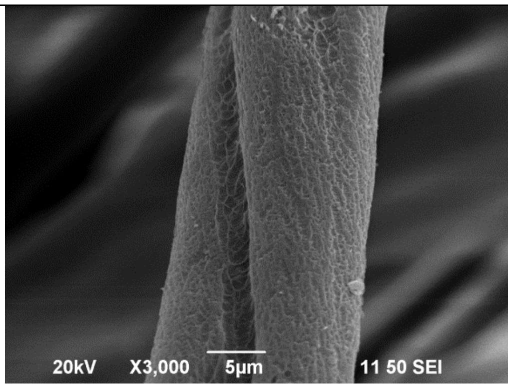
(c) Bleached



(d) 160W 0.2L/m

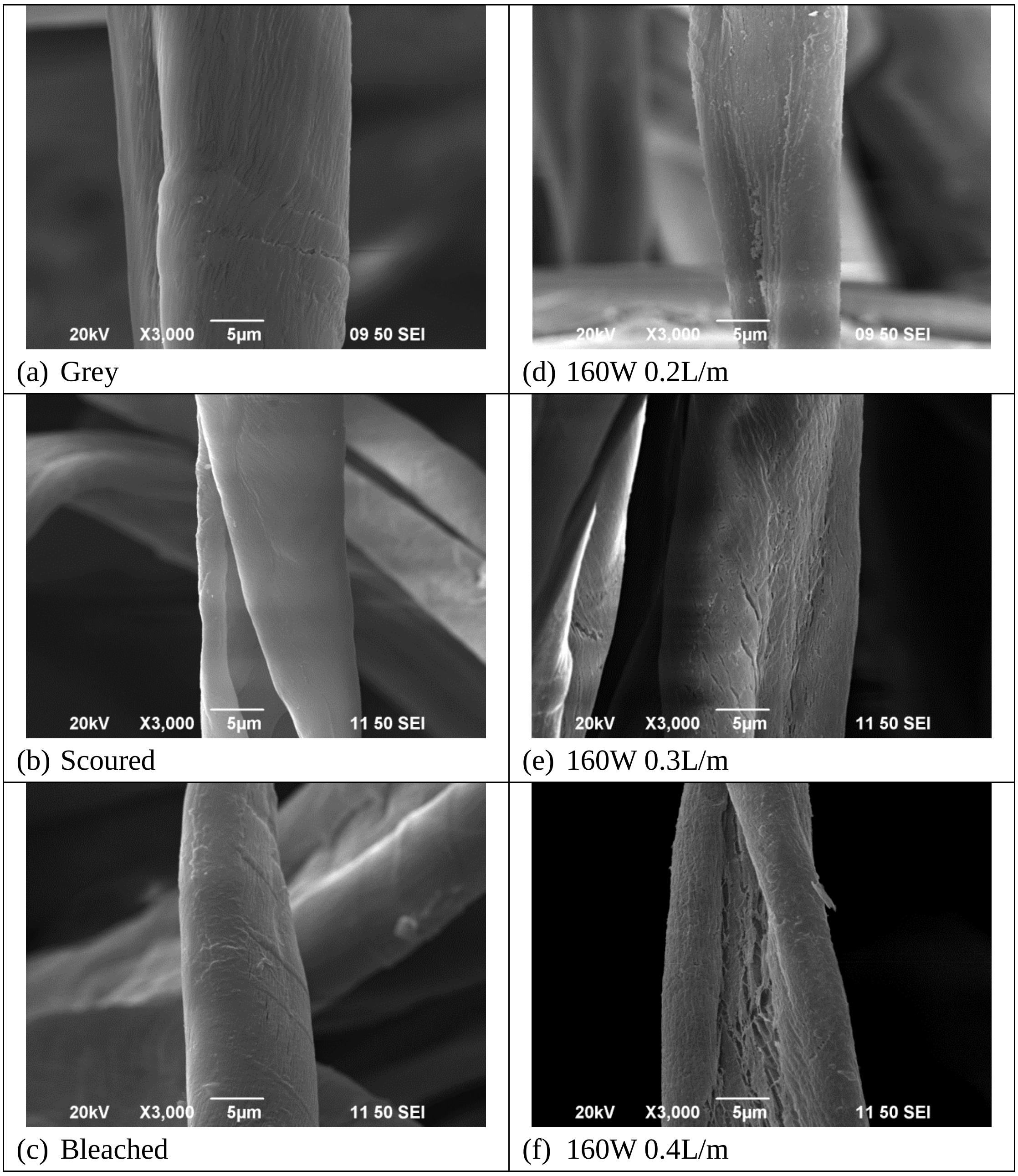


(e) 160W 0.3L/m



(f) 160W 0.4L/m

Figure 5.21 SEM photographs of single jersey knitted fabrics (a) grey (b) scoured (c) bleached; plasma treated with (d) 160W 0.2L/m (e) 160W 0.3L/m (f) 160W 0.4L/m



(a) Grey (d) 160W 0.2L/m
(b) Scoured (e) 160W 0.3L/m
(c) Bleached (f) 160W 0.4L/m

Figure 5.22 SEM photographs of interlock knitted fabrics (a) grey (b) scoured (c) bleached; plasma treated with (d) 160W 0.2L/m (e) 160W 0.3L/m (f) 160W 0.4L/m

Effect of conventional treatment

From the surface morphological images of the single jersey and interlock knitted fabrics, a smooth and slightly light reflected fiber surface is observed from the grey fabric (a), representing the wax and other hydrophobic impurities are covering the fiber surface. A cleaner fiber surface is shown after scouring (b) and bleaching (c) processes.

Effect of plasma treatment

The grey cotton knitted fabrics were subjected to plasma treatment with different parameters. Single jersey and interlock fabrics show a similar result in morphological changes. The surface morphological changes of the fiber after plasma treatment can be clearly seen from the SEM images (d-f). A large amount of microcracks can be observed from the fiber surface, reveling etching occurs on the fiber surface. Moreover, the appearance of fragmentation on the fiber surface is due to the partial breakdown of pectin and the length of the non-cellulose molecular chains is being cut into shorter lengths by the bombardment of plasma active species during and after plasma treatment (Tian et al., 2011). Moreover, the porous surface structure and microcracks are created by the plasmas etching process, resulting larger fiber surface area, thus the hydrophilicity of the plasma treated fabrics are greatly enhanced when compared with the grey and scoured knitted fabrics. The enhancement in hydrophilicity after plasma treatment has been evidenced in chapter 4.

5.3.2 Fourier transfer infrared spectroscopy (FTIR-ATR)

Figure 5.23 and 5.25 show the FTIR-ATR spectra of scoured and bleached single jersey and interlock knitted fabrics respectively; and Figure 5.24 and 5.26 show the FTIR-ATR spectra of grey and plasma treated single jersey and interlock knitted fabric under 150W output power and 0.4L/m oxygen flow rate respectively.

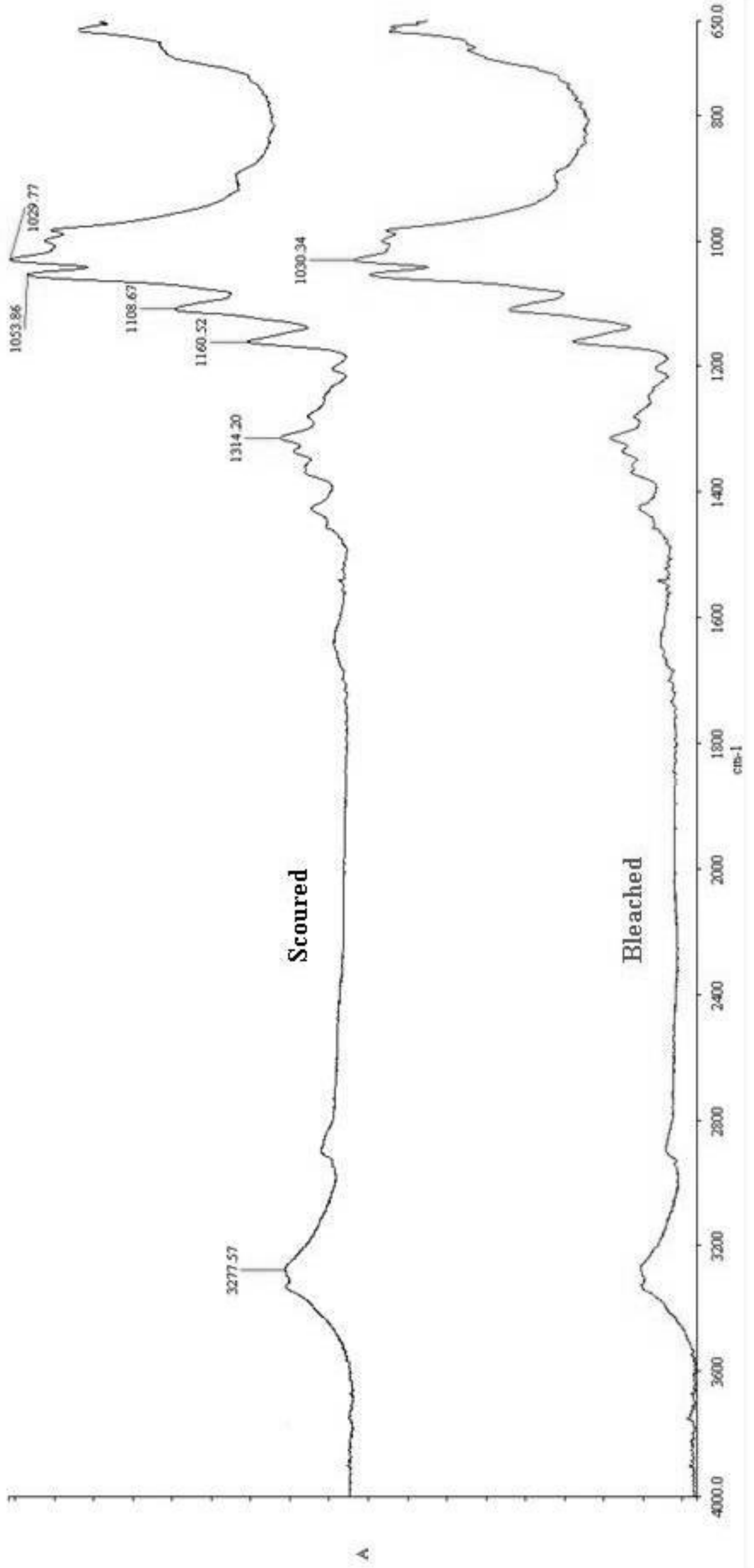


Figure 5.23 FTIR-ATR spectra of scoured and bleached single jersey knitted fabric

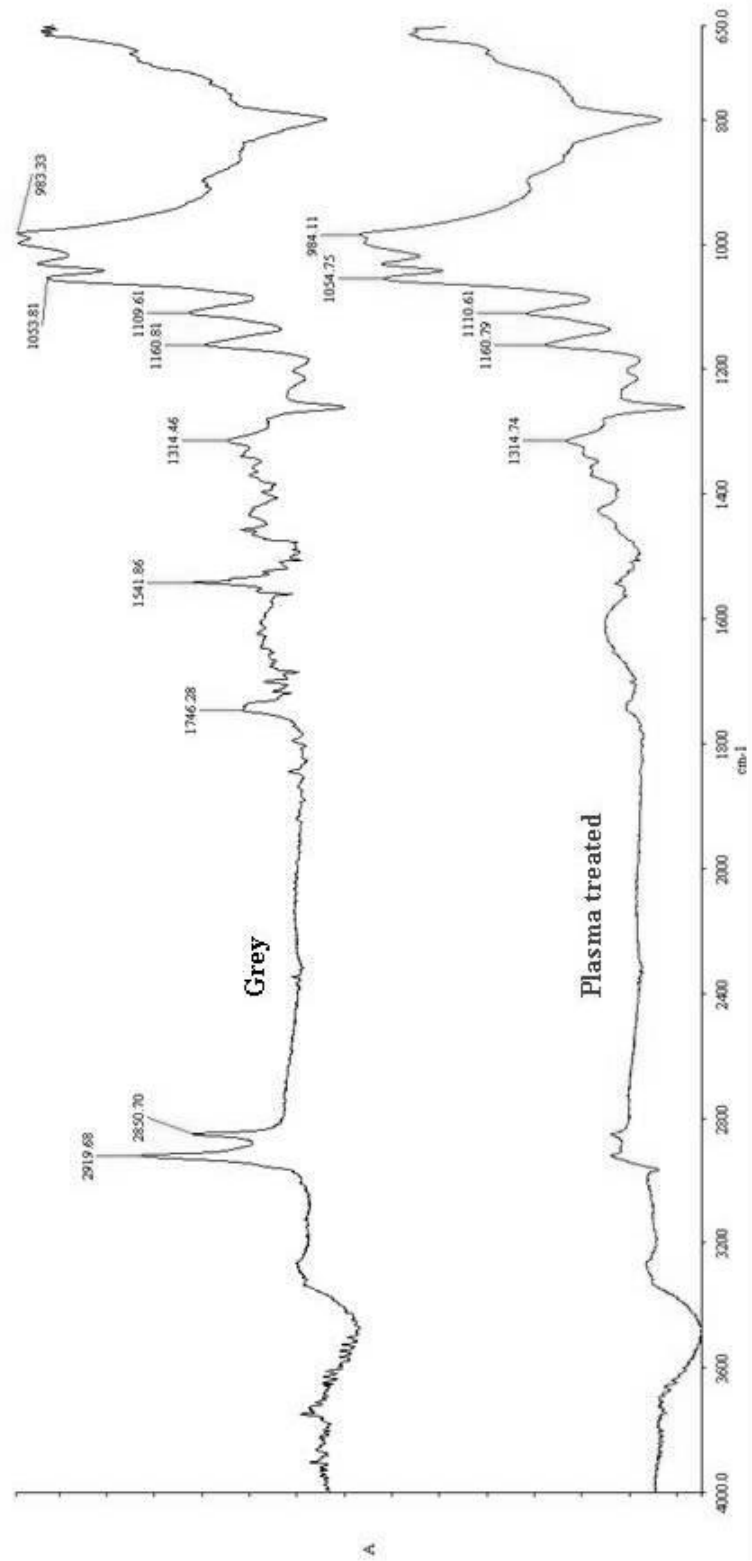


Figure 5.24 FTIR-ATR spectra of grey and plasma treated single jersey knitted fabric under 150W power and 0.4L/m oxygen flow rate

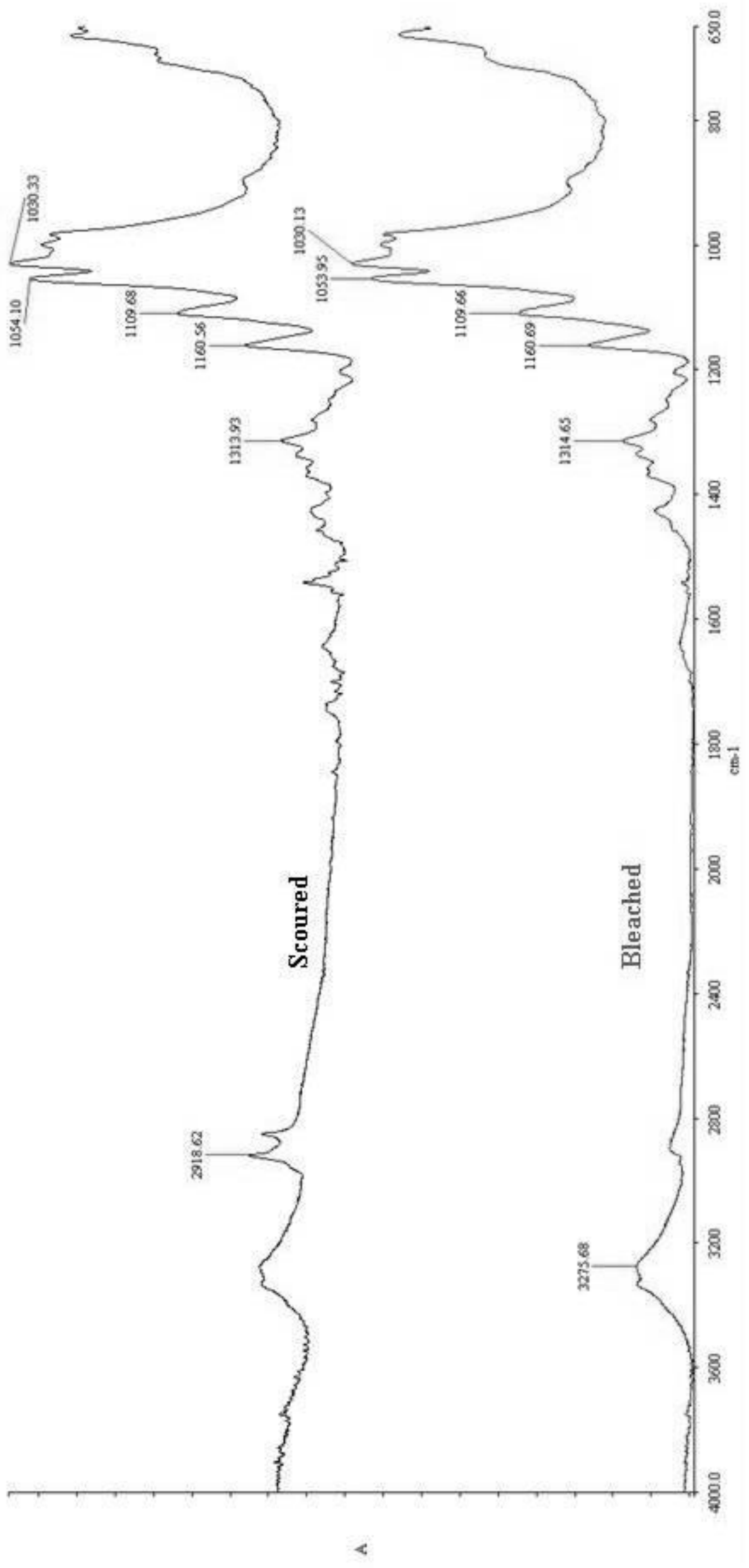


Figure 5.25 FTIR-ATR spectra of scoured and bleached interlock knitted fabric

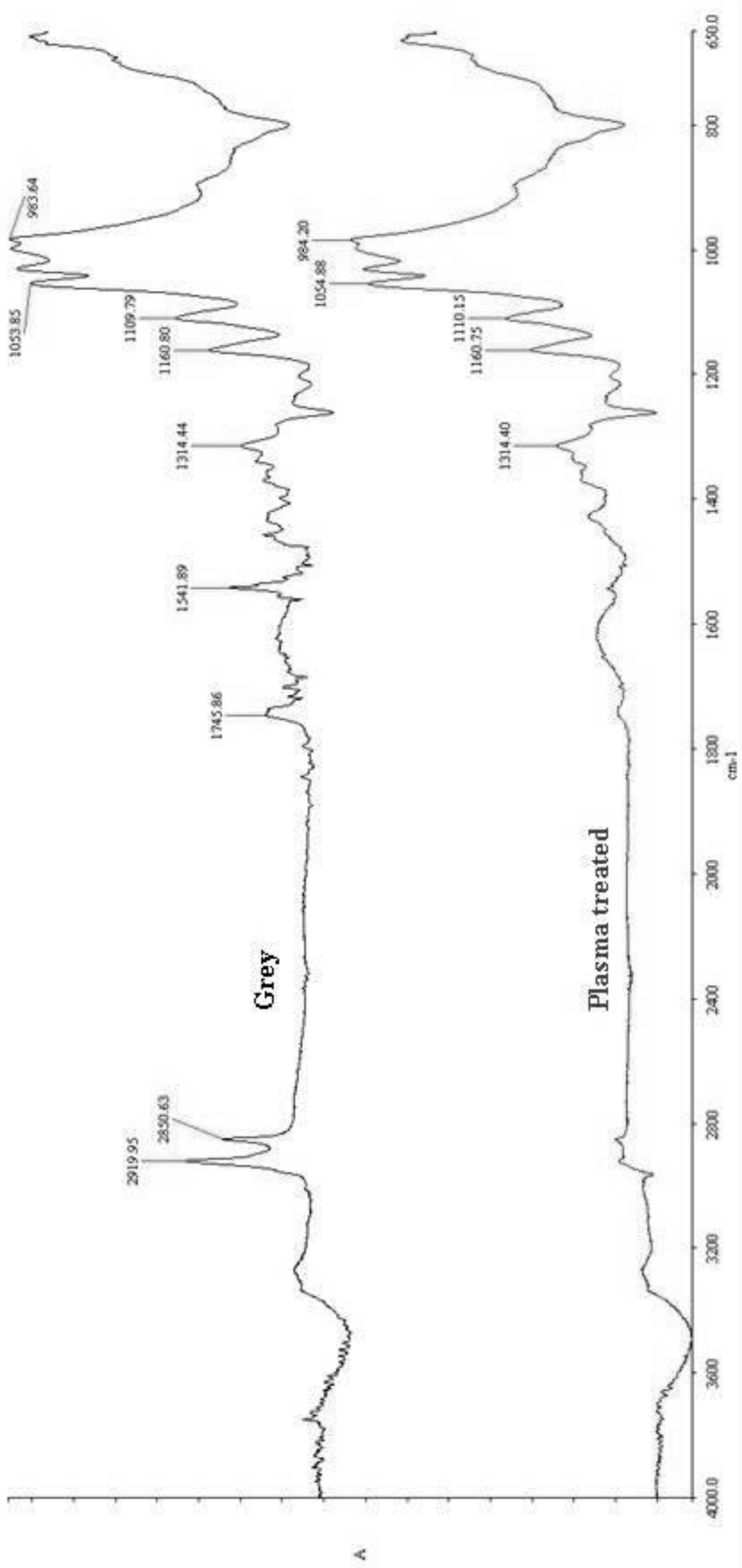


Figure 5.26 FTIR-ATR spectra of grey and plasma treated interlock knitted fabric under 150W power and 0.4L/m oxygen flow rate

Figure 5.23 and 5.25 show the spectra of scoured and bleached single jersey and interlock fabrics respectively. The interactions between the cotton knitted fabrics and the plasma species are confirmed by the analysis of FTIR-ATR spectra. Figure 5.24 and 5.26 show the spectra of the knitted grey fabrics and the fabrics plasma treated with 150W output power and 0.4L/m oxygen flow rate. The FTIR-ATR spectra of the single jersey and interlock fabrics show a similar result under the same treatment. Generally speaking, the intensities of the adsorption peaks at the ranges of 3400-3200cm^{-1} of the plasma treated knitted fabrics are higher than the grey fabric, revealing additional O-H stretch has been introduced by the oxygen plasmas. The peaks in the regions 1657-1605cm^{-1} are increased and a small peak is appeared after plasma treatment, indicating the C=O band is increased by the plasma oxidation effect. After removing the waxes, the cellulose is oxidized by the plasma active species, such as oxygen ions or oxygen free radicals, thus a relatively large amount of C=O band is produced (Samanta et al., 2009; Tian et al., 2011). Moreover, higher peaks are observed in the regions 1330-1000cm^{-1} from plasma treated fabrics, which regions are ascribed to the oxygen-containing groups of C-O stretch. The increase in C=O band and C-O stretch reveals that additional polar groups have been induced onto the fiber surface by oxygen plasmas, which could lead to the enhancement of hydrophilicity of fabric, as a result the plasma treated knitted fabric is more hydrophilic than the grey fabric. The findings agree with the results in the wettability test (see chapter 4).

5.3.3 X-ray phtoelectron spectroscopy (XPS)

Table 5.3 Surface elemental analysis and atomic ratios of knitted fabrics

Element concentration (%)				
	C_{1s}		O_{1s}	
Fabric sample	Single jersey	Interlock	Single jersey	Interlock
Grey	0.75	0.75	0.25	0.25
Scoured	0.47	0.49	0.53	0.51
Bleached	0.37	0.42	0.63	0.58
Plasma*	0.71	0.59	0.29	0.41
Atomic ratio (O/C)				
Fabric sample	Single jersey		Interlock	
Grey	0.25		0.32	
Scoured	1.13		1.05	
Bleached	1.71		1.36	
Plasma	0.41		0.70	

*Fabric plasma treated with 150W output power and 0.4L/m oxygen flow rate

Table 5.3 shows the elemental compositions of the grey, conventional treated and plasma treated woven fabrics. For the single jersey and interlock fabrics, the concentrations of C_{1s} are decreased and O_{1s} are increased after plasma treatment when comparing with the grey fabrics. The reduction in C_{1s} reveals that some of the carbon bonds present on the fabric surface such as the natural impurities have been broken or removed during the plasma treatment through etching effect; and the increase in O_{1s} reveals that the oxygen-containing groups such as C=O, -C=O, O-C-O and O-C=O are formed on the fiber surface by the oxygen plasma species (Morent et al., 2008; Wong et al., 1999; Inbakumar et al., 2010). The etching effect occurrs on the fiber surface can be evidenced from the SEM images from the previous section (5.3.1). The surface elemental compositions have been changed by the plasma species physically and chemically. The reduction in C_{1s}, increase in O_{1s}

and increase in O/C ratios of the plasma treated knitted fabrics result in the drastic enhancement in the fabric hydrophilicity, and even has a better wettability performance than the grey fabrics.

5.4 Conclusion

In this chapter, scanning electron microscope (SEM), fourier transfer infrared spectroscopy (FTIR-ATR) and x-ray photoelectron spectroscopy (XPS) have been applied to make an in-depth analysis on the surface and chemical changes on the conventional and plasma treated fabrics. The fabric surface morphology is found to be changed by plasma species, which the occurance of etching result in breaking the sizes into small fragments and creating microcracks on fiber surface. The increase in fabric hydrophilicity due to the introduction of polar groups by oxygen plasmas has been evidenced by the findings in FTIR and XPS.

As the fabric surface morphology and chemical compositions are found to be affected by the cleaning and etching effect of plasma species, the dyeing performances would also be affected. The dyeability of the plasma treated woven and knitted fabrics will be studied and compared with conventional treated fabrics in next chapter.

Chapter 6 Dyeing properties

6.1 Introduction

In order to have an in-depth analysis on how the plasma treatment affects the dyeability of the cotton woven and knitted fabrics, dyeing was carried out with reactive dyes in two colors. The dyeing properties of the grey, conventional treated and plasma treated cotton fabrics were interpreted by the reflectance values, K/S sum values, L*a*b* values and the relative unlevelness index (RUI). The results are shown according to the fabric type and color dyed.

6.2 Woven fabrics

6.2.1 Fabric images (blue color)

Figure 6.1 shows the images of the blue dyed grey, enzyme desized, scoured, bleached and plasma treated with 150W output power and 0.4L/m oxygen flow rate woven fabrics. The images are taken in the light box under daylight illuminant D65. Similar results are given by different types of woven fabrics. The color shade of the blue dyed fabric is decreased after each conventional wet treatment and the plasma treated fabric has a similar color shade with the enzyme desized fabric by eye observation.

Poplin 32s

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

Poplin 40s

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

2/1 twill

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

2/2 twill

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

Figure 6.1 Fabric images of woven fabrics (blue color)

6.2.2 Reflectance values (blue color)

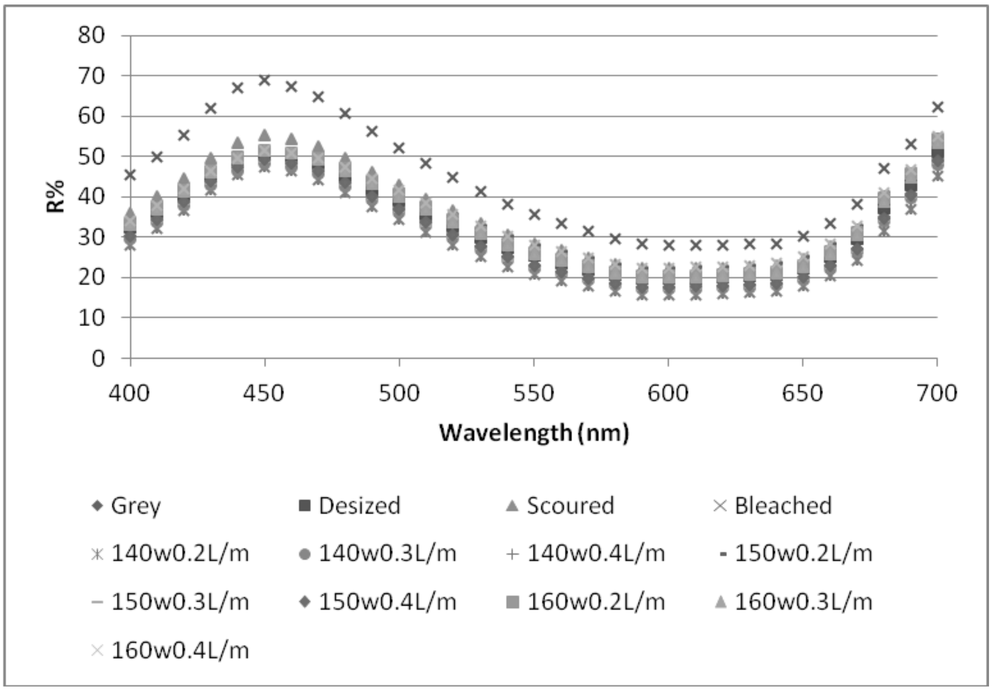


Figure 6.2 Reflectance values of poplin 32s woven fabric (blue color)

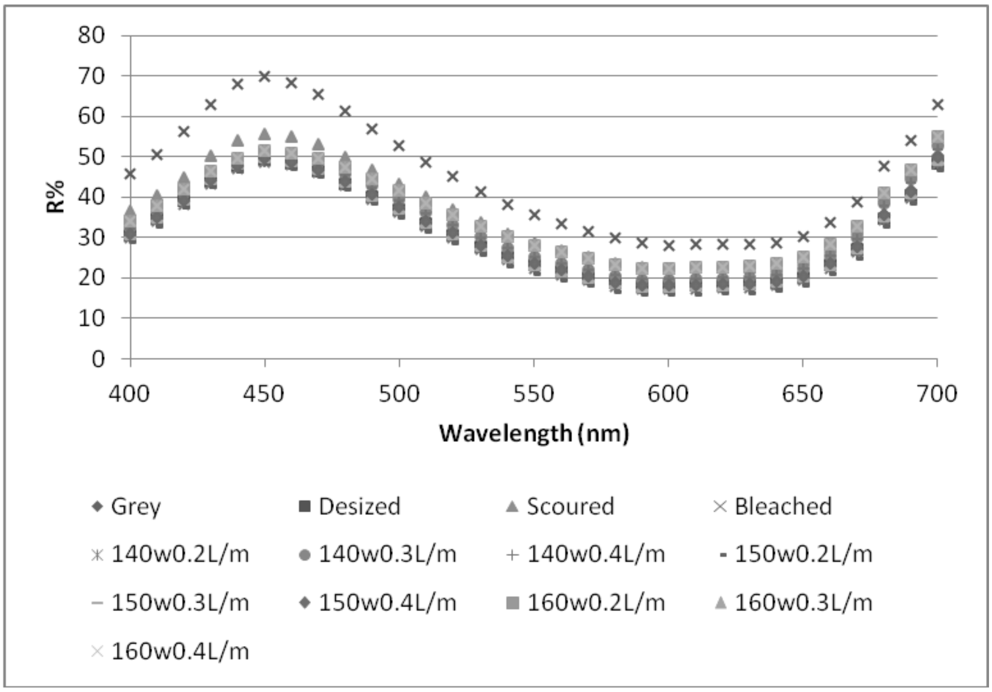


Figure 6.3 Reflectance values of poplin 40s woven fabric (blue color)

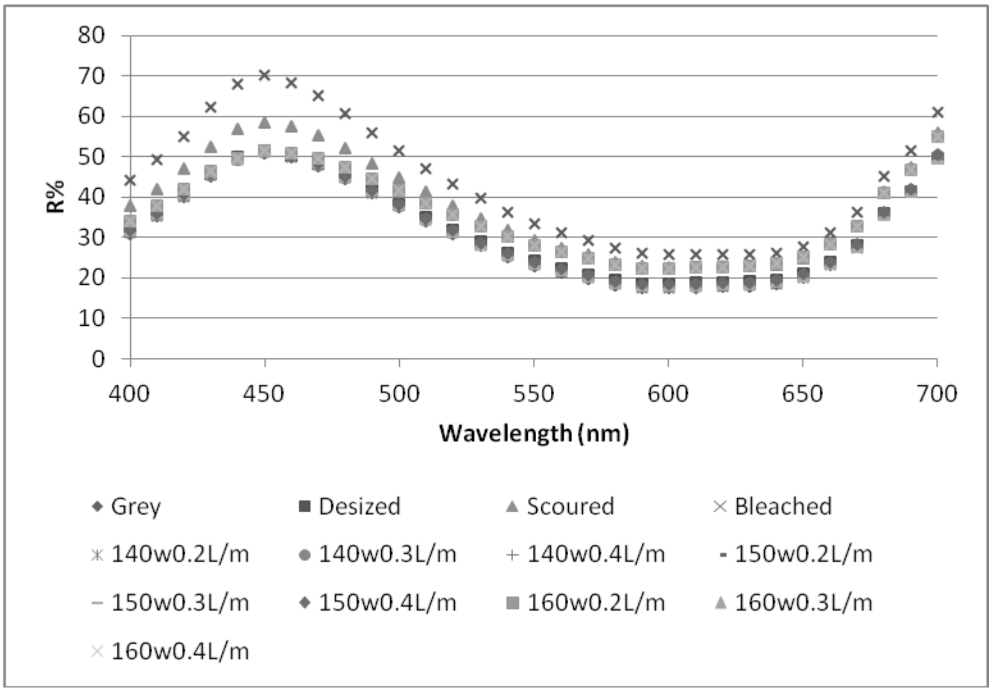


Figure 6.4 Reflectance values of 2/1 twill woven fabric (blue color)

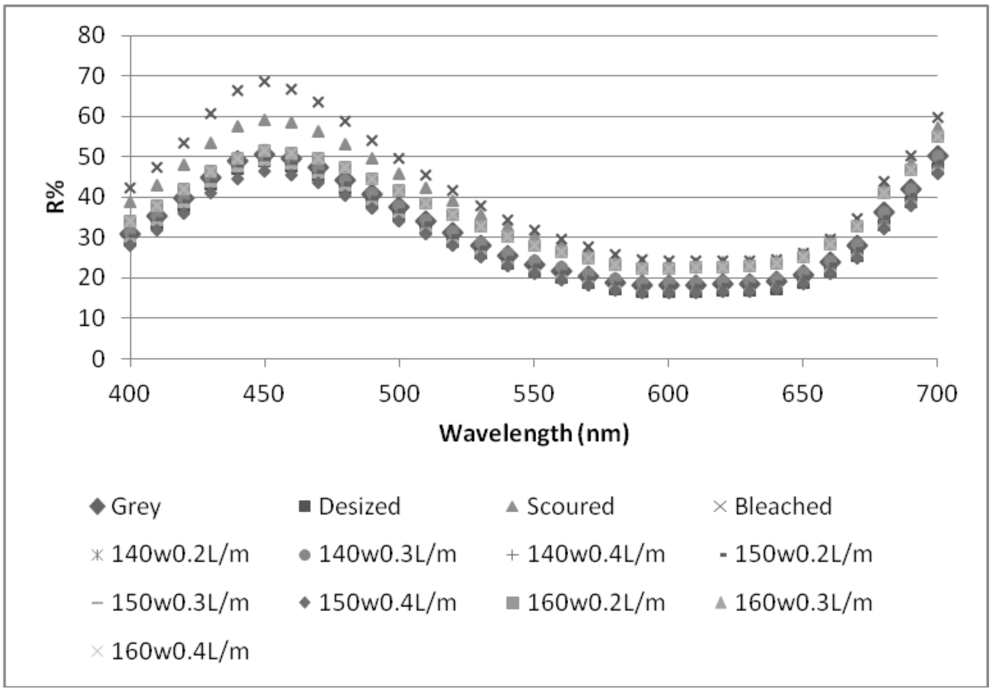


Figure 6.5 Reflectance values of 2/2 twill woven fabric (blue color)

6.2.3 K/S sum values (blue color)

Table 6.1 K/S sum values of cotton woven fabrics (blue color)

Treatment	Poplin 32s	Poplin 40s	2/1 twill	2/2 twill
Grey	32.49	29.97	28.60	27.99
Desized	26.02	29.36	28.26	32.60
Scoured	21.54	20.99	20.33	18.85
Bleached	13.94	13.59	16.20	17.19
140W0.2L/m	33.82	31.81	28.16	32.45
140W0.3L/m	30.53	26.43	28.25	29.14
140W0.4L/m	32.07	27.33	27.90	28.82
150W0.2L/m	25.02	33.76	22.34	30.54
150W0.3L/m	31.81	31.92	30.65	32.97
150W0.4L/m	30.24	29.08	27.92	27.89
160W0.2L/m	24.16	21.82	20.76	22.30
160W0.3L/m	25.53	23.91	21.80	26.92
160W0.4L/m	24.34	21.02	22.51	23.15

From the reflectance values of the blue color dyed cotton woven fabrics (Figure 6.2 to 6.5), the same type of woven fabrics treated with different plasma parameters show similar shapes of reflectance curves, which mean the color shade of those plasma treated fabrics are similar. Moreover, the plasma treated fabrics get more or less the same reflectance values with the enzyme desized fabrics which results agree with the fabric colors by eye observation (see section 6.2.1). In addition, some of the plasma treated fabrics, especially for the fabrics treated with 160W output power, give a higher reflectance values than the grey and enzyme desized fabrics, and even have similar reflectance values with the scoured fabrics. The higher the reflectance value, the lighter shade of the fabric will be.

K/S sum values of the blue color dyed woven cotton fabrics are shown in Table 6.1. The K/S sum value has a linear relationship with the concentration of colorant in the medium; the higher the K/S sum value, the darker shade of the fabric color will be.

From the results of those blue dyed woven fabrics, the K/S sum values of the woven fabrics decrease after each conventional wet treatment, i.e. the grey fabric has the darkest shade and the bleached fabric has the lightest shade. The lighter in color shade after each conventional wet treatment is due to the removal of natural yellowing matters. The K/S sum values of the fabrics treated with different plasma parameters are varied. The K/S sum values of the plasma treated woven fabrics give similar or even higher values than the enzyme desized fabrics, revealing the desizing efficiency of the plasma treatment is comparable to the enzyme desizing. Moreover, given that ether groups can be covalently formed by the reaction between reactive dyes and hydroxyl groups of cotton fiber, the number of hydroxyl groups in the fiber surface can be modified by plasma treatment and reactive free radical sites can be generated on the fabric surface by oxygen plasma species (Patiño et al., 2011; Martinez-Gomez et al., 2009). The increase in hydroxyl groups by plasma treatment could allow a higher number of dye molecules to bind on fiber surface and the hydrophilicity of the fiber surface is enhanced by oxygen plasma species, thus a faster dye adsorption and diffusion from the dyebath to fiber can be achieved. In addition, the fiber surface impurities have been removed by plasma etching and the effective surface area is created by the rougher surface, thereby facilitating the interaction and diffusion of dye molecules to fiber (Bhat et al., 2011b). As a result, a darker shade can be obtained from the plasma treated fabrics. The removal of size and impurities by plasmas can be evidenced from the reduction in fabric weight after plasma treatment (see section 4.2.2.2) and SEM images (see section 5.2.1). The increase in hydroxyl groups by oxygen plasma species can be evidenced from the enhancement in wettability (see section 4.2.4).

From the K/S sum values, poplin 32s fabric treated with 140W output power and

0.2L/m flow rate; poplin 40s fabric, 2/1 twill fabric and 2/2 twill fabric treated with 150W output power and 0.3L/m flow rate give the highest K/S sum values among other set of treatment parameters when compare with the same type of fabric.

6.2.4 L*a*b* values (blue color)

Table 6.2 CIE color coordinates L*a*b* values of cotton poplin 32s woven fabrics (blue color)

Treatment	L*	a*	b*
Grey	57.14	-4.10	-27.11
Desized	60.09	-4.28	-24.46
Scoured	62.88	-4.83	-24.46
Bleached	68.64	-4.14	-26.31
140w0.2L/m	56.58	-3.73	-27.44
140w0.3L/m	57.95	-4.12	-26.21
140w0.4L/m	57.30	-3.94	-26.64
150w0.2L/m	60.64	-4.79	-24.44
150w0.3L/m	57.42	-3.90	-26.86
150w0.4L/m	58.10	-4.12	-26.14
160w0.2L/m	61.09	-4.84	-24.12
160w0.3L/m	60.38	-4.68	-24.96
160w0.4L/m	60.99	-4.81	-23.73

Table 6.3 CIE color coordinates L*a*b* values of cotton poplin 40s woven fabrics (blue color)

Treatment	L*	a*	b*
Grey	58.23	-4.20	-27.01
Desized	58.44	-3.86	-25.97
Scoured	63.20	-4.64	-24.76
Bleached	68.94	-4.04	-26.84
140w0.2L/m	57.39	-3.95	-26.83
140w0.3L/m	59.91	-4.58	-25.13
140w0.4L/m	59.45	-4.36	-25.18
150w0.2L/m	56.58	-3.73	-27.64
150w0.3L/m	57.33	-3.81	-27.05
150w0.4L/m	58.61	-4.12	-25.85
160w0.2L/m	62.43	-4.96	-23.36
160w0.3L/m	61.24	-4.77	-24.12
160w0.4L/m	62.93	-5.10	-22.54

Table 6.4 CIE color coordinates L*a*b* values of cotton 2/1 twill woven fabrics (blue color)

Treatment	L*	a*	b*
Grey	58.88	-3.84	-27.51
Desized	59.03	-3.65	-26.99
Scoured	63.72	-4.63	-25.89
Bleached	67.05	-4.13	-29.30
140w0.2L/m	59.10	-4.02	-26.99
140w0.3L/m	59.04	-3.95	-26.81
140w0.4L/m	59.19	-3.97	-26.29
150w0.2L/m	62.15	-4.42	-24.85
150w0.3L/m	58.01	-3.76	-27.92
150w0.4L/m	59.20	-3.84	-26.95
160w0.2L/m	63.07	-4.58	-24.03
160w0.3L/m	62.44	-4.57	-24.11
160w0.4L/m	62.05	-4.47	-24.67

Table 6.5 CIE color coordinates L*a*b* values of cotton 2/2 twill woven fabrics (blue color)

Treatment	L*	a*	b*
Grey	59.04	-3.68	-26.60
Desized	57.05	-3.40	-27.80
Scoured	64.72	-4.77	-25.60
Bleached	66.27	-4.09	-29.55
140w0.2L/m	57.08	-3.41	-27.48
140w0.3L/m	58.53	-3.76	-26.08
140w0.4L/m	58.65	-3.71	-25.70
150w0.2L/m	57.87	-3.62	-26.42
150w0.3L/m	56.86	-3.49	-27.21
150w0.4L/m	59.10	-3.84	-25.44
160w0.2L/m	62.04	-4.41	-23.11
160w0.3L/m	59.58	-4.09	-24.95
160w0.4L/m	61.57	-4.46	-23.07

The CIE coordinates L*a*b* values of the blue dyed woven fabrics are shown in Table 6.2 to 6.5 according to the fabric type. Generally speaking, for the same type of woven fabric, the L* values of plasma treated fabrics are mostly similar with the grey and enzyme desized fabric, and some of the plasma treated fabrics are even given a slightly higher L* value than the enzyme desized fabric, especially for the fabric treated with 160W output power. The increase in L* value means that the fabric lightness is increased and thus paler shade is obtained. The increase in the fabric lightness of the enzyme desized fabric is due to the removal of sizing material; for the plasma treated fabrics, the increase in lightness may not only due to the removal of sizing material, but also the removal of the protruding fibers surface (Kan and Yuen, 2012; Karahan et al., 2009; Nithya et al., 2011). As the atmospheric pressure plasma treatment is a surface etching process, the protruding fiber surface could be removed, and thus smoother fiber surface and higher lightness due to the enhancement of the light reflection from the fiber surface could be obtained. The results of L* values agree with the reflectance values and K/S sum measurement from the previous section 6.2.2 and 6.2.3 respectively.

The a* value represents the redness and greenness of the fabric. The lower the negative a* value, the greener of the fabric shade will be. Most of the a* values of the plasma treated fabrics are slightly lower (more negative) than the grey fabric, which mean a slightly greenish shade is obtained after plasma treatment. A greenish shade appears on the plasma treated fabric may due to the color mixing of the natural yellowish color of grey fabric and the blue color dye.

The b* value represents the yellowness and blueness of the fabric. The higher the positive value of b*, the yellowish of the fabric shade will be. In general, the b* values of the plasma treated fabrics are slightly increased (more positive) when compare with grey fabric, especially for the fabrics treated with 160W output power, which may because of the oxidation effect induced by the plasmas with a higher output power. Although plasma treatment may lower the yellowish color of the grey fabric by removing sizing material and other impurities, the plasma species would induce a certain degree of yellowness due to the thermal oxidation on the fiber surface (Kan et al., 2011; Kan and Yuen, 2012). Moreover, the original yellowish color of the grey fabric is still remained even after plasma treated. As a result, a yellowish shade would be imparted after plasma treatment.

6.2.5 Relative unlevelness index (blue color)

Table 6.6 RUI of cotton woven fabrics (blue color)

Treatment	Poplin 32s	Poplin 40s	2/1 twill	2/2 twill
Grey	0.55	0.61	0.58	0.55
Desized	0.48	0.49	0.54	0.55
Scoured	0.49	0.50	0.54	0.54
Bleached	0.55	0.58	0.66	0.67
140W0.2L/m	0.55	0.54	0.56	0.58
140W0.3L/m	0.53	0.52	0.55	0.51
140W0.4L/m	0.53	0.50	0.52	0.50
150W0.2L/m	0.51	0.39	0.39	0.52
150W0.3L/m	0.53	0.54	0.57	0.53
150W0.4L/m	0.52	0.52	0.55	0.50
160W0.2L/m	0.53	0.49	0.50	0.46
160W0.3L/m	0.52	0.50	0.53	0.49
160W0.4L/m	0.48	0.46	0.51	0.45

With reference to the suggested interpretation of RUI (see Table 3.14), from Table 6.6, the RUI of all blue dyed grey, conventional treated and plasma treated woven fabrics have poor levelness which values are within the range 0.5-1.0. Theoretically, a better RUI could be obtained after each conventional treatment as some of the impurities are removed after each treatment, but the bleached woven fabrics have a poor RUI than the enzyme desized and scoured fabrics, which may due to the shrinkage problem caused by wet chemical treatment. The woven fabric will shrink after going through high temperature wet treatment and the fabric structure will be changed and even destroyed if operating with inappropriate treatment conditions, causing unlevel dyeing.

Although the calculated RUI values are not satisfactory, all of the plasma treated woven fabrics have a smaller RUI than the grey fabrics, and some even closer to the RUI of scoured fabrics. Due to the presentation of sizing material and impurities on the fiber surface, unlevel dyeing occurs on the grey fabric. Although the effects of plasma treatment on the enhancement on level dyeing is not proportional to its hydrophilicity incremental effect and the RUIs of plasma treated fabrics are not significantly smaller, the RUI of the plasma treated grey fabrics are lower than the grey fabrics, indicating plasma treatment gives aid in facilitating levelness dyeing by improving fiber surface hydrophilicity. The blue dyed woven fabrics have poor RUI may because of 1% blue dye concentration is not enough for dyeing the woven fabric samples.

6.2.6 Fabric images (black color)

The images of the black dyed grey, enzyme desized, scoured, bleached and plasma treated with 150W output power and 0.4L/m oxygen flow rate woven fabrics are shown in Figure 6.6. The images are taken in the light box under daylight illuminant D65. Similar results are obtained from different types of woven fabrics. From the color images of the black dyed woven fabrics, the color shade of the black dyed fabric is decreased after each conventional wet treatment and the plasma treated fabric has a similar color shade with the enzyme desized fabric by eye observation.

Poplin 32s

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

Poplin 40s

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

2/1 twill

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

2/2 twill

(a)Grey (b)Desized (c)Scoured (d)Bleached (e)Plasma treated

Figure 6.6 Fabric images of woven fabrics (black color)

6.2.7 Reflectance values (black color)

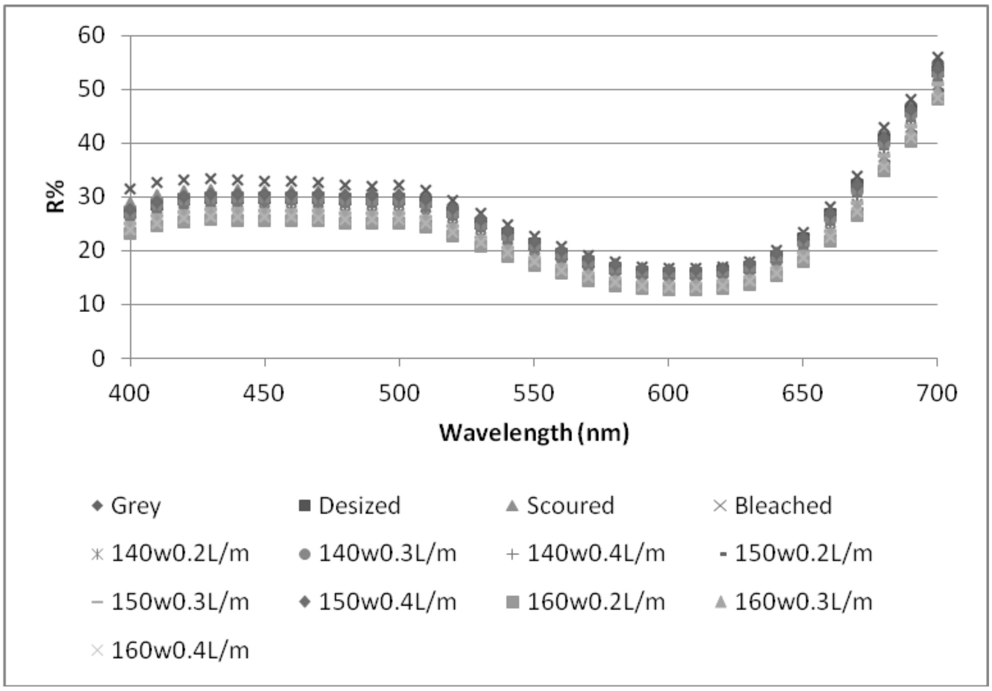


Figure 6.7 Reflectance values of poplin 32s woven fabric (black color)

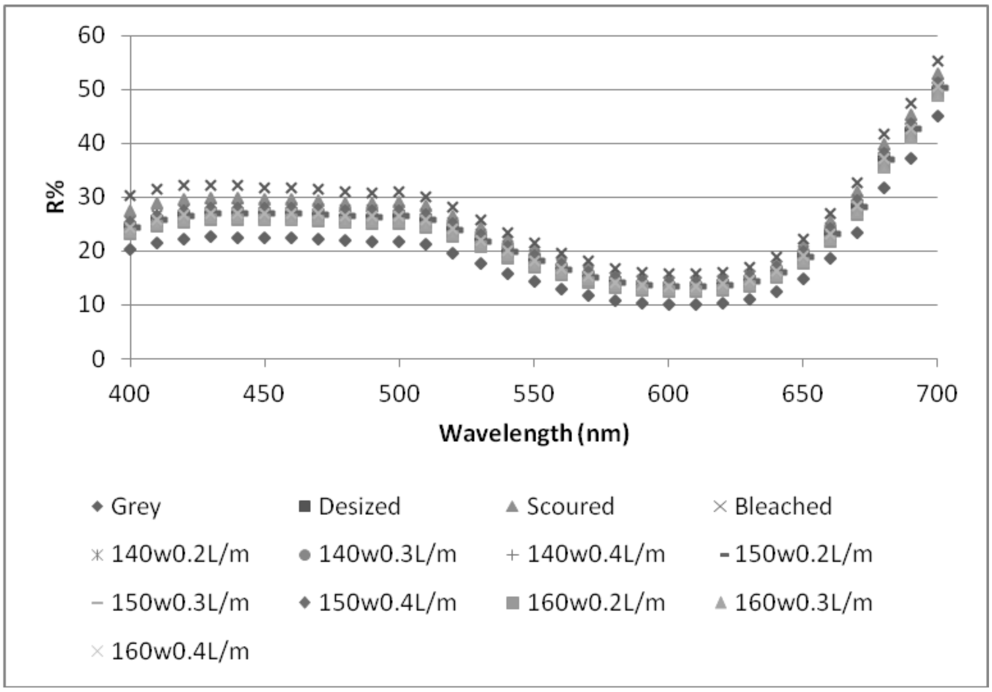


Figure 6.8 Reflectance values of poplin 40s woven fabric (black color)

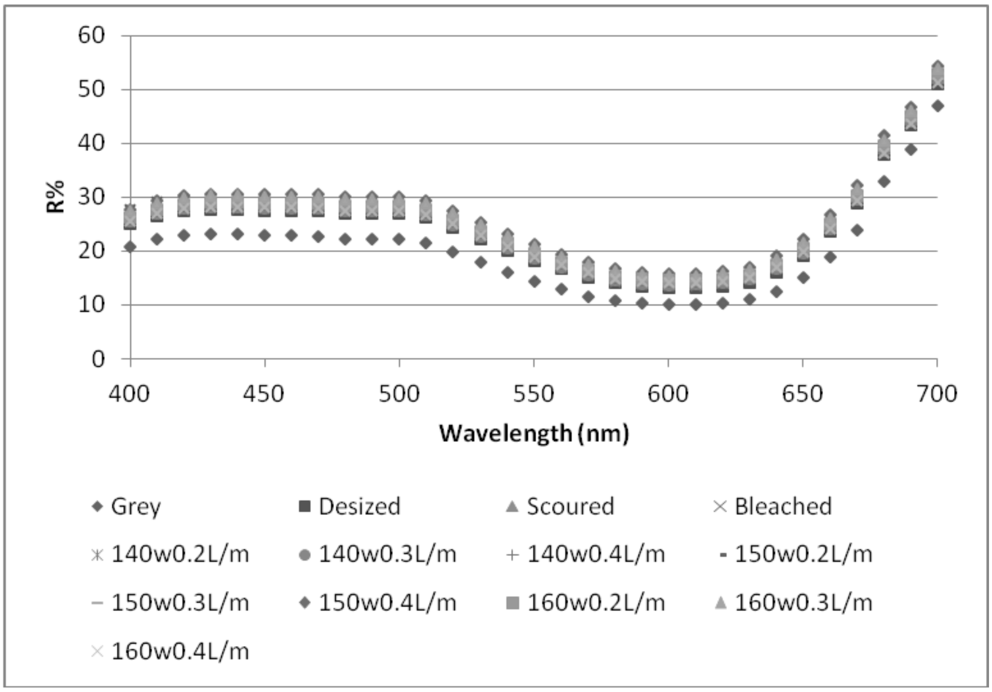


Figure 6.9 Reflectance values of 2/1 twill woven fabric (black color)

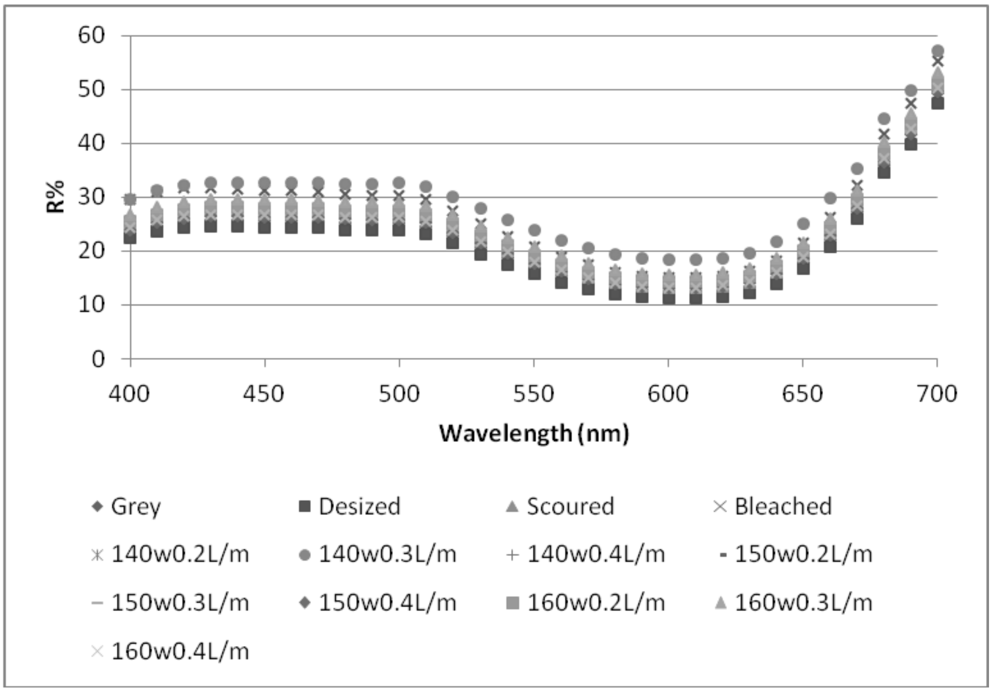


Figure 6.10 Reflectance values of 2/2 twill woven fabric (black color)

6.2.8 K/S sum values (black color)

Table 6.7 K/S sum values of cotton woven fabrics (Black color)

Treatment	Poplin 32s	Poplin 40s	2/1 twill	2/2 twill
Grey	36.80	64.36	65.60	50.82
Desized	36.13	48.37	44.96	55.71
Scoured	35.65	38.34	40.54	45.68
Bleached	31.59	35.89	42.59	37.45
140W0.2L/m	45.39	43.55	43.75	45.96
140W0.3L/m	39.87	48.69	43.54	29.82
140W0.4L/m	42.86	47.90	43.88	43.35
150W0.2L/m	46.35	47.21	41.23	46.00
150W0.3L/m	44.16	47.50	42.45	45.81
150W0.4L/m	35.77	42.06	36.79	44.69
160W0.2L/m	48.82	47.58	42.97	43.85
160W0.3L/m	44.67	48.28	38.15	38.53
160W0.4L/m	46.30	45.60	42.72	44.24

From the reflectance values of the woven fabrics dyed with black color (Figure 6.7 to 6.10), similar shapes of reflectance curves are obtained from the same type of fabrics treated with different plasma parameters, revealing the color shades of the plasma treated fabrics are similar. Among the same type of woven fabric, the plasma treated woven fabrics dyed with black color give more or less the same reflectance values with the enzyme desized fabrics.

The K/S sum values of the black color dyed woven cotton fabrics are shown on Table 6.7. The K/S sum values of the fabrics treated with different plasma parameters are varied. When comparing between different types of woven fabrics, the plasma treated poplin 40s, 2/1 twill and 2/2 twill fabrics both give a lower K/S sum value than the grey fabrics, but the plasma treated poplin 32s fabrics give a higher K/S sum value than the grey fabric. Obtaining a higher K/S sum value than the grey fabric may due to the fabric structure. Poplin 32s fabric has the most balanced structure among the four types of woven fabrics so the plasma species can be more evenly distributed on the fabric surface which may help to facilitate the absorption of dye from the dye bath to fabric surface, thus a darker shade can be obtained.

From the results of K/S sum values, poplin 32s fabric treated with 160W output power and 0.2L/m flow rate; poplin 40s fabric treated with 140W output power and 0.3L/m; 2/1 twill fabric treated with 140W output power and 0.4L/m flow rate; and 2/2 twill fabric treated with 150W output power and 0.2L/m flow rate give the highest K/S sum values among other set of treatment parameters when compare with the same type of fabric. The relationship between different plasma parameters and dyeability is hard to be observed from the reflectance values and the K/S sum values of the black color dyed fabrics.

6.2.9 L*a*b* values (black color)

Table 6.8 CIE color coordinates L*a*b* values of cotton poplin 32s woven fabrics (black color)

Treatment	L*	a*	b*
Grey	54.34	-7.57	-12.74
Desized	54.58	-7.37	-12.58
Scoured	54.79	-7.44	-13.37
Bleached	56.47	-7.21	-14.15
140w0.2L/m	51.23	-7.24	-13.35
140w0.3L/m	53.16	-7.30	-12.96
140w0.4L/m	52.09	-7.34	-13.12
150w0.2L/m	50.91	-7.27	-13.34
150w0.3L/m	51.62	-7.22	-13.35
150w0.4L/m	54.76	-7.27	-12.47
160w0.2L/m	50.13	-7.10	-13.33
160w0.3L/m	51.47	-7.21	-13.06
160w0.4L/m	50.94	-7.15	-13.16

Table 6.9 CIE color coordinates L*a*b* values of cotton poplin 40s woven fabrics (black color)

Treatment	L*	a*	b*
Grey	46.03	-7.19	-14.41
Desized	50.27	-7.44	-13.85
Scoured	53.70	-7.38	-13.65
Bleached	54.63	-7.34	-14.68
140w0.2L/m	51.84	-7.36	-13.45
140w0.3L/m	50.17	-7.30	-13.85
140w0.4L/m	50.43	-7.41	-13.83
150w0.2L/m	50.64	-7.39	-13.75
150w0.3L/m	50.55	-7.32	-13.69
150w0.4L/m	52.36	-7.31	-13.04
160w0.2L/m	50.52	-7.24	-13.58
160w0.3L/m	50.32	-7.27	-13.53
160w0.4L/m	51.14	-7.31	-13.67

Table 6.10 CIE color coordinates L*a*b* values of cotton 2/1 twill woven fabrics (black color)

Treatment	L*	a*	b*
Grey	45.76	-7.39	-15.18
Desized	51.36	-7.56	-14.02
Scoured	52.90	-7.64	-14.53
Bleached	52.17	-7.65	-15.53
140w0.2L/m	51.74	-7.42	-14.03
140w0.3L/m	51.80	-7.37	-14.04
140w0.4L/m	51.70	-7.38	-14.00
150w0.2L/m	52.62	-7.41	-13.79
150w0.3L/m	52.20	-7.40	-13.93
150w0.4L/m	54.29	-7.32	-13.29
160w0.2L/m	52.01	-7.37	-13.93
160w0.3L/m	53.77	-7.36	-13.44
160w0.4L/m	52.11	-7.32	-13.65

Table 6.11 CIE color coordinates L*a*b* values of cotton 2/2 twill woven fabrics (black color)

Treatment	L*	a*	b*
Grey	49.52	-7.34	-13.78
Desized	48.17	-7.47	-14.39
Scoured	51.13	-7.58	-14.62
Bleached	54.02	-7.58	-15.06
140w0.2L/m	51.01	-7.24	-13.44
140w0.3L/m	57.34	-7.11	-11.86
140w0.4L/m	51.88	-7.23	-13.20
150w0.2L/m	50.99	-7.21	-13.41
150w0.3L/m	51.06	-7.22	-13.41
150w0.4L/m	51.45	-7.23	-13.00
160w0.2L/m	51.72	-7.23	-13.27
160w0.3L/m	53.63	-7.22	-12.77
160w0.4L/m	51.58	-7.24	-13.19

The results of the CIE coordinates L*a*b* values of the black dyed woven fabrics are similar with the blue dyed fabrics, which are shown in Table 6.8 to 6.11 according to fabric type. Generally speaking, the L* values of the plasma treated fabrics are increased and even higher than the enzyme desized fabrics. The increase in fabric lightness may due to the removal of the sizing material and protruding fibers. As the atmospheric pressure plasma treatment is a surface etching process, the protruding fiber surface could be removed, and thus smoother fiber surface and higher lightness due to the enhancement of the light reflection from the fiber surface could be obtained. The L* values of the plasma treated poplin 32s fabrics are lower than the grey fabrics, indicating the plasma treated poplin 32s fabrics have darker shade than the grey fabric, which may due to the balanced structure of poplin 32s fabric; and the plasma treated poplin 40s, 2/1 twill and 2/2 twill fabrics both have higher L* values than the grey fabrics, thus lighter shade can be observed from the plasma treated fabrics. The L* values agree with the reflectance values (section 6.2.8) and K/S sum values (section 6.2.9).

The black dyed plasma treated poplin 32s fabrics have a more positive a* value and more negative b* value than the grey and enzyme desized fabrics. The plasma treated poplin 32s fabrics show a redder and bluer fabric color because the yellowness of the grey fabric have been reduced by removing the yellow coloring impurities on fabric surface, which yellowness results can be observed in section 4.2.3. The a* and b* values of the poplin 40s, 2/1 twill and 2/2 twill fabrics are similar with the grey fabrics.

6.2.10 Relative unlevelness index (black color)

Table 6.12RUI of cotton woven fabrics (black color)

Treatment	Poplin 32s	Poplin 40s	2/1 twill	2/2 twill
Grey	0.36	0.36	0.39	0.36
Desized	0.34	0.36	0.38	0.38
Scoured	0.36	0.37	0.40	0.40
Bleached	0.38	0.40	0.43	0.42
140W0.2L/m	0.34	0.36	0.38	0.35
140W0.3L/m	0.34	0.36	0.29	0.33
140W0.4L/m	0.34	0.36	0.38	0.35
150W0.2L/m	0.35	0.36	0.37	0.35
150W0.3L/m	0.35	0.36	0.38	0.35
150W0.4L/m	0.32	0.34	0.36	0.34
160W0.2L/m	0.34	0.35	0.38	0.35
160W0.3L/m	0.34	0.29	0.36	0.32
160W0.4L/m	0.34	0.36	0.36	0.35

From the RUI of the black dyed woven fabrics in Table 6.12, all of grey, conventional treated and plasma treated fabrics have good levelness as their RUI are both in the range 0.2-0.49 with reference to the suggested interpretation of RUI table (see Table 3.14). The black dyed bleached woven fabrics show a poor RUI than the grey fabrics may because of the shrinkage problem which caused by wet chemical treatment. The woven fabric will shrink after going through high temperature wet treatment and the fabric structure will be changed and even destroyed, thus causing unlevel dyeing.

The plasma treated woven fabrics give a similar or even lower RUI than the grey and enzyme desized fabrics, which mean a more uniform dye distribution on the plasma treated fabric surface is observed. Leveling dyeing can be achieved on the plasma treated grey fabric because of the enhancement in hydrophilicity on the fiber surface by oxygen plasmas and removal of protruding fiber by plasma etching process.

6.3 Knitted fabrics

6.3.1 Fabric images (blue color)

The blue dyed knitted fabrics images, in the order of grey, scoured, bleached and plasma treated with 150W output power and 0.4L/m oxygen flow rate, are shown in Figure 6.11 according to the fabric type. By the eye observation under daylight illuminant D65, the plasma treated single jersey and interlock fabrics both show a darker shade than the grey, scoured and bleached fabrics.

Single jersey

(a)Grey (b)Scoured (c)Bleached (d)Plasma treated

Interlock

(a)Grey (b)Scoured (c)Bleached (d)Plasma treated

Figure 6.11 Fabric images of knitted fabrics (blue color)

6.3.2 Reflectance values (blue color)

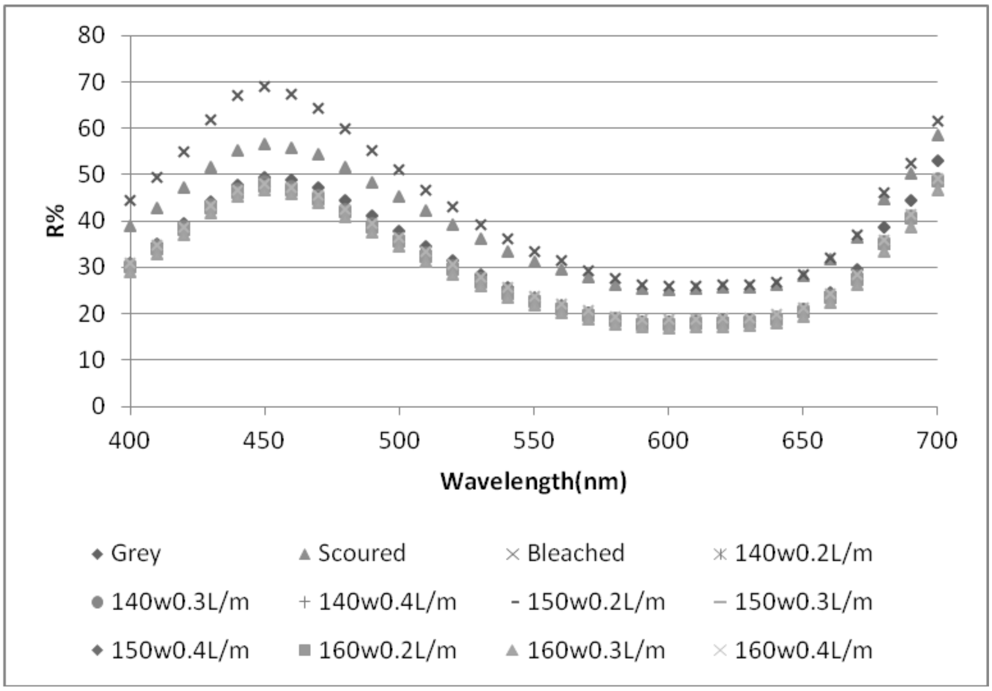


Figure 6.12 Reflectance values of single jersey knitted fabrics (blue color)

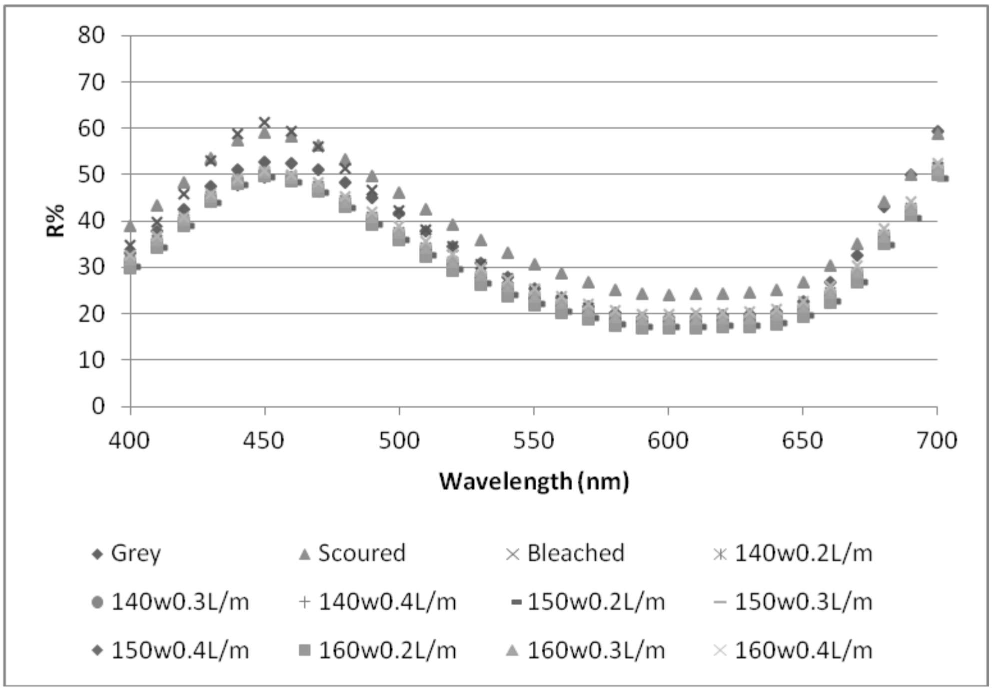


Figure 6.13 Reflectance values of interlock knitted fabrics (blue color)

6.3.3 K/S sum values (blue color)

Table 6.13 K/S sum values of cotton knitted fabrics (blue color)

Treatment	Single jersey	Interlock
Grey	27.66	21.06
Scoured	17.51	18.32
Bleached	15.67	25.90
140W0.2L/m	29.20	31.92
140W0.3L/m	32.16	28.02
140W0.4L/m	29.32	26.15
150W0.2L/m	31.36	32.18
150W0.3L/m	30.16	27.84
150W0.4L/m	29.65	29.85
160W0.2L/m	30.86	28.87
160W0.3L/m	30.74	28.86
160W0.4L/m	30.60	27.71

Figure 6.12 to 6.13 show the reflectance values of the cotton knitted fabrics with blue color dyed. The single jersey and interlock knitted fabrics treated with different plasma parameters give more or less the same shape of reflectance curves among

the same type of fabric, which indicate the shades of the dyed fabrics are similar. Moreover, the reflectance values of all the plasma treated fabrics are lower than the grey, scoured and bleached fabrics, which mean the plasma treated knitted fabrics have a darker shade than the grey, scoured and bleached fabrics.

For the blue dyed single jersey and interlock fabrics, all of the plasma treated fabrics show a higher K/S sum value than the grey, scoured and bleached fabrics. Obtaining a higher K/S sum value not only because of the removal of the hydrophobic impurities by the plasmas, but also may due to the creation of porous surface structure by the plasma etching and the enhancement of the hydrophilicity of the fiber surface. The fiber surface area is increased by the porous surface structure and additional polar groups are induced by the oxygen plasmas, thus the hydrophilicity of the fiber surface can be enhanced. As a result, a faster adsorption of dye from the dyestuff to the fiber and a darker shade can be obtained. The reflectance and K/S sum values of the blue dyed knitted fabrics agree with the fabric colors by eye observation (see section 6.3.1).

From the results of K/S sum values, single jersey treated with 140W output power and 0.3L/m flow rate and interlock fabric treated with 150W output power and 0.2L/m flow rate give the highest K/S sum values among other set of treatment parameters when compare with the same type of fabric.

6.3.4 L*a*b* values (blue color)

Table 6.14 CIE color coordinates L*a*b* values of cotton knitted fabrics (blue color)

Treatment	Single jersey			Interlock		
	L*	a*	b*	L*	a*	b*
Grey	59.21	-4.62	-25.32	63.02	-5.98	-23.72
Scoured	65.29	-4.31	-22.37	65.00	-4.75	-24.82
Bleached	67.27	-4.02	-27.91	61.22	-4.39	-31.29
140W0.2L/m	58.40	-3.46	-25.29	57.32	-3.31	-27.55
140W0.3L/m	57.08	-3.27	-25.87	59.04	-3.51	-25.90
140W0.4L/m	58.32	-3.49	-24.41	59.99	-3.72	-25.21
150W0.2L/m	57.41	-3.29	-25.70	57.22	-3.32	-27.43
150W0.3L/m	57.91	-3.27	-25.27	59.16	-3.54	-26.25
150W0.4L/m	58.18	-3.40	-24.93	58.21	-3.45	-26.43
160W0.2L/m	57.62	-3.29	-25.22	58.65	-3.39	-26.72
160W0.3L/m	57.67	-3.29	-25.34	58.64	-3.32	-26.39
160W0.4L/m	57.74	-3.33	-25.53	59.19	-3.51	-25.95

The CIE coordinates L*a*b* values of the blue dyed knitted fabrics are shown in Table 6.14. The L* values of the single jersey and interlock fabrics treated with different plasma parameters are both lower than the grey, scoured and bleached fabrics, indicating a darker shade is obtained after plasma treatment. The findings agree with the reflectance and K/S sum values showing in section 6.3.2 and 6.3.3 respectively. The a* values of the plasma treated single jersey and interlock fabrics are increased, revaling a redder shade is obtained after plasma treatment. The overall b* values of the single jersey are similar with the grey fabric and the plasma treated interlock fabrics have a more negative b* value than the grey and enzyme desized fabric. The plasma treated interlock fabrics have a bluer shade which may due to the yellowness of the grey fabric is slightly reduced after plasma treatment as showing in section 4.3.2.

6.3.5 Relative unlevelness index (blue color)

Table 6.15 RUI of cotton knitted fabrics (blue color)

Treatment	Single jersey	Interlock
Grey	0.53	0.54
Scoured	0.43	0.52
Bleached	0.61	0.71
140W0.2L/m	0.48	0.54
140W0.3L/m	0.46	0.50
140W0.4L/m	0.44	0.49
150W0.2L/m	0.48	0.54
150W0.3L/m	0.47	0.51
150W0.4L/m	0.46	0.51
160W0.2L/m	0.46	0.53
160W0.3L/m	0.47	0.51
160W0.4L/m	0.48	0.50

For the single jersey and interlock fabrics dyed with blue color, the RUI of the plasma treated fabrics are all better than the grey fabric, suggesting a more levelness dyeing can be achieved after plasma treatment as the hydrophilicity of the fiber surface is enhanced by the oxygen plasmas. The bleached knitted fabrics have the worst RUI may because of the shrinkage problem that caused by several wet chemical treatments and the fabric structure has been affected; and also may due to the presentation of impurities and chemical residuals on the fiber surface, leading to unlevel dyeing.

With reference to the suggested interpretation of RUI table (see Table 3.14), the singer jersey and interlock fabrics have good levelness (0.2-0.49) and poor levelness (0.5-1.0) respectively. The interlock fabrics have poor levelness than the single jersey fabrics may due to the higher thickness value. As the interlock fabric is too thick for the active plasma species to penetrate from the face to back side, leading to poor migration of dye molecules into the fiber during dyeing. The back side of the interlock fabric is unaffected by plasma species can be evidenced from the water drop test results in the previous section 4.3.3. Moreover, the 1% blue dye may be not enough for dyeing the interlock fabric, so poor levelness is obtained.

6.3.6 Fabric images (black color)

The black color dyed knitted fabric images of grey, scoured, bleached and plasma treated with 150W output power and 0.4L/m oxygen flow rate are shown in Figure 6.14 according to fabric type. The plasma treated single jersey and interlock fabrics both show a darker shade than the grey, scoured and bleached fabrics by eye observation under daylight illuminant D65.

Single jersey

(a)Grey (b)Scoured (c)Bleached (d)Plasma treated

Interlock

(a)Grey (b)Scoured (c)Bleached (d)Plasma treated

Figure 6.14 Fabric images of knitted fabrics (black color)

6.3.7 Reflectance values (black color)

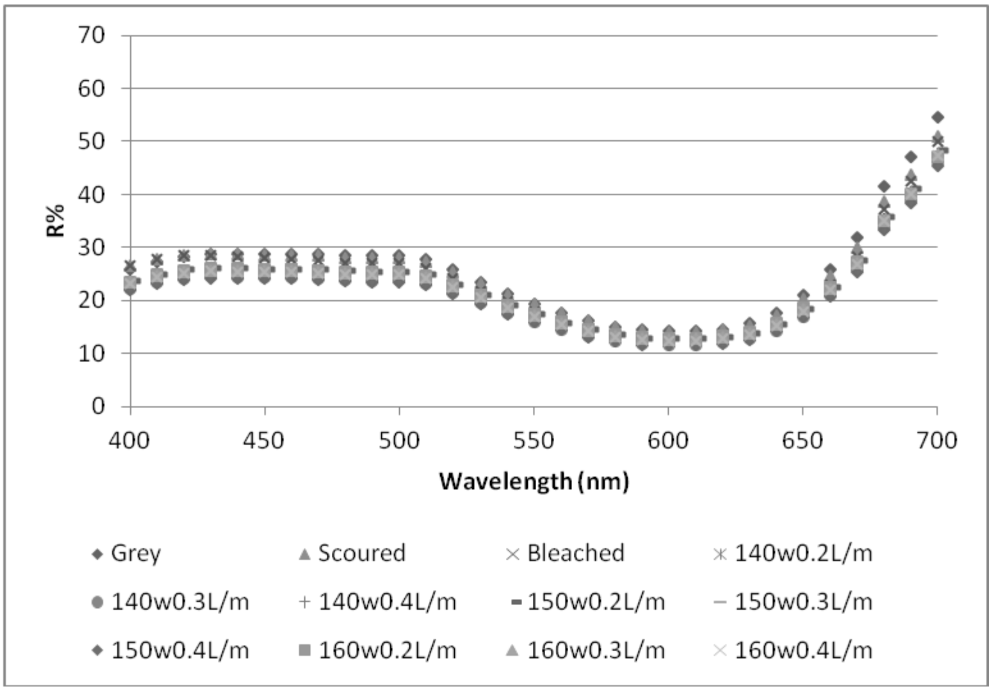


Figure 6.15 Reflectance values of single jersey knitted fabrics (black color)

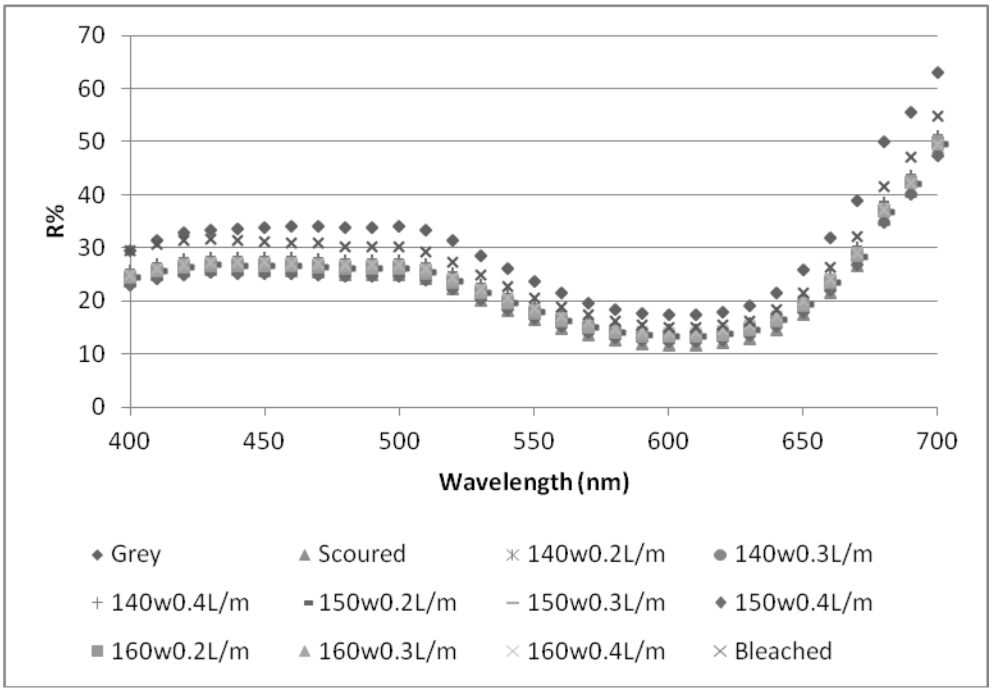


Figure 6.16 Reflectance values of interlock fabrics (black color)

6.3.8 K/S sum values (black color)

Table 6.16 K/S sum values of cotton knitted fabrics (black color)

Treatment	Single jersey	Interlock
Grey	41.59	30.19
Scoured	41.69	33.10
Bleached	46.39	37.05
140W0.2L/m	47.54	44.92
140W0.3L/m	49.38	46.56
140W0.4L/m	48.62	45.06
150W0.2L/m	51.44	45.45
150W0.3L/m	50.58	42.33
150W0.4L/m	55.62	51.98
160W0.2L/m	50.47	49.48
160W0.3L/m	50.43	46.56
160W0.4L/m	47.25	42.67

For single jersey and interlock knitted fabrics dyed with black color, the reflectance curves (Figure 6.15 and 6.16) give a more or less the same shape under different treatments, which mean the colors reflected from the different treated fabrics are similar. The plasma treated fabrics give a lower reflectance values and thus have a darker shade than the grey, scoured and bleached fabrics.

Because of the removal of hydrophobic impurities and introduction of polar groups by oxygen plasmas on the fiber surface, the hydrophilicity and dyeability of the plasma treated knitted fabrics are improved. As a result, the fabrics can be dyed with darker shade due to the faster adsorption of dye from the dyestuff to the fiber, so the K/S sum values of all the black color dyed plasma treated single jersey and interlock fabrics are higher than the grey, scoured and bleached fabrics.

From the results of K/S sum values, single jersey and interlock fabrics treated with 150W output power and 0.4L/m flow rate give the highest K/S sum values among other set of treatment parameters when compare with the same type of fabric.

6.3.9 L*a*b* values (black color)

Table 6.17 CIE color coordinates L*a*b* values of cotton knitted fabrics (black color)

Treatment	Single jersey			Interlock		
	L*	a*	b*	L*	a*	b*
Grey	52.45	-7.57	-13.42	57.19	-8.43	-12.81
Scoured	52.47	-7.52	-13.74	49.37	-7.65	-14.61
Bleached	50.91	-7.60	-15.68	54.10	-7.25	-14.59
140W0.2L/m	50.50	-7.10	-12.87	51.32	-7.09	-12.84
140W0.3L/m	49.91	-7.11	-13.30	50.76	-7.13	-13.42
140W0.4L/m	50.16	-7.13	-13.05	51.26	-7.10	-13.20
150W0.2L/m	49.31	-7.16	-13.44	51.12	-7.10	-13.36
150W0.3L/m	49.57	-7.21	-13.44	52.18	-7.04	-12.96
150W0.4L/m	48.17	-7.17	-13.54	49.15	-7.18	-13.47
160W0.2L/m	49.58	-7.09	-13.30	49.86	-7.12	-13.58
160W0.3L/m	49.61	-7.20	-13.52	50.76	-7.14	-13.39
160W0.4L/m	50.57	-7.09	-13.16	52.07	-7.09	-12.97

From Table 6.17, the L*values of the plasma treated black color dyed single jersey and interlock fabrics are lower than the grey fabrics, thus a darker shade can be obtained. The results agree with the reflectance and K/S sum values shown in the previous section 6.3.7 and 6.3.8 respectively. The colors of the knitted fabrics are slightly redder than the grey fabrics after plasma treatment as they all have an overall higher a* values than the grey fabrics. The b* values of the plasma treated single jersey fabrics are similar with the grey fabrics, and the interlock fabrics have a more negative b* values after plasma treatment, which results are matched with the yellowness values obtained in the previous section 4.3.2. The reduction in b* values reveals the yellowish color of the original grey fabric can be effectively covered by the 1% black dye.

6.3.10 Relative unlevelness index (black color)

Table 6.18 RUI of cotton knitted fabrics (black color)

Treatment	Single jersey	Interlock
Grey	0.39	0.43
Scoured	0.37	0.40
Bleached	0.43	0.41
140W0.2L/m	0.33	0.33
140W0.3L/m	0.34	0.32
140W0.4L/m	0.34	0.35
150W0.2L/m	0.35	0.36
150W0.3L/m	0.35	0.35
150W0.4L/m	0.34	0.35
160W0.2L/m	0.34	0.36
160W0.3L/m	0.35	0.36
160W0.4L/m	0.30	0.34

From Table 6.18, the black dyed plasma treated single jersey and interlock fabrics give similar RUI under different plasma parameters. The RUI of the plasma treated knitted fabrics are satisfactory as both have a better levelness index than the grey, scoured and bleached fabrics, evidencing plasma treatment is helpful in promoting levelness dyeing. The levelness dyeing of the plasma treated woven fabrics is attributed to the introduction of polar groups by oxygen plasmas.

6.4 Conclusion

In this chapter, the woven and knitted fabrics have been dyed with two types of reactive dyes with two dye concentrations. The dyeability of the plasma treated and concentional treated fabrics have been assessed by the reflectance values, K/S sum values and L*a*b* values. The plasma treated woven and knitted fabrics are found to have darker shade than the grey fabrics, no matter for blue dyed or black dyed. Moreover, the dyeing levelness has been reflected by the relative levelness index. All of the dyed woven and knitted fabrics have better RUI than the grey fabrics and/or enzyme desized fabrics. For both of the woven and knitted fabrics, the black dyed fabrics are found to have better RUI than the blue dyed fabrics.

Chapter 7 Conclusion and recommendations

7.1 Conclusion

In the past few decades, many efforts have been put in the investigations for improving the surface properties of textile materials without changing the bulk properties by low temperature plasma. In this study, atmospheric pressure plasma was employed on the cotton woven and knitted grey fabrics to determine the efficiency on removing the sizing materials and/or impurities on the fiber surface. Four kinds of cotton woven fabrics (poplin 32s, poplin 40s, 2/1 twill and 2/2 twill) and two kinds of cotton knitted fabrics (single jersey and interlock) were used for analyzing and comparing. The woven and knitted grey fabrics were treated with oxygen (reactive gas) and helium (carrier gas) gases under atmospheric pressure and different plasma parameters (varied output powers and oxygen flow rates) were applied. Plasma treated grey fabrics were subjected to different evaluation tests, including weight loss measurement, wettability, yellowness values, etc., to determine the effects of plasma treatment on fabric desizing and/or scouring. Moreover, the surface and chemical changes of the plasma treated fabrics were observed by using characterization techniques, such as SEM, FTIR and XPS. Beside those physical and chemical evaluations, dyeing properties of the plasma treated fabrics were also studied through reflectance values, K/S sum values, L*a*b* values and the RUI, so as to know more about how the dyeability changes after plasma treatment. In order to investigate the plasma treatment for cotton fabric preparation, the woven and knitted fabrics were also subjected to the conventional desizing (only for woven fabrics), scouring and bleaching processes, and the conventional treated fabrics were also gone through the same tests with the plasma treated fabrics. The results given by the conventional treated and plasma treated fabrics have been compared and the summary of each test are given in the following sections.

7.1.2 Physical properties

7.1.2.1 Weight loss measurement

The weight loss of the plasma treated starch sized and industrial sized fabrics indicated that plasma treatment played a role on removing the sizing materials. Although the weight loss percentages of the plasma desized fabrics were fewer than the enzyme desized fabrics due to different desizing conditions, the results given by the plasma treated fabrics were comparable with the enzyme desized fabrics. Weight loss was also occurred on the plasma treated knitted fabrics, revealing the hydrophobic impurities on the fiber surface were removed by the plasmas.

The results of washing and scouring of the plasma treated woven and knitted fabrics both showed that plasma treatment could help to reduce the usage of chemicals (chemical desizing process can be skipped) and energy consumption by at least 20% (lower treatment temperature and shorter treatment duration can be applied) in the scouring process. The sizing materials and impurities were being etched and broken into small fragments by plasmas, which can be hydrolyzed and dissolved in further wet process more easily, helping to improve the wet process efficiency.

7.1.2.2 Yellowness values

The yellowness values of the poplin 32s and poplin 40s woven fabrics were found to be decreased after plasma treatment and the colors of 2/1 twill and 2/2 twill fabrics only turned to be slightly yellower after plasma treatment; the single jersey knitted fabrics showed a slightly yellower surface color after plasma treatment and all of the yellowness values of the plasma treated interlock fabrics were reduced. Those results of woven and knitted fabrics indicated that plasma treatment not only did not lead to serious degradation on fabric color, but also helped to improve the yellowness values on the poplin woven fabrics and interlock knitted fabrics.

7.1.2.3 Wettability

From the results of the wettability tests of woven and knitted fabrics, both showed that the wettability of those fabrics was greatly enhanced after plasma treatment when compared with the fabrics treated with conventional desizing and scouring processes.

For the woven fabrics, better wetting results were obtained by the poplin fabrics than the twill fabrics in the drop test, which was due to poplin fabrics having smaller inter-yarn spaces and more compact structure. From the wicking results, the warp yarns of those woven fabrics were found to have better results than the weft yarns because of fewer yarn twist and closer packing of yarns. Among different output powers, 160W output power gave a more significant result in the wetting improvement of woven fabrics than 140W and 150W output powers. The optimum gas flow rate was hard to be determined. Different optimum plasma parameters were found under different fabric structures, so addition investigations are needed for understanding the relation between those plasma parameters for the specify fabric structure.

The wettability of the face and back sides of the single jersey fabrics were both greatly enhanced after plasma treatment. However, the interlock fabrics only showed wetting enhancement on the fabric face side as interlock fabric had a high thickness value, fabric back side cannot be affected by the plasmas. Among different output powers, 140W was found to be the optimum power of the single jersey and interlock knitted fabrics.

7.1.3 Surface and chemical characterizations

From the SEM images of the plasma treated woven and knitted fabrics, both showed that the sizes and/or impurities were apparently removed and broken into fragments, and also microcracks were produced on the fiber surface. The changes on the fiber surface result in the wettability improvement. The plasma desizing was comparable with the enzyme desizing because the surface characteristics of the plasma desized fabrics and enzyme desized fabrics were similar. The removal of sizing materials and introduction of polar groups by oxygen plasmas were evidenced by the FTIR-ATR and XPS results.

7.1.4 Dyeing properties

For the woven fabrics, the blue dyed fabrics showed a similar reflectance values and K/S sum values with the enzyme desized fabrics, except the fabrics treated with

160W output power. Thermal oxidation effect may be caused by plasmas under higher output power and the 1% blue dye may not enough for covering the yellowish shade, thus paler shade was obtained.

The black dyed plasma treated woven, blue dyed knitted fabrics and black dyed knitted fabrics both gave a better result than the plasma treated woven fabrics dyed with blue color. Higher K/S sum values than the scoured and bleached fabrics were given by most of the black dyed plasma treated woven and knitted fabrics, indicating a deeper shade can be obtained after plasma treatment, thus the same color can be achieved with less amount of dye concentration after plasma treatment.

The RUI of both woven and knitted fabrics dyed with blue and black colors showed that plasma treatment is helpful in facilitating levelness dyeing as the RUI of all the plasma treated fabrics were lower than the grey fabrics.

7.2 Recommendations

The objectives of this research study have been achieved. From the present works, the efficiency of plasma desizing on different types of woven grey fabrics and the influences of plasma treatment on different types of knitted grey fabrics have been studied and compared with the results of conventional wet treatment. However, further work is necessary for the improvement and development of more effective techniques for industrial application. Several recommendations for future work are suggested as follows:

1. Vary plasma parameters

   (a) Nozzle to substrate distance

   The nozzle to substrate distances in this study were fixed at 2mm for woven fabrics and 3mm for knitted fabrics. As different types of woven and knitted fabrics have different fabric structures and thickness values, thus different nozzle to subject distances should be applied on different types of fabrics for finding out the optimum combination of plasma parameters for each type of fabric more easily and precisely.

   (b) Treatment duration

   Treatment time is defined as the duration for a substrate being exposed to plasma afterglow. The treatment duration is one of the important factors to affect the concentration of plasma active species reacted with the fabric surface, as time is required for accumulating sufficient plasma active species on fabric surface. In the present work, the treatment time for woven and knitted fabrics was fixed at 1mm/s. A longer treatment time can be employed such as 0.5mm/s and 0.3mm/s for further analyzing the relationship between the concentration of plasma active species and plasma desizing efficiency.

2. Analysis on cost, energy and/or water consumption

   Apart from determine the optimum plasma parameters for each type of fabric, the consumption of cost, energy and/or water in the plasma pre-treatment is needed to be evaluated in real world application.

3. Application of other instrumental analysis methods

   SEM has been used for observing the surface morphological changes of the treated fabric in the present study. In order to have an in-depth analysis on the topographical changes on the treated fabric, atomic force microscopy (AFM) can be used for studying the fiber surface topographically in nanometers scale by imaging and manipulating the atoms and structures on the fabric surface, thus the penetration power of plasmas can also be evaluated.

4. Future study on fabric physical property changes

   Although plasma treatment would not affect fabric bulk properties, some physical properties may be altered during and/after plasma treated. Future investigations on fabric physical properties can be conducted, such as fabric hand feel value, dimensional stability, strength and elongation.

5. Further study in dyeing

   Two types of reactive dyes with the same dye concentration, i.e. 1%, were used for dyeing the woven and knitted fabrics in present study. A higher dye concentration can be used for further analyze the dyeability of the plasma treated fabrics, especially for the blue color dye. Moreover, from the results of present study, darker shade was found on the plasma treated grey fabrics, implying a lower dyeing temperature could be employed after plasma pretreatment. Different dyeing temperatures can be applied to observe the possibility in reducing energy consumption during dyeing process. Also, different types and colors of reactive dyes and other dyes can also be applied. In addition, the color fastness of plasma treated fabrics is important in the real world application. Evaluation tests, such as color fastness to light, to rubbing and to washing, can be operated.

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