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SURFACE MODIFICATION OF FABRICS BY RF PLASMA FOR INK ABSORPTION

Miss Porntapin Pransilp

A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	SURFACE MODIFICATION OF FABRICS BY RF PLASMA FOR INK ABSORPTION
By	Miss Porntapin Pransilp
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Assistant Professor Boonchoat Paosawatyanyong, Ph.D.
Thesis Co-advisor	Professor Suda Kiatkamjornwong, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

………………………………………….. Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

………………………………………….. Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

…………………………………….……. Thesis Advisor
(Assistant Professor Boonchoat Paosawatyanyong, Ph.D.)

………………………………………….. Thesis Co-advisor
(Professor Suda Kiatkamjornwong, Ph.D.)

………………………………………….. Examiner
(Assistant Professor Varawut Tangpasuthadol, Ph.D.)

………………………………………….. External Examiner
(Associate Professor Khemchai Hemachandra, Ph.D.)

พรเทพิน ปรานศิลป์ : การดัดแปรผิวของผ้าด้วยพลาสมาอาร์เอฟสำหรับการดูดซึมหมึกพิมพ์. (SURFACE MODIFICATION OF FABRICS BY RF PLASMA FOR INK ABSORPTION) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.บุญโชติ เผ่าสวัสดิ์ยรรยง, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ. ดร.สุดา เกียรติกำจรวงศ์, 119 หน้า.

งานวิจัยนี้ได้ศึกษาการดัดแปรลักษณะเชิงผิวด้านกายภาพและสมบัติทางเคมีของผ้าฝ้ายและผ้าพอลิเอสเทอร์ด้วยพลาสมา 3 ชนิด ได้แก่ พลาสมาของออกซิเจน ไนโตรเจน และซัลเฟอร์เฮกซะฟลูออไรด์ เพื่อปรับปรุงสมบัติการดูดซึมหมึกพิมพ์ฐานน้ำประเภทสารสี ศึกษาอิทธิพลของตัวแปรของพลาสมาแต่ละชนิด ได้แก่ กำลังไฟฟ้า ระยะเวลาดัดแปร และความดันระหว่างการดัดแปรด้วยพลาสมาแต่ละชนิดที่มีต่อสมบัติเชิงผิวด้านกายภาพและเคมีของผ้า ศึกษาหมู่ฟังก์ชันโดยใช้เทคนิคของ X-ray photoelectron spectroscopy (XPS) และ scanning electron microscopy ใช้เทคนิค attenuated total reflection Fourier transform infrared spectroscopy ศึกษาหมู่ฟังก์ชันของสารสี และเทคนิค color spectroscopy ศึกษาความเข้มของสีพิมพ์ที่ติดอยู่บนผ้าพิมพ์ ผลทดสอบแสดงให้เห็นว่า ผ้ามีสมบัติชอบน้ำและพลังงานผิวมากขึ้นหลังจากปรับปรุงผิวด้วยออกซิเจนพลาสมา และไนโตรเจนพลาสมา ผลจาก XPS แสดงหมู่ฟังก์ชันของ C-O, O-C-O/C=O และ O-C=O บนผิวมากขึ้นเมื่อดัดแปรด้วยพลาสมาออกซิเจน และเกิด C-N, O=C-NH ขึ้นด้วยพลาสมาไนโตรเจน พลาสมาออกซิเจนทำให้ผ้ามีสมบัติชอบน้ำมากที่สุดซึ่งส่งผลให้ผ้าสามารถดูดซึมหมึกพิมพ์ฐานน้ำได้มากขึ้น และค่า K/S เพิ่มขึ้นเมื่อเปรียบเทียบกับผ้าที่ไม่ได้รับการดัดแปรผิวด้วยพลาสมา ผ้าที่ผ่านการดัดแปรผิวด้วยพลาสมาซัลเฟอร์เฮกซะฟลูออไรด์จะไม่ชอบน้ำจึงทำให้ผ้าดูดซึมหมึกพิมพ์ฐานน้ำได้น้อย ความขรุขระที่เกิดจากการกัดผิวของพลาสมา ทำให้ผิวผ้ามีพื้นที่ในการรับหมึกได้มากขึ้นเป็นผลให้การติดสีเพิ่มขึ้นด้วย ผ้าฝ้ายแสดงการติดสีพิมพ์และแกมุตสีกว้างขึ้นเมื่อดัดแปรผิวผ้าด้วยพลาสมาออกซิเจนโดยเทียบกับผลการดัดแปรผิวผ้าด้วยพลาสมาไนโตรเจน ส่วนผ้าพอลิเอสเทอร์แสดงการติดสีพิมพ์และมีความกว้างของแกมุตสีที่ดีเมื่อดัดแปรผิวผ้าด้วยพลาสมาไนโตรเจนเมื่อเทียบกับการดัดแปรผิวผ้าด้วยพลาสมาออกซิเจน

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต
ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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PORNTAPIN PRANSILP: SURFACE MODIFICATION OF FABRICS BY RF PLASMA FOR INK ABSORPTION. ADVISOR: ASST. PROF. BOONCHOAT PAOSAWATYANYONG, Ph.D., CO-ADVISOR: PROF. SUDA KIATKAMJORNWONG, Ph.D., 119 pp.

The physical and chemical properties of cotton and polyester fabrics were modified by three types of gas plasma pretreatment to improve ink absorption of pigmented water-based inks. Oxygen (O_2), nitrogen (N_2), and sulfur hexafluoride (SF_6) gas plasmas were used in this research. Effects of each gas plasma parameter, namely, power, exposure time, and gas pressure during exposure were investigated on physical and chemical pr1operties of the treated fabrics. X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy were used to identify functional groups on the fabrics. Attenuated total reflection Fourier transform infrared spectroscopy was used to study the functional groups of the pigments. Color spectroscopic technique was used to investigate color ink strength absorbed on the printed fabrics. The results indicated that O_2 plasma and N_2 plasma increased the fabric hydrophilicity and surface energy with the increases of C-O, C=O, and O-C=O groups on the fabrics after the treatment by O_2 plasma. C-N and O=C-NH_2 groups were given by the N_2 plasma. The increased hydrophilicity of the fabric by O_2 plasma induced greater water-based ink absorption than by N_2 plasma. The K/S values were increased as well when comparing with those of the untreated fabrics. The SF_6 plasma-treated fabrics were hydrophobic which caused less ink absorption. The fabric surface roughness, caused by plasma etching increased fabric surface areas to capture more ink and thus increased more ink adhesion. The cotton fabrics exhibited higher ink adhesion and wider color gamut after the O_2 plasma treatment comparing with those from the N_2 plasma. More ink adhesion and wider color gamut were found on printed polyester fabrics with N_2 plasma treatment than the O_2 plasma treatment did.

Field of study : Petrochemistry and Polymer Science Student's Signature ....
Academic Year : 2011 Advisor's Signature ....
Co-advisor's Signature ....

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CHAPTER I

INTRODUCTION

1.1 Statement of the purpose

Cotton and poly(ethylene terephthalate) (PET) fabrics are popular textile fabrics in the applications such as clothing, bed lining, furniture covering and advertising [Shishoo, 2008]. The advantages of polyester fabric are high strength, abrasion resistance, and softy appearance. However, the eye-catching of fabric is very important as the selling point of the final product. Hence, fabrics usually pass color application to improve aesthetic appearance and values. Textile printing is one of color applications in the form of a design or pattern on textile substrate.

In the past decade, ink-jet printing has interested many designers because it has many advantages which are excellent printed pattern quality, considerably little pollution, low cost, simple process, and especially fast response to cloth fashion or application [Ujiie, 2006; Wang and Wang, 2010; Zhang and Fang, 2009]. Generally, the sharpness, color appearance and other properties of ink-jet printed images are very important roles in showing the selling point of product. Thus, the pretreatment of fabric is required in textile ink-jet printing to improve printing qualities. Conventional pretreatment is a chemical process such as sizing process with thickener. This technique usually involved toxic chemical substance and take long time [Fang and Zhang, 2009; Ujiie, 2006].

Recently, plasma techniques have been used in textile research and industry for surface modification of fabric materials. Compared with conventional techniques, plasma treatment has many advantages. Plasma treatment can modify the outermost layer of substrate, while the bulk properties will be kept. Furthermore, plasma technique does not generate waste water, hence this process is environmentally friendly process. The plasma interactions with the substrate are etching, grafting, cross-linking, deposition, fictionalization and sterilization [Hwang, 2004; Sparavigna, 2003]. New functional groups can be produced by plasma species. The rough surface is another parameter which can occur. The wettability of fabric can be changed by plasma process. Therefore, plasma treatment is an alternative method that could replace conventional method [Shishoo, 2008; McCord et al., 2002; Wang and Wang, 2010].

In this research, we use plasma to modify the surface of textile material to enhance the absorption of water-based inks, providing intense color appearance. In the first step, textile fabrics were surface modified by RF plasma. In the second step, the wettability and surface energy of fabric would be investigated. Then, the surface property such as morphology was analyzed. The surface chemical and functional groups were carried out. In the third step, the samples were printed with water-based ink-jet pigmented inks. After that, the ink absorption ability, color strength (K/S value) and color gamut of sample fabric were studied.

1.2 Research objectives

The objectives of the research are as follows:

1.2.1 To modify the printing color performance of fabric by plasma process.

1.2.2 To study the surface modification of fabric on physical and chemical quality of fabric by using plasma.

1.2 Scope of the investigation research

The detail of the experiment of this work was carried out as follows:

1.3.1 Literatures survey for related research work of the plasma treatment and ink-jet printing fabric.

1.3.2 Fabrics treating with various gases and under different conditions.

1.3.3 The wettability of fabrics was analyzed by contact angle and surface energy measurement.

1.3.3 Fabrics characterizing by various techniques such as SEM, AFM and XPS to investigate the morphology and functional groups.

1.3.4 Fabrics printing with ink-jet water-base inks and determination of color value of printed samples.

1.3.5 Analysis of color properties of printed fabric.

1.3.6 Discussion of the results and summary.

CHAPTER II

THECRETICAL BACKGROUD

2.1 Plasma

Plasma is the forth state of matter. A commonly accepted definition of plasma is a partially ionized gas composed of highly excited atomic, molecular, ionic and radical species, as well as photons and electrons [Goldston and Rutherford, 2003]. The plasma may be classified as hot and cold plasma. Hot or thermal plasma are characterized by a condition of thermal equilibrium between all the different species contained in the gas. In the thermal plasma, temperatures can reach several thousand degrees. Hence, thermal plasma destroys nature properties of materials Contrarily, cold or non-thermal plasma is produced at room temperature or just above room temperature. In cold plasma, electron acquires higher energies than ions and molecules. Their energies range from sub to few electron volts. Cold plasma is suitable for textile processing without excessive heat which can cause substrate degradation [Shishoo, 2008; Kamlangkla, 2010].

2.1.1 Different types of cold plasma

Different types of cold plasma include dielectric barrier discharge, corona discharge, glow discharge and atmospheric pressure plasma jet. Dielectric barrier discharge is an atmospheric-pressure plasma source. Pulsed higher voltage is applied between electrodes that one or both of which is covered by a dielectric layer. The purpose of the dielectric layer is to terminate rapidly the arcs that form in the region between electrodes. Corona discharge is obtained at atmospheric pressure. Low frequency, D.C., or pulsed high voltage between two electrodes of very different sizes could be applied. The corona consists of a series of rapid, non-uniform, non-arcing discharges. Plasma density drops rapidly with increasing distance from the electrodes. In case of glow discharge, it is obtained at low pressure, typically less than 10 mbar. The plasma is generated by antenna, fed with electromagnetic fields at frequencies of

40 kHz or 13.56 MHz or microwave (2.45 GHz). Glow discharge can be generated using wide range of plasma sources which are DC plasma (direct current discharge), radio frequency (RF) discharge and microwave (MW) discharge, depending on the application. Atmospheric pressure plasma jet (APPJ) which is a jet at atmospheric pressure while glow discharge plasma is produced in continuously flowing gases. However, cold plasma or low temperature, is one of the earliest applications on plasma treatment of fabric [Shishoo, 2008; Mather and Wardman, 2010].

2.1.2 Interaction of cold plasma and textile surface

- **Cleaning or etching**

For cleaning process, inert gas, N_2 or O_2 plasma is typically used. The bombardment of the substrate with the plasma species causes the breakdown of the covalent bond. The surface contaminants as polymer undergo abstraction of hydrogen with free radical formation and repetitive chain scission under the influence of free radicals, ions and electron of the plasma (Figure 2.1). Detachments of low molecular weight species (ablation) take places. Contaminant or even thin layers of the substrate are removed producing clean surfaces, modification in the surface area. The seven processes of etching reaction can be concluded in steps [Verdonck, 1998] as follows:

1) Formation of the reactive particles
2) Arrival of the reactive particles at the surface to be etched
3) Adsorption of the reactive particles at the surface
4) Chemisorption of the reactive particles at the surface, i.e. a chemical bond is formed
5) Formation of the product molecules
6) Desorption of the product molecules
7) Removal of the product molecules from the reactor.

- Activation

Interaction with plasma may induce the formation of active sites on the polymer surface (radicals or other active groups, such as hydroxyl, carboxyl, carbonyl, amine groups) which can give rise to chemical reactions. Figures 2.1 and 2.2 shows that the surface of polyethylene consisting of carbon and hydrogen atoms was treated with plasma, and the surface may be activated and anchored on its functional groups. For examples, the advantage of activation plasma process is to provide enhanced adhesive strength and permanency and a great increase in the production of functional fabric [Sparavigna, 2003].

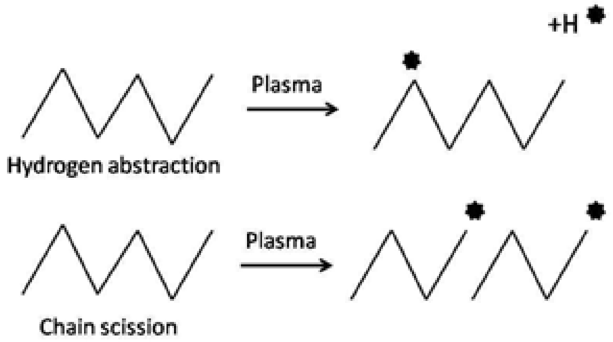


Figure 2.1 Plasma induced hydrogen abstraction or chain scission on a polymer chain [Sparavigna, 2003]

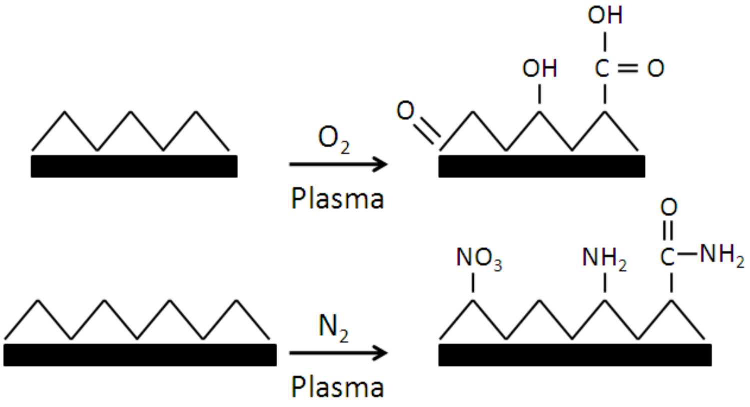


Figure 2.2 Plasma induced functional groups in the presence of a particular gas [Sparavigna, 2003]

- **Grafting**

The radical species present in the plasma may be directly grafted onto the polymer surface or open ways to introduce special functionalities with extremely diversified reactivities. In addition, activated species created active sites on the substrate which could be used to initiate copolymerization reaction with different monomers.

- **Polymerization**

This reaction occurs by using a specific molecule through a process known as plasma enhanced chemical vapor deposition. These specific such as C_2F_4, C_3F_6 molecules, activated by the plasma, may react with themselves forming a polymer chain attached directly on the surface of the substrate. Depending on the different experimental conditions, chemical, permeation, adhesion and other properties of the starting material can be modified.

As a consequence of the very complex cold plasma, a multiplicity of very different phenomena can occur depending on the nature of the gas and the operating condition, such as, pressure of the system, discharge power, etc. [Shishoo, 2007].

Sun and Stylios [2006] have studied the low temperature plasma that modified on wool and cotton fabrics. The process was performed by O_2 plasma and C_2F_6 plasma. O_2 plasma can produce etching, ablation effect and polar groups on the treated surface. C_2F_6 plasma introduces polymer-like product deposit on the surface. It can call C_2F_6 plasma that plasma polymerization. The SEM results indicated that fabric treated with C_2F_6 plasma had smooth surface from the deposited plasma polymer, whereas the specimen of fabrics treated by O_2 plasma became rougher because of bombardment of O_2 species. For the wettability changed, the research reported that O_2 plasma improved surface free energy of fabric surface because plasma produced oxygen-containing functional groups on surface.

2.2 Ink-jet Printing

Ink-jet printing for textile fabrics is an emerging technology that presents both opportunities and challenges. Ink-jet is a technology that enables the delivery of liquid ink to a material whereby only the ink drops make contact with the material. It is therefore a nonimpact printing method by nature. Ink-jet has three basic components, all of which need to work well in order to produce an acceptable output. These three components are the print head, the ink, and the printing substrate.

Ink-jet technologies are typically classified into two classes which are continuous ink-jet (CIJ) and drop-on-demand ink-jet (DOD). Continuous ink-jet, ink is acquired through nozzles at a constant speed by applying a constant pressure. The jet of ink is naturally unstable and breaks up into droplets shortly after leaving the nozzle. The drops are left to go to the material or deflected to a gutter for recirculation depending on the image being printed. The deflection is usually achieved by electrically charging the drops and applying an electric field to control the trajectory. The name continuous originates in the fact that drops are ejected at all times.

In a drop-on-demand ink-jet, drops are ejected only when needed to form the images. The two main drop ejector mechanisms used to generate drops are piezoelectric ink-jet and thermal ink-jet. In a piezoelectric ink-jet, the volume of an ink chamber inside the nozzle is quickly reduced by means of piezoelectric actuator, which squeezes the ink droplet out of the nozzle. For the thermal ink-jet, an electrical heater located inside each nozzle is used to raise the temperature of the ink to the point of bubble nucleation. The explosive expansion of the vapor bubble propels the ink outside the nozzle [Ujiie, 2006].

2.3 Ink

Ink for ink-jet printing are developed from the same colorants used in traditional dyeing and printing, however, dyes and pigments that are used in ink-jet inks require high purity which submicron particle size and high tinctorial strength are required for print head operation and print quality. In addition, the inks chemical characteristic and physical must be suitable with the fiber chemistry. In printing, four ink systems are usually used.

2.3.1 Ink system

- **Reactive dyes**

Reactive dyes are widely used for cellulose fabric where they can produce bright shade with good fastness for washing and light. Under alkaline condition, the dyes can form covalent bonds with fiber. Wool, nylon and silk may also be printed with the reactive dye.

Reactive dyes in a liquid form are not suitable for ink-jet printing because the commercial dye contains quite high levels of salt and this can cause corrosion of jet nozzles. Even with reduced salt concentration, dye solubility in the reactive dye inks can be a problem for ink nozzles.

- **Acid dyes**

Acid dye is water-soluble anionic dyes which are the common choice for printing wool, silk and nylon. The attraction of fiber and acid dye is the positive charges of dye and the negative charges of fiber. The shades are often deeper and brighter than those of the reactive dyes.

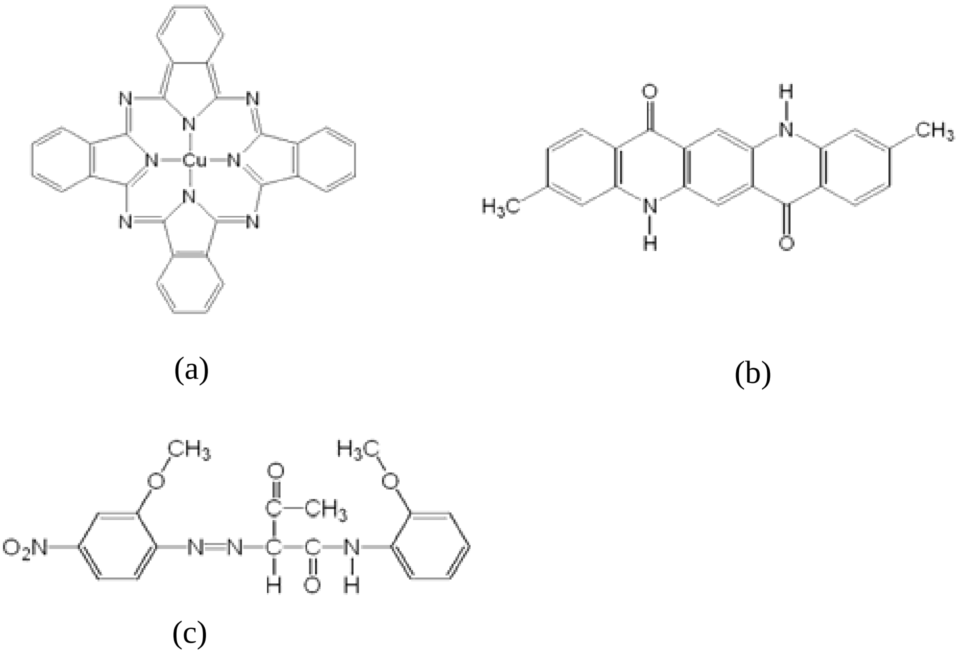
- **Disperse dyes**

Disperse dyes have limited water-solubility. These dyes are applied to synthetic-fiber textile such as polyester fiber.

- **Pigment dyes**

Pigments are insoluble in water or any solvents and are applied to textiles as finely divided dispersions. They are adhered to their outer surface by means of a polymeric, self-cross-linking binder. When the binder is also included in the ink, the risk of blockages can increase. Solvent-based inks have been in used in the graphics industry for some time. The pigments should have good color strength, good light fastness, stability towards chemical attack, fine particle size and dispersibility in normal ink vehicles [Ujiie, 2006].

Typical pigments commonly used in ink-jet ink are carbon black, copper phthalocyanine, dimethyl quinacridone and monazo for black ink, cyan ink, magenta ink and yellow ink, respectively [Lichtenberger, 2004; Momin, 2008; Cabot, 2012]. The structures of three pigments usually used in industry, C.I. pigment blue 15 (copper phthalocyanine), C.I. pigment red 122 (dimethyl quinacridone) and C.I. pigment yellow 74 (monoazo) are displayed in Figures 2.3 (a) – (c).



(a) (b)

(c)

Figure 2.3 Typical pigments used for ink-jet printing; (a) C.I. pigment blue 15 (copper phthalocyanine), (b) C.I. pigment red 122 (dimethyl quinacridone) and (d)C.I. pigment yellow 74 (monoazo)

2.3.2 Types of pigment [Thompson, 1998].

- **Carbon black**

Carbon blacks are basically soot or elemental carbon and are available in several forms. Carbon blacks have two types, furnace black and channel black. Furnace blacks are produced by burning either oil or natural gas in a furnace with a limit supply of O_2 to prevent the carbon particles combusting fully to carbon dioxide. The particle size of furnace black is about 30-150 µm which are collected electrostatically. Channel blacks are also made from natural gas but the particles are collected on moving iron channel. In addition, their particle sizes are smaller than furnace black that is about 20-30 µm. Channel black produces the best quality, long flowing black. Basically, carbon black is valuable due to good color strength and high resistance to light, heat, moisture and chemicals.

- **Inorganic pigments**

Dirty yellow to reddish brown of hue ranging are obtained from complex mixtures of hydrated ferric oxide and silicates. The bronze blue is also inorganic pigment that is based on ferric ferrocyanide. In general, inorganic pigments are very hard and cause wearing of plate surfaces. They are often difficult to grind and may have poor working qualities. The advantage is that they are thick, light, chemical resistant and cheap.

- **Organic pigments**

Organic pigments are the major source of industrial colorants, based on benzene, toluene, naphthalene and anthracence compounds. Typical classes include the azo dyes and pigments giving the hansa yellow, benzidene yellows, permanent reds, lithol rubines and lake red C. The phthalocyanines give a range of blue to green pigments including that are used to formulate the cyan process ink.

- **Vehicles**

The vehicle is a liquid for pigment to disperse in order to give it the mobility necessary to transport it through the printing press and onto the substrate. A vehicle also has the role of binding the pigment particles together and to the substrate as well as imparting gloss to the finished ink film. The vehicle can be a simple solvent into which dissolved a suitable binder. The binder is a resin and is the nonvolatile part of the vehicle that solidifies and holds the pigment particles in a dried film. The solvent, which imparts mobility to the vehicle, is only required until the ink film is formed after which it must dissipate.

Table 2.1 A typical press-ready ink composition [Thompson, 1998]

Component	Solvent-based ink (%)	Water-based ink (%)
Solvent/water	70	60
Resin	15	15
Pigment	10	20
Additives	5	5

A water-based ink must contain at least 85% water in its volatile component in order to quantify as a non solvent-based ink. It typically contains 5% or more of alcohol to improve resin solvency and substrate wetting [Thompson, 1998].

2.3.3 Ink penetration and drying model

The ideal model of ink-jet ink penetrates into media and dry on surface can be explained as follow:

- The stable pigment ink jets from ink-jet head.
- The ink hits on the media, then wets on the media and finally penetrates into the media.

For the ink penetration into media, the non-colored ink vehicle which is resin or binder, penetrates into the material more than other component. The pigment will stratify with some penetration into media and spreads on the media surface. Then, once stratified and dried the pigment and non-volatile ink components to form a cohesive network with each other and adhesive bond with the media.

The schematic of ink penetration and drying is shown in Figure 2.4. The droplet of ink jets from ink-jet head, hits and then wets on the material, which occur for short time (msec). After printing process, ink will occur the spreading on surface, absorption into material and evaporation of additive for msec to sec. Ink penetration process, is using time for sec to min and dry process for min to hours [Kowalski, 2001].

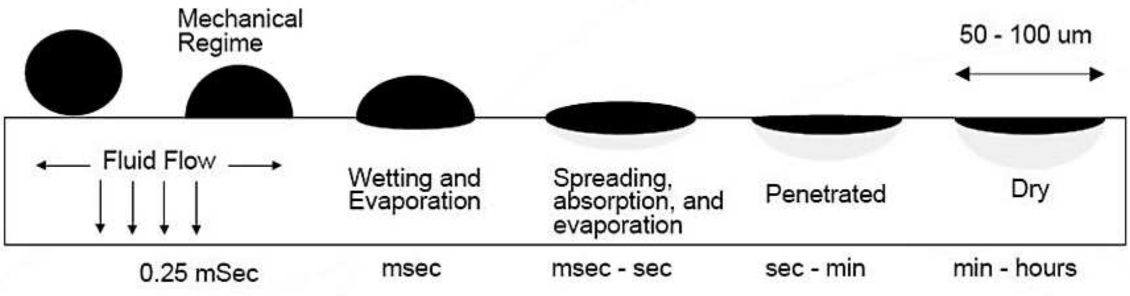


Figure 2.4 Schematic diagram of ink penetration and drying [Kowalski, 2001]

However, if the material has high the wettability, ink may penetrate and spread on the surface. When ink is absorbed (more penetration) into material more than spreading (x-axis > y-axis), the sharpness image will be obtained. On the other hand, if the surface poorly absorb ink (less or slow penetrate) into material, ink will spread (x-axis <y-axis) on the surface. This is resulting to blur image.

2.4 Structure and composition of polyester fabric

Polyester fiber is filament, which is long-chain synthetic polymer, composed of at least 85% by weight of an ester [Lowan and Jungerman, 1980]. Polyester as a specific material most commonly referred to poly(ethylene terepthalate) or PET. Polyester is formed by the polycondensation of ethylene glycol and terepthalate acid, a petroleum product. The equation of polycondensation and the structure of polyester are shown in Figure 2.5.

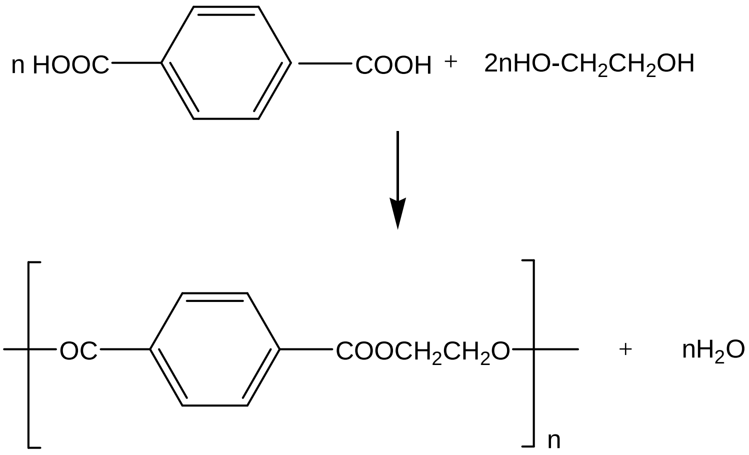


Figure 2.5 Polycondensation and the structure of polyester

For the fiber processing, polyesters are melt extruded. Extrusion is carried out at temperature above the melt temperature of polymer. Thus, poly(ethylene terephthalate) filaments are extruded at 250-260 °C because PET has a T_m of 270 °C and T_g at 270 °C [Odian, 2004]. The spinneret holes in the extruder are generally 0.2-

0.4 mm in the cross-section direction. Extrusion velocity varies according to the strength of yarn filament required. For low-oriented PET yarn, extrusion velocity is 500-1500 m.min^{-1}. At the other extreme, fully oriented PET yarn enquires velocities of above 6000 m.min^{-1}. Extruded PET filaments are generally amorphous, but drawing process brings the PET chain closer, with the result that some crystallinity is induced.

The morphology of polyester fibers is smooth and luster. They have low water absorbency, presenting a challenge to dye, to be printed and finishing. The chemical properties of polyester are mostly governed by the ester group in the polymer chains. Polyesters are resistance to acids but are more susceptible to alkalis. For the physical properties, polyesters are strong and show good resistance to abrasion. The tenacity of fiber is 35-56 cNtex^{-1}. Some properties are shown in Table 2.2.

Table 2.2 The properties of polyester [Mather and Wardman, 2010]

Specific gravity	1.38
Tenacity	35-56 cN tex^{-1} normally, but up to 100 cN tex^{-1} for high tenacity yarns.
Elongation at break	15-40%; 5-10% for high tenacity yarns.
Elastic recovery	80% from an 8% stretch
Resilience	High
Abrasion resistance	High
Moisture regain	0.4%
Launder ability	PET garments can withstand vigorous washing treatments, because of their high strength and abrasion resistance. The conditions for laundering blends of PET and other fibers are largely governed by the other fibers.

PET fibers are used in a whole application: apparel, house-hold, medical and industrial. PET fibers are often blended with other fibers such as cotton and wool [Lowan and Jungerman, 1980; Mather and Wardman, 2010].

2.5 Structure and composition of cotton

Cotton is a seed fiber, obtained from the seed of a species of plant of the genus *Gossypium*. Cotton has been woven from prehistoric days to the present. Cotton is quite sensitive about the conditions it requires for growth, favoring warm, humid climates and land. The quality of cotton has been affected by the fineness and the length of the fiber. The high-quality fibers having lengths varied between 25-65 mm were Sea Island and Egyptian cotton. The standard quality cotton, length of between 13-33mm, is typically from the Americas. The shorter fiber length is between 10-25 mm, produced in the Asian country.

Cotton cross sectional morphology as illustrated in Figure 2.6 exhibits three main features, primary wall, secondary wall and lumen. The primary wall is a very thin layer, consisting of a network of cellulose fibrils covered with an outer layer, or cuticle of pectin, protein, mineral matter and wax. The secondary wall constituents the bulk of nature fiber of about 20% to 45%. The lumen is the main pore through which is made up of a sap, a dilute solution of sugar, proteins and mineral pass, during the growth stage [Mather and Wardman, 2010].

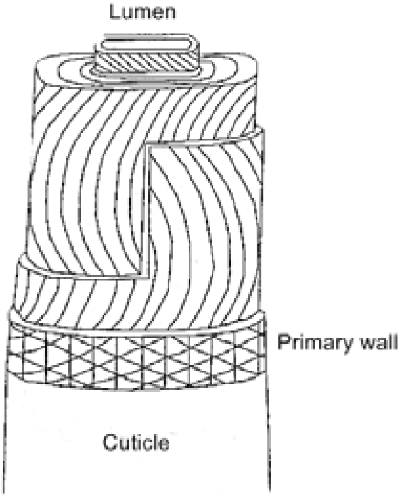


Figure 2.6 Schematic representation of cotton morphology [Mather and Wardman, 2010]

The cotton is composed mostly of long-chain carbohydrate molecule cellulose. Cellulose is a polysaccharide with the formula of the $(C_6H_{10}O_5)_n$, containing three hydroxyl groups: one primary and two secondary groups. Cellulose is formed by the condensation polymerization of β-D glucopyranose, with the six-membered rings joined through 1,4-glycosidic bonds. The repeating unit of cellulose is formed from cellubiose as shown in Figure 2.7, which is made up of two glucopyranose units.

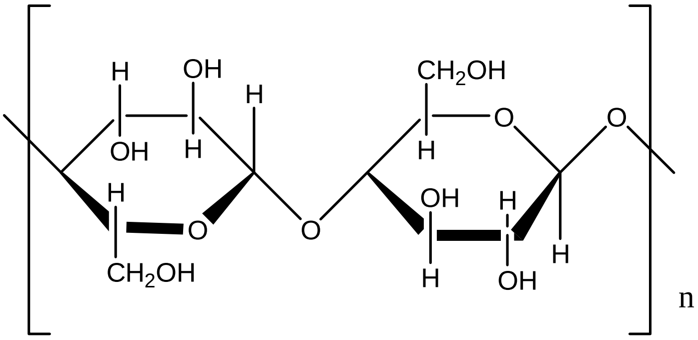


Figure 2.7 The chemical structure of cotton cellulose

The main properties of cotton fiber are shown in Table 2.3. In general terms, cotton fibers are fairly strong but they are 10-20% stronger when wet. The popularity of cotton results from its softness and absorbency. However, cotton fiber is subjected to attack by various agents. Acids are the most destructive agent for cellulose, attacking the glycosidic linkage by an acid-catalyzed hydrolysis reaction. Contrary, cotton is much more stable in alkali. Cotton fiber is stable to temperature of up to 150 °C, but above this temperature, the tensile strength as thermal degradation intensifies.

Table 2.3 Physical properties of cotton fiber [Mather and Wardman, 2010]

Fiber length	High quality cottons: 25-60mm. American upland cottons: 13-33mm. Indian and Asiatic cottons: 9-25 mm.
Fineness	10-20 µm.
Specific gravity	1.54 (one of the heavier fiber type).
Tenacity	25-40 cN tex^{-1}, but up to 20% stronger when wet.
Elongation at break	5-10%
Elastic recovery	Fairly inelastic. Only 45% recovery from 5% stretch.
Resilience	Low, but abrasion resistance is good.
Moisture regain	8.5%
Reaction to heat	Cotton has no melting point, it is relatively heat resistant (iron up to 200 ^{o}C), but will yellow with a very hot iron. It burns very readily when it gives a smell like burnt paper.
Launderability	Cotton garments can be washed, boil washed, dry cleaned and tumble dried. They dry slowly and crease easily. They often shrink during the first few washes-so the fabrics are often pre-shrunk prior to garment making.

In addition, cotton is often blended with other fiber; such as polyester, nylon, viscose or modal of increased advantage properties to another.

2.6 Characterization

2.6.1 Surface wetting phenomena

Wetting is the term that means liquid covering a surface. The wetting process involves with surface and interface. Figure 2.8 shows that surface tension is form by water molecule pull each other, resulting in liquid form dome on surface

Surface energy is important characteristics of a liquid penetrant. It indicates the ability to freely wet the surface of the object being inspected. The surface of material will be wet when its surface energy is higher than surface tension of liquid [Kwok and Neumann, 2000; Lichtenberger, 2004; Shishoo, 2008].

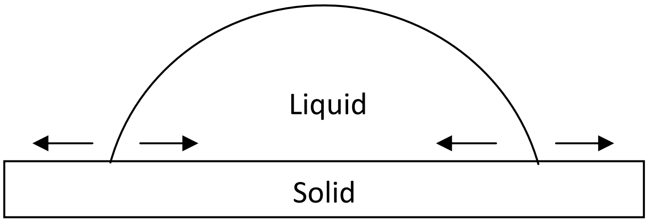


Figure 2.8 Surface tension of liquid [สุดา เกียรติกำจรวงศ์ และสุภาภรณ์ นพคุณดิลกรัตน์, 2551]

Surface energy is a function of surface area and the amount of electronic charge present, made up by the molecules at that surface. All of solid material surface have surface energy. For the liquid, all liquids have surface tension. The surface tension is a measure of the interaction energies between the molecules of liquid when at the gas/liquid interface. The most common unit used to measure surface energy and surface tension is energy per unit area.

To evaluate the surface energy of material, one can calculate according to the geometric theory equation. This theory takes into account the dispersive and polar parts of the surface energy by using two different test liquids. The surface energy of material is determined by sum of the polar and dispersive parts. The Owen-Wendt geometric theory equation which used to indicate surface energy of material as follows:

$$\gamma_l(1+\cos\theta_1) = 2[(\gamma_s^d\gamma_l^d)^{\frac{1}{2}} + (\gamma_s^p\gamma_l^p)^{\frac{1}{2}}] \tag{2.1}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{2.2}$$

where , γ_s is the total surface energy of the printing substrate

γ_l is the surface tension of the test liquid

γ_s^d is the dispersion contribution component of the surface energy

γ_l^d is the dispersion contribution component of the test liquid

γ_s^p is the polar contribution component of the surface energy

γ_l^p is the polar contribution component of the test liquid and θ is the contact angle [Kwok and Neumann, 2000; Jittiwattanapong et al., 2011].

To obtain γ_s^d and γ_s^p of material surface, the contact angle of two liquids with known surface tension component (γ_l, γ_l^d, γ_l^p) on the material must be decided. Generally, the testing is measured by using water and diiodomethane (CH_2I_2) as test liquid. The surface tension of water is 72.8 mNm^{-1} and CH_2I_2 is 50.8 mNm^{-1}. The dispersion contribution component of the surface energy of water is 21.8 mNm^{-1} and CH_2I_2 is 46.6 mNm^{-1}. The polar contribution component of the surface energy of water is 51 mNm^{-1} and CH_2I_2 is 4.2 mNm^{-1}.

For instance, the surface energy of fabric that had 33˚ of water contact angle and 30˚ of the CH_2I_2 contact angle, were calculated by follow:

From $\gamma_l(1+\cos\theta_1) = 2[(\gamma_s^d\gamma_l^d)^{\frac{1}{2}} + (\gamma_s^p\gamma_l^p)^{\frac{1}{2}}]$

Water, 72.8 (1+cos33) = $2(21.8\,\gamma_s^d)^{1/2} + 2(51\,\gamma_s^p)^{1/2}$

CH_2I_2, 50.8 (1+cos30) = $2(46.6\,\gamma_s^d)^{1/2} + 2(4.2\,\gamma_s^p)^{1/2}$

When γ_s^d is “x”

γ_s^p is “y”

Hence,

water, $133.86 = 9.34x^{1/2} + 14.28y^{1/2}$ (1)

CH_2I_2, $94.79 = 13.65x^{1/2} + 4.10y^{1/2}$ (2)

(1)-(2), $39.07 = -4.31x^{1/2} + 10.18y^{1/2}$

$$y^{1/2} = \frac{39.07 + 4.31x^{1/2}}{10.18} \quad (3)$$

Substitute (3) in (1),

$$133.86 = 9.34x^{1/2} + 14.28\left(\frac{39.07 + 4.31x^{1/2}}{10.18}\right)$$

$$= 9.34x^{1/2} + \left(\frac{557.92 + 61.55x^{1/2}}{10.18}\right)$$

$$= 9.34x^{1/2} + 54.81 + 6.04x^{1/2}$$

$$x^{1/2} = \frac{133.86 - 54.81}{9.34 + 6.04}$$

$$= 5.14$$

$$x = 26.42$$

Therefore,

$$y^{1/2} = \frac{39.07 + 4.31(5.14)}{10.18}$$

$$= 6.011$$

$$y = 36.12$$

Hence,

γ_s^d is 26.42 mNm^{-1}

γ_s^p is 36.12 mNm^{-1}

Finally,

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

$$= 26.42 + 36.12$$

$$= 62.54 \text{ mNm}^{-1}$$

Yang et al. [2009] studied low pressure air plasma to improve polyethylene terephthalate (PET) surface properties. The surface energy was measured. The result showed that the contact angle for water and diiodometane on surface decrease after treated with plasma, resulting in decreasing surface energy. The result revealed the variation in surface energy of PET surface as a function of the plasma treating time. The plasma process could increase the contribution of polar components (γ_s^p). They reported that it was due to the incorporation of polar groups onto the surface.

Pandiyaraj and Selvarajan [2008] studied modified grey cotton by atmospheric air plasma for hydrophilicity improvement. They used contact angle and surface energy to estimate the wettability of the plasma treated and untreated fabric. The result showed the total surface energy (γ_s) increase significantly with increase in plasma treating time, discharge potential and pressure (from 3.86 mNm^{-1} for untreated fabric to 71.54 mNm^{-1} for plasma-treated fabric).

2.6.2 Contact angle

The most useful method for characterizing wettability on a solid polymer surface is the contact angle technique which measure liquid drop on a solid surface, the angle formed by the solid surface and the tangent line to the upper surface at the end point constitute an angle. It is known that the angle (θ) is greater than 90 degrees or a water droplet could not to touch a large area of the surface and the shape of droplet would be spherical which are known as hydrophobicity. This condition is exemplified for poor wetting, poor adhesiveness and the solid surface free energy is low. Whereas, the hydrophillicity surface, contact angle (θ) below 90 degrees indicates water droplet would spread more on that surface. This condition reflects good wetting, good adhesiveness and high surface energy. In 1805, Thomas Young described the three-phase equilibrium as shown in Figure 2.9, the surface tension forces of water droplet, due to the balance of surface tension force at interfaces between solid/liquid (γ_{SL}), solid/vapor (γ_{SV}) and liquid/vapor (γ_{LV}) at equilibrium. It is resulted to equation as following:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \qquad (2.3)$$

Dynamic contact angle are formed namely, advancing and receding contact angle. The advancing angle is the contact angle when the three-phase lines is moving forward, while the receding contact angle is the three-phase line is withdrawn over a pre-wetted surface[Garbassi, Morra, and Occhiello, 1994].

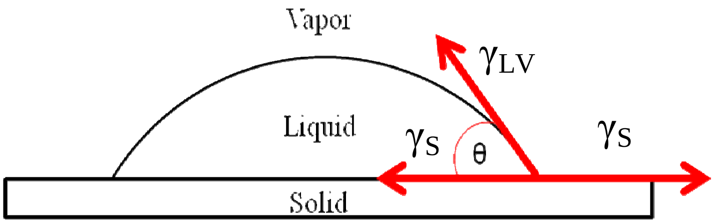


Figure 2.9 The schematic diagram of the contact angle [Garbassi, 1994]

2.6.3 Wicking of fiber

Wicking is a term given to the movement of a liquid by capillary forces. Small capillaries exist in fibrous assemblies between the yarns in a woven or knitted fabric structure or between the individual fibers in yarns or in non-woven structure. Wicking can only take place if the liquid is first capable of wetting the surface of the capillaries. The transport of a liquid through a fabric has significant implications for the effectiveness of many wet-processing treatments for textiles. In comparison with gas capillary tubes, textile fabrics are complex structures because wicking can take place not only in the capillaries between the fiber filaments that constitute the yarn, but also in the capillaries between the yarns themselves. Transverse wicking is the transport of water through the thickness of a fabric [Mather and Wardman, 2011].

Kan and Yuen [2011] studied the wettability of polyamide and polyester fabrics were treated with atmospheric pressure plasma by using longitudinal wicking test and contact angle. The contact angles of both fabrics were decreased from about 85˚ to 0˚ after treated with plasma for short time (3 sec). Then, the wicking test showed that both fabric had significant improvement in the wicking rate after using atmospheric pressure plasma. The wicking rate increased with increasing treating time. The research explained that this improvement could be from the introduction of hydrophilic functional group onto surface and they may also be attributed to the etching effect on fiber surface which increases surface area and enhances the capillary effect.

2.6.4 X-ray photoelectron spectroscopy (XPS)

XPS is a spectroscopic technique that provides quantitative information about the surface chemistry of material. The XPS spectrum is obtained by irradiating the sample with monochromatic X-ray source. A focused beam of X-ray at 1.5 eV is directed at the surface, and the number and kinetic energy of the photo-emitted electron from the top 10-12 nm are measured. From their kinetic, the binding energy of the electrons is determined. The kinetic energy of emitted electrons can be measured with an electron spectrometry and the binding energy of the electron can be obtained from the relationship of

$$\text{B.E.} = h\upsilon - \text{K.E.} - \text{ø} \qquad (2.4)$$

where B.E. is the binding energy of the emitted electron, $h\upsilon$ is the X-ray energy, K.E. is the kinetic energy of the ejected electron, and ø is the work function of material. Each element emits electrons from its core (inner shell) orbital at characteristic binding energies which cannot be detected. The spectrum is produced as a plot of the number of electrons at each binding energy which indicates the elements presence and their relative amounts in the area of the surface analyzed.

The XPS instrumentation consists of an ultra-high vacuum chamber containing a sample holder, X-ray gun and electron analyzer. The K_α lines of Mg (1253.6 eV) and Al (1486.6 eV) ensure both good resolution and sensitivity.

XPS technique can detect all elements, except H and He. From photoemission spectra, qualitative (functional group) and quantitative (surface concentration) information can be obtained. Figure 2.10 displays an XPS survey spectrum of poly(ethylene terephthalate) which is observed in the spectrum as C1s, O1s and high resolution spectra of the core level C1s, an evaluation of the relative amount of different functional groups [Garbassi, Morra and Occhiello, 1994].

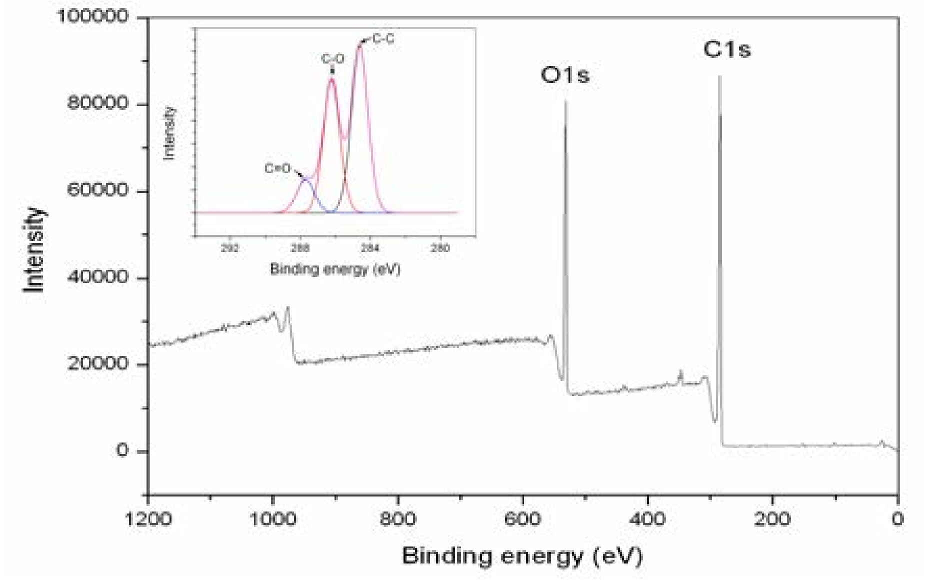


Figure 2.10 XPS survey spectrum of poly(ethylene terephthalate) in this research, and high resolution spectra of C1s of poly(ethylene terephthalate) in the inset figure

Regarding to Gogoi et al. [2011], the research based on the enhancement of hydrophobicity and tensile strength of muga silk by Argon plasma. This research used XPS to investigate the functional group before and after plasma treatment. XPS revealed that oxygen and nitrogen concentration on surface were increased and carbon concentration was decreased by increasing RF working power. XPS also showed the decovolution of C1s peak which the intensity of C-C, O-C=O were decreased after treated with plasma.

Inbakumar et el. [2009] also using XPS to investigate the functional group of cotton fabric after plasma (DC glow discharge obtained in air). The XPS result showed new functional group (O-C=O) on the surface which improve wettability of cotton fabric.

2.6.5 Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR generates information about the chemical nature of the surface material. It is used when the sample poorly transmits infrared radiation or when the sample cannot be dissolved [Twardowski and Anzenbacher, 1994]. In this technique, the sample is mounted on a crystal, typically made of germanium, through which the infrared beam is directed. The depth of penetration of the radiation beam into the sample is less than 5µm. Each time when the beam strikes the surface of the crystal in the contact with the sample, it forms an evanescent wave that penetrates the top micrometer layer of the sample, before reflecting back into the crystal. In combination with FTIR, an absorption spectrum of the sample surface is obtained. The wavelengths of IR radiation of each compound have a characteristic plot of reflection against wavelength.

2.6.6 Zeta potential

A particle in contact with aqueous solution is likely to obtain a surface change for various reasons. Particles with similar charge give repulsion, which is the origin of colloid stability in many cases. The most importance assumption is that the interaction between charged particles depends on the zeta potential (ζ). Zeta potential is a scientific term for electrokinetic in colloid system. The most useful for characterizing particle charge is the electrophoresis technique, and several commercial instruments are available such as the Zeta Meter, Zetasizer. Instrument is base on that the suspension obtain the potential. If particle surface have negative charge, its counterion will move to anode and charge in electrical double layer will move to cation. The zeta potential must be obtained by measure the particle velocity in dielectric by Smoluchowski equation [Adamson, 1976; Gregory, 2006] as follow:

$$\upsilon = \frac{E\varepsilon_r \varepsilon_o \xi}{\eta_1} \qquad (2.5)$$

When ε_r = Dielectric constant of the medium

ε_o= Dielectric constant of Free space

ζ = Zeta potential

η = Liquid viscosity

The molecule or particle has high zeta potential (negative or positive) that will produce stability. The solution or dispersion will resist aggregation when zeta potential has low [Adamson, 1976; Gregory, 2006].

Supaporn [Supaporn et al., 2010] presented the zeta-potential of pigment ink in her research. The zeta potential of inks was found to be negatively charged. The zeta potential of four inks (cyan, magenta, yellow and black) were about -34 to -56 mV. From this research, it can be illustrated that these inks have good dispersion stability.

2.6.7 Scanning electron microscopy (SEM)

SEM is a long-established technique that is capable of providing images of the sample of excellent resolution at very high levels of magnification. SEM makes use of a primary beam of electrons that interact with the specimen of interest, resulting in the emission of secondary electrons. The secondary electrons ejected from the specimen surface are collected and displayed to provide a high-resolution micrograph. The depth and resolution of the image are determined by beam current, beam energy interaction volume and the final spot size [Wei, 2009].

The sample must be conductivity, so the fabrics sample must be coated with a very thin metallic layer (usually gold) to provide conductivity for the electrons before a measurement. The sample has to be mounted in an evacuated chamber. [Mather and Wardman, 2010].

Based on Kamlangkla research [Kamlangkla at al., 2010], he presented the surface morphology of cotton fibers before and after SF_6 plasma treatment by SEM. The SEM images displayed that untreated cotton fibers were smooth while the treated fibers had granulars and grooves appearances on the surface (as shown in Figure 2.11). The roughness surfaces were caused by etching effect.

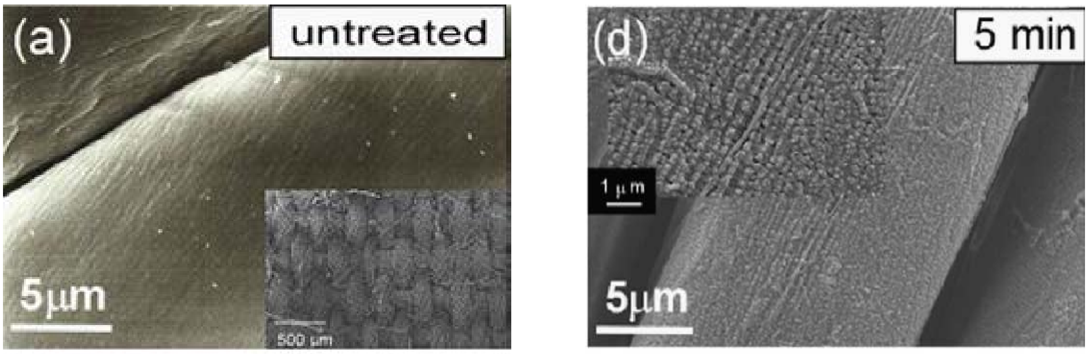


Figure 2.11 The SEM micrograph of cotton fiber with magnification of 5000 and 15,000. (a) untreated, (b) treated with 0.5 torr of SF6, and RF power of 50 watt for 5 min [Kamlangkla at al., 2010]

2.6.8 Atomic force microscopy (AFM)

AFM uses a sharp tip that scans over a surface. The tip is a part of a cantilever that can measure force down to the lower $1x10^{-9}$ N. The image of the surface topology of the sample is obtained by scanning the sharp tip which is made of silicon nitride, at the end of a cantilever across its surface, as illustrated in Figure 2.12. The forces generated as the tip undulates across the surface are recorded, so a type of relief map of the surface is generated. The technique is relatively more straightforward than the SEM technique because no surface coating is required and measurement can be made at normal atmospheric pressure. The diagram of AFM can be seen in Figure 2.12. [Mather and Wardman, 2010].

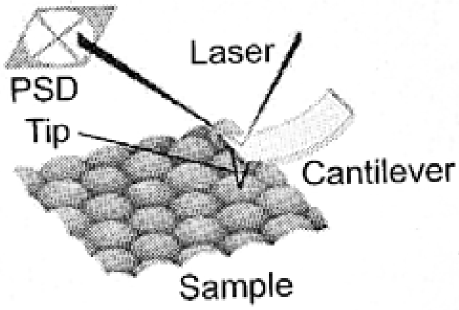
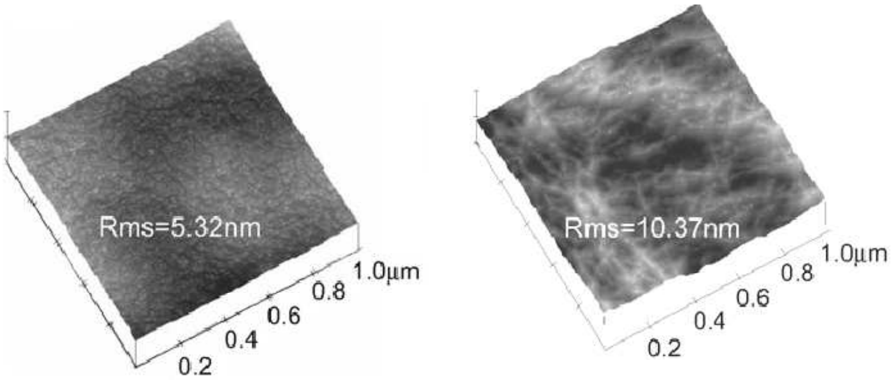


Figure 2.12 Schematic view of Atomic force microscopy (AFM) [Wei, 2009]

Kamlangkla [Kamlangkla et al., 2010] studied on the morphology of cotton fiber after SF_6 plasma, not only SEM but also AFM analysis was used. The AFM result reported that the topography of surface in term of roughness and the root mean square (RMS) of cotton fiber increased after plasma treatment. The instance of AFM images are shown in Figure 2.13.



(a)

(b)

Figure 2.13 AFM images 1 μm× 1 μm of cotton fibers (a) untreated and (b) treated with SF_6 plasma at 50 watt, 0.5 torr for 5 min [Kamlangka et al., 2010]

2.6.9 Tensile properties

Tensile strength is the mechanical property to measure the maximum force that the material can support. The maximum tensile force recorded in extending a test piece to breaking points is named tensile strength at break. The force at which a specimen breaks is directly proportional to its crossectional area, therefore, when comparing the strength of different fibers; yarns and fabrics allowances have to be made for this property. The tensile force recorded at the moment of rupture is sometimes referred to as the tensile strength at break as defined above. Figure 2.14 shows that the tensile properties of the specimen may continue after the maximum tensile force [Saville, 2006].

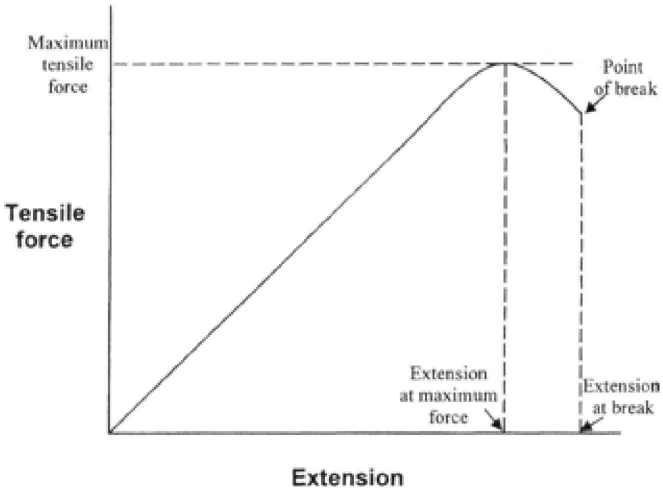


Figure 2.14 The tensile properties of the specimen after the maximum tensile force [Saville, 2006]

2.6.10 K/S

The commonly applied theory for most practical images composed of inks and dye is "Kubelka-Munk" theory. The Kubelka-Munk theory which has been used to predict the reflectance of inks, paints, plastic, textiles and other material models, affects the processes under the assumption of a one-dimensional light flux; hence isotopic scattering within the material is achieved. The scattering of light in the hardest copy images is an important part of the optics of these systems. Most substrates, such as paper and many colorants (colorant are dyes, toners and pigments) also scatter light. Thus, both absorption of light by colorants and scattering of the light are important to the appearance of images. Under this assumption, the material layer is characterized by a wavelength dependent scatter coefficient and absorption coefficient. Figure 2.15 shows the photometric model. So, the Kubellka-Munk equation defines a relationship between spectral reflectance (R_∞) of a sample and its absorption (K) and scattering (S) characteristics, as follows:

$$\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \qquad (2.6)$$

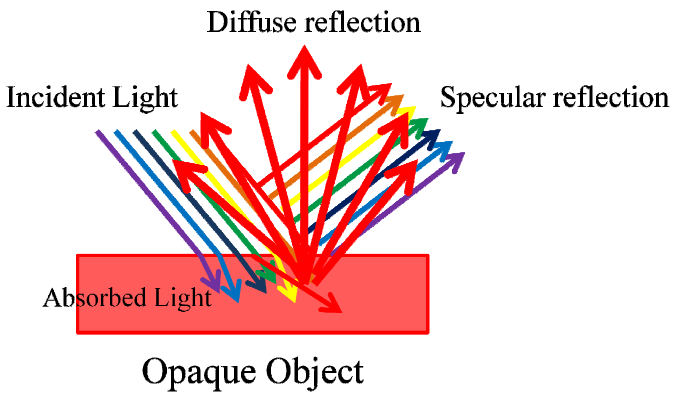


Figure 2.15 Light interactions with red material [Sabic, 2012]

Basically, the color yield (K/S) can be obtained by measuring with a color spectrophotometer. The spectrophotometer connects to a build-in computer which displays the intensity of diffusely reflected (or scattered) light at each wavelength. Thus, the spectrophotometer can measure the amount of light absorbed by a medium where the light is reflected by an object. Then, reflectance value of a sample which is characterized by a spectrophotometer is calculated to give the K/S value. Generally, the higher the K/S value is, the greater the color yield will be [Gilbert and Haeberli, 2006: Liao and Chen, 2011].

Kamel et al., [2010] used K/S to determined the dyeability of polyester fabrics. The fabrics were modified by atmospheric plasma treatment with O_2 gas. The result indicated that plasma process can improve the dyeability of fabric with reduce dyeing temperature.

Kan and Yuen studied the modified-cotton fabrics for digital ink-jet printing. His research enhanced the deposition of printing paste using atmospheric pressure plasma. Their research used K/S to indicate the improvement of final color properties of ink-jet printed cotton fabrics. The result showed that atmospheric pressure plasma pretreatment could increase the color yield of ink-jet printed cotton fabrics.

Fang and Zhang [2009] used atmospheric pressure plasma for enhancing ink-jet printing performance of polyester fabric. The fabric printed with pigment ink. The result showed that the color strength (K/S) of printed-fabric increased after plasma treatment.

2.6.11 Color gamut (color space)

A color gamut plot as shown in Figure 2.16 illustrates the overall range of shade that can be achieved when measuring an image printed with CMYK inks. The extent of the gamut can be considerably expanded if additional inks, comprising brighter primaries such as orange, yellowish-red, reddish-blue and yellowish-green are included. This idea was first promoted with the Pantone Hexachrome and Heptatone colors which give additional bright red, purple and green colors.

The visual quality of the textile prints on fabric should also be quite good when both the printer and the ink set are optimized for printing on fabrics. The fineness and sharpness of detail (fineness of line, saturation and quality of the color) must also be acceptable.

The CIE L*a*b* color system is also used in many applications. L* is the lightness, a* is the red-green colors and b* is the yellow-blue colors of a set of specific colors. The lighter of the color is the higher of L* values, the redder of the color is the higher of a* values and the more yellow of color is the higher of b* values as shown in Figure 2.16 [Ujiie and Dawson, 2006]

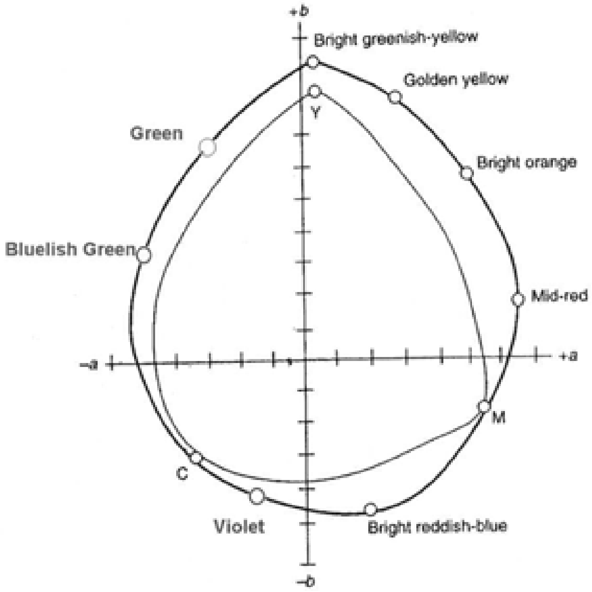


Figure 2.16 The schematic diagram of a color gamut in the CIE L*a*b* color system [Ujiie and Dawson, 2006]

2.6.12 Color fastness

Color fastness is the term used in dyeing or printing of textile fabric. It means resistance of color to fading. It also refers to the notion of an object having a color that retains its original hue without fading or losing its color saturation. The color adhesion property can be one of the attributes to color fastness. The term is usually used in the context of clothes. Color fastness can be applied to many aspects, such as wash fastness, light fastness, rub fastness and perspiration fastness. To evaluation such a property, many international standards are available for quantifying this property as AATCC, ISO, DIN and BS. In this work, rubbing fastness and wash fastness of the printed fabrics after the plasma pretreatment are the necessary properties to evaluate by the ISO standards.

2.7 Literature review

Between 2004 to 2008, there are many researches about wettability of textile fabric modified by plasma process. The hydrophilic and hydrophobic properties of modified fabric were investigated. For hydrophilic property, surface modification of poly(ethylene terephthalate) fabric by an atmospheric-pressure plasma source was studied. The change in contact angles was studied. The effects of radio frequency (RF) powers, O_2 concentrations and exposure durations on changes in wettability were studied by contact angle measurement. The resultant contact angles decreased with higher RF power, longer exposure duration and higher O_2 concentration [Yang and Gupta, 2004]. Moreover, increases in surface energy of the cotton yarn surface modified with DC glow discharge in ambient air by plasma were found. Degree of hydrophilic behavior of the treated cotton quantified by a wicking rate test tended to be higher in the vicinity of the electrode. Moreover, the wicking rate increased with increasing exposure times and discharge powers [Temmerman and Lcys, 2005].

On the other hand, the hydrophobic property of fabric by plasma process had been reported by several researchers. Hodak used radio-frequency inductively coupled SF_6 plasma to modify the surface of Thai silk fabric for the enhancement of hydrophobic property. After the SF_6 plasma treatment, the contact angles increased and morphology was changed. The RMS surface roughness of the fiber increased from 10 to 30 nm. XPS spectra of the silk treated with SF_6 plasma exhibited clearly that the F1S peak was the only visible one on the samples after the treatment. Surface fluorination of the fabric is the main reaction for the enhancement of hydrophobicity [Hodak et al., 2008].

In 2008, Pandiyaraj and Selvarajan researches on improvement of dyeing properties of grey cotton fabric pretreated by air plasma process were conducted. The fabric treated with air plasma possessed more wettability and good dyeability. The color strengths (K/S values) increased with increasing exposure times which might be caused by penetration of the dye molecules into the fabric surface induced by the plasma treatment to increase the polar groups on the surfaces which were strongly bonded with the dye molecules. In addition, the etching effect also caused weight loss of the treated fabrics. SEM images showed the formation of cracks, holes and increases in the micro-roughness on the fabric surface [Pandiyaraj and Selvarajan, 2008].

Recently, Yuen and Kan [2007] used low temperature plasma treatment on textile fabrics followed by padding with sodium alginate solution that was used generally in a traditional chemical process. Influences of the low temperature plasma on color appearance (color yield and color sharpness) and color performance properties (color fastness) of ink-jet printed cotton fabric were investigated [Yuen and Kan, 2007]. Later, Fang studied influences of exposure time of the low temperature plasma treatment on silk fabrics by O_2 plasma on the similar color appearance (color yield and color sharpness) and color fastness of ink-jet printed cotton fabric [Fang et al., 2007]. The composite atmosphere comprising 90% air and 10% Ar was used to modify surface of polyester fabric [Zhang and Fang, 2009]. The surface-modified polyester fabrics exhibited enhanced color yield and excellent pattern sharpness. SEM and XPS analyses indicated that the improved color performance was contributed by the etching effect of O_2 gas which produced oxygen containing polar groups on the fiber surface.

From previous works, there are few literatures concerning the plasma pretreatment on PET fabric on inkjet printing properties and the fabric performance.

In this work, three types of gases plasma were used to modify fabric surfaces for improving printed color performance. Wettability changes of the treated fabric were investigated by various methods. We thus investigated influences of plasma operating conditions on color yield of PET fabric. Parameters of gas, treating power, exposure time and operating pressure of the plasma were studied. Two types of fabrics, namely cotton and polyester were used substrates for comparison of fabric types.

CHAPTER III

EXPERIMENTAL METHOD

3.1 Plasma Reactors

Figures 3.1 to 3.2 show the schematic diagram of radio-frequency (RF) plasma generatior. The main components of the system are the reactor chamber, impedance matching network, RF generator and gas supply system. The reactor has several stainless steel ports for gas feeding and plasma diagnostic equipment to be attached to the system reactor. The top stainless steel plate has a circular quartz window (20 cm in diameter) for let the RF field from planar coil place above the quartz plate to couple into the plasma. A flat coil (7 turns) is mounted directly on top of the quartz window to induce the plasma at 13.56 MHz power. The matching network connected the induction coil to the power source and allowed the coil to be tuned to match the source resistance. A base pressure at $3x10^{-5}$ torr was achieved using a turbo molecular pump backed by a rotary pump. Gas is allowed to enter the chamber via a set of mass flow controllers.

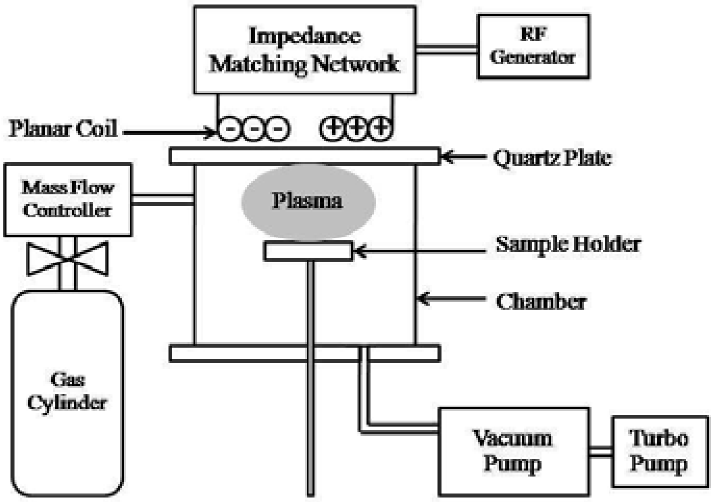


Figure 3.1 Schematic diagram of the radio-frequency inductively coupled plasma reactor

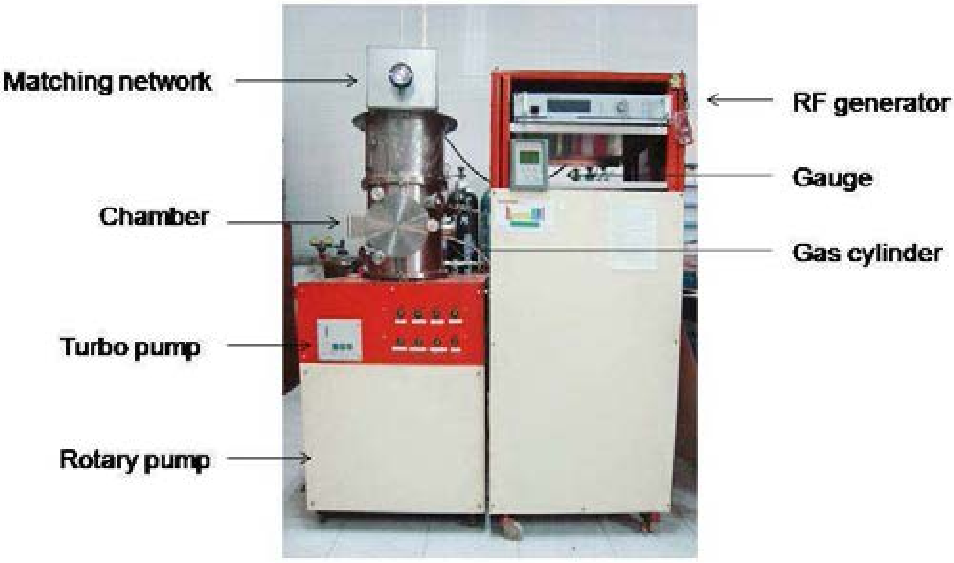


Figure 3.2 Components of the radio-frequency inductively coupled plasma reactor

3.2 Materials

3.2.1 Textile Fabrics

In this research, three types of fabrics used are polyester (PET), cotton and combination of PET and cotton fabric (TC). The 100% polyester woven fabric used had a density of 164.8 g.m^{-2}. The densities of warp and weft were 15 ends/cm and 26 picks/cm, respectively. The cotton woven fabric was 100% cotton which has a density of 88.76 g.m^{-2}. The density of warp and weft were 48 ends/cm and 48 picks/cm, respectively. Commercial TC composing of 65% cotton and 35% polyester woven fabric were used, had a density of 115.1 g.m^{-2}. The density of warp and weft were 44 ends/cm and 28 picks/cm, respectively. All of fabric samples were cut to a size of A5 (14.8 cm. x 21 cm). During the plasma treatment, the fabric samples were held stretch in a horizontal plane with the aid of quadrilateral frame as shown in Figure 3.3. The plasma power used was in the range of 50-150 watts RF power. The distance between the sample and quartz window was 3 cm. To carry out the treatment, the chamber was evacuated down to a pressure of 3x10^{-5} torr. Then, the chamber was filled with the required gas to reach the desired pressure. The samples were exposed to the plasma for various times in the of range 30 s to 20 min. The pressures was adjusted in the 0.1-1.0 torr range.

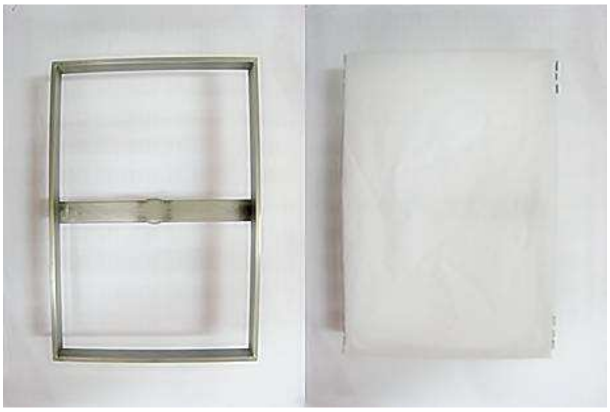


Figure 3.3 The quadrilateral frame for holding the fabric samples, (left) quadrilateral frame and (right) fabric stretch on the frame

3.2.2 Ink-jet printing procedure

After the plasma pretreatment, the fabric samples were printed with a set of four-color, pigmented ink-jet inks (cyan, magenta, yellow and black), using a commercially available water-based ink, Inkman from International Connected Trade Co., Ltd (Thailand). The samples were printed by the EPSON Stylus T13 printer. A color test chart, Gretag test chart 294 colors (as shown in Figure 3.4) was used for investigating the quality of the printed fabrics.

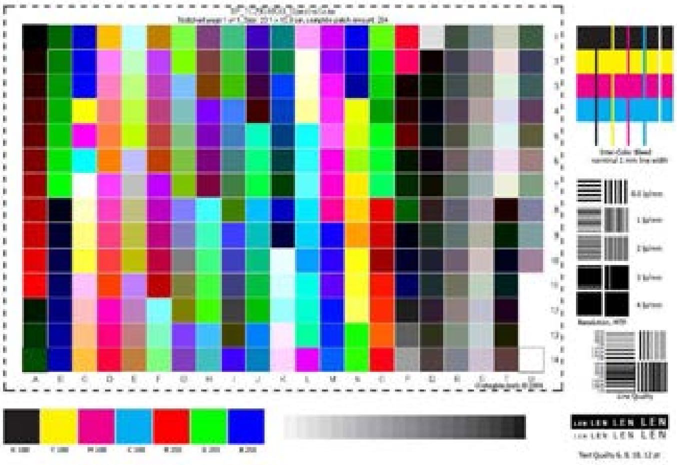


Figure 3.4 The Gretag test chart with 294 color batches and other control elements

3.3 Characterization technique

3.3.1 Physical-chemical properties of the fabric surface and pigment ink

3.3.1.1 Surface analysis

- **Contact angle and surface energy**

To investigate the wettability properties, contact angles of the water droplet on the samples surfaces were evaluated by a standard goniometry (200-F1, Ramé-Hart, U.S.A.). Distilled water (3 µl) and CH_2I_2 was dropped on the fabrics surface using a micro-syringe, and the contact angles were read. The surface energy of fabric surfaces was calculated using geometric theory of material in equation (2.1).

- **Capillary rise method**

The test was conducted using a vertical wicking tester according to DIN53924 method [Das et al., 2008: 225-231]. A strip of fabric (20 cm x 2.5 cm) was suspended vertically with its lower end immersed in a reservoir of distilled water (3 cm). The movement of water was measured by the clamped scale. The three samples were evaluated for averaging.

- **Zeta potential measurement**

The ink-jet ink and the fabrics were all measured for zeta potential, using a Zeta Nanoseries model S4700 (Malvern Instrument, UK) in a U-shaped cell with each wall accommodating one small piece of a Cu electrode. The fabrics were prepared before measure the zeta potential by cutting the fibers which pulling out from the piece of fabric, into small pieces. They were then immersed in de-ionized water for 72 h. The suspended fiber was used for characterizing the zeta potential of fabric.

3.3.1.2 Surface morphology

- **Scanning electron microscopy (SEM)**

The morphology changes of the plasma-treated fabrics were observed using a scanning electron microscope (JEOL-JSM 6400). All the samples were coated with gold before SEM experiments.

- **Atomic Force Microscopy (AFM)**

AFM (model Veeco Nanoscope-IV) is used to obtain the surface roughness of the fabric. The measurement is operated in a tapping mode. The top and end of the fiber was stocked on the glass slide before the measurement.

3.3.1.3 Surface chemistry

- **Attenuated total reflection Fourier transforms infrared (ATR-FTIR)**

The functional group of the ink and the changes of functional groups caused by the plasma treatment of fabric were evaluated by an attenuated total reflection Fourier transform infrared spectrometry (Thermo Scientific-NICOLET; S10)

- **X-ray photoelectron spectroscopy (XPS)**

The most sensitive technique to measure chemical composition and bonding structure of a material is X-ray photoelectron spectroscopy (XPS). This technique is used in a variety of applications to identify element and bonding structure in the outermost atomic layer. In the research, AXIS ULTRA^{DLD}, Kratos analytical was used to verify the changes in surface chemical composition of the fabric. The base pressure in XPS analysis chamber was about 6x10^{-9} torr. The samples were excited with X-rays Hybrid Mode on a 700 x 300 µm spot area with a monochromatic Al K$_{\alpha1,2}$ radiation at 1.4 keV.

3.3.1.4 Mechanical property

- **Tensile strength**

Tensile strength was examined using the guidelines of ASTM D5035-95 (2003) [American Society for Testing and Materials, 2003] standard. This method covers reveled strip test procedure. It can determine the maximum load, breaking force and elongation of fabric. In this work, the samples were cut into 25 mm x 150 mm (test on warp side) and clamped in a tensile testing machine (Lloyd, Universal Testing Machine, UK). The distance between the clamps was set at 75 ± 1 mm. The loading rate of testing machine was set at 300 ± 10 mm.min^{-1}. The three specimens were applied the force until it break. Values for the stress at maximum load of the sample are obtained from machine scale.

- **Viscosity of ink**

The viscosity of water-based pigment inks were analyzed by viscosity meter (DV III, programmable rheometer, USA). The testing condition was set at 25˚C. The motor speed was set to vary from 10 rpm to 250 rpm within 12 min.

3.3.2. Color performance of the printed fabrics

3.3.2.1 Ink absorption in fabric

The performance of ink adsorption in fabric was measured by height of the ink in printed fabric. The printed fabric was cut and stuck onto a glass slide. Then, the samples were brought to view through a digital microscope in the cross-section direction and the ink adsorption was captured via a digital camera. The captured images were measured for the penetration depth of ink absorption which was then computed to percentage of ink absorption.

3.3.2.2 Color strength (K/S)

Color strength of the inkjet-printed fabrics was measured by color spectroscopy (X-rite Premier 8400). The fabric samples were measured under the illuminant D50, the CIE 1931 2^o observer in a specular light excluded mode. The color strength of inks was resolved as a K/S value which is the Kubelka-Munk equation, defined as a relationship between the infinite spectral reflectance (R_∞) of the sample and its scattering (S) and absorption (K) characteristics. The K/S value can be calculated according to equation 2.6:

$$K/S = (1-R_\infty)^2/2R_\infty \qquad (2.6)$$

3.3.2.3 Color gamut evaluation

The color test chart of each printed fabric was measured for the tristimulus values by the same spectrophotometer. The tristimulus values (X, Y, Z) were transformed to the chromaticity coordinate (x,y,z) for creating a color gamut in a two-dimensional color space. The L^*, a^* and b^* color values are used to calculate a gamut volume.

3.3.2.4 Color fastness test

- **Rubbing fastness test**

ISO 105-X12 was the standard to the rubbing fastness. The samples were cut into size 10 cm x 5 cm. The testing was carried out by two conditions, wet rub and dry rub. A white cotton fabric was laid on the tester (Crock meter) and rubbed against the printed fabric sample for 10 cycles. The amount of color transfer from printed sample onto the white cotton fabric was revealed by using the ISO Gray scale.

- **Washing Test**

The color fastness of washing on printed fabrics was investigated based on ISO 105-C06-1994. The samples were washed in washing machine (Rotawash) in 5 g/l solution of commercial non-ionic detergent with 20 metallic balls and temperature of water at 40^oC for 30 min and rinse by de-ionized water.

CHAPTER IV

INKS ANALYZATION

4.1 Viscosity of the inks

The viscosity of the inks was measured by viscometer at 25 ˚C. The results is ahown in Figure 4.1 for the viscosity values of cyan, magenta, yellow and black ink. For the cyan, magenta and yellow ink, their viscosity did not change when changing the shear stress. The viscosity of cyan, magenta and yellow inks indicate Newtonian flow behavior at the appropriate shear force. Newtonian flow is where viscosity remain more or less constant as shear force is applied [Lichtenbergaer, 2004]. Cyan, magenta and yellow inks were giving viscosity values of approximately 3 mPas as change shear force. The viscosities of these three inks agree well with Chakvattanatham’s research [Chakvattanatham et al., 2010] in which their viscosity showed Newtonian flow and giving viscosity values of about 2.5 mPas.

However, Figure 4.1 indicates black ink as non-Newtonian flow behavior because of its viscosity non linear change when changing shear stress. The viscosity decreased with increasing shear stress. This viscosity behavior seems like the thixotropic flow. Thixotropic flow is the viscosity that decrease when there is an increase in shear. Lichtenberger [2004] indicate that most water-based ink will show the viscosity of thixotropic behavior.

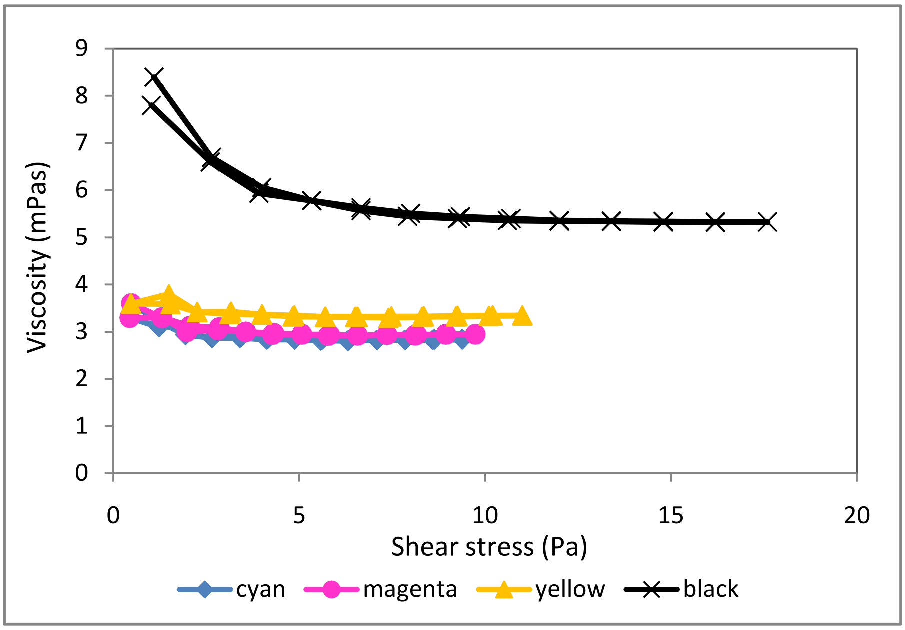


Figure 4.1 The variation of viscosity with shear stress of cyan, magenta, yellow and black inks

The result showed low-viscosity which are about 2.8, 3.4, 3.0 and 5.3 mPas for cyan, magenta, yellow and black inks, respectively. The low-viscosity ink (2-5 mPas) can be well printed by the ink-jet printing [Kamalakar, 2009; Chakvatttanatham, 2010; Jalindre; 2011].

4.2 Zeta potential, particle size and surface tension of the inks

Table 4.1 shows the zeta potential, size and surface tension of inks. The result reveals that zeta potential of all four inks (stored in the storage about 1 year) have negative charge. The magenta color has the highest negative value (-43.4 mV). Material with high zeta potential will show good stabilization because of it has high electrostatic repulsion between the particles [Baez et al., 2009]. However, black and cyan shows low negative charge. The low level of charge may cause to low repulsive force between particles, leading to coagulation of pigment.

The particles sizes of all four inks were measured by zetasizer. The result also shows in Table 4.1. The cyan, magenta and yellow pigments sizes are similar at around 145 nm whereas the black pigment has the biggest size around 251 nm. However, the pigments are usually ground to particle size between 5 µm to 10 nm depending on the properties need. The smaller the particle are, the brighter the color will be [Lichtenberger, 2004]. Thus, the black ink will provide darker shade than other ink.

Table 4.1 Characterization of pigment ink used

Ink	Zeta potential (mV)	Particle size (nm)	Surface tension (mNm^{-1})
Cyan	-3.3 ± 0.9	142 ± 3	26 ± 1.0
Magenta	-43.1 ± 1.0	147 ± 3	32 ± 0.5
Yellow	-31.6 ± 0.7	145 ± 8	30 ± 0.5
Black	-1.9 ± 0.7	251 ± 2	28 ± 0.5

The surface tension of four inks used in this research was investigated by tensiometer. Table 4.1 shows the surface tension result that cyan ink provides the lowest (26 mNm^{-1}) tension and magenta ink provided the highest (32 mNm^{-1}) tension. However, the surface tensions of all inks are within the standard range of 30-40 mNm^{-1}. It is acceptable for ink performance, i.e. droplet formation and spreading on printing substrates [Jittiwattanapong et al., 2011; Jalindre, 2011].

4.3 Analysis of the functional group of pigment ink

In this research, the functional groups of pigments were characterized by ATR-FTIR. The cyan-pigment spectrum is shown in Figure 4.2. It reveals that the peak at 3037 cm^{-1} corresponded to C-H stretching in aromatic, 1607 cm^{-1} for C=N stretching, 1501 cm^{-1} for C=C stretching in aromatic and 1330 cm^{-1} for C-N stretching, respectively. This spectrum indicate that the functional groups of cyan blue 15 (Copper phthalocyanine) which is the widely used as cyan pigment [Momin, 2008; Cabot, 2012]. Moreover, Chakvattanatham et al. [2010] used C.I. cyan blue 15 in his research which the FTIR-fingerprint is similarly with our research. Hence, this cyan-pigment ink might be the C.I cyan blue 15 which is the commonly pigment for cyan ink.

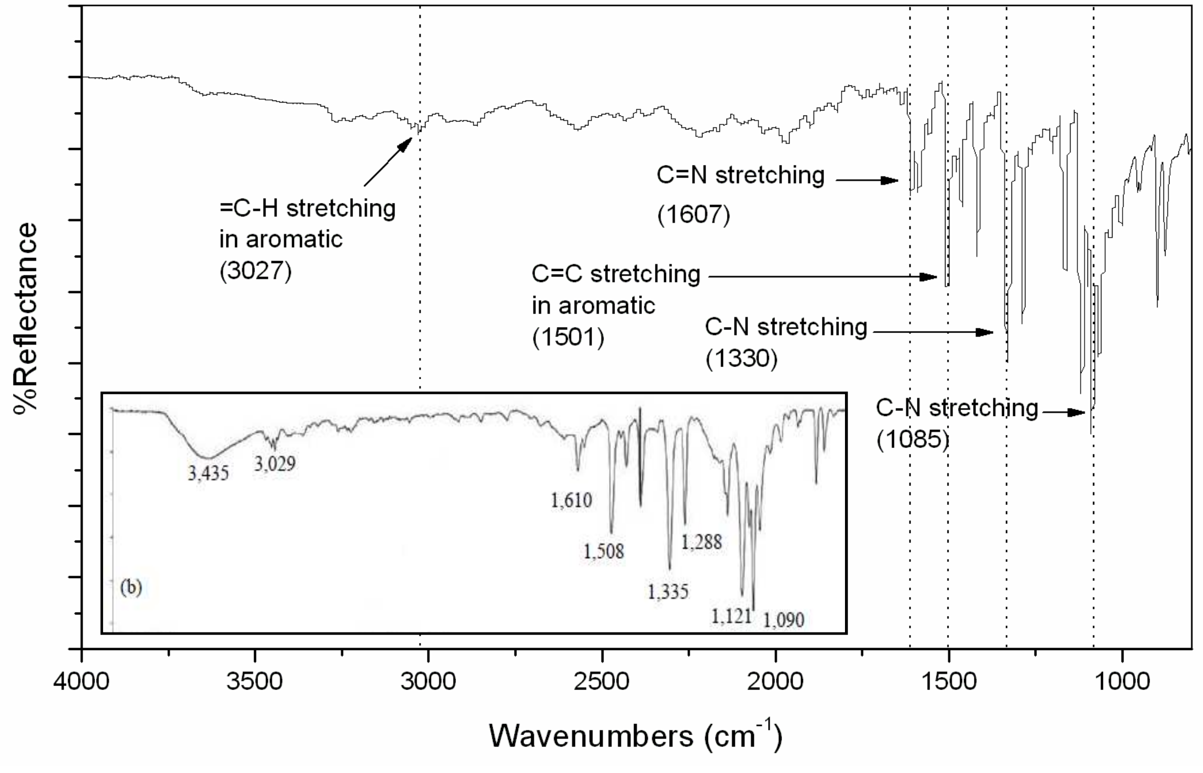


Figure 4.2 ATR-FTIR spectra of cyan pigment of this research, and the cyan pigment of Chakvattanatham et al. [2010] in the in set figure.

The ATR-FTIR spectrum of magenta-pigment is illustrated in Figure 4.3. The spectrum shows the functional groups of quinacridone pigment which is the main class of colorant of magenta [Cabot, 2012]. Figure 4.4 reveals five significant peaks which are 3098 cm^{-1} corresponding to =C-H stretching in aromatic, 2962 cm^{-1} for the C-H stretching for alkane, 1728 cm^{-1} for C=O stretching in aromatic, 1578 cm^{-1} for N-H stretching and 1463 cm^{-1} for C=C stretching in aromatic. This ATR-IR result is agreed well with the magenta-pigment of Chavattanatham's research [Chakvattanatham, 2010]. Chakvattanatham's results shows IR spectrum of C.I. pigment red 122 (as dimethyl quinacridone). This result indicates that the magenta-pigment which is used in this research could be C.I. pigment red 122 (dimethyl quinacridone).

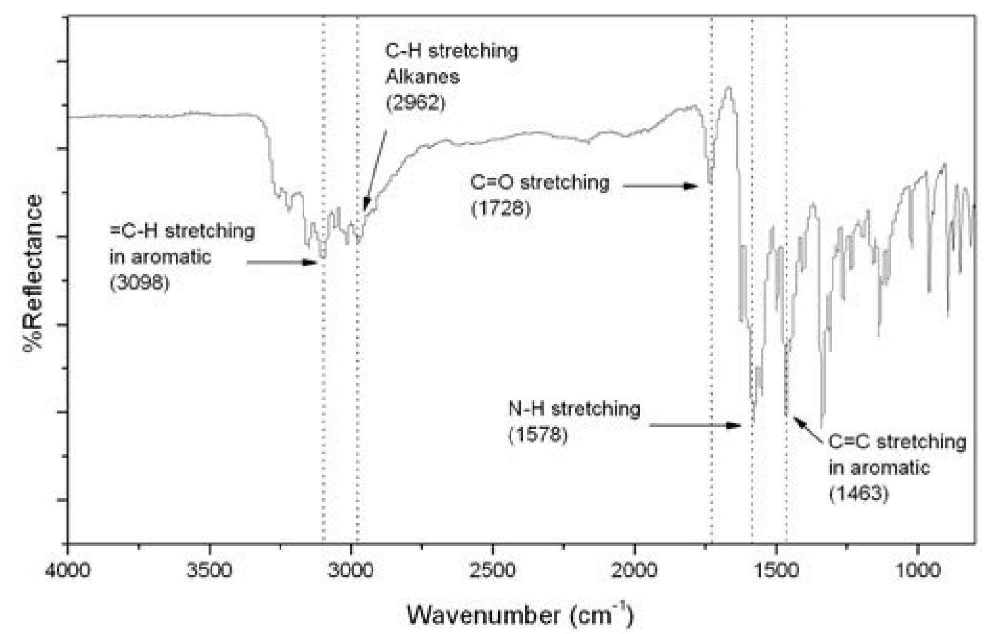


Figure 4.3 ATR-FTIR spectrum of magenta pigment.

In the case of yellow-pigment as in Figure 4.4, the ATR-FTIR spectrum shows various peaks, at 3127, 1672, 1650, 1507 and 1250 cm^{-1}, representing, =C-H stretching in aromatic, C=O stretching, N-H bending in amide, N-O stretching and C-O-C, respectively. All fingerprint peaks are similar to those for C.I. yellow 74 pigment, as in monoazo pigment. This pigment type is the most widely used as yellow pigment [Cabot, 2012; Momin, 2008].

Figure 4.5 shows ATR-FTIR spectrum of black pigment. From the literature [Cabot, 2012; Lichtenberger, 2004], they reported that black ink always made by the carbon black. Figure 4.6 shows that the spectrum of black-pigment is carbon black spectrum [Shimadzu, 2012]. Therefore, the black pigment in this research may be produced by carbon black.

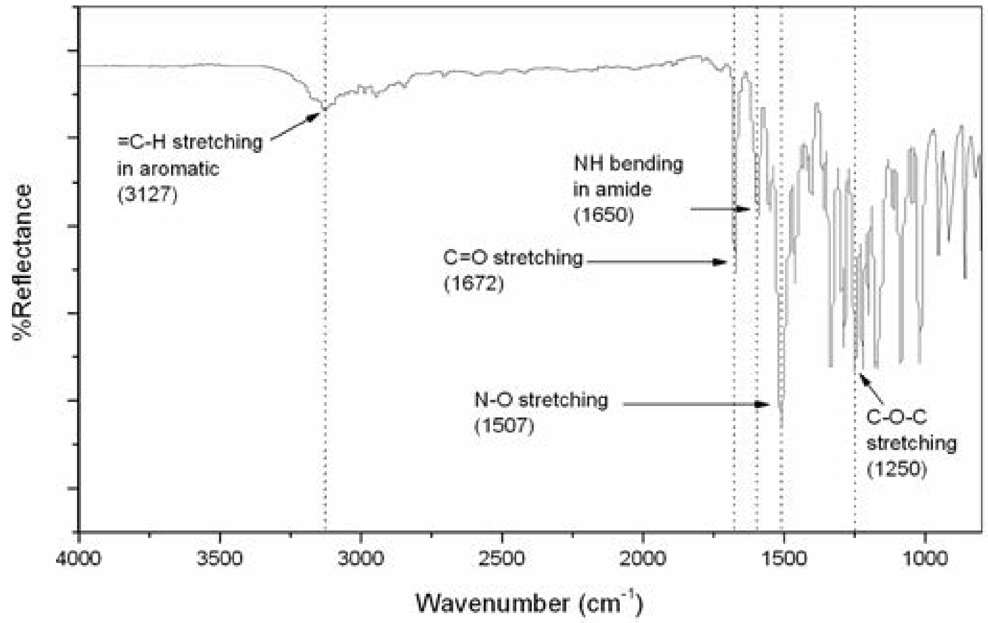


Figure 4.4 ATR-FTIR spectrum of yellow pigment.

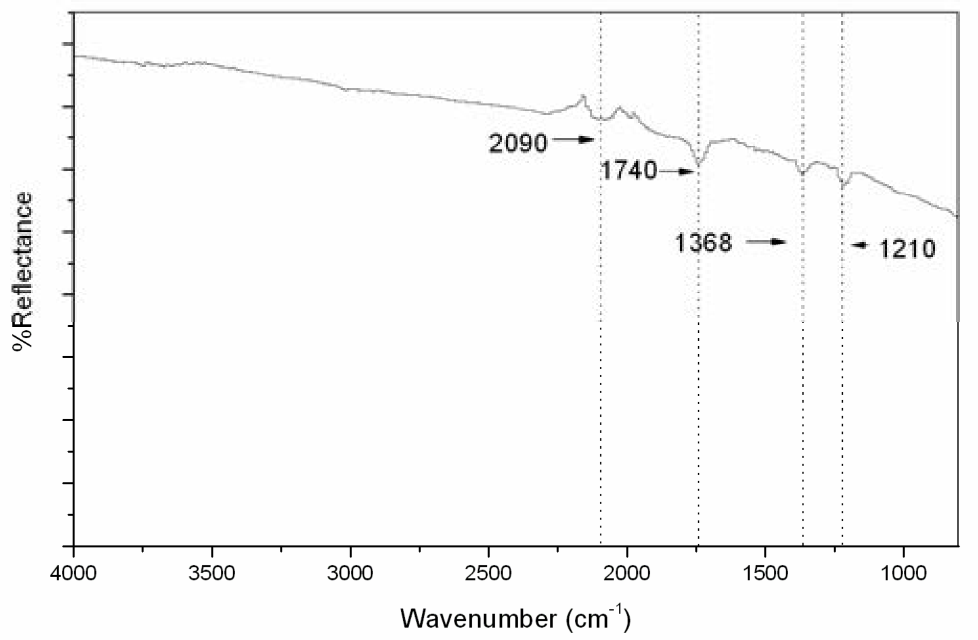


Figure 4.5 ATR-FTIR spectrum of black pigment.

CHAPTER V

COTTON FABRICS

5.1 Effect of plasma treatment on fabrics.

5.1.1 Wettability of fabric

5.1.1.1 Contact angle

The wettability modification of plasma modified cotton fabric surface was investigated by contact angle measurement. The contact angle of water and CH_2I_2 droplet on cotton fabric for different treatment time, working power and operating pressure of plasma treatment is shown in Table 5.1. The initial contact angles of untreated fabric are 77˚ and 25˚ for water and diiodomethane (CH_2I_2) as a test liquid, respectively. The contact angle of the both test liquid decreased after O_2 and N_2 plasma treatment while increased after treated with SF_6 plasma. The experimental results of decreasing contact angle of treated O_2 and N_2 plasma fabric by operating pressure and increasing exposure time are shown in Table 5.1. The result agreed agreement with Pandiyarai and Selvarajan [2008] study which reported the contact angle of water and glycerol of cotton fabric treated with air plasma decreased at increasing exposure time. On the other hand, when increase working power, the contact angle of treated fabric with N_2 plasma slightly increased. For the SF_6 plasma treatment, the contact angle of both test liquid increased when increased power and pressure conditions.

Decreasing contact angle suggested the formation of polar groups on the plasma treated surface which increase the hydrophilic property. For the SF_6 plasma treatment, it has effect to increase the contact angle, then result to hydrophobic property.

Table 5.1 Contact angles of the untreated and plasma treated-cotton fabrics

Condition			Contact angle (˚)					
Power (watt)	Pressure (torr)	Time (min)	O_2 plasma		N_2 plasma		SF_6 plasma	
			H_2O	CH_2I_2	H_2O	CH_2I_2	H_2O	CH_2I_2
Untreated fabric			77	25	77	25	77	25
50	0.5	0.5	53	0	64	20	113	95
50	0.5	5	0	0	33	30	138	125
50	0.5	10	0	0	29	0	138	119
50	0.5	20	0	0	27	0	134	118
50	0.5	5	0	0	33	30	138	125
100	0.5	5	0	0	52	0	133	135
150	0.5	5	0	0	52	30	130	120
50	0.1	5	0	0	50	28	125	114
50	0.5	5	0	0	33	30	138	125
50	1	5	0	0	0	0	126	125

The number of replication = 3

5.1.1.2 Surface energy

Using contact angle and Owen-Wendt geometric equation (2.1), the total surface energy (γ_s), dispersion component (γ_s^d) and polar component (γ_s^p) of untreated and treated fabrics were calculated and are shown in Table 5.2

It can be seen from Table 5.2 that the untreated cotton fabric has a relatively low polar contribution component of surface energy 6.4 mNm^{-1}. The total surface energy of untreated fabric is 46.61 mNm^{-1}. The literature [Pandiyarai and Selvarajan, 2008] reported that good wettability is obtained when the value of polar component is high. Therefore, the untreated cotton had low wettability. After O_2 and N_2 plasma treatments, the polar component was increased and the total surface energy was also increased. The surface energy of fabric treated with O_2 and N_2 plasma as a function of the plasma treating time and operating pressure. The surface energy was increased from 46.41 mNm^{-1} to 73.65 mNm^{-1} after treated with O_2 plasma 50 watt, 0.5 torr for 5 min. After such treatment 0˚ contact angle of both testing liquid were observed. From the result, the high surface energy fabric provides high hydrophilicity. The phenomenon was due to that surface energy of fabric was higher than surface tension of liquid [Shishoo, 2008] (72.8 mNm^{-1} for water and 50.8 mNm^{-1} for CH_2I_2).

SF_6 plasma treatment effected to low surface energy. The surface energy decreased to 2.02 mNm^{-1} after treated with SF_6 plasma for 5 min, 50 watt, 0.5 tor. The low surface energy is related to hydrophobicity. Yang et al. [2009] reported that the properties such as wettability, printability, adhesion, etc. depend on the surface energy. High surface energy leads to high wettability. The high surface energy was due to the incorporation of polar group by plasma treatment which leads more hydrophilicty on surface. Accordingly, the low surface energy lead to hydrophobicity. The functional groups of fabric induced by plasma process that has affected the surface energy will be discussed in our XPS analysis section (Topic 5.2).

Table 5.2 Surface energies of cotton fabric at various plasma conditions

Conditions			Surface energy (mNm^{-1})								
			O_2 plasma			N_2 plasma			SF_6 plasma		
Power (watt)	Pressure (torr)	Time (min)	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s
Untreated			40.01	6.4	46.41	40.01	6.4	46.41	40.01	6.4	46.41
50	0.5	0.5	38.56	16.84	55.4	39.39	10.37	49.76	16.64	2.34	18.98
50	0.5	5	29.7	43.95	73.65	26.42	36.12	62.54	2.22	0.12	2.34
50	0.5	10	29.7	43.95	73.65	32.55	34.11	66.66	3.49	0.01	3.50
50	0.5	20	29.7	43.95	73.65	32.26	35.4	67.66	3.53	0.11	3.64
50	0.5	5	29.7	43.95	73.65	26.42	36.12	62.54	2.22	0.12	2.34
100	0.5	5	29.7	43.95	73.65	38.56	17.64	56.2	0.59	0.56	1.15
150	0.5	5	29.7	43.95	73.65	31.34	21.16	52.5	2.69	0.56	3.25
50	0.1	5	29.7	43.95	73.65	31.47	22.28	53.75	3.88	4.76	8.64
50	0.5	5	29.7	43.95	73.65	26.42	36.12	62.54	2.22	0.12	2.34
50	1	5	29.7	43.95	73.65	29.7	43.95	73.65	1.37	2.02	3.39

5.1.1.3 Wicking test

With O_2 plasma treatments, the fabrics exhibited 0° contact angle when treated for longer than 5 min and the surface energy of those conditions were not different (73.65 mNm^{-1}). Consequently, wicking test or capillary rise method will be an alternative method to demonstrate the wettability of O_2 plasma treatment. Wicking test results of untreated and treated cotton fabrics according to DIN53924 method are illustrated in Figures 5.1 (a) and 5.2 (b). It is shown that the vertical wicking height of untreated fabric was 6.7 cm. When fabric treated with plasma, the wicking rate was changed. The study of the different operating condition (exposure time and working power), the wicking rate decreased when increased the treating time as shown in Figure 5.1(a). The highest wicking rate was at treating time of 5 min. For different operating RF power as shown in Figure 5.1(b), cotton fabrics treated with 50 watt have the highest vertical wicking. When working power was higher than 50 watt, the wicking rate would be decreased. It might be related to decrease the hydrophilic property. These results were described by the effect of plasma on the surface. The changing of hydrophilic property will be discussed in next XPS analysis section (Topic 5.1.2)

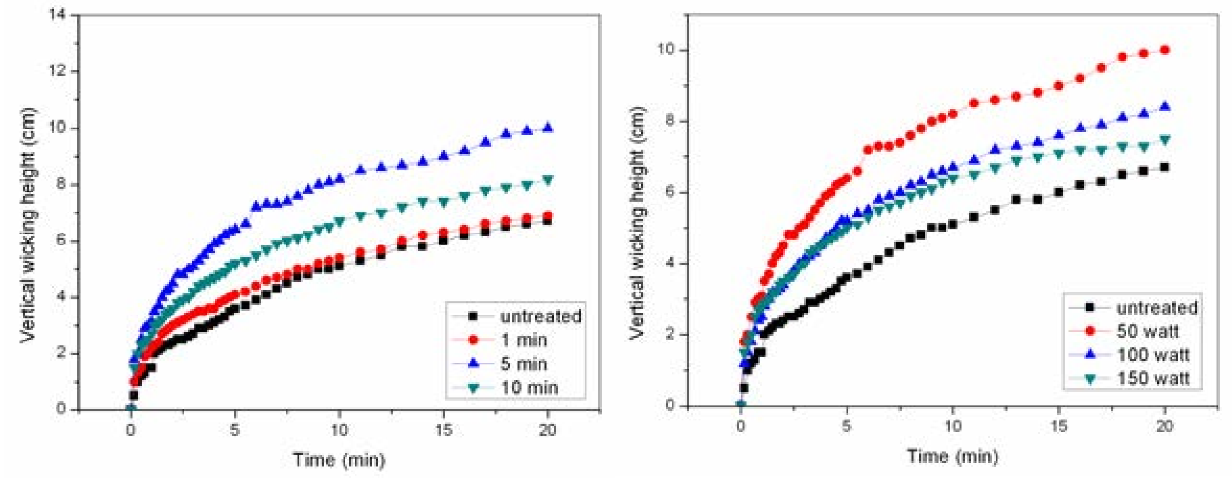


Figure 5.1 The vertical wicking of cotton fabric treated with O_2 plasma at the various (a) exposure times and (b) working powers

5.1.2 Functional groups of fabric surface

Changing of chemical composition of the cotton surface that affect to wettability and surface energy were analyzed by XPS. Figure 5.2 shows the survey spectra of the cotton fibers by O_2, N_2 and SF_6 plasma treatment. It shows that the untreated fabric exhibit two peaks of C1s and O1s. Both peaks are the main structure of the cotton and can be seen in all of cotton fabric after treating with plasma. The sample exhibited the N1s signal after treating with N_2 plasma. The distinct-F1s-peak has been detected on the spectrum of sample treating by SF_6 plasma. The high intensity of O1s peak can be observed after treated with O_2 plasma. The spectra indicate that these elements (nitrogen, oxygen, fluorine) incorporate on each fabric. From the results of contact angle and surface energy (sections 5.1.1 and 5.1.2) are relative to the type of gas plasma. For example, O_2 and N_2 plasma producing polar groups in cotton surface would contributed to an increasing of hydrophilicity and surface energy, whereas fluorine producing non-polar groups on cotton surface would increase hydrophobicity and provide to low surface energy.

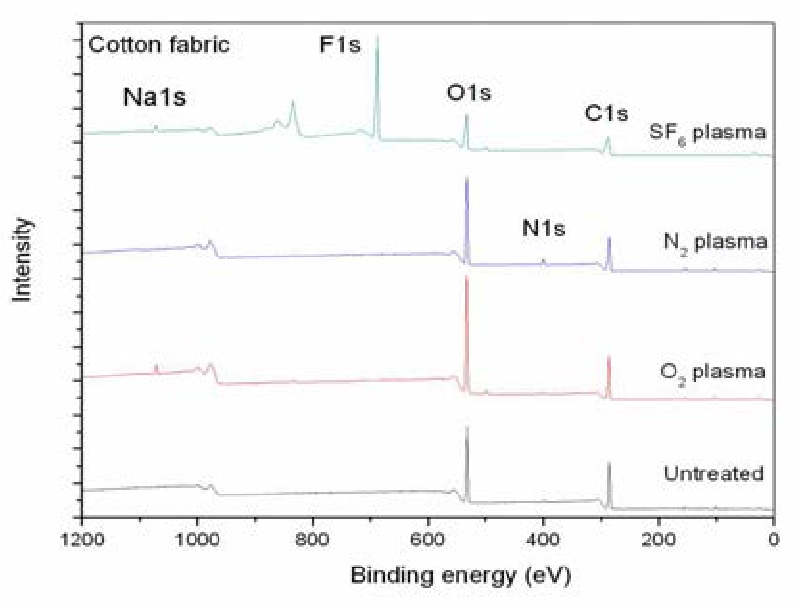


Figure 5.2 Survey spectra for untreated, O_2, N_2 and SF_6 plasma treated cotton fabric at RF treating power of 50 watt, operating pressure 0.5 torr and exposure time 5 min

The percentage summary of atomic concentration of various treating conditions is shown in Table 5.3. The results showed that fabrics treated with O_2 plasma have %O on surface increased from 31.3% (untreated fabric) to about 44% after treated with plasma at the operating condition of 0.5 torr of pressure, 50 watt of RF power, and 5 min of exposure time. Comparison with treated for 5 min, %O was slightly decreased when treated for the longer time exposure to 20 min. Fang [Fang et al., 2007] explained that at fixed input power but prolong exposure time, the dissociative reaction rate increased and led to further the increasing of high speed electron before reached the maximum. As treatment continued to the longer period, this reaction led to the saturation of plasma effect on fabric surface. Moreover, the %O also slightly decreased when increase in the RF power to 100 watt.

Table 5.3 Chemical composition by XPS analysis for untreated and treated fabric by O_2, N_2 and SF_6 plasma

Type of plasma	Condition			Elements on treated cotton fabric surface (%)				
	Power (watt)	Pressure (torr)	Time (min)	C	O	N	F	other
untreated				70.9	31.3	-	-	4.9
O_2	50	0.5	5	45.4	44.2	-	-	10.4
	50	0.5	20	53.5	41.0	-	-	9.1
	100	0.5	5	60.6	37.1	-	-	4.8
N_2	50	0.5	5	58.1	34.4	4.2	-	6.5
	50	0.5	20	56.2	37.6	4.8	-	1.4
	100	0.5	5	62.2	30.0	3.9	-	3.9
SF_6	50	0.5	5	42.3	18. 8	-	37.8	1.1
	50	0.5	20	42.5	18.1	-	38.7	1.1
	100	0.5	5	42.8	16.2	-	40.4	0.6

For N_2 plasma-treated fabric, nitrogen of about 4% can be detected after treated with the plasma at operating pressure of 0.5 torr, RF power of 50 watt, and treatment times of 5 min and 20 min. Also, %N slightly decreased when use high RF power (100 watt).

For cotton fabric treated with SF_6 plasma, the data report 38% of fluorine when treated at 50 watt power, 0.5 torr pressure, for 5 and 20 min. The results are agree well with the literature [McCord et al., 2010] that reported fluorine composition on fabric increasing with increasing CF_4 plasma exposure time. Furthermore, this result showed that %F is increasing after treated with high RF power.

From section 5.1.2, the high surface energy was due to the polar component of surface which was obtained by the incorporation of polar groups by plasma process [Yang et al., 2009]. Figure 5.3 shows the relation between element from N_2 plasma and surface energy. It can be observed in the similar treading. The result show that not only can plasma process improve %element on modified fabric by forming new functional groups, but it also leads to high wettability and surface energy improvement.

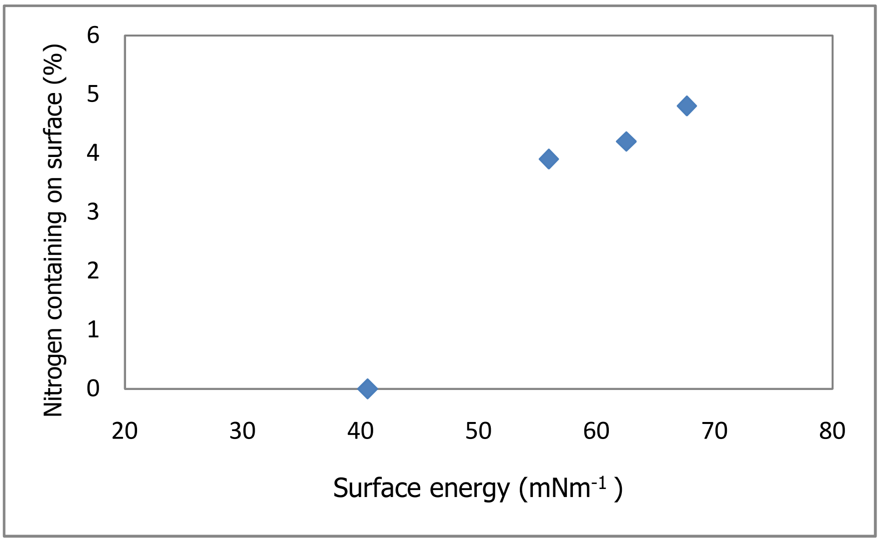


Figure 5.3 The relationship between N_2 containing percentage on fabric and the surface energy of fabric treated with N_2 plasma

To understanding the functional groups on fabric surface after treating with various plasmas, the deconvolution of C1s spectra were studied. The summaration of peak areas of C1s fitted curve which can predict the amount of functional groups by various conditions, are shown in Table 5.4.

From Table 5.4, the untreated cotton exhibits three functional groups which are cellulose structure (C-C or C-H, C-OH and O-C-O groups) as shown in section 2.5. For fabric treated with O_2 plasma for 5 min, 0.5 torr, and 50 watt, it shows four functional groups on the surface. When compare with untreated fabric, the C-C on the treated surface decreased while C-O/C-OH and O-C-O increased. Moreover the treated fabric showed new functional group of O-C=O on the surface. The result may be due to active species in plasma collide with the molecule on cotton surface and then C-C bonds on fiber surface are broken and finally, the radical species in plasma would interact with radicals on fabric. [Fang and Zhang, 2009; Hwang, 2003; Kamlangkla, 2010]. Thus, C-O and O-C-O is increased. As the exposure time increase to 20 min, results yields high amount of C-O and O-C-O but the percentage of O-C=O decreased. The results are related to the decrease in the O_2 concentration on cotton surface with increasing exposure time. This behavior suggests that chemical reaction would occur by chain scission. As working power increase to 100 watt, four functional groups are still observed. Compare between 50 watt and 100 watt, fabric treated at 100 watt, the functional groups of C-O, O-C-O and O=C-O was lower than that of one treated with 50 watt plasma. The wicking test of fabric treated at 100 watt was lower than at 50 watt. Hence, the result can be noted that in the fabric that has low polar groups, the wettbaility would be low.

Table 5.4 Percentage of the chemical groups present on the surface of untreated and plasma-treated cotton fabrics

Types of plasma	Condition (at pressure of 0.5 torr)		% of functional group								
	Power (watt)	Time (min)	C-C/C-H	C-O/C-OH	O-C-O/C=O	O=C-O	C-N	O=C-NH	C-F	C-F_2	C-F_3
Untreated			49.9	39.5	10.6	-	-	-	-	-	-
O_2	50	5	16.2	59	18.8	6	-	-	-	-	-
	50	20	18.3	57.3	19	5.3	-	-	-	-	-
	100	5	31.1	50.4	13.1	4.7	-	-	-	-	-
N_2	50	5	24.8	-	21.2	4.2	39.8	10.1	-	-	-
	50	20	22.7	-	24.7	4.3	39	9.2	-	-	-
	100	5	57.6	-	13.8	-	28.5	-	-	-	-
SF_6	50	5	13.8	34.6	12.6	-	-	-	16.5	16.7	5.9
	50	20	16.8	29.2	11.8	-	-	-	17.9	18	6.2
	100	5	15.4	27.8	10.7	-	-	-	20	18.3	7.8

In N_2 plasma treated fabric, the result show new functional group on the cotton surface. For the fabric treated with N_2 plasma at 50 watt, 0.5 torr and 5 min, XPS analysis indicate based functional group of cotton structure and two new functional group by plasma treatment, C-N bond and O=C-NH. This new functional group is in good agreement with literature reported [Pertile et al., 2010]. Pertile work reported that N_2 plasma can induces the incorporation of various chemical functionalities onto the polymer surface such as amine, imine, amide and nitrile on different materials.

For the cotton fabric treated at longer time of 20min, functional group was similar to one treated at a shorter time 5 min while the percentage of C-C, O-C=O, C-N and O=C-NH slightly decreased. For increasing power (100watt), XPS showed that O-C=NH and O-C=O disappeared from the treated surface. However, this result is relative to the decrease in N_2 concentration on cotton surface according to Table 5.3. It can be explained that a higher input power improved the plasma effect on surface [Fang at el., 2008]. Plasma has more effect of ion bombardment, resulting in chain scission as well the breakage of functional groups [Gogoi, 2011]. The polar groups (O-C=O and O=C-NH) was disappeared when increasing working power relate to the wettability and surface energy of fabric as described in the section 5.1.2. The fabric has low polar group, resulting to low surface energy and wettability.

In cotton treated with SF_6 plasma, there are six functional groups on surface which are based structure of cotton fabric (C-C, C-O and O-C-O) and new functional group from SF_6 plasma (CF, CF_2 and CF_3). The CF, CF_2 and CF_3 molecule result in hydrophobic property of fabric [McCord et al., 2002], resulting in fabric treated with SF_6 plasma providing high water contact angle and low surface energy. Compare between two exposure times (5 and 20 min), the percentage of CF, CF_2 and CF_3 of 20 min is higher than that of 5 min. The percentage of CF, CF_2 and CF_3 is relative to the increase in fluorine concentration on cotton surface according to Table 5.3. The fitted C1s spectrum of sample treated with increase working power show higher the peak area of CF, CF_2 and CF_3 than the fabric treated at 50 watt. The surface had high fluorine species. The XPS shows the result correlated well with the literature [Selli et al., 2001] which show that high of plasma power (100 watt) sample would have higher fluorine containing on the surface than one treated with low plasma power (50 watt).

From the results, O_2 and N_2 plasma treatment can produce new functional groups, such as C=O, O-C=O and C-N onto the fabric surface. The new functional group has an effect to improve hydrophilic properties and surface energy of cotton treated-fabric. The treated cotton can absorb water easier and faster which corresponds with wicking rate test. On the other hand, hydrophobicity of fabric is produced by fluorination of SF_6 plasma treatment, resulting in improvement of contact angle and lessens the surface energy.

5.1.3 Roughness surface

Plasma treatment has the effect on the change of morphology of material surface [Mather and Wardman, 2010; Shishoo, 2008]. The atomic force microscopy was used to measure the root mean square (RMS) surface roughness. The surface topography of untreated and treated cotton fibers at the condition of 0.5torr, 50 watt, and 5 min are shown in Figure 5.4. After plasma treatment, the RMS roughness of cotton increased from 6.9 to 16 nm. The RMS roughness of treating fabric by N_2 plasma is 7.695 nm, O_2 plasma is 11.153 nm, and SF_6 plasma is 16.431 nm after treated at the plasma condition of 50 watt, 0.5 torr for 50 min. The rough surface of treated fabric occurred by etching process [Poletti et al., 2003]. Moreover, Table 5.5 revealed that RMS of fabric increased with increasing exposure time. The surfaces have much more roughness. Rough surface may be due to the etching process continues to the longer period.

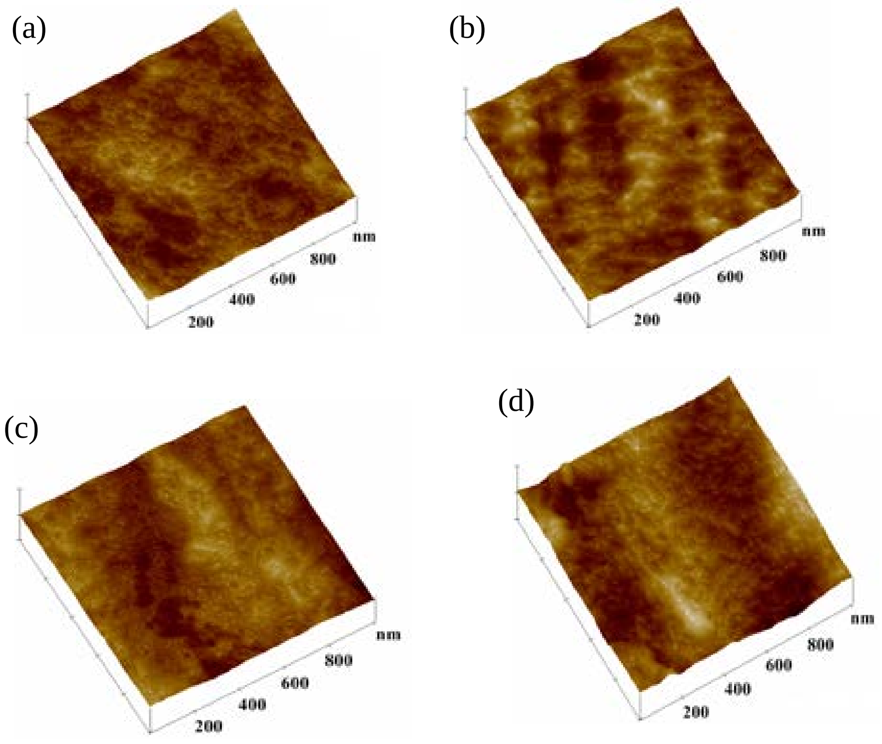


Figure 5.4 AFM images of untreated cotton fabric (a) and after treated with (b) O_2 plasma, (c) N_2 plasma and (d) SF_6 plasma treatment at the condition of 0.5 torr, 50 watt, and 5 min

Table 5.5 The RMS surface roughness of cotton fabric treated at the condition of 50 watt 0.5 torr for studied exposure time.

Treatment time (min)	Root mean square (nm)	
	O_2 plasma	N_2 plasma
Untreated	6.93	6.93
5	11.53	7.62
20	14.07	7.95

The cotton morphology was investigated by SEM. The result shows that the untreated cotton has a little wrinkle on the surface and the fiber like ribbon. For cotton fabric treated with plasma, the feature of cotton textiles having a scratch-like and grooves is produced by etching effect by bombardment on surface fiber [Hwang, 2004] as shown in Figure 5.5. Comparing between all gases used in the experiment, N_2 plasma has a lower effect than other. The result related with the RMS value that AFM analyzed. The cotton surface treating by N_2 plasma is rather smooth and has little small grooves on the fiber surface while O_2 and SF_6 plasma have outstanding of the grooves. The surfaces of O_2 and N_2 plasma treatment change to rough surface. It may cause by etching process by bombarding with high energy species creates the grooves along the fibers. The roughening is increased the surface. The etching process continues to the longer period, the surfaces have much more roughness. It seems like the factor of plasma power, if the process used high power, the grooves will increase.

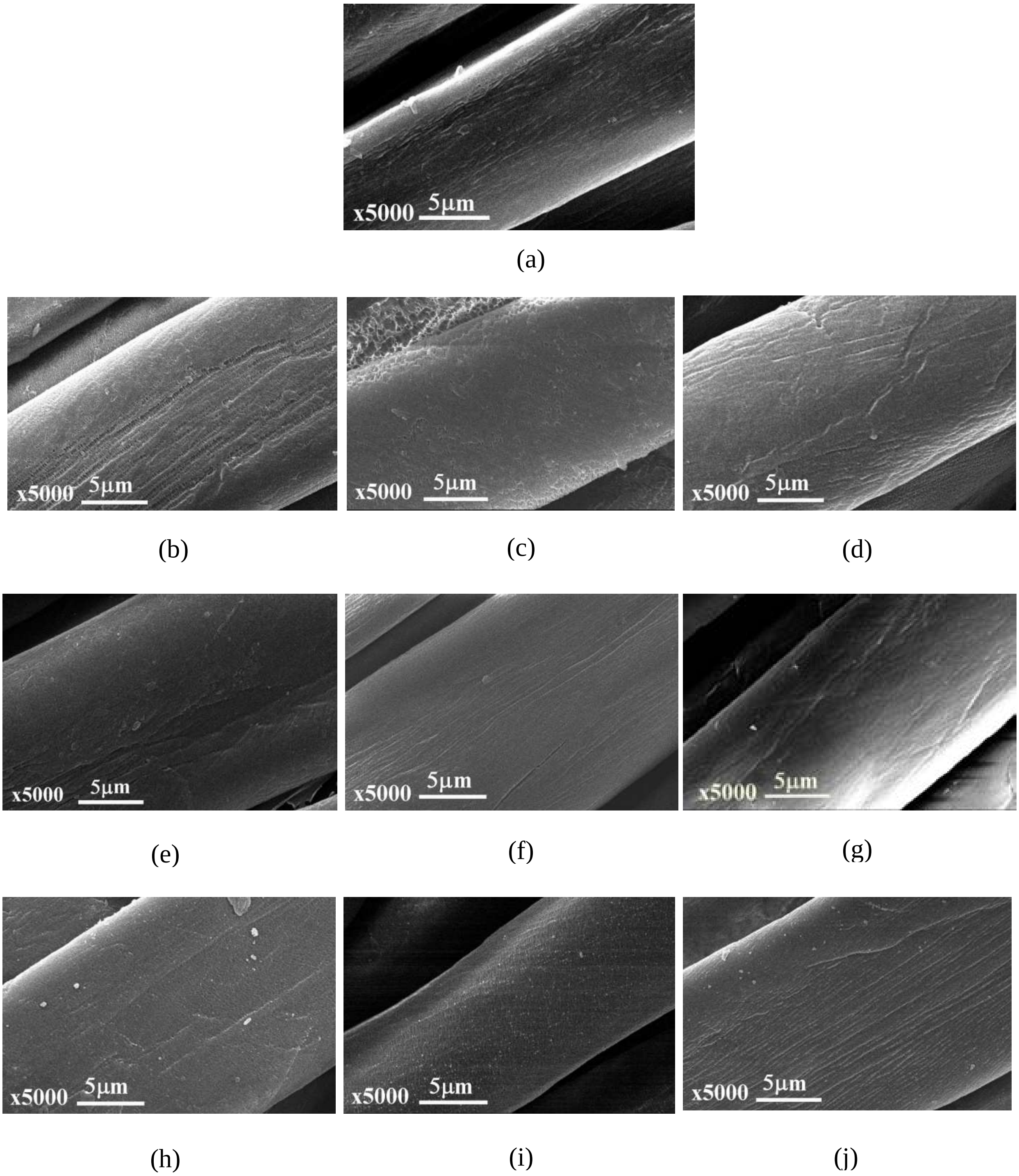


Figure 5.5 SEM photomicrographs of cotton fiber for (a) untreated fabric and treated fabric by (b) O_2 plasma at 50 watt, 0.5 torr for 5 min, (c) for 20 min, (d) at 100 watt, 5 min, 0.5 torr, (e) N_2 plasma at 50 watt, 0.5 torr for 5 min, (f) for 20 min, (g) at 100 watt, 5 min, 0.5 torr, (h) SF_6 plasma at 50 watt, 0.5 torr for 5 min, (i) for 20 min and (j) at 100 watt, 5 min, 0.5 torr

5.1.4 Tensile strength

Table 5.6 presents tensile properties of untreated cotton and plasma-treated fabrics according to the guidelines of ASTM D5035-95 (R2003). It could be seen that the tensile strength slightly increased after treating for a short period and then decreased after treating for long time. The untreated cotton fabric has a maximum tensile force of 283.1 N, while the N_2 plasma treated fabric with 5 min, 50 watt, and 1 torr has the highest maximum tensile force (339.2 N). This result is noticeable that the tensile force value increases after plasma treatment for short time, could be due to increasing in surface roughness after plasma treatment. It brings about increasing mechanical interlocking effect of fiber [Demir, 2010]. Hence, surface roughening by plasma process can increase fiber-to-fiber friction which results in the increase of tensile force [Hwang, 2004]. However, after long treating time or using high power, the tensile strength decreased because these conditions caused more etching effect. The fabric would be damaged.

Table 5.6 Tensile properties of cotton untreated and plasma treated fabrics

Conditions			Maximum tensile force (N)		
Power (watt)	Pressure (torr)	Time (min)	O_2 plasma	N_2 plasma	SF_6 plasma
Untreated			283.1	283.1	283.1
50	0.5	0.5	314.5	323.9	288.2
50	0.5	5	286.5	324.3	310.3
50	0.5	10	260.5	312.4	265.6
50	0.5	20	175.5	314.5	180.2
50	0.5	5	286.5	324.3	310.3
100	0.5	5	289.0	288.2	311.5
50	0.5	5	286.5	324.3	310.3
50	1	5	321.7	339.2	307.7

5.2 Effect of plasma treatment on printed cotton fabric

5.2.1 Effect of surface energy of fabric on ink absorption

After plasma treatment, the surface energy of fabrics was changed. The wettability and printability of fabric depend on surface energy [Pandiyaraj, 2008; Shishoo, 2008; Yang, 2009]. Ink can wet, absorb and adhesive on the substrate when the surface energy of substrate is higher than that of ink surface tension. Therefore, the relationship between surface and ink absorption of fabric is shown in Figure 5.6. It indicated that ink absorption of fabric increase with increasing surface energy. The O_2 plasma treatment could provide the highest ink absorption percentage while SF_6 plasma treatment provided the lowest. SF_6 plasma is poor to absorb ink because its surface energy is lower than surface tension of the inks (cyan is 26 mNm^{-1}, magenta is 32 mNm^{-1}, yellow is 30 mNm^{-1} and black is 28 mNm^{-1})

The ink absorption percentage was increased when the fabric had high surface energy. It was due to surface energy of fabric has the impact to fabric absorbed water-based ink. The results can infer that for fabric with high surface energy and hydrophilicity, the high water – based ink absorption would be observed.

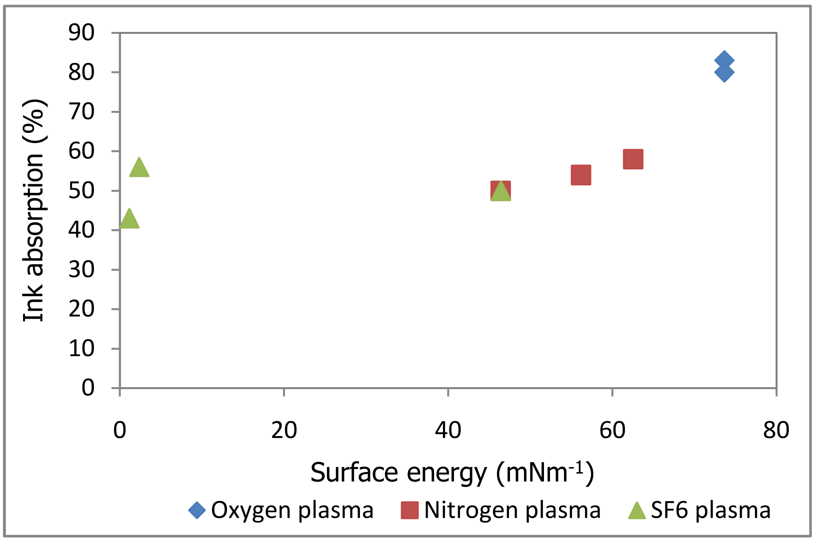


Figure 5.6 The relationship of surface energy and ink absorption of cotton printed fabric

5.2.2 Effect of surface energy of fabric on color strength

The fabric could absorb ink when it had high surface energy. Then the correlation of surface energy and color strength of printed fabric would be observed. The color strength of printed fabrics were characterized by color spectroscopy and shown in K/S value. Figure 5.7 show the relationship of surface energy and color strength (K/S) of fabric. It showed that printed fabric had high color strength when surface energy was improved. The highest color strength was obtained by O_2 plasma treatment which had the surface energy about 73 mNm^{-1}. The fabric treated with SF_6 plasma which was impact to hydrophobicity, had low color strength. It was due to fabric could not be wet and cannot absorb ink. Moreover, the surface energy was lower than surface tension of the printed-ink. Hence, SF_6 plasma treated fabric provided low color strength after printing.

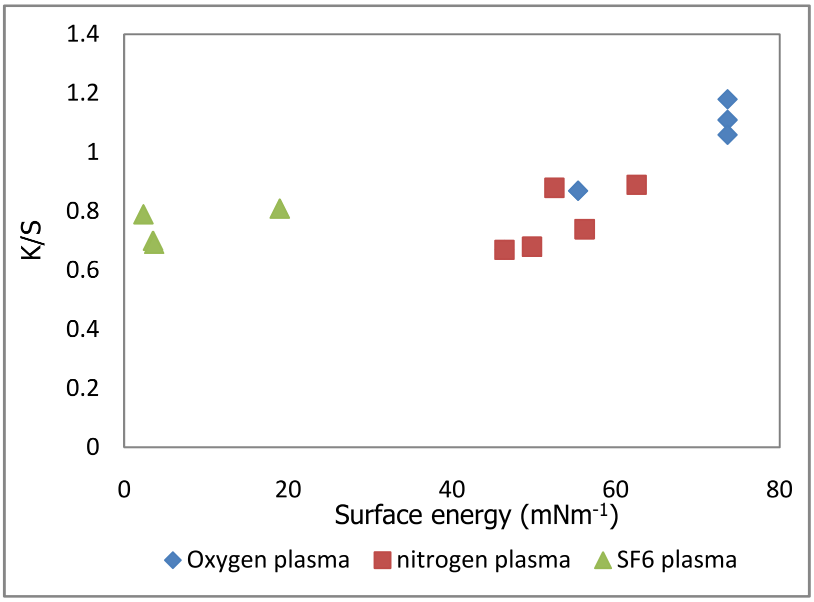


Figure 5.7 The correlation of surface energy and color strength of cotton printed fabric

From the results in section 5.1.1 and 5.1.2, it can imply that cotton fabric can get ink though the fabric and provide high color strength when the fabric has high surface energy. And the high surface energy was obtained by modified fabric with O_2 plasma and N_2 plasma. O_2 and N_2 plasma may provide the polar group on the fabric surface to improve hydrophilicity, resulting in an increase on polar component of surface energy. The functional groups of fabric after plasma treatment would be discussed in section 5.1.2 and then, the effect of functional group on printing properties will be addressed in next section.

5.2.3 Effect of functional groups by plasma treatment on ink absorption

From Table 5.7, considering the results between plasma treatment with various gases (condition at 0.5 torr, 50 watt, and 5 min) and %ink absorption, the plasma-treated surfaces have different functional groups. SF_6 plasma will yield the functional group of fluorine (CF, CF_2, and CF3) on the surface, and cause the fabric to become hydrophobic with low surface energy which show poor ink absorption. A value of %ink absorption in cotton treated with SF_6 plasma is not much different in comparison with the value of untreated cotton. In this work, the effects of plasma treatment with O_2 and N_2 gases on ink absorption were studied. These gases have an effect on fabric to wettability and surface energy, cause to %ink absorption increases.

By considering the functional group which comes from the effect of plasma with ink, the result of %ink absorption of untreated fabric with the functional group of cotton (C-C/C-H, C-O/O-C-O) has the %ink absorption depending on colors as cyan with 50%, magenta with 70%, yellow with 53% and black with 53% .

Table 5.7 The ink adsorption of untreated and treated cotton fabric

Plasma treatment	Ink absorption (%)			
	Cyan	Magenta	Yellow	Black
Untreated	50 ± 5	70 ± 5	53 ± 4	53 ± 3
O_2	83 ± 6	84 ± 4	89 ± 6	85 ± 6
N_2	81 ± 6	74 ± 10	83 ± 8	73 ± 2
SF_6	34 ± 4	51 ± 3	56 ± 5	49 ± 2

O_2 plasma

The oxygen content and %ink absorption of fabric treated with O_2 plasma were shown in Table 5.8. The surface had an increasing amount of oxygen when compare with the untreated fabric. A new oxygen functional group was found, O-C=O. In comparison of amount of functional group, the treated fabric had the group of C-O/C-OH and O-C-O/C=O higher than the untreated one, which leads to hydrophilicity of the fabric. The ink-absorbing percentage showed around 83, 84, 89 and 85% for cyan, magenta, yellow and black, respectively, after treated with the power of 50 watt, pressure of 0.5 torr, and treating time of 5 min. In comparison with different working power, at the ink absorption on fabric treated with 100 watt was lower than one treated at 50 watt. It may be due to the fabric treated with 50 watt had higher oxygen composition on surface than one treated with 100 watt plasma. The results can imply that cotton fabric had high oxygen containing which cause more hydrophilicity, then, fabric can absorb more water-base ink and the high ink absorption would be obtained.

Table 5.8 The ink adsorption of untreated and O_2 plasma-treated cotton fabric

RF power	O_2 containing on surface (%)	Ink absorption (%)			
		Cyan	Magenta	Yellow	Black
untreated	31.3	50 ± 5	70 ± 5	53 ± 4	53 ± 3
50 watt	44.2	83 ± 6	84 ± 4	89 ± 6	85 ± 6
100 watt	37.1	80 ± 5	80 ± 4	74 ± 5	68 ± 6

N_2 plasma

For the fabric treating with N_2 plasma, there was a new functional group on the surface. The modified fabric with 50 watt of power, 0.5 torr in pressure and both 5 and 20 min in treating time had C-N and O=C-NH forming on its surface. However, by XPS, O-C/C-H and O-C-O/C=O were also detected on the surface in case of the plasma treatment of with 5 min which has the highest amount of %C-N and O=C-NH. The %ink absorptions of this condition (as shown in Table 5.9) on each inks: cyan, magenta, yellow, and black, have percentage around 58, 74, 83 and 73, respectively. Between treating time of 5 and 20 min, the fabric treated for 5 min had higher ink adsorption than 20 min.

However, the fabric treated with N_2 plasma of 100 watt, 0.5 torr for 5 min did not show the same functional groups as mentioned above. The functional groups of C-N, O-C-O/C=O and C-C/C-H was detected by XPS while O=C-NH was not observed. By %ink absorptions of this condition, the percentages of cyan, magenta, yellow and black are 54, 73, 85, and 62%, respectively. A percentage ink absorption were lower than that of fabric treated at the condition of 50 watt in power, 0.5 torr of pressure, and 5 min of time which has the functional group of O=C-NH. This can be implied that %ink absorption depends on amount of polar groups of fabric. Then, the functional group of fabric treated with N_2 plasma at 100 watt, 0.5 torr and 5 min show low %ink absorption as seen in Table 5.9. This result implies that cotton fabric treated by N_2 plasma had polar group resulting in high ink absorption.

Table 5.9 The ink adsorption of untreated and N_2 plasma-treated cotton fabric

RF power	N_2 containing on surface (%)	Ink absorption (%)			
		Cyan	Magenta	Yellow	Black
untreated	0	50 ± 5	70 ± 5	53 ± 4	53 ± 3
50 watt	4.2	58 ± 6	74 ± 4	83 ± 6	73 ± 6
100 watt	3.9	54 ± 5	73 ± 8	85 ± 4	62 ± 4

5.2.4 Effect of functional groups by plasma treatment on color strength

The result of color strength (K/S) before and after plasma treatment (at condition of 0.5 torr, 50 watt, 5 min) are shown in Figure 5.8. The maximum K/S of all printed-colors obtained in cotton treated with O_2 plasma. Moreover, SF_6 plasma treatment presented the minimum K/S because fluorine has corporate on cotton surface that produce hydrophobicity and low surface energy.

Therefore, the effect of both N_2 plasma and O_2 plasma are taken into account for studying color strength because the both treatment provide K/S value more than untreated-printed fabric. The K/S value of untreated-printed fabric is 0.67, 1.81, 1.81 and 2.45 for cyan, magenta, yellow and black, respectively.

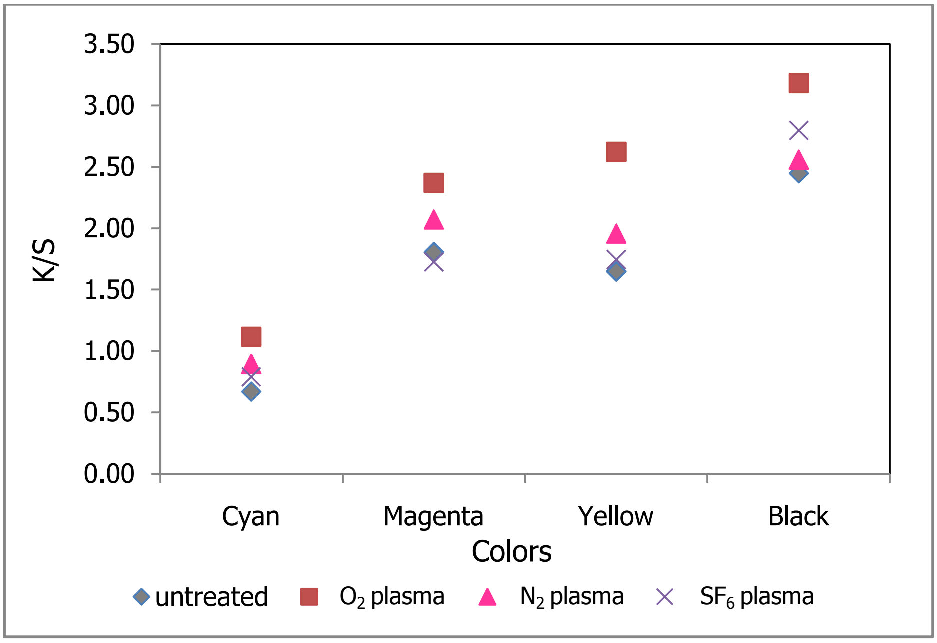


Figure 5.8 The color strength (K/S) of untreated and plasma-treated cotton fabrics that printed by water-based ink.

O_2 plasma

The fabric treated with O_2 plasma at 50 watt of power, 0.5 torr of pressure and 5 min for exposure time which has high polar groups on surface provide the higher K/S value than the untreated and N_2 plasma treated fabric. The treated fabric with O_2 plasma of this condition provide the value of color strength up to 65% with cyan, 31% with magenta, 58% with yellow and 29% with black. One can clearly see that O_2 plasma modification can improve the color yield of printing fabric at least 29% (as shown in Table 5.10).

For treatment at 100 watt of power, the fabric had similar functional groups as in 50 watt (O=C, O=C-O, C-O, C-C) but show different in oxygen containing percentage on surface. The treated fabric at the condition of 100 watt provide the value of color strength up to 54% with cyan, 23% with magenta, 37% with yellow and 21% with black when comparing with untreated fabric. The condition of 100 watt had lower K/S than 50 watt plasma. It may be due to low O_2 content on surface was observed at the power of 100 watt providing low hydrophilicity and also led to low color strength.

Table 5.10 The color strength (K/S) of untreated and O_2 plasma-treated cotton fabric

RF power	O_2 containing on surface (%)	Color strength			
		Cyan	Magenta	Yellow	Black
untreated	31.3	0.67 ± 0.04	1.81 ± 0.03	1.65 ± 0.02	2.45 ± 0.05
50 watt	44.2	1.11 ± 0.02	2.37 ± 0.03	2.62 ± 0.02	3.18 ± 0.04
100 watt	37.1	1.03 ± 0.03	2.22 ± 0.01	2.26 ± 0.02	2.97 ± 0.03

N_2 plasma

Color strength of printed fabric which modified by N_2 plasma, are shown in Table 5.11. For the fabric treated with 50 watt, 0.5 torr and 5 min show the new functional groups of O=C-NH and C-N on the surface. The fabric had higher K/S value than untreated fabric. The K/S values of cyan, magenta, yellow and black are 0.89, 2.07, 1.96 and 2.56, respectively. The N_2 plasma treated fabric with of this condition yields the printed fabric increase K/S value up to 33%, 14%, 18% and 4% for cyan, magenta, yellow and black, respectively.

The K/S value of 100 watt, 0.5 torr for 5min was 0.74, 1.81, 1.79 and 2.58 for cyan, magenta, yellow and black, respectively. The functional group of O=C-NH was not observed, confirmed by XPS. The color strength of treated fabric was higher than that of the untreated fabric in all colors, except the magenta. Moreover, the color strength of this condition is lower than the condition of 50 watt, 0.5 torr, 5 min which had more polar group on surface. The results can imply that the polar group can improve the color strength of printed fabric. The printed-treated fabric with 50 watt had higher color strength than 100 watt despite similar in %nitrogen containing on surface (about 4%). Nevertheless, the fabric treated with 50 watt had more polar group (O=C-NH) than 100 watt.

Table 5.11 The color strength (K/S) of untreated and N_2 plasma-treated cotton fabric

RF power	N_2 containing on surface (%)	Color strength			
		Cyan	Magenta	Yellow	Black
untreated	0	0.67 ± 0.04	1.81 ± 0.03	1.65 ± 0.02	2.45 ± 0.05
50 watt	4.2	0.89 ± 0.03	2.07 ± 0.02	1.96 ± 0.03	2.56 ± 0.03
100 watt	3.9	0.74 ± 0.04	1.81 ± 0.02	1.79 ± 0.01	2.58 ± 0.01

Figure 5.9 showed that fabric had high oxygen composition on surface which results in hydrophilicity and the improvement of the K/S. The results show the wettability is affected to color strength on printed fabric. The fabric treated with O_2 plasma whose posses the highest hydrophilicity always provides the highest K/S value while SF_6 whose posses highest hydrophobicity provides the lowest K/S value.

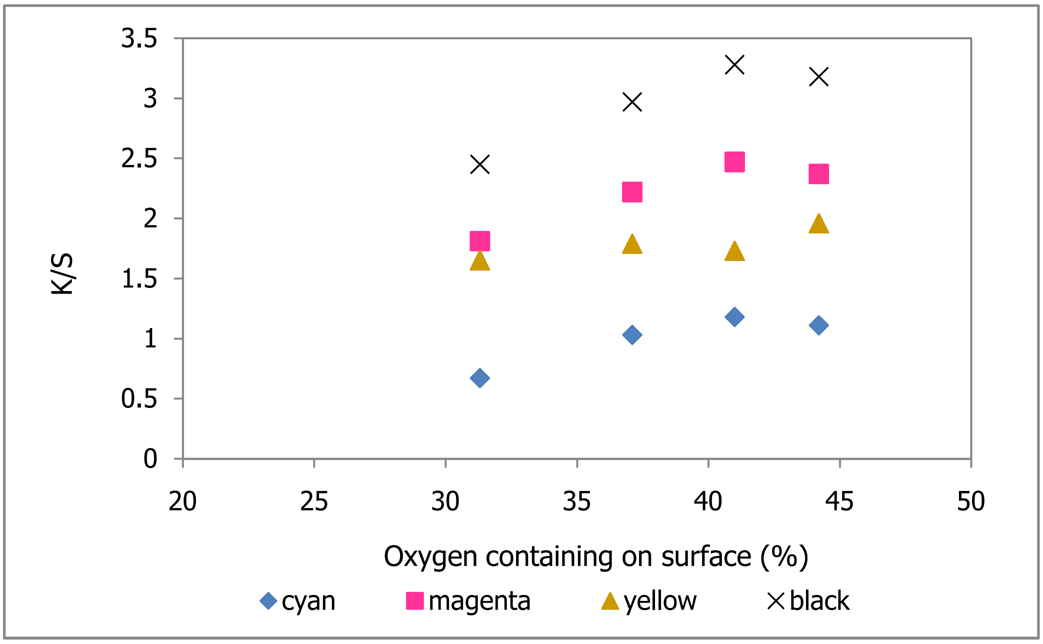


Figure 5.9 The relationship of color strength and oxygen containing on surface

Figure 5.10 also show the relationship of ink absorption and color strength of printed cotton fabric. It showed that when the percentage of ink absorption increased, the color strength was increased. It can be consider that cotton fabric had high color strength, leading to better ink absorption into the fabric.

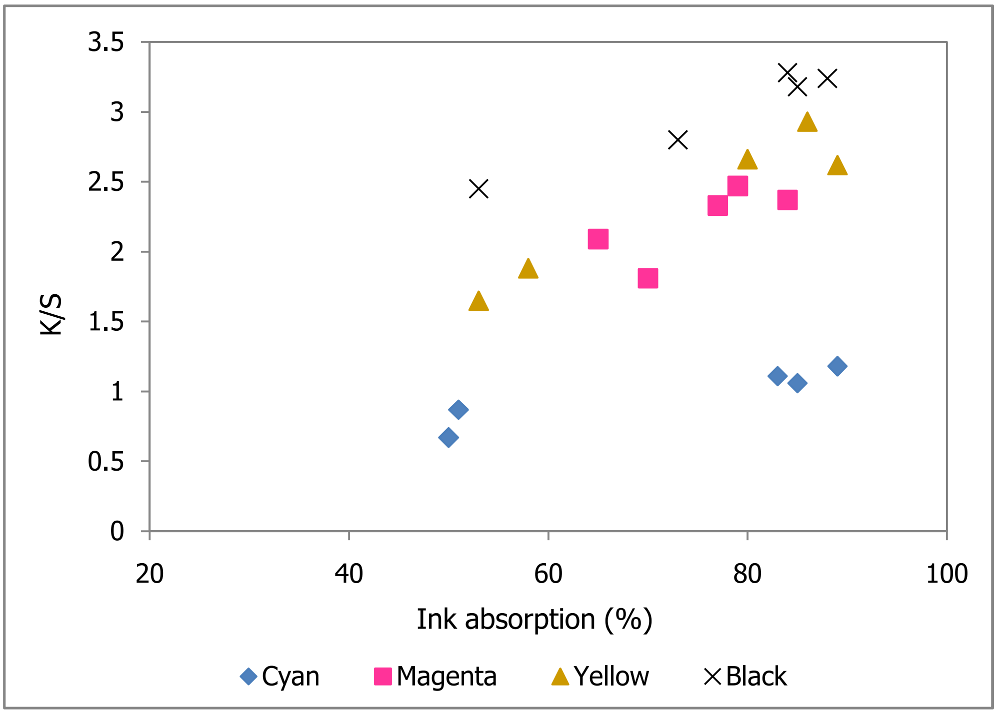


Figure 5.10 The correlation of ink absorption and color strength of printed- O_2 plasma-treated fabric

5.2.5 Effect of rough surface on color strength

The effect of roughness of printed fabric was studied. Table 5.12 show the K/S values of printed fabric treated with O_2 and SF_6 plasma at the condition of 0.5 torr, 50 watt, and 5 min. The comparison between color strength of fabrics treated with SF_6 plasma (RMS value of 16.4 nm) and fabric treated with O_2 plasma (RMS value of 11.5 nm) were observed. The color strength result showed that the K/S of SF_6 plasma was lower than that of fabric treated with O_2 plasma despite of the fact that SF_6 plasma provided high roughness on surface. This result can imply that the roughness is not the main factor to provide high color strength of printed cotton. The fabric had hydrophobic property which had low water contact angle and surface energy. The hydrophobicity could not facilitate the adsorption of water-based ink into fabric because of surface had lower surface energy than surface tension of ink. Then, ink did not contact and wet into fabric, leading to low color strength.

Table 5.12 The effect of roughness surface by plasma treatment on color strength

Plasma treatment	RMS (nm)	Contact angle (˚)	Color strength			
			Cyan	Magenta	Yellow	Black
untreated	6.9	77	0.67	1.81	1.65	2.45
O_2	11.5	0	11.1	2.37	2.62	3.18
SF_6	16.4	138	0.79	1.73	1.74	2.8

However, roughness may be the reason for providing capacity for fabric to contain ink. The result showed in Table 5.13. The fabric treated with O_2 plasma for 20 min which contain polar groups (C-O/C-OH and O=C-O) and oxygen containing on surface was lower than did of 5 min. However, the K/S value of treating at 20 min was higher than 5 min. The RMS value of plasma-treated-fabric for 20 min was about 14 nm while treating for 5 min was about 11 nm. The result caused by fabric treated with plasma for 20 min, had capacity for capture ink more than the other one. Hence, it can provide high color strength after printed with water-based ink. Thus, the improvement of color strength of cotton fabric not only depends on wettability but also on the roughness of surface.

Table 5.13 The effect of roughness surface after treated with O_2 plasma on color strength

Treating time (min)	RMS (nm)	O_2 on Surface (%)	Contact angle (˚)	Color strength			
				Cyan	Magenta	Yellow	Black
untreated	6.9	31.3	77	0.67	1.81	1.65	2.45
5	11.5	44	0	11.1	2.37	2.62	3.18
20	14.2	37	0	0.79	1.73	1.74	2.8

This result implies that the polar groups, hence wettability is the main factor to provide high color strength of printed cotton, which facilitates the adsorption of water-based ink into fabric. The roughness surface contributes as the supporter (not main reason) that provides capacity for fabric to contain ink.

5.2.6 Zeta potential

This research found zeta potential changed after plasma process. The zeta potential of material may improve printing property. The zeta potential of cotton fabric which characterized by zetasizer are shown in Table 5.14. The cotton fabric treated with O_2 and N_2 plasma has positive charge. The zeta potential of fabric are around 1.56 and 0.71 for O_2 and N_2 plasma, respectively. It is clear that O_2 and N_2 plasma has a dominant effect to cotton fabric. The zeta potential of all four inks show negative charge (cyan is -3.3 mV, magenta is -43.4 mV, yellow is -31.6 mV and black is -1.9 mV). As a result, the pigment and treated cotton could have electric charge for their interaction, may resulting in improving the color strength of fabric. Moreover, O_2 plasma provides higher positive potential than N_2 plasma. The cotton fabric treating with O_2 plasma has higher color strength than N_2 plasma treating. For SF_6 plasma, zeta potential is decreased after treatment, resulting in repulsing between charge of fabric and ink, and then it has low color strength.

Table 5.14 Zeta potential of materials

Types of materials	Zeta potential, ζ (mV)
Fabric	
- Untreated	-12.6
- O_2 plasma	1.6
- N_2 plasma	0.7
- SF_6 plasma	-17.5

5.2.7 Color gamut

Color gamut in CIE $L^*a^*b^*$ system were investigated to show a more complete color information. Figure 5.11 shows color gamut in term of the CIE a^*b^*. Among three color gamut, the O_2 plasma treated fabric gave the widest gamut followed by N_2 plasma treated fabric, SF_6 plasma treated fabric and untreated fabric, respectively. The O_2 plasma can produce more saturating in all shade color, orange, lemon magenta and cyan colors than that of the untreated fabric by about 5 units of color scales. N_2 plasma treated fabric show higher gamut area than that of untreated fabric but lower than that of O_2 plasma treatment. For the SF_6 plasma treatment, printed fabric did not show any different color gamut from untreated printing fabric.

However, plasma pretreatment can increase color performance of cotton fabrics. Fabric can get more ink and exhibits high color strength by pretreated with O_2 plasma. It was due to O_2 plasma modified surface fabric showed wettability and more roughness on the surface resulting in more capacities for ink absorption. Therefore, the penetration of pigment particles into fabric was increased. Moreover, it has electric charge interaction between ink and treated fabric. On the other hand, SF_6 plasma treatment induced hydrophobicity and did not have electric-charge interaction between ink and surface due to likeness of negative charge. Hence, an absorption performance of fabrics was decreased, and poorly color strength and color gamut.

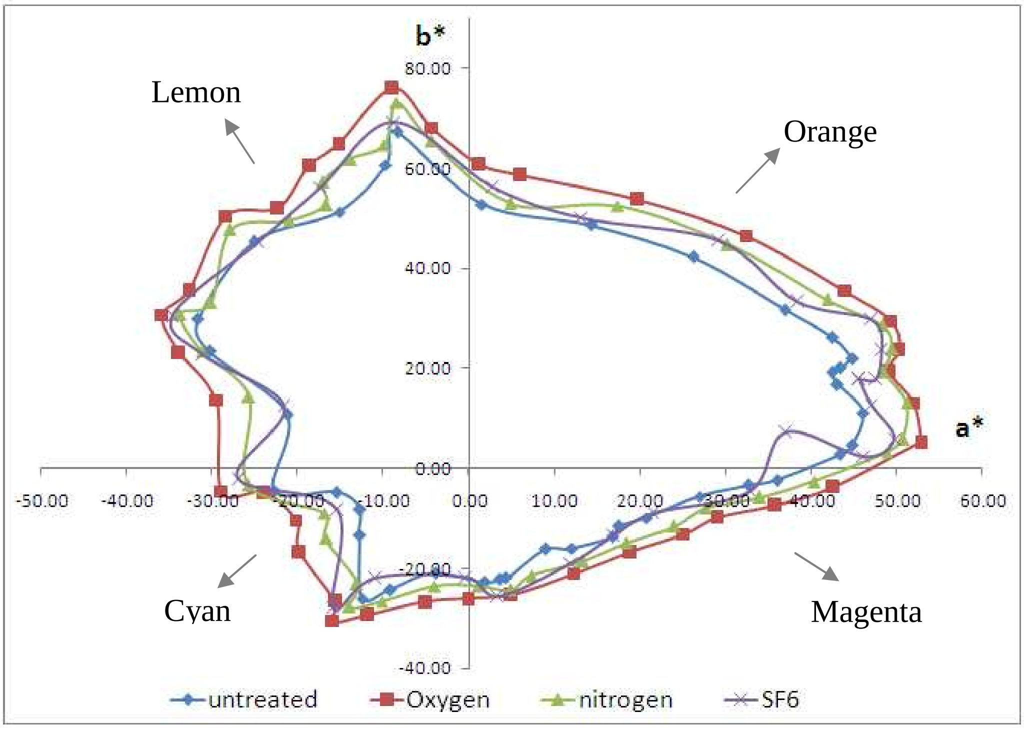


Figure 5.11 The color gamut of the printed PET fabrics as a^*b^*

5.2.8 Color fastness

Fastness for rubbing and washing of printed cotton fabrics based on ISO 105-X12: 2001 and 105-C06-1994, are given in Table 5.15. The results are based on the 5 rating system of 5 for no staining/color change, 4 for slightly staining/color change, 3 for noticeable staining/color change, 2 for considerable staining/color change and 1 for excessive staining/color change [Noppakundilograt et al., 2010]. The results of color fastness to rubbing showed that the color fastness of ink-jet printed cotton fabric with the plasma treatment were achieved resulting in improvement in the color fastness properties than the untreated one. Among all gases, O_2 and N_2 plasma pretreatment gave the high color fastness; the results show the level of 4 while untreated fabric showed level of 3 and 3-4 for SF_6 plasma treatment. It might be due to the ink being able to highly penetrate into the fiber and thus, the fastness for rubbing improves. However, the color fastness to washing is not good. It shows level

1 in color change. Result indicates that pigment and fiber interact with Van der Waal force. This is weak attractive force to pigment and fiber because of color on fabric was changed after testing. Moreover, the mechanical force by metallic ball in testing standard may be the reason of low wash fastness.

Table 5.15 Color fastness of printed cotton fabric

Types of plasma	Rub fastness on color staining		Wash fastness	
	Dry condition	Wet condition	Color change	Color staining
Untreated	3	1-2	1	4-5
O_2	4	2	1	4-5
N_2	4	2	1	4-5
SF_6	3-4	2	1	4-5

From this result of printed cotton, we conclude that wettability, surface energy, zeta potential and roughness of fabric is the effect to modify the printing color performance. In addition, the wettability by plasma process is the important factor for cotton fabric to improve the color printing performance. The result showed that O_2 plasma treatment can provide the highest color performance for cotton printing fabric.

CHAPTER VI

PET FABRICS

6.1 Effect of plasma treatment on PET fabrics.

6.1.1 Wettability of fabric

6.1.1.1 Contact angle

The plasma modification of PET fabric for wettability was illustrated by contact angle measurement. Water and diiodomathane (CH_2I_2) was used as the test liquid. The initial contact angles were 130˚ and 45˚ for water and CH_2I_2, respectively. The contact angle of the both test liquids decreased after O_2 and N_2 plasma. Then, the treated fabric could improve the surface wettability. However, the fabric treated with SF_6 plasma had the contact angle higher than that of untreated fabric. Table 6.1 shows the variation in the contact angle of PET fabric for different conditions and for two test liquids. The contact angles of fabrics treated with O_2 and N_2 plasma were considerably decreased as the function of plasma conditions. For fabric treated with O_2 plasma, the fabric shows complete wetting. The contact angle was zero when treated with treatment time for 5 min. It indicates that O_2 plasma caused the hydrophilicity on the fabrics which is in good agreement with the literature [Wei et al., 2007]. Wei reported on the effect of plasma treatment to wettability of fabric that the water contact angel was reduced when treated with O_2 plasma. Conversely, SF_6 plasma treatment caused the hydrophobicity. The contact angle of test liquids increased with increasing exposure time. The contact angle increased to 137˚ after a short exposure time (0.5 min) and increased to 156˚ at treated for longer period (20min). The SF_6 plasma-treated fabric showed non-wetting. It may be due to the function of non-polar groups by plasma species incorporation on the surface, resulting in hydrophobic property.

Table 6.1 Contact angles of the untreated and plasma treated-PET fabrics

Condition			Contact angle (°)					
Power (watt)	Pressure (torr)	Time (min)	O_2 plasma		N_2 plasma		SF_6 plasma	
			H_2O	CH_2I_2	H_2O	CH_2I_2	H_2O	CH_2I_2
Untreated fabric			130	45	130	20	130	45
50	0.5	0.5	44	0	126	8	137	85
50	0.5	5	0	0	33	0	146	115
50	0.5	10	0	0	14	0	153	120
50	0.5	20	0	0	2	0	156	110
50	0.5	5	0	0	33	0	150	115
100	0.5	5	0	0	32	0	141	116
150	0.5	5	0	0	0	0	145	120
50	0.1	5	0	0	40	0	135	110
50	0.5	5	0	0	33	0	150	115
50	1	5	0	0	0	0	138	133

The number of replication = 3

6.1.2.2 Surface energy

The surface energy of PET fabrics (γ_s) was calculated from the surface tension and contact angle of testing liquid in section 6.1.2.1. The results of total surface energy (γ_s), dispersion component (γ_s^d) and polar component (γ_s^p) of untreated and treated fabric were shown in Table 6.2.

Table 6.2 reveals that the surface energy of untreated PET fabric is 60.68 mNm^{-1} with sum of high dispersion component (52.27 mNm^{-1}) and low polar component (8.41 mNm^{-1}). However, the polar component was increased to 23.52 mNm^{-1} and dispersion component was decreased to 35.82 mNm^{-1} after treated with O_2 plasma for a short time (0.5 min). When fabric treated for the longer time, the polar component increased to 43.95 mNm^{-1} and the highest surface energy (73.65 mNm^{-1}) was obtained. For N_2 plasma treatment, it is clearly seen that the surface energy increased significantly with an increase in plasma treating time, working power and operating pressure. For the fabric treated with O_2 and N_2 plasma result, it is mainly due to the incorporation of polar groups such as OH, COO, CO, O=C-N on the surface [Deshmukh and Bhat, 2003]. It caused to hydrophilic property and complete wetting of fabric

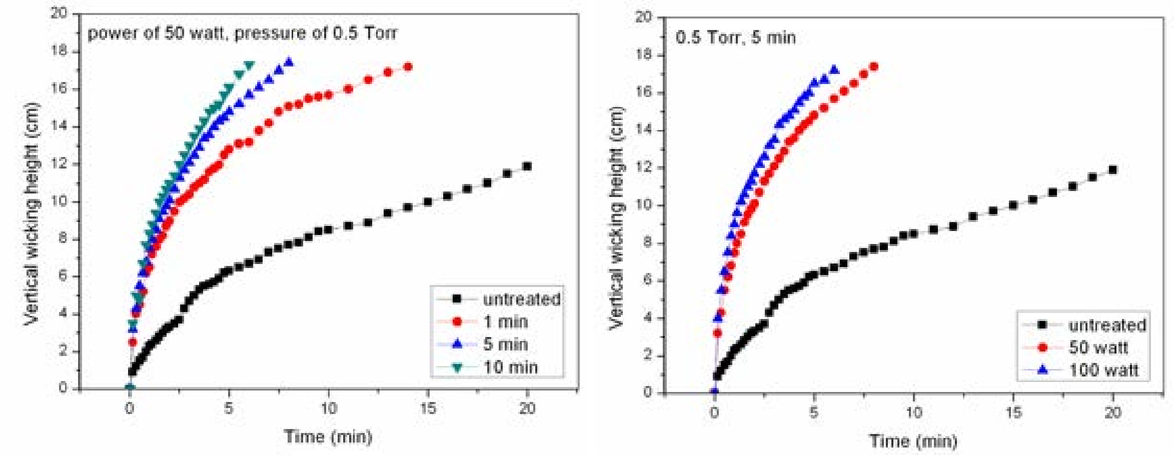
In the case of SF_6 plasma treatment, the result showed different from O_2 and N_2 plasma, like the contact angle (pervious section). The surface energy decreased after treating with SF_6 plasma and showed lower than that of surface tension of liquids, resulted to high contact angle and hydrophobic property [Kwok and Neumann, 2000]. It was due to SF_6 plasma introduced non-polar groups on surface.

Table 6.2 Surface energies of PET fabric at various plasma conditions

Conditions			Surface energy (mNm^{-1})								
			O_2 plasma			N_2 plasma			SF_6 plasma		
Power (watt)	Pressure (torr)	Time (min)	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s
Untreated			52.27	8.41	60.68	52.27	8.41	60.68	52.27	8.41	60.68
50	0.5	0.5	35.82	23.52	59.34	57.15	8.12	65.27	20.43	2.53	22.96
50	0.5	5	29.7	43.95	73.65	34.22	31.69	65.91	5.52	0.37	5.89
50	0.5	10	29.7	43.95	73.65	30.91	41.70	72.61	4.49	0.67	5.16
50	0.5	20	29.7	43.95	73.65	30.47	44.22	74.69	10.69	1.61	12.3
50	0.5	5	29.7	43.95	73.65	34.22	31.69	65.91	5.52	0.37	5.89
100	0.5	5	29.7	43.95	73.65	33.52	32.33	65.85	4.70	0.08	4.78
150	0.5	5	29.7	43.95	73.65	29.7	43.95	73.65	3.84	0.14	3.98
50	0.1	5	29.7	43.95	73.65	35.05	26.63	61.68	6.20	0.02	6.22
50	0.5	5	29.7	43.95	73.65	34.22	31.69	65.91	5.52	0.37	5.89
50	1	5	29.7	43.95	73.65	29.7	43.95	73.65	0.99	0.45	1.44

6.1.2.3 Wicking test

With O_2 plasma treatment, the fabrics exhibited low contact angle with zero. Therefore, wicking test would be an alternative method to demonstrate the wettability. Figures 6.1(a) and (b) show the effect of the O_2 plasma treated PET fabrics on the various exposure times and working power according to DIN53924 method. The results showed that the wicking rate increased with increasing exposure time and RF power. A high wicking rate was achieved for short time testing (1 min). Then, wicking test can be used for the alternative method for water contact angle. The result shows that PET fabric had more hydrophilicity when treating with long time and high power.



(a) (b)

Figure 6.1 The vertical wicking of PET fabric treated with O_2 plasma at the various (a) exposure times and (b) working powers

6.1.2 Functional groups of fabric surface

X-ray photoelectron spectroscopic (XPS) was chosen to analyze functional groups of PET fabric. Figure 6.2 shows survey spectrum for untreated and O_2, N_2 and SF_6 plasma treated PET fabric, respectively at the condition on the pressure of 0.5 torr, the RF power of 50 watt and the treatment time of 5 minutes. It is clearly seen that the peak of C1s and O1s is observed in all of spectra while N_2 plasma treatment shows N1s peak in the spectrum. For SF_6 plasma, F1s fluorine peak is shown in XPS spectrum. For O_2 plasma treatment, intensity of O1s peak is higher than that of all spectra. These results indicate that the incorporation of these elements in the treated fabrics. It implies that the introduction of oxygen and nitrogen containing polar groups on PET surface could contribute to increasing in the hydrophillicity [Pappas, 2006; Yang, 2009] and fluorine could contribute in the hydrophobicity. These results are related well with the wettability and surface energy of fabric as discussed above.

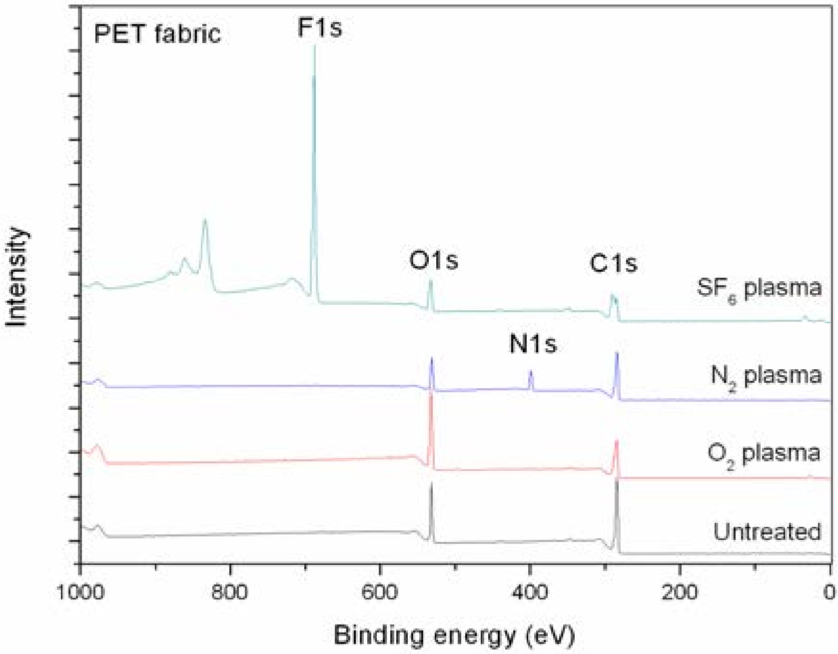


Figure 6.2 XPS survey spectrums for untreated, O_2, N_2 and SF_6 plasma treated cotton fabric at RF treating power of 50 watt, operating pressure 0.5 torr and exposure time 5 min

The summary of %atomic concentration is showed in Table 6.3. The results indicate that fabrics treated with O_2 plasma had accrue %O on surface and oxygen content increased with increasing the exposure times. In addition, %O increased when increasing the RF power to 100 watt (constant operating pressure and time at 0.5 torr and 5 min). Hence, %O on fabric surface increased when the treatment time or treatment power also increased. The result has the same tendency on previous work [Li et al., 2012] that oxygen content on treated surface (with He/O_2 plasma jet) increased with increasing exposure time from 20 - 50 sec. The summary of %F concentration of SF_6 plasma treatment is also shown in the Table 6.3. %F on surfaces treated by SF_6 plasma showed the same trending for O_2 plasma treatment. The concentration of fluorine on fabric surface increased when the treatment time or treatment power increased. However, PET fabric treated with N_2 plasma was different from both treatments. The nitrogen concentration after treating with N_2 plasma was slightly increased with increasing exposure time and decreasing RF power. Vesel reported that the changing nitrogen concentration may be due to the removal of the surface contamination and the incorporation of new species from plasma into the surface of the sample [Vesel, 2010].

Table 6.3 Chemical composition for fabrics treated by O_2, N_2 and SF_6 plasma

Type of plasma	Condition			Elements on treated cotton fabric surface (%)				
	Power (watt)	Pressure (torr)	Time (min)	C	O	N	F	other
untreated				79.6	19.7	-	-	0.7
O_2	50	0.5	5	64.6	34.5	-	-	0.9
	50	0.5	20	63.8	36.0	-	-	0.3
	100	0.5	5	64.2	35.2	-	-	0.6
N_2	50	0.5	5	71.7	13.9	14.5	-	0
	50	0.5	20	67.0	17.3	15.8	-	0
	100	0.5	5	70.9	27.8	6.9	-	0
SF_6	50	0.5	5	44.3	9.3	-	45.9	0.5
	50	0.5	20	43.6	9.2	-	46.9	0.5
	100	0.5	5	35.5	7.8	-	46.8	0

For understand the functional group on the sample surface, the deconvolutions of C1s were investigated and the peak area was calculated for the determination of the percentage of functional group by peak area. Table 6.4 shows a detailed C1s peak area as the percentage of functional groups for the untreated and plasma treated PET fabric.

Table 6.4 shows the untreated PET fabric had three different types of carbon atom in the structure. The XPS showed functional groups of carbon atom bond only carbon or hydrogen (C-C/C-H), carbon atom bonded to oxygen, C-O or C-OH and O=C-O bond. The three peaks are the structure of poly (ethylene terephthalate).

Table 6.4 Percentage of the chemical groups present on the surface of untreated and plasma-treated PET fabrics

Types of plasma	Condition (at pressure of 0.5 torr)		% of functional group								
	Power (watt)	Time (min)	C-C/C-H	C-O	O-C-O/C=O	O=C-O	C-N	O=C-NH	C-F	C-F_2	C-F_3
Untreated			57.4	33.6	-	9	-	-	-	-	-
O_2	50	5	43.7	31.9	24.4	-	-	-	-	-	-
	50	20	41.4	24.4	34.2	-	-	-	-	-	-
	100	5	27.4	42.2	20.7	9.8	-	-	-	-	-
N_2	50	5	48.8	-	32.8	-	18.4	-	-	-	-
	50	20	36.7	-	18.3	-	41.6	3.4	-	-	-
	100	5	61.5	-	16	-	22.5	-	-	-	-
SF_6	50	5	19.7	19.9	-	24.4	-	-	20.2	15	1
	50	20	13.3	17.3	-	25	-	-	20.5	17.5	6.4
	100	5	24.9	16.3	-	25.2	-	-	24.6	8.9	-

Table 6.4 shows the percentage of functional group of the O_2 plasma treated PET fabric. It reveals that fabric treated with O_2 plasma for 5 min, 0.5 torr and 50 watt demonstrated the percentage of C-C and C-O decreased and could not found O-C=O on the treated surface. However, XPS analysis found O-C-O/C=O on the treated surface. It may be due to active species would collide with the molecules on surface and then C-C bonds and C-O bonds in fiber surface are broken by the plasma treatment. The radical species in plasma would interact with radicals on fabric [Hwang, 2003; Fang, 2009]. An increase in the exposure time of treatment was also increased the concentration of oxygen, C-O and O-C-O/C=O could detected in high percentage. As improving treating power to 100 watt (5min, 0.5 torr), it can be found 9.8% of O-C=O. The percentage of C-O on treated surface increased while C-C and O-C-O decreased. It may be due to higher input power increased the number of high speed electrons in the plasma, then improved the plasma treatment effects [Fang, 2008].

For N_2 plasma treated fabric, the new chemical group of C-N was found on treated surface. For the condition of 5 min, 50 watt, 0.5 torr, XPS analysis found 18% of C-N on the treated surface. However, XPS also detect C-C and O-C-O/ C=O that were still shown in the fabric surface. As the treatment continued to a longer period, 20 min at treating power 50 watt and operating pressure 0.5 torr, the C-N increased and found news function group on the surface corresponding to O=C-NH. As improving treating power, 100 watt, it found three chemical group corresponding to C-C, C=O or O-C-O and C-N group. Comparing treating power of 50 watt with 100 watt, treating power of 100 watt was higher the C-C and C-N percentage than 50 watt while C=O/O-C-O was lower.

PET fabrics treated by SF_6 plasma show the new functional group similar to the cotton treated fabric. XPS found fluorine atom bond to carbon atom on the surface after treating with SF_6 plasma for all conditions. In the condition of 0.5 torr, 50 watt and 5min, XPS revealed six chemical groups on the surface which were the functional groups of PET (C-C, C-O, O and C=O) and new functional groups of CF, CF_2 and CF_3. It is possible that fluorine atoms are responsible for the surface chemical changes. To compare between two exposure time (5 and 20 min), the percentage of fluorine atom bonded to carbon (CF, CF_2 and CF_3) corresponding to treating time with 20 min is higher. The XPS of sample treated with SF_6 plasma at operating power of 100 watt, treating pressure of 0.5 torr and exposure time of 5 min has five chemical groups which are C-C, O-C-O/C=O, O-C=O, C-F and C-F_2 respectively. The percentage of C-F_2 was lower than treating with 50 watt while C-F is higher. This result same tendency to the literature [McCord et al., 2002], which reported that cotton fabric treated with CF_4 plasma at high power could not find CF_2 and CF_3 on the surface while fabric treated with lower power, CF, CF_2 and CF_3 can found. It is implied that fabric treated on high condition may be deteriorated to sample.

From the studies carried above, O_2 plasma and N_2 plasma treatment can produce new functional groups that are polar groups such as C-O, C=O, O-C=O and C-N onto the fabric surface. It improves hydrophilic properties, resulting in high surface energy. On the other hand, hydrophobicity of fabric is produced by fluorination of SF_6 plasma treatment due to the incorporation of reactive species of fluorine atoms on to the surface.

6.1.3 Roughness surface

AFM analysis was used to indicate the root mean square (RMS) surface roughness of fiber by plasma effect. RMS surface roughnesses of fibers (1.0 µm x 1.0µm area) are shown in Figure 6.3. The untreated fiber had relatively smooth surface. The RMS surface roughness of O_2, N_2 and SF_6 plasma treated fiber exhibited the roughness of surface increased after plasma treatment. The O_2 plasma and SF_6 plasma produced more surface roughness than that of N_2 plasma. This implied that O_2 and SF_6 plasma had a stronger etching effect. For a representation condition of 0.5 torr 50 watt 5 minute, the RMS surface roughness values increased from 0.55 nm for untreated fabric to 1.82, 3.37 and 3.23 nm after treating with N_2, O_2 and SF_6 plasma respectively. Table 6.5 showed RMS of fabrics increased with increasing working power. Kan and Yuen [2006] reported that the degree of etching will occur when altering parameter. Then the excited atom may occur when increasing working power, lead to high etching effect.

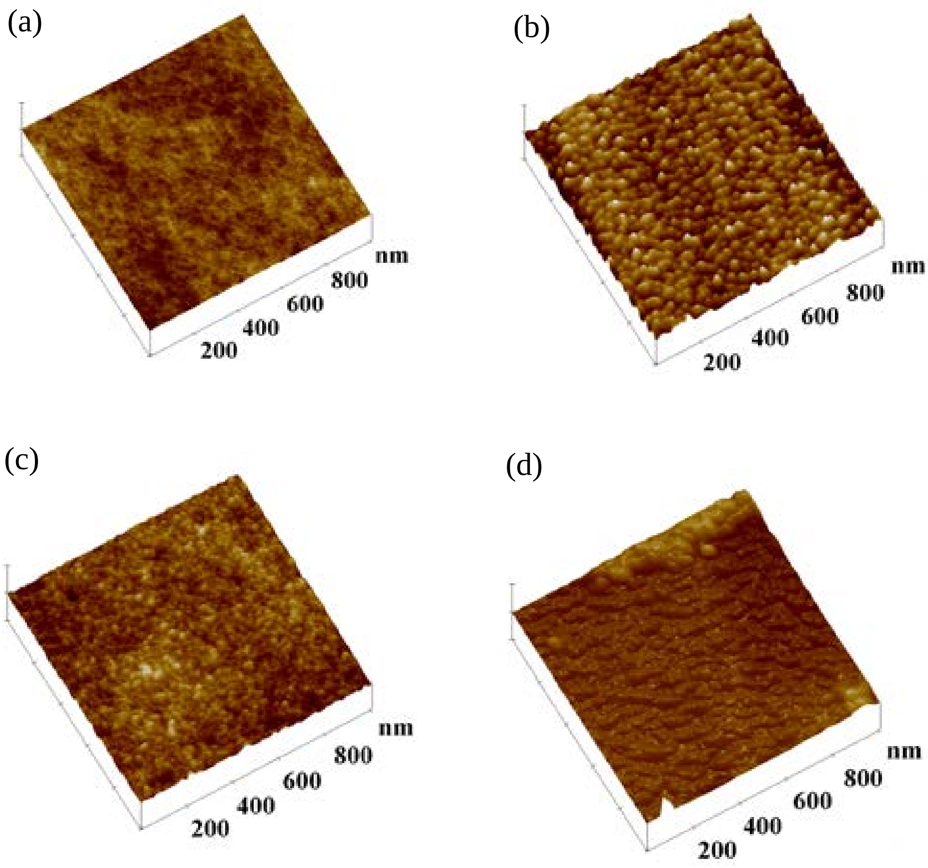
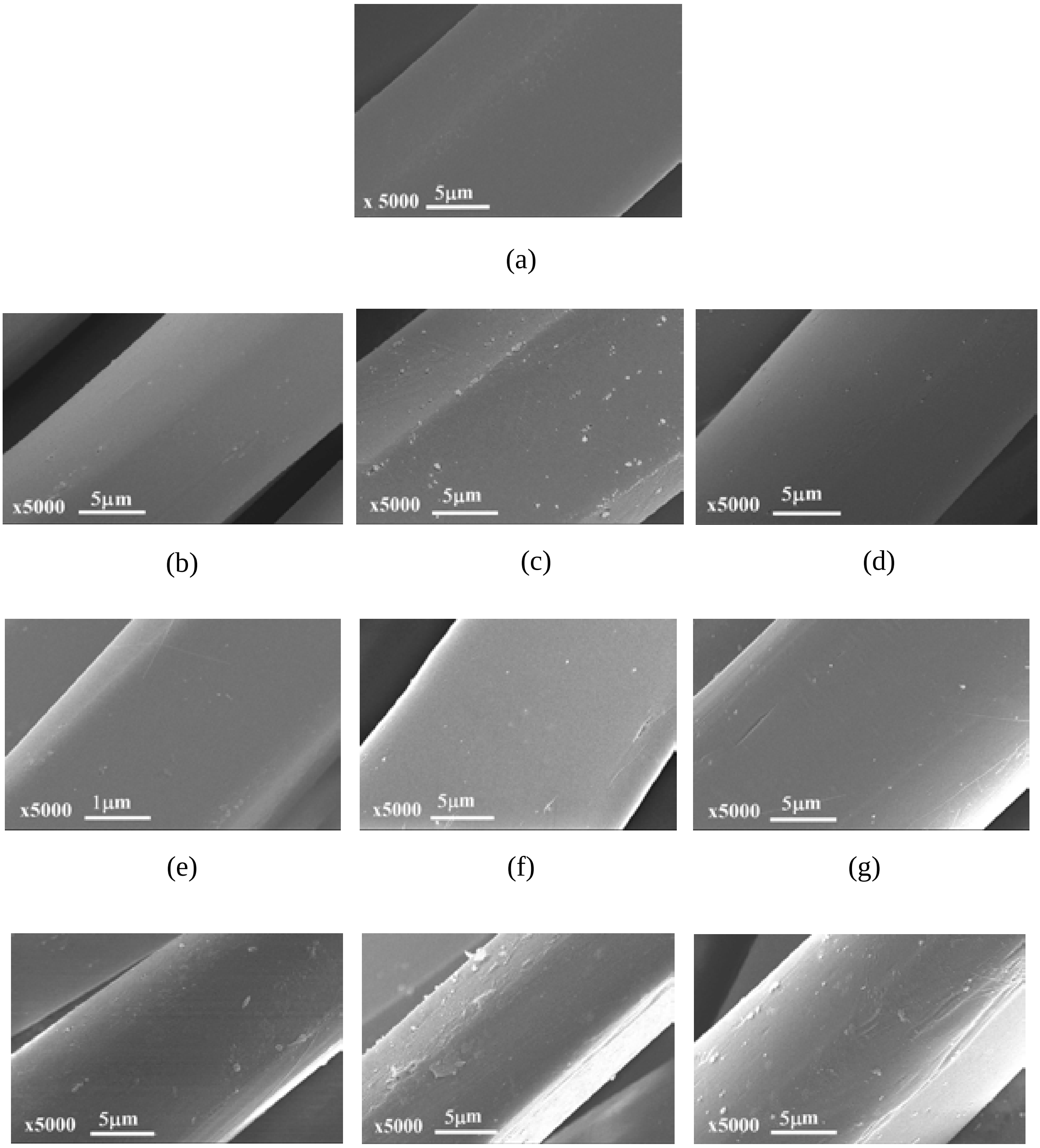


Figure 6.3 AFM images of untreated PET fabric (a) and after treated with (b) O_2 plasma, (c) N_2 plasma and (d) SF_6 plasma treatment at the condition of 0.5 torr, 50 watt, and 5 min

Table 6.5 The RMS surface roughness of PET fabric treated at the condition of 0.5 torr for 5 min

Working power (watt)	Root mean square (nm)		
	O_2 plasma	N_2 plasma	SF_6 plasma
Untreated	0.55	0.55	0.55
5	3.37	1.82	3.23
20	6.03	3.41	4.43

The SEM images as shown in Figures 6.4 (a)-(j) are observed to comprehend the changes of the untreated surface and the plasma treated surface of PET fiber. The untreated PET fiber exhibits a smooth surface as seen in Figure 6.4 (a) while fabric treated with plasma [Figures 6.4 (b) - (j)] shows the roughened surface. The roughness on surface was produced by bombardment with the plasma species [Wang and Qiu, 2012]. The rough surface consists of small grooves. Comparison with the different gases plasma, O_2 plasma produced more abrasion on the surface the same as SF_6 plasma and the both of gases have more abrasion on the surface than that of the N_2 plasma treatment. For the different operating condition, rough surface by plasma bombardment increased with increasing exposure time, operating power and pressure.



(a)

(b) (c) (d)

(e) (f) (g)

(h) (i) (j)

Figure 6.4 SEM images of PET fiber for (a) untreated fabric and treated fabric by (b) O_2 plasma at 50 watt, 0.5 torr for 5 min (c) for 20 min, (d) at 100 watt, 5 min, 0.5 torr, (e) N_2 plasma at 50 watt, 0.5 torr for 5 min, (f) for 20 min, (g) at 100 watt, 5 min, 0.5 torr, (h) SF_6 plasma at 50 watt, 0.5 torr for 5 min, (i) for 20 min and (j) at 100 watt, 5 min, 0.5 torr

6.1.4 Tensile strength

Tensile properties of PET untreated and plasma treated fabrics are presented in Table 6.6. It can report the mechanical changing properties on fabric after plasma treatment process. The maximum tensile force of untreated PET fabric was 582.3 N. When fabrics were treated by O_2 plasma, tensile force of PET fabric increased for short time, 0.5 min. For increasing power and pressure, tensile force trend to slightly increase. The increasing tensile force could be due to increasing in surface roughness after plasma treatment. It became increasing mechanical interlocking effect of fiber [Demir et al., 2010]. Hence, surface roughening by plasma process can increase the friction of interfiber which results in the increase of tensile force [Hwang, 2004]. For N_2 plasma, when increasing exposure time, the tensile strength also increase and reach to the maximum (5min) as treatment continued to a longer period, the tensile strengths were drop. Likewise with O_2 plasma, when an increase in power and pressure, the tensile force are increased. For SF_6 plasma, the greatest treating time that provides the highest tensile force was 20 min, tensile force was 669.6 N and increased as treating with higher power and pressure.

Table 6.6 Tensile properties of PET untreated and plasma treated fabrics

Conditions			Maximum tensile force (N)		
Power (watt)	Pressure (torr)	Time (min)	O_2 plasma	N_2 plasma	SF_6 plasma
Untreated			582.3	582.3	582.3
50	0.5	0.5	660.0	691.2	663.2
50	0.5	5	600.0	697.6	624.0
50	0.5	10	609.6	635.2	668.8
50	0.5	20	684.0	637.6	669.6
50	0.5	5	600.0	697.6	624.0
100	0.5	5	686.8	701.6	639.2
50	0.5	5	600.0	697.6	640.0
50	1	5	645.6	650.4	768.0

6.2 Effect of plasma treatment on printed PET fabric

6.2.1 Effect of surface energy of fabric on ink absorption

Plasma process had impact to wettability and surface energy of treated-surface that illustrated in previous topic (6.1). Literature [Kwok, 2000; Pandiyaraj, 2008; Shishoo, 2008; Yang, 2009] reported that wettability and printability of fabric are depending on surface energy. The liquid can be wet on surface when its surface tension is lower than surface energy of the surface. Then, the study of effect of surface energy on ink absorption of printed fabric was investigated. Figure 6.5 reveals PET fabric can absorb more ink when surface had high surface energy. Similar with cotton section, SF_6 plasma treatment provided the lowest ink absorption percentage of printed fabric while O_2 plasma treatment could provide the highest. It was due to the surface energy of O_2 plasma treatment is higher than surface tension of the inks and higher than other gas plasmas. Ink could wet on the surface and then penetrate into fabric because treated fabric had high wettability and surface energy. Thus, O_2 plasma treatment could provide the highest ink absorption.

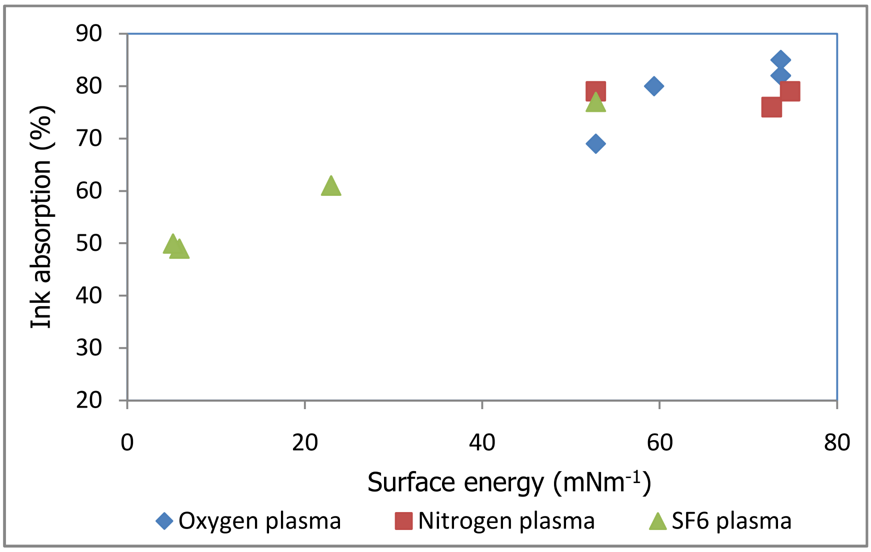


Figure 6.5 The effect of surface energy on ink absorption of cotton printed fabric

6.2.2 Effect of surface energy of fabric on color strength

Fabric treated with plasma is affected to surface energy. Furthermore, surface energy had effect on ink absorption, the percentage of ink absorption is the function of surface energy. Then, the correlation between surface energy on color strength of printed fabric is also studied. Figure 6.6 displays the relationship of surface energy and color strength (K/S). The results of printed-PET fabric are different the cotton section. It showed that the highest color strength of printed-PET fabric was obtained by treating with N_2 plasma. The highest of color strength was set by about the total surface energy of 66 mNm^{-1}. It may be considered that the high surface energy is impact to pigment and vehicle more penetrate into the fabric. Moreover, ink can be penetrated though the inter-yarn of fabric. Then, pigment can penetrate into fabric more than dried on the surface, resulting in low color strength.

However, the color strength of SF_6 plasma treated fabric is the lowest, like cotton section. This result may explain that fabric had lower surface energy than the surface tension of ink, leading the poor ink absorption. Hence, printed-fabric had poor color strength after SF_6 plasma treatment.

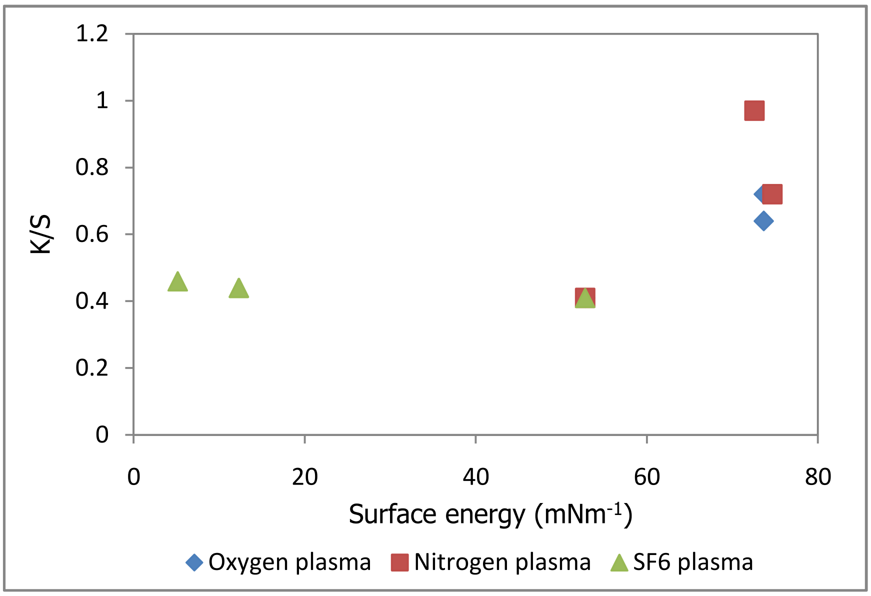


Figure 6.6 The correlation of surface energy and color strength of PET printed fabric

In the section 6.1.2, the functional group by plasma treatment had the impact to change wettability and surface energy of fabric. The plasma treatment can introduce the new functional groups onto the surface. O_2 and N_2 plasma provided the polar groups such as O=C-O, C=O and O-C=N on the fabric surface which improve hydrophilicity. Therefore, the effect of functional group on printing properties will be described

6.2.3 Effect of functional groups by plasma treatment on ink absorption

Table 6.7 shows some of the ink absorption percentage of the printed fabrics. It shows that O_2 and N_2 plasma could provide fabric to absorb ink more than untreated one while ink absorption of fabric treated with SF_6 plasma was not clearly different from untreated fabric. The ink absorption percentage sometime slightly increased after treated with SF_6 plasma (black ink). Considering the results, plasma was affected to the functional group of surface. Fabric treated with SF_6 plasma, had the fluorine functional group on surface. It caused fabric to become hydrophobic, resulting in poor ink absorption on fabric. For N_2 plasma and O_2 plasma, these gases increase polar group on fabric lead to hydrophilic surface. The percentage of ink adsorption became increasing. Therefore, the effect of O_2 plasma and N_2 plasma modification surface on ink absorption would be studied.

Table 6.7 The ink adsorption of untreated and treated PET fabrics

Plasma treatment	Ink absorption (%)			
	Cyan	Magenta	Yellow	Black
Untreated	79 ± 4	66 ± 10	63 ± 9	55 ± 8
O_2	80 ± 7	78 ± 6	73 ± 5	85 ± 7
N_2	79 ± 5	76 ± 6	76 ± 5	78 ± 7
SF_6	61 ± 5	58 ± 6	65 ± 5	67 ± 4

O_2 plasma

The PET fabric modified with O_2 plasma, XPS showed that surface had more oxygen containing functional group on surface. XPS found the functional group of C-C/C-H, C-O and O-C-O/C=O on fabric with 50 watt of power, 0.5 torr of pressure and both of 5 min and 20 min for treating time. Comparison between 5 min and 20 min treated fabric, the case of condition for 20 min had higher amount of oxygen containing functional group on surface more than 5 min case. The %ink absorption of 20 min treating time was higher than 5min. In the case of treating time for 20 min, the treated fabric can absorb black ink more than other ink and the value was higher than untreated about 60%. The summaries of ink absorption of PET fabric treated with O_2 plasma are shown in Table 6.8.

However, XPS showed that fabric treated with 100 watt of power had functional group different from above mentioned. XPS indicated the functional group of C-C/C-H, C-O, C=O/O-C-O and O-C=O. The percentages of all ink were higher than untreated fabric. Comparison with working power 50 min and power 100 watt (50 min case did not have O-C=O), %ink adsorption is slightly different. It may be due to the both cases had similar oxygen containing percentage and contact angle which lead to similar hydrophilic property and surface energy. From this result can imply that amount of oxygen containing on surface by plasma effect had impact to improvement in ink absorption of printed PET fabric.

Table 6.8 The ink adsorption of untreated and O_2 plasma-treated PET fabrics

Condition		Oxygen on Surface (%)	Surface energy (mNm^{-1})	Color strength			
Power (watt)	Time (min)			Cyan	Magenta	Yellow	Black
untreated		20	60.7	79 ± 4	66 ± 10	63 ± 9	55 ± 8
50	5	34	73.7	80 ± 7	78 ± 6	73 ± 5	85 ± 7
50	20	36	73.7	85 ± 4	84 ± 6	77 ± 4	88 ± 4
100	5	35	73.7	76 ± 6	84 ± 6	78 ± 4	83 ± 10

N_2 plasma

Table 6.9 reveals ink absorption of PET fabric treated with N_2 plasma by two conditions. PET fabric treating with N_2 plasma had new functional groups on surface when treating in the condition of 50 watt of power, 0.5 torr of pressure and 20 min for treating time. XPS detected the 15.8% of N_2 containing on the surface and indicated functional group of C-N, O=C-NH, O-CO and C-C on surface. It caused fabric to have more hydrophilicity and ink absorption. The %ink absorptions were 81, 76, 83, and 70% for cyan, magenta, yellow and black. In this case the treated fabric can absorb yellow ink more than others. The ink absorption value can up to 30% when comparing with the untreated fabric.

However, fabric treated with the condition of 50 watt, 0.5 torr, 5 min did not have functional groups of O=C-NH. It had 14.5% of nitrogen containing on surface. Comparison between the treating condition for 5 min and 20 min, the treated fabric for 20 min has more polar group and nitrogen containing on surface. The result of fabric treated for 20 min is higher %ink absorption than 5 min treating. It is due to that the hydrophilic group and amount of nitrogen containing on surface of fabric treating for 20 min had higher than 5 min, resulting in fabric had high hydrophilicity and surface energy. Therefore, the fabric could absorb water-based ink though the fabric deeply.

From the result, it can be explained similar with the cotton section that ink could be penetrated into fabric depending on amount of polar groups on the surface which lead to hydrophilicity and surface energy of fabric. The ink absorption become highly when fabric had high surface energy and wettability.

Table 6.9 The ink adsorption of untreated and N_2 plasma-treated PET fabrics

Treating time (min)	Nitrogen on Surface (%)	Surface energy (mNm^{-1})	Color strength			
			Cyan	Magenta	Yellow	Black
untreated	0	60.7	79 ± 4	66 ± 10	63 ± 9	55 ± 8
5	14.5	65.9	79 ± 5	76 ± 6	76 ± 5	76 ± 7
20	15.8	74	81 ± 3	76 ± 5	82 ± 3	70 ± 6

6.2.4 Effect of functional groups by plasma treatment on color strength

The section 6.2.2 showed color strength of printed-PET fabric. The result of PET fabric is different from the cotton. The N_2 plasma-treated fabric will have the highest K/S value. However, when the fabric was modified with SF_6 plasma, K/S had the lowest value because of it has hydrophobicity and low surface energy as same as cotton. Therefore the effect of both N_2 and O_2 plasmas are taken into account for studying color strength in the same conditions as %ink absorption.

O_2 plasma

Table 6.10 showed K/S of PET fabric treated with O_2 plasma. It shows fabric treated with 50 watt, 0.5 torr, for 5 min which did not have O-C=O group on its surface but had the highest oxygen containing on surface, seem provide lower color strength than others.

To consider with fabric treated with O_2 plasma at 100 watt, 0.5 torr, for 5 min, the functional groups are C-C, C-O, O-C-O and O-C=O. In comparison with untreated fabric, the K/S of treated one for cyan, magenta and black increase to 70%, 2% and 19%, but yellow turning decreases. Comparison with the fabric treating for 20 min, 50 watt that mentioned above, fabric treated 100 watt has color strength slightly more than that one. Among all conditions, the fabric treated with the condition of 50 watt, power, 0.5 torr, pressure and 5 min, exposure time usually provided higher color strength than other. It notices that this condition produced the wicking rate (section 6.1.2.3) and oxygen containing on surface was lower than other conditions. The high hydrophilicity may be the reason for poor printing property of fabric.

Table 6.10 The color strength (K/S) of untreated and O_2 plasma-treated PET fabrics

Condition		O_2 on Surface (%)	Surface energy (mNm^{-1})	Color strength			
Power (watt)	Time (min)			Cyan	Magenta	Yellow	Black
untreated		20	60.7	0.41 ± 0.02	1.41± 0.02	1.82± 0.02	1.61± 0.03
50	5	34	73.7	0.72 ± 0.01	1.45± 0.01	1.61± 0.02	1.80± 0.01
50	20	36	73.7	0.66 ± 0.01	1.29± 0.02	1.60± 0.01	1.98± 0.01
100	5	35	73.7	0.70 ± 0.01	1.44± 0.01	1.55± 0.04	1.90± 0.01

N_2 plasma

Table 6.11 displays the K/S values of N_2 plasma modification fabrics. The K/S value of fabric treated with the condition of 50 watt, 0.5 torr, 20 min which had the functional groups of C-N, O=C-NH, O-C-O and C-C, are 0.49, 1.61, 1.95 and 2.05 for cyan, magenta, yellow and black, respectively.

For treated fabric at the condition of 50 watt, 0.5 torr, 5 min, the functional group of O=C-NH was not observed and the K/S value in cyan, magenta, yellow higher than fabric treated with the condition of 50 watt, 0.5 torr, 20 min but yellow and black are lower. However, the both conditions provide the color strength of printed fabric higher than untreated-printed-fabric.

Table 6.11 The color strength (K/S) of untreated and N_2 plasma-treated PET fabrics (at working power 50 watt and operating pressure 0.5 torr)

Treating time (min)	N_2 on Surface (%)	Surface energy (mNm^{-1})	Color strength			
			Cyan	Magenta	Yellow	Black
untreated	0	60.7	0.41 ± 0.02	1.41 ± 0.02	1.82 ± 0.02	1.61± 0.03
5	14.5	65.9	0.72 ± 0.01	1.62 ± 0.04	1.83 ± 0.03	1.70± 0.04
20	15.8	74	0.49 ± 0.04	1.61 ± 0.02	1.95 ± 0.02	2.05± 0.03

Moreover, comparison with O_2 plasma, fabric treated with N_2 plasma always provides higher color strength than that of O_2 plasma. From literature [Sparavigna, 2003], an increase of fabric's wettability may contribute to high color yield. This theory is investigated to correct in section of cotton fabric (Chapter 5) but not in this section. The O_2 plasma gives fabric with the highest hydrophilicity, but K/S value of the O_2 plasma is lower than N_2 plasma treated fabric does. Therefore, the degree of pigment adhesion on PET fabric is not quite dependent on surface wettability. The PET fabric had much more hydrophilicity and high surface energy, ink can quickly penetrate though fabric. Then, pigment dried on surface in low level, result to low color strength. My previous report [Pransilp et al., 2012] found that the color strength of the O_2 plasma treatment in back side was higher than N_2 plasma treatment despite the fact that N_2 plasma treatment provided color strength in the printed side higher than that of O_2 plasma treatment. Thus, fabric had slightly low in hydrophilicity and surface energy, ink may spreading on surface (x-axis) and then dry on surface, resulting to high color strength.

6.2.5 Effect of rough surface on color strength

Owing to plasma treatment produced more grooves on the fiber surface. Several literatures were explained that grooves plausible had the ability of holding more inks on the fabric surface and also facilitate the penetration of colorant particles into the fabrics [Fang et al, 2008; Fang and Zhang, 2009; Zhang and Fang, 2009]. In this section, SF_6 plasma and O_2 plasma show the high level of rough surface. However, both of treated fabrics did not provide high K/S value. For the SF_6 plasma treated, fabric has hydrophobicity and low surface energy, thus, ink was poor wetting on surface and also poor absorbing water-based ink into fabric. For the O_2 plasma treated PET fabric, the treated surface has highly hydrophilicity and roughness surface, may be effect to pigment water-base ink deeply penetrate into fabric. The pigment deeply penetrate into fabric, result to pigment could not deposit on the surface [Leelajariyakul et al., 2007]. When the fabric had more roughness, the printed fabric will show low color strength (as shown in Figure 6.7).

However, N_2 plasma treatment showed slightly roughness improvement but the color strength of printed fabrics had the highest. Moreover, the color strength of fabric treated with N_2 plasma increased as the function of RMS roughness value. The result shows in Figure 6.7. It can imply that roughness can improve color strength of printed fabric when fabric had suitable wettability and surface energy.

Likewise with cotton section, the wettability is the main factor to provide high color strength of printed fabric and roughness surface contributes as the supporter that provides capacity for fabric to contain ink.

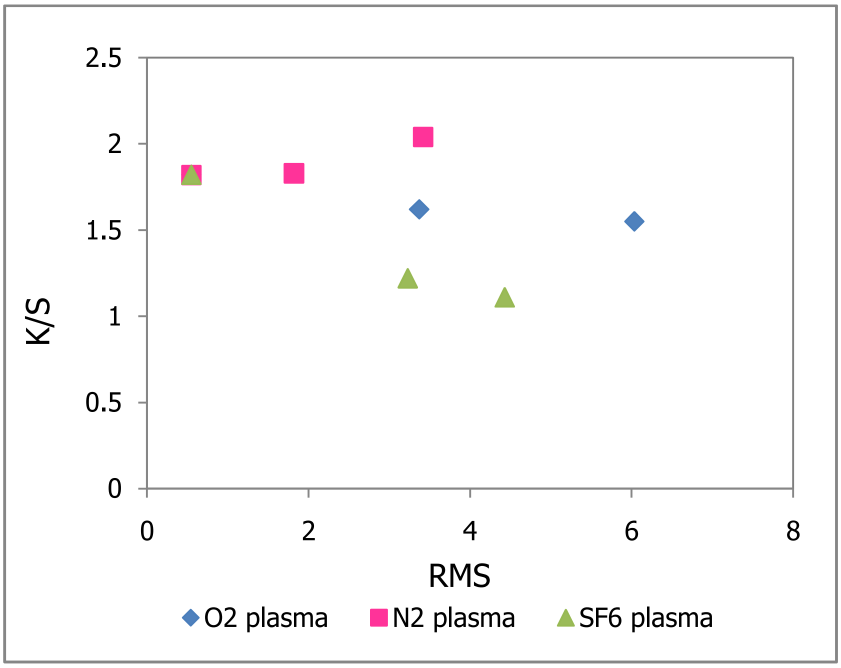


Figure 6.7 The effect of roughness surface on color strength of printed fabric after O_2 plasma, N_2 plasma and SF_6 plasma treatment

6.2.6 Color gamut

A significant effect of color is the color gamut in CIE L^* a^* b^* system. The a*b* types of color gamut is showed in Figure 6.8. Among all gases used, the N_2 treatment can provide the widest gamut area while SF_6 plasma treated fabrics shows the narrowest. Untreated fabric and N_2 plasma treated fabric had the same gamut while the N_2 plasma treated fabric shows a slight different in lemon area. In case of O_2 plasma treatment, the treated fabric gave a slightly difference from untreated sample in orange lemon and cyan areas. For O_2 plasma treated, printed fabric produced saturated cyan higher than that of the untreated fabric by about 6 units but saturate in orange and lemon lower than that about 8 and 7 units, respectively. The saturation in cyan of O_2 plasma-treated printing fabric relate with the result of K/S. On the other hand, printed fabric of the SF_6 plasma pretreatment produced orange and lemon lower saturated than that did the untreated fabric by about 7 units of scales.

N_2 plasma is the best gases plasma types for modified the PET fabric to get ink and improve color performance due to improvement of color strength (K/S) and provide a wider color spaces. Therefore, plasma process can be used to increase color performance of PET fabrics.

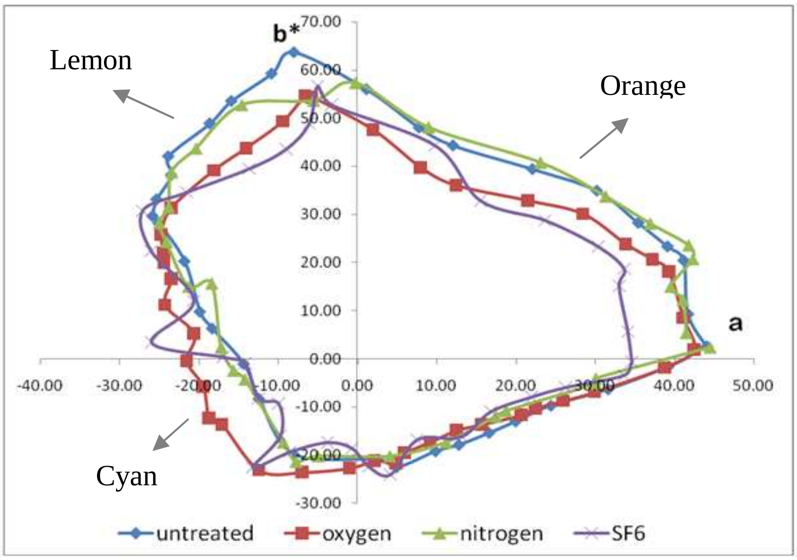


Figure 6.8 The color gamut of the printed PET fabrics as a^*b^* for untreat and plasma treatment

6.2.7 Color fastness

Based on the 105-C06-1994 and ISO 105-X12: 2001 for evaluating color fastness to washing and rubbing, respectively. The result was presented on Table 6.12. The value of 5 levels of evaluation was given as following:

Class 5 – No staining/color change
Class 4 – Slightly staining/color change
Class 3 – Noticeable staining/color change
Class 2 – Considerable staining/color change
Class 1 – Excessive staining/color change

The untreated and plasma-treated-printed fabrics gave low color fastness to washing. The color changes are in level 1. It may be due to there was weak inter-action force between fabric and ink.

For rub fastness, the treated fabric gave the higher color fastness to rubbing (dry and wet) than the untreated one. The O_2 plasma treatment gave the better color fastness for rubbing of printed PET fabric than N_2 plasma treatment. This result might be contributed by hydrophilicity as the pigment penetration though fiber in deeper than those of untreated or N_2 plasma treated printing fabric. Moreover, the rough surface was produced by plasma such as O_2 and SF_6 providing more capacities for ink as colorant particle deposit in deep surface, resulting to improvement rubbing fastness. This result indicates that plasma treatment has the effect on improvement the rub fastness of ink-jet printed PET fabric.

Table 6.12 Color fastness of PET printed fabrics

Types of plasma	Rub fastness on color staining		Wash fastness	
	Dry condition	Wet condition	Color change	Color staining
Untreated	2	1	1	4-5
O_2	2-3	3-4	1	4-5
N_2	2-3	2-3	1	4-5
SF_6	2-3	2-3	1	4-5

6.3 Printing performance of combination of polyester and cotton fabric

The color strength of treated combination of PET and cotton fabric (ratio 35: 65) at treating power of 50 watt, working pressure of 0.5 torr, exposure time for 5 min is showed in Table 4.20. The results of fabric after treated with N_2 and O_2 plasma have a higher K/S values than untreated fabrics while SF_6 plasma provides the lowest K/S values on water-based ink-jet printed fabric.. The highest K/S values of cyan, magenta and black colors were found in combination fabric treated with O_2 plasma and N_2 plasma, resulting in the highest K/S value of yellow.

Table 4.20 The color strength (K/S) of printed cotton-polyester combination fabrics before and after plasma treatment

Color/ λmax	K/S at λ_{max} of cotton-polyester combination fabric pretreatment			
	Untreated	O_2 plasma	N_2 plasma	SF_6 plasma
Cyan/620 nm	0.70	1.11	0.95	0.67
Magenta/560 nm	2.04	2.29	2.29	1.49
Yellow/420 nm	2.01	2.72	2.77	1.63
Black/560 nm	2.31	3.28	3.12	2.52
Blue/570 nm	1.50	1.95	1.77	1.55
Green/420 nm	1.40	2.05	1.94	1.08
Red/560 nm	1.53	2.51	2.49	1.81

Among all used gas, the combination fabrics treated with O_2 plasma provide the highest K/S values. The cotton is the main structure of the combination fabrics, so the K/S would be increase when fabric treated with O_2 plasma. It is similar to 100% cotton. Moreover, the study of water contact angle showed that the angle of untreated, O_2 plasma, N_2 plasma and SF_6 plasma treated fabrics is 89°, 0°, 60° and 130°, respectively. The results indicated that O_2 and N_2 plasma is affected to hydrophilicity whereas SF_6 plasma is affected to hydrophobicity and the wettability is the important effect to combination fabric adsorbs the ink and provide high color strength.

CHAPTER V

CONCLUSION

5.1 Conclusion

In this research, the ink adsorption properties of fabrics can be modified by plasma process. The pretreatment by plasma process can improve the color strength (K/S value) of the water-based ink-jet printed fabric. In the present work, the effects of three plasmas at plasma conditions on chemical and physical properties of the untreated and treated fabrics were investigated.

Effect on cotton fabric

The O_2 plasma modified the cotton fabric surface and enable more ink absorption yield the higher color strength than did the other gases. The K/S values were increased to 1.11 (cyan), 2.37 (magenta), 2.62 (yellow) and 3.18 (black) from 0.67 (cyan), 1.81 (magenta), 1.65 (yellow) and 2.45 (black), after treating with the O_2 plasma at 0.5 torr pressure, 50 watt and 5 min of exposure. The cotton fabric after the O_2 plasma treatment became more hydrophilic with a higher surface wettability. XPS exhibited more abundant intensity of oxygen peak after being treated by the O_2 plasma. The O_2 plasma generated polar groups on the surface, such as, C-OH, C=O and O-C=O, resulting in higher hydrophilic property on the fabric surface. Furthermore, the O_2 plasma has the etching effect by O^+ bombardment, resulting in the rougher surface. The hydrophilicity and roughness on the fabric surface facilitated deeper penetration of ink into the fabric and then fabric could capture more ink on the surface.

The N_2 plasma treated fabrics gave less color strength than did the O_2 plasma pretreatment. XPS analysis of the treated samples indicated the N_2 containing spectra. The C1s fitted peaks revealed polar groups on the surface, such as, NH, O=C-NH. AFM analysis indicated that the root-mean square (RMS) roughness is slightly increased. Moreover, zeta potential of the fabric treated with the O_2 and N_2 plasmas provided positive charges while ink the negative charges. Therefore, electric charge interaction could also contribute to the higher ink adhesion on the fabric.

On the other hand, the SF_6 plasma treated cotton fabrics produced the lower color strength and ink absorption. Its surface was thus hydrophobic after the SF_6 plasma treatment The XPS characterization gave an abundance of fluorine containing surface while the zeta potential gave the negative charge, similar to those of the ink. Cracks and scratches were found on the fabric surface on the AFM images. The RMS of the SF_6 plasma treatment was not different from that of the O_2 plasma treatment. Thus, the hydrophilicity and zeta potential of cotton fabric were the main attributes for the fabric to absorb more ink. Moreover, rough surface with cavities had the capacity of capturing more ink onto their surfaces.

Effect on PET fabric

PET fabric revealed good color strength when treating with the N_2 plasma under the plasma condition of 5 min of exposures time, 0.5 torr pressure and 100 watt of the plasma treating power. The K/S values increased from 0.41 (cyan), 1.41 (magenta), 1.82 (yellow) and 1.61 (black) for the untreated printed fabric to 0.0.54 (cyan), 1.81 (magenta), 2.04 (yellow) and 2.19 (black) for the treated fabric with N_2. It was found that the surface analyses by SEM and AFM had little grooves and slightly increase in the RMS roughness after treating with the N_2 plasma. The XPS showed the new functional groups. The N_2 plasma produced the N_2 containing species incorporated on the fabric surface, such as, C-N, O=C-NH. These functional groups increased the fabrics wettability, i.e., the contact angles were decreased while the wicking rates were increased.

On different gas plasmas, the O_2 plasma treatment imposed some impacts to the surface, having similar rough surface like the SF_6 plasma treatment but the wettability of the both treatments were different. The O_2 plasma affected hydrophilicity whereas SF_6 plasma affected hydrophobicity. Increases in surface hydrophilicity and surface roughness of the cotton treated fabric enhanced ink absorption. Comparison between the O_2 and N_2 plasmas, the O_2 plasma produced more hydrophilicity and roughness than did the N_2 plasma; while the N_2 plasma pretreated PET fabric produced the higher color strength than did the O_2 plasma. As a result, the N_2 plasma improved more color strength of the ink-jet printed PET fabric than did the O_2 plasma.

5.2 Suggestion for future work

Research areas that could be further explored might be in the following aspects:

- Other fabrics, such as, cotton blended PET fabric to observe the effect of mixed textile fabrics on color reproduction.
- The investigation of color strength of printed fabric by upscale operation for industry

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VITAE

Miss Porntapin Pransilp was born on August 26, 1986 in Chanthaburi, Thailand. She received the Bachelor’s degree from the Department of Textile Science and Technology, Faculty of Agro-Industry, Kasetsart University, Thailand in 2008. She was admitted to the Master Degree in Petrochemical and Polymer Science, Faculty of Science, Chulalongkorn University, and completed the program in 2012.

ISI journal publication:

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Her present address is 7/1 Moo 6, Tambol Kohkwang, Muang District, Chanthaburi, Thailand 22000, Tel. 039-454086, E-mail: lookpad_hae@hotmail.com