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# SURFACE MODIFICATION OF FABRICS BY AIR PLASMA AND ARGON PLASMA GENERATED FROM THETA-PINCH DEVICE

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การดัดแปรผิวผ้าพอลิเอสเทอร์ ผ้าฝ้าย และผ้าพอลิเอสเทอร์ผสมฝ้ายสามารถทำได้โดยใช้พลาสมาอากาศและพลาสมาอาร์กอนอุณหภูมิสูงที่กำเนิดจากเครื่องทีตาพินช์ โดยมีการปรับเปลี่ยนจำนวนครั้งของการยิงพลาสมาตั้งแต่ 10 20 30 และ 40 ครั้ง ในภาวะความดัน 2 พาสคัล กระแส 125 กิโลแอมแปร์ และความต่างศักย์ 20 กิโลโวลต์ สเปกตรัมเอทีอาร์ฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรสโกปีของผ้าที่ดัดแปรผิวด้วยพลาสมาทั้งหมดแสดงให้เห็นถึงการเกิดหมู่ฟังก์ชันที่ชอบน้ำ เช่น หมู่คาร์บอนิล แอมีน และแอลดีไฮด์ ซึ่งขึ้นกับชนิดของแก๊สและชนิดของผ้า นอกจากนี้ ภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงให้เห็นถึงการเกิดการเฉือนและการตกสะสมของชิ้นส่วนเส้นใยที่ถูกเฉือนด้วยพลาสมากลับลงมาบนผิวผ้า ซึ่งทำให้เกิดความขรุขระของผิว และยังพบว่า ความสามารถในการเปียกดีขึ้น เมื่อจำนวนครั้งของการยิงพลาสมาเพิ่มขึ้น อย่างไรก็ตาม ความสามารถในการย้อมสีและความคงทนต่อการซักยังขึ้นกับชนิดของผ้าอีกด้วย โดยผ้าที่มีความชอบน้ำสูง ดังเช่น ผ้าฝ้าย การดัดแปรผิวด้วยพลาสมาอากาศและพลาสมาอาร์กอนไม่ส่งผลต่อสมบัติทั้งสองนี้ สำหรับผ้าพอลิเอสเทอร์และผ้าพอลิเอสเทอร์ผสมฝ้ายที่ผ่านการย้อมสีแล้ว พบว่า ความเข้มสีมีค่าสูงสุดเมื่อดัดแปรผ้าทั้งสองด้วยพลาสมาอากาศที่จำนวนครั้งของการยิงพลาสมา 20 ครั้ง

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CHIRAPHORN WAIPEETA: SURFACE MODIFICATION OF FABRICS BY AIR PLASMA AND ARGON PLASMA GENERATED FROM THETA-PINCH DEVICE THESIS PRINCIPAL ADVISOR : ASSOC. PROF. VIMOLVAN PIMPAN, Ph.D., THESIS CO-ADVISOR : ASST. PROF. RATTACHAT MONGKOLNAVIN, Ph.D., 135 pp.

Polyester, cotton and polyester/cotton blended (T/C) fabrics were surfaced-modified by high temperature-pulsed air plasma and argon plasma generated from a theta-pinch device. The number of plasma shot applied to the fabric was varied from 10, 20, 30 and 40 shots. The theta-pinch device was operated with the pressure of 2 Pa, the maximum input current of 125 kA and the charging voltage of 20 kV. Attenuated total reflectance fourier transform infrared spectra of all plasma-treated fabrics indicated the formation of hydrophilic functional groups such as carbonyl, amine and aldehyde groups depending on the gas type and the fabric type. In addition, scanning electron microscopic photographs revealed the etching and the redeposition of etched fragments on the fabric surface resulting in surface roughness. It was found that better wettability was achieved with increasing the number of plasma shot. However, dyeability and colorfastness to washing properties were also depended on the fabric type. It was found that highly hydrophilic fabric such as cotton, air and argon plasma treatments had no effects on these two properties. In the case of polyester and T/C fabrics, after dyeing with selected dyes, it was found that the highest color strengths were achieved when they were modified by 20 shots of air plasma.

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Field of study: Applied Polymer Science and Textile Technology Principal Advisor's signature: Vimolvan Pimpan

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# CHAPTER I

# INTRODUCTION

Surface modification of textile materials has been utilized to provide desired single or multi-characteristics for various applications [1]. Plasma treatment is a very effective technology in the field of surface modification for a variety of materials. Plasma contains activated species, such as electrons, ions, radicals and photons which are able to initiate chemical and physical modifications at the fiber surface. These either directly or indirectly participate in plasma-chemical reactions which produce specific functional groups on the surface for specific interactions with other functional groups and increase hydrophobicity or hydrophilicity, or modify surface morphology by physical interaction. With an increasing economical and environmental concern, plasma treatment of textile materials has emerged as a major possibility for replacing many processes due to advantages over conventional or wet processes. The advantage of this technique is that plasma treatment only alters the uppermost atomic layers of a material surface without changing the bulk properties. In addition, the process is water free and avoids the need for costly effluent treatment. Plasma treatment provides an environmental friendly and low energy alternative to improve surface properties of textiles such as wettability, adhesion, printing and dyeing properties. Furthermore, this process can be used to modify textile products in many forms including fiber or fabric. Moreover, almost all compounds including inert gases such as He and Ne and non polymer forming gases can be used as working gases in plasma treatment.

Recently, many scientific literatures have shown a potential of surface modification of textile fibers and fabrics. These works have emphasized on the modification methods using cold plasma generated from several devices. Because these plasma generating processes are continuous, the control of plasma exposure is difficult. In 2005 and 2006, high temperature pulsed plasma generated from a theta-pinch device was employed in surface modification of fibers and fabrics including polypropylene, silk, nylon and polyester [2-5]. The dynamic of this device is governed by an increase in magnetic field which induces an electric field opposing to the direction of the discharge current. This produces plasma current that rapidly compresses toward the tube axis. The ions produced are of high energy such that they can be used for modifying material surface. Since the theta-pinch device produces plasma in pulses, it is easier to control plasma exposure on a material.

With the reference to previous research exposure synthetic and natural fabrics to a plasma environment of pure gases such as oxygen and nitrogen can produce more reactive surfaces. The gas type showed significant effect on surface characteristics and properties of plasma-treated fibers and fabrics [2-5]. Therefore, the main objectives of this research are to study the possibility of this method for industrial application by using air instead of pure gas such as oxygen and nitrogen as previously done and study the mechanism of plasma-substrate reaction by compare the plasma-treated fabrics properties after treated with air and argon plasma. The effects of modification parameters including the type of gases and the number of plasma shots on morphology and properties of surface-modified polyester, cotton and polyester/ cotton blended fabrics were also investigated and compared to those of the unmodified ones.

# CHAPTER II
# THEORY AND LITERATURE REVIEW

## 2.1 Conventional Modification of Textile Materials

The modification of textiles consists of the application of a wide variety of treatments and special processes that give to the fabric some quality that is needed to enhance its aesthetic, performance properties and surface characteristics. The modification results in either physical or chemical changes of the fiber or fabric which can be achieved through various techniques, both chemical and physicochemical [1].

### 2.1.1 Chemical Processes

In general, chemical modification is defined by direct chemical reaction with a given solvent or by the covalent bonding of suitable macromolecular chains to the substrate surface. Chemical process usually involves the development of specified chemical solutions, which exploit specific liquid-polymer interactions [6]. Over-exposure to chemical agents may lead to discoloration, irreversible fiber damage, and deterioration of mechanical properties.

*1. Coating* This method is an easily and low chemical consumes method because only fiber or yarn surface are coated. Coated fibers or yarn not durable since the chemical agents or additives which on the surface are rubbed. Thus the additives will be off.

*2. Chemical Treatment* Using the chemical which cause oxidation reaction on the fiber or yarn surface. The oxidized surface can react with other chemicals or materials so the surface properties are improved. But this method is not favored because it affect to environment.

3. *Graft Copolymerization* Different polymer can graft on fiber by initiator or irradiation for free radical polymerization. Graft fiber is high durable, for polymer formed the covalent bond with fiber.

Disadvantages of Chemically-Modified Textiles [1] In addition to alterations in the aesthetics and mechanical properties of chemically modified textiles, there are other disadvantages to this form of processing. These disadvantages include the use of large amounts of chemicals, high temperature treatments, increased cost, and environmental concerns. Environmental problems arise from both air born particulate emission during processing, and water pollution caused by the discharge of untreated effluents. These concerns and limitations have led to the further development of alternative physicochemical processing methods.

### 2.1.2 Physicochemical Processes

Physicochemical techniques have become more commercially attractive and have begun to supercede conventional wet chemical methods for properties modification. High-energy treatments including corona discharge, flame treatments, UV irradiation, hot or cold gaseous plasmas, are much more diverse in application.

The formation of high-energy electromagnetic fields close to charged thin wires with consequent ionization in their proximity, can lead to an electrical-corona discharge [6]. It generates electrons and ions via ionization. Electrons, ions, excited neutrals, and photons occurred by the discharge react with the polymer surface to create surface radicals. Then, these surface free radicals rearrange to form functional groups, thus physicochemical modification of the surface can be achieved. Due to corona discharges modification can be generated at atmospheric pressure; therefore, it has been widely used for surface modification of textile materials.

The polymer/fabric surface can also be oxidized by flame treatments, a process much similar to corona discharge in providing oxidation. Due to high heat activation of radicals, ions, and molecules in excited states, this form of modification can be accomplished [6]. Flame treatment is commonly used for enhanced adhesion. Variables that must be controlled for property optimization include air-to-gas ratio, flow rate, distance of the flame from the sample, and exposure time [7].

UV exposure to polymeric surfaces has been used to promote photon-activated cross-links and fragmentation of coatings. Wettability and adhesion, as well as antistatic characteristics can be enhanced by UV irradiation in the presence of oxygen leading to photo-oxidation of the surface. Additionally, by conducting UV irradiation in the presence of polymerizable organic vapors, surface polymerization is also possible by creating a thin polymeric film layer on the surface [8]. Like most high-energy sources, UV exposure may result in the deterioration of physical properties and promotes photo-degradation [9].

In light of environmental regulations and concerns, the textile industry has become more interested in plasma applications as a novel finishing technology that significantly reduces toxic-chemical pollution [10]. Plasma technology received enormous attention as a solution for environmental problems in textiles, and there has been rapid development and commercialization of plasma technology over the past decade. Due to plasma treatment is a dry process; therefore, it does not require water or wet chemicals. Additionally, plasma is able to change properties of the surface (such as micro-roughness and functionalization) without affecting bulk properties. Plasma surface modifications (such as desizing, wettability enhancement, water/soil-repellency, printability, dyeability, shrink-resistance, adhesion enhancement and sterilization etc.) can be achieved over large textile areas.

## 2.2 Plasma Applications to Textile Materials

For textile materials, surface modification has been used to provide desired single or multi-features for various applications. It is a highly focused area of research in which alterations to physical and/or chemical properties lead to new textile products that provide new applications or satisfy specific need. These processes, however, are usually involving numerous chemical, some of which are toxic to humans and hazardous to the environment. Additionally, the degradation and/or weakening of the treated surface may be occurred [11].

With increasing awareness of environmental regulations and concerns, alternative techniques have been investigated over the past two decades, to reduce toxic-chemical pollution or eliminate dependency on chemical treatments. One recent alternative, involving non-aqueous processing, is plasma treatment of textile materials.

Plasma technology has received enormous attention as a solution for environmental problems in textiles due to its advantages when compared to conventional wet processes such as coating and graft copolymerization. These advantages are as follows. Surface layers of the substrate can be homogeneously modified in seconds or minutes without affecting of its bulk properties, different types of chemical modification are possible by choosing the appropriate gases, chemical consumption is low, and since the process is performed in a dry and closed system, it is safer as well as environmentally friendly [12].

### 2.2.1 Definition of Plasma

The term "Plasma" was first used by Irving Langmuir in 1926 to describe the inner region of an electrical discharge [13]. Later definition was broadened by Crookes in 1879; to define a gaseous state of matter (the "4th stated of matter) [10,14].Plasma may be defined as an ionized gas containing both charged and neutral species, including free electrons, positive and/or negative ions, atoms, and molecules. Ion and radical formation results from electron and ion impact [7]. Electron impact, defined as collisional processes in plasma, is the impact of electrons on other plasma species, including non-ionized neutrals (atoms and molecules). In order to form and sustain plasma, an energy source capable of producing the required degree of ionization must be used. Either direct current (dc) or alternating current (ac) power supplies may be used to generate the electric field required for plasma generation [15]. For many industrial types of plasma, radio frequency (RF) power supplies are used, usually at a standard frequency of 13.56 MHz. Plasma generations may also be performed at various pressures including low (vacuum), atmospheric, or high pressure.

Plasma can be found easily in the universe, including solar coronas, lightening bolts, and nuclear fusion. Plasma also appears in man-made devices such as fluorescent lamps, neon tubes, welding arcs and gas lasers. Plasma technology plays a prominent role in various industrial areas, especially in the electronics industry, such as production or modification of computer chips, semiconductors, aircraft and automobile parts, machine tools, medical implants, and integrated circuits. Recently, plasma techniques are utilized in lighting and large-screen television.

Many types of plasma can be used for industrial processing. They are different in the way they are formed and the range of their characteristics after they are produced. Generally, all plasma is characterized by the same basic parameters no matter the system to which they are coupled. These parameters can be categorized as either internal (qualities of the plasma itself) or external (qualities of the operating control parameters). The main internal parameters of concern are plasma temperature (the average individual temperature of the electrons or ions in the plasma), plasma density (the number of activated species in a plasma), and plasma frequency and collision frequency. The external parameters are the potential (or voltage between the electrodes), distance between the plates, chamber pressure, power, operating frequency, and the type of gas used [16].

### 2.2.2 Classification of Plasma

Plasma may be classified as “hot” or “cold”. Plasma temperature is expressed in units of electronvolts “eV’ (1eV = 11600 K). Cold or non-thermal, plasma contains very hot free electrons of several eV, which generate high chemical reactivity while neutrals and ions remain near room temperature (0.025 eV). Cold plasma is also partially-ionized with a low fractional ionization. On the other hand, hot or thermal equilibrium plasma contains constituents, which are all at approximately the same temperature so that the heat content, and therefore overall temperature, is high (>10000 K, close to 1eV) and they are close to maximal degrees of ionization (100%) [7,15]. Solar coronas and nuclear fusion generated by thermonuclear reaction are the examples of hot plasma [10] . In the case of a glow discharge, the temperature of the ions and molecules is roughly ambient, while that of the electrons is higher by a factor of 10 to 100. Consequently, plasma produced by glow discharge is called cold plasma because the electron temperature is much higher than the gas temperature [14].

Cold or hot plasma can be used for surface treatment. Due to low heat resistance of most textile/polymeric materials, hot plasma treatment has little to no applicability in surface modification. Cold plasma conducted under low pressure or atmospheric pressure has been used in a wide variety of applications such as surface etching and material processing [10]. However, its generating system involves continuous processes; therefore, the exposure of the material surfaces to the plasma is difficult to control [17-18].

In previously published results, hot plasma generated in pulse from theta-pinch and plasma focus devices have been utilized to modify the surface of textile materials since plasma exposure can be easily controlled. Thus, low heat resistance of most textile/polymeric materials can be modified by this system. From this point of view, pulsed-plasma treatment and its resulting surface modifications will be the main focus of this work in later sections.

### 2.2.3 Plasma-Substrate Interactions

The reactive species (positive and negative ions, neutral species, atoms, metastables and free radicals) in plasma bulk are generated by ionization, fragmentation and excitation. They lead to chemical and physical interactions between plasma and substrate surface, depending on plasma conditions such as gas, power, pressure, and exposure time. Different plasma species exhibit very different interaction ranges with the polymer surface. The possible mechanisms for plasma-substrate interaction are illustrated in Figure 2.6. When a polymer is exposed to plasma of non-polymerizable gases (Ar, He, $O_2$, $N_2$, $CO_2$, etc.) surface morphology of the polymer changed. As a result, the surface of modified polymer becomes rough. Ions and neutral species in plasma play an important role in colliding with the molecules on the substrate surface and physically etch the surface.

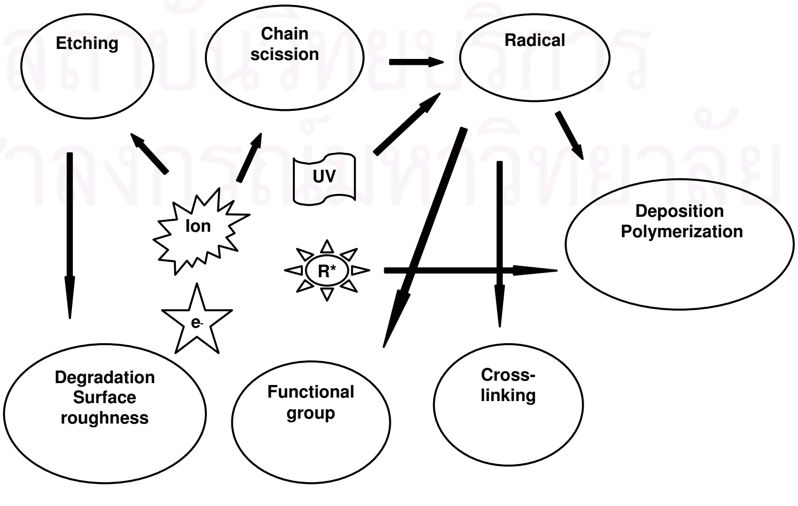


Figure 2.1 Mechanisms of Plasma-Substrate Interaction [10].

This phenomenon is well-known as etching effect. In addition, this reactive species bring about the breaking of the long molecular chains into short ones namely chain scission. This leads to chemical interaction with the surface of the molecules, generating new functional groups (functionalization) and radicals. Radicals obtained by chain scission mechanism and oxidation reaction would lead to chemical interaction with surface molecules, including new functional groups (functionalization) formation and inducing cross-linking generation on the uppermost few mono-layers of polymer. Besides, hydrocarbon and fluorocarbon gases can be been used to achieve deposition, and plasma polymerization can be obtained by using a polymerizable [10].

### 2.2.3.1 Physical Phenomena in Plasma Surface Modifications

#### 2.2.3.1.1 Effects of Plasma Etching

Plasma etching is a physical removing process of a material on the surface of a substrate. This process is dependent on the chemical combination of the solid surface being etched and the active gaseous species produced in the discharge. Molecular weight of the resulting etched material will be decreased due to the topmost layer will be stripped. Etching in plasma treatment has no unfavorable effect on the physical properties of substrate because only few hundred Å layers are etched away [19].

It is well known that etching process results in surface morphology and micro-roughness, preferring to remove amorphous region: that is, selective etching. The etched particles, however, would be re-deposited on substrate surface again, and lead to undesirable results on etching processing [20].

##### 2.2.3.1.1.1 Etching and Re-deposition Mechanism

Etching and deposition rates are exactly dependent on the ion energy flux and deposition species; that is to say, the reactive species collide with the molecules on substrate surface, and the etching species could be re-deposited by interaction with the active particles on the substrate surface. The etched species would be dissociated or ionized, and then deposited on the substrate surface. Consequently, the deposited species would generate new polymer layers or tiny particles. The new polymer layers would be etched by the ions in plasma, and deposited again. The etching and deposition processes are repeatedly conducted.

#### 2.2.3.1.1.2 Effects of Plasma Parameters on Etching

Plasma etching is dependent on the type of gas, pressure, exposure time, etching rate, uniformity, and selectivity of the substrate. By changing these parameters, system optimization can be achieved and controlled.

The effect of gas on etching process includes both gas type and its flow rate. The different forms and degrees of etching can be achieved by altering either parameter. Specifically, the gas type can determine whether the treatment will induce a higher or lower degree of etching, as well as promote etching in favor of deposition/polymerization. Reactive gases such as $O_2$ and $CF_4$, can have a much greater etching effect. However, the composition of these reactive gases must be balanced in order to optimize the etching and/or polymerization balance [1].

The influence of the flow rate must be also considered. In general, the rate of etching will rise rapidly with increasing flow rate to a maximum value, followed by a decrease at higher flow rates. Initially, in low flow region, there is an inadequate supply of reactant gas, creating a high utilization rate. This is steadily overcome and etching is maximized at the optimum flow rate.

Pressure can also play an important role in etching mechanism. As pressure is lowered below 0.1 Torr, as in most vacuum plasma systems, the sheath potential is dramatically increased. Given that the pressure is inversely proportional to the mean-free path, this rise in potential translates into a higher energy ion flux [21]. As a result, the ion bombardment promotes etching by physical sputtering or damage-induced mechanisms versus those of chemical etching [22].

#### 2.2.3.1.2 Changes in Surface Morphology and Roughness

As already mentioned, plasma etching of polymer surfaces can lead to morphological and topographical changes. Since most polymers are semi-crystalline; that is to say, they contain both crystalline and amorphous regions. Thus, morphology changes due to selective etching can be occurred [1].

Poletti, G., et al. [23] investigated the morphology changes, mainly root mean square (rms) surface roughness and surface area, of the surface of poly(ethylene terephthalate) (PET) fabrics due to cold plasma treatments, using Atomic force microscopy (AFM). The morphology changes on PET fabrics surface due to cold plasma have been measured as a function of treatment time and as a function of gas pressure. The changes in morphology in the cases of air, He and Ar gases seems to be due mainly to etching effects. The situation is different for $SF_6$ and $CF_4$ gases where reorganization of the surface, possibly due to fluorine atoms grafting, seems to be effective.

Chen Y.Y., et al. [24] studied the structure, morphology and properties of degummed *Bombyx mori* silk treated by low temperature oxygen plasma. The results showed that slight flutes appeared on the surface of *B. mori* silk fiber and that its surface structure changed after plasma treatment. Because of etching, the weight of the fiber decreased but the breaking strength slightly changed little after short-time treatment. In addition, its conformation changed and its degree of crystallinity decreased as well.

#### 2.2.3.1.3 Chain Scission of Molecules on Polymer Surface

Chain-scission is defined as any event that leads to the breakage of one polymer molecule into two or more parts [25]. This can be occurred through a direct rearrangement of the backbone into two separate entities, or by the loss of side groups and consequent rearrangement, which results inherently in molecular division. Both processes can be occurred because of etching via plasma exposure. The first interaction involves ion bombardment which is a main reason to break off molecular chains on substrate surface, resulting in functionalization. Additionally, chain scission is strongly related to etching effects on polymer surface, leading to weight loss and reduction of molecular weight.

Ward et al. [26] suggested the mechanisms of cellulose chain breakage by RF plasma treatment, based on radical formation process. Mainly, the chain breakages of cellulose molecules are carried out at glycosidic bond oxygen. Another possibility of chain scission would be ring-opening.

### 2.2.3.2 <u>Chemical Phenomena in Plasma Surface Modifications</u>

#### 2.2.3.2.1 <u>Radical Formation</u>

In addition to physical modifications, plasma exposure results in changing of the elemental composition of the polymer surface. The active species would collide with the molecules on substrate surface. UV-radiation and the collisions bring about the radical formation by chain scission of molecules and abstraction (taking-off of atoms on molecular chain) [27]. The formation of radical sites occurs through ionization or excitation of the polymers through electrostatic interaction between fast moving electrons and the orbital electrons in the polymers [1]. The consequent ionization leads to molecular fragmentation and the formation of a free radical. In the same way, excitation results in dissociation of the excited polymers, also forming free radicals.

$$\text{e-} + \text{AB} \xrightarrow{\text{radiation}} \text{AB+} + \text{e-} \text{ (Ionization)}$$

$$\text{e-} + \text{AB} \xrightarrow{\text{radiation}} \text{A+} + \text{B} + \text{e-}$$

$$\text{AB} \xrightarrow{\text{radiation}} \text{AB*} \text{ (Excitation)}$$

$$\text{AB*} \longrightarrow \text{A}\cdot + \text{B}\cdot \text{ (Dissociation)}$$

Free radicals generated in plasma treatment on polymeric materials play an important role in surface modification. Radical species would react with the radicals on substrate molecules, and then new functional groups are generated. Moreover, these active radicals can also induce the chain cross-linking by re-combination between radicals and initiate graft polymerization of vinyl monomers [28]. After plasma treatment on the substrate, unstable free radicals would recombine rapidly with other active species while stable free radicals remain as living radicals [29].

Wilken, R. and Wakida, T. [28,30] found that the free radical intensity of plasma treated fibers is related to plasma parameters (gas, pressure, and exposure time), fiber structures and chemical composition of fibers. The intensity of free radical increased in the following order: cotton>wool>silk>nylon 6 = PET.

2.2.3.2.2 Grafting

Plasma grafting, often referred to as plasma graft-copolymerization, can occur through either of the following two mechanisms [31]. One is the creation of active species on the polymer surface, followed by reaction with a monomer as shown in Figure 2.2. In this mechanism, free radicals are formed on the polymer surface as a result of inert gas plasma treatment. These radicals can either directly initiate grafting or be converted into peroxide or hydroperoxides by the inclusion of an oxidative gas. These activated peroxides will also initiate grafting in the presence of the monomer species [32].

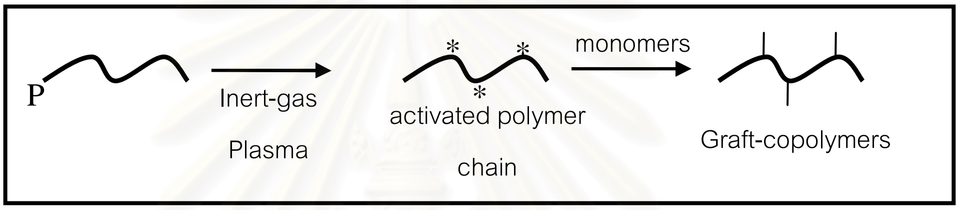


**Figure 2.2** The mechanism of plasma grafting
through active species created by plasma [32].

The other is direct grafting of the polymer with common or unconventional monomers under monomer-plasma conditions as illustrated in Figure 2.3. Unlike the previous method, this involves a combined plasma and monomer exposure in one step by the use of gaseous monomers in the working gas mixture. Both of these techniques have shown great advantages over conventional grafting by offering a large range of chemical compounds to be used as monomers, varying thickness of monomer layers, and limited destruction [33].

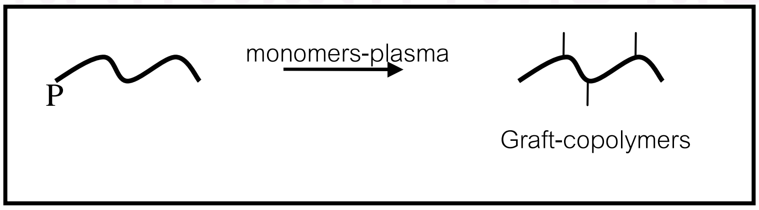


**Figure 2.3** The mechanism of plasma grafting
through gaseous monomers in the working gas mixture [32].

Man, W. H., and et al. [34] prepared chitosan-grafted poly(ethylene terephthalate) using plasma glow discharge. PET texture was exposed to oxygen plasma glow discharge to produce peroxides on its surface. These peroxides were then used as catalysts for the polymerization of acrylic acid (AA) in order to prepare a PET introduces by a carboxylic and acid group (PET-A). Chitosan and quaternized chitosan (QC) were then coupled with the carboxyl groups on the PET-A to obtain chitosan-grafted PET and QC-grafted PET, respectively.

#### 2.2.3.2.3 Cross-linking Formation

It is well-known that the radical formation is strongly related to ion bombardment and UV-radiation. Cross-linking can be achieved by recombination of molecular radicals, resulting in increasing molecular weight of the molecules, while chain scission lead to a decrease in molecular weight. Furthermore, chain scission occurs at the surface while cross-linking is dominated in the subsurface [35]. Ion bombardment produces the radicals introducing mainly surface functionalization, while UV photons have sufficient energy to penetrate much deeper into the polymer substrate, and then generate radicals.

##### 2.2.3.2.3.1 Cross-linking Mechanism

When two polymer molecules join to form one large molecular network, cross-linking will be occurred. Cross-linking results in an improvement of mechanical properties, a decrease in solubility, elimination of melting point, and resistance to corrosive attack, all of which are desirable properties [36]. Figure 2.4 illustrates an increase in cross-linking mechanism for PET.

As shown in Figure 2.2, cross linking of PET results from the recombination of two benzene ring radicals obtained by hydrogen abstraction from the benzene ring. In PET film treated by oxygen plasma, cross-linking reactions are expected from the destruction of benzene ring and ester groups, the combination of ethylene units and benzene ring, and the formation of peroxide [36].

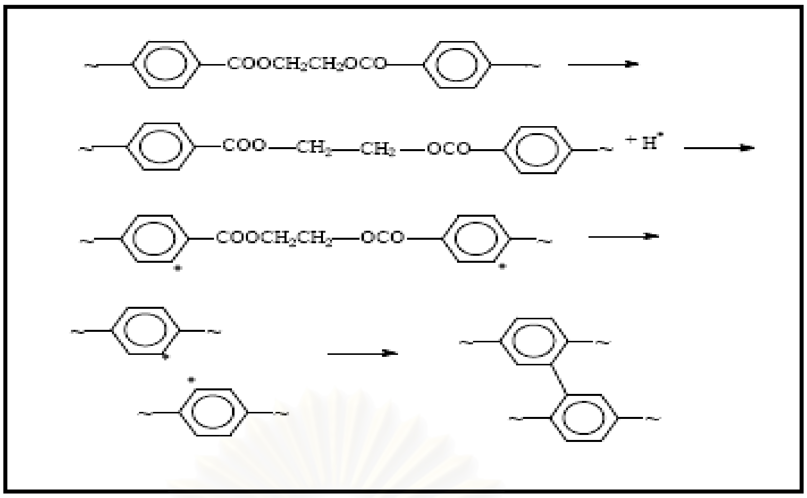


Figure 2.4 Cross-linking by recombination of two aryl radicals obtained by hydrogen abstraction from benzene ring in PET [36].

2.2.3.2.4 Functionalization on Polymer Surface

2.2.3.2.4.1 Hydrophilic Functionalization

2.2.3.2.4.1.1 Oxygen and Oxygen-Containing Plasmas

Oxygen and oxygen-containing plasmas are most commonly employed to modify polymer surfaces. In addition, they are very effective at increasing the surface energy of polymers. It has been reported that oxygen plasma can react with a wide range of polymers to introduce a variety of oxygen functional groups, including C-O, C=O, O-C=O, C-O-O, and $CO_3$ at the surface. For oxygen plasma, it is well-known that two processes occur simultaneously: etching of the polymer surface through the reactions of atomic oxygen with the surface carbon atoms, giving volatile reaction products; and the formation of oxygen functional groups at the polymer surface through the reactions between the active species from the plasma and the surface atoms. Depending on operation parameters of a given experiment, the balance of these two processes can be achieved [14].

In oxygen plasma, the various active particles of oxygen molecules can be obtained by dissociation and combination reactions in oxygen plasma. However, the radicals generated by plasma can interact with oxygen and $H_2O$ in air after plasma exposure, and then hydrophilic functional groups can be introduced on substrate surface.

#### 2.2.3.2.4.1.2 Nitrogen and Nitrogen-Containing Plasmas

Nitrogen and nitrogen-containing plasmas are widely used to introduce nitrogen functionalities on polymer surfaces such as amino, amine, imine and amide groups on polymer surface. Different nitrogen-containing plasmas have been shown to produce different nitrogen functional groups on a polymer surface [14].

Oxygen-functionalities are always incorporated in nitrogen-plasma-treated polymer surface after and during non-oxygen-plasma treatments due to free radicals created on a polymer surface which can react with oxygen during a plasma treatment and when the modified surface is brought to atmosphere.

### 2.2.3.2.4.2 Hydrophobic Functionalization

#### 2.3.3.2.4.2.1 Fluorine and Fluorine-Containing Plasmas

Fluorine and fluorine-containing plasmas are not only employed to decrease the surface energy but the hydrophobicity of polymer surfaces can be increased as well. When the surface energy of a material is changed, a wide range of commercially important properties may be altered in the direction of greater utility.

Surface reactions in fluorine-containing plasma, including, etching, plasma polymerization, and functionalization can carry out simultaneously. Which reactions predominate will depend on gas feed and operating parameters [14]. In the plasma of tetrafluoromethane gas ($CF_4$) plasma, the functionalization on the surface can be generated by competition, etching, and deposition. Etching can increase crystallinity rate and roughness on the polymer surface, while deposition results in functionalization, leading to hydrophobicity on the polymer surface.

Sun D., and Stylios G.K. [37] used the hexafluoroethane ($C_2F_6$) to treat wool and cotton fabrics. The increased contact angle of the $C_2F_6$ treated samples attributes to the fluorine containing surface caused by the $C_2F_6$ plasma treatment which produced a plasma polymer on the treated wool and cotton fabric surface. SEM observations showed smoother surface for the $C_2F_6$ treated wool and cotton fabrics comparing with the untreated. The smoother surface of the $C_2F_6$ treated fibers caused by the plasma polymer which deposited on the surfaces.

### 2.2.3.2.4.3 Aging Effect

The functional groups generated on the polymer surface by plasma treatment are not stable and have higher mobility than in polymer bulk. In order to become stable after plasma treatment, the surface is likely to be reoriented by the migration of short chain oxidized molecules and the diffusion of oxidized functional groups into polymer bulk [38-39] .

The aging effect of functional groups on plasma treated polymer surface can be reduced at low storage temperature and in oxygen atmosphere [40-41]. The lower storage temperature could lead to slower aging by reduction of the polymer chain mobility [42]. Yasuda, H., et al. [43] found that the decay of wettability was related to degree of cross-linking on polymer treated by oxygen plasma. Aging mechanisms of plasma treated polymers depending on molecular structure of the polymer are shown in Figure 2.5.

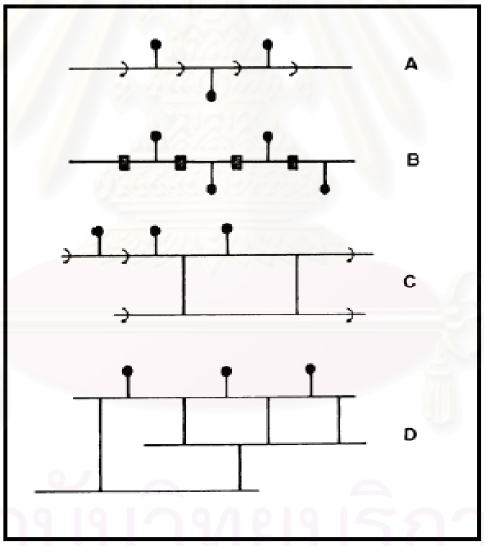


**Figure 2.5** Models of molecular mobility on polymer surface by Yasuda [43].

The main molecular chain with hydrophilic groups rotated along the axis of the macromolecule are shown in Model A. Model B illustrates the macromolecule with rigid backbone containing hydrophilic groups, as a consequence, the hydrophilic groups can not be freely rotated into polymer bulk. Model C represents a cross-linked macromolecule with hydrophilic groups on polymer surface. Free rotation along the axis of a polymer chain is limited due to cross-linking. Model D is for the cross-linked network of polymer having hydrophilic groups on polymer surface. No rotation of hydrophilic groups is in this model.

Nakamatsu, K. J., et al. [44] studied the aging of plasma surface modification of polytetrafluoroethylene (PTFE) surfaces by keeping the samples in four different environments, some samples were immersed in water at room temperature and at $90^{o}$C, and others kept in air at room temperature (20-$22^{o}$C) and an oven at $100^{o}$C. The results showed that the wettability decreases with time due to molecular movement in the polymer and this ageing process is reversible since the character of the treated surface changes when the environment changes (i.e., from water to air).

#### 2.2.3.3 The Effects of Plasma Treatment on Physical Properties

As already mentioned, functionalization can lead to desire chemical properties on the polymer surface while cross-linking, chain scission and etching are strongly related to physical property changes of the polymer substrate; especially, morphology and mechanical properties. In general, it is well-known that plasma treatment does not alter bulk properties of the substrate. However, in the extreme conditions of plasma, the bulk properties can be deteriorated. In order to overcome the defects of plasma, the optimum conditions should be considered to achieve advantages of plasma treatment [6].

Joanne, Y., et al. [45] treated Nylon 6 fabrics with low temperature plasma (LTP) with three non-polymerizing gases: oxygen, argon and tetrafluoromethane. Low-stress mechanical properties obtained by means of the Kawabata evaluation system fabric (KES-F) were investigated. Tensile properties decreased at shorter exposure time, but increased at higher exposure time. Bending and shear properties showed same behavior. At short exposure time, the slight reduction of all properties might be related to smoothing effect. The considerable enhancement of all properties resulted from higher etching effects of oxygen and argon plasma at higher exposure time, resulting in higher fiber-to-fiber and yarn-to-yarn frictions. However, the further increase of exposure time showed no enhancement of tensile, bending and shearing properties because etching was dominated over cross-linking.

Wong, K., et al. [46] found that fabric strength of plasma treated linen fabric treated with oxygen and argon decreased at longer exposure time, and linearly depended on weight loss. The fabric strength increased slightly at 10 min. exposure time because of the increase of interfacial friction, resulting from roughness of fibers by etching effect. However, after 20 min. plasma exposure time at higher discharge power, the apparent reduction of tensile strength was achieved. It is seemed that the severe plasma conditions could deteriorate bulk molecular structures due to more severe surface etching by bombardment of ions and excited particles.

In atmospheric pressure plasma, there have been a few studies of handling and physical properties of fabric treated. McCord, M., et al. [47] found that the tensile strength of nylon 66 fabrics treated by helium and helium/oxygen atmospheric plasma increased at some conditions with no surface morphology change. It is expected that the cross-linking would be related to the increase of tensile strength not due to frictions fiber-to-fiber or yarn-to-yarn.

Cioffi. M.O.H., et al. [48] studied the effect of cold plasma treatment on mechanical properties of polyester using oxygen and argon gases. The influence of treatment times is almost the same for both gases: the average tensile strength is always lower than for the untreated fibers but, after a drop for short treatment times, there is a tendency to elevate the tensile strength for treatments during 20–30 seconds, followed by an additional drop for larger periods. For cold plasma treated PET fibers using oxygen or argon gases, the higher average tensile strength was obtained for treatment time of 20 seconds.

### 2.2.4 Altering Surface Energy

Many commercial applications of plasma surface treatment are usually intended to increase the surface energy of materials. Increasing surface energy can be achieved by plasma cleaning, by altering the chemical nature of the surface with plasma active species, by embedding or removing charge; or by otherwise using active species to change the physical characteristics of the surface at the atomic scale of size [49].

The different types of gas or mixtures of gases that can be used for plasma treatment of polymers include argon, helium, hydrogen, nitrogen, ammonia, nitrous oxide, oxygen, carbon dioxide, sulfur dioxide, water, and tetrafluoromethane. Each gas produces a unique modified surface. Oxygen, nitrogen, and fluorine plasmas are frequently used to alter surface energy of polymeric materials.

#### 2.2.4.1 Wettability Enhancement

The most probably important surface-energy-related characteristic is wettability, which is a requirement for other important functional characteristics of surface. Wettability is the ability to absorb a liquid on a solid surface, or to absorb the liquid in the bulk of fibrous materials such as fabrics. Wettability implies a high surface energy (50-70 dynes/cm) and a low contact angle [49].

Ferrero F. [50] improved the water uptake of polyester fabric by plasma treatment. Power range from 5 to 150 W, exposure time 30, 60 and 90 seconds and working gases nitrogen, air and oxygen were used. The results shown that wettability of polyester after plasma treatment in air are lower than wettability in nitrogen and, except for one again become lower in oxygen. In the presence of oxygen plasma, surface oxidation occurs, which should intensify the initial water uptake of a polyester fabric. At the same time, crosslinking reactions were observed which are probably responsible for the decreased surface activity. Therefore, the results of wettabllity on plasma treated polyester fabric in the presence of oxygen lower than in nitrogen.

Carmen Almazan-Almazan, M., et al. [51] studied the textural and chemical surface modification produced by oxygen and carbon dioxide plasma on the surface of poly(ethylene terephthalate), (PET). The surface-modified samples were characterized by infrared spectroscopy, atomic force microscopy, and inverse gas-solid chromatography. The main difference between the effects of oxygen and carbon dioxide plasma were mainly related to the time scale of the surface degradation, which was considerably faster for the former. Aggregate globular features revealed by AFM were produced by different treatments due to chain scission and further recombination of evolved products; as a consequence, the specific component of the surface free energy was clearly observed to increase after these long treatments.

Sun, D. and Stylios, G.K., et al. [52] studied the effect of low temperature plasma treatment on the scouring and dyeing of natural fabrics. The contact angles of treated fabrics decreased considerably after $O_2$ plasma treatment compared to those of untreated cotton samples in both scouring and dyeing bath. This indicated that the surface free energy increased for the plasma-treated fabrics. Morphology changes produced by this modification were small. Plasma oxidation reactions produced oxygen-containing functional groups, which attached to the polymer surface. These functional groups formed and play an important role in increasing hydrophilic properties of the fabrics.

Wrobel, A. M., et al. [21] treated poly(ethylene terephthalate) by plasma initiated in various gases: nitrogen, oxygen, air, carbon dioxide and ammonia. Plasma-treated fabric showed a considerable change in surface structure and wettability. It was observed that the change in the surface structure of polyester fiber was closely dependent on the gas type and treatment conditions. The wetting time of plasma treated fabric considerably dropped in comparison to that of untreated fabric and the best results were obtained by treatment in nitrogen, oxygen and air plasma. A good correlation existed between change in the surface structure of the fabric and its wettability. Infrared ATR spectroscopy showed some differences in the spectra of plasma treated fabrics but these changes were only moderately dependent on the gas type and plasma conditions.

Wang C.X. and Qiu Y.P. [53] studied the influence of processing parameters on plasma penetration of wool fabrics by atmospheric pressure plasma jet. After plasma treatment, the water-absorption time for both sides of the fabrics was reduced. The decrease of water-absorption time can be attributed to the destruction of the scale structure due to plasma etching on the wool fiber surface and the introduction of more polar groups such as hydroxyl groups due to plasma chemical modification. Water absorption time of the two sides of the treated fabric was affected by jet-to-substrate distance. When the distance between the plasma jet nozzle and the fabric surface was too small, the flow of the gas from the nozzle was almost blocked by the fabric and the gas could only be bounced off the surface and flew out in a more parallel to the fabric surface direction, which greatly reduced the effectiveness of the treatment. On the other hand, when the distance too far, the velocity and the activity of the active species in the plasma jet greatly decreased when reaching the top side of the fabric and thus was not effective either.

2.2.4.2 Water Repellent Finishing

Fluorocarbon, hydrocarbon and mixtures of fluorocarbon and hydrocarbon gases have been used to increase hydrophobicity of polymer substrates in plasma. Compared to oxygen and air plasma treatment, plasma of fluorocarbon and mixtures of fluorocarbon and hydrocarbon gases plasma showed higher durability in air exposure [12,54].

Iriyama et al. [55] studied the water-repellency of nylon fabrics treated in fluorocarbon plasma ($CF_4$, $C_2F_4$, $C_3F_6$ and $C_6F_{14}$). The durability of water-repellency after 30 min. washing was better in fabrics treated with saturated fluorocarbon plasma than those treated with the unsaturated one. The saturated fluorocarbon plasma introduced longer chains of the polymer on fabric surface, leading to better hydrophobicity and durability.

Kim Y., et al. [56] improvedof hydrophobic properties of polyethylene (LLDPE) and poly(ethylene terephthalate) (PET) films with $CF_4$ gas. After CF4-PSII treatments, the water contact angle values of LLDPE and PET markedly increased to $\theta = 123°$ and $\theta = 103°$, respectively, indicating an increase in surface hydrophobicity. As expected, $CF_4$ as a working gas produced hydrophobic surface due to the incorporation of more hydrophobic groups such as CF, $CF_2$, and $CF_3$ onto the polymer surface.

Regardless of good results from previous research works, fluorocarbon plasma treatments have not been used commercially to improve water-repellency or oil repellency of textile materials. First, fluorocarbon plasma can generate a Teflon-like film not only on the substrate surface, but also on the inside of the plasma chamber. The fluorocarbon coating on the chamber, which is hard to remove, can block gas nozzles and contaminate inside of the plasma chamber. Therefore, use of fluorocarbon plasma for industrial scaled-low-pressure plasma system is not recommended [34]. Secondly, the durability against washing was not examined for water-repellent finishing of textiles although most of plasma applications to textiles have not been available to satisfy commercial needs yet. In order to overcome these issues against fluorocarbon plasma applications, it is suggested that a new plasma system designed, plasma conditioning and pre-conditioning of fabrics should be considered to optimize durability of washing for textile industrial requirement [10].

### 2.2.4.3 Dyeability Enhancement

Dyeability is the ability of a porous or fibrous material such as a fabric to be dyed in bulk. It requires both a high degree of surface adsorptivity and bulk absorptivity. Dyeing affects the surfaces of all fibers throughout a fabric, and may involve chemical reactions with the bulk material of the fibers as well. Dyeing is most effectively done if the fabric to be dyes is wettable and wickable to dyeing solution [49].

Dyeing in textile industry requires the development of environmentally friendly and economical processes due to pollution and economic limitations. Plasma techniques have been used as alternative technique to replace or aid the conventional wet dyeing process.

Dyeability of textile materials can be enhanced by using low-pressure plasma in various approaches; including, non-polymerizable gas plasma treatment before dyeing, plasma-induced graft polymerization before dyeing, etching/sputtering on dyed fabrics, and atmospheric pressure plasma also showed feasibility for dyeing applications.

Antonio R. A., et al. [57] investigated the surface chemical and topographical modifications induced on poly(ethylene terephthalate), (PET) fabrics by treatment with air radio frequency (RF) plasma of both a reactive and an inert gas under different operating condition, to correlate them to the plasma-induced variation of the dyeing properties of PET fabrics. An increase in color depth upon dyeing was obtained after treating PET fabrics with two gases used. This may be easily related to optical effects connected to plasma-induced surface roughness. Additionally, an increase of surface area and the introduction of hydrophilic groups may increase water swelling capability and affinity of PET fibers for dyes containing polar groups.

Okuno, T., et al. [58] observed that an increase in crystallinity of PET fiber resulted in the reduction of dyeability. Etching of plasma treatment was dominant in amorphous region, a dyeable domain, and led to an increase of crystallinity of PET fiber.

Wakida, T., et al. [59-61] extensively investigated the effect of plasma treatment on dyeing properties of nylon 6 fibers. Compared to acid dyes, oxygen plasma treatment enhanced the dye uptake, dyeing rate and dye exhaustion for nylon fibers dyed with basic dyes. Oxygen plasma treatment incorporated –OH and –COOH functional groups on the nylon fiber surface, leading to electronegativity on the fiber surface. Thus, the adsorption of basic dye can be higher than that of acid dye for oxygen plasma treated nylon fibers.

Byrne, G., et al. [62] showed that plasma-induced graft polymerization with acrylic acid improved dyeability of PET fabric using basic dye, as well as anti-soiling and soil release.

Park, J., et al. [63] explained that generation of carboxylic acid groups (-COOH) on PET surface could result in dyeability enhancement. When acrylic acid was grafted on PET fabric in plasma, higher wettability resulted form the generation of hydrophilic functional groups, such as carboxylic acid groups was observed. These increase the interaction with basic dye, resulting in enhancement of dyeability.

Seto, F., et al. [64] and Park, S., et al. confirmed that the concentration of carboxylic acid generated by acrylic acid grafting had a significant relationship to an increase of dyeability when basic dye was used, resulting in the acid-base intermolecular interaction between acidic functional groups and basic dyes.

Navaneetha P.K. and Selvarajan V. [65] used non-thermal plasma treatment for hydrophilicity improvement of grey cotton fabrics. When the fabric was plasma treated its dyeability increased substantially. This may be due to increase in the dye molecule penetration into the fabric surface caused by the plasma treatment and the increase in polar groups on the surface which are strongly bonded with dye molecules.

### 2.2.5 Altering Adhesive Properties

Adhesion is the interaction of two surfaces, close to each other or in contact, which causes them to stick together. Adhesion results from a combination of factors, which may include mechanical, electrostatic, chemical, permeation, diffusive, surface roughness, or micro-profile contributions. Adhesion as well as surface energy is normally increased by exposing a surface to the active species of plasma. For adhesion improvement, atomic oxygen appears to be the most important plasma active species [66].

The enhancement of the adhesion between a polymer matrix and plasma-treated fibers is due to both physical and chemical modifications. The physical modification is the surface roughening of the fiber by sputtering effect, producing an enlargement of contact area that increases the friction between the fiber and the polymer matrix. Chemical modification increases the concentration of functional groups on the fiber surface, hence, causing a large number of chemical bonds to be formed between fiber and polymer matrix [67].

Saurabh G., et al. [68] wool and polyester fabrics were pretreated with atmospheric plasma glow discharge (APGD) to improve the ability of the substrate to bond with anthraquinone-2-sulfonic acid doped conducting polypyrrole (PPy) coating. The results shown that plasma-treated wool fabric have a thin layer of conductive polymer bonded to the exocuticle which is not present in the untreated fiber. This improvement in coating coverage led to improved conductivity. The improved adhesion of the polymer layer could be caused by the increase of amino groups ($–NH_2$), other reactive groups and radicals on the fiber surface. In contrast to wool fabrics, PPy coated PET fabrics showed only a slight improvement in appearance after plasma treatment.

### 2.2.6 Altering Electrical Characteristics

Many polymeric fabrics are capable of strongly retaining surface static charge. Their utility for carpeting, upholstery, and clothing is greatly enhanced if the static charge drains off quickly. This can be accomplished through an increase in surface electrical conductivity induced by, for example, bonding copper compounds to plasma-treated fibers to produce conductive fabrics [49].

## 2.3 Surface Modification of Textile Materials Using A Theta-pinch Device

Theta-pinch, a plasma generating device, is relatively simple in structure compared with other devices and originated from the research in the field of controlled thermonuclear fusion. The high density pulsed plasma can be achieved; that is to say, it produces fully ionized gas having density in excess of about $10^{16}$ particles/cm$^3$ and temperature in excess of some $10^6$ K (1 eV= 11,600 K).

**Figure 2.6** Front view (left) and side view (right view) of theta-pinch device used in this research [17].

This device has been utilized in various applications, for instance, the deposition of thin films, including amorphous carbon film, $\alpha$-Si film, diamond like carbon film, etc. Besides, it has been used to process the superconducting films for lithography, which reveals its potential advantages over other methods [69].

### 2.3.1 Dynamic Process of Theta-pinch Discharge

Figure 2.12 shows the basic dynamic process of theta-pinch discharge. This process begins when the capacitor bank is charged to a voltage of a few ten kVs by the charger, The switching of the spark gap controlled by a triggering unit is closed, resulting in discharging to a single turn coil. Because of this, the rapidly increasing axial magnetic field that accompanies the current in the coil induces an electric field. The maximum electric field usually occurs near the wall of quartz tube, and ionizes the neutral gas there most likely; consequently, a plasma current sheath is initiated, which flows opposite to the direction of the discharge current in the coil. Subsequently, the force rapidly compresses the plasma current sheath toward the tube axis, and the neutral gas is simultaneously ionized by the confliction of the sheath. At last, the plasma density and temperature are simultaneously enhanced [69].

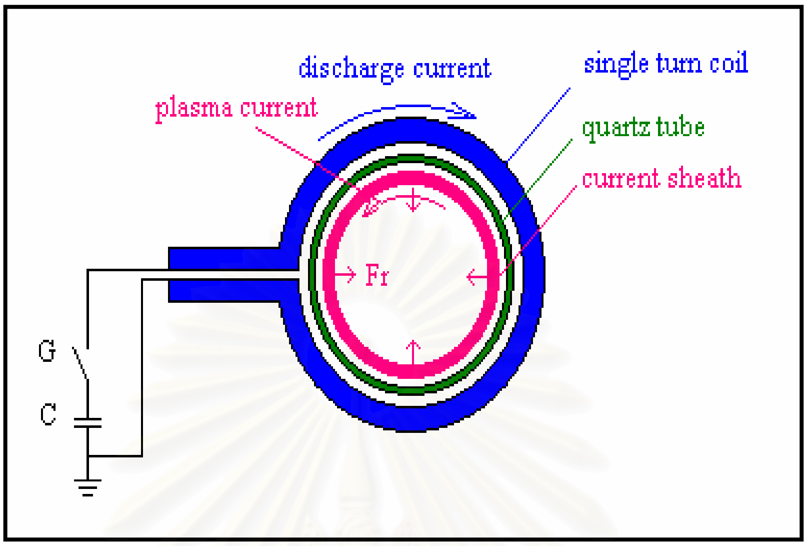


**Figure 2.7** Dynamic process of theta-pinch discharge [69].

As already mentioned, there have been several reports on surface modification of textile materials with hot plasma generating devices because they have several advantages over cold plasma generating devices. Therefore, the main focus of this research is to modify the fabrics using theta-pinch device.

In 2004, Pimpan, V., Chuenchon, S., Kamsing, P., and Mongkolnavin, R. [17] applied theta-pinch device to modify the surface of man-made fibers, including polypropylene, polyester, and rayon fibers. The properties and morphology of treated fibers were investigated. Oxygen and nitrogen plasma generated at different number of plasma shots caused and increased in the roughness of the fiber surface. Because of this, tensile properties, linear density and diameter of plasma-treated fibers were affected by the both type of gases and the number of plasma shots. However, the flammability of both treated and untreated fibers were comparable.

In 2004, Mongkolnavin, R., Srisawat, J., Ngamrungroj, D., and Pimpan, V. [18] improved the adhesion between the components of a composite using a UNU/ICTP plasma focus device. The surface of PP nonwoven was modified with nitrogen gas at a pressure of 1.5 mbar under different the number of plasma shots. The plasma focus device produced reactive nitrogen plasma which bombarded the surface of the fabric at a supersonic speed, resulting in increasing of hydrophilicity of PP. When surface modified PP nonwoven was laminated with polyester/cotton (PET/C) nonwovens by compression molding at 190°C for 12 minutes, PP-PET/C composites were obtained. From mechanical properties tests, it was found that tensile and flexural properties prepared from surface-modified PP were higher than those of the composites prepared from the unmodified one. However, impact strength of both composites was comparable.

Also in 2005, Khaymapanya, P., Pimpan, V., Kamsing, P., and Mongkolnavin, R. [71] employed high temperature pulsed plasma generated from a theta-pinch device to modified fabrics surface. 20 and 40 shots of plasma oxygen and nitrogen plasmas were used to modified fabrics surface including polypropylene, silk, nylon and polyester. SEM photographs revealed etching effect on the surface of all plasma-treated fabrics causing the surface roughness. The wetting time measurement indicated an enhancement of the surface hydrophilicity with increasing number of plasma shots due to the formation of hydrophilic groups on the fabric surface. This is confirmed by FTIR spectroscopy.

## 2.4 Textile Materials

### 2.4.1 Cotton [71-73]

Cotton is the most versatile and the most widely used textile fiber, processing more ideal properties than any other fiber. There are several qualities of cotton, but they can be conveniently grouped into three types as follows:

*1. Long staple cotton* This is the best quality type which goes up to about 55 millimeters in length. There are the finest, softest and strongest cotton.

*2. Medium staple cotton* This is the largest group comprising well over 50% of cotton. This type is about 25 millimeters in length, not fine, soft or strong as the long type but much cheaper and much more plentiful.

*3. Short staple cotton* This type of cotton is mostly less than 25 millimeters in length and is coarser and harsher than medium type.

2.4.1.1. Molecular Structure

Cotton is composing of cellulose, the foundation of plant. It is a pure plant cell material consisting of macromolecules of at least several hundreds to several thousands of anhydroglucose units. Cellulose is a polymer of β-D-glucopyranosyl units which are linked together by 1,4-β-D glycosidic bond, with the elimination of water, to form chains of 2,000-4,000 units, as shown in Figure 2.8

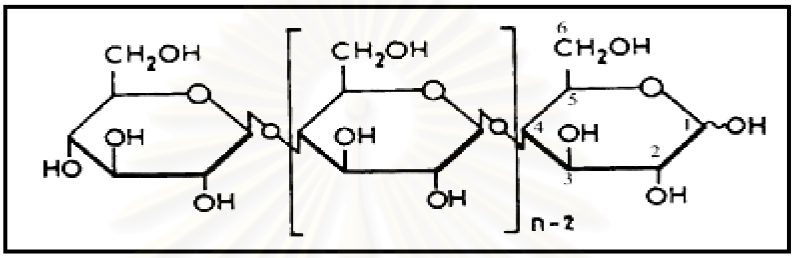


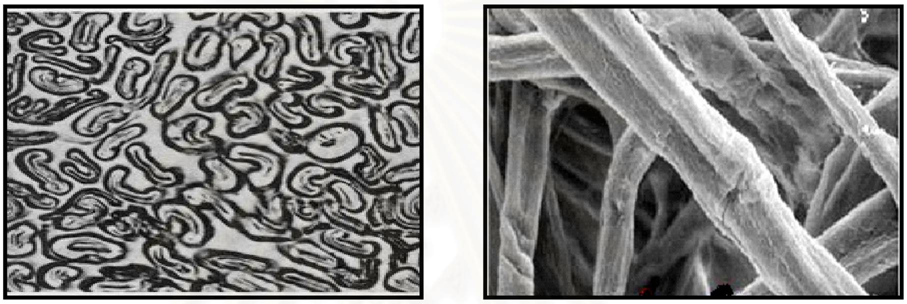
**Figure 2.8** Molecular structure of cellulose.

The cellulose molecules form into fibrils or bundles of molecular chains combining in groups to form cellulose fiber. Each fiber consists of many cellulose molecules. There arrangements are not in a completely parallel manner; rather, certain portions of the fiber may have the molecules lying parallel, while other areas are characterized by a somewhat random molecular arrangement. The molecules within the fiber tend to be held in place by hydrogen bonding. When cellulose fibers are bent, the hydrogen bonds are broken and new ones form, which results in creases or wrinkles that do not hang out.

The chemically reactive units in cellulose are the hydroxyl groups. These groups may undergo substitution reactions in procedures to modify the cellulose fibers or in the application of some finishes and dyestuffs. Substitution occurs when one or more hydroxyl groups are removed and other ions or radicals, atom, or groups of atoms, attach themselves to the carbon atoms. Modification can occur when the hydrogen of hydroxyl group is removed by chemical reaction and other elements or compounds hook to the remaining oxygen.

#### 2.4.1.2 Microscopic Properties

Cotton fibers are composed of an outer cuticle (skin) and primary wall, secondary wall, and a central core or lumen. Immature fibers exhibit thin wall structures and large lumen whereas the mature fibers have thick walls and small lumen that may not continuous due to the fact that the wall closes the lumen in some sections as shown in figure 2.9a. The longitudinal view of fiber shows a ribbonlike shape with twist at irregular intervals. The fiber diameter narrows at the fiber tip. Their lumen may appear as a shaded area or as striation as Figure 2.9b.



a) b)

**Figure 2.9** Photomicrographs of regular cotton

a) cross section and b) longitudinal view [72].

#### 2.4.1.3 Physical Properties

Color Cotton fiber is generally white or yellowish in color.

Shape Cotton fiber is fairy uniform in width for natural fiber. It varies between 12-20 microns and the central portion of the fiber is wider than either end. The fiber length as used in yarn and fabric manufacture varies from 0.5 inch into 2.5 inches with the majority of fibers in the 0.88 inch into 1.25 inches range.

Luster The luster of cotton is low unless finishes have been added.

Strength Cotton has a tenacity of 3.0 to 5.0 gram per denier. When wet, cotton increases in strength may have a wet strength about 110 to 120 percent of its dry strength. Its strength can be increased by a process called mercerization in which yarns or fabrics held under tension are treated with controlled solutions of sodium hydroxide.

Elasticity and Resilience The elasticity and elastic recovery of cotton are low. Not only does cotton stretch relatively little but it also does not recovery well from stretching.

Its resilience is low. Therefore, cotton fabrics wrinkle easily and do not recover well from wrinkling.

Specific Gravity Cotton is a fiber of relatively high density, having a specific gravity of 1.54. This means that cotton fabrics will feel heavier in weight than comparable fabrics made from polyester or nylon whose specific gravities are 1.38 and 1.14, respectively.

Absorbency and Moisture Regain Cotton fiber is composed primarily of cellulose which is very absorbent and its hollow center or lumen aids in conveying moisture so the fiber becomes very absorbent. The moisture regain for cotton at standard condition is 8.5 percent.

Dimensional Stability Cotton fiber exhibit neither shrinkage nor stretching in their natural state. Woven or knitted cotton fabrics may shrink in the first few laundering because the laundering releases tensions created during weaving or finishing. The relaxation of these tensions may cause changes in the fabric dimensions. Cotton fabrics require treatment to render them resistant to shrinkage.

Drapability Cotton does not intrinsically have the body and suppleness require for good drapability. However, the nature and compactness of the fabric construction can improve it. This can enhance further by sizing and other finishes.

#### 2.4.1.4 Thermal Properties

Heat and Electrical Conductivity Cotton has a relatively high degree of heat conductivity which makes the fabric comfortable in hot weather. It does not build up static electrical charges.

Effect of light Cotton fiber oxidizes, turning yellow and losing strength from exposure to sunlight over a protracted period of time.

#### 2.4.1.5 Biological Properties

Resistance to Mildew Especially cotton sized fabrics, mildew readily when permitted to remain in a damp condition. Small greenish-black or rust colored spots caused by mildew fungus develop and a musty odor may be detected. Other bacteria that grow in soiled, moist areas will also deteriorate or rot cotton fabrics. Therefore, cotton material should be kept in dry atmosphere.

Resistance to insects Cotton is not digestible by moth larvae and beetle. Silverfish will eat cellulose, especially if heavily starched, but do more damage to paper and other products composed of cellulose molecules.

#### 2.4.1.6 Chemical Properties

Reaction to Alkalies Cotton is highly resistant to alkalies. The majority of detergents and laundry aids are alkaline; thus, cotton can be laundered in these solutions with no fiber damage.

Reaction to Acids Strong acids destroy cotton and hot dilute mineral acids will cause disintegration. Cold dilute acids cause gradual fiber degradation, but volatile organic acids does not damage cotton fabrics.

Affinity for Dyes Cotton has a good affinity for dyes. Azoic and reactive dyes can also be affectively used. Colorfastness is generally good.

### 2.4.2 Poly(ethylene terephthalate) (PET) [71-73]

Polyester fibers dominate the world synthetic fibers industry. It is inexpensive, easily produces from petrochemical sources and has a desirable range of physical properties. Its versatility is legendary. Both as continuous filament yarn and staple fiber, it is used in countless varieties, blend and forms of textile apparel fibers, household and furnishing fabrics.

#### 2.4.2.1 Molecular Structure

Polyester is defined as condensation or step-growth polymer containing in chain ester units as their essential polymer-forming chain linkage. PET is a polycondensation product of ethylene glycol and terephthalic acid (or dimethyl terephthalate).

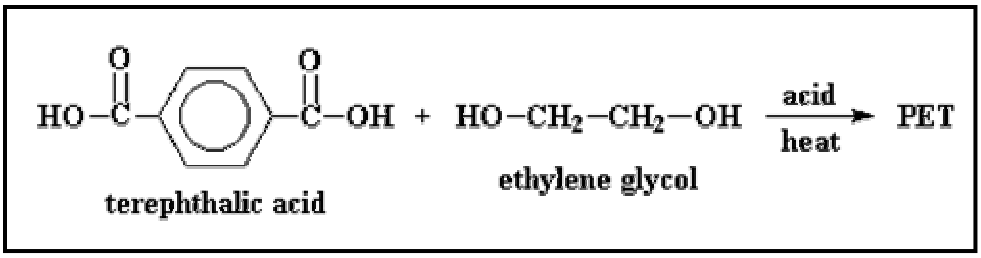
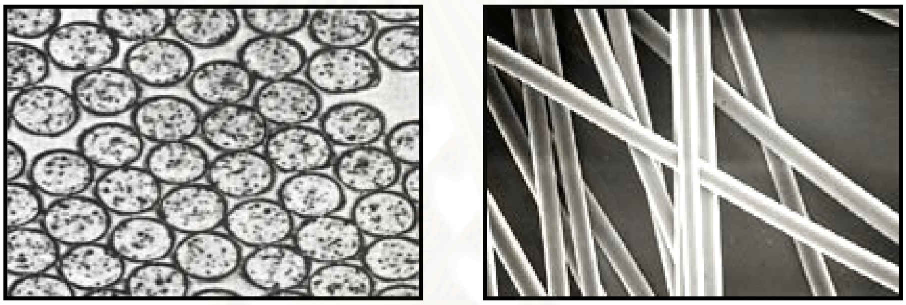


Figure 2.10 The polycondensation stage of PET production

2.4.2.2 Microscopic Properties

A longitudinal view of polyester fiber exhibits uniform diameter, smooth surface and rodlike appearance.



a) b)

Figure 2.11 Photomicrographs of regular polyester fiber

a) cross-section and b) longitudinal view [72].

The cross section usually round. Variations will be encountered in trilobal and pentalobal polyester. Fiber with dull or semidull appearance due to inclusion of pigment in the melt solution has a speckled effect due to change in the light reflection caused by the presence of pigment.

2.4.2.3 Physical Properties

Shape and Appearance Polyester fibers are generally round and uniform. They can be of any length or diameter as required by fiber producers and yarn and fabric manufacturers. The fiber is partially transparent and white of slightly off-white in color.

Strength Regular and high strength fibers are produced by several manufacturers. Polyester fibers can be characterized as relatively strong fibers. Its strength varies from a low of 2.5 grams per denier to a high of 9.5 grams per denier. There is no loss of strength when fibers are wet.

Elasticity and Resilience Stronger fibers have lower degree of elongation. Polyester fibers do not have a high degree of elasticity. In general, polyester fiber is characterized as having a high degree of stretch resistance, which means that polyester fabrics are not likely to stretch out of shape too easily. The property resilience from creasing and wrinkling is excellent for polyester fibers. Furthermore, heat setting can stabilize fibers and yarns so they need little or no pressing to retain smooth appearance.

Specific Gravity The specific gravity (1.38 or 1.22 depending on type) is moderate. Fabrics made from polyesters are medium in weight.

Absorbency and Moisture Regain The moisture regain of polyester is low, only 0.2 to 0.8 percent. Although polyesters are nonabsorbent, they do have wicking ability. In wicking, moisture can be carried on the surface of the fiber without absorption. Multilobal fiber cross sections improve the wicking qualities of fiber.

Dimensional Stability Polyesters that have been given heat-setting treatments have excellent dimensional stability, so long as the heat-setting temperature is not exceeded. If polyester fabrics have not been heat-set, they may shrink at high temperatures.

Drapability Polyester fabrics have satisfactory draping qualities. The trilobal type is supple and imparts better drapability.

#### 2.4.2.4 Thermal Properties

Heat Conductivity The basic polyester fiber is round. This results in a smoother yarn woven into fabrics with fewer air spaces and less insulation.

Effect of light Polyester has good resistance to degradation by sunlight. Over prolonged of exposure to direct sunlight; however, they will be gradual deterioration of the polyester fiber.

#### 2.4.2.5 Biological Properties

Resistance to Mildew Polyester fabrics are absolutely resistant to mildew. They will not be stained or weakened. Should mildew form on the fabric, it would be due to the finish; but mildew should readily wash of the fabric without any deterioration to it. However, they may be some discoloration.

Resistance to insects Polyester is unaffected by moths, carpet beetles, silverfish or other insects.

2.4.2.6 Chemical Properties

Reaction to Alkalies Polyester has good resistance to weak alkalies at hot as well as room temperature. It exhibits only moderate resistance to strong alkalies at room temperature and is degraded at elevated temperatures.

Reaction to Acids Depending upon the type, polyester has excellent-to-good resistance to mineral and organic acids. Highly concentrates solution of mineral acid such as sulfuric acid, at relatively high temperature will result in degradation.

Affinity for Dyes Polyester can be dyed with appropriate disperses and developed dyes at high temperatures.

2.4.3 Polyester/cotton blended fabric (T/C)

In attempt to improve the consumer acceptance of polyester in apparel, the technique development for blending polyester and cotton in the same yarn give improved comfort and better dyeability while maintaining the wrinkle resistance and dimensional stability of 100 percent polyester. The cotton contributes a high level of moisture absorption to the blend as well as a better hand. Cotton producers found that the suitable fabrics may by produce from a wide range of polyester/cotton blend ratios. The most popular ratios for apparel are 65/35 and 50/50 blends although blends high as 80/20 or as low as 20/80 have proved useful.

Increasing the polyester content gives greater wrinkle resistance, higher elasticity and dimensional stability, faster drying times and better abrasion resistance. These advantages are accompanied by decrease comfort, a slicker, more synthetic hand, less brilliant colors and a tendency to grey. Higher levels of cotton promote a drier, more natural hand, increases comfort, more brilliant colors, and tendency to absorb oil-borne dirt. The disadvantages are increased need for ironing, a tendency to shrink upon laundering and absorption of water-borne stains. Stain removal is a problem with all polyester/cotton blended fabrics.

# CHAPTER III

# EXPERIMENT

## 3.1 Scope of The Experiments

In this chapter, the polyester (PET), cotton and polyester/cotton blended (T/C) fabrics were surface-modified by air or argon plasma. The morphology and properties of untreated and plasma-treated fabrics were then characterized and compared. The flow chart of the entire experimental procedure is shown below in Figure 3.1

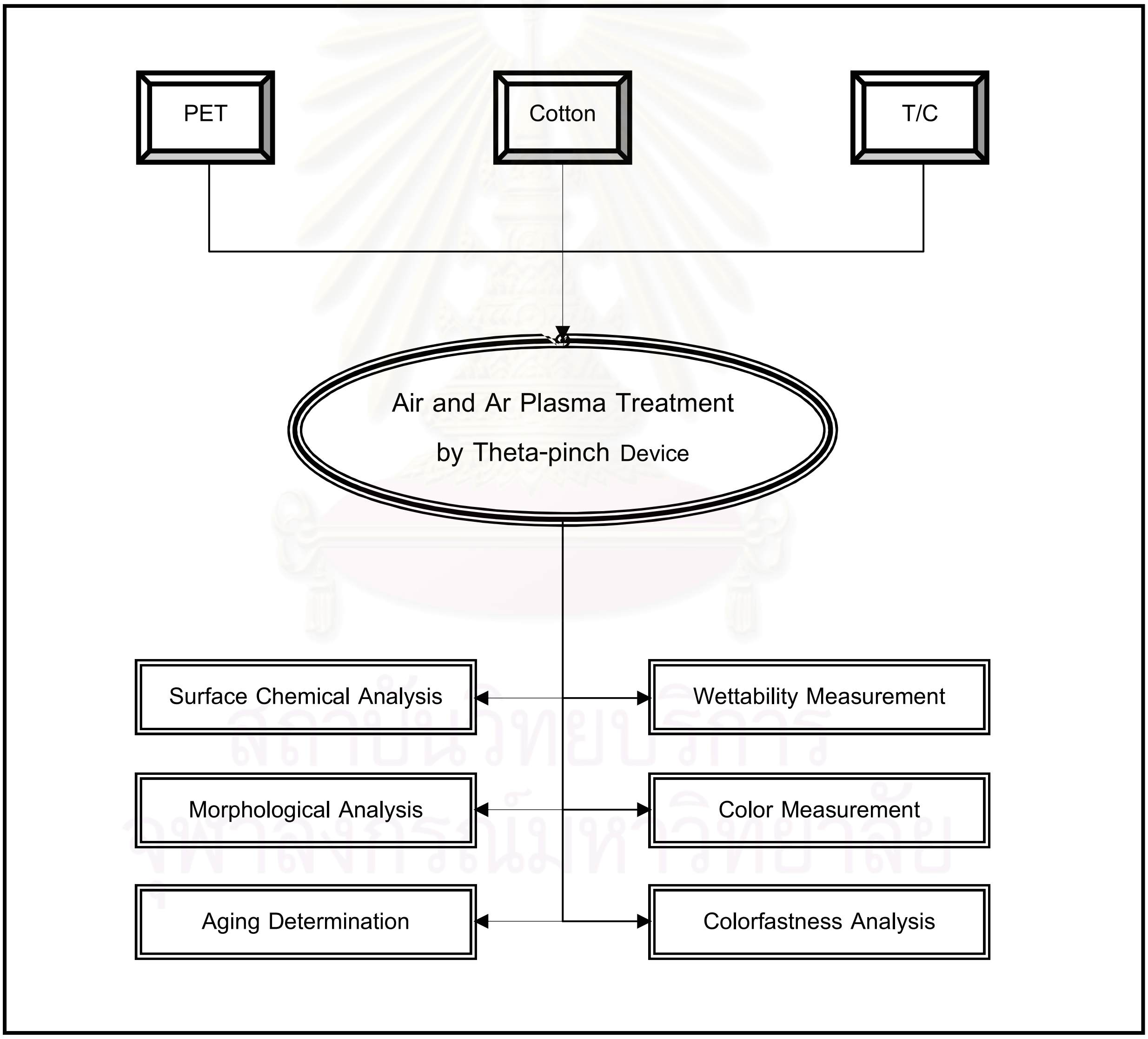


Figure 3.1 The scope of experiment

## 3.2 Materials

### 3.2.1 Samples

3.2.1.1 Polyester (PET) woven fabric (plain); THAI TAFFETA Co., Ltd.

Yarn count : Warp 70/24 dtex, Weft 160/90 dtex

Density : Warp 118 ends/cm, Weft 80 picks/cm

Weight : 89 g/$m^2$

3.2.1.2 Cotton woven fabric (plain); Jim Thomson Co., Ltd

Density : Warp 35 ends/cm, Weft 20 picks/cm

Weight : 234 g/$m^2$

3.2.1.3 Polyester/cotton blended (T/C) woven fabric (plain) (65/35)

Density : Warp 46 ends/cm, Weft 30 picks/cm

Weight : 101 g/$m^2$

### 3.2.2 Dyes

3.1.2.1 Disperse dye, Dianix Blue XF; DyStar Thai Ltd.

3.1.2.2 Reactive dye, Levafix Navy CA gran; DyStar Thai Ltd.

### 3.2.3 Chemicals

**Table 3.1** Analytical grade chemicals used in this research

| Chemicals | Company |
|---|---|
| acetic acid | MERCK |
| anti-migration agent | DyStar Thai Ltd. |
| citric acid | DyStar Thai Ltd. |
| leveling agent | CIBA Specialty Chemicals Inc. |
| sodium carbonate | SEELZE-HANNOVER |
| sodium hydrosulfite | APS Ajax Finechem |
| sodium hydroxide | Ajax Finechem |
| sodium sulfate | AnalaR® |
| standard soap (WOB) | SDC Enterprises Limited |

## 3.3 Machines and Equipments

3.3.1 Theta-pinch device supported by Asian African Association for Plasma Training (AAAPT)

3.3.2 Scanning electron microscope (SEM): JSM-6400, Jeol Co, Ltd.

3.3.3 ATR/FT-IR spectrophotometer, Thermo Nicolet Nexus 670

3.3.4 CHNS/O Analyzer, Perkin Elmer PE2400 Series II

3.3.5 Laboratory exhausted dyeing machine, Labtec®

3.3.6 Macbeth reflectance spectrophotometer, COLOR-EYE® 7000

3.3.7 Crock meter, ATLAS ELECTRIC DEVICES Co, Ltd.

3.3.8 Washing machine, Gyrowash®

3.3.9 Electrical analytical balance, Precisa 300C

3.3.10 Hot plate, Fermo-Geratetechnik M21/1

## 3.4 Glassware

3.4.1 Beaker

3.4.2 Buret

3.4.3 Cylinder

3.4.4 Dropper

3.4.5 Stirring rod

## 3.5 Procedure

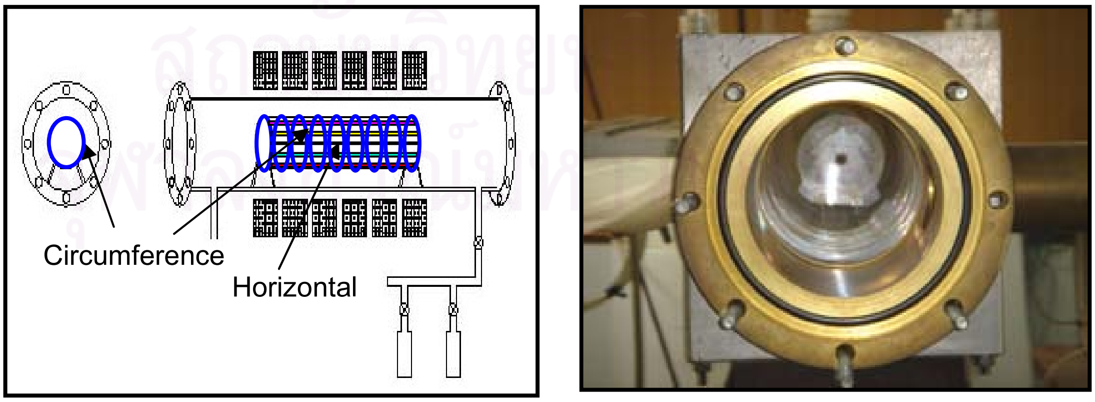
### 3.5.1 Surface Modification of Fabrics Using Theta-pinch Device

Each type of fabric was cut into the required dimension, 48×26 cm. Fabric sample was then wound around a sample holder. In the middle of reaction chamber of theta-pinch device, a sample fabric was placed as shown in Figure 3.2. Before starting the process, air and old gases had to be pumped out by the vacuum pump, thus almost a vacuum level was created in the reaction chamber. Afterward, air or argon gas was introduced into this chamber. All the treatments were performed using the following conditions shown in Table 3.2

**Table 3.2** The operating conditions of theta-pinch device

| Operating Conditions of Theta-pinch Device | |
|---|---|
| Pressure | 2 Pa |
| Maximum Input | 125 kA |
| Charging Voltage | 20 kV |

When the treatment completed, the fabric was taken out of the chamber and was further tested and characterized.



a) b)

**Figure 3.2** Configuration of theta-pinch device (a) and position of fabric sample in chamber (b)

In order to investigate the effect of high temperature pulse-plasma on the properties of each fabric, the operating parameters; especially, the type of the gas and the number of plasma shots were varied. Table 3.3 shows the conditions used for surface modification of fabrics.

**Table 3.3** Modification conditions used in surface modification of synthetic and natural-fiber fabrics

| Gas<br>Type of Fabric | Number of Plasma Shots | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Air | | | | Argon | | | |
| PET | 10 | 20 | 30 | 40 | 10 | 20 | 30 | 40 |
| Cotton | 10 | 20 | - | - | 10 | 20 | - | - |
| T/C | 10 | 20 | - | - | 10 | 20 | - | - |

3.5.2 Characterization and Testing

3.5.2.1 Wettability Measurement

In order to investigate the wettability (or hydrophilicity) of untreated and treated fabrics, a water droplet absorption time measurement was applied according to AATCC standard test method 79 (Absorbency of Bleached Textiles).

A distilled droplet was allowed to fall from a buret held 10-mm height from the stretched fabric surface. The time for the disappearance of water-mirror on the surface was measured as the wetting time. The averages of wetting time at different positions on the sample surface were recorded. In the cases of PET and T/C, the studied area of the fabric was divided as shown in Figure 3.3 and 3.4 and the wetting time of each area was determined. First, the area horizontal to the chamber was divided into 9 parts, including I, II, III, IV, middle, V, VI, VII, and VIII, as illustrated in Figure 3.3. Additionally, each horizontally divided area was separated into seven areas, specified as P.1, P.2, P.3, P.4, P.5, P.6, and P.7 which can be seen in Figure 3.4

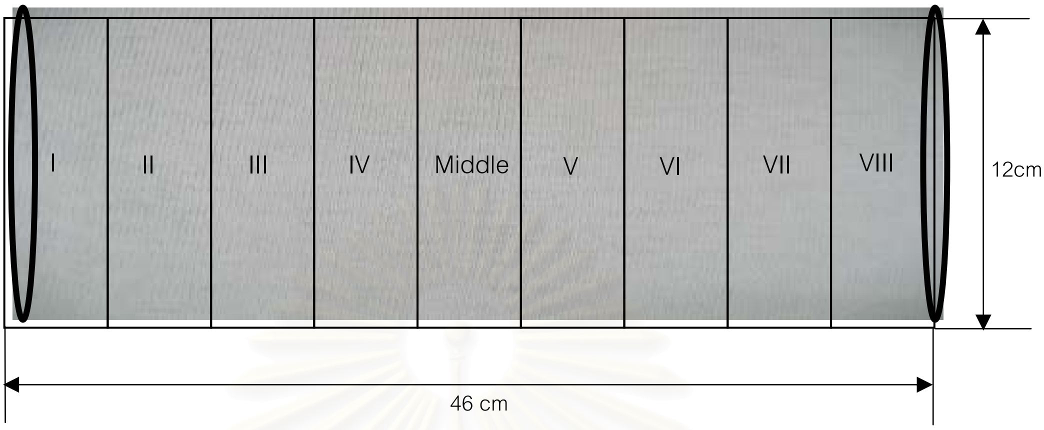


Figure 3.3 Horizontally divided areas of the fabric

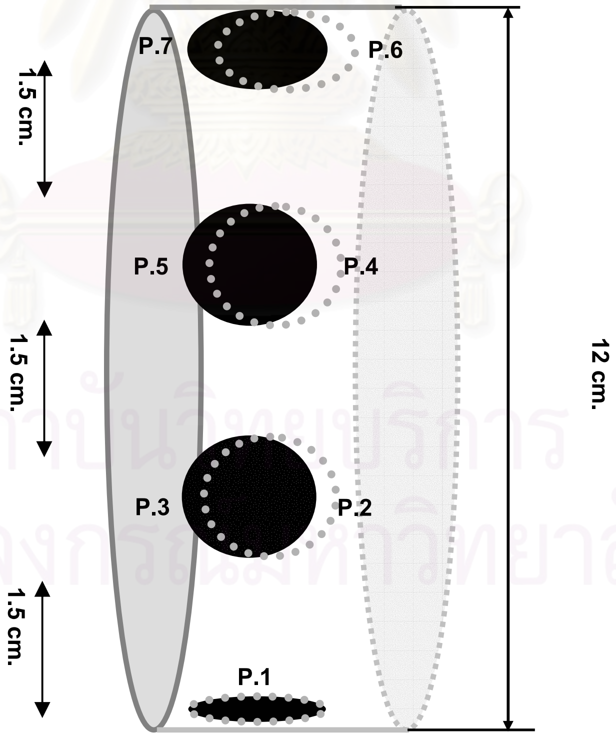


Figure 3.4 Seven areas of each horizontally divided position

3.5.2.2 Morphological Analysis

In order to observe the influence of the gas type and the number of plasma shots on surface morphology of plasma-treated fabrics, scanning electron microscope (SEM) (JSM-6400) was used to characterize the sample morphology.

All of the fabric samples were coated with thin evaporated layer of gold in order to improve conductivity and prevent electron charging on the surface before SEM analysis. The operation was at 5 keV acceleration voltages. SEM photographs were taken at different angles of view with magnification of 1500X.

**Figure 3.5** Scanning electron microscope (JSM-6400)

3.5.2.3 Surface Chemical Analysis

The changes in surface chemical structure of the fabric samples were characterized using Attenuated total reflection/Fourier transform infrared spectroscopy (ATR-FTIR) (Thermo Nicolet Nexus 670 spectrophotometer). The samples were scanned at the frequency range of 4000-600 $cm^{-1}$ with 300 consecutive scans and 4 $cm^{-1}$ resolution.

3.5.2.4 Determination of aging effect of functional groups

In order to investigate the aging effect of functional groups on plasma-treated fabrics surface, the plasma-treated fabrics which treated by various gas and number of plasma shots were collected at room temperature for 30 days. Functional group on fabric surface was detected by ATR-FTIR.

**Figure 3.6** ATR-FTIR Spectrophotometer

(Thermo Nicolet Nexus 670 spectrophotometer)

3.5.2.5 Elemental Analysis

Elements of the plasma-treated fabric surface were analyzed by CHNS/O Analyzer (Perkin Elmer PE2400 Series II). Fabrics samples were pyrolyzed in oxygen atmosphere and the pyrolzed substances were separated by chromatographic column.

**Figure 3.7** Elemental Analyzer (Perkin Elmer PE2400 Series II)

#### 3.5.2.6 Dyeability Testing

##### 3.5.2.6.1 Dyeing of Untreated and Plasma-treated Polyester (PET) Fabrics

PET fabrics were dyed with disperse dye (Dianix Blue XF supplied by DyStar Thai Ltd.), carried out using 1.5 g of fabric and 1:20 liquor ratio. Exhausted dyeing machine was used. Solution, containing 2% o.w.f. of the dye, 2 g/l wetting agent (Sera Wet C-AS supplied by DyStar Thai Ltd.) and 50 ml/l of citric acid (Sera Gel M-IP supplied by DyStar Thai Ltd.) for pH adjustment was employed for dyeing PET fabric.

The following dyeing solutions were adopted. Initial temperature was 50°C, followed by a temperature increase 2°C/min up to 130°C, holding for 30 min. After dyeing, the samples were taken out from the dyeing tubes. The dyed fabrics were reduction cleared for 20 min at 80°C using a water solution containing 5 g/l of NaOH and 2g/l of $Na_2S_2O_4$. Dyed fabrics were soaped for 15 min at 60°C with a water solution containing 2 g/l of a standard non-ionic detergent to eliminate any residual dye from their surface and allowed to dry in opened air. The dyeing process is illustrated in Figure 3.9

**Figure 3.8** Laboratory exhausted dyeing machine, Labtec®

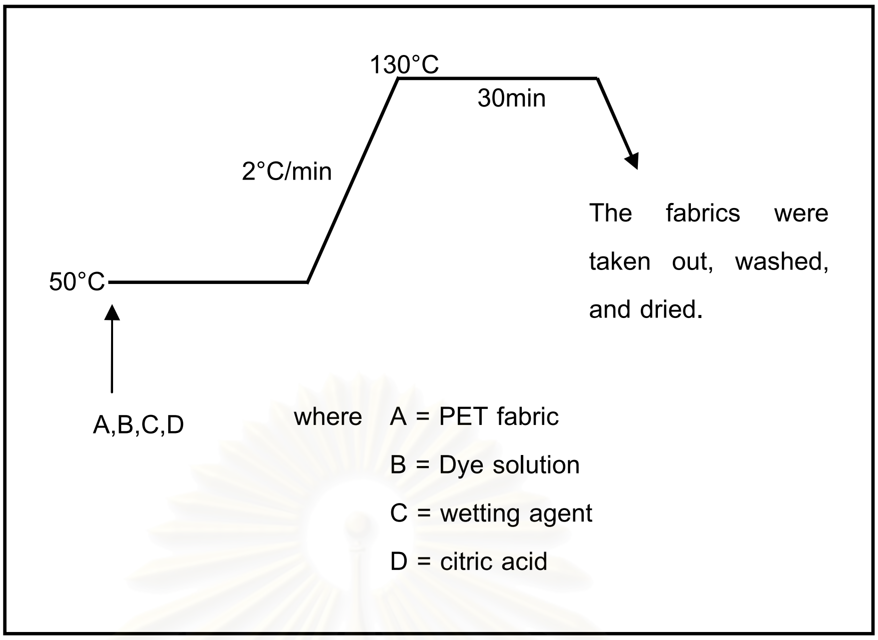


**Figure 3.9** Disperse dyeing process of untreated and plasma-treated PET fabrics

3.5.2.6.2 Dyeing of Untreated and Plasma-treated Cotton Fabrics

Dyeing of cotton fabrics were carried out using a reactive dye (Levafix Navy CA gran supplied by DyStar Thai Ltd.) and 1:20 liquor ratio. Aqueous solution, containing 2% o.w.f. of the dye, 15 g/l of salt was employed for dyeing cotton fabrics in sealed stainless steel dyeing tubes of 300 $cm^3$ capacity housed in a laboratory exhausted dyeing machine (Labtec®).

The following dyeing solutions were adopted. Initial temperature was 30°C and held for 30 min, followed by a temperature increase 2°C/min up to 60°C. At this temperature, 5 g/l $Na_2CO_3$ was added in dyeing tubes. The dyeing continued for 30 min. At the end of dyeing, the samples were taken out from the dyeing tubes. Dyed fabrics were washed with 5 g/l of non-ionic surfactant at 100°C for 15 min. and rinsed again with hot distilled water and allowed to dry in opened air. The dyeing process is illustrated in Figure 3.10

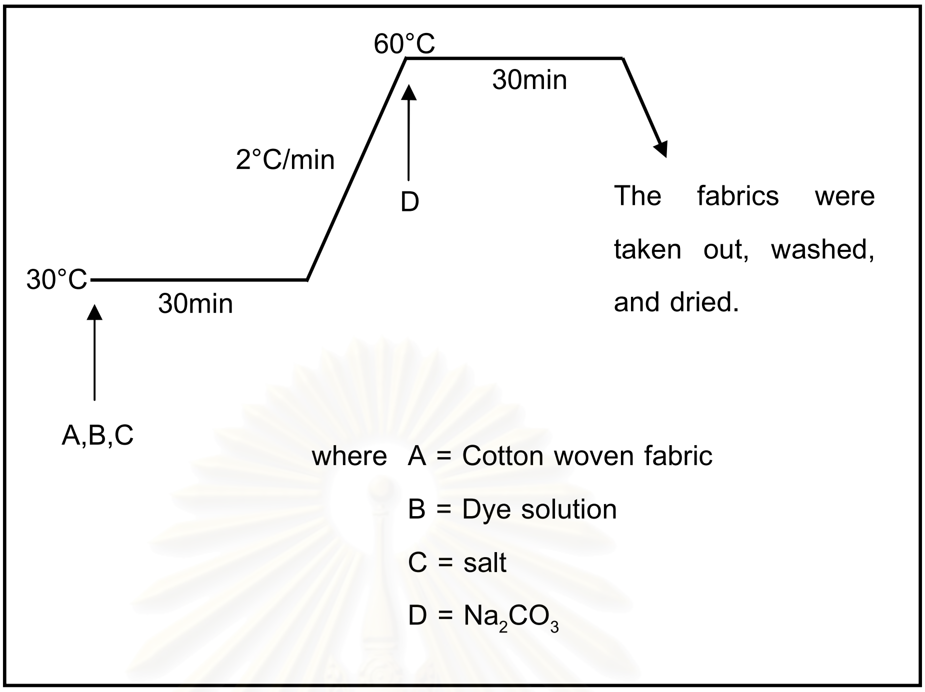


**Figure 3.10** Reactive dyeing process of untreated and plasma-treated cotton fabrics

#### 3.5.2.6.3 Dyeing of Untreated and Plasma-treated Polyester/Cotton (T/C) Fabrics

In this research, Untreated and plasma-treated T/C fabrics were dyed twice. Firstly, disperse dye (Dianix Blue XF supplied by DyStar Thai Ltd.) was used to dye polyester fibers which 65 percent containing in fabrics. Next, cotton fibers were dyed by a reactive dye (Levafix Navy CA gran supplied by DyStar Thai Ltd.). Both dyeing process were used as describe before.

#### 3.5.2.7 Color Measurement

The reflectance values of dyed samples were measured using an Instrument Color System (I.C.S.) Macbeth reflectance spectrophotometer (Figure 3.10) connected to a digital personal computer, to measure the reflectance of the employed sample and the wavelength corresponding to the maximum absorbance of the employed dye.

**Figure3.11** Macbeth reflectance spectrophotometer

Each fabric sample was folded once leading to a total of two thicknesses of fabric. Each reflectance value was determined as the average of four measurements. Percent reflectance values (R) were converted into *K/S* values, the color strength of the fabric, according to the Kubelka-Munk equation:

$$K/S = \frac{(1-R^2)}{2R}$$

Where K is the absorption coefficient.

S is the scattering coefficient.

R is the reflectance of the fabric at the wavelength of maximum absorption ($\lambda_{max}$)

3.5.2.8 Determination of Colorfastness to Washing (AATCC Test Method 61)

A laundering test was performed to evaluate the resistance of dyed fabrics to change in any of its color characteristics as a result of the exposure of fabric samples to laundering.

**Figure 3.12** Gyrowash® washing machine

The dyed fabric was cut into the size of 2.0 to 4.0 inch and immersed in solution containing a 0.37% of AATCC standard reference detergent WOB (without fluorescent whitening agent and without phosphate) in 400 ml. Stainless steel lever lock canister containing 0.25 inch. stainless steel balls and the number of balls were 10. These canisters were housed in a washing machine shown in Figure 3.12, for rotating closed canisters in a thermostatically controlled water bath at 40°C for 45 min. Colorfastness to washing was evaluated at 10, 20,and 30 cycles of washing for each sample.

The color difference between two fabrics can be evaluated by $\Delta E$, the distance between two colors in the color space, with $L^*$, $a^*$, and $b^*$ indicating the brightness (black-white), red-green, and yellow-blue, respectively. The $\Delta E$ value between sample 1 and sample 2 can be calculated using following equation:

$$\Delta E = \sqrt{(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2}$$

if $L^*_1-L^*_2$ = (+) is lighter
(-) is darker

$a^*_1-a^*_2$ = (+) is redder
(-) is greener

$b^*_1-b^*_2$ = (+) is yellower
(-) is bluer

3.5.2.9 Colorfastness to Crocking test (AATCC 8-2005)

Crock meter was used to determine the amount of color that transferred from the surface of dyed fabrics. The dyed fabric was cut at least into 5 x 13 centimeters and two pieces of bleached cotton were used as reference cut into 5x5 centimeters, one for dry and wet test. Each sample was rubbed for 10 turns. The color transferred to the cotton was assessed by a comparison with the AATCC Gray Scale for staining and a grade was assigned.

**Figure 3.13** Crock Meter

# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Properties and Morphology of Untreated and Plasma-treated Polyester Fabrics

### 4.1.1 Fabric Appearance

Figure 4.1 reveals that the color of polyester fabrics treated with 30 and 40 shots of air and argon plasma became darker due to degradation caused by higher electron bombardment as the number of plasma shots was increased. The results suggest that the suitable numbers of plasma shots for plasma treatment should be 10 and 20 shots.

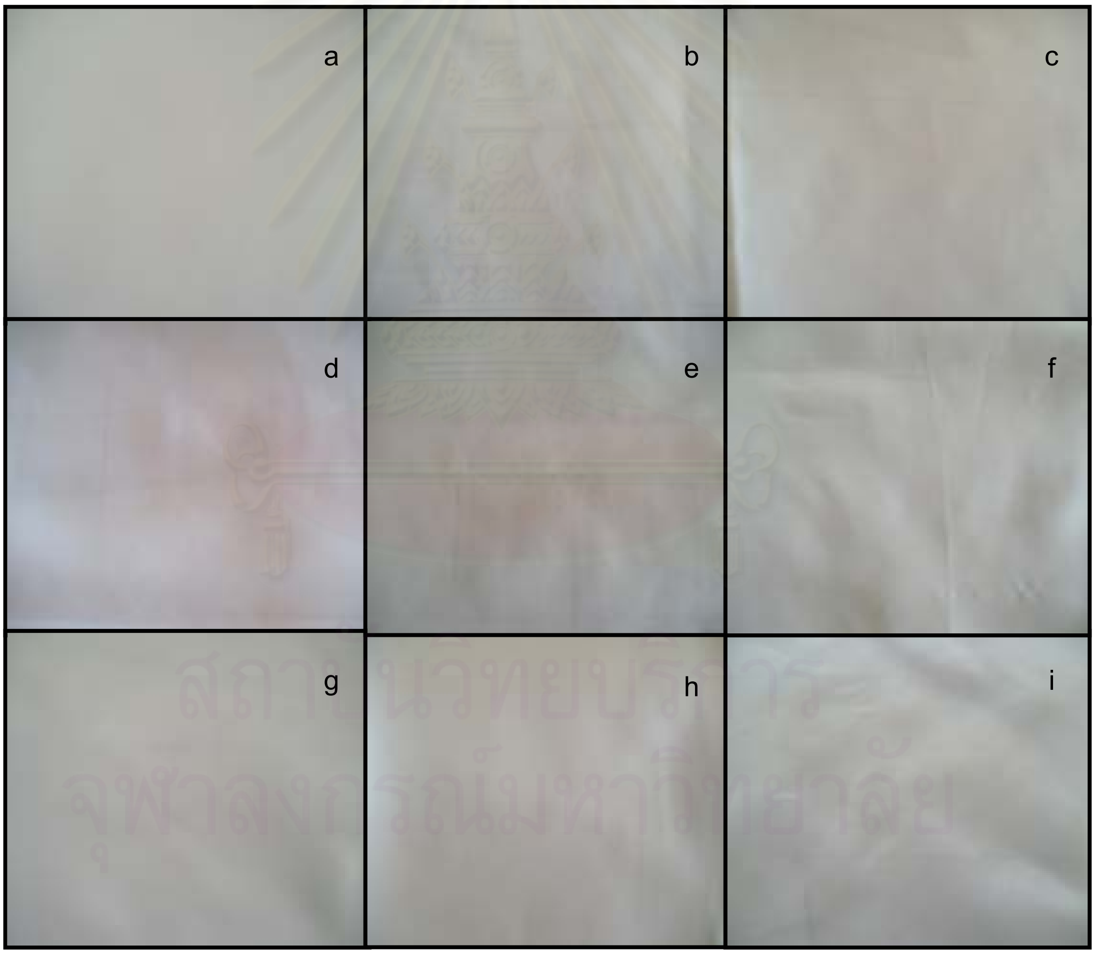


**Figure 4.1** Images of untreated PET fabric (a), PET fabrics treated with 10 (b), 20 (c), 30 (d), and 40 (e) shots of air plasma, PET fabrics treated with 10 (f), 20 (g),30 (h), and 40 (i) shots of argon plasma.

### 4.1.2 Surface Chemical Structure

The attenuated total reflection infrared spectroscopic (ATR-FTIR) studies were performed to analyze the changes in chemical structures of PET molecules at fabric surface after subjecting to plasma treatment. These changes include the introduction of any new functional groups, or the alteration of existing groups.

ATR-FTIR spectra of untreated and plasma-treated polyester fabrics are shown in Figures 4.2 and 4.3 while all the interpretations of ATR-FTIR spectra of these fabrics are given in Table 4.1. When polyester fabric was treated with 10 shots of air plasma, the peak around 1605 $cm^{-1}$ which can be assigned to C=O stretching appears near C=O stretching of ester groups of PET molecules as seen from Figure 4.2(a) and 4.2(b). The intensity of this peak increases with increasing the number of plasma shots to 20 shots as shown in Figure 4.2(c). These results suggest that oxygen containing groups, such as carbonyl groups were attached to polyester fabric surface when it was treated with air plasma. In case of polyester fabric treated with 10 and 20 shots of argon plasma, the similar peaks were observed as shown in Figure 4.3. This suggest that argon plasma caused chain scission of PET molecules and scission fragments then reacted with PET surface resulting in the formation of carbonyl groups.

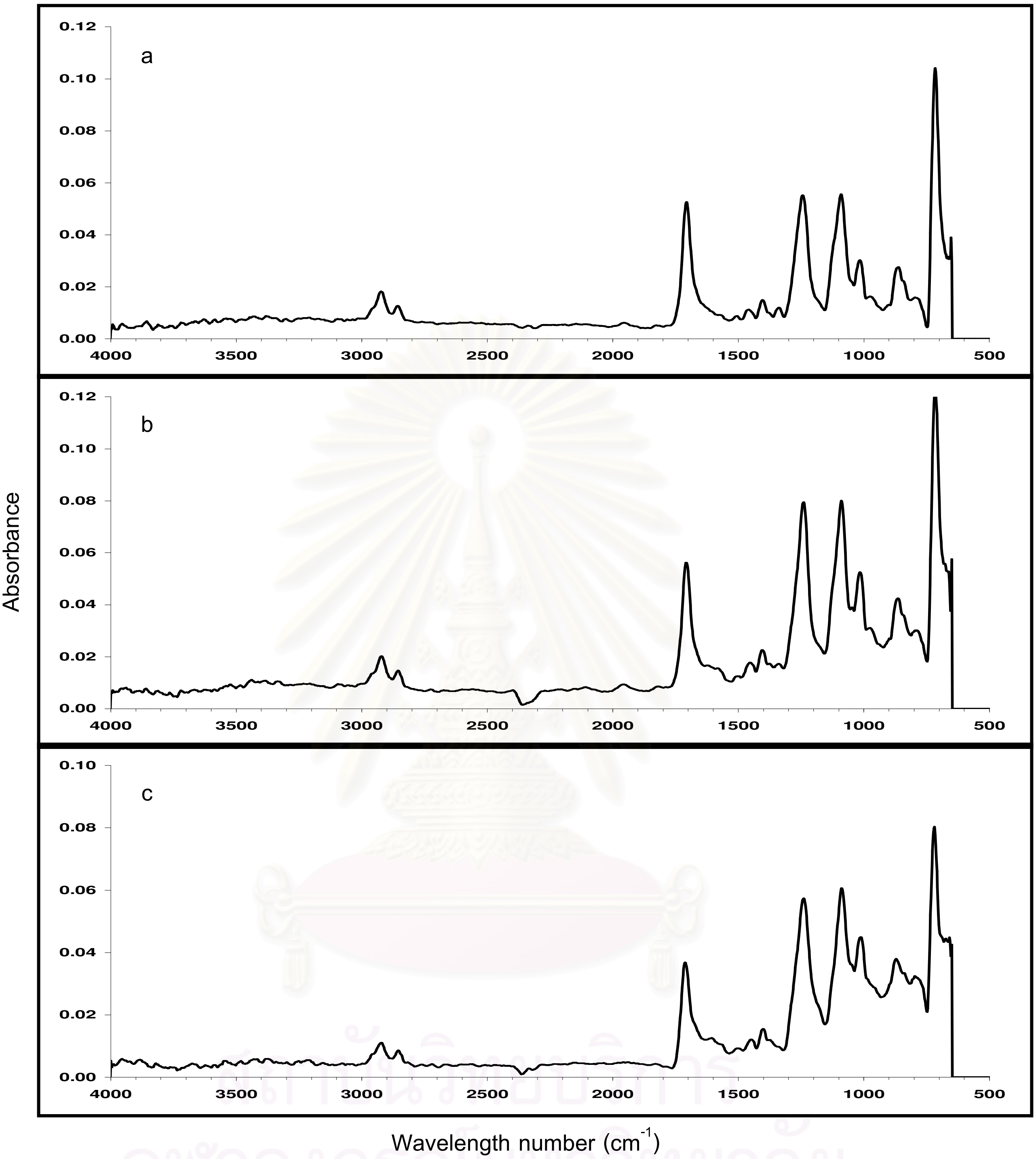


Figure 4.2 ATR-FTIR spectra of untreated PET fabric (a), PET fabrics treated with 10 (b), and 20 (c) shots of air plasma.

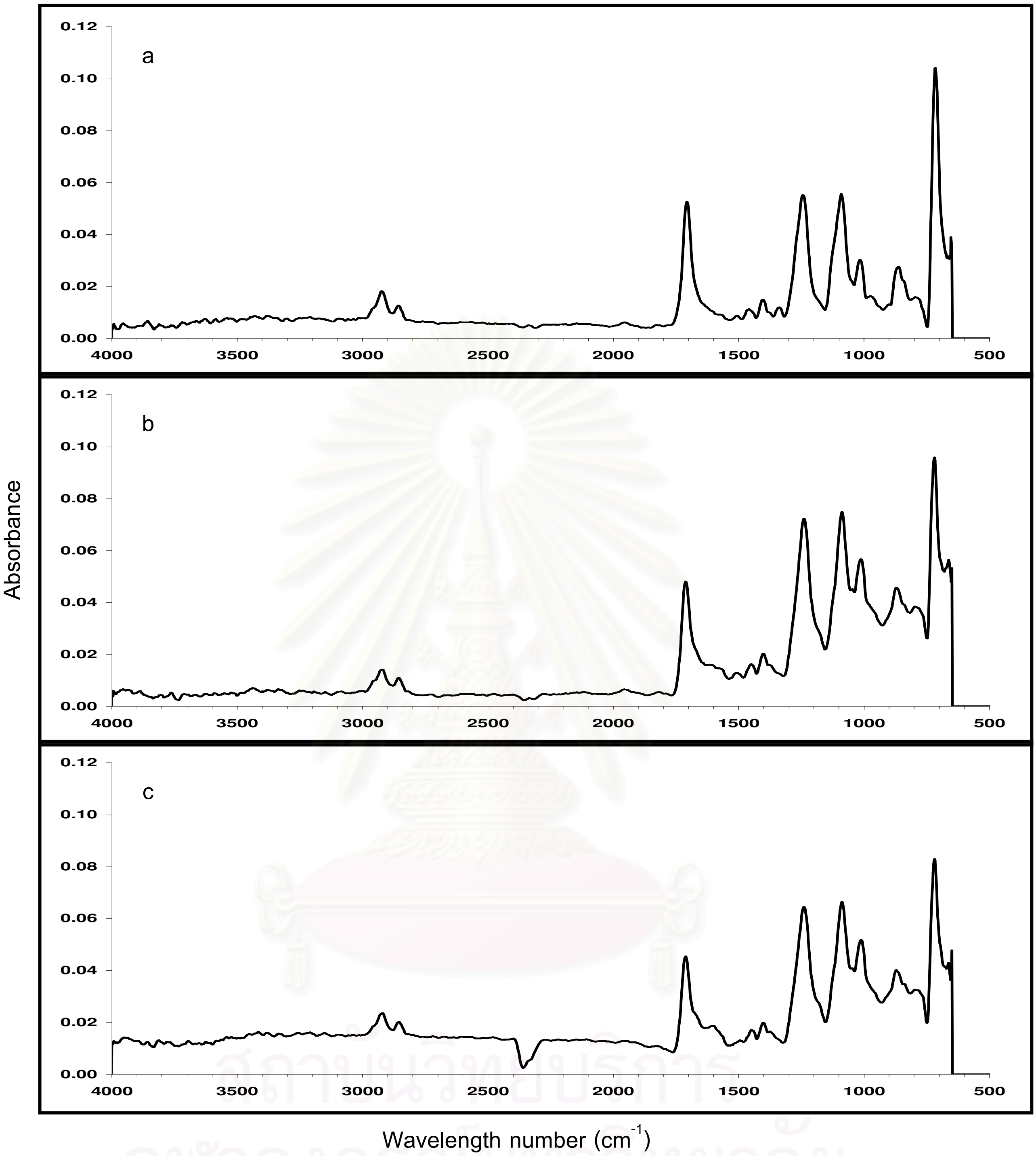


**Figure 4.3** ATR-FTIR spectra of untreated PET fabric (a),

PET fabrics treated with 10 (b), and 20 (c) shots of argon plasma.

**Table 4.1** The interpretation of ATR-FTIR spectra of untreated and plasma-treated PET fabrics

| Wavenumber ($cm^{-1}$) | | | Interpretation |
|---|---|---|---|
| Untreated | Air Plasma | Ar Plasma | |
| 2992 | 2922, 2857 | 2921, 2855 | Saturated C-H stretching |
| 1706 | 1706 | 1712 | C=O stretching of ester group of polyester molecule |
| - | 1605 | 1605 | C=O stretching of the carbonyl group |
| 1459,1403 | 1444,1405 | 1442,1406 | C-H bending for $CH_2$ |
| 1244, 1091 | 1244, 1091 | 1239, 1068 | C-O-C stretching of the ester |
| 980 | 982 | 980 | Skeleton vibration involved in C-O stretching |
| 863 | 863 | 871 | Out of plane C-H of p-disubstituted aromatic rings |

### 4.1.3 Morphological Analysis

Surface morphological changes induced by air and argon plasma treatments on PET fabrics were observed by scanning electron microscope (SEM) and the results are shown in Figure 4.4.

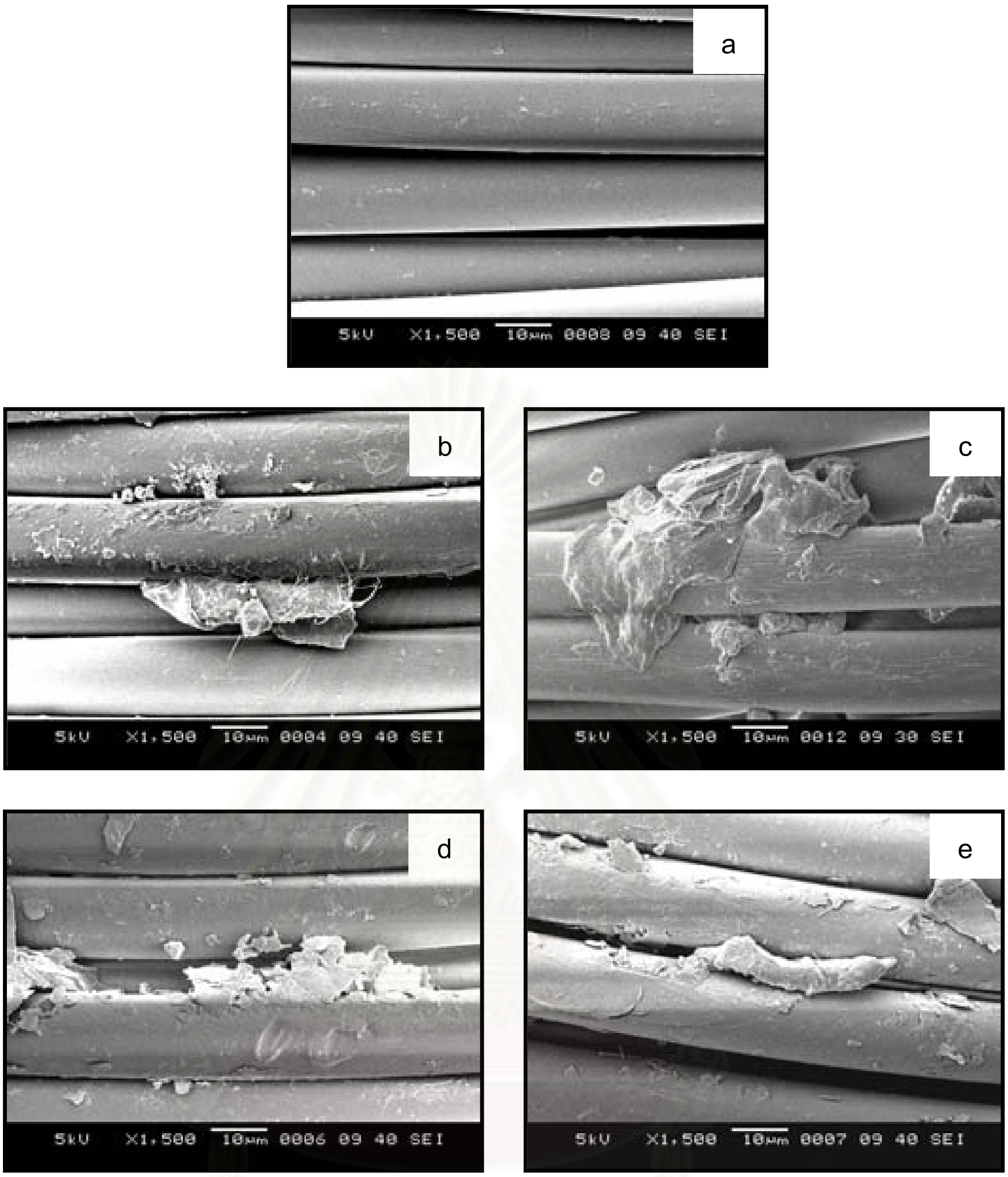


**Figure 4.4** SEM images at X1500 of untreated PET fabric (a), PET fabric streated with 10 (b), and 20 (c) shots of air plasma, PET fabric treated with 10 (d), and 20 (e) shots of argon plasma.

As illustrated in Figure 4.4(a) the original surface of untreated polyester is smooth. After treatment with air plasma, an increase in surface roughness was observed as shown in Figure 4.4(b). Furthermore, when 20 shots of air plasma were applied, the surface roughness increased as seen in Figure 4.4(c). These results can be attributed to the etching process caused by the bombardment of air plasma reactive species on the fabric surface. In addition, the redeposition of etched fragments onto the fabric surface is also clearly seen in these images. Figures 4.4(d) and 4.4(e) show SEM images of polyester fabrics treated by argon plasma at 10 and 20 shots, respectively. It is obviously seen that argon plasma also caused the changes in surface roughness of PET surface similar to air plasma. The bombardment of plasma species can be enhanced by increasing the number of plasma shots. Therefore, it can be concluded that the changes in surface morphology of the plasma-treated fabrics depend on the number of plasma shots.

### 4.1.4 Aging of Functional Groups

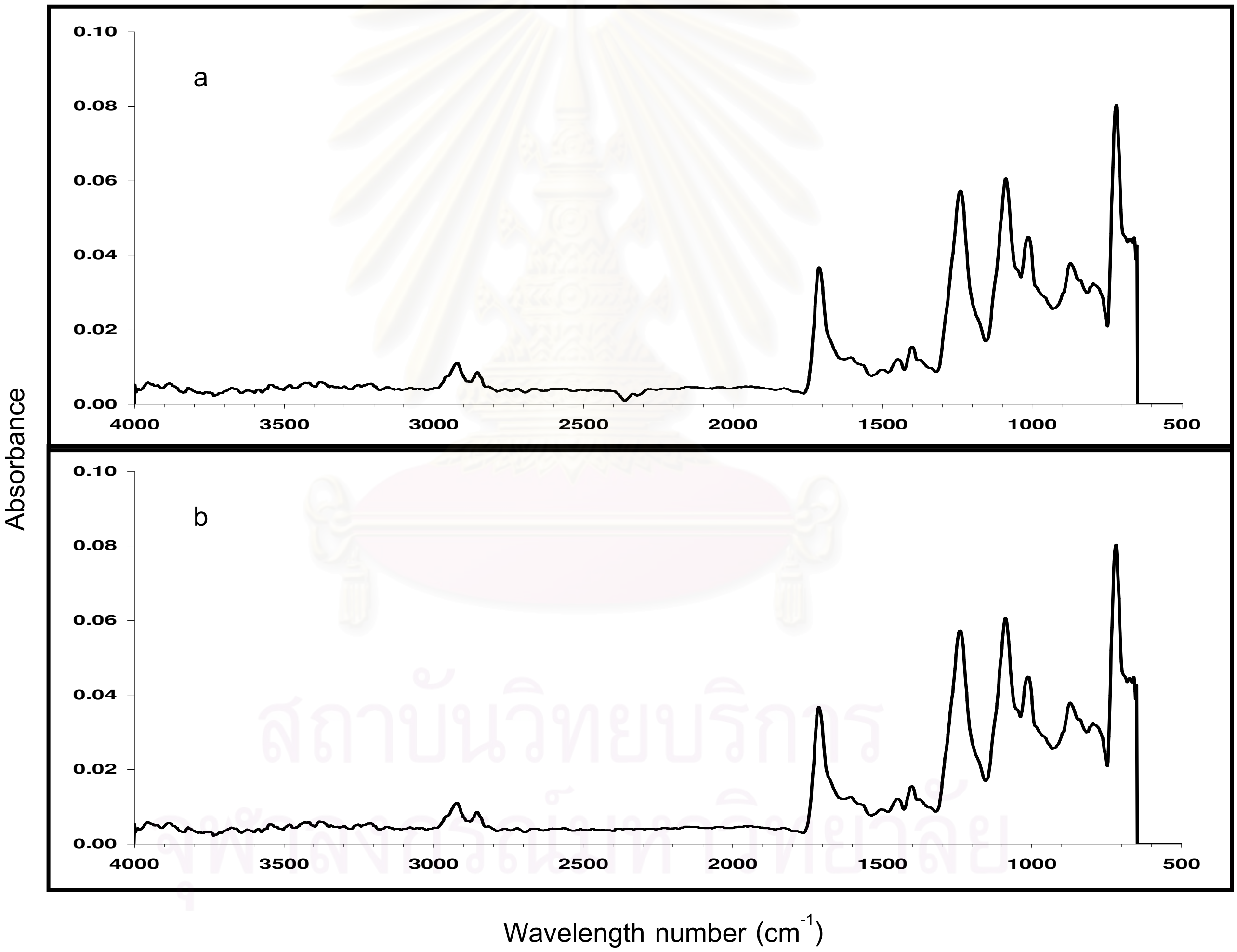


**Figure 4.5** ATR-FTIR spectra of PET fabrics treated with 20 (a) shots of air plasma, and PET fabrics treated with 20 (b) shots of air plasma after 30 days.

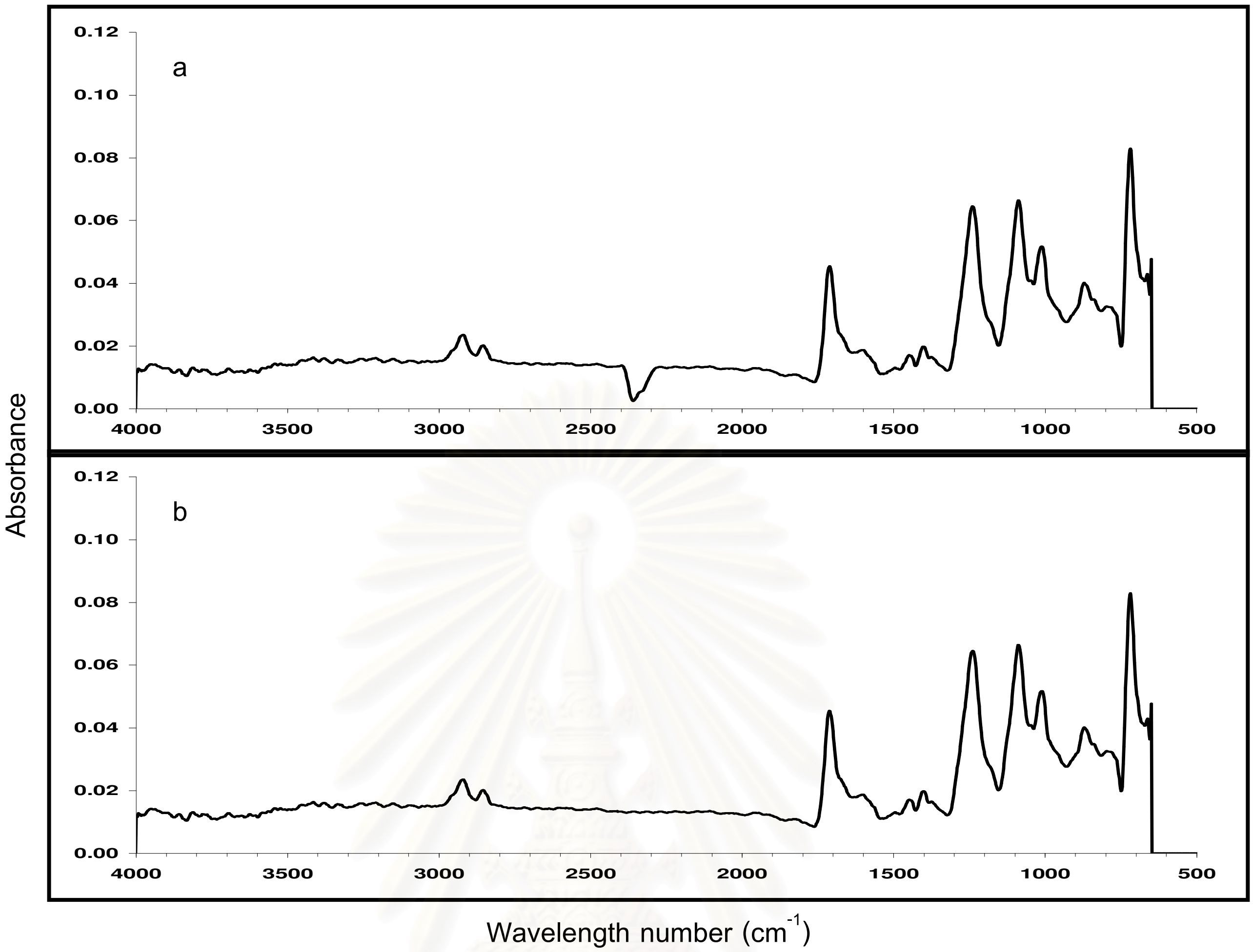


**Figure 4.6** ATR-FTIR spectra of PET fabrics treated with 20 (a) shots of argon plasma, and PET fabrics treated with 20 (b) shots of argon plasma after 30 days.

As shown in Figures 4.5 and 4.6, the peaks corresponding to C=O functional groups resulted from air and argon plasma treatment still appear at wavenumber around 1605 $cm^{-1}$. This indicates that these functional groups are stable over 30 days.

### 4.1.5 Wettability

The surface wettability of untreated and plasma-treated polyester fabrics was characterized by the measurement of the wetting time directly after the plasma treatment. As previously described in Chapter III, the wettability of untreated and plasma-treated synthetic-fiber fabrics were both investigated in horizontal and circumference areas.

4.1.5.1 Wettability in Horizontal Area

As shown in Figure 4.7, it can be obviously seen that the wetting time of untreated PET fabric is higher than that of air and argon plasma-treated PET fabrics, indicating that untreated PET fabric was more hydrophobic. After air or argon plasma treatments, the results show that the wetting time significantly decreased. Additionally, the wetting time of air and argon plasma-treated PET fabrics apparently decrease with increasing the number of plasma shots because both air and argon plasma led to the formation of new hydrophilic functional groups on polyester surface as confirmed by ATR-FTIR spectroscopy. In addition, due to higher amount of hydrophilic functional groups formed and surface roughness with increasing number of plasma shots, fabrics treated with 20 shots of both plasmas have lower wetting times than those treated with 10 shots. However, it can be seen that PET surface treated at the middle position of theta-pinch chamber has better wettability than those treated at other positions. Since maximum plasma density and energy of plasma usually occurs at the middle position of the chamber; therefore, PET fabric can be modified effectively at this position.

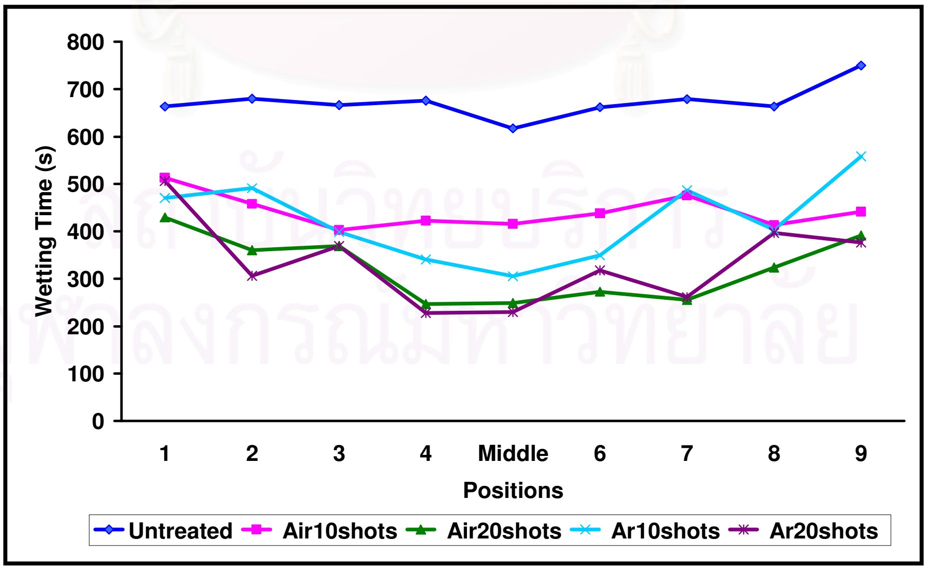


Figure 4.7 The wettability of untreated and plasma-treated PET fabrics measured in horizontal area

#### 4.1.5.2 Wettability in Circumference Area

Figure 4.8 shows the wettability of plasma-treated PET fabrics measured in circumference area. Treating PET fabrics with air and argon plasma results in effectively increasing hydrophilicity since higher degree of modification occurred. It can be seen that the modification of PET fabrics by air and argon plasmas using theta-pinch device led to the changes in surface properties of PET fabric from hydrophobic to hydrophilic; consequently, the wetting times of all circumference area on the surface decrease.

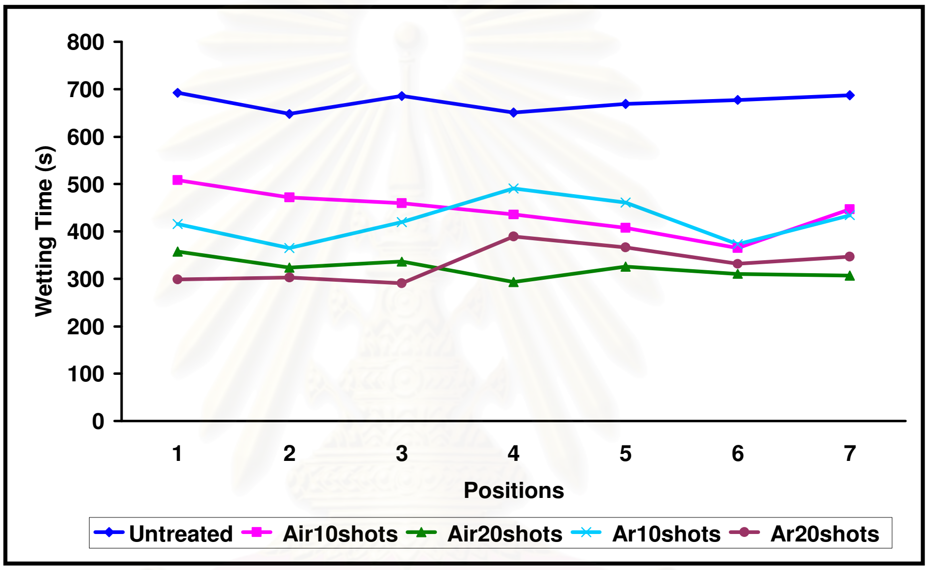


Figure 4.8 The wettability of untreated and plasma-treated PET fabrics measured in circumference area

### 4.1.6 Dyeability

The dyeability of PET fabrics after air and argon plasma treatments was evaluated in this study. After treatment with air and argon plasmas, PET fabrics were dyed with a disperse dye previously described in Chapter III. Table 4.2 summarizes the results for color measurements of plasma-treated PET fabrics dyed with disperse dye (Dianix XF, supplied by DyStar Thai Ltd.). They are expressed in term of K/S at maximum absorption wavelength and CIE lab values.

**Table 4.2** Color measurement of untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix Blue XF, supplied by DyStar Thai Ltd.)

| Conditions | $\lambda_{max}$ (nm) | K/S | L* | a* | b* |
|---|---|---|---|---|---|
| Untreated | 620 | 13.88±0.16 | 26.60±0.08 | 0.28±0.04 | -18.51±0.13 |
| 10 Shots of Air Plasma | 610 | 13.77±0.06 | 26.63±0.24 | 0.55±0.13 | -18.72±0.45 |
| 20 Shots of Air Plasma | 610 | 16.24±0.46 | 24.48±0.49 | 0.68±0.10 | -18.07±0.45 |
| 10 Shots of Argon Plasma | 620 | 15.28±0.19 | 25.14±0.32 | 0.90±0.10 | -18.48±0.45 |
| 20 Shots of Argon Plasma | 610 | 13.49±0.21 | 26.46±0.18 | 0.46±0.02 | -17.50±0.06 |

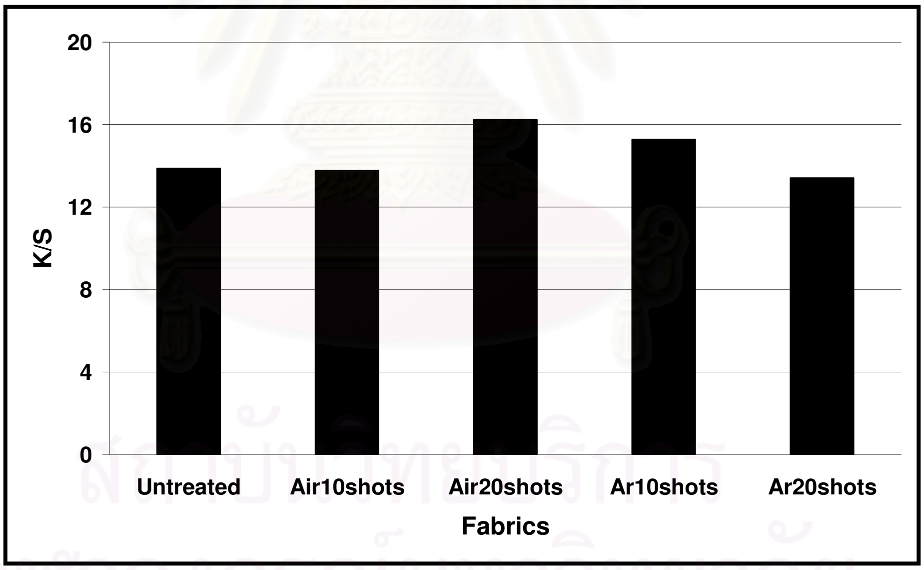


**Figure 4.9** K/S values of untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix Blue XF, supplied by DyStar Thai Ltd.)

After treatment with air and argon plasma, polyester fabrics were dyed with a disperse dye as described. Color strength of dyed samples was measured. The results in Figure 4.9 indicate that the color strengths of dyed fabrics treated with 20 shots of air plasma and 10 shots of argon plasma prior to dyeing are higher than that of untreated fabric. This may be due to increasing the surface roughness by plasma treatment, the amount of dye more penetrated into fiber.

However, the fabric treated by 20 shots of argon plasma shows comparable color strength as the untreated fabric instead of higher color strength as one might expect. This is because the etching effect of plasma treatment. When the surface of a material is subjected to plasma, the amorphous region of the material is easier to be removed than the crystalline region [3]. Since the dye molecules can penetrate the former than the latter; consequently, less amorphous region causes a decrease in saturation dye uptake value of the fabric.

### 4.1.7 Colorfastness to Washing

The colorfastness to washing of PET fabrics treated with air and argon plasmas and dyed with disperse dye (Dianix XF, supplied by DyStar Thai Ltd.) in terms of $\Delta$E and gray scale rating is summarized in Table 4.3 and Figure 4.10.

**Table 4.3** K/S values and $\Delta$E after washing of untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix Blue XF, supplied by DyStar Thai Ltd.)

| Conditions | Cycles | K/S | L* | a* | b* | $\Delta$E | Color Change |
|---|---|---|---|---|---|---|---|
| Untreated | 0 | 13.88 | 26.60 | 0.28 | -18.51 | - | - |
| | 10 | 13.66 | 26.81 | 0.30 | -18.68 | 0.37 | 4.5 |
| | 20 | 13.27 | 27.07 | 0.28 | -18.43 | 0.48 | 4.5 |
| | 30 | 13.18 | 22.14 | 0.35 | -18.65 | 0.67 | 4.5 |

**Table 4.3** K/S values and $\Delta$E after washing of untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix Blue XF, supplied by DyStar Thai Ltd.) (con't)

| Conditions | Cycles | K/S | L* | a* | b* | $\Delta$E | Color Change |
|---|---|---|---|---|---|---|---|
| 10 Shots, Air Plasma | 0 | 13.77 | 26.63 | 0.55 | -18.72 | - | - |
| | 10 | 13.56 | 25.14 | 0.48 | -18.28 | 0.37 | 4.5 |
| | 20 | 13.28 | 26.81 | 0.49 | -18.39 | 0.48 | 4.5 |
| | 30 | 13.24 | 26.98 | 0.42 | -18.50 | 0.67 | 4.5 |
| 20 Shots, Air Plasma | 0 | 16.24 | 24.82 | 0.61 | -18.39 | - | - |
| | 10 | 15.42 | 25.21 | 0.65 | -18.45 | 0.89 | 4.5 |
| | 20 | 13.33 | 26.85 | 0.35 | -18.09 | 2.45 | 3.5 |
| | 30 | 13.13 | 27.08 | 0.34 | -18.19 | 2.64 | 3.5 |
| 10 Shots, Argon Plasma | 0 | 15.28 | 25.14 | 0.90 | -18.48 | - | - |
| | 10 | 13.68 | 26.55 | 0.65 | -18.53 | 1.45 | 4 |
| | 20 | 13.76 | 26.58 | 0.58 | -18.73 | 1.69 | 4 |
| | 30 | 13.07 | 27.13 | 0.69 | -18.82 | 2.11 | 3.5 |
| 20 Shots, Argon Plasma | 0 | 13.41 | 26.46 | 0.46 | -17.50 | - | - |
| | 10 | 13.25 | 26.63 | 0.48 | -17.53 | 0.20 | 5 |
| | 20 | 12.98 | 26.82 | 0.46 | -17.38 | 0.38 | 4.5 |
| | 30 | 12.78 | 27.02 | 0.49 | -17.49 | 0.56 | 4.5 |

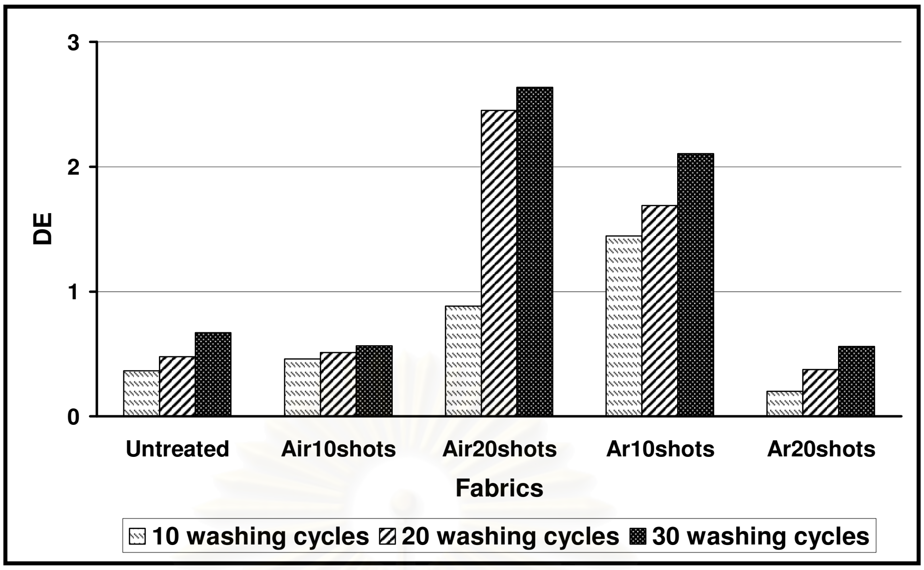


Figure 4.10 ΔE of untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix XF, supplied by DyStar Thai Ltd.) after washing.

Although PET fabrics treated with 20 shots of air plasma and 10 shots of argon plasma have higher color strength than untreated fabric and fabrics treated with other conditions, they exhibited worse colorfastness property. This may be because during washing, the etched fragments which also absorbed dye molecules were removed as confirmed by Figure 4.11. In this figure, the removal of etched fragments on fabric surface was observed after washing.

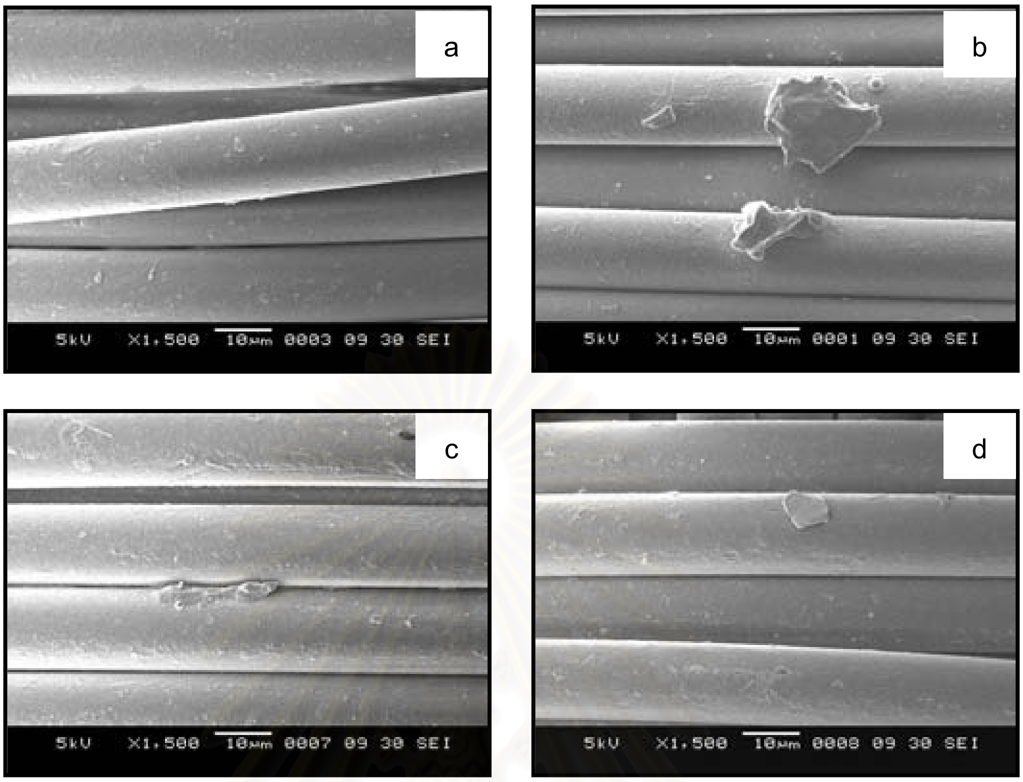


**Figure 4.11** SEM images at X1500 of PET fabrics treated with 20 shots of air plasma after washing (a) and (b), and 10 shots of argon plasma after washing (c) and (d).

### 4.1.8 Colorfastness to Crocking

**Table 4.4** Color stain values untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix XF, supplied by DyStar Thai Ltd.)

| Fabrics | Conditions | Color stain | |
|---|---|---|---|
| | | Dry | Wet |
| PET | Untreated | 5 | 4.5 |
| | 10 Shots, Air Plasma | 5 | 4.5 |
| | 20 Shots, Air Plasma | 5 | 4.5 |
| | 10 Shots, Argon Plasma | 5 | 4.5 |
| | 20 Shots, Argon Plasma | 5 | 4.5 |

All plasma-treated fabrics and untreated fabric were measured for color stain after dyeing. From Table 4.4, it can be seen that there is no difference between untreated and all plasma-treated fabrics. This indicates that the rubbing resistance of the fabric surface was not affected by plasma treatment suggesting that the modification occurred only on the fabric surface.

## 4.2 Properties and Morphology of Untreated and Plasma-treated Cotton Fabrics

### 4.2.1 Fabric Appearance

From Figure 4.12, it can be seen that treating T/C fabric with 10 and 20 of air and argon plasma did not affect their color.

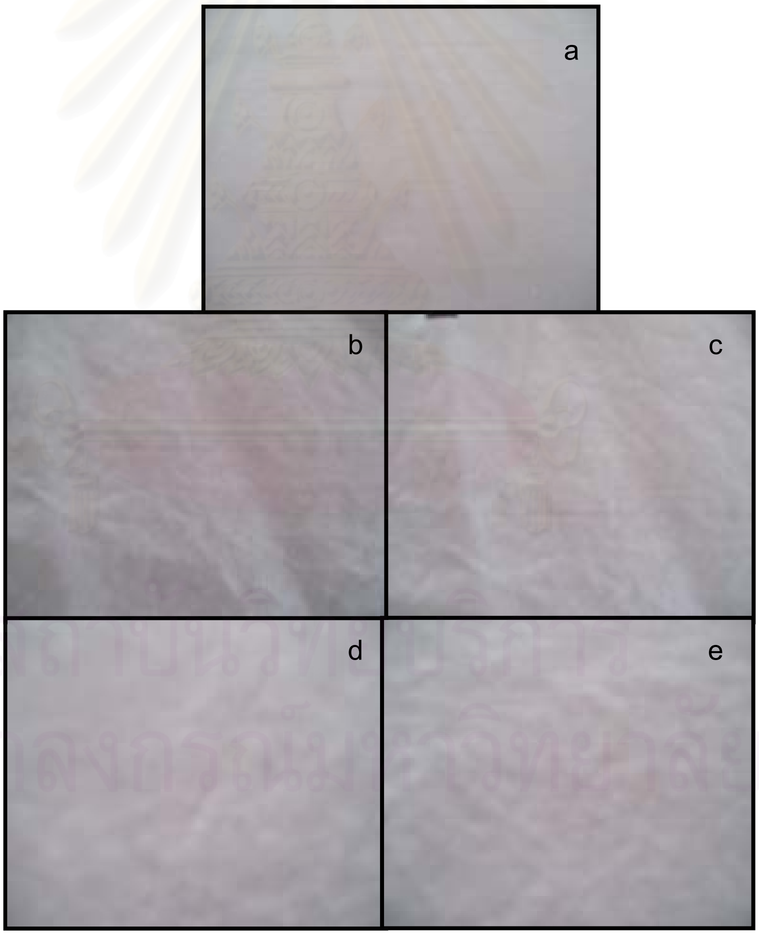


**Figure 4.12** Images of untreated cotton fabric (a), cotton fabrics treated with 10 (b) and 20 (c) shots of air plasma, cotton fabrics treated with 10 (d) and 20 (e) shots of argon plasma.

### 4.2.2 Surface Chemical Structure

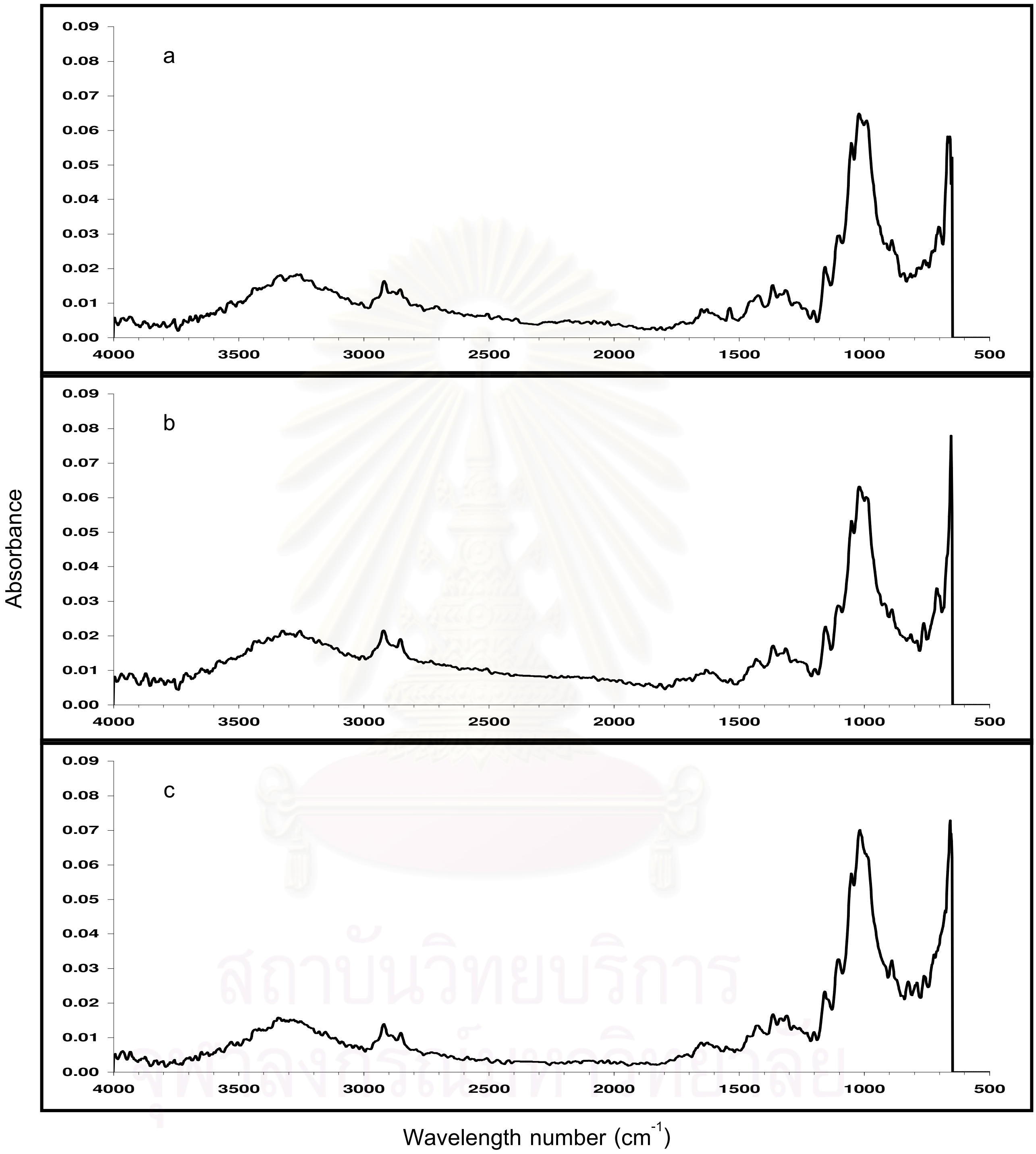


**Figure 4.13** ATR-FTIR spectra of untreated cotton fabric (a), cotton fabrics treated with 20 (b) shots of air plasma, and cotton fabrics treated with 20 (c) shots of argon plasma.

**Table 4.5** The interpretation of ATR-FTIR spectra of untreated and plasma- treated cotton fabrics

| Wavenumber ($cm^{-1}$) | | | Interpretation |
|---|---|---|---|
| Untreated | Air plasma | Ar plasma | |
| 3254 | 3256 | 3298 | O-H stretching : intermolecular hydrogen bonding |
| 2919 | 2922 | 2922 | C-H stretching of $-CH_2$ |
| 1304 | 1313 | 1313 | O-H in plane bending |
| 1157 | 1156 | 1157 | Anti-symmetrical bridge C-O-C |
| 1052 | 1052 | 1052 | C-O stretching of primary alcohol |
| - | 763 | - | C-N bending of primary amine |
| - | - | 825 | CH-O bending of aldehyde |

As shown in Figure 4.13 and Table 4.5, the spectrum of cotton fabric treated with 20 shots of air plasma exhibits the peak at 763 $cm^{-1}$ which can be assigned to primary amine. In case of argon plasma-treated cotton fabric, the new peak at 825 $cm^{-1}$ attributed to aldehyde group occurs. These results suggest that nitrogen and oxygen containing groups were introduced to the fabric surface after air and argon plasma treatment.

#### 4.2.2.1 Surface Elemental Analyze

The nitrogen containing groups appeared on cotton fabric treated with 20 shots of air plasma was confirmed by elemental analysis. The results are shown in Table 4.6. It can be seen that the amount of nitrogen on fabric surface increases after treating with 20 shots of air plasma when compared the untreated one. This confirms that air plasma treatment causes nitrogen functional groups on plasma treated-fabric surface.

**Table 4.6** Element Precentage of untreated and plasma- treated cotton fabrics

| Fabrics | % Element | | |
|---|---|---|---|
| | Carbon | Hydrogen | Nitrogen |
| Untreated | 41.810 | 7.030 | 0.037 |
| 20 Shots, Air Plasma | 41.905 | 6.952 | 0.220 |

### 4.2.3 Morphological Analysis

As shown in Figure 4.14(a) the original surface of untreated cotton is smooth. When it was exposed to 10 shots of air plasma, its surface was etched and redeposited with etched fragments, resulting in surface roughness as shown in Figure 4.14(b).

When 20 shots of air plasma were applied, the breaking of the fiber was observed as seen in Figure 4.14(c). These results can be attributed to the etching process or ablation effect caused by bombardment of air plasma reactive species on the fabric surface. Argon plasma also caused the changes in surface roughness of cotton surface similar to air plasma as shown in Figures 4.14(d)-(e).

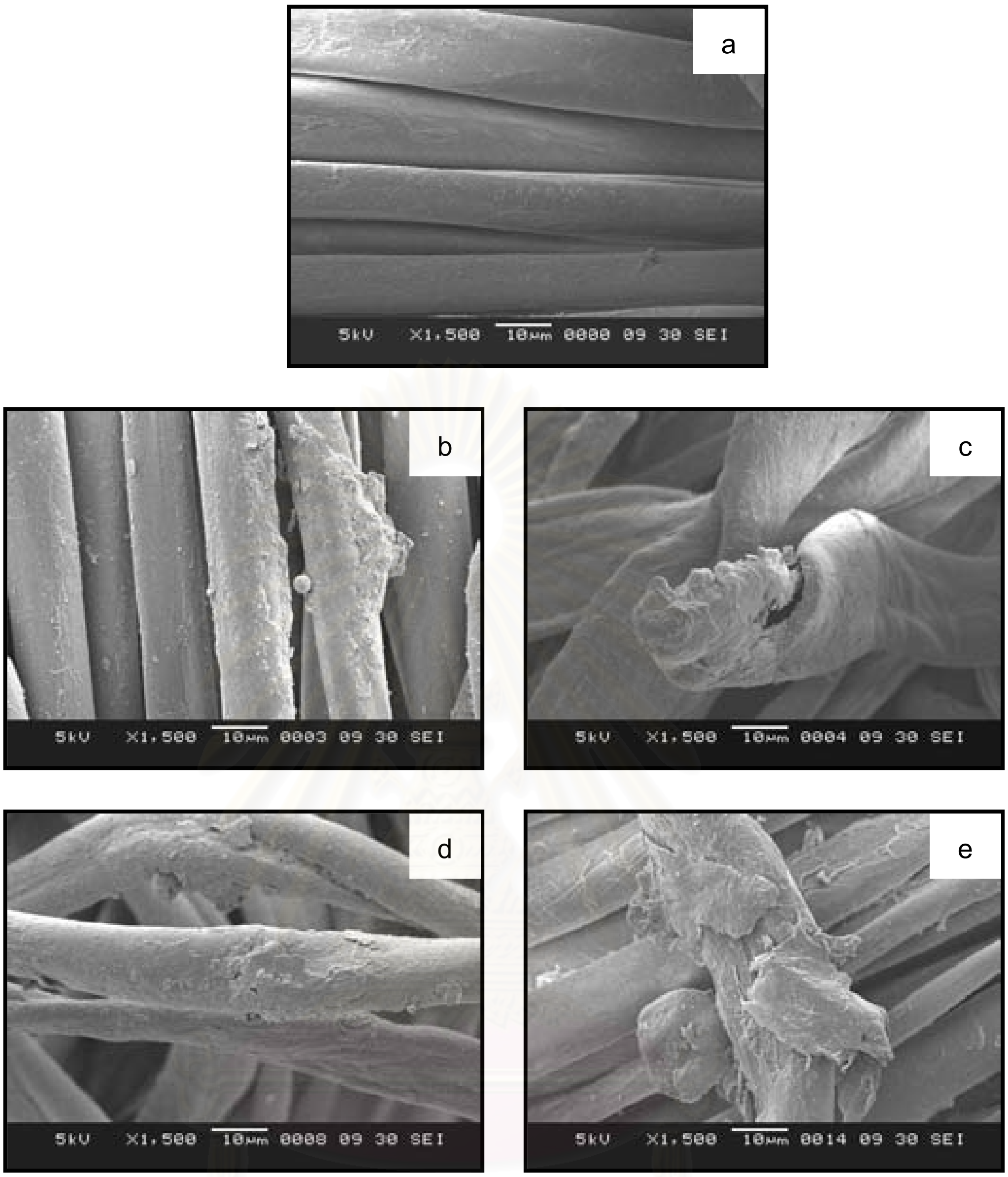


**Figure 4.14** SEM images at X1500 of untreated cotton fabric (a), cotton fabrics treated with 10 (b) and 20 (c) shots of air plasma, cotton fabrics treated with 10 (d) and 20 (e) shots of argon plasma.

### 4.2.4 Aging of Functional Groups

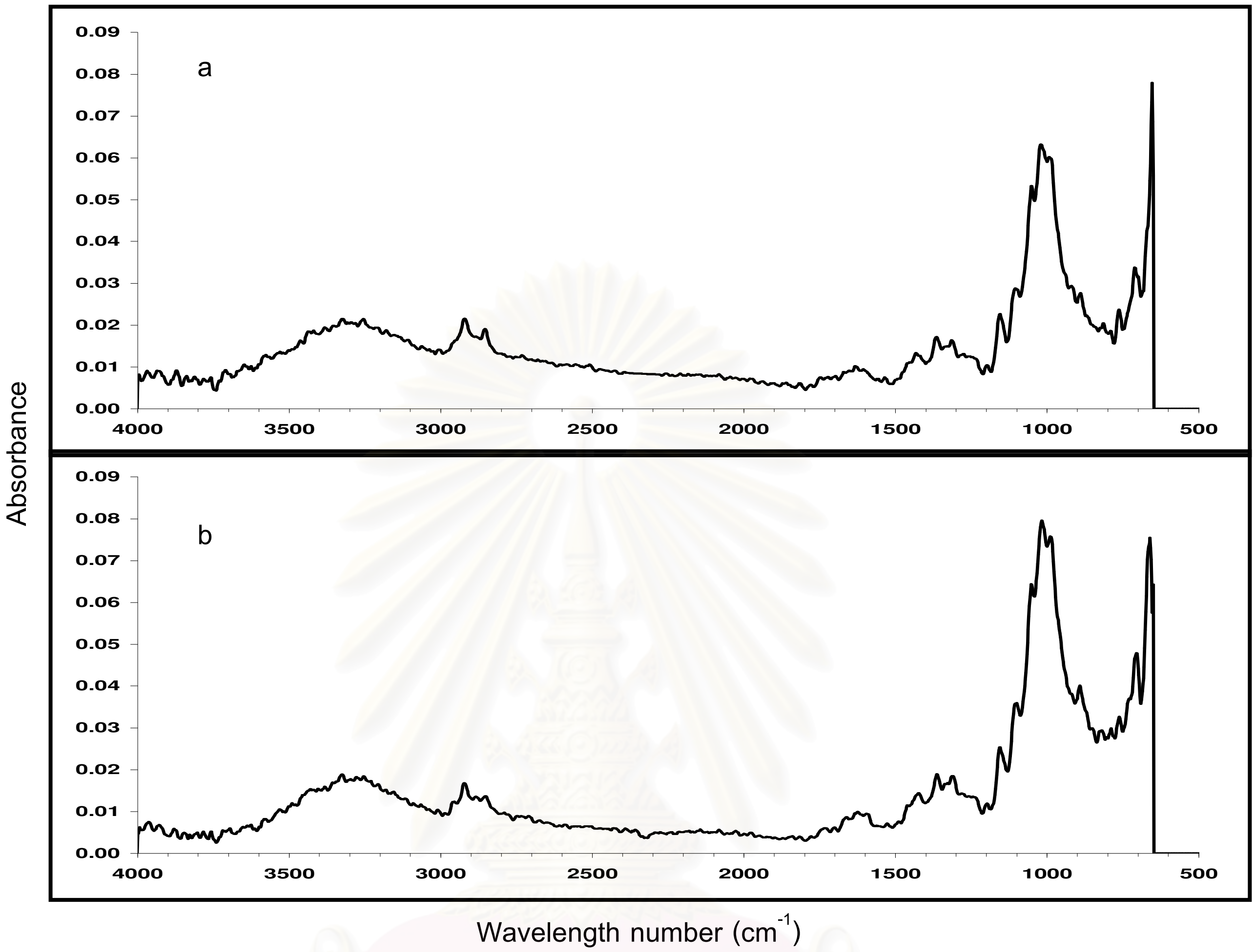


**Figure 4.15** ATR-FTIR spectra of cotton fabrics treated with 20 (a) shots of air plasma, and cotton fabrics treated with 20 (b) shots of air plasma after 30 days.

After 30 days, the intensity of the peak at 763 cm$^{-1}$ of the cotton fabric treated with 20 shots of air plasma decreases as shown in Figure 4.15. On the other hand, there is no change in intensities of the peak corresponding to aldehyde functional groups of argon plasma-treated fabric after 30 days as shown in Figure 4.16. This may be because the amine groups formed during air plasma treatment are more hydrophilic than aldehyde groups formed during argon plasma treatment; therefore, they can interact with higher amount of moisture in the atmosphere.

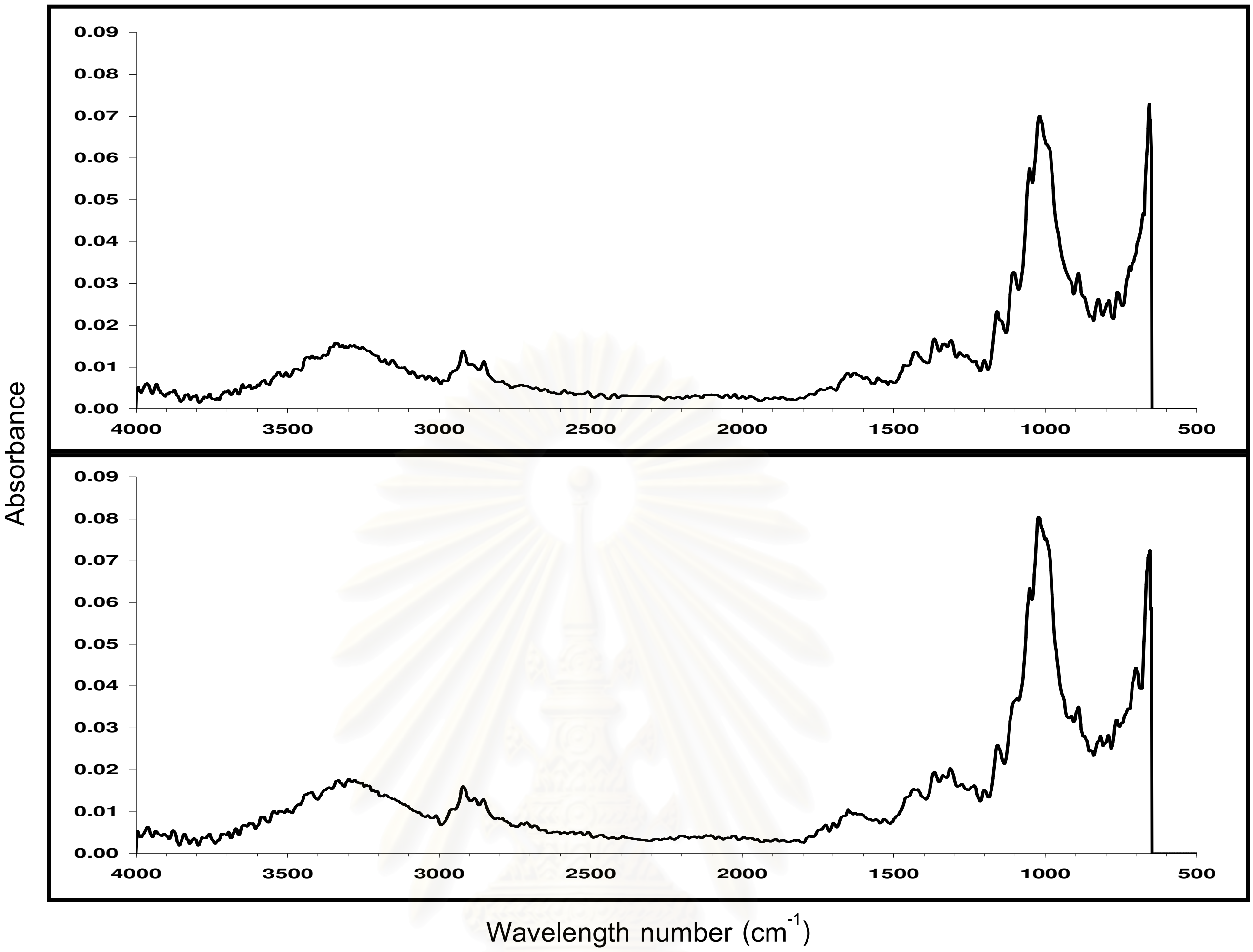


**Figure 4.16** ATR-FTIR spectra of cotton fabrics treated with 20 (a) shots of argon plasma, and cotton fabrics treated with 20 (b) shots of argon plasma after 30 days.

4.2.5 Wettability

Figure 4.17 shows the wettability of untreated and plasma-treated cotton fabrics. The wettability of air and argon plasma-treated cotton fabrics was not different from the untreated one. The changes in wettability of plasma-treated cotton fabric cannot be seen obviously. This is possibly due to the fact that cotton already possesses hydrophilic characteristics.

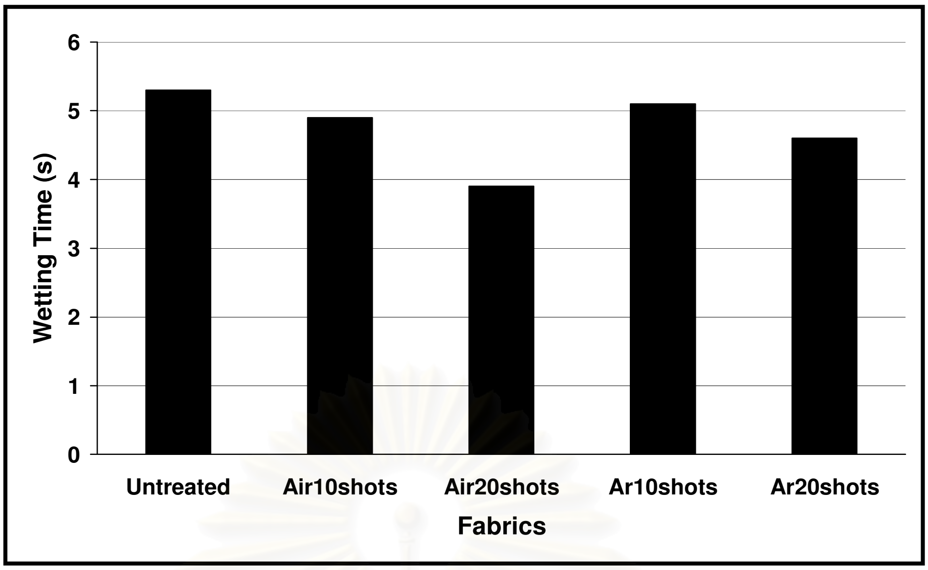


Figure 4.17 The wettability of untreated and plasma-treated cotton fabrics

4.2.6 Dyeability

Table 4.7 Color measurement of untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

| Conditions | $\lambda_{max}$ (nm) | K/S | L* | a* | b* |
|---|---|---|---|---|---|
| Untreated | 620 | 2.88±0.60 | 53.06±2.92 | -8.42±0.3 | -17.56±0.57 |
| 10 Shots of Air Plasma | 620 | 2.65±0.45 | 53.85±2.44 | -8.17±0.08 | -16.92±0.35 |
| 20 Shots of Air Plasma | 620 | 2.67±0.52 | 53.74±2.71 | -8.23±0.05 | -16.75±0.46 |
| 10 Shots of Argon Plasma | 620 | 2.47±0.37 | 55.08±2.34 | -8.26±0.13 | -16.81±0.34 |
| 20 Shots of Argon Plasma | 620 | 2.81±0.83 | 53.22±4.12 | -8.17±0.02 | -17.10±0.88 |

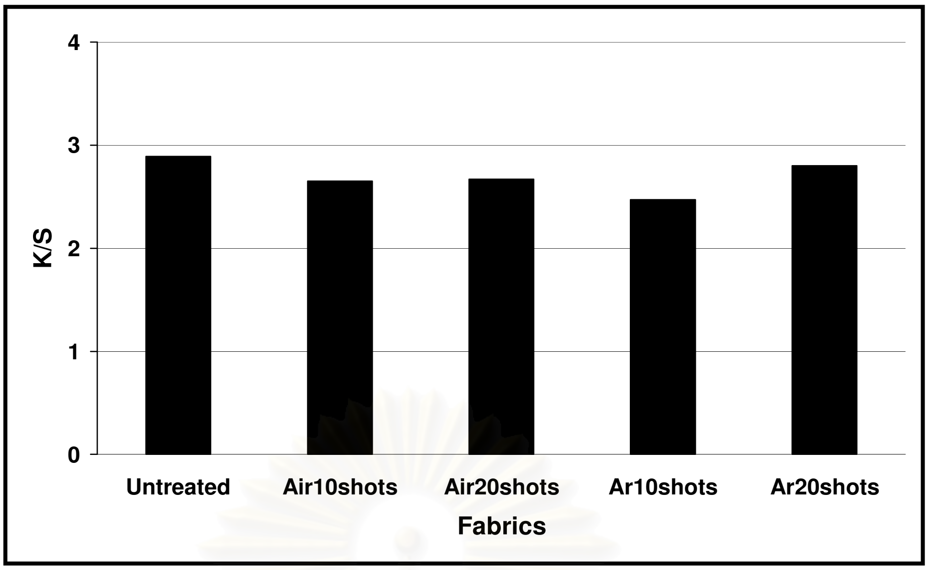


**Figure 4.18** K/S values of untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

Since the nature of cotton is already highly hydrophilic, dyeability of all plasma-treated fabrics is comparable to that of the untreated one but tends to be slightly lower as shown in Table 4.7 and Figure 4.18. A reason given for this event is that the plasma induces etching on the non-crystalline (i.e. amorphous) regions of the fiber. These regions are the ones inherently responsible for the dyeing of cotton or any other cellulosic fibers.

### 4.2.7 Colorfastness to Washing

As shown in Table 4.8 and Figure 4.19, cotton fabrics treated with air and argon plasmas have comparable colorfastness to washing as the untreated fabric. The results suggest that air and argon plasma treatments do not affect dyeability of cotton fabric since the nature of cotton is already highly hydrophilic.

**Table 4.8** K/S values and ΔE after washing of untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

| Conditions | Cycles | K/S | L* | a* | b* | ΔE | Color Change |
|---|---|---|---|---|---|---|---|
| Untreated | 0 | 2.88 | 53.06 | -8.42 | -17.56 | - | - |
| | 10 | 2.69 | 53.74 | -8.20 | -17.21 | 0.57 | 4.5 |
| | 20 | 2.59 | 54.22 | -8.15 | -17.02 | 1.31 | 4 |
| | 30 | 2.38 | 55.12 | -7.93 | -16.56 | 2.36 | 4 |
| 10 Shots, Air Plasma | 0 | 2.65 | 53.85 | -8.17 | -16.92 | - | - |
| | 10 | 2.55 | 54.38 | -8.19 | -16.89 | 0.57 | 4.5 |
| | 20 | 2.42 | 54.92 | -7.94 | -16.54 | 1.17 | 4 |
| | 30 | 2.29 | 55.53 | -7.85 | -16.27 | 1.86 | 4 |
| 20 Shots, Air Plasma | 0 | 2.67 | 53.74 | -8.23 | -16.75 | - | - |
| | 10 | 2.47 | 54.74 | -8.03 | -18.17 | 1.03 | 4.5 |
| | 20 | 2.37 | 55.29 | -8.01 | -16.55 | 1.59 | 4 |
| | 30 | 2.26 | 55.81 | -7.82 | -17.77 | 2.17 | 4 |
| 10 Shots, Argon Plasma | 0 | 2.47 | 55.08 | -8.26 | -16.81 | - | - |
| | 10 | 2.35 | 55.47 | -8.12 | -16.67 | 0.63 | 4.5 |
| | 20 | 2.27 | 55.79 | -7.99 | -16.42 | 1.02 | 4 |
| | 30 | 2.19 | 56.26 | -7.90 | -16.28 | 1.52 | 4 |
| 20 Shots, Argon Plasma | 0 | 2.81 | 53.22 | -8.17 | -17.10 | - | - |
| | 10 | 2.55 | 54.39 | -8.00 | -16.74 | 1.24 | 4 |
| | 20 | 2.44 | 54.74 | -7.82 | -16.29 | 1.77 | 4 |
| | 30 | 2.33 | 55.42 | -7.76 | -16.33 | 2.37 | 3.5 |

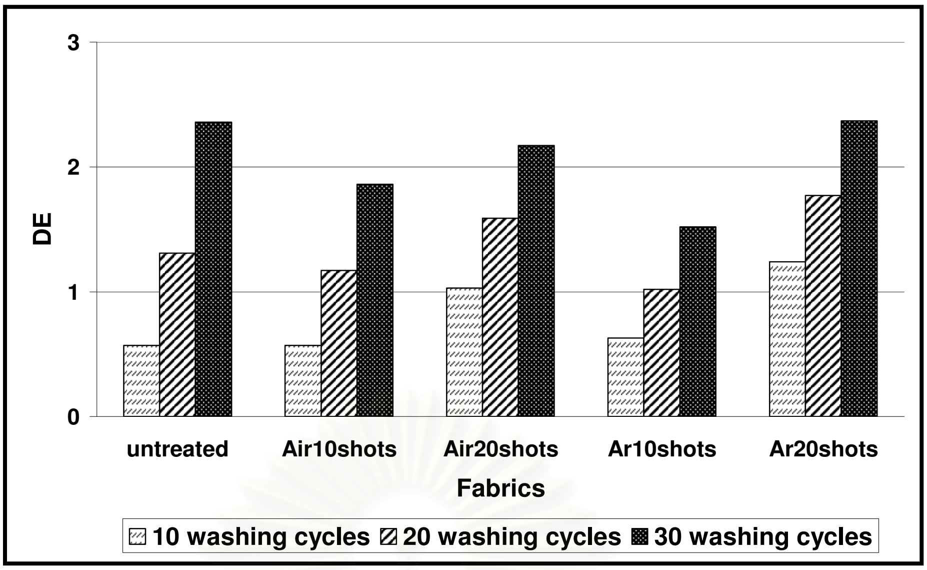


Figure 4.19 ΔE of untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.) after washing.

4.2.8 Colorfastness to Crocking

As shown in Table 4.9, the color stain value of all dyed plasma-treated fabrics is comparable to that of the untreated fabric. This indicates that the rubbing resistance of the fabric surface was not affected by plasma treatment suggesting that the modification occurred only on the fabric surface.

Table 4.9 Color stain values untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

| Fabrics | Conditions | Color stain | |
|---|---|---|---|
| | | Dry | Wet |
| Cotton | Untreated | 5 | 4.5 |
| | 10 Shots, Air Plasma | 4.5 | 4.5 |
| | 20 Shots, Air Plasma | 5 | 4.5 |
| | 10 Shots, Argon Plasma | 4.5 | 4.5 |
| | 20 Shots, Argon Plasma | 5 | 4.5 |

## 4.3 Properties and Morphology of Untreated and Plasma-treated Polyester/Cotton Blended (T/C) Fabrics

### 4.3.1 Fabric Appearance

From Figure 4.20, it can be seen that treating T/C fabric with 10 and 20 of air and argon plasma did not affect their color.

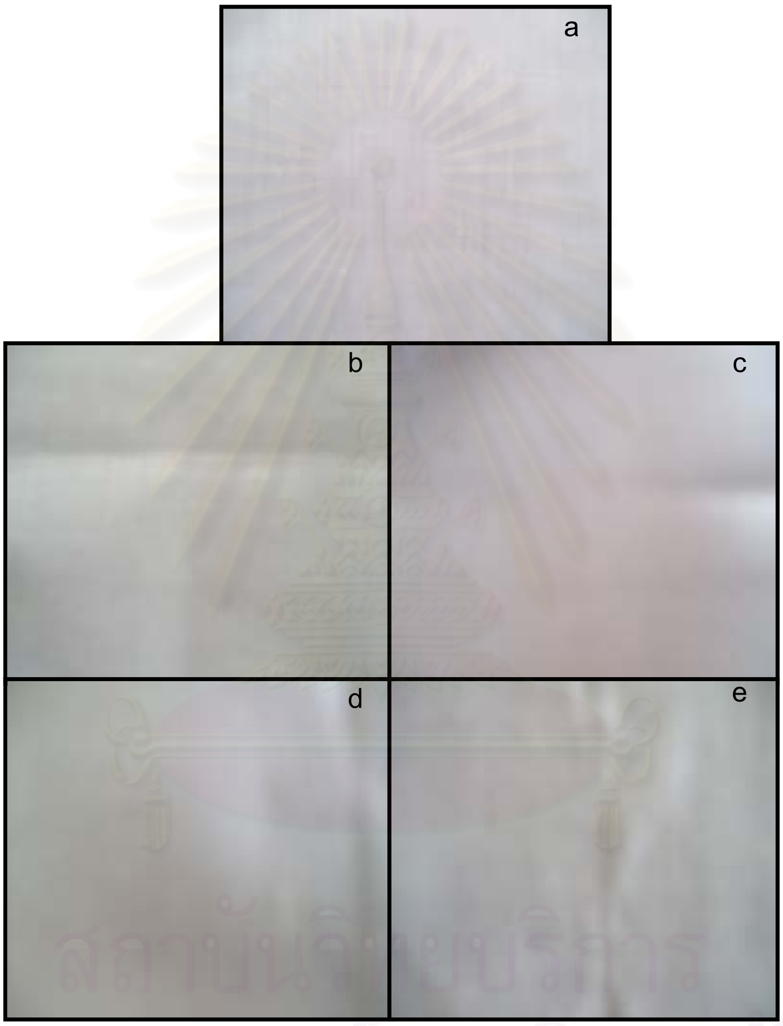


**Figure 4.20** Images of untreated T/C fabric (a), T/C fabrics treated with 10 (b), and 20 (c) shots of air plasma, T/C fabrics treated with 10 (d), and 20 (e), shots of argon plasma.

### 4.3.2 Surface Chemical Structure

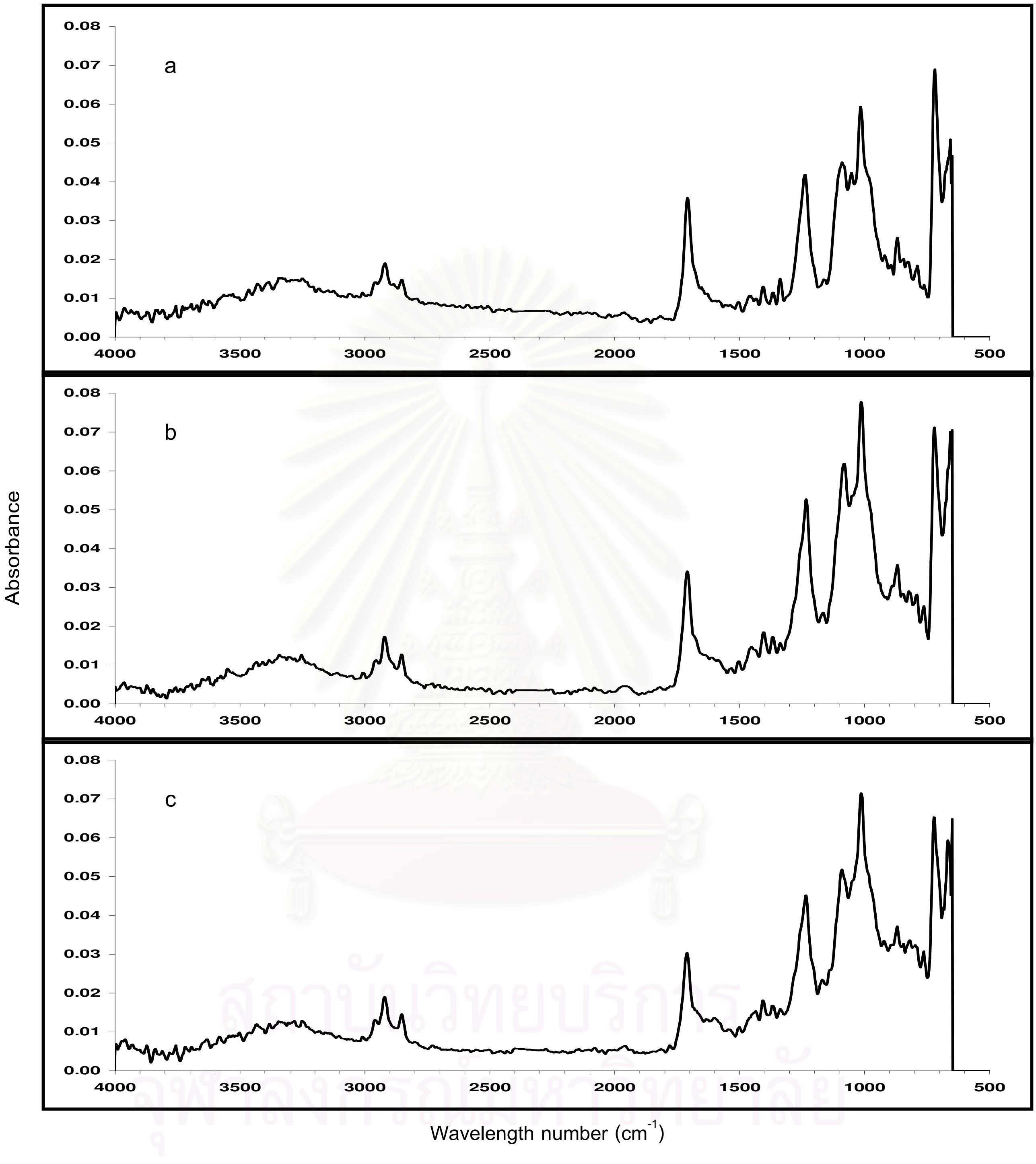


**Figure 4.21** ATR-FTIR spectra of untreated T/C fabric (a), T/C fabrics treated with 20 (b) shots of air plasma, and T/C fabrics treated with 20 (b) shots of argon plasma.

ATR-FTIR spectra of untreated and plasma-treated T/C fabrics are shown in Figure 4.21. After treating with 20 shots of air and argon plasma, the peak at wave number 1600 cm$^{-1}$ which can be assigned to C=O stretching appears. In addition, the intensities of the peak at 1366 cm$^{-1}$ and 658 cm$^{-1}$ increase. These peaks correspond to the bending of methyl ketone and out of plane bending of the carbonyl substituents on the aromatic ring, respectively. On the other hand, a decrease in the intensity of the peak at 1338 cm$^{-1}$ assigned C-H plane bending substituted aromatic rings was also observed. All other interpretations of ATR-FTIR spectra of untreated and plasma-treated polyester/cotton blend fabrics are given in Table 4.10.

**Table 4.10** The interpretation of ATR-FTIR spectra of untreated and plasma- treated polyester/cotton blend fabrics

| Wavenumber (cm$^{-1}$) | | | Interpretation |
|---|---|---|---|
| Untreated | Air plasma | Ar plasma | |
| 3343 | 3342 | 3251 | O-H stretching : intermolecular hydrogen bonding |
| 2919,2852 | 2922,2853 | 2921,2853 | C-H stretching of -CH$_2$ |
| 1709 | 1710 | 1711 | C=O stretching of the ester carbonyl group |
| - | 1629 | 1592 | C=O stretching of the carbonyl group |
| 1442,1411 | 1442,1405 | 1442,1411 | C-H bending for CH$_2$ |
| 1366 | 1368(increase) | 1369(increase) | Bending of methyl ketone |

**Table 4.10** The interpretation of ATR-FTIR spectra of untreated and plasma- treated polyester/cotton blend fabrics (con't)

| Wavenumber ($cm^{-1}$) | | | Interpretation |
|---|---|---|---|
| Untreated | Air plasma | Ar plasma | |
| 1338 | 1335(decrease) | 1335(decrease) | C-H in plane bending in substituted aromatic rings and skeleton vibrations involving C-O |
| 1239,1091 | 1235, 1091 | 1234, 1083 | C-O-C stretching of the ester |
| 870 | 869 | 874 | Out of plane C-H of p-disubstituted aromatic rings |
| 720,658 | 722,658(increase) | 722,667(increase) | Out of plane bending of the two carbonyl substituents on the aromatic ring |

### 4.3.3 Morphological Analysis

Figures 4.22 (b) and (c) shows SEM images of T/C fabrics surface treated by air plasma at 10 and 20 shots, respectively. It can be obviously seen that air plasma also caused the changes in surface roughness of T/C surface similar to argon plasma.

However, the surface of T/C fabric treated with air plasma is rougher that that of argon plasma-treated fabric. This may be due to the fact that the etching rate and surface roughness depend on the type of plasma and the energy of plasma which are applied.

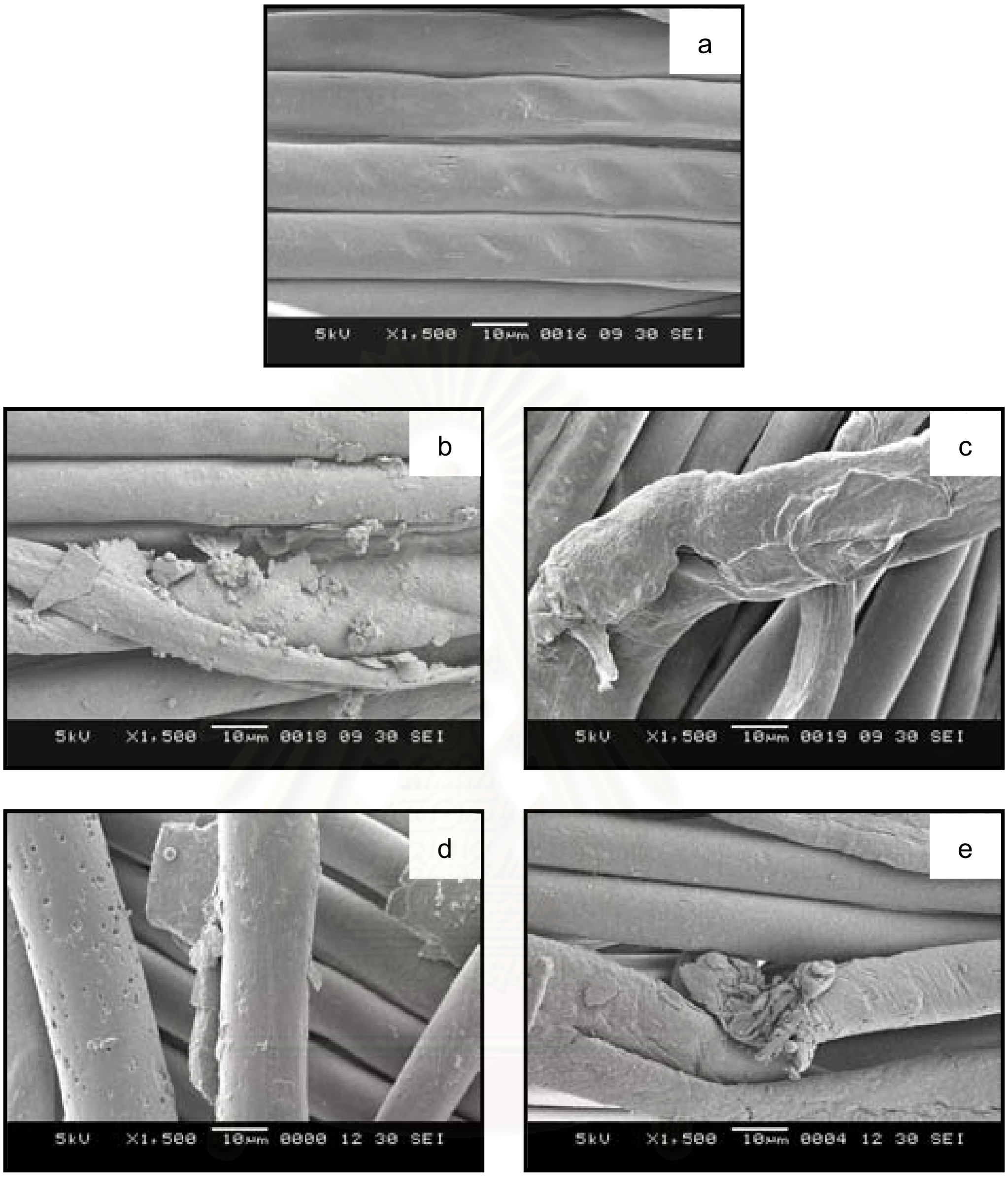


**Figure 4.22** SEM images at X1500 of untreated T/C fabric (a), T/C fabrics treated with 10 (b), and 20 (c) shots of air plasma, T/C fabrics treated with 10 (d), and 20 (e) shots of argon plasma.

### 4.3.4 Wettability

Figures 4.23 and 4.24 illustrate the changes in wettability of T/C fabrics treated with air and argon plasma measured in circumference and horizontal areas, respectively.

#### 4.3.4.1 Wettability in horizontal area

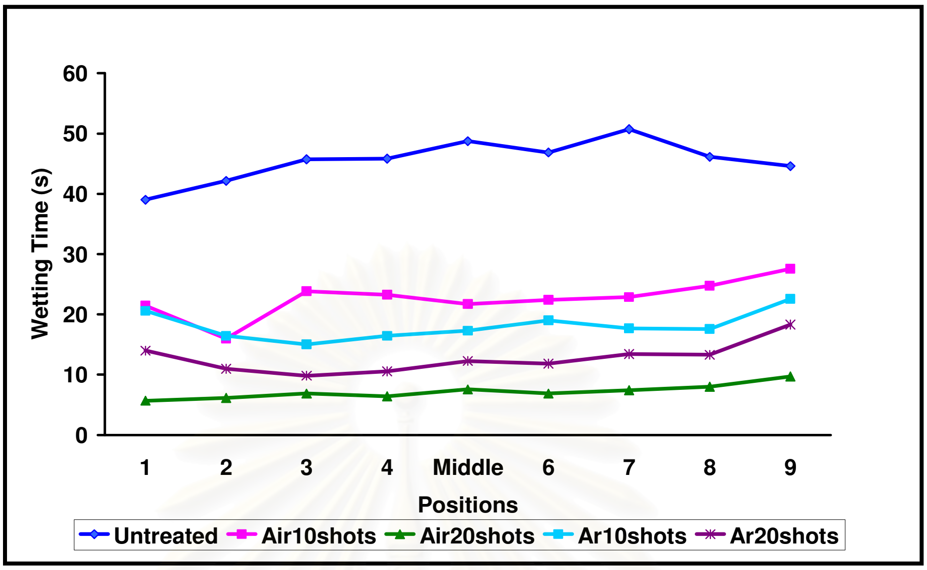


Figure 4.23 The wettability of untreated and plasma-treated T/C fabrics measured in horizontal area

#### 4.3.4.2 Wettability in Circumference Area

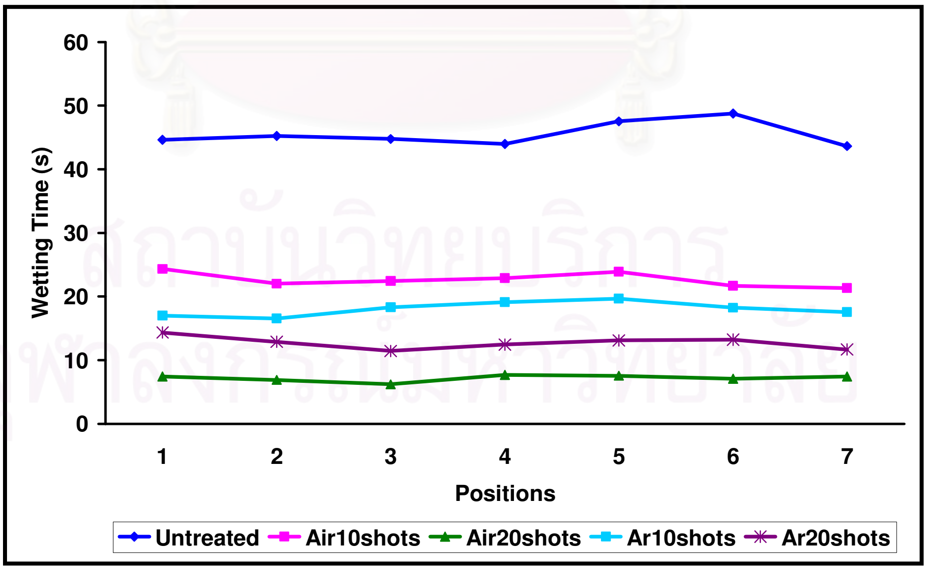


Figure 4.24 The wettability of untreated and plasma-treated T/C fabrics measured in circumference area

As shown in Figures 4.23 and 4.24, wetting time measurement demonstrated an enhancement of surface hydrophilicity with increasing the number of plasma shots. The enhancement of hydrophilicity can be explained by the formation of polar functional groups; leading to improved wettability as a result of better interaction with water molecules. However, the wetting time of 10 shots of argon plasma-treated fabric lower than 10 shots of air plasma. This may be because the fabric was affected by etching effect more than functionalization.

### 4.3.5 Dyability

**Table 4.11** Color measurement of untreated and plasma-treated T/C fabrics dyed with disperse dye and reactive dye (Dianix Blue XF and Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

| Conditions | $\lambda_{max}$ (nm) | K/S | L* | a* | b* |
|---|---|---|---|---|---|
| Untreated | 620 | 5.83±0.12 | 39.09±0.28 | -3.55±0.17 | -15.91±0.27 |
| 10 Shots of Air Plasma | 620 | 5.86±0.04 | 38.27±0.02 | -3.26±0.13 | -13.98±0.12 |
| 20 Shots of Air Plasma | 620 | 6.17±0.06 | 37.65±0.01 | -3.29±0.16 | -14.21±0.21 |
| 10 Shots of Argon Plasma | 620 | 5.77±0.21 | 39.38±0.87 | -3.65±0.13 | -16.07±0.69 |
| 20 Shots of Argon Plasma | 620 | 5.85±0.21 | 38.81±0.70 | -3.47±0.32 | -15.25±0.01 |

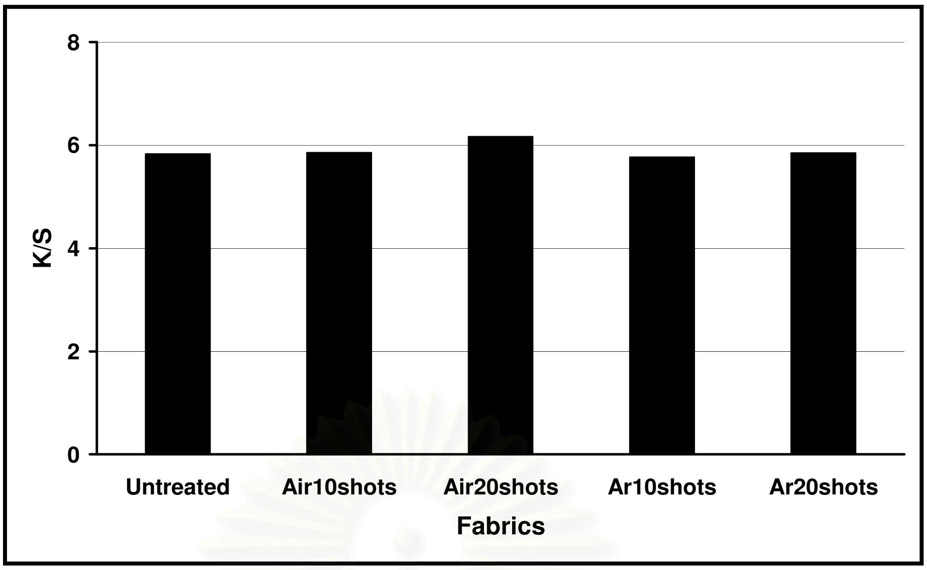


**Figure 4.25** K/S values of untreated and plasma-treated T/C fabrics dyed with disperse dye and reactive dye (Dianix Blue XF and Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

The color strengths of air and argon plasma-treated T/C fabrics are comparable to that of the untreated fabric as seen from Table 4.11 and Figure 4.25. This may be due to the nature of cotton which is already highly hydrophilic and easily to absorb dye molecules.

### 4.3.6 Colorfastness to Washing

As shown in Table 4.12 and Figure 4.26, T/C fabrics treated with air and argon plasma have comparable colorfastness to washing as the untreated fabric. These results indicate that their characteristics remain unchanged. Therefore, surface modification by air and argon plasma treatments does not affect colorfastness to washing of T/C fabrics.

**Table 4.12** K/S values and $\Delta$E after washing of untreated and plasma-treated T/C fabrics dyed with disperse dye and reactive dye (Dianix Blue XF and Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

| Conditions | Cycles | K/S | L* | a* | b* | $\Delta$E | Color Change |
|---|---|---|---|---|---|---|---|
| Untreated | 0 | 5.83 | 39.09 | -3.55 | -15.91 | - | - |
| | 10 | 5.72 | 39.25 | -3.46 | -15.58 | 0.41 | 4.5 |
| | 20 | 5.58 | 39.51 | -3.44 | -15.35 | 0.75 | 4.5 |
| | 30 | 5.51 | 39.66 | -3.38 | -15.38 | 0.83 | 4.5 |
| 10 Shots, Air Plasma | 0 | 5.86 | 38.27 | -3.26 | -13.98 | - | - |
| | 10 | 5.70 | 38.69 | -3.14 | -14.28 | 0.57 | 4.5 |
| | 20 | 5.65 | 38.81 | -3.12 | -14.32 | 0.69 | 4.5 |
| | 30 | 5.55 | 39.28 | -3.35 | -14.37 | 1.12 | 4 |
| 20 Shots, Air Plasma | 0 | 6.17 | 37.65 | -3.29 | -14.21 | - | - |
| | 10 | 6.09 | 37.68 | -3.17 | -13.90 | 0.36 | 4.5 |
| | 20 | 5.97 | 38.11 | -3.17 | -14.46 | 0.87 | 4.5 |
| | 30 | 5.80 | 38.71 | -3.29 | -14.92 | 1.42 | 4 |
| 10 Shots, Argon Plasma | 0 | 5.77 | 39.38 | -3.65 | -16.07 | - | - |
| | 10 | 5.62 | 39.48 | -3.41 | -15.77 | 0.56 | 4.5 |
| | 20 | 5.58 | 39.62 | -3.48 | -15.58 | 0.62 | 4.5 |
| | 30 | 5.45 | 39.91 | -3.49 | -15.65 | 0.78 | 4.5 |
| 20 Shots, Argon Plasma | 0 | 5.85 | 38.81 | -3.47 | -15.25 | - | - |
| | 10 | 5.66 | 39.15 | -3.44 | -14.95 | 0.48 | 4.5 |
| | 20 | 5.61 | 39.28 | -3.46 | -14.94 | 0.58 | 4.5 |
| | 30 | 5.50 | 39.67 | -3.54 | -15.04 | 1.09 | 4.5 |

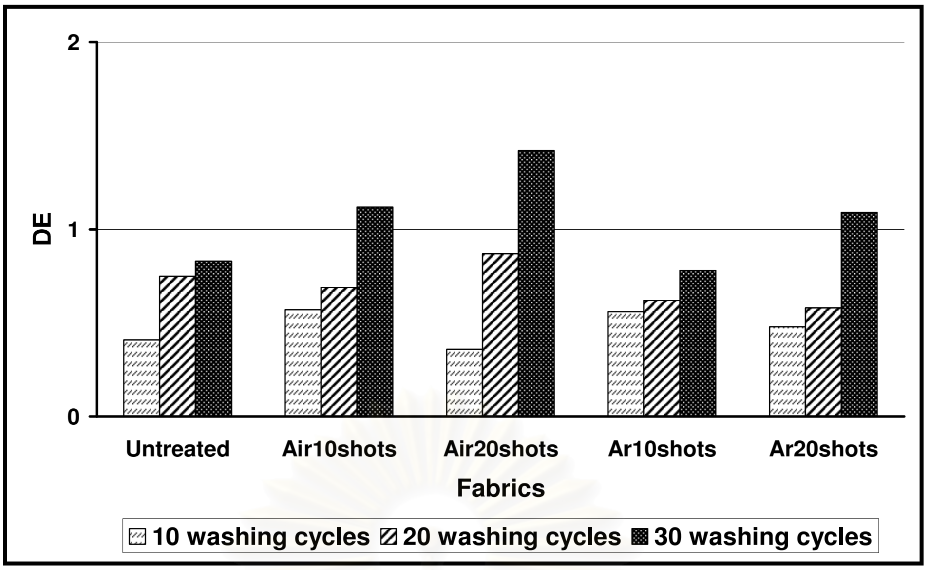


Figure 4.26 ΔE of untreated and plasma-treated T/C fabrics dyed with disperse dye and reactive dye (Dianix Blue XF and Levafix Navy CA gran, supplied by DyStar Thai Ltd.).

### 4.3.7 Colorfastness to Crocking

Table 4.13 Color stain values untreated and plasma-treated T/C fabrics dyed with disperse and reactive dye (Dianix Blue XF and Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

| Fabrics | Conditions | Color stain | |
|---|---|---|---|
| | | Dry | Wet |
| T/C | Untreated | 5 | 5 |
| | 10 Shots, Air Plasma | 5 | 4.5 |
| | 20 Shots, Air Plasma | 5 | 4.5 |
| | 10 Shots, Argon Plasma | 4.5 | 4.5 |
| | 20 Shots, Argon Plasma | 4.5 | 4.5 |

As shown in Table 4.13, the color stain value of all dyed plasma-treated fabrics is comparable to that of the untreated fabric. This indicates that the rubbing resistance of the fabric surface was not affected by plasma treatment suggesting that the modification occurred only on the fabric surface.

# CHAPTER V
# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

Morphology and properties of polyester, cotton and polyester/cotton blended fabrics after treatments by high temperature-pulsed air plasma and argon plasma generated from theta-pinch device were investigated. The results can be concluded as follows:

1. Surface modification of textile fabrics using air and argon plasmas generated from theta-pinch device resulted in the etching of the fabric surface and the redeposition of etched fragments on the fabric surface which were confirmed by SEM photographs. In addition, the formation of hydrophilic functional groups on the fabric surface was also observed as shown in ATR-FTIR spectra. In the cases of polyester and T/C fabrics treated with air and argon plasma, the functional groups baring C=O bonds were formed at wavenumbers around 1,600 $cm^{-1}$. For plasma-treated cotton fabrics, amine and aldehyde functional groups were observed after air and argon plasma treatment, respectively. These functional groups were stable on the surface over one month.

2. As the consequences of an increase in surface roughness caused by etching and redeposition combining with the formation of hydrophilic functional groups, the wettability of plasma-treated polyester, cotton and T/C fabrics was clearly observed. With increasing the number of plasma shots, this characteristic was significantly improved.

3. For all selected dyes used in this research, it was found that the gas types and the number of plasma shots significantly affected dyeing properties of plasma-treated polyester fabrics. However, due to highly hydrophilic property of cotton, dyeabilities of both untreated and plasma-treated cotton and T/C fabrics are comparable.

4. Due to the removal of etched fragments redeposited on the fabric surface, it was found that the colorfastness to washing of polyester was worse than those of untreated fabrics and plasma-treated fabrics with other conditions. However, due to

highly hydrophilic property of cotton, colorfastness to washing of both untreated and plasma-treated cotton and T/C fabrics are comparable.

5. After crocking test, it was observed that the rubbing resistance of the fabric surface was not affected by plasma treatment. This indicates that the modification occurred only on the fabric surface.

6. The results suggested that 20 shots of air plasma were suitable for improving wettability of PET and T/C fabrics. However, for a fabric which are already highly hydrophilic such as cotton, air and argon plasma treatments slightly improved or had no effects on the wetting time and dyeability.

## 5.2 Recommendations

1. The improvement of textile properties such as flame retardance should be investigated by treatment with high temperature pulsed-plasma generated from theta-pinch device using other types of gases.

2. Surface modification by air and argon plasmas generated from theta-pinch device of other forms of textile products such as yarn should be studied.

# REFERENCES

[1]. Matthewa, S. R. Plasma Aided Finishing of Textile Materials. Doctoral Dissertation, Department of Fiber and Polymer Science, North Carolina State University, 2005.

[2]. Tomasino, C.; Cuomo, J. J.; and Smith, C. B. Plasma Treatments of Textile. Journal of Coated Fabrics 25 (1995): 115-127.

[3]. Shishoo, R. Plasma Treatment – Industrial Application and Its Impact on the C&L Industry. Journal of Coated Fabrics 26 (1996): 26-35.

[4]. Eastman, T.E. “Perspectives on Plasma–The Fourth State of Matter.” [Online]. Available from: http://www.plasmas.org (1999).

[5]. Glane, J. “The Pervasive Plasma State.” [Online]. Available from: http://w3fusion.ph.utexas.edu/aps/plasmaState/PPSPage1.html (1996).

[6]. Muralidharan, B.; Mathanmohan, T.; and Ethiraj, J. Effect of Acetonitrile Pretreatment on The Physicochemical Behavior of 100% Polyester Fabric. Journal of Applied Polymer Science 91 (2004): 3871-3878.

[7]. Chan, C. M., Polymer Surface Modification and Characterization. New York: Hanser/Gardner Publications, 1994.

[8]. Feast, W. J. New Generation Atmospheric Pressure Plasma Technology for Industrial on-line Processing. In H. S. Munro (ed.), Polymer Surfaces and Interfaces. Chichester: John Wiley and Sons, 1987.

[9]. Walter, H. W.; Larry, R. E.; James, G. G.; and Derek, S. Polymer Surface Modification. Rubber Chem. and Technology 65 (1992): 687.

[10]. Yoon, J. H. Characterization of Atmospheric Pressure Plasma Interactions with Textile/Polymer Substrates. Doctoral Dissertation, Department of Fiber and Polymer Science, North Carolina State University, 2003.

[11]. Tyrone, L. V. Textile Processing and Properties: Dyeing, Finishing, and Performance. Amsterdam: Elsevier, 1994.

[12]. Inagaki, N.; Tasaka, S.; and Takami, Y. Durable and Hydrophobic Surface Modification by Plasma Polymers Deposited from Acetone/Hexafluoroacetone, Ethylene/Hexafluoroacetone, and Ethane/Hexafluoroacetone Mixture. Journal of Applied Polymer Science 41 (1990): 965-973.

[13]. Bengi, K.; and Aysun, C. “Plasma Technology in Textile Processing.” [Online]. Available from: http://www.ft.vslib.cz (1990).

[14]. Chan, C. M.; Ko, T. M.; and Hiraoka, H. Polymer Surface Modification by Plasmas and Photons. Surface Science Reports 24 (1996): 1-54.

[15]. Ferencz, S. D.; and Sorin, M. Macromolecular Plasma-Chemistry: an Emerging Field of Polymer Science. Progress in Polymer Science 29 (2001): 305-341.

[16]. LAURA, K. C. Non Aqueous Treatment of Fabrics Utilizing Plasmas. Master’s Thesis, Department of Textile Engineering and Science, North Carolina State University, 2000.

[17]. Pimpan, V., Chuenchon, S., Kamsing, P., and Mongkolnavin, R. Properties and Morphology of Surface-Modified Polypropylene Fibers Using Theta-Pinch Device. International Meeting on Frontiers of Physics 2005 (IMFP 2005), pp. 70-71. Kuala Lampur, Malaysia, July 25-29, 2005.

[18]. Mongkolnavin, R. Srisawat, J., Ngamrungroj, D., and Pimpan, V. A Plasma Focus Application for Enhancing Lamination Process of Polypropylene/polyester/cotton Composites. International Meeting on Frontiers of Physics 2005 (IMFP 2005), pp. 72. Kuala Lampur, Malaysia, July 25-29, 2005.

[19]. Riekerink, M.; Terlingen, J.; Engbers, H.; and Feijen, J. Selective Etching of Semicrystalline Polymers: $CF_4$ Gas Plasma Treatment of Poly (ethylene). Langmuir15 (1999): 4847-4856.

[20]. Gray, D.; Mohindra, V.; and Sawin, H.Redeposition Kinetics in Fluorocarbon Plasma Etching. Journal of Vacuum Science and Technology A-Vacuum Surfaces and Films 12 (1994): 354-364.

[21]. Wrobel, A. M.; Kryszewski, M.; Rakowski, W.; Okoniewski, M.; and Kubacki, Z. Effect of Plasma Treatment on Surface Structure and Properties of Polyester Fabric. POLYMER 19 (1978): 908-912.

[22]. Dennis, M. M.; and Daniel, L. Plasma Etching: An Introduction. San Diego: Academic Press, 1989.

[23]. Poletti, G.; Orsini, F.; Raffaele-Addamo, A.; Riccardi, C.; and Selli, E. Cold Plasma Treatment of PET Fabrics: AFM Surface Morphology Characterisation. Applied Surface Science 219 (2003): 311-316.

[24]. Chen, Y. Y.; Lin, H.; Ren, Y; Wang, H. W.; and Zhu, L. J. Study on *Bombyx mori* Silk Treated by Oxygen Plasma. Journal of Zhejiang University SCIENCE 5 (2004): 918-922.

[25]. Roger L. Clough and Shalaby W. Shalaby, Eds., Irradiation of Polymers*:* Fundamentals and Technological Applications. Washington, D.C.: American Chemical Society, 1996.

[26]. Ward, T.; Jung, H.; Hinojosa, O.; and Benerito, R. Characterization and Use of Radio Frequency Plasma-Activated Natural Polymers. Journal of Applied Polymer Science 23 (1979): 1987-2003.

[27]. Inagaki, N.; Tasaka, S.; Narushima, K.; and Teranishi, K. Surface Modification of Poly (tetrafluoroethylene) with Pulsed Hydrogen Plasma. Journal of Applied Polymer Science 83 (2002): 340-348.

[28]. Hudis, M. Surface Cross-linking of Polyethylene Using Hydrogen Glow Discharge. Journal of Applied Polymer Science 16 (1972): 2397-2415.

[29]. Chen, J. Free Radicals of Fibers Treated with Low Temperature Plasma. Journal of Applied Polymer Science 42 (1991): 2035-2037.

[30]. Wilken, R.; Hollander, A.; and Behnisch, J. Surface Radical Analysis on Plasma-Treated Polymers. Surface and Coatings Technology 116-119 (1999): 991-995.

[31]. Simionescu, C.I.; and Denes, F. The Use of Plasma-Chemistry in The Field of Synthesis and Modification of The Natural Macromolecular Compounds. Cellulose ChemIcal Technology 14 (1980): 285.

[32]. Jagur-Grodzinski, J. Heterogenous modification of polymers*:* Matrix and surface reactions. Chichester, UK*:* John Wiley and Sons Ltd., 1997.

[33]. Christofor, I. S.; Ferencz, D.; Mihaela, M. M.; and Ioan, N. “Surface Modification and Grafting of Natural and Synthetic Fibers and Fabrics Under Cold Plasma Conditions. Makromol. Chemical Supply 8 (1984): 17.

[34]. Man, W. H., Inn-kye, K., Du, H. L., Woo, S. K., Dong, H .L., Lee, S. P., Kyung, E. M., and Kwan, H. S. Journal of Applied Polymer Science 81 (2001): 2769-2778.

[35]. Friedrich, J.; Loeschcke, I.; Frommelt, H.; Reiner, H.; Zimmermann; H.; and Lutgen, P. Ageing and Degradation of Poly(ethylene terephthalate) in An Oxygen Plasma. Polymer Degradation and Stability 31 (1991): 97-114.

[36]. Roger L. Clough and Shalaby W. Shalaby, Eds., Irradiation of polymers: Fundamentals and technological applications. Washington, D.C.: American Chemical Society, 1996.

[38]. Sun, D. and Stylios, G.K. Fabric surface properties affected by low temperature plasma treatment. Journal of Materials Processing Technology 173 (2006) 172–177.

[39]. Foerch, R.; Kill, G.; and Walzak, M. Plasma Surface Modification of Polypropylene: Short-Term vs. Long-Term Plasma Treatment. Journal of Adhesion Science and Technology 7 (1993): 1077-1089.

[40]. Mas, A.; Jaaba, H.; and Schue, F. Modification of Poly (3-hydroxybutyric acid)-co (3-hydroxyvaleric acid) Film Surfaces in An Oxygen Low Pressure Plasma. Macromolecular Chemistry and Physics 197 (1996): 2331-2341.

[41]. Piao, D.; Uyama, Y.; and Ikada, Y. Aging of Plasma Treated Polymers. Kobunshi Ronbunshu 48 (1991): 529-534.

[42]. Poncin-Epaollard, F.; Brosse, J.; and Falher, T. Reactivity of Surface Groups Formed onto A Plasma Treated Poly (propylene) Film. Macromolecular Chemistry and Physics 200 (1999): 989-996.

[43]. Brennan, W.; Feast, W.; Munro, H.; and Walker, S. Investigation of The Aging of Plasma Oxidized Peek. Polymer 32 (1991): 1527-1530.

[44]. Yasuda, H.; Sharma, A.; and Yasuda, T. Effect of Orientation and Mobility of Polymer Molecules at Surfaces on Contact Angle and Its Hysteresis. Journal of Polymer Science-Polymer Physics Edition 19 (1981): 1285-1291.

[45]. Nakamatsu, J. K.; Delgado-Aparicio, L. F.V.; Da-Silva, R. A.; and Soberon, F. V. P. " Ageing of Plasma-Treated Polytetrafluoroethylene Surfaces." [Online]. Available from: plasma@pucp.edu.pe

[46]. Joanne, Y.; Kwong, C.; Kwan, M. S.; and Kai, S. L. Low Temperature Plasma-Treated Nylon Fabrics. Journal of Materials Processing Technology 123 (2002): 5-12.

[47]. Wong, K.; Tao, X.; Yuen, C.; and Yeung, K. Low Temperature Plasma Treatment of Linen. Textile Research Journal 69 (1999): 846-855.

[48]. McCord, M.; Hwang, Y.; Hauser, P.; Qiu, Y.; Cuomo, J.; Hankins, O.; Bourham, M.; and Canup, L. Modifying Nylon and Polypropylene Fabrics with Atmospheric Pressure Plasma. Textile Research Journal 72 (2002): 491-498.

[49]. Cioffi, M.O.H.; Voorwald, H.J.C.; Hein, L.R.O.; and Ambrosio, L. Effect of Cold Plasma Treatment on Mechanical Properties of PET/PMMA Composites. Composites: Part A Applied Science and Manufacturing 36 (2005) 615–623.

[50]. Ferrero., F. Wettability Measurements on Plasma Treated Synthetic Fabrics by Capillary Rise Method. Polymer Testing 22 (2003) 571–578.

[51]. Carmen Almazan-Almazan, M. Effect of Oxygen and Carbon Dioxide Plasmas on The Surface of Poly(ethylene terephthalate). Journal of Colloid and Interface Science 287 (2005): 57-66.

[52]. Sun, D.; and Stylios, G. K. Effect of Low Temperature Plasma Treatment on The Scouring and Dyeing of Natural Fabrics. Textile Research Journal 74 (2004): 751 756.

[53]. Wang, C.X.; and Qiu, Y.P. Two Sided Modification of Wool fabrics by Atmospheric Pressure plasma Jet: Influence of Processing Parameters on Plasma Penetration. Surface & Coatings Technology 201 (2007) 6273–6277.

[54]. Sarmadi, M.; and Kwon, Y. Improved Water Repellency and Surface Dyeing of Polyester Fabrics by Flasma Treatment. Textile Chemist and Colorist 25 (1993): 33-40.

[55]. Iriyama, Y.; Yasuda, T.; Cho, D.; and Yasuda, H. Plasma Surface Treatment on Nylon Fabrics by Fluorocarbon Compounds. Journal of Applied Polymer Science 39 (1990): 249-264.

[56]. Kim, Youngsoo.; Lee, Yeonhee.; Han, Seunghee.; and Kim, Kang-Jin. Improvement of Hydrophobic Properties of Polymer Surfaces by Plasma Source Ion Implantation. Surface & Coatings Technology 200 (2006) 4763 – 4769.

[57]. Antonio, R. A.; Elena, S.; Ruggero, B.; Claudia, R.; Francesco, O.; Giulio, P.; Laura, M.; Maria, R.; and Bruno, M. Cold Plasma-Induced Modification of The Dyeing Properties of Poly(ethylene terepthalate) Fibers. Applied Surface Science In Press.

[58]. Okuno, T.; Yasuda, T.; and Yasuda, H. Effect of Crystallinity of PET and Nylon 66 Fibers on Plasma Etching and Dyeability Characteristics. Textile Research Journal 62 (1992): 474-480.

[59]. Wakida, T.; Lee, M.; Niu, S.; Kobayashi, S.; and Ogasawara, S. Microscopic Observation of Cross-section of Dyed Wool and Nylon 6 Fibers After Treatment with Low-Temperature Plasma. Sen'i Gakkaishi 50 (1994): 421-423.

[60]. Wakida, T.; Lee, M.; Sato, Y.; Ogasawara, S.; Ge, Y.; and Niu, S. Dyeing Properties of Oxygen Low-Temperature Plasma-Treated Wool and Nylon 6 Fibers with Acid and Basic Dyes. Journal of the Society Dyers and Colourist 112 (1996): 233-236.

[61]. Wakida, T.; Cho, S.; Choi, S.; Tokino, S. and Lee, M. Effect of Low Temperature Plasma Treatment on Color of Wool and Nylon 6 Fabrics Dyed with Natural Dyes. Textile Research Journal 68 (1998): 848-853.

[62]. Byrne, G.; and Brow, K. Modifications of Textiles by Glow-Discharge Reactions. Journal of the Society Dyers and Colourist 88 (1972): 113-117.

[63]. Park, J.; Kim, J.; and Song, S. Surface Modification of Polyester Fabric by Plasma Polymerization of Acrylic Acid in The Presence of Oxygen. Journal of Korean Fiber Society 33 (1996): 790-797.

[64]. Seto, F.; Muraoka, Y.; Sakamoto, N.; Kishida, A.; and Akashi, M. Surface Modification of Synthetic Fiber Nonwoven Fabrics with Poly(acrylic acid) Chains Prepared by Corona discharge Induced Grafting. Angewandte Makromolekulare Chemie 266 (1999) : 56-62

[65]. Navaneetha Pandiyaraj, K.; and Selvarajan, V. Non-Thermal Plasma Treatment for Hydrophilicity Improvement of Grey Cotton Fabrics. Journal of materials processing technology 1999 (2008) : 130-139.

[66]. Kubota, S.; and Emori, K. Abrasive Finishing of Cotton fiber by Low Temperature Plasma. Sen'i Gakkaishi 50 (1994): 57-62.

[67]. Shijian, L. Surface Modification of Textile Fibers and Cords by Plasma Polymerization for Improvement of Adhesion to Polymeric Matrices. Doctoral Dissertation, Department of Materials Science and Engineering, University of Cincinnati, 2002.

[68]. Garg, Saurabh.; Hurren, Chris; and Kaynak, Akif. Improvement of Adhesion of Conductive Polypyrrole Coating on Wool and Polyester Fabrics Using Atmospheric Plasma Treatment. Synthetic Metals 157 (2007) 41–47.

[69. Yin-an, L.; Mao-fu, Y.; and Feng-zhi, X. Introduction to Theta-pinch Discharge. : Beijing : Asian-African Association for Plasma Training Research and Training Center, 2002. (Mimeographed)

[70]. Khaymapanya, P.; Kamsing, P.; Mongkolnavin, R.; and Pimpan, V. Surface Modification of Polyester Fabric Using Plasma Generated from Theta-Pinch Device. The 14th Academic Symposium of Faculty of Science. Chulalongkorn University, 2006.

[71]. Phyllis, G. T. Understanding textiles. United States of America: Macmillan Publishing, 1978.

[72]. Majory, L. J. Introductory textile science. 2nd ed. United States of America: Holt, Rinehart and Winston, 1972.

[73]. Bernard, P. C. Textiles fiber to fabric. 6th ed. Singapore: Mc Graw-Hill, 1985.

# APPENDICES

# Appendix A

## The Wetting Time of Untreated and Plasma-Treated Synthetic and Natural-Fiber Fabrics

**Table A1.** Data of The Wetting Time of Untreated Polyester Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 0 | 1 | 634 | 692 | 683 | 755 | 616 | 705 | 728 | 662 | 756 | 692 | 50 |
| | 2 | 628 | 622 | 696 | 576 | 612 | 636 | 705 | 646 | 708 | 648 | 46 |
| | 3 | 657 | 787 | 723 | 690 | 621 | 629 | 654 | 649 | 763 | 686 | 59 |
| | 4 | 728 | 612 | 645 | 608 | 611 | 612 | 636 | 685 | 722 | 651 | 49 |
| | 5 | 686 | 707 | 616 | 717 | 614 | 623 | 628 | 672 | 757 | 669 | 52 |
| | 6 | 674 | 718 | 641 | 656 | 616 | 705 | 695 | 623 | 769 | 677 | 50 |
| | 7 | 636 | 621 | 662 | 728 | 630 | 724 | 706 | 705 | 773 | 687 | 52 |
| | Mean | 663 | 680 | 667 | 676 | 617 | 662 | 679 | 663 | 750 | | |
| | S.D. | 36 | 65 | 37 | 66 | 7 | 47 | 39 | 27 | 25 | | |

**Table A2.** Data of The Wetting Time of 10 Shots Air Plasma-treated Polyester Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 10 | 1 | 637 | 598 | 446 | 486 | 460 | 542 | 510 | 446 | 450 | 508 | 70 |
| | 2 | 700 | 367 | 411 | 619 | 455 | 491 | 400 | 376 | 429 | 472 | 115 |
| | 3 | 451 | 412 | 442 | 420 | 405 | 471 | 680 | 376 | 477 | 459 | 89 |
| | 4 | 412 | 529 | 445 | 394 | 456 | 405 | 434 | 393 | 455 | 436 | 43 |
| | 5 | 526 | 429 | 396 | 315 | 390 | 347 | 483 | 306 | 476 | 408 | 77 |
| | 6 | 463 | 406 | 354 | 305 | 315 | 341 | 331 | 407 | 366 | 365 | 51 |
| | 7 | 400 | 464 | 329 | 420 | 427 | 471 | 490 | 590 | 435 | 447 | 71 |
| | Mean | 513 | 458 | 403 | 423 | 415 | 438 | 475 | 413 | 441 | | |
| | S.D. | 115 | 80 | 47 | 107 | 52 | 76 | 109 | 89 | 38 | | |

**Table A3.** Data of The Wetting Time of 20 Shots Air Plasma-treated Polyester Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 20 | 1 | 456 | 463 | 408 | 316 | 288 | 299 | 291 | 330 | 365 | 357 | 69 |
| | 2 | 407 | 386 | 456 | 195 | 226 | 295 | 216 | 333 | 400 | 324 | 95 |
| | 3 | 441 | 398 | 478 | 217 | 222 | 288 | 263 | 346 | 376 | 337 | 95 |
| | 4 | 409 | 317 | 315 | 191 | 163 | 297 | 253 | 267 | 429 | 293 | 88 |
| | 5 | 423 | 291 | 288 | 307 | 299 | 260 | 252 | 327 | 486 | 326 | 78 |
| | 6 | 431 | 352 | 311 | 240 | 250 | 250 | 231 | 356 | 371 | 310 | 71 |
| | 7 | 440 | 314 | 328 | 262 | 293 | 220 | 282 | 308 | 313 | 307 | 60 |
| | Mean | 430 | 360 | 369 | 247 | 249 | 273 | 255 | 324 | 391 | | |
| | S.D. | 18 | 60 | 77 | 51 | 49 | 30 | 26 | 29 | 55 | | |

Table A4. Data of The Wetting Time of 10 Shots Ar Plasma-treated Polyester Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 10 | 1 | 426 | 286 | 454 | 408 | 364 | 391 | 419 | 424 | 570 | 416 | 76 |
| | 2 | 321 | 432 | 442 | 345 | 183 | 363 | 370 | 294 | 533 | 365 | 99 |
| | 3 | 656 | 450 | 396 | 299 | 300 | 241 | 438 | 401 | 596 | 420 | 137 |
| | 4 | 475 | 726 | 496 | 349 | 330 | 319 | 760 | 400 | 560 | 491 | 165 |
| | 5 | 470 | 776 | 359 | 276 | 311 | 360 | 487 | 440 | 671 | 461 | 167 |
| | 6 | 457 | 327 | 266 | 307 | 274 | 357 | 398 | 441 | 529 | 373 | 90 |
| | 7 | 488 | 442 | 378 | 399 | 374 | 415 | 536 | 424 | 450 | 434 | 53 |
| | Mean | 470 | 491 | 399 | 340 | 305 | 349 | 487 | 403 | 558 | 416 | 76 |
| | S.D. | 99 | 188 | 75 | 50 | 64 | 56 | 133 | 51 | 68 | | |

Table A5. Data of The Wetting Time of 20 Shots Ar Plasma-treated Polyester Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 20 | 1 | 326 | 308 | 332 | 266 | 203 | 259 | 287 | 399 | 310 | **299** | **55** |
| | 2 | 782 | 191 | 340 | 223 | 12 | 288 | 140 | 390 | 358 | **303** | **216** |
| | 3 | 556 | 205 | 343 | 149 | 139 | 346 | 206 | 333 | 340 | **291** | **131** |
| | 4 | 509 | 401 | 558 | 361 | 348 | 337 | 269 | 401 | 321 | **389** | **92** |
| | 5 | 575 | 361 | 367 | 187 | 233 | 352 | 331 | 440 | 450 | **366** | **116** |
| | 6 | 394 | 304 | 316 | 222 | 329 | 307 | 199 | 456 | 457 | **332** | **91** |
| | 7 | 401 | 375 | 325 | 185 | 344 | 336 | 398 | 359 | 397 | **347** | **67** |
| | Mean | **506** | **306** | **369** | **228** | **230** | **318** | **261** | **397** | **376** | | |
| | S.D. | **152** | **82** | **85** | **69** | **125** | **34** | **87** | **43** | **60** | | |

Table A6. Data of The Wetting Time of Untreated and Plasma-treated Cotton Fabrics

| Conditions | The Wetting Time (s) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Mean | S.D. |
| Untreated | 4 | 9 | 3 | 9 | 4 | 4 | 4 | 6 | 5 | 5 | 5 | 2 |
| 10 Shots of Air Plasma | 9 | 6 | 5 | 6 | 4 | 3 | 4 | 6 | 4 | 2 | 5 | 2 |
| 20 Shots of Air Plasma | 4 | 5 | 4 | 4 | 4 | 4 | 4 | 3 | 4 | 3 | 4 | 1 |
| 10 Shots of Argon Plasma | 5 | 4 | 4 | 8 | 3 | 3 | 4 | 7 | 8 | 5 | 5 | 2 |
| 20 Shots of Argon Plasma | 3 | 3 | 6 | 3 | 5 | 10 | 4 | 4 | 5 | 3 | 5 | 2 |

**Table A7.** Data of The Wetting Time of Untreated Polyester/Cotton Blended Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 0 | 1 | 34 | 51 | 46 | 35 | 48 | 54 | 48 | 41 | 45 | 45 | 7 |
| | 2 | 40 | 41 | 49 | 47 | 49 | 46 | 42 | 47 | 46 | 45 | 3 |
| | 3 | 38 | 42 | 53 | 45 | 54 | 38 | 49 | 42 | 42 | 45 | 6 |
| | 4 | 39 | 42 | 38 | 48 | 43 | 49 | 52 | 44 | 41 | 44 | 5 |
| | 5 | 41 | 47 | 46 | 49 | 50 | 45 | 56 | 51 | 43 | 48 | 5 |
| | 6 | 48 | 41 | 47 | 49 | 45 | 49 | 55 | 57 | 48 | 49 | 5 |
| | 7 | 33 | 31 | 41 | 48 | 52 | 47 | 53 | 41 | 47 | 44 | 8 |
| | Mean | 39 | 42 | 46 | 46 | 49 | 47 | 51 | 46 | 45 | | |
| | S.D. | 5 | 6 | 5 | 5 | 4 | 5 | 5 | 6 | 3 | | |

**Table A8.** Data of The Wetting Time of 10 Shots Air Plasma-treated Polyester/Cotton Blended Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 10 | 1 | 28 | 11 | 27 | 19 | 28 | 26 | 24 | 28 | 28 | 24 | 6 |
| | 2 | 21 | 22 | 24 | 14 | 23 | 24 | 23 | 20 | 27 | 22 | 4 |
| | 3 | 17 | 18 | 22 | 24 | 19 | 22 | 26 | 23 | 31 | 22 | 4 |
| | 4 | 28 | 18 | 25 | 24 | 16 | 23 | 17 | 25 | 30 | 23 | 5 |
| | 5 | 20 | 16 | 25 | 28 | 26 | 25 | 22 | 26 | 27 | 24 | 4 |
| | 6 | 14 | 15 | 21 | 27 | 23 | 22 | 20 | 24 | 29 | 22 | 5 |
| | 7 | 22 | 12 | 23 | 27 | 17 | 15 | 28 | 27 | 21 | 21 | 6 |
| | Mean | 21 | 16 | 24 | 23 | 22 | 22 | 23 | 25 | 28 | | |
| | S.D. | 5 | 4 | 2 | 5 | 5 | 4 | 4 | 3 | 3 | | |

**Table A9.** Data of The Wetting Time of 20 Shots Air Plasma-treated Polyester/Cotton Blended Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 20 | 1 | 6 | 6 | 8 | 6 | 7 | 8 | 7 | 7 | 12 | 7 | 2 |
| | 2 | 6 | 6 | 7 | 8 | 7 | 5 | 8 | 7 | 8 | 7 | 1 |
| | 3 | 4 | 5 | 6 | 7 | 6 | 6 | 7 | 8 | 7 | 6 | 1 |
| | 4 | 5 | 6 | 8 | 5 | 8 | 7 | 6 | 11 | 13 | 8 | 3 |
| | 5 | 8 | 6 | 6 | 6 | 9 | 6 | 9 | 8 | 10 | 8 | 2 |
| | 6 | 6 | 6 | 7 | 6 | 8 | 7 | 7 | 7 | 10 | 7 | 1 |
| | 7 | 5 | 8 | 6 | 7 | 8 | 9 | 8 | 8 | 8 | 7 | 1 |
| | Mean | 6 | 6 | 7 | 6 | 8 | 7 | 7 | 8 | 10 | | |
| | S.D. | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | | |

Table A10. Data of The Wetting Time of 10 Shots Ar Plasma-treated Polyester/Cotton Blended Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 10 | 1 | 22 | 13 | 14 | 17 | 18 | 18 | 19 | 15 | 17 | 17 | 3 |
| | 2 | 22 | 15 | 12 | 19 | 15 | 16 | 15 | 17 | 18 | 17 | 3 |
| | 3 | 22 | 17 | 17 | 16 | 15 | 22 | 18 | 15 | 23 | 18 | 3 |
| | 4 | 18 | 17 | 17 | 18 | 16 | 21 | 16 | 22 | 27 | 19 | 4 |
| | 5 | 21 | 16 | 16 | 14 | 20 | 24 | 20 | 19 | 27 | 20 | 4 |
| | 6 | 19 | 20 | 15 | 15 | 17 | 16 | 19 | 19 | 24 | 18 | 3 |
| | 7 | 20 | 17 | 14 | 16 | 20 | 16 | 17 | 16 | 22 | 18 | 3 |
| | Mean | 21 | 16 | 15 | 16 | 17 | 19 | 18 | 18 | 23 | | |
| | S.D. | 2 | 2 | 2 | 2 | 2 | 3 | 2 | 3 | 4 | | |

Table A11. Data of The Wetting Time of 20 Shots Ar Plasma-treated Polyester/Cotton Blended Fabrics

| Number of plasma shots | Position | Wetting Time (s) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | Middle | 6 | 7 | 8 | 9 | Mean | S.D. |
| 20 | 1 | 21 | 10 | 10 | 13 | 16 | 12 | 12 | 14 | 21 | 14 | 4 |
| | 2 | 12 | 10 | 10 | 10 | 12 | 13 | 12 | 15 | 22 | 13 | 4 |
| | 3 | 12 | 11 | 8 | 11 | 12 | 8 | 13 | 13 | 15 | 11 | 2 |
| | 4 | 12 | 12 | 10 | 10 | 12 | 12 | 16 | 13 | 15 | 12 | 2 |
| | 5 | 15 | 11 | 9 | 11 | 12 | 13 | 16 | 11 | 20 | 13 | 3 |
| | 6 | 13 | 11 | 10 | 11 | 13 | 16 | 14 | 13 | 18 | 13 | 3 |
| | 7 | 13 | 12 | 12 | 8 | 9 | 9 | 11 | 14 | 17 | 12 | 3 |
| | Mean | 14 | 11 | 10 | 11 | 12 | 12 | 13 | 13 | 18 | | |
| | S.D. | 3 | 1 | 1 | 2 | 2 | 3 | 2 | 1 | 3 | | |

## Appendix B

**Table B1.** Data of Color Measurement of Untreated and Plasma-treated Polyester Fabrics Dyed with Disperse Dye

| Conditions | Maximum wavelength (nm) | K/S | L* | a* | b* |
|---|---|---|---|---|---|
| Untreated | 620 | 13.99 | 26.54 | 0.25 | -18.64 |
| | 610 | 13.77 | 26.65 | 0.3 | -18.38 |
| | Mean | 13.88 | 26.60 | 0.28 | -18.51 |
| | S.D. | 0.16 | 0.08 | 0.04 | 0.13 |
| 10 Shots of Air Plasma | 610 | 13.81 | 26.46 | 0.64 | -18.4 |
| | 610 | 13.72 | 26.8 | 0.46 | -19.04 |
| | Mean | 13.77 | 26.63 | 0.55 | -18.72 |
| | S.D. | 0.06 | 0.24 | 0.13 | 0.45 |
| 20 Shots of Air Plasma | 610 | 15.91 | 24.82 | 0.61 | -18.39 |
| | 610 | 16.56 | 24.13 | 0.75 | -17.75 |
| | Mean | 16.24 | 24.48 | 0.68 | -18.07 |
| | S.D. | 0.46 | 0.49 | 0.10 | 0.45 |
| 10 Shots of Argon Plasma | 620 | 15.14 | 25.36 | 0.86 | -18.86 |
| | 620 | 15.41 | 24.91 | 0.94 | -18.1 |
| | Mean | 15.28 | 25.14 | 0.90 | -18.48 |
| | S.D. | 0.19 | 0.32 | 0.06 | 0.54 |
| 20 Shots of Argon Plasma | 610 | 13.64 | 26.33 | 0.47 | -17.46 |
| | 610 | 13.34 | 26.59 | 0.44 | -17.54 |
| | Mean | 13.41 | 26.46 | 0.46 | -17.50 |
| | S.D. | 0.21 | 0.18 | 0.02 | 0.06 |

**Table B2.** Data of Colorfastness to Washing of Untreated and Plasma-treated Polyester Fabrics Dyed with Disperse Dye

| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| Untreated | 10 | 1 | 13.72 | 26.84 | 0.41 | -19.06 | 0.54 | 4.5 |
| | | 2 | 13.59 | 26.78 | 0.19 | -18.3 | 0.19 | 5 |
| | | Mean | 13.66 | 26.81 | 0.30 | -18.68 | 0.37 | |
| | | S.D. | 0.35 | 0.04 | 0.16 | 0.54 | 0.25 | |
| | 20 | 1 | 13.1 | 27.22 | 0.2 | -18.45 | 0.7 | 4.5 |
| | | 2 | 13.43 | 26.91 | 0.35 | -18.4 | 0.26 | 5 |
| | | Mean | 13.27 | 27.07 | 0.28 | -18.43 | 0.48 | |
| | | S.D. | 0.21 | 0.22 | 0.11 | 0.04 | 0.15 | |
| | 30 | 1 | 13.1 | 27.36 | 0.37 | -19.1 | 0.95 | 4.5 |
| | | 2 | 13.26 | 16.92 | 0.32 | -18.19 | 0.39 | 5 |
| | | Mean | 13.18 | 22.14 | 0.35 | -18.65 | 0.67 | |
| | | S.D. | 0.11 | 7.38 | 0.04 | 0.64 | 0.42 | |
| 10 Shots of Air Plasma | 10 | 1 | 13.72 | 26.55 | 0.54 | -18.53 | 0.19 | 4.5 |
| | | 2 | 13.39 | 23.72 | 0.42 | -18.02 | 0.73 | 4.5 |
| | | Mean | 13.56 | 25.14 | 0.48 | -18.28 | 0.46 | |
| | | S.D. | 0.23 | 2.00 | 0.08 | 0.36 | 0.59 | |
| | 20 | 1 | 13.30 | 26.74 | 0.52 | -18.43 | 0.31 | 5 |
| | | 2 | 13.26 | 26.88 | 0.45 | -18.34 | 0.71 | 4.5 |
| | | Mean | 13.37 | 26.81 | 0.49 | -18.39 | 0.51 | |
| | | S.D. | 0.23 | 0.10 | 0.05 | 0.06 | 0.28 | |
| | 30 | 1 | 13.30 | 26.98 | 0.41 | -18.48 | 0.57 | 4.5 |
| | | 2 | 13.18 | 26.98 | 0.42 | -18.51 | 0.56 | 4.5 |
| | | Mean | 13.24 | 26.98 | 0.42 | -18.50 | 0.57 | |
| | | S.D. | 0.08 | 0.00 | 0.01 | 0.02 | 0.01 | |

**Table B3.** Data of Colorfastness to Washing of Untreated and Plasma-treated Polyester Fabrics Dyed with Disperse Dye (Con't)

| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| 20 Shots of Air Plasma | 10 | 1 | 15.04 | 25.5 | 0.55 | -18.38 | 0.68 | 4.5 |
| | | 2 | 15.79 | 24.91 | 0.75 | -18.51 | 1.09 | 4.5 |
| | | Mean | 15.42 | 25.21 | 0.65 | -18.45 | 0.89 | |
| | | S.D. | 0.53 | 0.42 | 0.14 | 0.09 | 0.21 | |
| | 20 | 1 | 13.14 | 26.95 | 0.34 | -17.92 | 2.2 | 3.5 |
| | | 2 | 13.51 | 26.75 | 0.35 | -18.25 | 2.7 | 3.5 |
| | | Mean | 13.33 | 26.85 | 0.35 | -18.09 | 2.45 | |
| | | S.D. | 0.26 | 0.14 | 0.01 | 0.23 | 0.35 | |
| | 30 | 1 | 12.91 | 27.31 | 0.35 | -18.34 | 2.51 | 3.5 |
| | | 2 | 13.34 | 26.85 | 0.32 | -18.03 | 2.76 | 3.5 |
| | | Mean | 13.13 | 27.08 | 0.34 | -18.19 | 2.64 | |
| | | S.D. | 0.30 | 0.33 | 0.02 | 0.22 | 0.18 | |
| 10 Shots of Argon Plasma | 10 | 1 | 13.72 | 26.67 | 0.64 | -19.03 | 1.34 | 4 |
| | | 2 | 13.64 | 26.43 | 0.66 | -18.03 | 1.55 | 4 |
| | | Mean | 13.68 | 26.55 | 0.65 | -18.53 | 1.45 | |
| | | S.D. | 0.06 | 0.17 | 0.01 | 0.71 | 0.15 | |
| | 20 | 1 | 13.39 | 26.78 | 0.45 | -18.33 | 1.57 | 4 |
| | | 2 | 14.12 | 26.38 | 0.7 | -19.13 | 1.81 | 4 |
| | | Mean | 13.76 | 26.58 | 0.58 | -18.73 | 1.69 | |
| | | S.D. | 0.52 | 0.28 | 0.18 | 0.57 | 0.17 | |
| | 30 | 1 | 12.91 | 27.19 | 0.71 | -18.61 | 1.85 | 4 |
| | | 2 | 13.22 | 27.06 | 0.66 | -19.03 | 2.36 | 3.5 |
| | | Mean | 13.07 | 27.13 | 0.69 | -18.82 | 2.11 | |
| | | S.D. | 0.22 | 0.09 | 0.04 | 0.30 | 0.36 | |

Table B4. Data of Colorfastness to Washing of Untreated and Plasma-treated Polyester Fabrics Dyed with Disperse Dye (Con't)

| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| 20 Shots of Argon Plasma | 10 | 1 | 13.39 | 26.53 | 0.45 | -17.56 | 0.23 | 5 |
| | | 2 | 13.1 | 26.73 | 0.51 | -17.49 | 0.17 | 5 |
| | | Mean | 13.25 | 26.63 | 0.48 | -17.53 | 0.20 | |
| | | S.D. | 0.21 | 0.14 | 0.04 | 0.05 | 0.04 | |
| | 20 | 1 | 13.02 | 26.73 | 0.47 | -17.32 | 0.42 | 4.5 |
| | | 2 | 12.91 | 26.9 | 0.44 | -17.43 | 0.33 | 5 |
| | | Mean | 12.97 | 26.82 | 0.46 | -17.38 | 0.38 | |
| | | S.D. | 0.08 | 0.12 | 0.02 | 0.08 | 0.06 | |
| | 30 | 1 | 12.72 | 27.04 | 0.53 | -17.41 | 0.71 | 4.5 |
| | | 2 | 12.83 | 26.99 | 0.45 | -17.56 | 0.41 | 4.5 |
| | | Mean | 12.78 | 27.02 | 0.49 | -17.49 | 0.56 | |
| | | S.D. | 0.08 | 0.04 | 0.06 | 0.11 | 0.21 | |

**Table B5.** Data of Color Measurement of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dye

| Conditions | Maximum wavelength (nm) | K/S | L* | a* | b* |
|---|---|---|---|---|---|
| Untreated | 620 | 3.3 | 50.99 | -8.44 | -17.96 |
|  | 620 | 2.45 | 55.12 | -8.4 | -17.15 |
|  | Mean | 2.88 | 53.06 | -8.42 | -17.56 |
|  | S.D. | 0.60 | 2.92 | 0.03 | 0.57 |
| 10 Shots of Air Plasma | 620 | 2.96 | 52.12 | -8.11 | -17.17 |
|  | 620 | 2.33 | 55.57 | -8.22 | -16.67 |
|  | Mean | 2.65 | 53.85 | -8.17 | -16.92 |
|  | S.D. | 0.45 | 2.44 | 0.08 | 0.35 |
| 20 Shots of Air Plasma | 620 | 3.03 | 51.82 | -8.26 | -17.07 |
|  | 620 | 2.3 | 55.65 | -8.19 | -16.42 |
|  | Mean | 2.67 | 53.74 | -8.23 | -16.75 |
|  | S.D. | 0.52 | 2.71 | 0.05 | 0.46 |
| 10 Shots of Argon Plasma | 620 | 2.73 | 53.42 | -8.35 | -17.05 |
|  | 620 | 2.2 | 56.73 | -8.17 | -16.57 |
|  | Mean | 2.47 | 55.08 | -8.26 | -16.81 |
|  | S.D. | 0.37 | 2.34 | 0.13 | 0.34 |
| 20 Shots of Argon Plasma | 620 | 3.39 | 50.31 | -8.18 | -17.72 |
|  | 620 | 2.22 | 56.13 | -8.15 | -16.47 |
|  | Mean | 2.81 | 53.22 | -8.17 | -17.10 |
|  | S.D. | 0.83 | 4.12 | 0.02 | 0.88 |

**Table B6.** Data of Colorfastness to Washing of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dye

| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| Untreated | 10 | 1 | 3.05 | 51.9 | -8.23 | -17.65 | 0.98 | 4.5 |
| | | 2 | 2.33 | 55.58 | -8.17 | -16.77 | 0.16 | 4.5 |
| | | Mean | 2.69 | 53.74 | -8.20 | -17.21 | 0.57 | |
| | | S.D. | 0.51 | 2.60 | 0.04 | 0.62 | 0.58 | |
| | 20 | 1 | 2.89 | 52.54 | -8.1 | -17.3 | 1.71 | 4 |
| | | 2 | 2.29 | 55.9 | -8.2 | -16.73 | 0.91 | 4.5 |
| | | Mean | 2.59 | 54.22 | -8.15 | -17.02 | 1.31 | |
| | | S.D. | 0.42 | 2.38 | 0.07 | 0.40 | 0.57 | |
| | 30 | 1 | 2.54 | 54.09 | -7.86 | -16.64 | 3.42 | 3 |
| | | 2 | 2.22 | 56.15 | -8 | -16.47 | 1.3 | 4.5 |
| | | Mean | 2.38 | 55.12 | -7.93 | -16.56 | 2.36 | |
| | | S.D. | 0.23 | 1.46 | 0.10 | 0.12 | 1.50 | |
| 10 Shots of Air Plasma | 10 | 1 | 2.82 | 52.92 | -8.27 | -17.24 | 0.81 | 4.5 |
| | | 2 | 2.27 | 55.84 | -8.1 | -16.53 | 0.33 | 5 |
| | | Mean | 2.55 | 54.38 | -8.19 | -16.89 | 0.57 | |
| | | S.D. | 0.39 | 2.06 | 0.12 | 0.50 | 0.34 | |
| | 20 | 1 | 2.66 | 53.49 | -7.93 | -16.83 | 1.42 | 4 |
| | | 2 | 2.18 | 56.34 | -7.95 | -16.25 | 0.92 | 4.5 |
| | | Mean | 2.42 | 54.92 | -7.94 | -16.54 | 1.17 | |
| | | S.D. | 0.34 | 2.02 | 0.01 | 0.41 | 0.35 | |
| | 30 | 1 | 2.47 | 54.44 | -7.89 | -16.47 | 2.44 | 3.5 |
| | | 2 | 2.11 | 56.61 | -7.8 | -16.07 | 1.27 | 4.5 |
| | | Mean | 2.29 | 55.53 | -7.85 | -16.27 | 1.86 | |
| | | S.D. | 0.25 | 1.53 | 0.06 | 0.28 | 0.83 | |

**Table B7.** Data of Colorfastness to Washing of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dye (Con't)

| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| 20 Shots of Air Plasma | 10 | 1 | 2.79 | 52.94 | -8.08 | -17.02 | 1.13 | 4.5 |
| | | 2 | 2.15 | 56.54 | -7.97 | -19.32 | 0.92 | 4.5 |
| | | Mean | 2.47 | 54.74 | -8.03 | -18.17 | 1.03 | |
| | | S.D. | 0.45 | 2.55 | 0.08 | 1.63 | 0.15 | |
| | 20 | 1 | 2.65 | 53.47 | -7.94 | -16.71 | 1.72 | 4 |
| | | 2 | 2.08 | 57.11 | -8.08 | -16.39 | 1.46 | 4 |
| | | Mean | 2.37 | 55.29 | -8.01 | -16.55 | 1.59 | |
| | | S.D. | 0.40 | 2.57 | 0.10 | 0.23 | 0.18 | |
| | 30 | 1 | 2.54 | 54 | -7.82 | -16.51 | 2.29 | 3.5 |
| | | 2 | 1.97 | 57.62 | -7.81 | -19.03 | 2.04 | 4 |
| | | Mean | 2.26 | 55.81 | -7.82 | -17.77 | 2.17 | |
| | | S.D. | 0.40 | 2.56 | 0.01 | 1.78 | 0.18 | |
| 10 Shots of Argon Plasma | 10 | 1 | 2.53 | 54.41 | -8.16 | -16.91 | 1.02 | 4.5 |
| | | 2 | 2.16 | 56.52 | -8.08 | -16.42 | 0.23 | 5 |
| | | Mean | 2.35 | 55.47 | -8.12 | -16.67 | 0.63 | |
| | | S.D. | 0.26 | 1.49 | 0.06 | 0.35 | 0.56 | |
| | 20 | 1 | 2.44 | 54.68 | -7.98 | -16.61 | 1.38 | 4 |
| | | 2 | 2.1 | 56.89 | -8 | -16.22 | 0.66 | 4.5 |
| | | Mean | 2.27 | 55.79 | -7.99 | -16.42 | 1.02 | |
| | | S.D. | 0.24 | 1.56 | 0.01 | 0.28 | 0.51 | |
| | 30 | 1 | 2.35 | 55.2 | -7.93 | -16.46 | 1.92 | 4 |
| | | 2 | 2.02 | 57.32 | -7.86 | -16.09 | 1.11 | 4.5 |

**Table B8.** Data of Colorfastness to Washing of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dye (Con't)

| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| 20 Shots of Argon Plasma | 10 | 1 | 3 | 51.91 | -8.04 | -17.34 | 1.65 | 4 |
| | | 2 | 2.09 | 56.86 | -7.95 | -16.13 | 0.83 | 4.5 |
| | | Mean | 2.55 | 54.39 | -8.00 | -16.74 | 1.24 | |
| | | S.D. | 0.64 | 3.50 | 0.06 | 0.86 | 0.58 | |
| | 20 | 1 | 2.82 | 52.51 | -7.83 | -16.72 | 2.44 | 3.5 |
| | | 2 | 2.06 | 56.97 | -7.8 | -15.86 | 1.09 | 4.5 |
| | | Mean | 2.44 | 54.74 | -7.82 | -16.29 | 1.77 | |
| | | S.D. | 0.54 | 3.15 | 0.02 | 0.61 | 0.95 | |
| | 30 | 1 | 2.73 | 53.02 | -7.82 | -16.87 | 2.86 | 3.5 |
| | | 2 | 1.93 | 57.82 | -7.69 | -15.79 | 1.88 | 4 |
| | | Mean | 2.33 | 55.42 | -7.76 | -16.33 | 2.37 | |
| | | S.D. | 0.57 | 3.39 | 0.09 | 0.76 | 0.69 | |

**Table B9.** Data of Color Measurement of Untreated and Plasma-treated Polyester /Cotton Blend Fabrics Dyed with Disperse Dye and Reactive dye

| Conditions | Maximum wavelength (nm) | K/S | L* | a* | b* |
|---|---|---|---|---|---|
| Untreated | 620 | 5.74 | 39.29 | -3.67 | -15.72 |
| | 620 | 5.91 | 38.89 | -3.43 | -16.1 |
| | Mean | 5.83 | 39.09 | -3.55 | -15.91 |
| | S.D. | 0.12 | 0.28 | 0.17 | 0.27 |
| 10 Shots of Air Plasma | 620 | 5.88 | 38.28 | -3.35 | -14.06 |
| | 620 | 5.83 | 38.25 | -3.16 | -13.89 |
| | Mean | 5.86 | 38.27 | -3.26 | -13.98 |
| | S.D. | 0.04 | 0.02 | 0.13 | 0.12 |
| 20 Shots of Air Plasma | 620 | 6.21 | 37.64 | -3.4 | -14.36 |
| | 620 | 6.12 | 37.66 | -3.17 | -14.06 |
| | Mean | 6.17 | 37.65 | -3.29 | -14.21 |
| | S.D. | 0.06 | 0.01 | 0.16 | 0.21 |
| 10 Shots of Argon Plasma | 620 | 5.92 | 38.76 | -3.55 | -15.58 |
| | 620 | 5.62 | 39.99 | -3.74 | -16.56 |
| | Mean | 5.77 | 39.38 | -3.65 | -16.07 |
| | S.D. | 0.21 | 0.87 | 0.13 | 0.69 |
| 20 Shots of Argon Plasma | 620 | 5.7 | 39.3 | -3.69 | -15.24 |
| | 620 | 6 | 38.31 | -3.24 | -15.26 |
| | Mean | 5.85 | 38.81 | -3.47 | -15.25 |
| | S.D. | 0.21 | 0.70 | 0.32 | 0.01 |

Table B10. Data of Colorfastness to Washing of Untreated and Plasma-treated Polyester /Cotton Blend Fabrics Dyed with Disperse Dye and Reactive dye

| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| Untreated | 10 | 1 | 5.6 | 39.46 | -3.58 | -15.12 | 0.63 | 4.5 |
| | | 2 | 5.83 | 39.03 | -3.33 | -16.03 | 0.19 | 5 |
| | | Mean | 5.72 | 39.25 | -3.46 | -15.58 | 0.41 | |
| | | S.D. | 0.16 | 0.30 | 0.18 | 0.64 | 0.31 | |
| | 20 | 1 | 5.41 | 39.89 | -3.44 | -15.18 | 0.84 | 4.5 |
| | | 2 | 5.74 | 39.13 | -3.43 | -15.51 | 0.65 | 4.5 |
| | | Mean | 5.58 | 39.51 | -3.44 | -15.35 | 0.75 | |
| | | S.D. | 0.23 | 0.54 | 0.01 | 0.23 | 0.13 | |
| | 30 | 1 | 5.38 | 39.8 | -3.33 | -14.98 | 0.96 | 4.5 |
| | | 2 | 5.63 | 39.51 | -3.43 | -15.77 | 0.7 | 4.5 |
| | | Mean | 5.51 | 39.66 | -3.38 | -15.38 | 0.83 | |
| | | S.D. | 0.18 | 0.21 | 0.07 | 0.56 | 0.18 | |
| 10 Shots of Air Plasma | 10 | 1 | 5.69 | 38.68 | -3.05 | -14.39 | 0.6 | 4.5 |
| | | 2 | 5.7 | 38.7 | -3.23 | -14.17 | 0.53 | 4.5 |
| | | Mean | 5.70 | 38.69 | -3.14 | -14.28 | 0.57 | |
| | | S.D. | 0.01 | 0.01 | 0.13 | 0.16 | 0.05 | |
| | 20 | 1 | 5.63 | 38.86 | -3.03 | -14.55 | 0.83 | 4.5 |
| | | 2 | 5.66 | 38.76 | -3.21 | -14.09 | 0.55 | 4.5 |
| | | Mean | 5.65 | 38.81 | -3.12 | -14.32 | 0.69 | |
| | | S.D. | 0.02 | 0.07 | 0.13 | 0.33 | 0.20 | |
| | 30 | 1 | 5.59 | 39.43 | -3.49 | -14.8 | 1.37 | 4 |
| | | 2 | 5.5 | 39.12 | -3.2 | -13.94 | 0.87 | 4.5 |
| | | Mean | 5.55 | 39.28 | -3.35 | -14.37 | 1.12 | |
| | | S.D. | 0.06 | 0.22 | 0.21 | 0.61 | 0.35 | |

**Table B11.** Data of Colorfastness to Washing of Untreated and Plasma-treated Polyester /Cotton Blend Fabrics Dyed with Disperse Dye and Reactive dye (Con't)

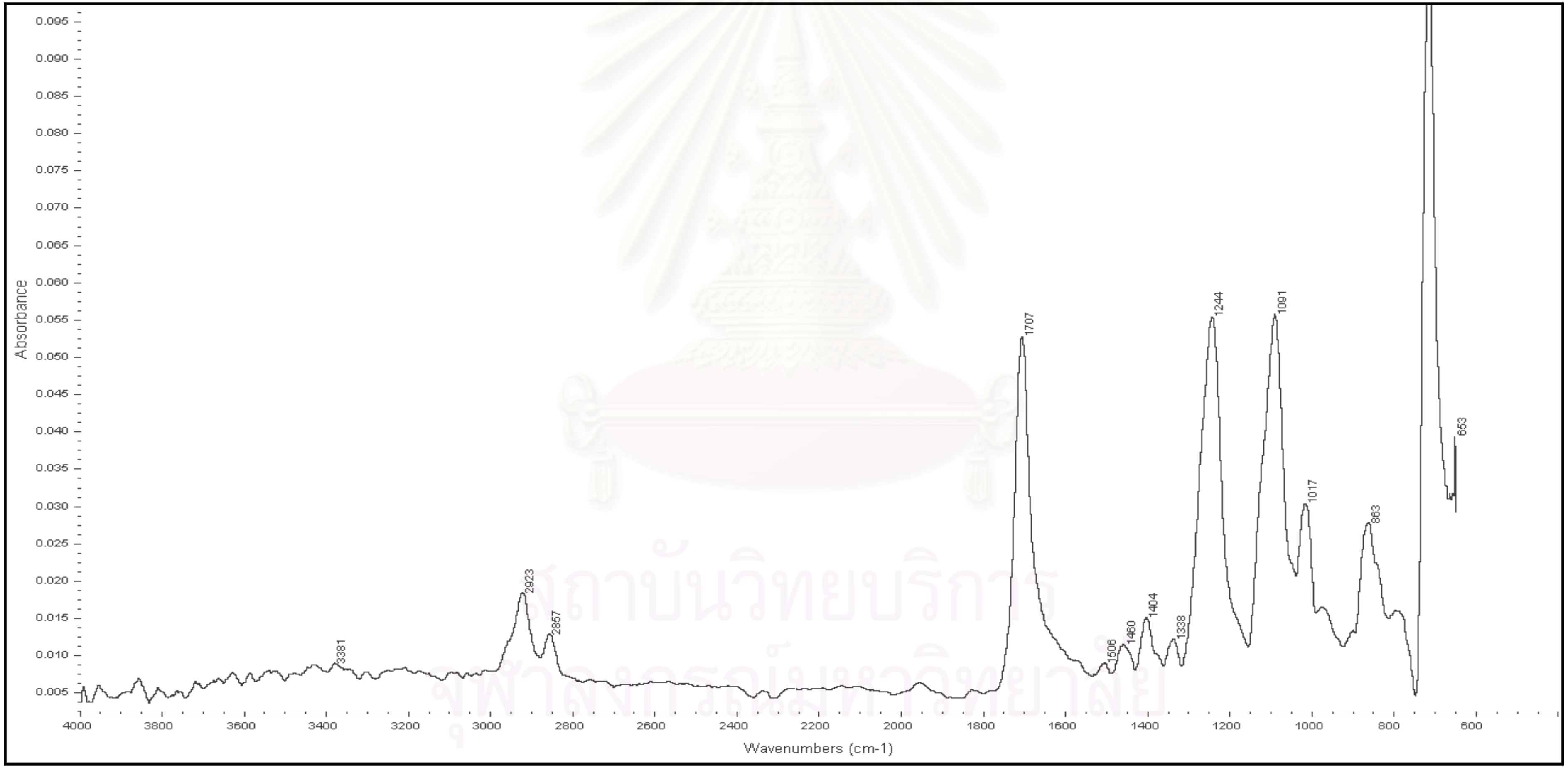
| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| 20 Shots of Air Plasma | 10 | 1 | 6.14 | 37.58 | -3.14 | -13.93 | 0.5 | 4.5 |
| | | 2 | 6.03 | 37.78 | -3.19 | -13.87 | 0.22 | 5 |
| | | Mean | 6.09 | 37.68 | -3.17 | -13.90 | 0.36 | |
| | | S.D. | 0.08 | 0.14 | 0.04 | 0.04 | 0.20 | |
| | 20 | 1 | 6.02 | 37.8 | -3.11 | -13.93 | 0.53 | 4.5 |
| | | 2 | 5.92 | 38.41 | -3.22 | -14.99 | 1.2 | 4.5 |
| | | Mean | 5.97 | 38.11 | -3.17 | -14.46 | 0.87 | |
| | | S.D. | 0.07 | 0.43 | 0.08 | 0.75 | 0.47 | |
| | 30 | 1 | 5.73 | 38.57 | -3.11 | -14.38 | 0.97 | 4.5 |
| | | 2 | 5.87 | 38.85 | -3.47 | -15.45 | 1.86 | 4 |
| | | Mean | 5.80 | 38.71 | -3.29 | -14.92 | 1.42 | |
| | | S.D. | 0.10 | 0.20 | 0.25 | 0.76 | 0.63 | |
| 10 Shots of Argon Plasma | 10 | 1 | 5.73 | 39.08 | -3.28 | -15.62 | 0.42 | 4.5 |
| | | 2 | 5.51 | 39.87 | -3.54 | -15.91 | 0.69 | 4.5 |
| | | Mean | 5.62 | 39.48 | -3.41 | -15.77 | 0.56 | |
| | | S.D. | 0.16 | 0.56 | 0.18 | 0.21 | 0.19 | |
| | 20 | 1 | 5.68 | 39.2 | -3.37 | -15.25 | 0.57 | 4.5 |
| | | 2 | 5.47 | 40.04 | -3.58 | -15.91 | 0.67 | 4.5 |
| | | Mean | 5.58 | 39.62 | -3.48 | -15.58 | 0.62 | |
| | | S.D. | 0.15 | 0.59 | 0.15 | 0.47 | 0.07 | |
| | 30 | 1 | 5.53 | 39.53 | -3.33 | -15.41 | 0.81 | 4.5 |
| | | 2 | 5.37 | 40.29 | -3.64 | -15.89 | 0.74 | 4.5 |
| | | Mean | 5.45 | 39.91 | -3.49 | -15.65 | 0.78 | |
| | | S.D. | 0.11 | 0.54 | 0.22 | 0.34 | 0.05 | |

**Table B12.** Data of Colorfastness to Washing of Untreated and Plasma-treated Polyester /Cotton Blend Fabrics Dyed with Disperse Dye and Reactive dye (Con’t)

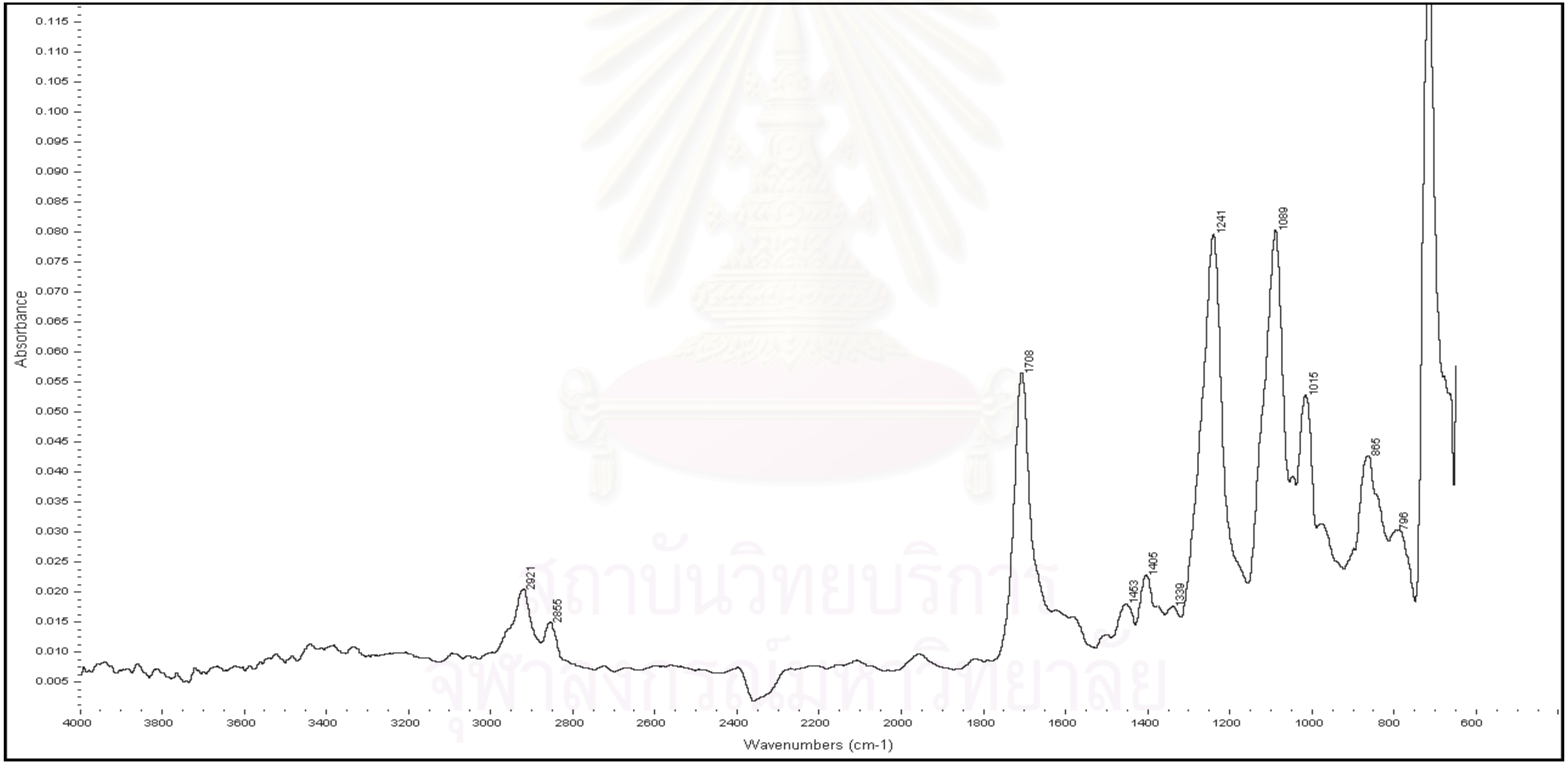
| Conditions | Cycles | Number of Testing | K/S | L* | a* | b* | ∆E | Color Change |
|---|---|---|---|---|---|---|---|---|
| 20 Shots of Argon Plasma | 10 | 1 | 5.5 | 39.61 | -3.62 | -14.81 | 0.54 | 4.5 |
| | | 2 | 5.81 | 38.69 | -3.26 | -15.09 | 0.42 | 4.5 |
| | | Mean | 5.66 | 39.15 | -3.44 | -14.95 | 0.48 | |
| | | S.D. | 0.22 | 0.65 | 0.25 | 0.20 | 0.08 | |
| | 20 | 1 | 5.42 | 39.83 | -3.65 | -14.8 | 0.69 | 4.5 |
| | | 2 | 5.8 | 38.73 | -3.26 | -15.08 | 0.46 | 4.5 |
| | | Mean | 5.61 | 39.28 | -3.46 | -14.94 | 0.58 | |
| | | S.D. | 0.27 | 0.78 | 0.28 | 0.20 | 0.16 | |
| | 30 | 1 | 5.31 | 39.91 | -3.45 | -14.54 | 0.96 | 4.5 |
| | | 2 | 5.68 | 39.43 | -3.63 | -15.53 | 1.21 | 4.5 |
| | | Mean | 5.50 | 39.67 | -3.54 | -15.04 | 1.09 | |
| | | S.D. | 0.26 | 0.34 | 0.13 | 0.70 | 0.18 | |

# Appendix C

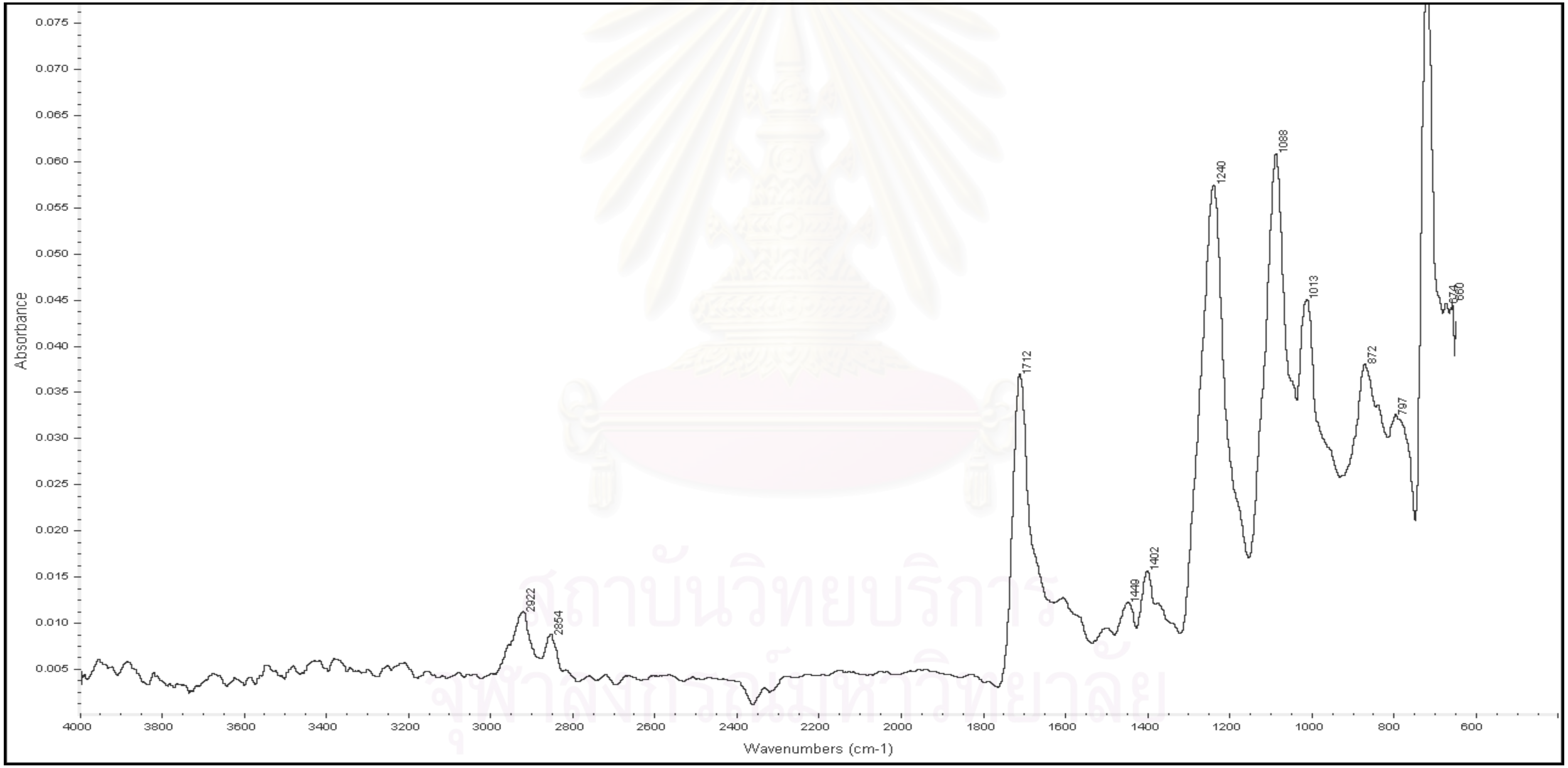
1. ATR-FTIR Spectra of untreated PET fabric



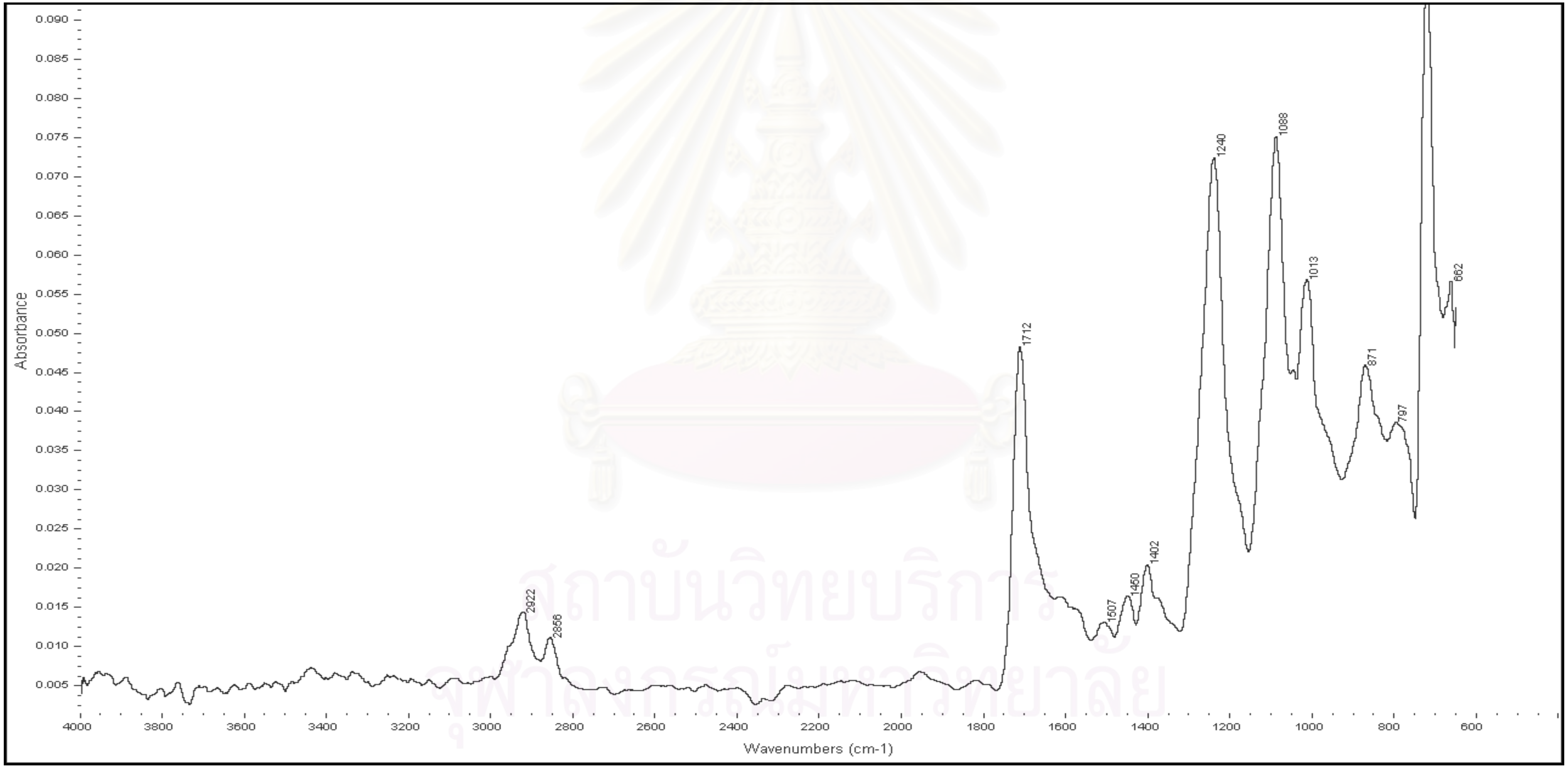
2. ATR-FTIR Spectra of air plasma-treated PET fabric for 10 shots



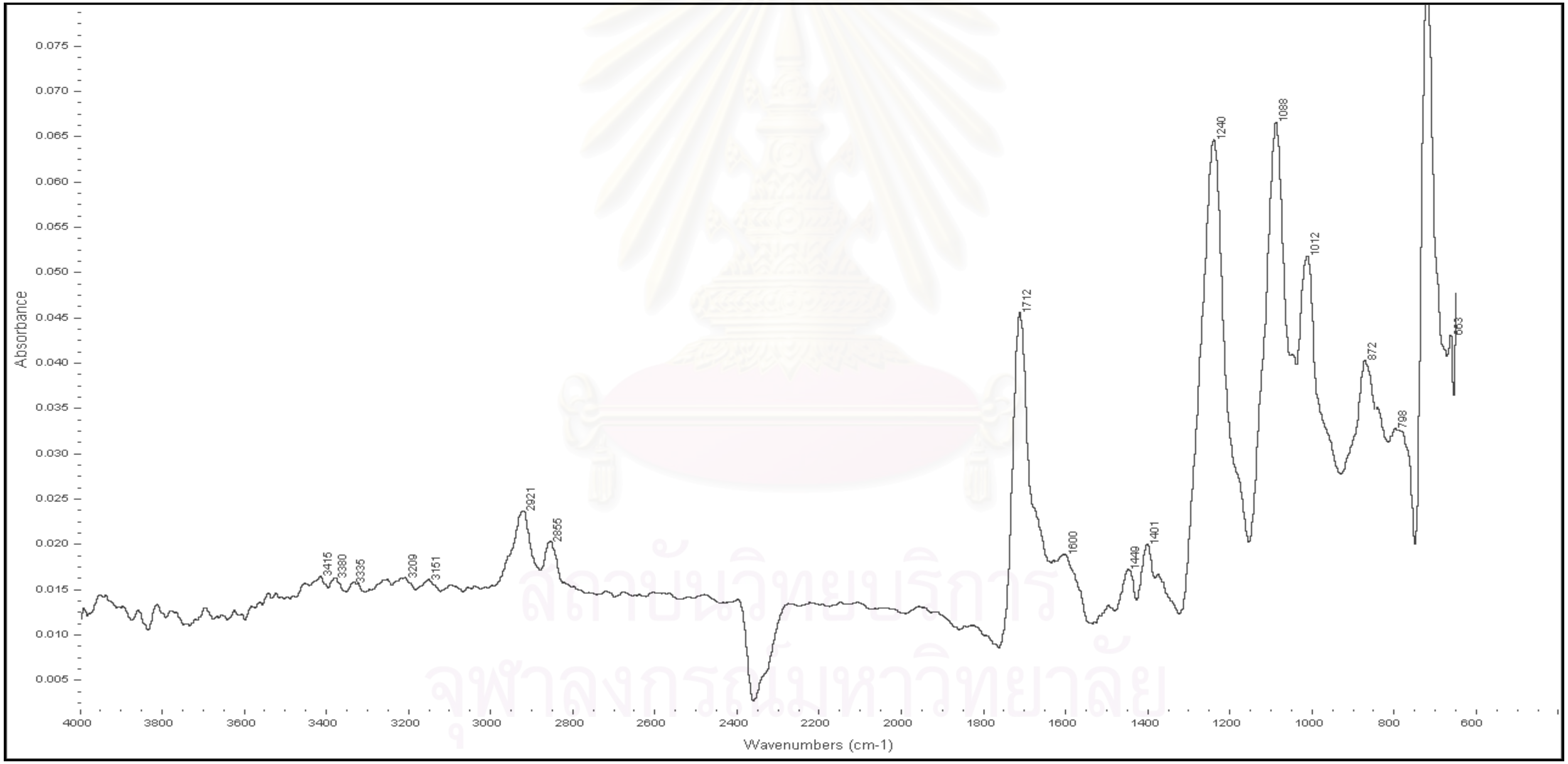
3. ATR-FTIR Spectra of air plasma-treated PET fabric for 20 shots



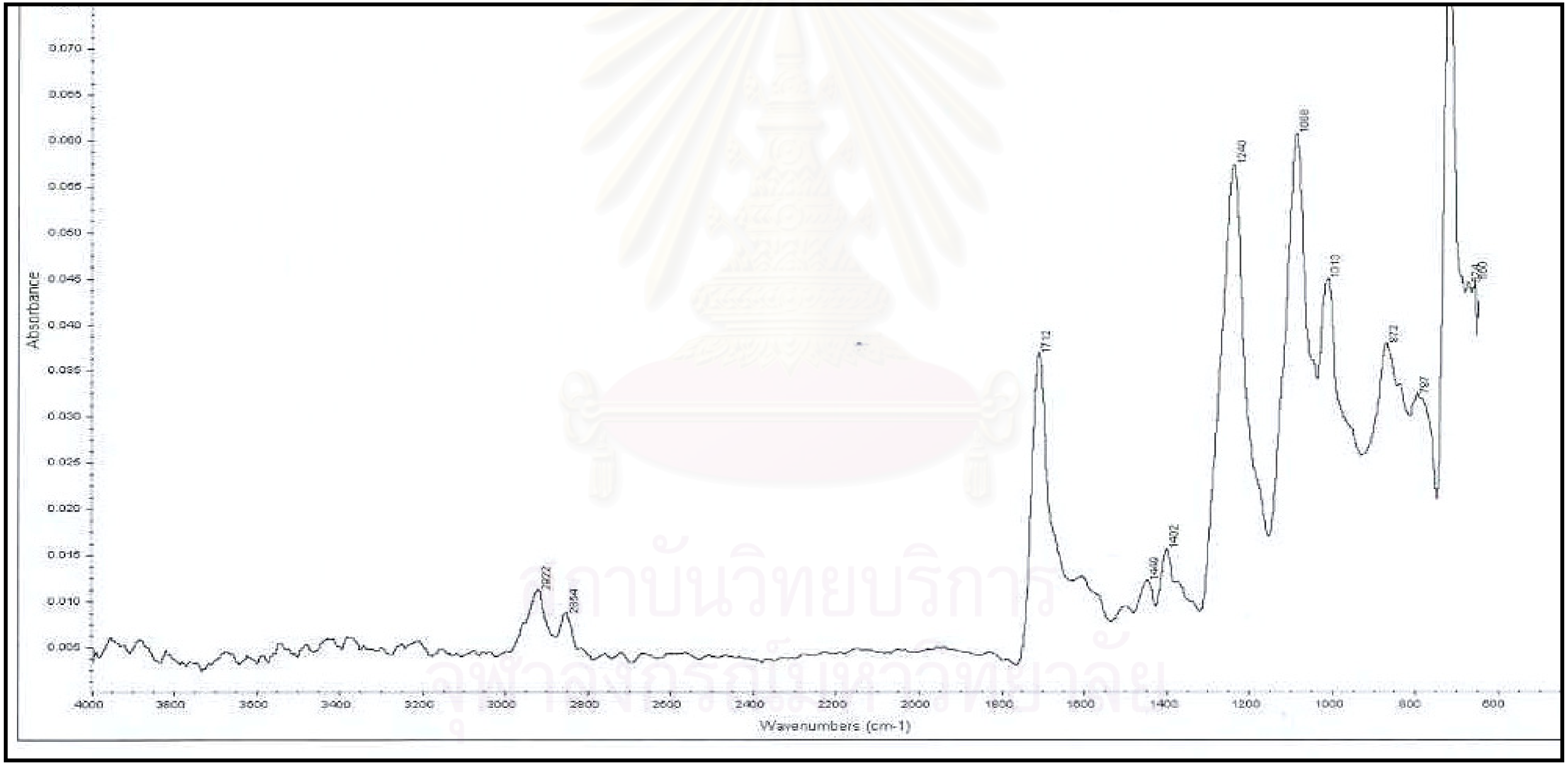
4. ATR-FTIR Spectra of argon plasma-treated PET fabric for 10 shots



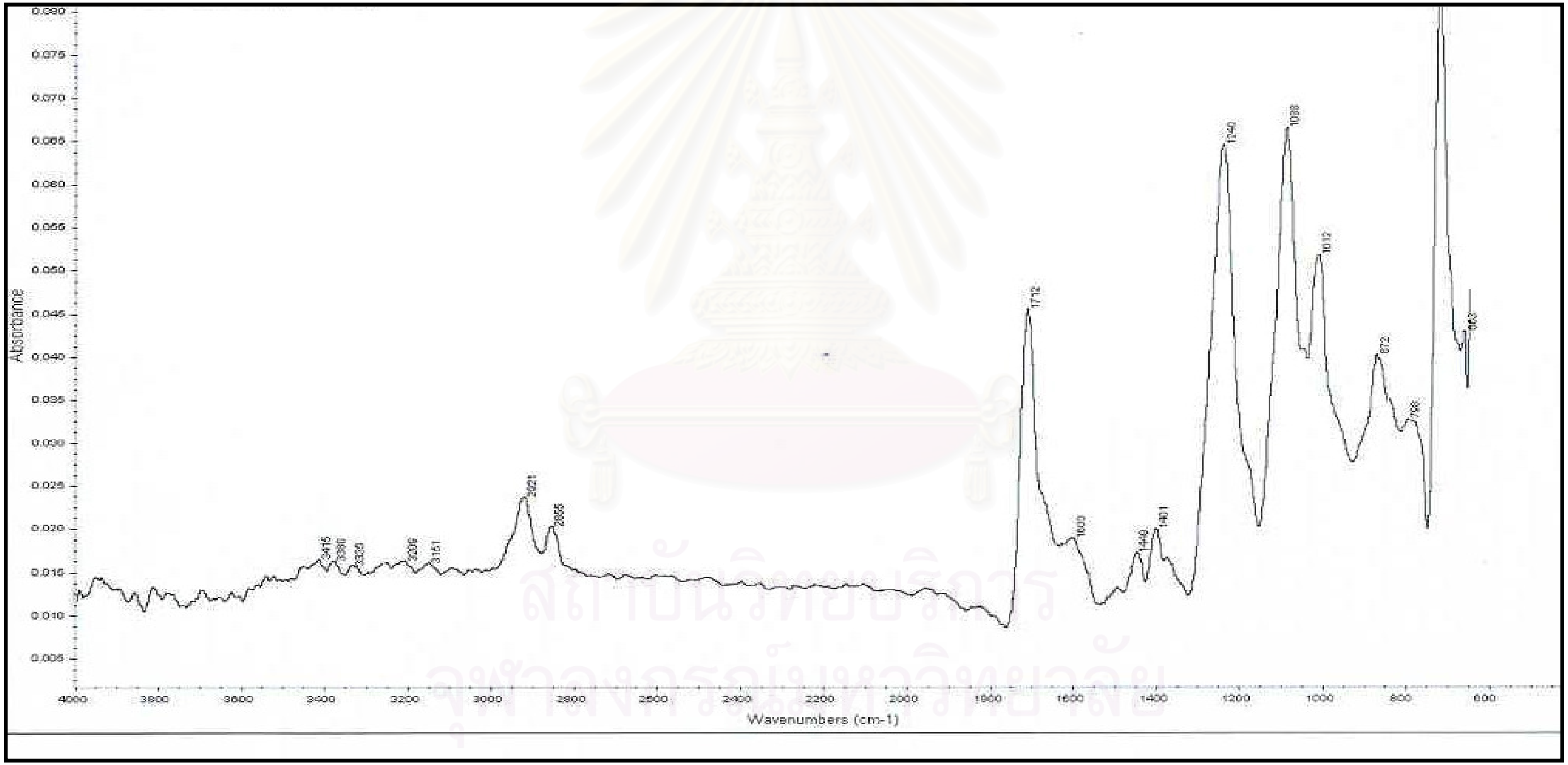
5. <u>ATR-FTIR Spectra of argon plasma-treated PET fabric for 20 shots</u>



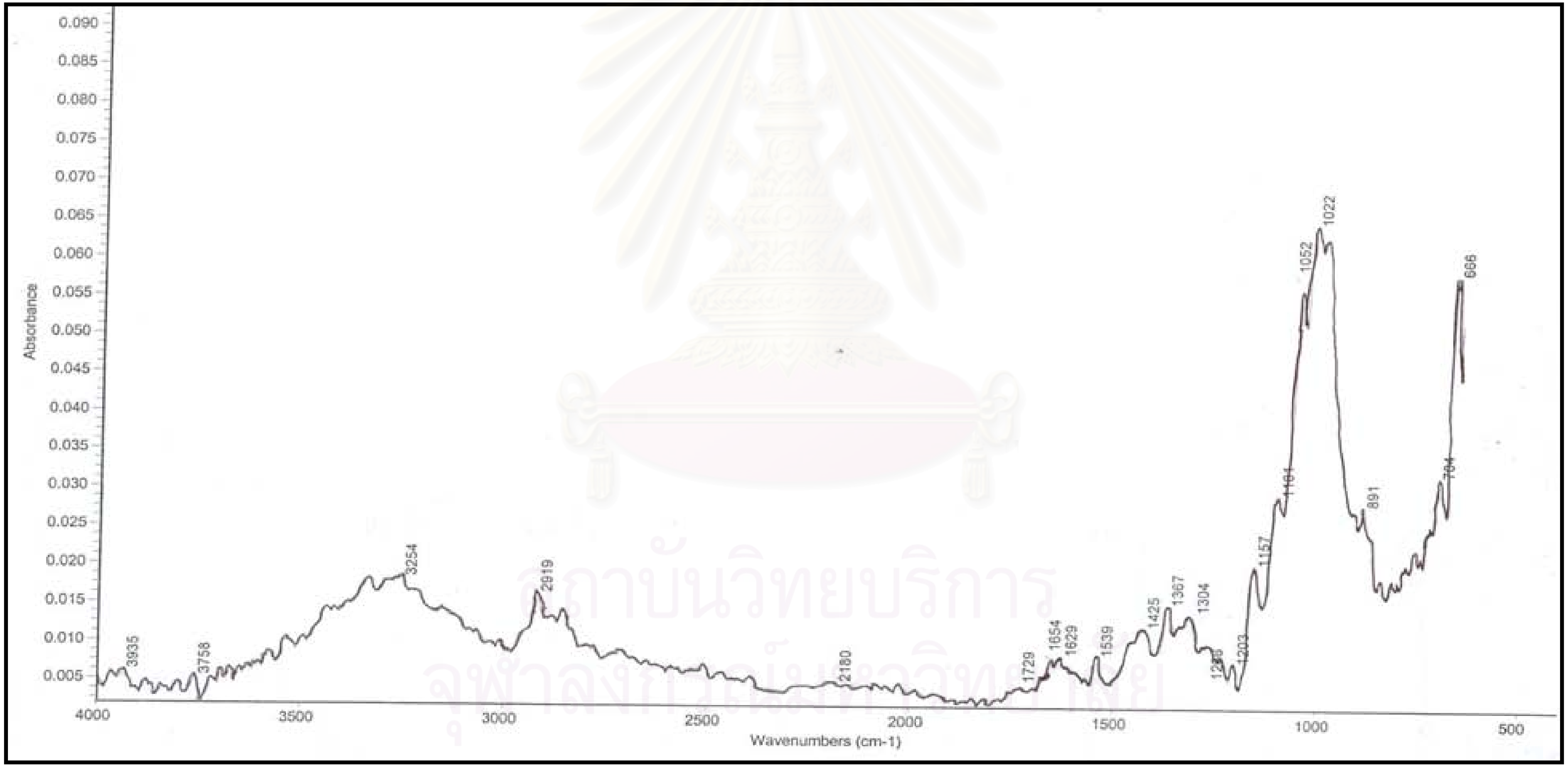
6. ATR-FTIR Spectra of air plasma-treated PET fabric for 20 shots after 30 days



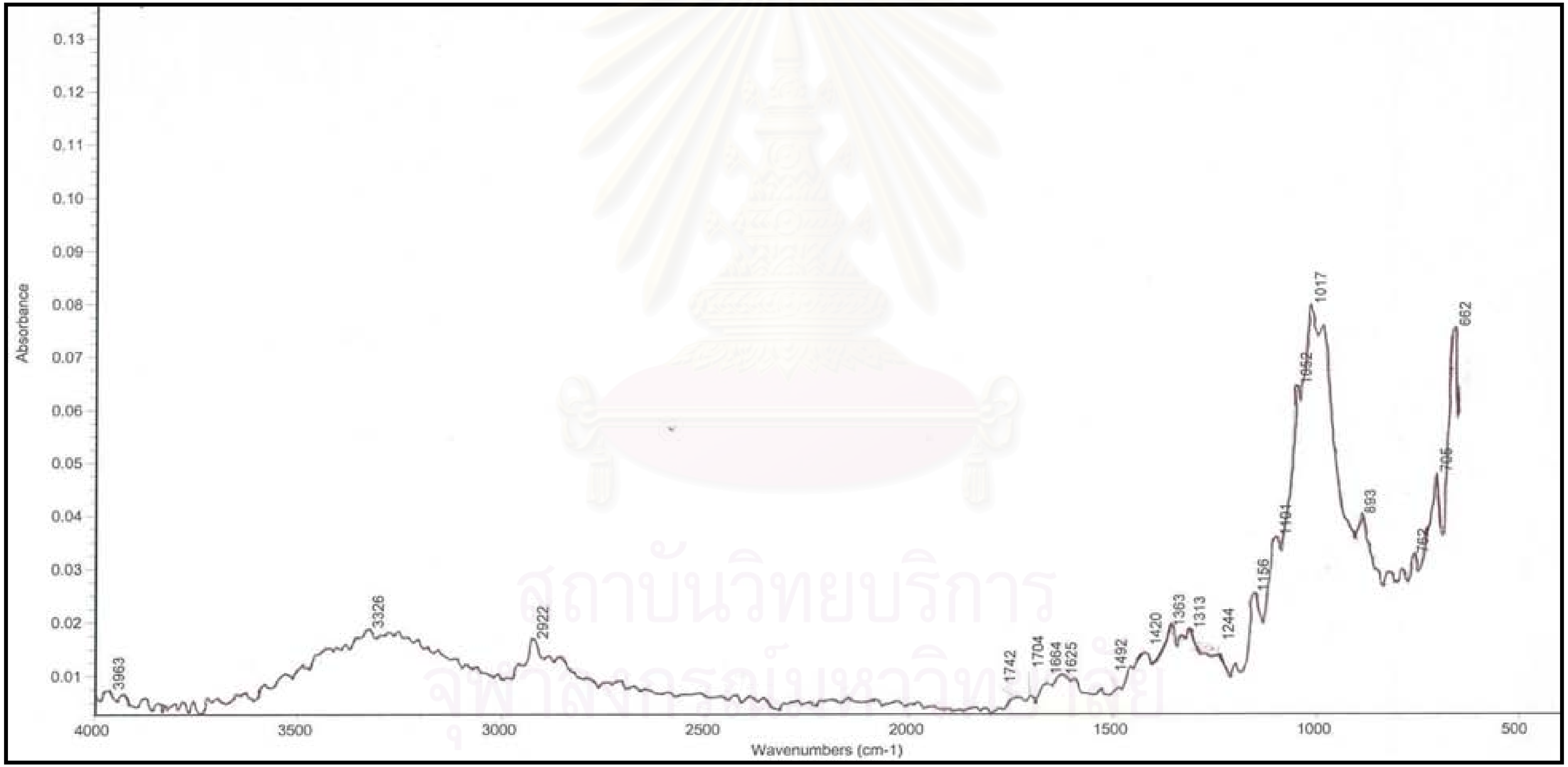
7. ATR-FTIR Spectra of argon plasma-treated PET fabric for 20 shots after 30 days



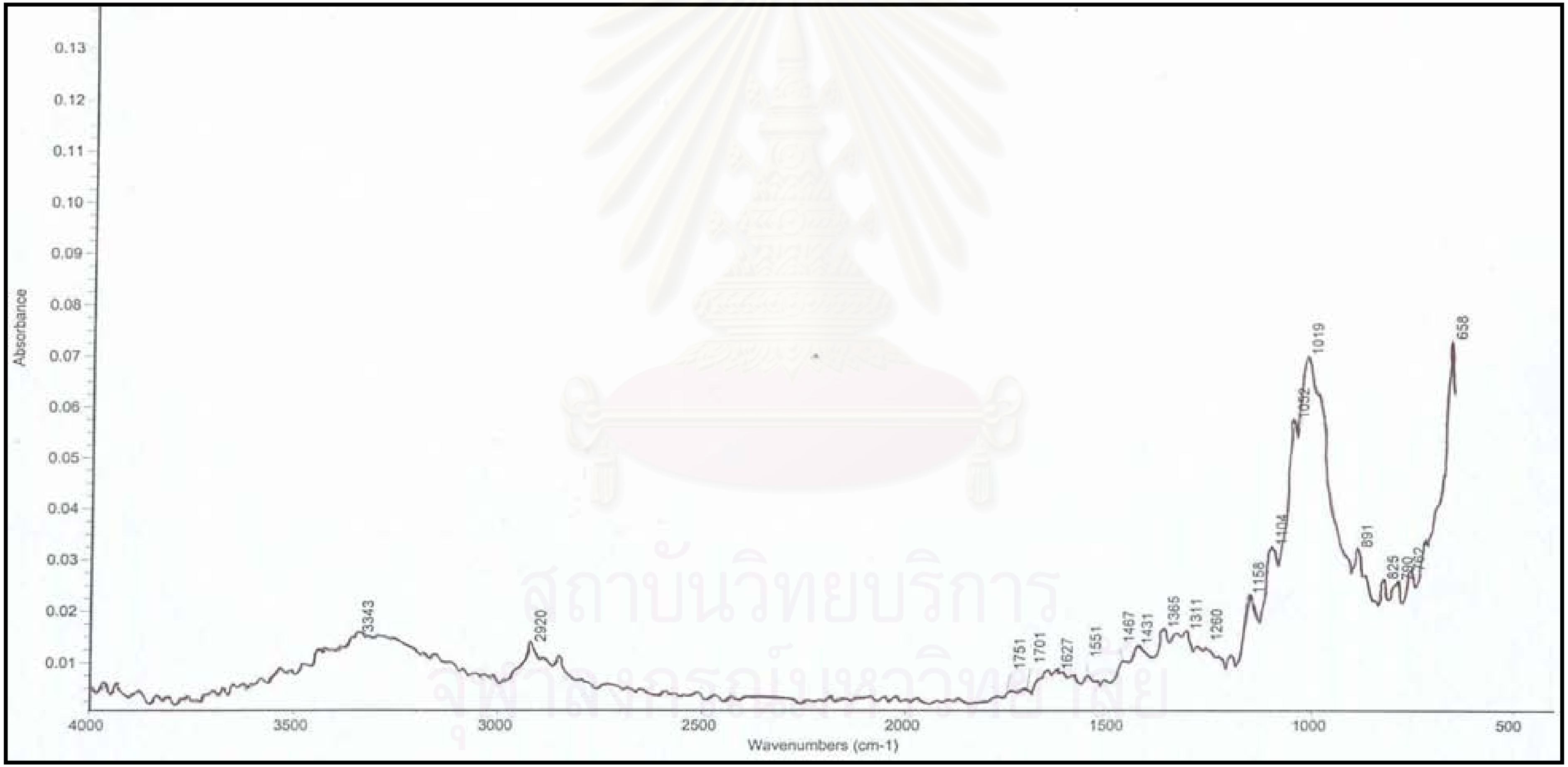
8. <u>ATR-FTIR Spectra of untreated cotton fabric</u>



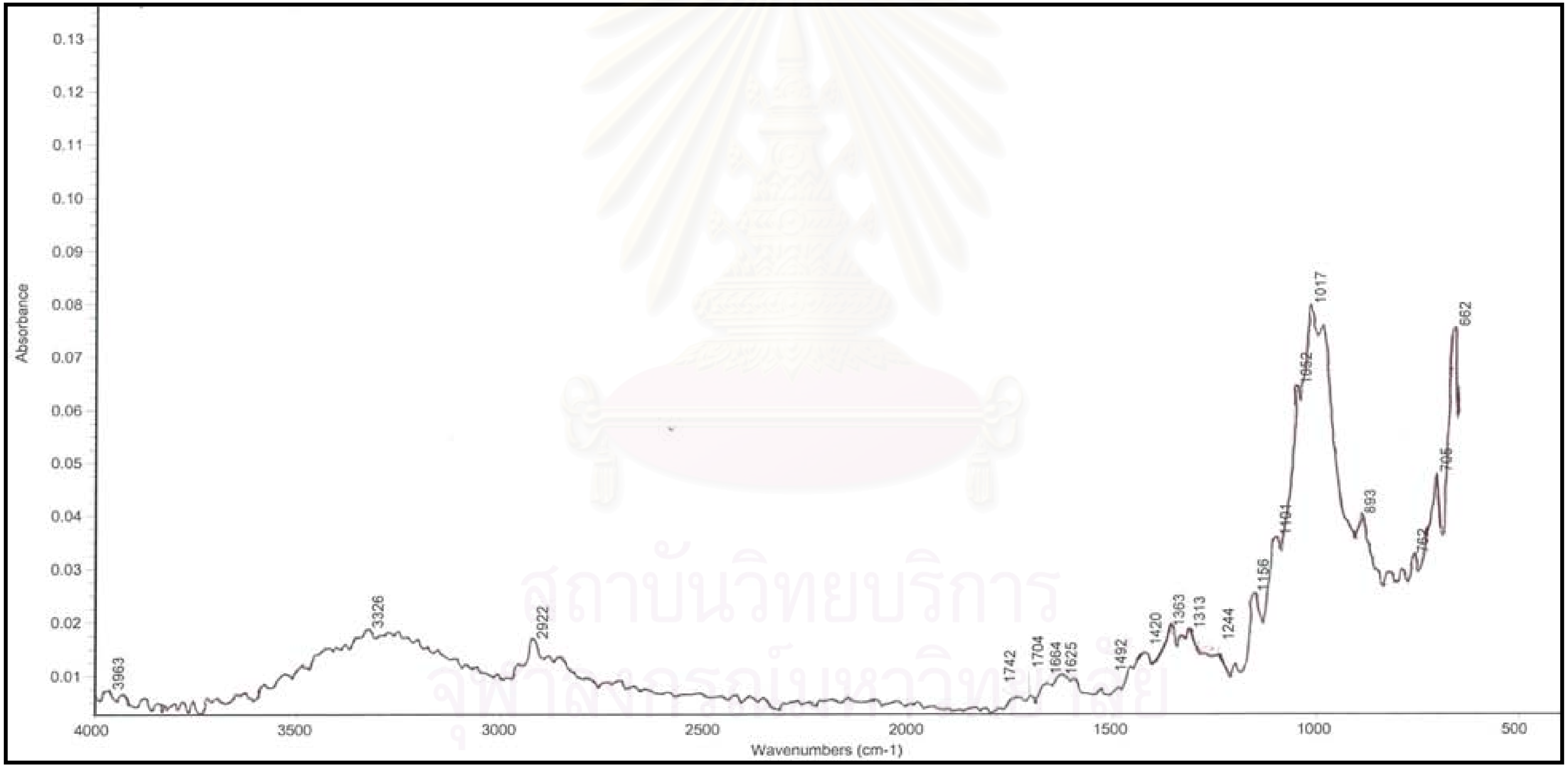
9. ATR-FTIR Spectra of air plasma-treated cotton fabric for 20 shots



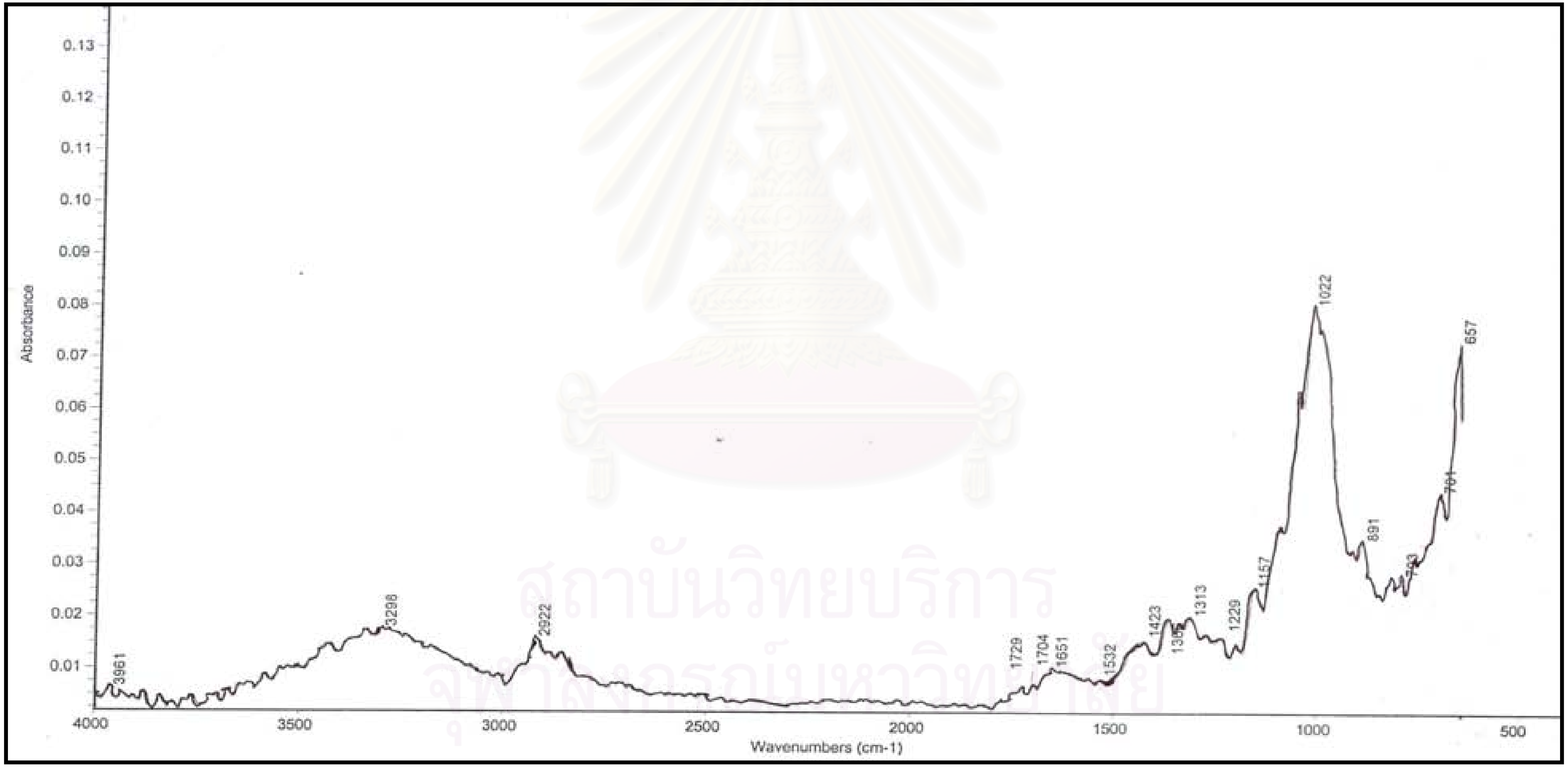
10. ATR-FTIR Spectra of argon plasma-treated cotton fabric for 20 shots



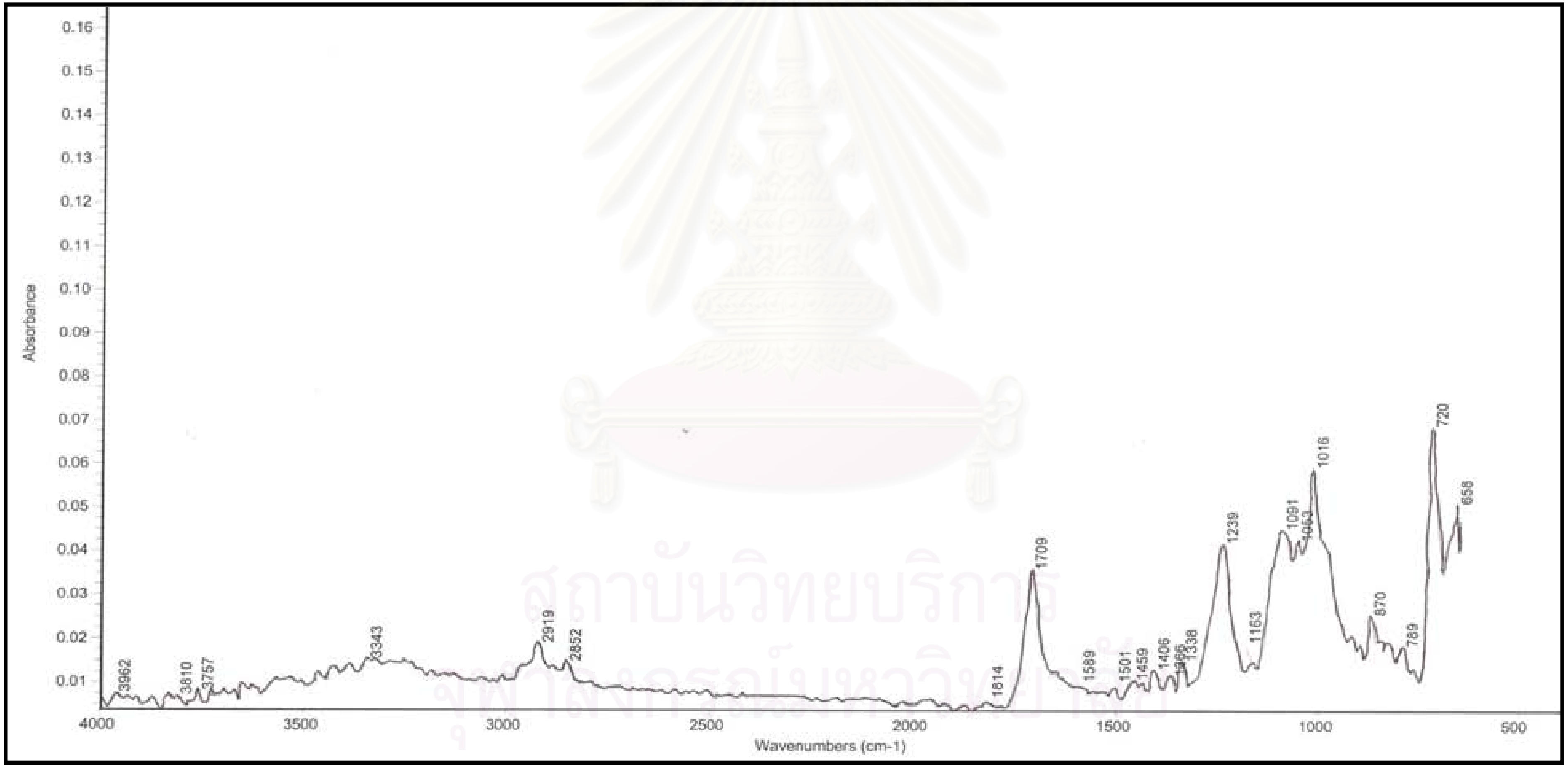
11. <u>ATR-FTIR Spectra of air plasma-treated cotton fabric for 20 shots for 30 days</u>



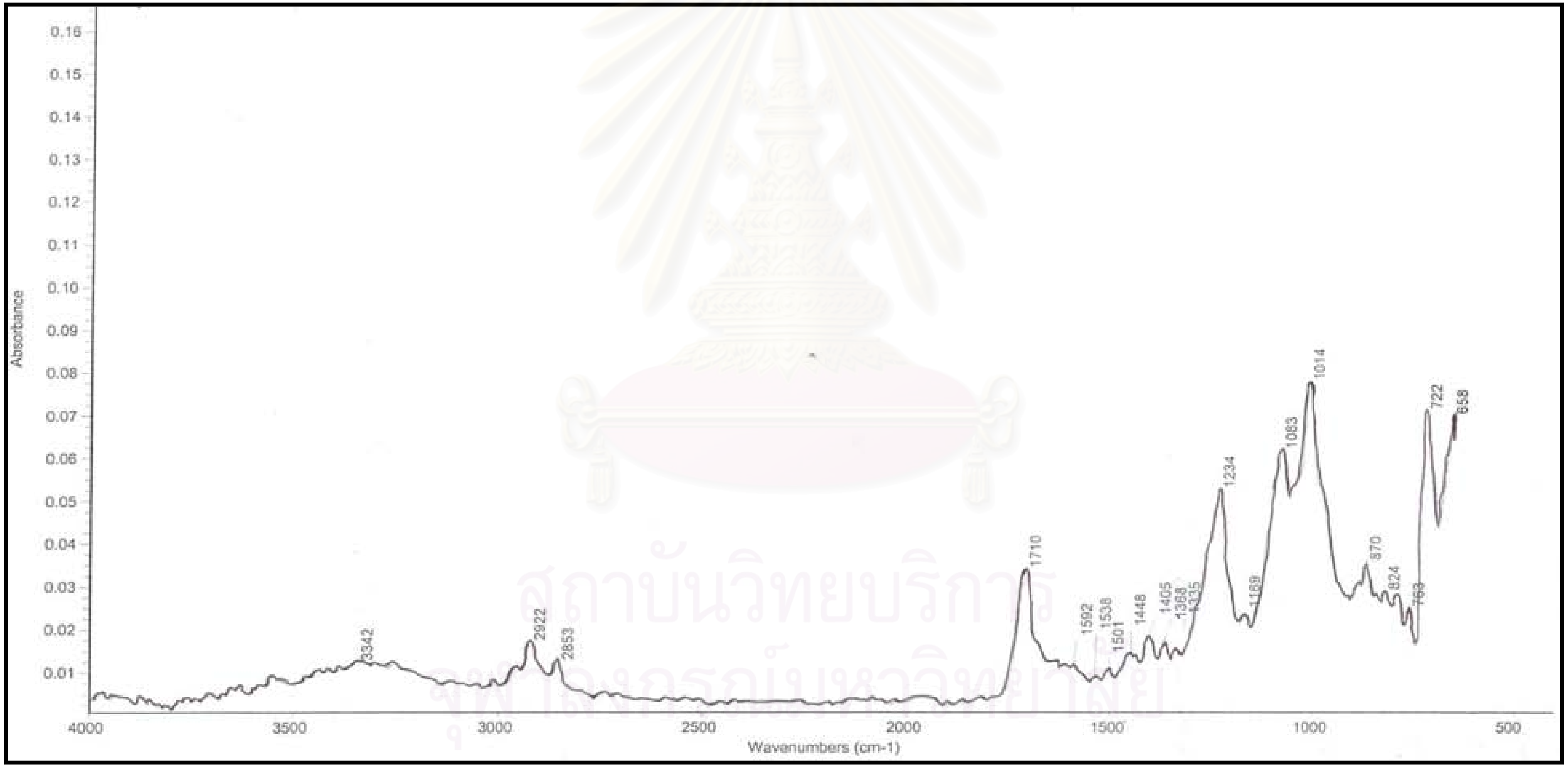
12. <u>ATR-FTIR Spectra of argon plasma-treated cotton fabric for 20 shots for 30 days</u>



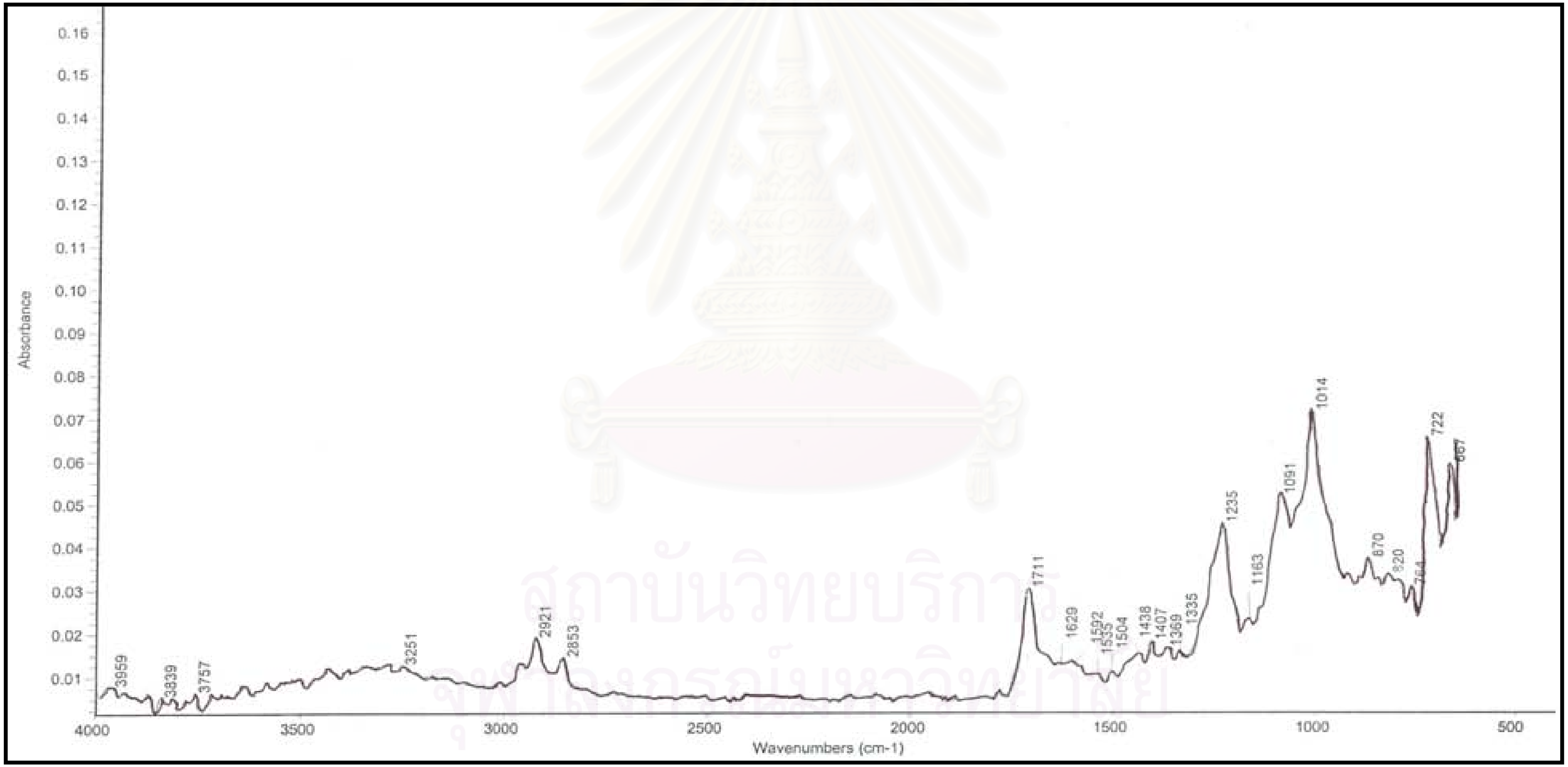
13. <u>ATR-FTIR Spectra of untreated polyester/cotton blended fabric</u>



14. ATR-FTIR Spectra of air plasma-treated polyester/cotton blended fabric for 20 shots



15. ATR-FTIR Spectra of argon plasma-treated polyester/cotton blended fabric for 20 shots



# VITA

Miss Chiraphorn Waipeeta was born on July 31, 1984 in Bangkok, Thailand as a daughter of Somboon Waipeeta and Somchit Waipeeta. She graduated from Rattanakosinsomphoch Ladkrabang School in March 2002 and received a Bachelor of Science degree with a major in Industrial Chemistry from King's Mongkut Institute of Technology Ladkrabang in March 2006. Pursuing her interests in textiles, she continued her education at Chulalongkorn University to achieve a Master of Science degree in Applied Polymer Science and Textile Technology in May 2006.