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SURFACE MODIFICATION OF SYNTHETIC AND NATURAL-FIBER FABRICS USING A THETA- PINCH DEVICE

Miss Parnnapa Khaymapanya

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By	Miss Parnnapa Khaymapanya
Field of study	Applied Polymer Science and Textile Technology
Thesis Advisor	Associate Professor Vimolvan Pimpan, Ph.D.
Thesis Co-advisor	Assistant Professor Rattachat Mongkolnavin, Ph.D.

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

.... Dean of Faculty of Science

(Professor Piamsak Menasveta, Ph.D.)

THESIS COMMITTEE

.... Chairman

(Associate Professor Saowaroj Chuayjuljit)

.... Thesis Advisor

(Associate Professor Vimolvan Pimpan, Ph.D.)

.... Thesis Co-advisor

(Assistant Professor Rattachat Mongkolnavin, Ph.D.)

.... Member

(Associate Professor Paiparn Santisuk)

.... Member

(Assistant Professor Usa Sangwatanaroj, Ph.D.)

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งานวิจัยนี้ เป็นการดัดแปรผิวผ้าพอลิเอสเทอร์ ไนลอน ไหม และ ฝ้าย ด้วยพลาสมาออกซิเจนและไนโตรเจนที่กำเนิดจากเครื่องทีตาพินช์ โดยใช้จำนวนครั้งของการยิงพลาสมาเท่ากับ 20 และ 40 ครั้ง ภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงให้เห็นถึงความขรุขระของผิวผ้า ซึ่งเป็นผลจากการเฉือนของพลาสมา ผลจากการวัดเวลาที่ทำให้เปียกบ่งชี้ถึงสมบัติความชอบน้ำที่เพิ่มขึ้นของผิวผ้าเมื่อจำนวนครั้งของการยิงพลาสมาเพิ่มขึ้น อันเนื่องมาจากการเกิดหมู่ฟังก์ชันที่ชอบน้ำบริเวณผิวผ้าซึ่งสามารถยืนยันได้จากเอทีอาร์ฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรสโกปี อย่างไรก็ตาม การดัดแปรผิวผ้าด้วยพลาสมานี้ไม่เปลี่ยนแปลงคุณลักษณะการเผาไหม้ของผ้า เมื่อนำผ้าไปย้อมสีด้วยสีย้อมที่เลือกใช้ พบว่าการดัดแปรผิวผ้าไหมและฝ้ายซึ่งเป็นผ้าที่มีความชอบน้ำสูงอยู่แล้วด้วยพลาสมาออกซิเจนและไนโตรเจน ไม่ส่งผลต่อสมบัติการย้อมสีและความคงทนของสีต่อการซักของผ้าดังกล่าว อย่างไรก็ตาม ชนิดแก๊สและจำนวนครั้งของการยิงพลาสมา ส่งผลอย่างมากต่อสมบัติทั้งสองนี้ของผ้าพอลิเอสเทอร์และไนลอน 6 โดยภาวะที่เหมาะสมต่อการดัดแปรผิวผ้าพอลิเอสเทอร์และไนลอน 6 ได้แก่ การดัดแปรด้วยไนโตรเจนพลาสมาที่จำนวนครั้งของการยิงพลาสมาเท่ากับ 20 และ 40 ครั้ง ตามลำดับ

ภาควิชาวัสดุศาสตร์ ลายมือชื่อนิสิต พรรณนภา เขมะปัญญา
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ลายมือชื่ออาจารย์ที่ปรึกษา วิมลวรรณ พิมพ์พันธุ์
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PARNNAPA KHAYMAPANYA : SURFACE MODIFICATION OF SYNTHETIC AND NATURAL-FIBER FABRICS USING A THETA-PINCH DEVICE. THESIS ADVISOR : ASSOC. PROF. VIMOLVAN PIMPAN, Ph.D., THESIS COADVISOR : ASST. PROF. RATTACHAT MONGKOLNAVIN, Ph.D., [PAGES] 161. ISBN 974-14-2070-6.

In this research, polyester, nylon, silk and cotton fabrics were surface-modified by 20 and 40 shots of plasma oxygen and nitrogen plasmas generated from a theta-pinch device. 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 ATR-FTIR spectroscopy. However, burning characteristics of all plasma-treated fabrics were unchanged after exposing to the plasma. After dyeing with selected dyes, it was found that oxygen and nitrogen plasma treatments did not affected dyeing properties and colorfastness to washing of highly hydrophilic silk and cotton fabrics. However, the gas type and the number of plasma shots significantly affected these two properties of PET and nylon 6 fabrics. In order to improve these properties, optimum conditions for surface modification of PET and nylon 6 fabrics were achieved when 20 shots and 40 shots of nitrogen plasma were applied, respectively.

Department Materials Science — Student's signature Parnnapa Khaymapanya

Field of study Applied Polymer science and Textile Technology — Advisor's Vimolvan Pimpan

Academic year 2005 — Co-advisor's signature........

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CHAPTER I

INTRODUCTION

Polymers have been applied successfully in fields, for example, coatings, biomaterials, composites and textiles as a consequence of excellent bulk physical and chemical properties. Furthermore, they are inexpensive and easy to process. However, polymers in some cases, do not possess the surface properties needed for some applications. Such properties include, hydrophilicity, roughness, and conductivity. For these reasons, polymer surface modification techniques, that can transform these inexpensive materials into valuable finished product, will become more important in the future as material cost becomes a substantial factor in determining the success of an industry. In recent years, many surface treatment techniques developed to alter the chemical and physical properties of polymer surfaces. These treatments have been employed to achieve many purposes which are, to produce specific functional groups on the surface for specific interactions with other functional groups, to increase surface energy, increase hydrophobicity or hydrophilicity, and modify surface morphology [1].

Surface modification of textile materials have been utilized to provide desired single or multi-characteristics for various applications [2]. A wide spectrum of surface modification techniques of textile materials is available, which can be classified into four groups: coating, chemical treatment, graft copolymerization, and plasma treatment. Textile surface can be modified by coating, which give a thin and uniform additive layer in the finishing stage. This technique requires a few amount of additives; however, often causes problem in fastness. Graft copolymerization give a good fastness. However, it may affect bulk properties and require much complicated steps because it involves a wet process [3-4]. Textile surfaces can also be chemically modified by chemicals which convert smooth hydrophobic polymer surfaces to rough hydrophilic surfaces by dissolution of amorphous regions and surface oxidations. Chemical treatment tends to degrade the polymer mechanical properties and is hazardous to environment [1]. The concern in textile industry over the reduction of water consumption and waste-water treatment in all areas of fiber, yarn, and fabric preparations has led to a continuous search for new non-aqueous treatments; that is, the plasma treatment of textile materials [5].

Plasma treatment of textile materials has emerged as a major possibility for replacing many current wet chemical processes. Plasma can be defined as gaseous state of matter that consists of a dynamic mix of ions, electrons, free radicals, metastable excited species, molecular and polymeric fragments, and large amounts of visible, UV, and IR radiation [6,7]. Decades of development have allowed researchers and scientists to contain and control such matter and to develop applications such as materials processing, waste reduction, and alternative energy sources [8,9]. Plasma modifies the surface of materials through the transfer of energy from the excited plasma particles to the substrate and can effectively achieve modification of near-surface region without affecting desirable bulk properties of the material. Through this method, it is possible to obtain both chemical and physical modification [2,10].

Most researches on plasma treatments of textile materials have been widely investigated using cold plasma systems generated from several devices. However, these devices generate plasma in the form of continuous processes; consequently, the control plasma exposure is probably difficult. Therefore, a new approach using high temperature pulsed-plasma generated from theta-pinch device has been developed for surface modification of textile fibers [11,12]. Since this hot plasma is generated in shots, the plasma exposure can be easily controlled. The basic dynamic process of theta-pinch discharge begins when the capacitor bank is charged and then discharged to a single turn coil by closing a tiggering unit. Because of this, the rapidly increasing axial magnetic field that accompanies the current in the coil induce an electric field; consequently, a plasma current sheath is initiated, which flows opposite to the direction of the discharge current in the coil. The neutral gas is simultaneously ionized by the confliction of the plasma current shealth compressed rapidly toward the tube axis by force. The ions produced are of high energy such that they can be used for modifying material surface [13].

In this research, plasma treatment was conducted by utilizing theta-pinch device for modifying synthetic and natural-fiber fabrics, including polyester, nylon, cotton, and silk fabrics. The effects of hot plasma modification parameters; especially, the gas types and the number of plasma shots on morphology, surface chemical structure, and properties of these fabrics were investigated and compared to those of the untreated ones.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Textile Materials

2.1.1 Industrial Fabrics and Fibers [14-15]

Fibers used in fabrics for garments and other domestic purposes can be classified based on their origins as either *natural* or *man-made*, and summarized in Figure 2.1. The natural fibers are subdivided into those of animal origin, which contain protein, and those of plant origin, which contain cellulose. Examples of *protein-based natural fibers* include wool and silk and examples of *cellulose-based natural fibers* include cotton, linen, and hemp.

Fibers created by man through technology are divided into two basic classifications. Regenerated man-made fibers are made from natural materials that cannot be used for textiles in their original form, but that can be regenerated into usable fibers by chemical treatment and processing. True synthetic man-made fibers are made or "synthesized" completely from chemical substances such as petroleum derivatives.

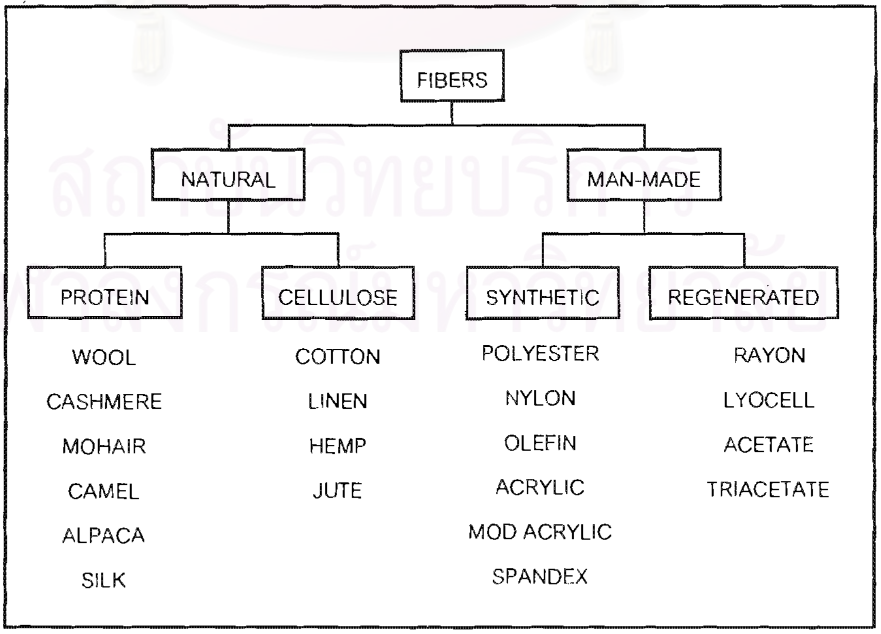


Figure 2.1 Classification of fibers used based on their origin [14].

Fabrics, whether made of natural or man-made fibers, can be classified based on the methods of assembling the fibers into a fabric, as either textiles or nonwovens, as shown in Figure 2.2. Textiles can be woven and knitted. For woven fabrics, two orthogonal layers of parallel fibers are assembled in such a way that the fibers of one set are interlaced alternately above and below the fibers of the second, orthogonal set. In case of knitted fabrics, a single yarn is knotted to itself to form a seamless fabrics.

Nonwovens can be felted, in which a fabric is made of matted, pressed fibers, usually fur or wool. In addition, nonwovens also can be spun-bonded; that is, man-made fibers are pressed together in an overlapping, non-parallel array while still molten so that bonding at the fiber contact points produces a cohesive fabric.

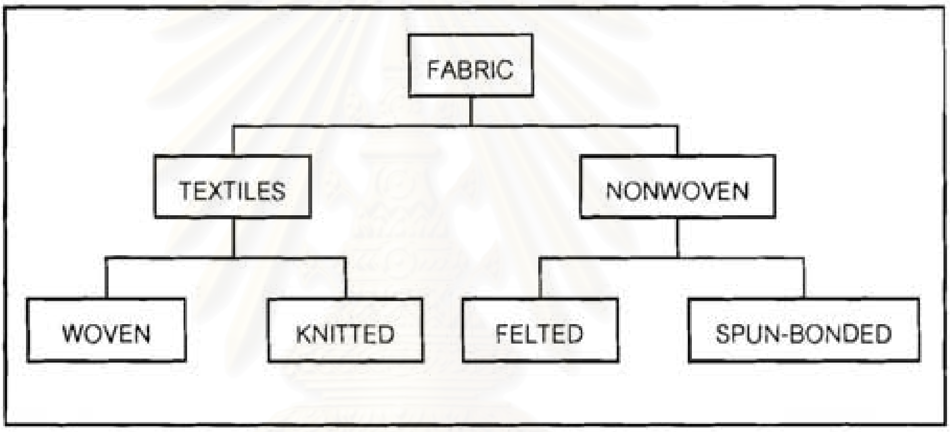


Figure 2.2 Classification of fabrics produced based on the methods of assembling the fibers into a fabric [14].

2.1.1.1 Natural Fabrics and Fibers

2.1.1.1.1 Cotton [15-17]

2.1.1.1.1.1 Molecular Structure

Cotton is the most widely used textile fiber, composing basically of a substance called *cellulose*. Cellulose is the most abundant of all naturally occurring organic polymers. 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 2.3.

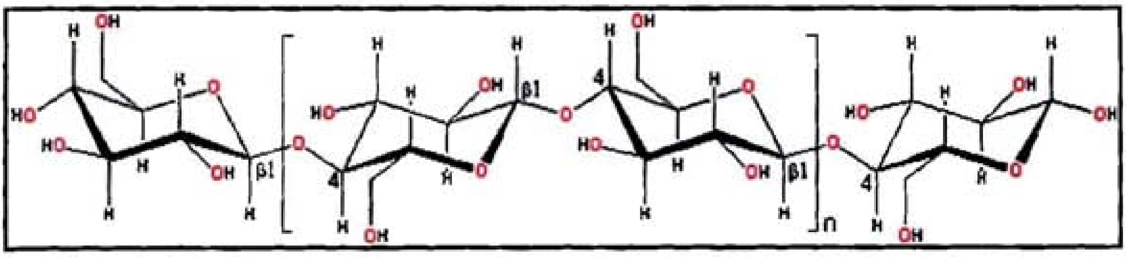


Figure 2.3 Molecular structure of cellulose [18].

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 hydrogens of hydroxyl groups are removed by chemical reaction and other elements or compounds hook to the remaining oxygens.

2.1.1.1.1.2 Microscopic Properties

The diameter of cotton fiber narrows at the tip. The longitudinal view of the fiber shows a ribbon-like shape with twist (convolutions) at irregular intervals. The lumen may appear as a shaded area or as striations; this is more obvious in immature fibers, as illustrated in Figure 2.4.

Figure 2.4 SEM and optical photographs of raw cotton fiber in a cross section (right) and a longitudinal view (left) [16].

2.1.1.1.1.3 Physical Properties

Color Cotton fiber is generally white or yellowish in color.

Shape The length of an individual cotton fiber is usually from 1,000 to 3,000 times its diameter. The diameter may range from 16 to 20 microns. In cross section, the shape of the fiber varies from a U-shape to a nearly circular form.

Luster The luster of cotton is low, unless it has been given special treatments or finishes. This is, in part, a consequence of the natural twist of cotton and its resultant uneven surface that breaks up and scatters light rays reflected.

Strength Strength of a fiber is indicated by the ability to resist being pulled or torn apart when subjected to stress or tension. Cotton has a tenacity of 3.0 to 5.0 grams per denier. This produces a fiber of moderate to above-average strength. In comparison to other cellulosic fibers, cotton is weaker than flax and stronger than rayon.

Cotton is 10 to 20 per cent stronger when wet than dry. 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. The alkali causes the fiber to swell, straighten out, and to become more lustrous and stronger.

Elasticity and Resillience Elasticity refers to the extent in which a fiber can be elongated by stretching and then returning to its former condition of size or length. Like most other cellulosic fibers, the elasticity and elastic recovery of cotton are low. Not only does cotton stretch relatively little but it also does not recover well from stretching. Resilience refers to the extent in which a fabric can be deformed by compression or crushing and return to its original condition.

Density and 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 The ease and extent to which moisture can penetrated into a fiber determines its absorbency. Cotton is an absorbent fiber. Its good absorbency makes cotton comfortable in hot weather, suitable for materials where absorbency is important (such as diapers and towels), and relatively slow to dry, because the absorbed moisture must be evaporated from the fiber. For the same reason, cotton fibers take waterborne dyes readily. The percentage moisture regain of cotton is 7 to 8%.

Dimensional Stability The ability of a fabric to hang easily and fall into graceful shape and folds indicates its drapability. Cotton fibers exhibit neither shrinkage nor stretching in their natural state. Woven or knitted cotton fabrics may shrink in the first few launderings because the laundering releases tensions created during weaving or finishing. The relaxation of these tensions may cause change in the fabric dimensions.

2.1.1.1.1.4 Thermal Properties

Effect of Heat Cotton is not thermoplastic and will not melt. Long exposure to dry heat above 149°C will cause the fiber to decompose gradually, and temperatures greater than 246°C will cause rapid deterioration. Excessively high ironing temperatures cause cotton to scorch or turn yellow. Cotton is combustible. It burns upon exposure to a flame and will continue to burn when the flame has been removed. Burning cotton fabric smells like burning paper, and a fluffy, gray ash residue remains. It is not possible to distinguish cotton from other cellulosic fibers by burning.

2.1.1.1.1.5 Chemical Properties

Effect of Alkalies Cotton is not harmed by alkalies. In fact, they are used in finishing and processing the fiber; for instance, a solution of sodium hydroxide is used to mercerize cotton, making it stronger, smoother, and more lustrous

Effect of Acids Cotton is not damaged by such volatile organic acids as acetic acid. However, it is tendered if such nonvolatile organic acids as oxalic and citric are allowed to remain on it, particularly if heat is also applied. They should therefore be rinsed with cool water as soon as possible. Concentrated cold or diluted hot mineral acids, such as sulfuric acid, will destroy cotton.

Effect of Organic Solvents Cotton is highly resistant to most organic solvents and to all those used in normal care and stain removal. It is, however, soluble in such compounds as cuprammonium hydroxide and cupriethylene diamine, and these are used for chemical analysis of cotton.

Effect of Sunlight, Age, and Miscellaneous Factors Cotton fiber oxidizes, turns yellow and loses strength from exposure to sunlight over a protracted period of time. If properly stored, cotton will retain most of its strength and appearance over a long period of time. It should be stored in dark, dry areas. Ages does not seriously affect cotton fabrics; however, it is important that the fabrics should be stored in clean condition and in dry areas to prevent mildew.

Affinity for Dyes Cotton has a good affinity for dyes. There are water-soluble dyes applied by a one-bath process without the use of mordants (direct dyes), water soluble dyes that form a chemical linkage with the fiber (reactive dyes).

2.1.1.1.1.6 Biological Properties

Resistance to Micro-organisms and Insects Cotton is damaged by fungi such as mildew and bacteria. Mildew will produce a disagreeable odor and will result in rotting and degradation of cotton. Certain bacteria encountered in hot, moist, and dirty conditions will cause the decay of cotton. Therefore, cotton material should be kept in a dry atmosphere. Where this is not possible, a mildew resistant finish or a mildew inhibitor is advisable when stored.

Moths and beetles will not attack or damage cotton. But in fabrics containing cotton and wool, the larvae may damage the cotton to get at the wool. Certain other insects that may be attracted to its cellulose content may damage cotton, but this is not common.

2.1.1.1.2 Silk [15-17]

2.1.1.1.2.1 Molecular Structure

Silk is natural protein fiber. The actual fiber protein is called fibroin, while the protein sericin is the gummy substance that holds the filaments together. Like wool, silk proteins are composed of amino acids, which, by condensation, form a polypeptide chain. Fibroin differs from wool keratin in that no cystine is involved, and hence there are no sulfur or cystine linkages.

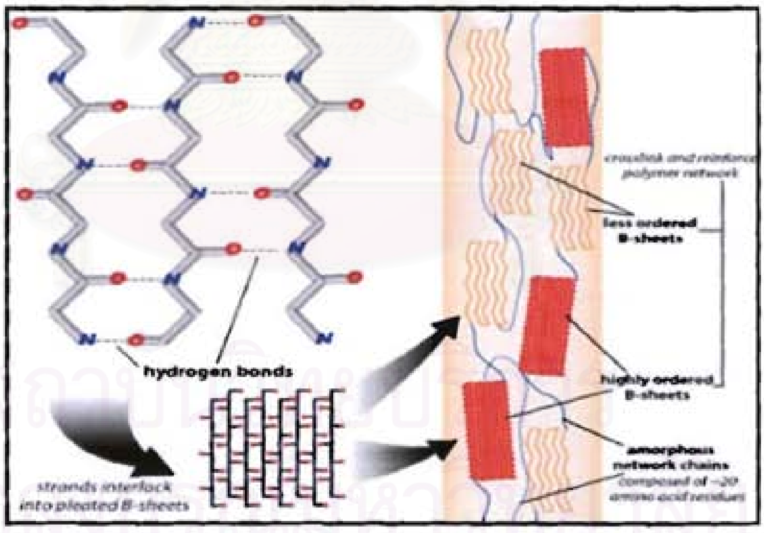


Figure 2.5 Molecular structure of silk [19].

Fibroin is composed of about fifteen amino acids. There is considerable difference of opinion among authorities about the arrangement of the acids; however, most agree that the simple amino acids such as glycine, alanine, serine, and tyrosine make up the largest part of the fiber. An important aspect of silk fiber is its high degree of molecular orientation, which accounts for the excellent strength of silk products.

2.1.1.1.2.2 Microscopic Properties

Cultivated degummed silk, viewed longitudinally under a microscope, resembles a smooth, transparent rod, as shown in Figure 2.6. If gum is still present, fiber surfaces are rough and irregular. Wild silk tends to be uneven and darker. It may have longitudinal striations.

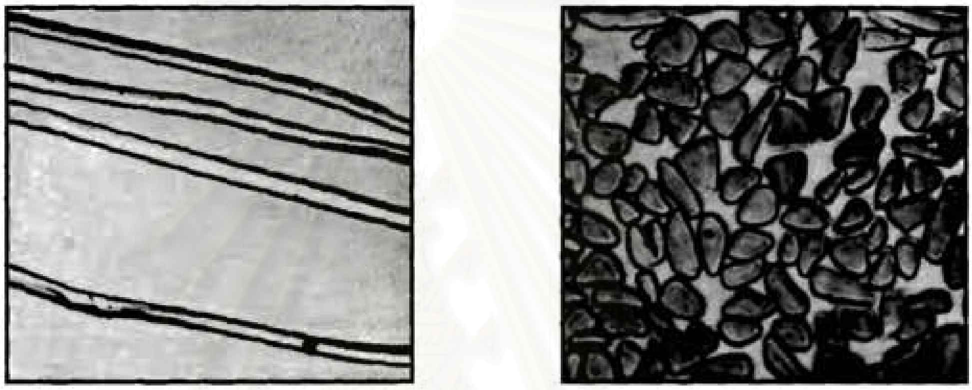


Figure 2.6 Optical photographs of raw silk fiber
in a cross section (right) and a longitudinal view (left) [16].

Cross-sectional views of silk show triangular fibers with no markings. Two filaments usually lie with their flat sides together. This can be explained by the fact that two filaments are extruded simultaneously by each silkworm, and they come together as indicated in Figure 2.6.

2.1.1.1.2.3 Physical Properties

Color The natural color of cultivated silk is off-white, cream or yellow. Wild silk is brown.

Shape In microscopic cross section, silk is triangular in shape. The double silk filaments lie with the flat sides of the triangles together. The fiber has a smooth, transparent rodlike shape with occasional swelling or irregularities along its length. It is fine, having a diameter of nine to eleven microns, and filaments may be as short as 300 meters or as long as 1,000 meters. Individual filaments as long as 3,000 meters have been measured.

Luster Silk filaments have a high natural luster of sheen.

Strength Silk is one of the strongest natural fibers. It has a tenacity of 2.4 to 5.1 grams per denier when dry, and its wet strength is about 80 to 85 percent of the dry.

Elasticity and Resilience Silk has good elasticity and moderate elongation. When it is dry, the elongation varies from 10 to 25 percent; when wet, silk will elongate as much as 33 to 35 percent. At 2%elongation, the fiber has a 92% elastic recovery.

Silk has medium resiliency. Creases will hang out relatively well but not as quickly or completely as in wool.

Density and Specific Gravity The specific gravity of silk of 1.25 is less than that of cellulose fibers and is similar to that of wool. Lightweight fabrics can be made of silk because of the fine diameter of the fiber and its high tenacity.

Absorbency and Moisture Regain Silk has a relatively high standard moisture regain of 11.0%. At saturation the regain is 25 to 35%. The absorption property of silk is helpful in the application of dyes and finishes and making it a comfortable fiber to wear.

Dimensional Stability Silk fabrics have good resistance to stretch or shrinkage when laundered or dry cleaned.

2.1.1.1.2.4 Thermal Properties

Effect of Heat When placed in a direct flame, silk will burn, but when the flame is removed it will not continue to support combustion. Therefore, silk is not considered to be and especially combustible fabric. Like wool, silk is damaged by dry heat and should be ironed damp, at low temperatures and using a press cloth.

2.1.1.1.2.5 Chemical Properties

Effect of Alkalies Silk is damages by strong alkalies and will dissolve in heated caustic soda (NaOH); however, silk reacts more slowly than wool, and frequently the identity of the two fibers can be determined by the speed of solubility in NaOH. Weak alkalies such as soap, borax and ammonia cause little or no damage to silk unless they remain in contact with the fabric for a long time.

Effect of Acids Silk protein can be decomposed by strong mineral acids. Medium concentrations of hydrochloric acid (HCl) will dissolve silk, and moderate concentrations of other mineral acids cause fiber contraction and shrinkage. The molecular arrangement in silk permits rapid absorption of acids but tends to hold the acid molecules so they are difficult to remove.

Effect of Organic Solvents Cleaning solvents and spot-removing agents do not damage silk.

Effect of Sunlight, Age, and Miscellaneous Factors Sunlight tends to accelerate the decomposition of silk. It increases oxidation and results in fiber degradation and destruction.

Silk requires careful handling and adequate protection in storage to withstand the ravages of age. Oxygen in the atmosphere causes a gradual decomposition of silk, and unless it is stored in carefully sealed containers, the fiber will lose strength and eventually be destroyed.

Silk is a poor conductor of electricity, which results in the buildup of static charges. Like other protein fibers, it has a lower thermal or heat conductivity than cellulosic fibers. This factor, coupled with certain methods of construction, creates fabrics that tend to be warmer than comparable fabrics of cellulosic fibers.

2.1.1.1.2.6 Biological Properties

Silk is resistant to attack by mildew and is relatively resistant to other bacteria and fungi. It is decomposed by rot-producing conditions.

2.1.1.2 Synthetic Fabrics and Fibers

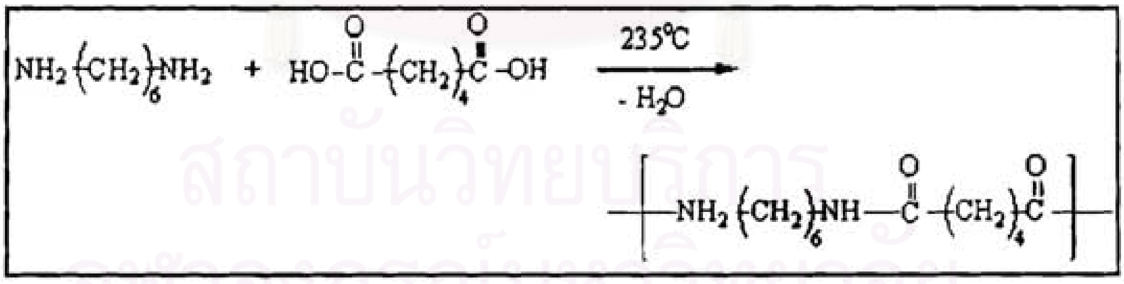
2.1.1.2.1 Nylon [15-17]

Nylons are one of the most common polymers used as a fiber. Nylon is found in clothing all the time, but also in other places, in the form of a thermoplastic. The chemical name for nylon is "Polyamide". The Textile Fiber Products Identification Act defines nylon as a manufactured fiber in which the fiber-forming substance is any long chain synthetic polyamide having recurring amide groups as an integral part of the polymer chain. This definition covers a variety of structures, two main classifications of which are used in the United States: nylon 6 and nylon 6,6.

2.1.1.2.1.1 Nylon 6,6

2.1.1.2.1.1 .1 Molecular Structure

The chemicals from which nylon 6,6 is synthesized are hexamethylene diamine and adipic acid, as illustrated in Figure 2.7. Note that there are six carbon atoms in each molecule of hexamethylene diamine and six carbon atoms in each molecule of adipic acid. For this reason, this nylon was designated as nylon 6,6 (six carbons in each molecule of reacting chemical). In time, it came to be known as nylon 6,6.



$$NH_2 \left(CH_2 \right)_6 NH_2 + HO-\overset{O}{\overset{\|}{C}}-\left(CH_2 \right)_4 \overset{O}{\overset{\|}{C}}-OH \xrightarrow[-\,H_2O]{235°C} \left[NH_2 \left(CH_2 \right)_6 NH-\overset{O}{\overset{\|}{C}}-\left(CH_2 \right)_4 \overset{O}{\overset{\|}{C}} \right]$$

Figure 2.7 The synthesis of nylon 6,6 [20].

2.1.1.2.1.2 Nylon 6

2.1.1.2.1.2 .1 Molecular Structure

Another common nylon is nylon 6 or polycaprolactam. It is special because it's not a condensation polymer, but instead is formed by ring-opening polymerization of caprolactam. In this process, the peptide bond within the caprolactam molecule is broken, with the active groups on each side re-forming two new bonds as the monomer becomes part of the polymer backbone. In this polymer, all amide bonds lie in the same direction, but the properties of nylon 6 are almost indistinguishable from those of nylon 6,6.

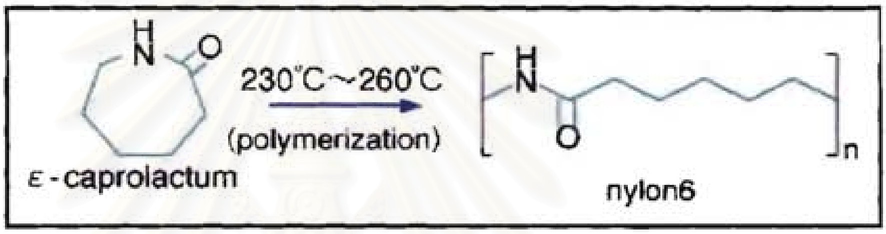


Figure 2.8 The synthesis of nylon 6 [21].

2.1.1.2.1.3 Microscopic Properties of Nylon 6,6 and Nylon 6

Nylon filaments are smooth and shiny. Normal nylon in microscopic appearance looks like a long smooth cylinder. When viewed in cross section, nylon is usually perfectly round. Longitudinal magnification shows relatively transparent fibers of uniform diameter with a slight speckled appearance.

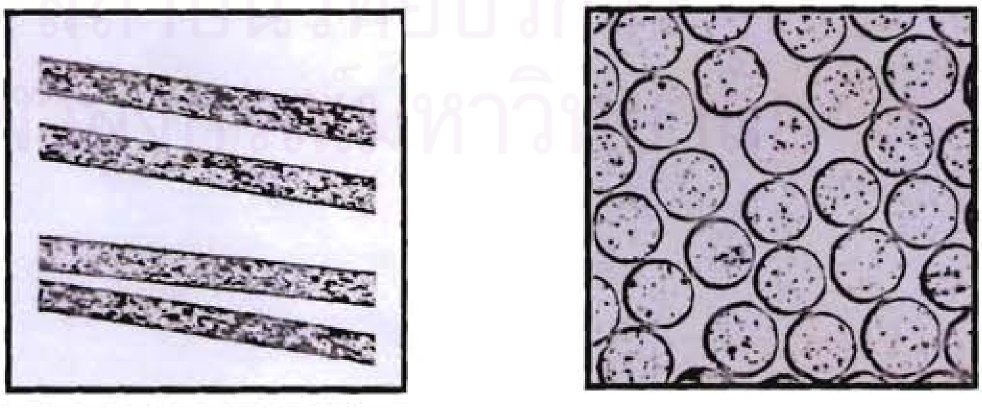


Figure 2.9 Photomicrographs of delustered, regular nylon 6

in a cross section (right) and a longitudinal view (left) [16].

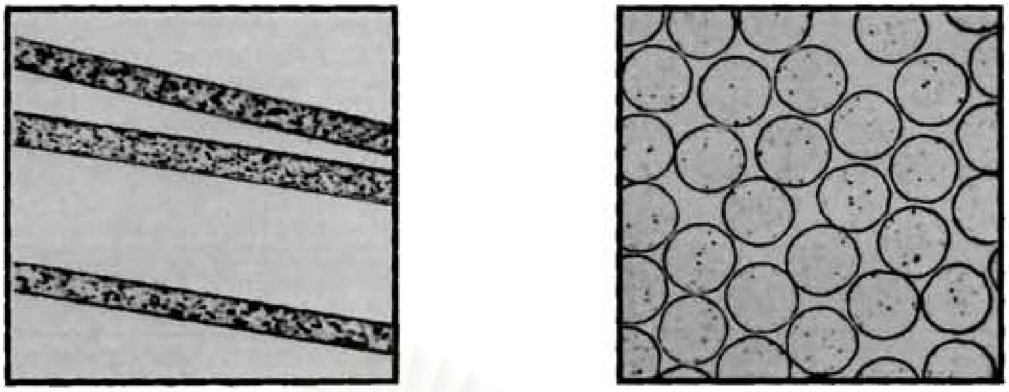


Figure 2.10 Photomicrographs of delustered, regular nylon 6,6 in a cross section (right) and a longitudinal view (left) [16].

2.1.1.2.1.4 Physical Properties of Nylon 6,6 and Nylon 6

Shape and Appearance Nylon is a man-made fiber; therefore the diameter and length of the filaments or staple fibers are determined by the manufacturer and by the ultimate end-use. It is transparent when produced and can be made bright or dull.

Strength One of the major advantages of nylon fibers is their strength. The tenacity or strength of nylon can be excellent. It is produced in a variety of tenacities. Regular-tenacity nylon is rated at 3.0 to 6.0 grams per denier (g/d); high-tenacity nylon is rated 6.0 to 9.5 g/d. Wet nylon retains much of its strength, but wet tenacity may drop to between 4.0 and 5.1g/d and to 7.6 g/d for high-tenacity fiber.

Elasticity and Resilience Contrary to most high-tenacity fibers, the elasticity of nylon is very high. Its resilience is good, although not quite as good as polyester. Nylon is a highly elastic fiber with relatively good elongation. The elastic recovery properties assure excellent shape retention of nylon fabrics. Nylon has good to very good recovery from creasing or wrinkling.

Density and Specific Gravity The specific gravity of nylon is 1.14, which is lower than most other fibers. Nylon can be made into very light, sheer fabrics, of good strength.

Absorbency and Moisture Regain Like many synthetics, nylon is low in absorbency which causes the fiber to resist some dyes. Other dyestuffs that are compatible with nylon have been developed. Nylon fabrics dry quickly after laundering. Compared with natural fibers, nylon has rather low moisture absorbency. Nylon 6,6 has a percentage moisture regain at standard conditions of 4.2 to 4.5; for nylon 6 the range is 3.5 to 5.0. At conditions of 95-percent relative humidity, nylon fibers will absorb approximately 8 percent moisture. Nylon 6 has a slightly higher absorbency than nylon 6,6 so it will accept dyes more easily. The low moisture regain of nylon results in fabrics that dry quickly after laundering. However, low moisture absorption and poor electrical conductivity cause an accumulation of static electric charges on nylon.

Dimensional Stability Nylon has good dimensional stability at low to moderate temperatures, neither shrinking nor stretching out of shape. At high temperatures, nylon fabrics may shrink. Washing and drying temperatures should be kept low.

2.1.1.2.1.5 Thermal Properties of Nylon 6,6 and Nylon 6

Effect of Heat Nylon 6,6 melts at approximately 250°C (480°F) and nylon 6 at 210°C (400°F). All nylon can withstand temperatures to 149°C (300°F) for long periods of time without damage, but when temperatures exceed 149°C (300°F) for a few hours, the fibers will discolor. If temperatures approach 177 to 205°C (350-400°F), the fiber softens, and discoloration and loss of strength occur quickly.

Nylon melts away from a flame and forms a gummy gray or tan ash that hardens as it cools. The fiber will burn if held in an open flame, but it does not support combustion. The smoke is white or grayish in color, and the odor is likened to that of cooking celery or green beans.

2.1.1.2.1.6 Chemical Properties of Nylon 6,6 and Nylon 6

Effect of Alkalines Nylon is substantially inert to alkalines.

Effect of Acids Mineral acids, such as hydrochloric, nitric, and sulfuric, will cause nylon to disintegrate or dissolve almost immediately. Even dilute solutions of hydrochloric acid will destroy the fiber. Organic acids, such as formic, will dissolve nylon in concentrations of 88 to 90 percent. Acid fumes in the air in industrial regions have been known to bring about fiber disintegration.

Effect of Organic Solvents Most organic solvents have little or no effect on nylon. Phenol, metacresol, and formic acid dissolve the fiber, but solvents used in stain removal and dry cleaning do not damage it.

Effect of Sunlight, Age, and Miscellaneous Factors Sunlight has destructive effect upon nylon, and there is marked loss of strength after extended exposure. If nylon is left in direct sun for several weeks, it may actually decompose. Bright nylon has better resistance to sunlight than the deluster one. These are important when the fiber must be subjected to the sun for long periods of time. Age appears to have no effect on the fiber. If stored away from light and other deleterious influences, nylon will last for many years. Soaps, synthetic detergents, and bleaches do not damage nylon fibers.

Affinity for Dyes Nylon 6 has greater affinity for dyes than nylon 6,6 and can be more easily dyed with a wider range of dyes. Both types of nylon retain their color and have good resistance to fading.

2.1.1.2.1.7 Biological Properties of Nylon 6,6 and Nylon 6

Resistance to Microorganisms and Insects Nylon is highly resistant to attack by most insects and microorganism. However, some insects normally found outdoors, including ants, crickets, and roaches, will eat nylon if they are trapped in folds or creases. Microorganism producing mildew may attack finishes used on nylon but do not damage the fiber itself. Bacteria have no effect on nylon.

2.1.1.2.1.8 Main Problems [5]

Nylon is a synthetic fiber and shares its common characteristics. Its chemical structure usually does not allow for it to be dyed easily. Also its wettability is usually poor due to a lack of hydrophilic groups and a negative charge on the surface. Furthermore, nylon has low surface energy resulting in poor adhesion properties, presenting difficulty when bonding, coating, printing, and dyeing.

2.1.1.2.2 Polyester [15-17]

2.1.1.2.2.1 Poly(ethylene terephthalate) (PET)

Poly(ethylene terephthalate) (PET) is the most common fiber-forming polyester. Poly(ethylene terephthalate) constitutes the majority of polyester fibers produced and consumed globally. The International Standard Organization (ISO) defines polyester fibers as those from polymers based on a diol and a terephthalic acid. The Federal Trade Commission (FTC) defines them as those which contain at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted terephthalic units and para-substituted hydroxybenzoate units.

2.1.1.2.2.2 Molecular Structure

The concept for forming the polyesters from diols and diacids was first described by Carothers in 1931 and was developed into a patent on PET by Whinfield and Dickson in 1941. PET is a polycondensation product of ethylene glycol and terephthalic acid (or dimethyl terephthalate).

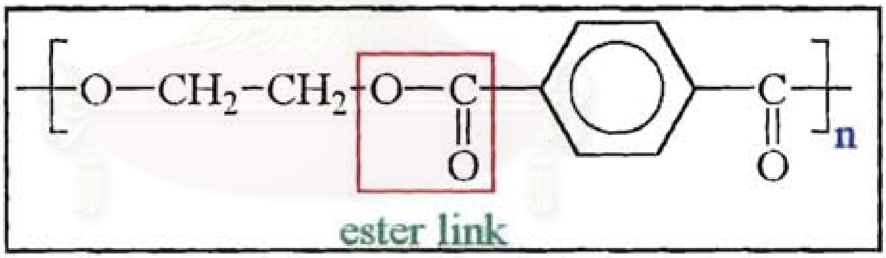


Figure 2.11 The repeating unit of PET [22].

Dimethyl terephthalate is more frequently used than terephtalic acid, because it is easier to obtain in pure form. The resulting polymer is of superior quality. The polycondensation stage of PET production is shown in Figure 2.12. Methanol is a by-product of this reaction.

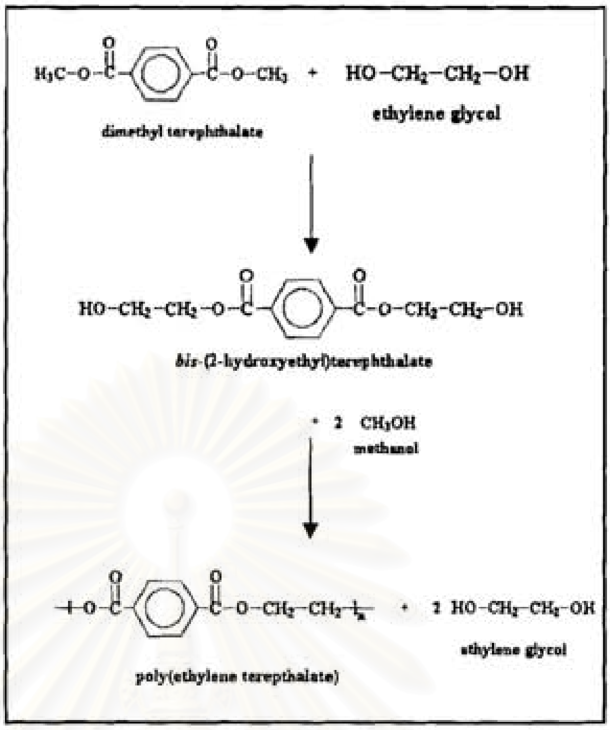


Figure 2.12 The polycondensation stage of PET production [23].

2.1.1.2.2.3 Microscopic Properties

Polyester fibers are manufactured in a variety of cross sections, including round, trilobal, and pentalobal. Under the microscope, round fibers appear as long, smooth rods with spots of pigment. This pigmented appearance decreases the luster or brightness of polyesters. Longitudinally, multilobal fibers appear striated.

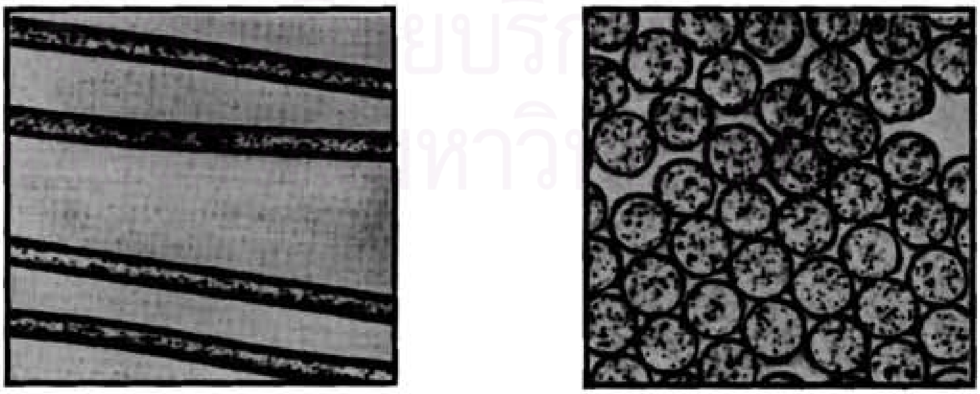


Figure 2.13 Photomicrographs of regular polyester fiber, cross-section (right) and longitudinal view (left) [15].

2.1.1.2.2.4 Physical Properties

Shape and Appearance Except for the multilobal varieties, polyesters 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. Optical brighteners are frequently added to produce clear, bright white polyester fibers.

Strength The strength or tenacity of polyester varies with the type of fiber; however, as a general category, polyester would be considered a relatively strong fiber. Regular filaments have a breaking tenacity of 4 to 6 g/d; high tenacity filaments are rated at 6.3 to 9.5 g/d.

Elasticity and Resilience 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. Polyester fiber has a high degree of resilience. Not only does a polyester fabric resist wrinkling when dry, it also resists wrinkling when wet.

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

Absorbency and Moisture Regain Polyester is one of the least absorbent fibers. Absorbency is quite low for polyester, ranging from 0.4 to 0.8 percent of moisture regain. This low absorbency has two important advantages. Polyester fabrics will dry very rapidly since almost all the moisture will lie on the surface rather than penetrate the yarns. Therefore, they are well suited for water-repellent purposes, such as rainwear. Furthermore, this low absorbency means that polyester fabrics will not stain easily. Fabrics of low absorbency generally have the disadvantage of being clammy and uncomfortable in humid weather because they will not absorb perspiration or atmospheric moisture.

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.

2.1.1.2.2.5 Thermal Properties

Effect of Heat Polyester fibers melt at temperatures from 238 to 290°C (460-554°F) depending upon type. As the fiber melts, it forms a gray or tawny-colored bead that is hard and noncrushable. Polyesters will burn and produce a dark smoke and an aromatic odor. However, they do not burn as rapidly as many other fabrics.

2.1.1.2.2.6 Chemical Properties

Effect of Alkalies At room temperature, polyester has good resistance to weak alkalies and fair resistance to strong alkalies. This resistance is reduced with increasing temperature. At boiling temperature, it has poor resistance to weak alkalies and dissolves in strong alkalies.

Effect of Acids Weak acids, even at the boiling point, have no effect on polyesters unless the fiber is exposed for several days. They have good resistance to strong acids at room temperature. Prolonged exposure to boiling hydrochloric acid destroys the fiber, and 96 percent sulfuric acid cause disintegration.

Effect of Organic Solvents Polyester is generally resistant to organic solvents. Chemicals used in cleaning and stain removal with not damage it, but hot *m*-cresol will destroy the fiber, and certain mixtures of phenol with trichlorophenol or tetrachlorethane will dissolve polyesters. Oxidizing agents and bleaches do not damage polyester fibers.

Effect of Sunlight, Age, and Miscellaneous Factors Polyester exhibits good resistance to sunlight when behind glass, so it is satisfactory for window coverings, but prolonged exposure to sunlight weakens the fiber. Polyester fibers are not affected by aging. One of the most seriously faults with polyester is its oleophilic quality. It adsorbs oily materials easily and holds the oil tenaciously. The fiber resists abrasion very well. Soaps, synthetic detergents, and other laundry aids do not damage it. It can be safely laundered in automatic washers and dried in controlled-temperature dryers. Control of both laundering and drying temperature dryers. Control of both laundering and drying temperatures is essential to prevent the formation of undesirable wrinkles.

Affinity for Dyes Polyester can be dyed with appropriate disperse and developed dyes at high temperatures. The dyeing of polyester fibers and fabrics with disperse dyes is a complex phenomenon and is often a challenge to the dyers, the main reasons for which are its high degree of crystallinity, its hydrophobic nature, the absence of dye sites, very low swelling, low diffusion of the dye molecules, high glass-transition temperature, and the absence of chemically reactive groups in the molecular chain.

2.1.1.2.2.7 Biological Properties

Resistance to Micro-organisms and Insects Insects will not destroy polyesters if there is other food available. However, if trapped, beetles and other insects will cut their way through the fabric as a means of escape. While microorganisms will not harm the fiber, they may attack finishes that have been applied. Usually, any discoloration is easily removed, since it does not penetrated the fiber.

2.1.1.2.2.8 Main Problems [18]

Of all the man-made fibers, polyester fiber is widely used because of its outstanding properties such as high strength, high wear resistance, pleasant appearance, and ease of washing. However, the inherent poor absorbency of polyester, 0.2-0.8%, lowers the comfort factor of skin-contact apparel and upholstery. Low moisture absorption is also associated with the high build-up of static charges that can add to discomfort and cause garments to drape improperly.

2.2 Conventional Modification of Textile Materials

The modification of woven, knitted, and nonwoven 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 [2].

2.2.1 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 [24]. Over-exposure to chemical agents may lead to discoloration, irreversible fiber damage, and deterioration of mechanical properties.

Besides, heat treatments are employed at various stages in the chemical modification process. This not only includes drying, but also the use of high temperatures to activate the chemicals and cure the finish. Wrinkle-resistant and flame-retardant finishes are the examples of the modification employed both chemical processing and heat treatments.

2.2.1.1 Disadvantages of Chemically-Modified Textiles [2]

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.

2.2.2 Physicochemical Processes

Physicochemical techniques have become more commercially attractive and have begun to supercede conventional wet chemical methods for properties modification. These techniques involve the alteration of the fiber/fabric surface by high energy and coating. Fabric coating processes are direct, indirect, or transfer coating which form a composite material consisting of fiber and matrix phases [25]. This technique provides a fabric with a construction that combines the beneficial properties of a textile material with those of a polymer. 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 electical-corona discharge [24]. It is known that the corona discharge is not exactly plasma. It generates electrons and ions via ionization. Electrons, ions, excited neutrals, and photons occured 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 archeived. Generally, surface modification by oxidation reaction can lead to enhanced wettability and adhesion. However, there are many problems occuring with this treatment, including non-uniformity, the creation of "pinholes", and difficulty in property control [26]. The variations in electron and ion energies, and their respective randomization, are the main reasons for non-uniformity of treated surfaces. Pinholes are essentially due to the impact of corona, i.e. small arcs, on the surface causing localized heat and penetration into the surface. Due to corona discharges modification can be generated at atmospheric pressure; therfore, 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 [24]. 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 [26].

UV exposure to polymeric surfaces has been used to promote photon-activated cross-links and fragmentation of coatings [24]. 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 [27]. Like most high-energy sources, UV exposure may result in the deterioration of physical properties and promotes photo-degradation [28].

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 [29]. 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.

2.3 Surface Modification of Textile Materials Using Plasma Treatment

2.3.1 Definition of Plasma

The term "Plasma" was first used by Irving Langmuir in 1926 to describe the inner region of an electrical discharge [30]. Later definition was broadened by Crookes in 1879, to define a gaseous state of matter (the "4th stated of matter) [1,29]. 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. Ions and radical formation results from electron and ion impact [26]. 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 [31]. For many industrial types of plasma, radio frequency (RF) power supplies are used, usually at a standard frequency of 13.56 MHz. Plasma generation 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 appear in man-made devices such as fluorescent lamps, neon tubes, welding arcs and gas lasers [29]. 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 are 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 [5].

2.3.2 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%) [26,31]. Solar coronas and nuclear fusion generated by thermonuclear reaction are the examples of hot plasma [29]. 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 are called cold plasma because the electron temperature is much higher than the gas temperature [1].

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 [29]. However, its generating system involves continuous processes; therefore, the exposure of the material surfaces to the plasma is difficult to control [11,12].

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.

2.3.3 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 2.14.

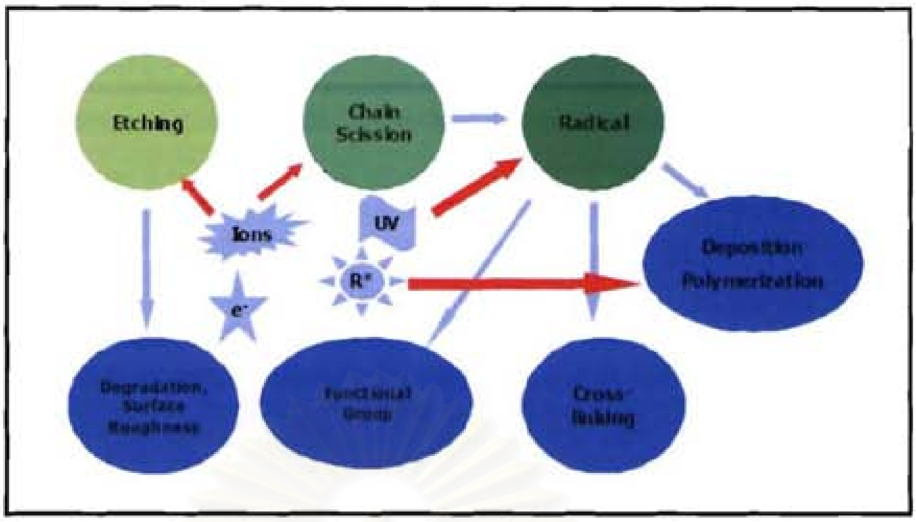


Figure 2.14 Mechanisms of Plasma-Substrate Interaction [29].

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. This phenomena 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 [29].

2.3.3.1 Physical Phenomena in Plasma Surface Modifications

2.3.3.1.1 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 [32].

It is well known that etching process results in surface morphology and micro-roughness, preferring to removing 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 [33].

2.3.3.1.1.1 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.

2.3.3.1.1.2 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 [2].

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 [34]. As a result, the ion bombardment promotes etching by physical sputtering or damage-induced mechanisms versus those of chemical etching [35].

2.3.3.1.2 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 [2].

Poletti, G., et al. [36] 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. [37] 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.

2.3.3.1.3 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 [38]. 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. [39] 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.

2.3.3.2 Chemical Phenomena in Plasma Surface Modifications

2.3.3.2.1 Radical Formation

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) [40]. 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 [2]. 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.

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

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

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

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

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 [41]. After plasma treatment on the substrate, unstable free radicals would recombine rapidly with other active species while stable free radicals remain as living radicals [42].

Wilken, R. and Wakida, T. [42,43] 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.

2.3.3.2.2 Grafting

Plasma grafting, often referred to as plasma graft-copolymerization, can occur through either of the following two mechanisms [45]. One is the creation of active species on the polymer surface, followed by reaction with a monomer as shown in Figure 2.15. 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 [46].

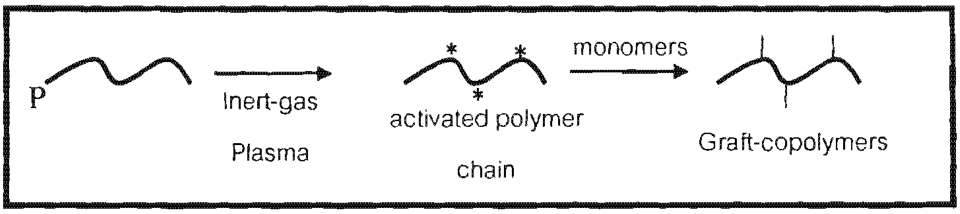


Figure 2.15 The mechanism of plasma grafting
through active species created by plasma [45].

The other is direct grafting of the polymer with common or unconventional monomers under monomer-plasma conditions as illustrated in Figure 2.16. 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 [47].

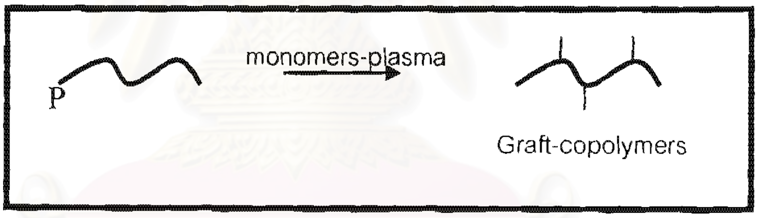


Figure 2.16 The mechanism of plasma grafting
through gaseous monomers in the working gas mixture [46].

Man, W. H., and et al [48] 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 oder 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.

2.3.3.2.3 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 [49]. 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.

2.3.3.2.3.1 Cross-linking Mechanism

When two polymer molecules join to form one large molecular network, cross-linking will be occured. 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 [50]. Figure 2.17 illustrates an increase in cross-linking mechanism for PET.

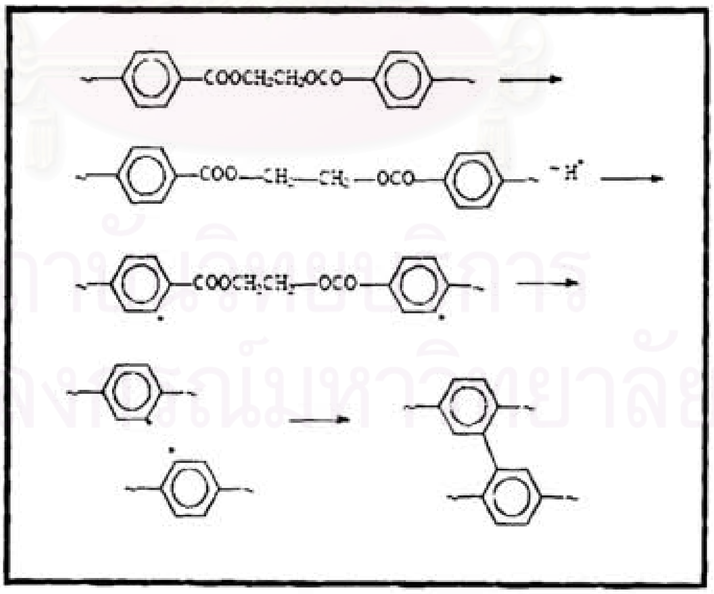


Figure 2.17 Cross-linking by recombination of two aryl radicals obtained by hydrogen abstraction from benzene ring in PET [50].

As shown in Figure 2.15, 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 [50].

2.3.3.2.4 Functionalization on Polymer Surface

2.3.3.2.4.1 Hydrophilic Functionalization

2.3.3.2.4.1.1 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 an 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 [1].

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.

2.3.3.2.4.1.2 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 [1].

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.

2.3.3.2.4.2 Hydrophobic Functionalization

2.3.3.4.2.1 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 a fluorine-containing plasma, including, etching, plasma polymerization, and functionalization can carry out simultaneously. Which reactions predominate will depend on gas feed and operating parameters [1]. 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 result in functionalization, leading to hydrophobicity on the polymer surface.

Chaivan, P., and et al [51] applied SF_6 low temperature plasma to improve hydrophobic property of Thai silk. The treated samples reach the limit of the absorption times at 180 min and increase the contact angle to 130-140°. These results show a significant increase in the hydrophobic property compared with the untreated one.

2.3.3.2.4.3 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 [52-53].

The aging effect of functional groups on plasma treated polymer surface can be reduced at low storage temperature and in oxygen atmosphere [54-55]. The lower storage temperature could lead to slower aging by reduction of the polymer chain mobility [56]. Yasuda, H., et al. [57] 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 2.18.

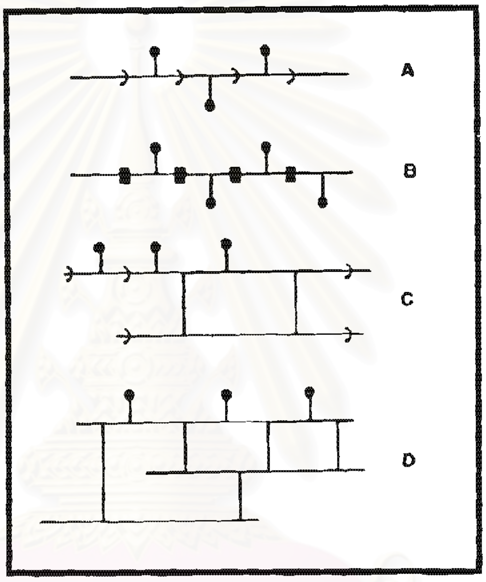


Figure 2.18 Models of molecular mobility on polymer surface by Yasuda [57].

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. [58] 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°C, and others kept in air at room temperature (20-22°C) and an oven at 100°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).

2.3.3.3 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 [24].

Joanne, Y., et al. [59] 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) was 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.

Yasuda, T., et al. [60] studied the effect of plasma treatment on fiber and fabrics using non-polymerizable gases (helium, air, nitrogen and tetrafluoromethane). For most of fibers treated by air plasma, it was found that weight loss increased with an increase of exposure time.

Wong, K., et al. [61] 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.

Negulescu, I., et al. [62] studied the physical property change of PET fabrics treated by $SiCl_4$ plasma. Kwabata Evaluation System (KES) measurement showed that the surface roughness of treated fabrics increased significantly in both filling and warp directions, resulting in a change of the handle properties of PET fabric after plasma treatment. While tensile, bending and compression properties were not changed, shear properties increased significantly because of higher friction and roughness.

In atmospheric pressure plasma, there has been a few study of handling and physical properties of fabric treated. McCord, M., et al. [63] 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.

2.4 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 involve 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 [64].

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 [65].

2.4.1 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 [14].

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.

2.4.1.1 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 [14].

Ricky, K. Y., et al [66]. altered the surface properties of Nylon 6 by modifying the molecular structure using oxygen/nitrogen plasma immersion ion implantation (PIII). The observed improvement in the wettability was due to the oxygenated and nitrogen (amine) functional groups created on the polymer surface by the plasma treatment. X-ray photoelectron spectroscopy (XPS) results showed that nitrogen and oxygen plasma implantation resulted in C-C bond breaking to form the imine and amine groups as well as alcohol and/or carbonyl groups on the surface. The water contact angle results revealed that more polar groups (alcohol > amine > amide) gave rise to better wetting properties.

Carmen Almazan-Almazan, M., et al. [67] 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. [68] 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 was 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.

Poll, H.U., et al. [69] investigated the penetration of oxygen plasma effects into cotton fabric layers put together tightly in order to simulate a total fabric thickness of approximately 1 mm. The hydrophilization was measured on both front and back sides of each fabric layer. With increasing plasma treatment time and pressure, the hydrophilization effects penetrated deeper into the fabric. This might be due to and increasing concentration of oxygen radicals per volume unit.

Wrobel, A. M., et al. [34] 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 droped 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.

2.4.1.2 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 [65,70].

Mccord M.G., et al [71] treated cotton fabrics by radio-frequency induced plasma of tetrafluoromethane (CF_4) and hexafluoropropene (C_3F_6) gases under different exposure times, pressures, and power levels. The hydrophobicity and water repellency were analyzed with measurements of the cosine of the contact angle (cos Θ) and wet-out time. The hydrophobicity was enhanced with treatments of both gases. X-ray photoelectron spectroscopy (XPS) revealed increases in the fluorine content of 1-2% for CF_4 plasma and of 2.3-7.8% for C_3F_6 plasma. The relative chemical composition of the C1s spectra after CF_4 and C_3F_6 plasma treatments showed an increase in the relative amounts of –C-O-C- and fluorocarbon groups, whereas peak areas for –COH and –COOH decreased. The hydrophobicity was enhanced by an increase in the fluorine content and fluorocarbon groups.

Iriyama et al. [72] 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.

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 [48]. 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 [29].

2.4.1.3 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 [14].

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, atmospheric pressure plasma also showed feasibility for dyeing applications.

Antonio R. A., et al. [73] 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.

Some studies, however, showed that plasma treatment did not increase dyeability of cotton. Kubota et al. [74] found that dyeability of reactive and direct dyes on cotton decreased after argon plasma treatment. The reduction of dyeability resulted from the increase of crystalline regions by etching away of dyeable amorphous regions, although water absorption of the cotton fiber increased after plasma treatment because of the capillary effect and hydrophilic group formation on the fiber surface. In addition, cross-linking could play important roles in deteriorating dyeability of cotton fabric [35].

Enzyme treatment and enzyme plus plasma treatment have been shown to increase dyeability of cotton fabrics at higher dyeing rate [75-76]. Enhancement of dyeability for PET fibers by air plasma treatment could be derived from a modification of microstructure on the fiber surface resulting in a disintegration of the diffusion barrier [77].

Okuno, T., et al. [78] 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. [79-81] 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. [82] 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. [83] 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. This increase the interaction with basic dye, resulting in enhancement of dyeability.

Seto, F., et al. [84] and Park, S., et al. [85] 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.

2.4.2 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 a plasma. For adhesion improvement, atomic oxygen appears to be the most important plasma active species [14].

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 [86].

Cueff, R., et al. [87] studied the chemical effects of a reactive plasma treatment on PET surface and investigated the chemical interactions involving at alumina/PET interface. The treatment of PET by carbon dioxide plasma introduces new oxygen reactive species on polymer surface. Evidence of this chemical modification was given by the appearance of additional carbonyl bonds. The interfacial study revealed a reaction of alumina with the oxygne atons of the carbonyl bonds of PET (plasma-induced carbonyl bonds and carbonyl bonds ot the ester groups). This chemical interaction resulted in the formation of Al-O-C interfacial bonds in the early stages of deposition.

2.4.3 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 [14].

Kyung, W.O., et al. [88] investigated the effect of plasma treatment on surface characteristics and electrical conductivity of polyaniline-nylon 6 composites fabrics. Oxygen plasma-treated nylon fabric retained the highest conductivity and polyaniline deposit. The surface of nylon 6 fiber was strongly etched by oxygen plasma treatment, and various functional groups such as COOH and C=O could be produced on nylon 6 surface, which was confirmed by XPS. Oxygen was revealed as the most aggressive and effective plasma gas compared with ammonia and argon plasma in this system. The conductivity of oxygen plasma-treated polyaniline-nylon 6 fabric was more stable with repeated washing and abrasion cycles than polyaniline-nylon 6 fabric without plasma pretreatment.

2.5 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 2.19 Front view (left) and side view (right view)

of theta-pinch device used in this research [11].

This device has been utilized in various applications, for instance, the deposition of thin films, including amorphous carbon film, α-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 [13].

2.5.1 Dynamic Process of Theta-pinch Discharge

Figure 2.20 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 induce 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. Subsuquently, 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 [13].

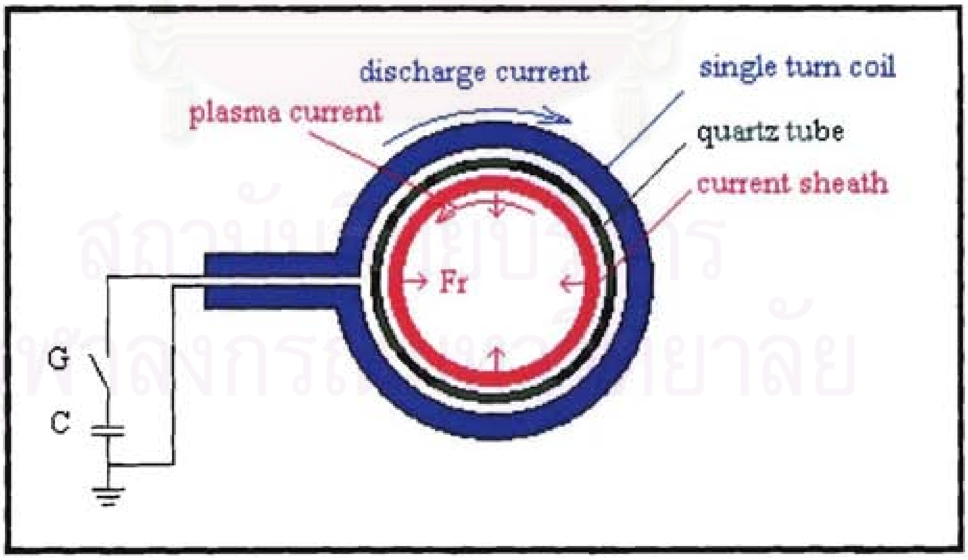


Figure 2.20 Dynamic process of theta-pinch discharge [13].

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 synthetic and natural-fiber fabrics using theta-pinch device.

In 2004, Pimpan, V., Chuenchon, S., Kamsing, P., and Mongkolnavin, R. [11] 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.

Also in 2004, Mongkolnavin, R., Srisawat, J., Ngamrungroj, D., and Pimpan, V. [12] 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.

CHAPTER III

EXPERIMENT

3.1 Scope of The Experiments

In this chapter, the synthetic and natural-fiber fabrics were surface-modified by oxygen or nitrogen 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

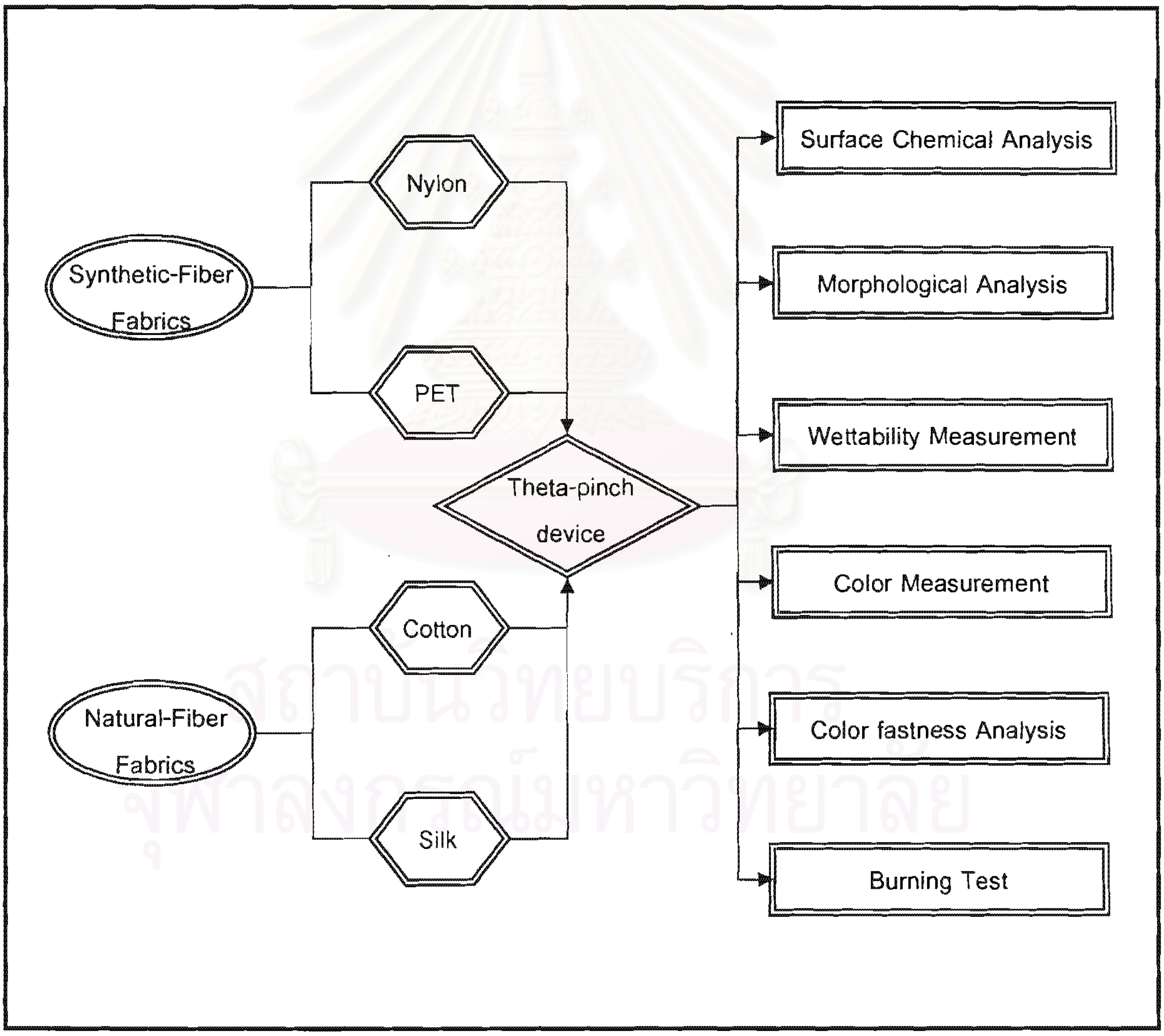


Figure 3.1 The scope of experiment

3.2 Materials

3.2.1 Samples

3.2.1.1 Polyester (PET) woven fabric (plain), supplied by 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 Nylon 6 woven fabric (plain), supplied by THAI TAFFETA Co., Ltd.

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

Density : Warp 110 ends/cm, Weft 80 picks/cm

Weight : 59 g/m^2

3.2.1.3 Bleach cotton knitted fabric (Single Jersey)

Yarn count : 20/1 (body size)

Weight : 1.98 g/m^2

3.2.1.4 Silk fabric, supplied by Jim Thomson Co., Ltd.

Yarn count : Warp organzine silk 3 ply, Weft native 150/200

Weight : 76-80 g/m^2

3.2.2 Dyes

3.1.2.1 Disperse dye, Dianix XF, supplied by Dystar Thai Ltd.

3.1.2.2 Acid dye, Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.

3.1.2.3 Reactive dye, Levafix Navy CA gran, supplied by 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.

Chemicals	Company
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 Laboratory exhausted dyeing machine, Labtec®

3.3.5 Macbeth reflectance spectrophotometer, COLOR-EYE® 7000

3.3.6 Padder mangle, Labtec®

3.3.7 H.T. STEAMERS, Rapid®

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

3.5 Procedure

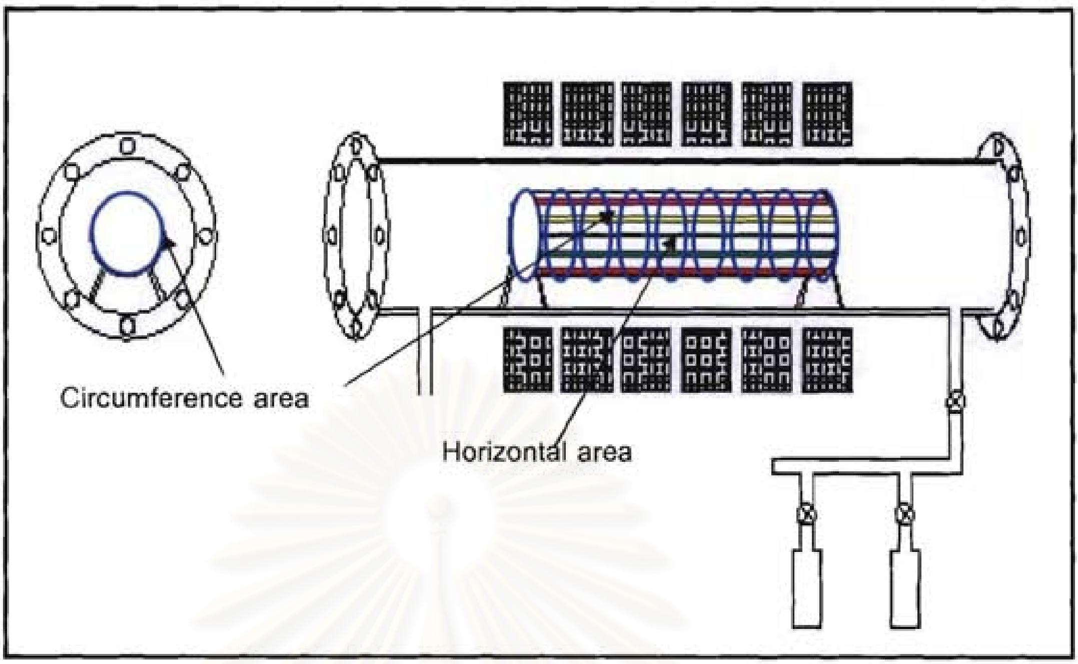
3.5.1 Surface Modification of Fabrics Using Theta-pinch Device

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, nitrogen or oxygen gas was introduced into this chamber. All the treatments were performed using the following conditions shown in Table 3.2

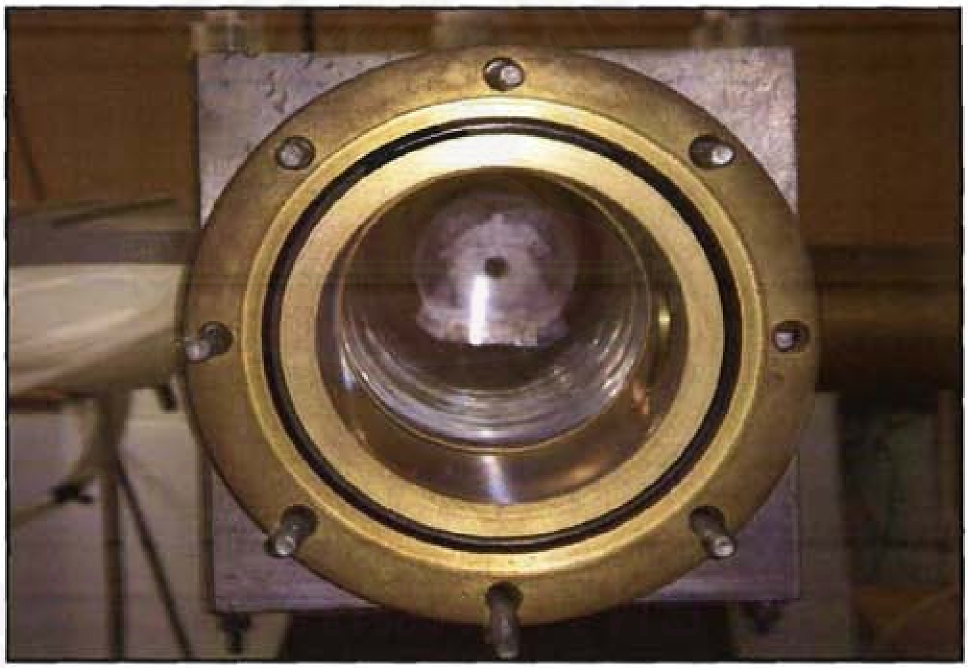
Table 3.2 The operating conditions of theta-pinch device

Operating Conditions of Theta-pinch Device	
Pressure	2 pascal
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	Number of Plasma Shots			
Type of Fabric	Nitrogen		Oxygen	
Polyester	20	40	20	40
Nylon	20	40	20	40
Silk	20	40	20	40
Cotton	20	40	20	40

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 burette 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 nylon, 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

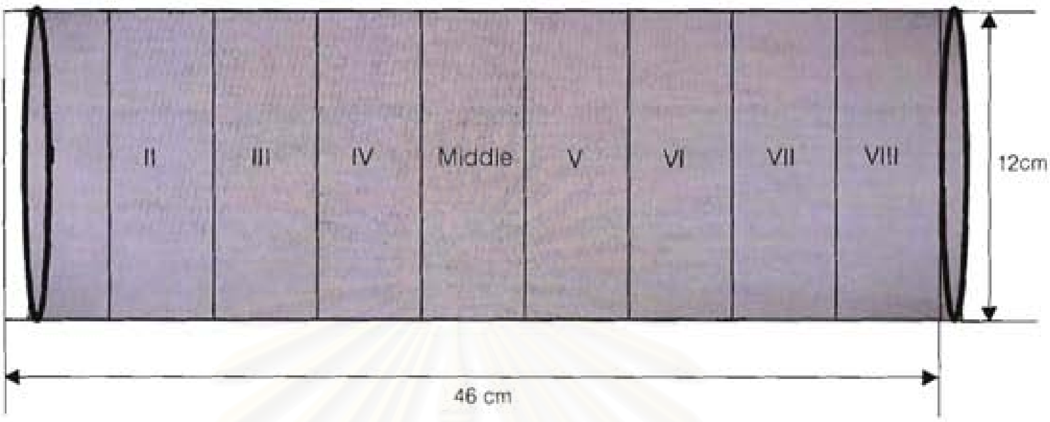


Figure 3.3 Horizontally divided areas of the fabric

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

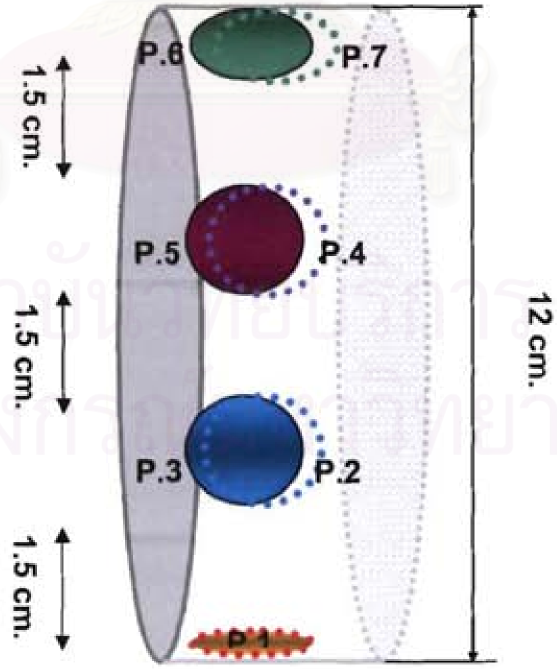


Figure 3.4 Seven areas of each horizontally divided position

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 15 keV or 10 keV acceleration voltages. SEM photographs were taken at different angles of view with magnification of 100X and 2000X.

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 by 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.

Figure 3.6 ATR-FTIR Spectrophotometer

(Thermo Nicolet Nexus 670 spectrophotometer)

3.5.2.4 Burning Test

To investigate the burning characteristics of the fabric samples, burning test was performed according to AATCC 20 standard. A few threads were removed from the sample fabrics and untwisted to form a loose mass. While holding the yarn with tweezers, the fiber mass was slowly brought to the edge of a flame and observed the behavior as the fibers approach the flame. Afterward, the sample was moved into the flame and it was noted whether the sample burnt when held in the flame. Then it was slowly and carefully removed from the flame and it was noted whether the sample continued to burn after removing from the flame. The odor, the color and the nature of any ash residue was examined and noted.

3.5.2.5 Dyeability Testing

3.5.2.5.1 Dyeing of Untreated and Plasma-treated Polyester Fabrics

Each PET fabric was dyed with disperse dye (Dianix Blue XF supplied by Dystar Thai Ltd.), carried out using 1.5 g of fabric. 50 ml of dispersion solutions, containing 20 g/l of the disperse 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, were employed for dyeing PET fabric. Migration inhibitors (2 g/l of Sara Wet C-AS) were required to reduce dye migration during drying.

In this research, thermosol processes were used to dye untreated and plasma-treated PET fabrics. At first, each fabric sample was immersed in dispersion solution described above. After impregnation with dye dispersion, it was taken to a padding mangle for padding with 70% wet-pick up. PET fabric was dried at 110°C for 2 min and then thermofixed for 60 seconds in the region of 210-220°C. Dyed fabric was 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. Medium and heavy depths were reduction cleared for 20 min at 80°C using a water solution containing 5 g/l of NaOH and 2g/l of $Na_2S_2O_4$ followed by soaping with 2g/l of non-ionic detergent at 1:50 liquor ratio and allowing to dry in opened air. The dyeing process used is shown in Figure 3.7.

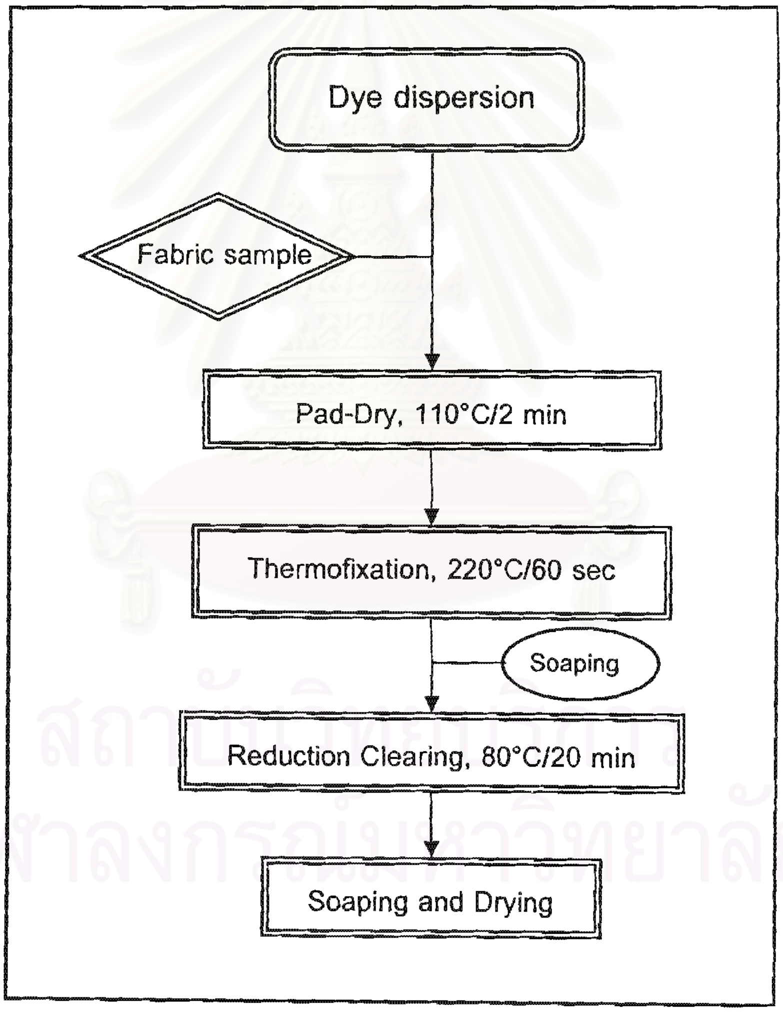


Figure 3.7 Dyeing process of untreated and plasma-treated PET fabrics

3.5.2.5.2 Dyeing of Untreated and Plasma-treated Nylon and Silk Fabrics

In this research, acid dye (Erionyl Blue A-R supplied by CIBA Specialty Chemical Co., Ltd.) was used to dye both untreated and plasma-treated nylon 6 or silk fabrics. Aqueous solution, containing 3% o.w.f. of the dye, 1 g/l of wetting agent and 2% o.w.f. of acetic acid for pH adjustment, and 1:20 liquor ratio (1 g of fabric in 20 ml of dye solution), was employed for dyeing nylon 6 and silk fabrics in sealed stainless steel dyeing tubes of 300 cm^3 capacity housed in a laboratory exhausted dyeing machine (Labtec®) shown in Figure 3.8.

Figure 3.8 Laboratory exhausted dyeing machine, Labtec®

The following dyeing solutions were adopted. Initial temperature was 40°C and held for 10 min, followed by a temperature increase 2°C/min up to 100°C, holding for 45 min at this temperature. After dyeing, the samples were taken out the dyeing tubes. Dyed fabrics were washed with 2g/l of wetting agent at 50°C for 15 min. and repeatedly rinsed in cold distilled water and allowed to dry in opened air. The dyeing process is illustrated in Figure 3.9

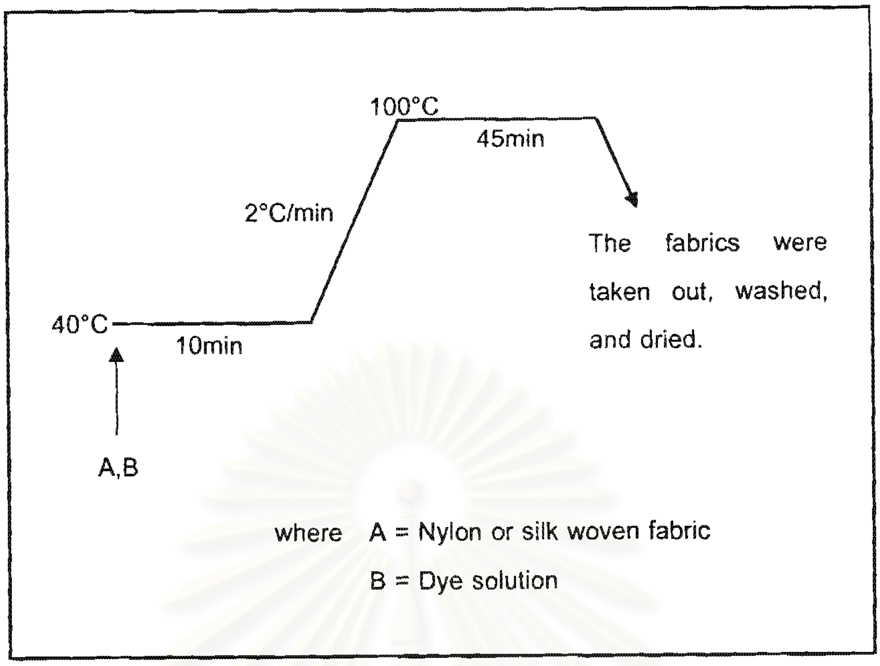


Figure 3.9 Dyeing process of untreated and plasma-treated nylon or silk fabrics

3.5.2.5.3 Dyeing of Untreated and Plasma-treated Cotton Fabrics

Dyeing of cotton fabrics was 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 Glauber's salt (Na_2SO_4) 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 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

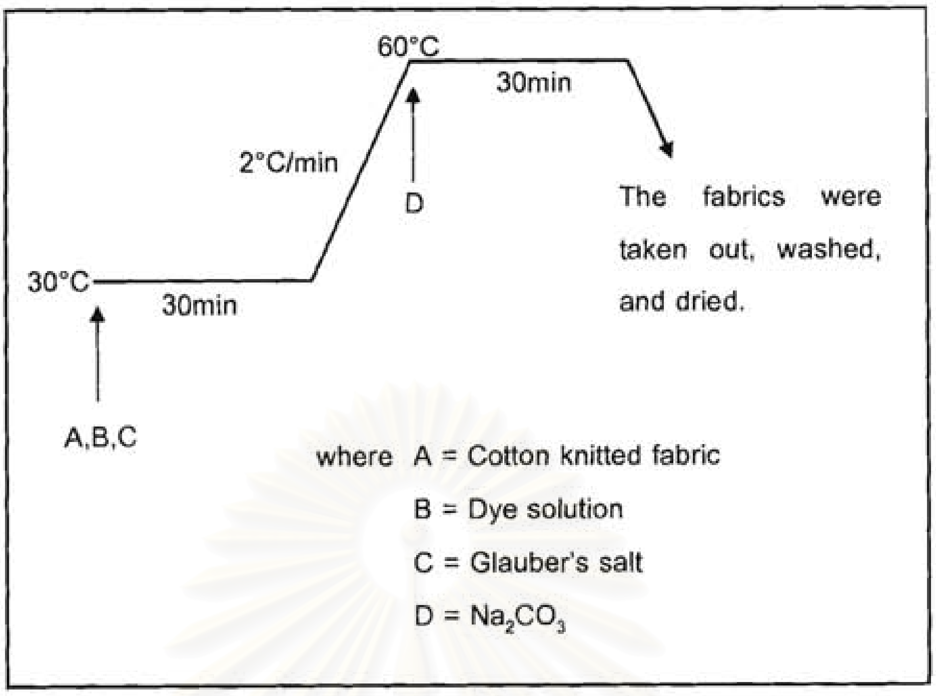


Figure 3.10 Dyeing process of untreated and plasma-treated cotton fabrics

3.5.2.6 Color Measurement

The reflectance values of dyed samples were measured using an Instrument Color System (I.C.S.) Macbeth reflectance spectrophotometer (Figure 3.11) 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.

Figure 3.11 Macbeth reflectance spectrophotometer

Each fabric sample was folded twice leading to a total of four 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 (λ_{max})

3.5.2.7 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

Each fabric sample was folded twice leading to a total of four 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:

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3.5.2.7 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 ΔE, 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 ΔE value between sample 1 and sample 2 can be calculated using following equation:

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

CHAPTER IV

RESULTS AND DISCUSSION

In the present work, surface chemical and morphological modifications induced on synthetic and natural-fiber fabrics by treatment with high temperature pulsed-plasmas of nitrogen and oxygen gases were investigated at different numbers of plasma shots, while other discharge parameters were kept constant in each experiment.

4.1 Properties and Morphology of Synthetic-fiber Fabrics

4.1.1 Properties and Morphology of PET Fabrics

4.1.1.1 Surface Chemical Structure

The attenuated total reflection infrared spectroscopic (ATR-FTIR) studies of untreated and plasma-treated PET fabrics were performed to assess any structural changes, the introduction of any new functional groups, or the alteration of existing groups on the surface of fabrics as a result of plasma modification using theta-pinch device.

Figure 4.1 shows ATR-FTIR spectra of untreated PET fabric (spectrum a), 40 shots of O_2 plasma-treated PET fabric (spectrum b), and 40 shots of N_2 plasma-treated PET fabric (spectrum c). Also, Table 4.1 presents the interpretation of ATR-FTIR spectra of these fabrics.

In case of PET fabric treated with 40 shots of O_2 plasma, the appearances of the peaks at wavenumber of 1041 and 1370 cm^{-1} are observed as shown in Figure 4.1 (b). These peaks correspond to C-O stretching of primary alcohol and bending of methyl ketone or acetate, respectively. Additionally, it is clearly seen that the peak corresponding to C-H in plane bending in substituted aromatic rings and skeleton vibrations involving C-O stretching (1338 cm^{-1}) displays a significant decrease in its intensity. These results suggest that oxygen containing groups, such as ketone and acetate groups were formed on the surface of PET treated with O_2 plasma.

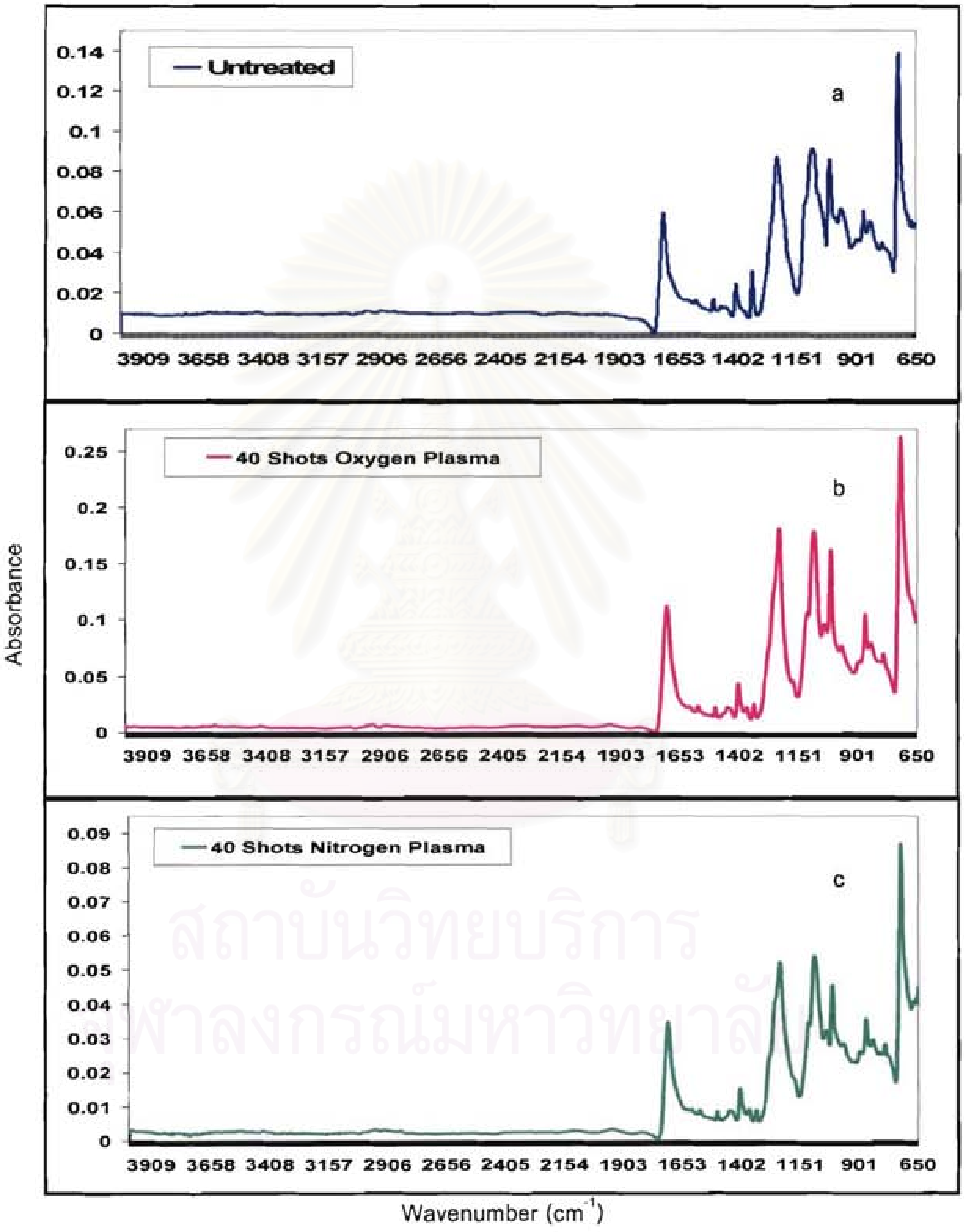

Figure 4.1 ATR-FTIR spectra of untreated PET fabric (a),

PET fabrics treated with 40 shots of O_2 plasma (b) and with 40 shots of N_2 plasma (c)

For PET fabric treated with 40 shots of N_2 plasma, as shown in Figure 4.1 (c), a decrease in intensity of the peak at 1339 cm^{-1}corresponding to C-H in plane bending in substituted aromatic rings and skeleton vibrations involving C-O stretching is also observed. In addition, the peak at intensity of 1370 cm^{-1} assigned to stretching of aromatic nitro group (N-O) is clearly seen as well. Besides, the new peaks at 1040 cm^{-1} attributed to C-N stretching of aliphatic amine group occurs. These results suggest that nitrogen containing groups; especially, nitro and amine group was mainly introduced to the surface of N_2 plasma-treated PET fabric.

It is generally accepted that new chemical functionalization may also occur consequently to the incorporation of polar groups either during the treatment in the case of chemically reactive plasmas and/or immediately after the plasma treatment on exposure to the atmosphere [89].

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

Wavenumber (cm^{-1})			**Interpretation**
Untreated	**O_2Plasma**	**N_2 Plasma**	
3425	3425	3437	Stretching of ethylene glycol end groups
-	-	Region 3400-3300	N-H stretching of amine groups
3072,3043	3072,3043	3072,3043	Aromatic C-H stretching
2962,2907,2868	2962,2907,2868	2960,2907, 2868	C-H stretching of methylene groups

Table 4.1 The interpretation of ATR-FTIR spectra of untreated and plasma-treated PET fabrics (con't)

Wavenumber (cm^{-1})			Interpretation
Untreated	O_2Plasma	N_2 Plasma	
-	-	Region 2105-2300	Different nitrogen functionalities, such as aryl nitriles, isonitriles, and isocyanates
1957,1886	1955,1886	1995,1886	Weak combination bands and overtone bands attributed to aromatic C-H
1713	1708	1711	C=O stretching of the ester carbonyl group
1576,1503	1577 , 1504	1577, 1503	Ring C-...C stretching in plane
1470,1407	1451,1407	1451, 1407	Skeleton vibrations of the conjugated system and related to the p-disubstituted benzene rings
-	1370	1370	bending of methyl ketone or acetate
			stretching of aromatic nitro group
1338 ,1014	1339 (decreased), 1015	1339 (decreased)	C-H in-plane bending in substituted aromatic rings and skeleton vibrations involving C-O stretching
-	1041	1040	C-O stretching of primary alcohol
			C-N stretching of aliphatic amine group
1235,1088	1234,1086	1237, 1091	The ester C-O-C asymmetric and symmetric stretching vibrations

Table 4.1 The interpretation of ATR-FTIR spectra of untreated and plasma-treated PET fabrics (con't)

Wavenumber (cm-1)			**Interpretation**
Untreated	**O_2Plasma**	**N_2 Plasma**	
967,843	970, 846	970, 843	Wagging vibrations corresponding to CH_2- and oxyethylene groups
871,791	870, 792	871, 792	Out of plane C-H of p-substitued aromatic rings
725,699	720, 699	724, 699	Out of plane bending of the two carbonyl substituents on the aromatic ring

4.1.1.2 Morphological Analysis

Surface morphological changes induced by oxygen and nitrogen plasma treatments on PET fabrics were observed by scanning electron microscopy (SEM). Figures 4.2(a)-(c) illustrate SEM images of morphological changes on PET surface treated with oxygen plasma at different number of plasma shots.

As shown in Figure 4.2 (a) the original surface of untreated PET is smooth. When it was exposed to 20 shots of oxygen plasma (Figure 4.2 (b)), its surface was etched, resulting in surface roughness. When 40 shots of oxygen plasma were applied, the breaking of the fiber was observed as seen in Figure 4.2 (c). These results can be attributed to the etching process or ablation effect caused by the bombardment of oxygen plasma reactive species on the fabric surface.

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.

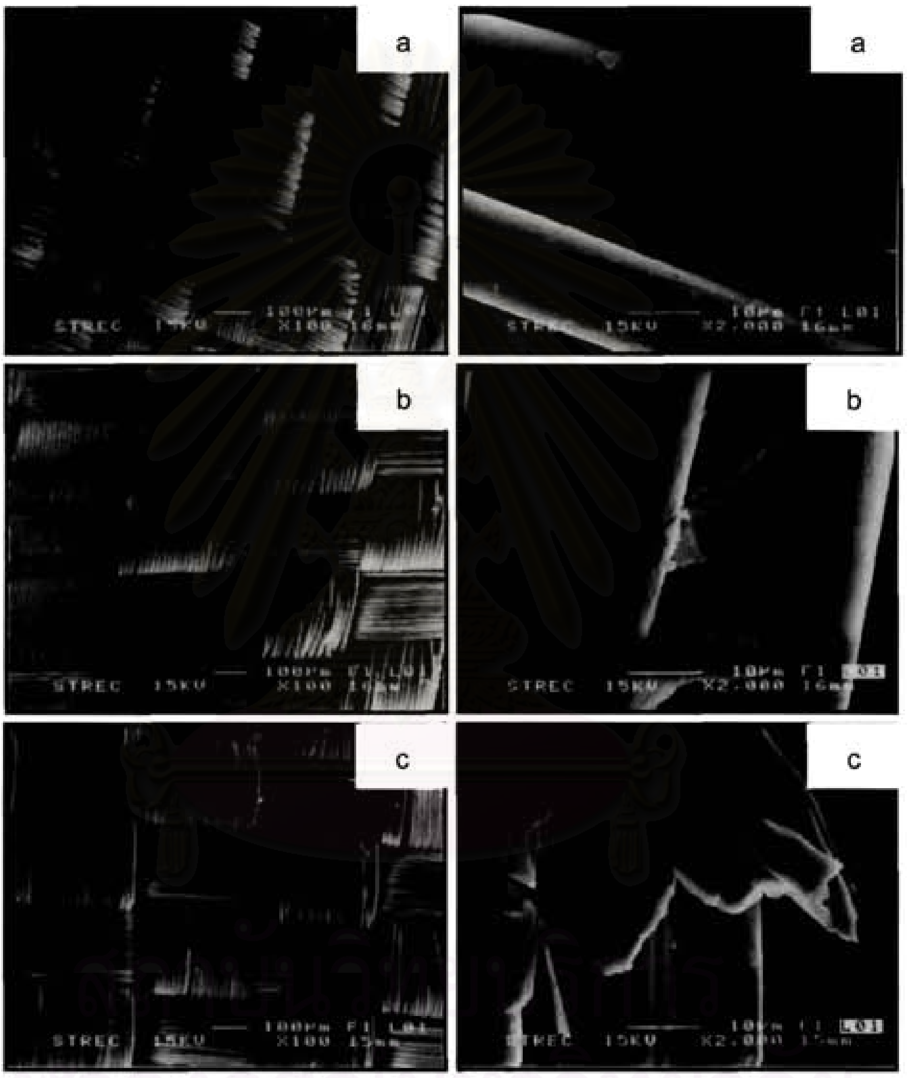

Figure 4.2 SEM photographs at X100 (left) and X2000 (right) of untreated PET fabric (a), PET fabrics treated with 20 (b), and 40 (c) shots of oxygen plasma

It is obviously seen from Figures 4.3 (b) and (c) that nitrogen plasma also caused the changes in surface roughness of PET surface similar to oxygen plasma.

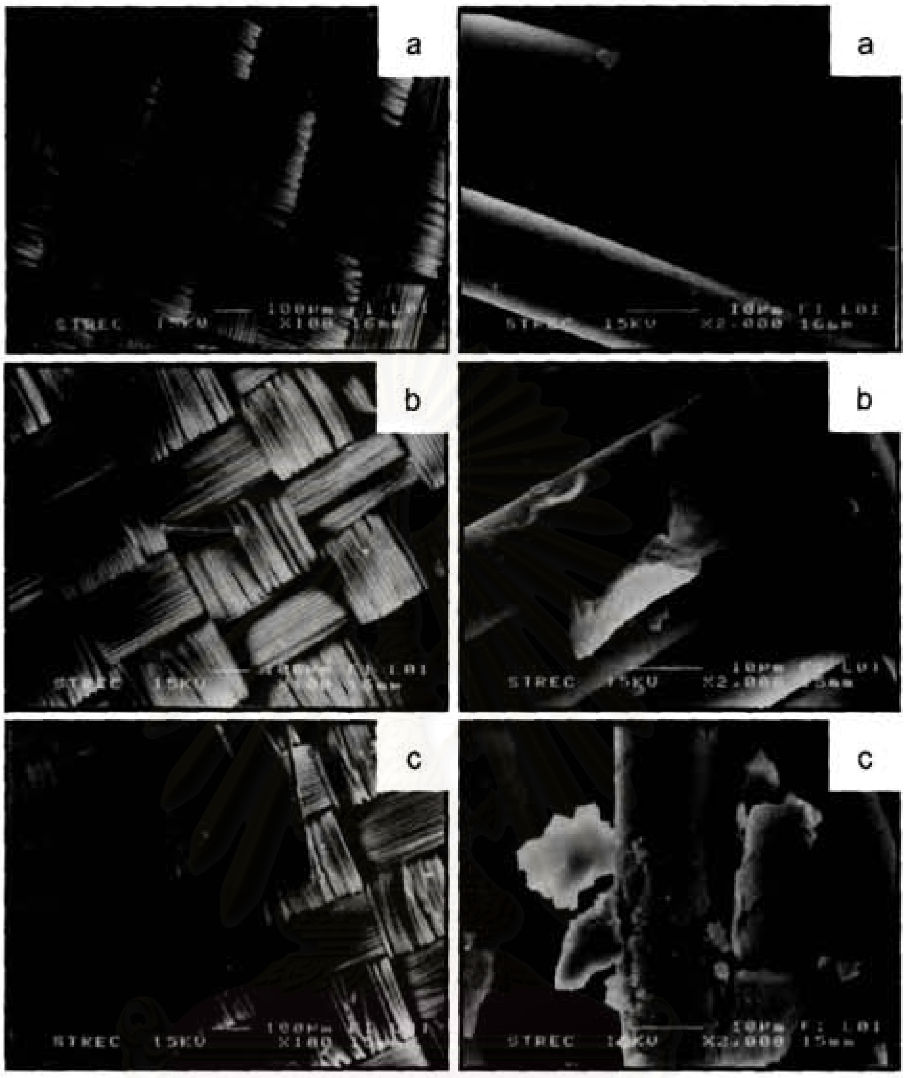

Figure 4.3 SEM photographs at X100 (left) and X2000 (right) of untreated PET fabric (a), PET fabrics treated with 20 (b), and 40 (c) shots of nitrogen plasma

The changes in the surface morphology of the fabrics observed after the plasma treatment can be explained by the localized degradation of polymer at the surface layer [90]. The degradation seems to be the effect of the interaction of plasma with a polymer surface. This process leads to an almost completed breakdown of relatively small numbers of molecules at the surface into low molecular components which eventually vaporize in the low pressure system.

4.1.1.3 Wettability

The degree of modification of plasma-treated fabric samples treated in this research was determined by measuring the wetting time directly after 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. Figure 4.4 shows the position of a fabric sample held in chamber of theta-pinch device.

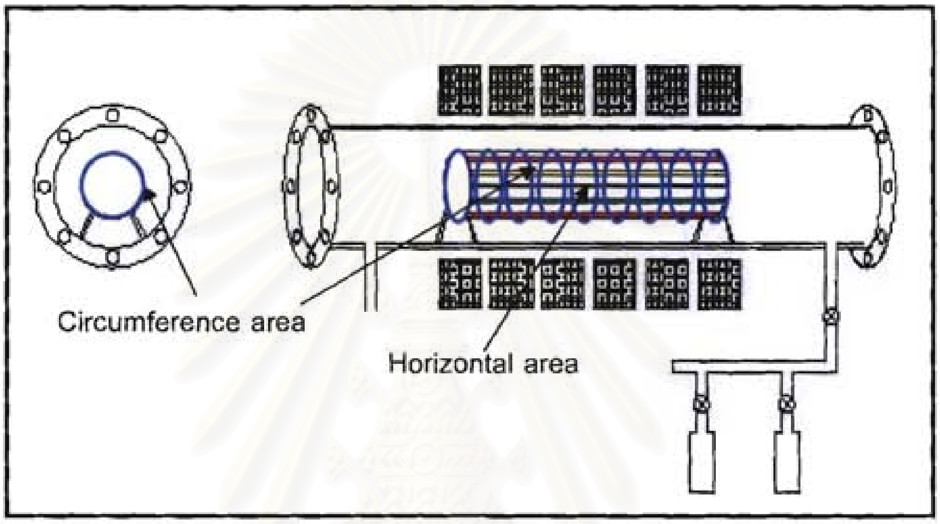

Figure 4.4 Configuration of theta-pinch device with the placement of a fabric sample

4.1.1.3.1 Wettability in Horizontal Area

As shown in Figure 4.5, it can be obviously seen that the wetting time of untreated PET fabric is higher than that of oxygen and nitrogen plasma-treated PET fabrics, indicating that untreated PET fabric was hydrophobic. After oxygen or nitrogen plasma treatments, the results show that the wetting time significantly decreased. Additionally, the wetting time of oxygen and nitrogen plasma-treated PET fabrics apparently decrease with increasing the number of plasma shots. Improved wettability of oxygen plasma-treated PET fabrics is possibly due to the formation of oxygen-containing groups such as hydroxyl groups on the treated surface which were confirmed by ATR-FTIR analysis. Exposing PET fabrics to nitrogen plasma caused the incorporation of nitrogen-containing groups; especially, amine and nitro groups onto PET surface.

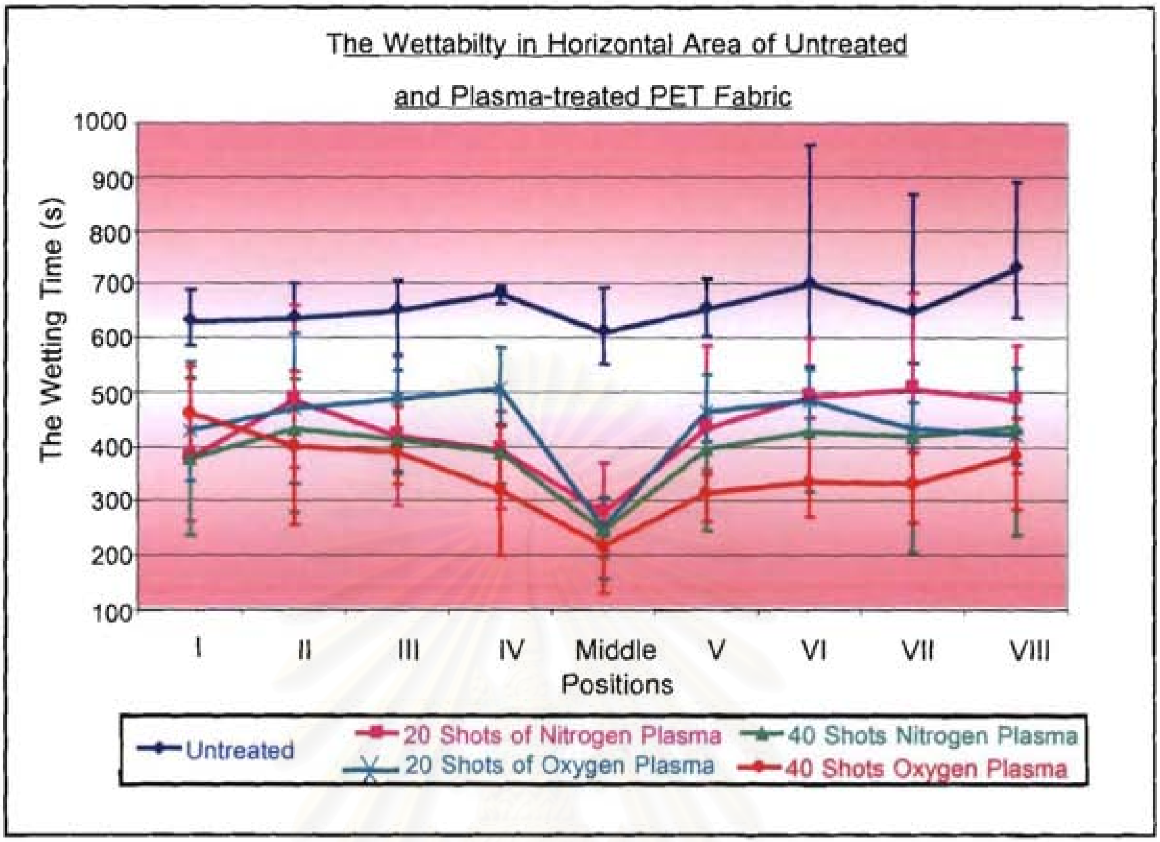

Figure 4.5 The wettability of untreated and plasma-treated PET fabrics measured in horizontal area

From Figure 4.5, it can be concluded that PET fabric treated with 40 shots of oxygen plasma results in better wettability compared with other conditions in this study. The main reason for enhancing the wettability of PET fabrics treated by oxygen plasma is an increase in the amount of carbonyl groups. It is known that carbonyl groups are more polar than amine groups occurred in nitrogen plasma treatment; thus, better wettability can be achieved by using oxygen plasma treatment [66].

From this Figure, 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. This can be explained by the dynamic process of theta-pinch discharge. Since maximum plasma density and energy of plasma usually occurs at the middle position of the chamber [13]; therefore, PET fabric can be modified effectively at this position.

4.1.1.3.2 Wettability in Circumference Area

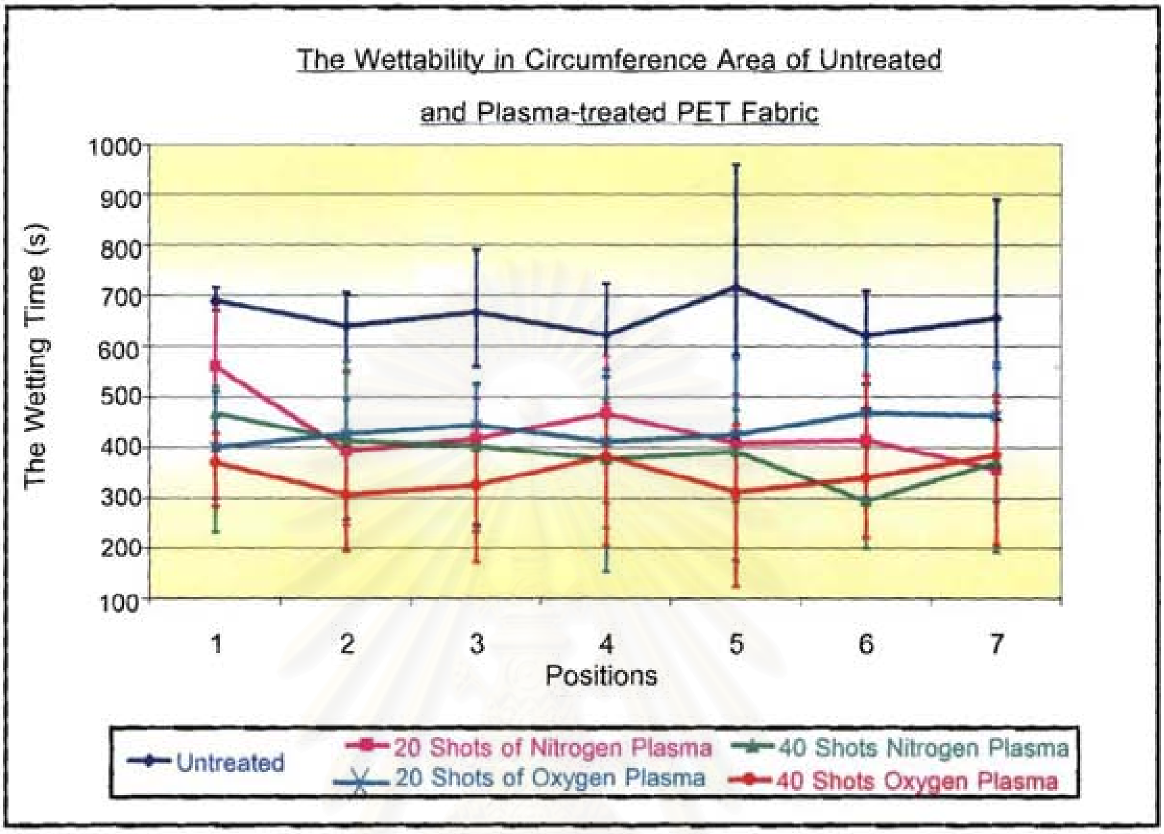

Figure 4.6 The wettability of untreated and plasma-treated PET fabrics measured in circumference area

Figure 4.6 shows the wettability of plasma-treated PET fabrics measured in circumference area. It can be seen that the modification of PET fabrics by oxygen and nitrogen 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. Treating PET fabrics with 40 shots of oxygen plasma results in effectively increasing hydrophilicity since higher degree of modification occurred.

4.1.1.4 Dyeability

The dyeability of PET fabrics after oxygen and nitrogen plasma treatments were evaluated in this study. After treatment with oxygen and nitrogen plasmas, PET fabrics were dyed with a disperse dye previously described in Chapter III. Table 4.2 summarizes the results for color measurement 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 XF, supplied by DyStar Thai Ltd.)

	λ_{max} (nm)	K/S	L*	a*	b*
Untreated	630	4.739±0.055	49.280±0.368	-0.940±0.410	-37.770±0.042
20 Shots of O_2 Plasma	630	2.804±0.344	57.535±3.415	-4.060±0.099	-32.080±1.230
40 Shots of O_2 Plasma	630	4.160±0.106	51.440±0.255	-4.600±0.028	-33.705±1.223
20 Shots of N_2 Plasma	630	3.379±0.268	53.845±1.407	-3.570±0.325	-33.985±0.629
40 Shots of N_2 Plasma	630	3.919±0.237	51.680±0.622	-3.900±0.580	-33.200±0.290

The above results indicate that the color strength of dyed PET fabrics decreases slightly when the fabrics were treated by oxygen or nitrogen plasmas prior to dyeing. This may be due to the fact that the amorphous regions of plasma-treated PET fabrics decrease because they are easier to be etched by plasma than the crystalline regions [78]. Since dye molecules can easily penetrate and be adsorbed in these amorphous regions; therefore, as these regions decrease, the saturation dye uptake value decreases.

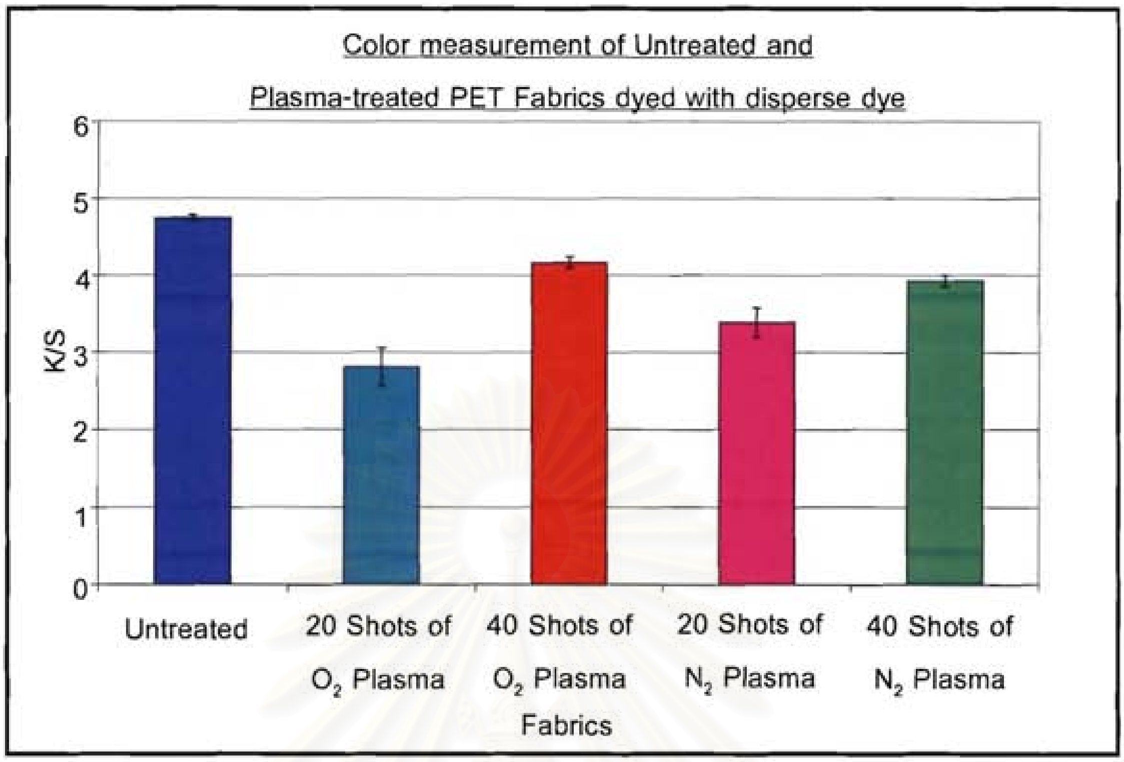

Figure 4.7 K/S values of untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix XF, supplied by DyStar Thai Ltd.)

4.1.1.5 Colorfastness to Washing

The colorfastness to washing for PET fabrics treated with oxygen and nitrogen plasmas and dyed with disperse dye (Dianix XF, supplied by DyStar Thai Ltd.) in terms of DE and gray scale rating is summarized in Table 4.3 and Figure 4.8.

After 30 washing cycles, it can be seen that PET fabrics treated with 20 and 40 shots of oxygen plasma and 20 shots of nitrogen plasma have better colorfastness to washing than those untreated and treated with 40 shots of nitrogen plasma. This is due to the difference in type and amount of functional groups incorporated onto the fabric surface at each condition.

It can be seen that using 40 shots of oxygen plasma and 20 shots of nitrogen plasma result in the fabrics having lower color strength and higher colorfastness than untreated fabric while using 20 shots of oxygen plasma yields the fabric having lowest color strength and 40 shots of nitrogen plasma yields that having worst colorfastness, However, when considering safety, time and energy consumption, it is better to use 20 shots of nitrogen plasma for surface modification of PET fabric.

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

Conditions	Cycles	K/S	L*	a*	b*	ΔE	Color Change
Untreated	0	4.739	49.280	-0.940	-37.770	-	-
	10	4.370	50.230	-1.170	-37.255	1.105	4.5
	20	3.916	51.290	-1.380	-36.120	2.638	3.5
	30	3.610	52.610	-1.850	-35.900	3.936	2.5
20 Shots, O_2 Plasma	0	2.804	57.535	-4.060	-32.080	-	-
	10	2.532	56.880	-3.070	-31.995	1.453	4.5
	20	2.478	57.410	-2.820	-32.470	1.331	4.5
	30	2.415	57.800	-2.950	-32.585	1.936	4
40 Shots, O_2 Plasma	0	4.160	51.440	-4.600	-33.705	-	-
	10	3.599	53.485	-3.730	-33.655	2.299	3.5
	20	3.446	53.850	-3.610	-34.355	3.034	3.5
	30	3.338	54.420	-3.335	-34.910	3.708	3
20 Shots, N_2 Plasma	0	3.379	53.845	-3.570	-33.985	-	-
	10	3.036	55.300	-2.880	-35.175	2.145	3.5
	20	2.937	55.640	-2.760	-34.935	2.612	3.5
	30	2.927	57.270	-2.975	-35.320	2.344	2.5
40 Shots, N_2 Plasma	0	3.919	51.680	-3.900	-33.200	-	-
	10	3.309	53.795	-3.280	-33.255	3.453	3
	20	2.816	55.370	-2.865	-32.865	4.539	2.5
	30	2.824	56.975	-3.143	-34.705	5.581	2.5

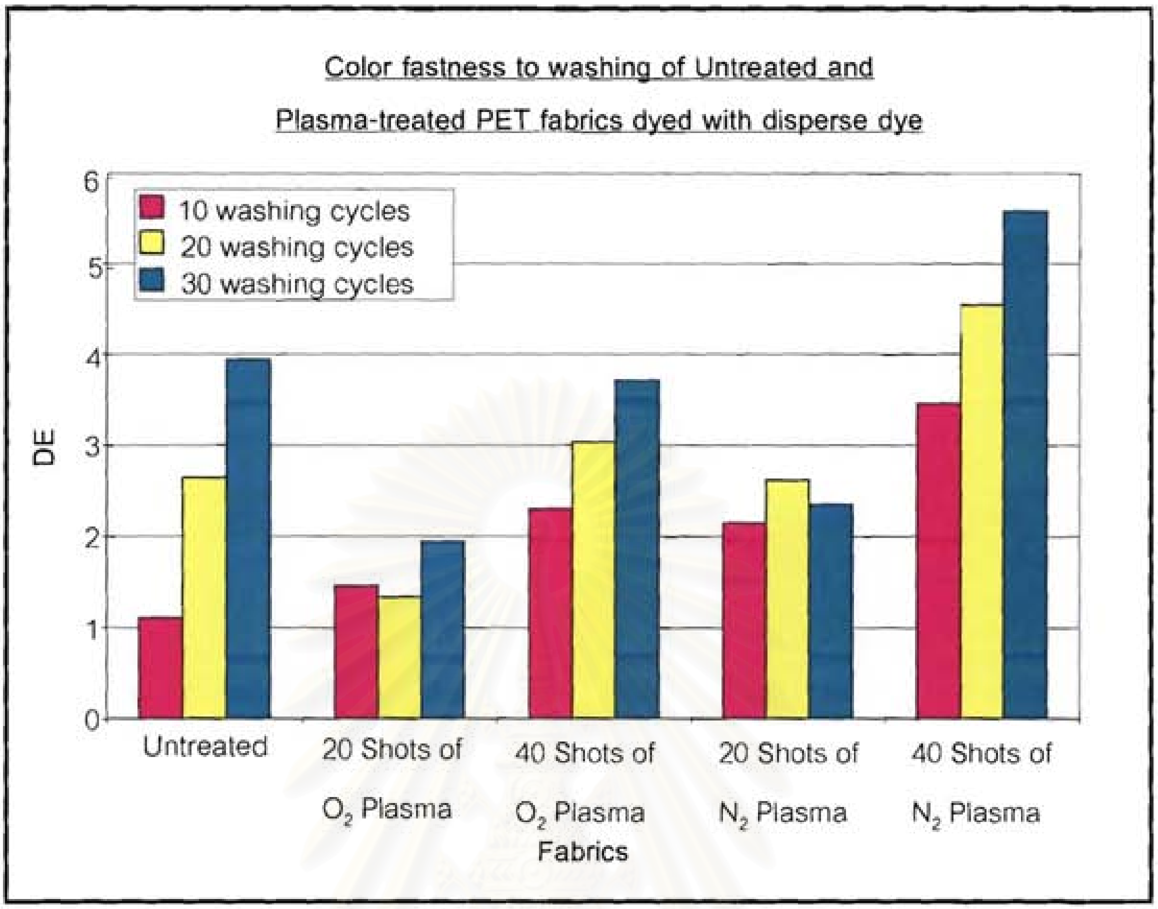

Figure 4.8 DE of untreated and plasma-treated PET fabrics dyed with disperse dye (Dianix XF, supplied by DyStar Thai Ltd.) after washing

4.1.1.6 Burning Characteristics

Burning characteristics of untreated and plasma-treated PET fabrics are given in Table 4.4. It can be seen that their characteristics are unchanged. Therefore, surface modification by oxygen and nitrogen plasma treatments does not affect burning characteristics of PET fabric.

Table 4.4 Burning characteristics of untreated and plasma-treated PET fabrics

Fabrics / Characteristics	Untreated	O_2/40	O_2/20	N_2/40	N_2/20
Approaching Flame	Melted and shrank from flame.	Melted and shrank from flame.	Melted and shrank from flame.	Melted and shrank from flame.	Melted and shrank from flame.
In Flame	Melted and burnt slowly.	Melted and burnt slowly.	Melted and burnt slowly.	Melted and burnt slowly.	Melted and burnt slowly.
Out of flame	Burnt slowly; melted and driped.	Burnt slowly; melted and driped.	Burnt slowly; melted and driped.	Burnt slowly; melted and driped.	Burnt slowly; melted and driped.
Odor	Slight sweet	Slight sweet	Slight sweet	Slight sweet	Slight sweet
Residue	Hard, shiny black or brown bead.	Hard, shiny black or brown bead.	Hard, shiny black or brown bead.	Hard, shiny black or brown bead.	Hard, shiny black or brown bead.

4.1.2 Properties and Morphology of Nylon 6 Fabrics

4.1.2.1 Surface Chemical Structure

ATR-FTIR spectra of untreated and plasma-treated nylon 6 fabrics are shown in Figure 4.9 and Table 4.5 presents the interpretation of ATR-FTIR spectra.

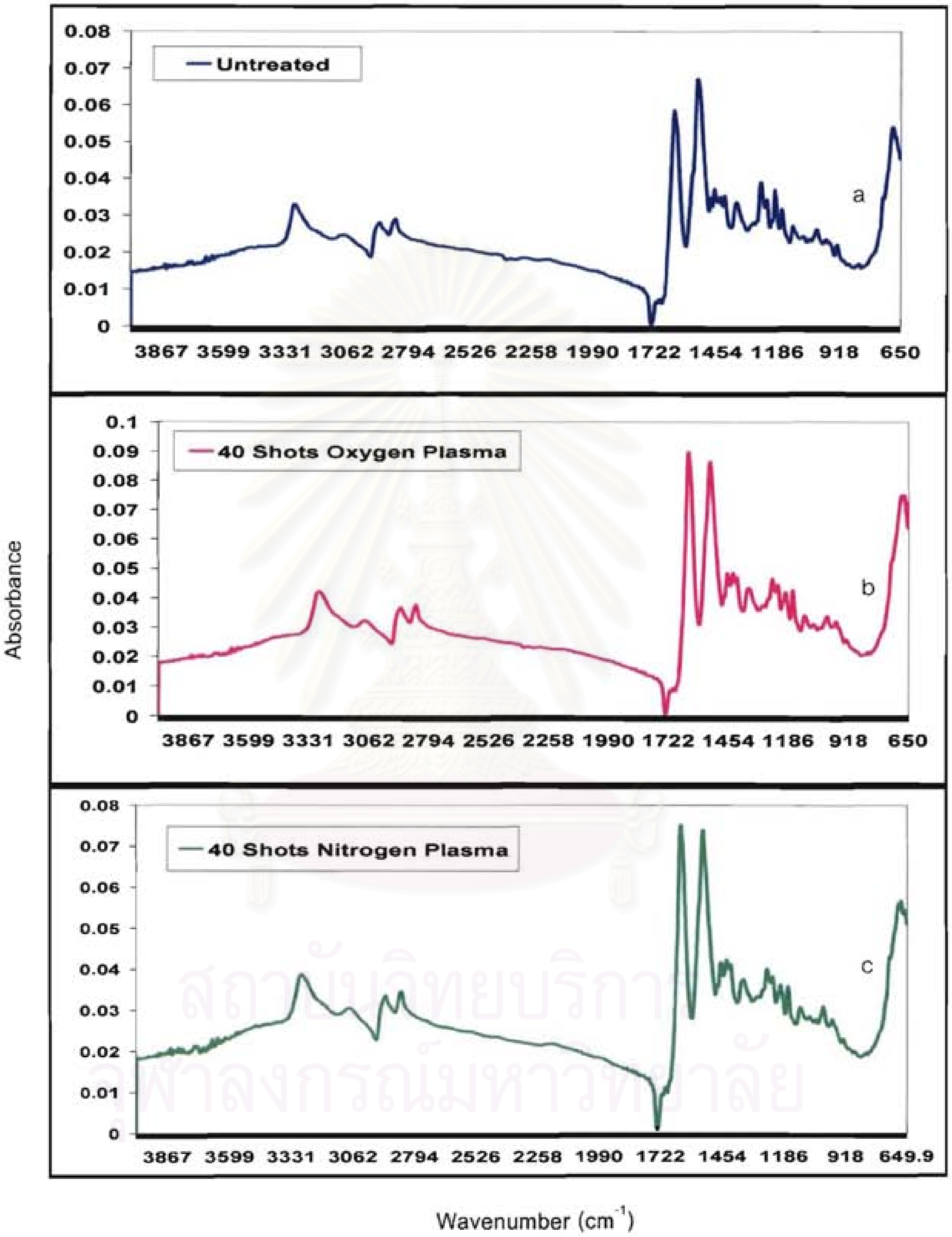

Figure 4.9 ATR-FTIR spectra of untreated nylon 6 fabric (a), nylon 6 fabrics treated with 40 shots of O_2 plasma (b) and with 40 shots of N_2 plasma (c)

Table 4.5 The interpretation of ATR-FTIR spectra of untreated and plasma-treated nylon 6 fabrics

Wavenumber (cm-1)			Interpretration
Untreated	O_2 plasma	N_2 plasma	
3294,3074	3286,3079	3286, 3079	N-H stretching of secondary amide
2919,2852	2920,2853	2919,2852	C-H stretching of methylene groups
1635	1633 (increased)	1633 (increased)	C=O stretching of secondary amide, and amine
			C=N stretching of imine group
1534	1537 (decreased)	1538 (decreased)	N-H in plane bending of secondary amide, and amine
1460	1460	1460	C-H bending of $-CH_2$ and $-CH_3$
1198	1220	1220	C-O stretching of carboxylic group
1260	1260	1260	C-N stretching of secondary amide, and amine
684	682,670	687,675	Out of plane N-H bending

When nylon 6 fabrics was treated with 40 shots of O_2 plasma, the intensity of the peak at 1635 cm^{-1} which can be related to C=O stretching of secondary amide or amine groups increases. However, the peak corresponding to N-H in plane bending (1537 cm^{-1}) decrease. These results indicate that oxygen containing groups, such as carbonyl groups were attached to nylon 6 surface when it was treated with oxygen plasma.

In case of nylon 6 fabric treated with 40 shot of N_2 plasma, the intensity of the peak at 1633 cm^{-1} assigned to C=N stretching of imine group increase. This suggests that nitrogen containing groups, such as imine groups were formed on nylon 6 surface when it was treated with nitrogen plasma.

Antonio, R. and et al. [73], have affirmed that when nylon 6 is subjected to high energy ion bombardment, reactive defects are created on the surface resulting in hydrogen abstraction, C-C bond breaking, and incorporation of reactive nitrogen species. It should be noted that the formation of the amine terminal and/or imine groups on the surface can be explained by hydrogen abstraction from the polymer.

4.1.2.2 Morphological Analysis

SEM photographs of nylon 6 fabric surface modified with oxygen and nitrogen plasmas are shown in Figure 4.10 and 4.11, respectively.

Figure 4.10 (b) shows etched surface of nylon 6 fibers, while an untreated sample presents a smooth surface as seen in Figure 4.10 (a). After increasing the number of plasma shots, the changes in surface morphology can be obviously seen as shown in Figure 4.10 (c). This phenomenon was a result of etching by reactive oxygen plasma.

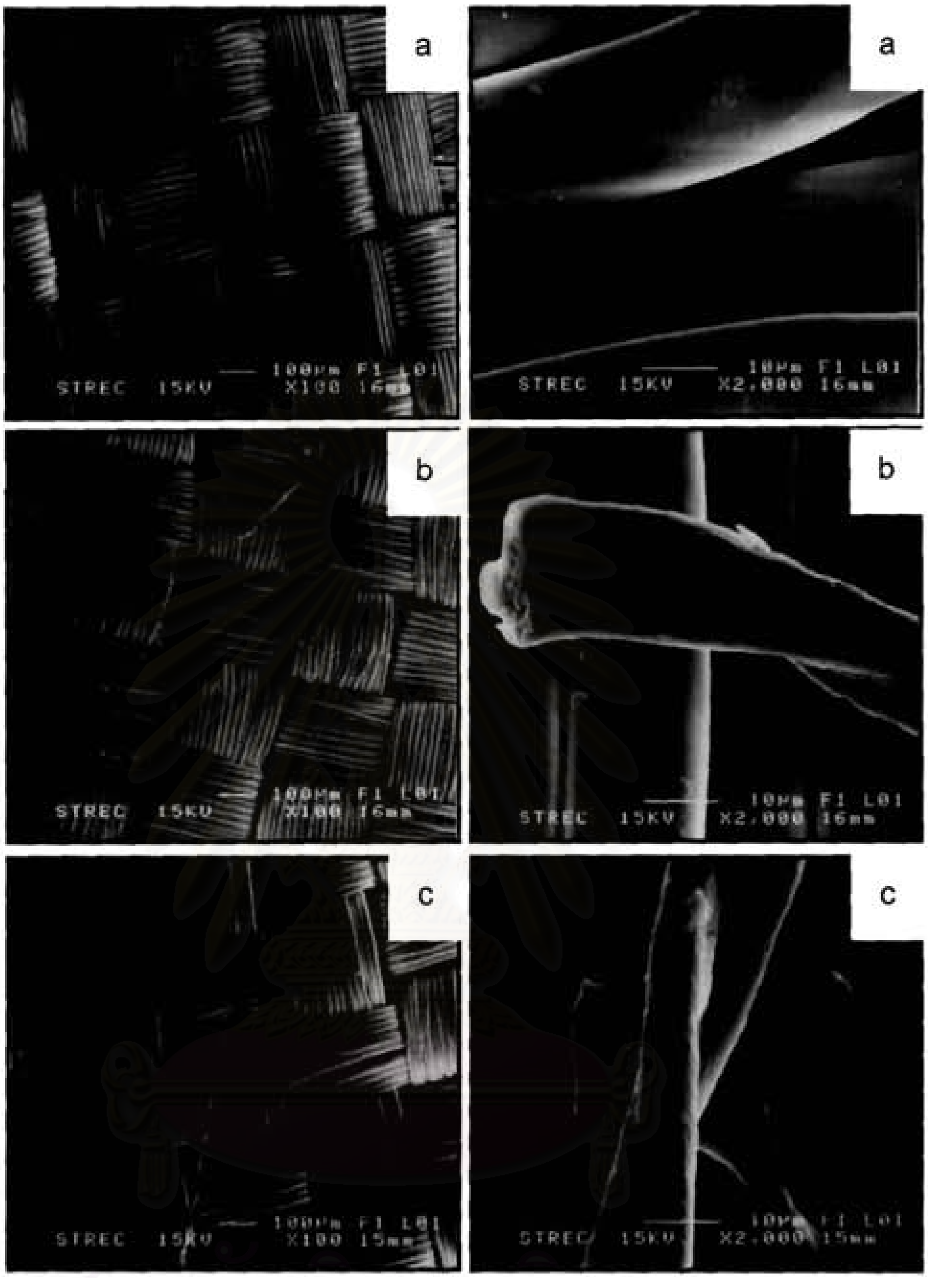

Figure 4.10 SEM photographs at X100 (left) and X2000 (right) of untreated nylon 6 fabric (a), nylon 6 fabrics treated with 20 (b), and 40 (c) shots of oxygen plasma

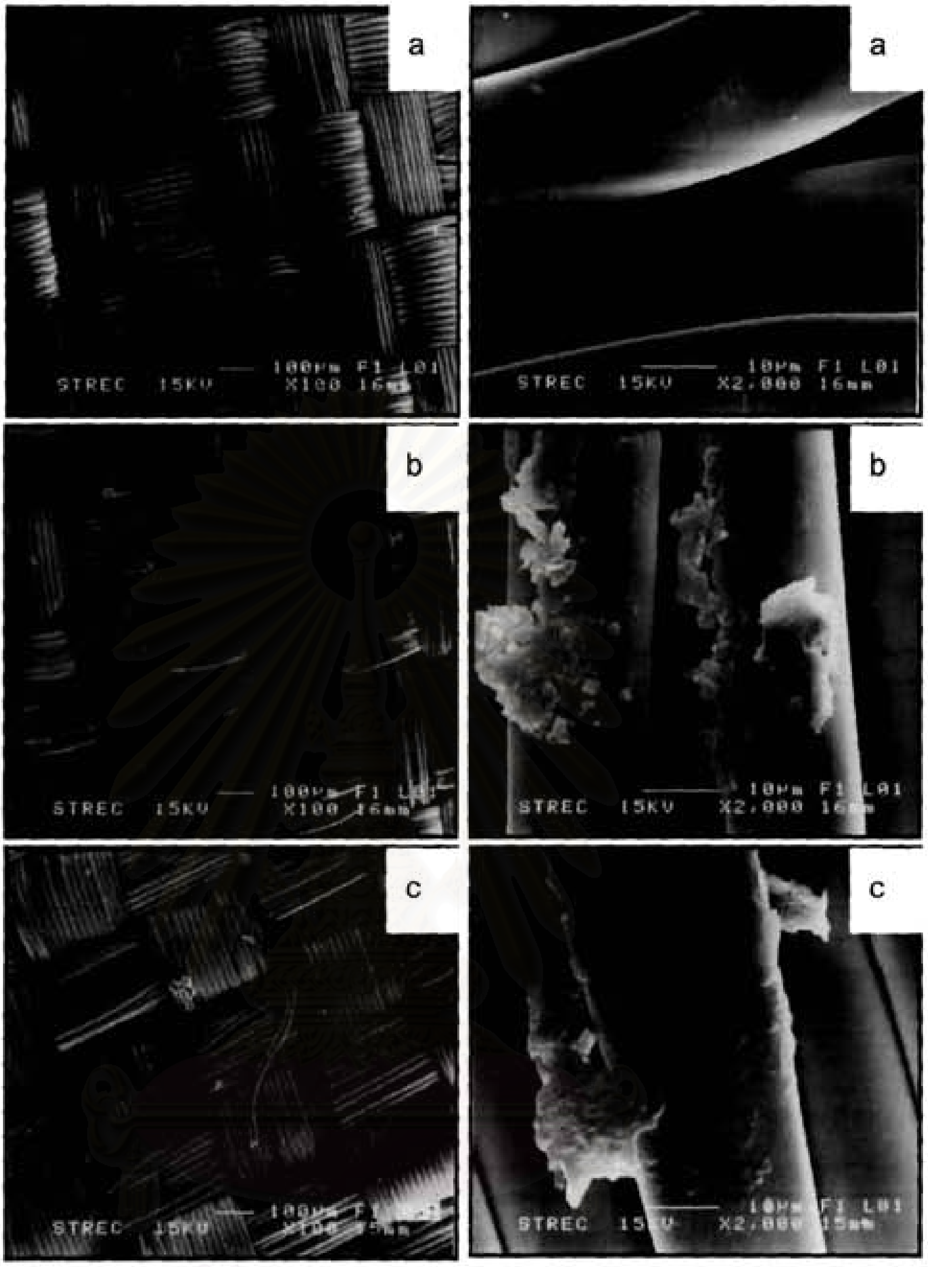

Figure 4.11 SEM photographs at X100 (left) and X2000 (right) of untreated nylon 6 fabric (a), nylon 6 fabrics treated with 20 (b), and 40 (c) shots of nitrogen plasma

Figure 4.11 shows SEM photographs of nylon 6 fabrics, both untreated and treated with nitrogen plasma. When it was exposed to 20 shots of nitrogen plasma, its surface was etched, resulting in surface roughness as shown in Figure 4.11 (b). When 40 shots of nitrogen plasma were applied, the breaking of the fiber was observed as seen in

Figure 4.11 (c). These results can be attributed to etching process or ablation effect caused by bombardment of nitrogen plasma reactive species on the fabric surface.

4.1.2.3 Wettability

Figures 4.12 and 4.13 illustrate the changes in wettability of nylon 6 fabrics treated with oxygen and nitrogen plasmas measured in circumference and horizontal areas, respectively.

As shown in Figures 4.12 and 4.13, 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.

4.1.2.3.1 Wettability in horizontal area

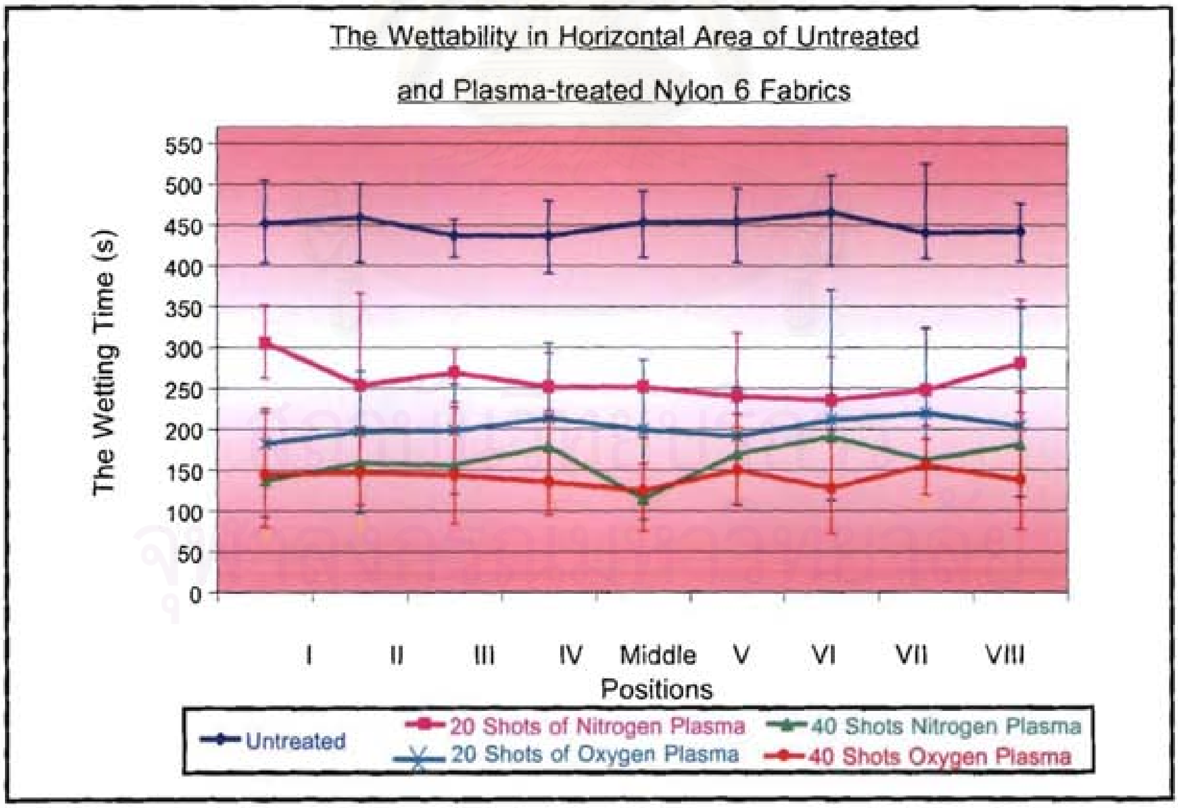

Figure 4.12 The wettability of untreated and plasma-treated nylon 6 fabrics measured in horizontal area

4.1.2.3.2 Wettability in circumference area

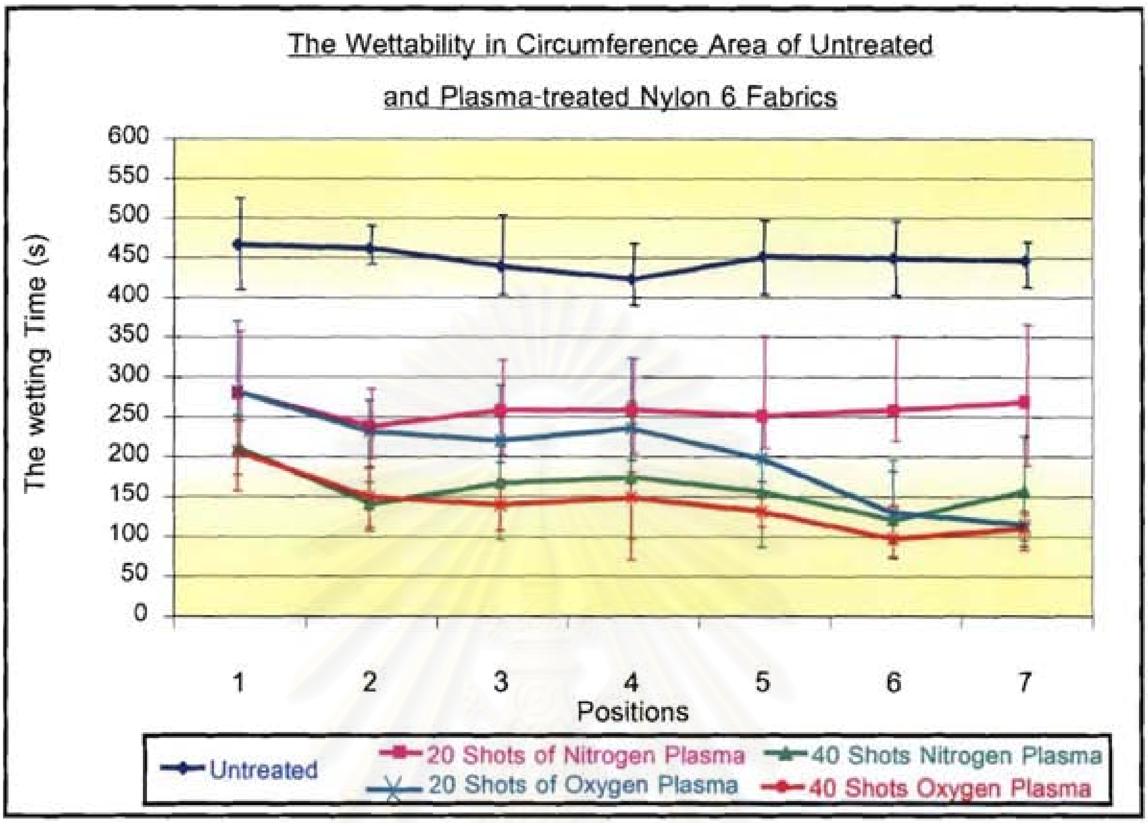

Figure 4.13 The wettability of untreated and plasma-treated nylon 6 fabrics measured in circumference area

The results of wettability in circumference and horizontal areas of nylon 6 fabric were different from those observed in plasma treatment of PET fabric. It can be seen from Figures 4.12 and 4.13 that the wetting times of all areas of plasma-treated nylon 6 fabric at each condition were comparable whereas PET fabric exhibited lower wetting times at the middle part of horizontal area. This may be because nylon is already more hydrophilic than PET, therefore, slight change in number of hydrophilic functional groups in different areas of plasma exposure does not significantly affect.

4.1.2.4 Dyability

It is well known that dyeing properties of plasma-treated fibers is correlated to their morphological characteristics, determined by SEM analysis, and to their chemical surface structure, determined by ATR-FTIR analysis [66]. Due to an increase in surface roughness and the formation of hydrophilic functional groups on nylon 6 surface after oxygen and nitrogen plasma treatments, the color strengths of oxygen and nitrogen plasma-treated nylon 6 fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.) are slightly higher than that of untreated nylon 6 fabric as seen from Table 4.6 and Figure 4.14.

Table 4.6 Color measurement of untreated and plasma-treated nylon 6 fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.)

Conditions	λ_{max} (nm)	K/S	L*	a*	b*
Untreated	630	14.905±0.713	30.785±0.884	15.795±0.615	-46.630±0.141
20 Shots of O_2 Plasma	590	15.503±0.150	29.820±0.085	14.705±0.290	-44.150±0.242
40 Shots of O_2 Plasma	590	15.572±0.077	30.360±0.071	15.815±0.021	-46.595±0.035
20 Shots of N_2 Plasma	590	15.463±0.153	29.885±0.064	15.820±0.240	-45.710±0.276
40 Shots of N_2 Plasma	590	15.518±0.153	30.020±0.170	16.080±0.297	-46.240±0.113

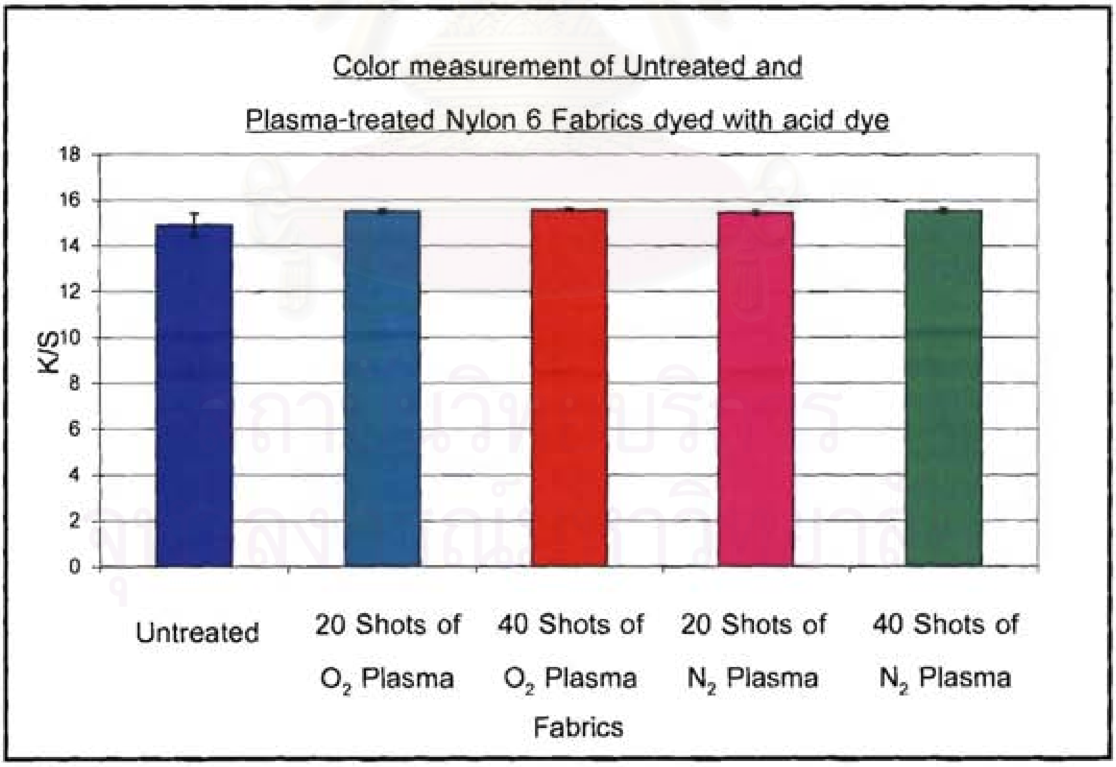

Figure 4.14 K/S values of untreated and plasma-treated nylon 6 fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.)

4.1.2.5 Colorfastness to Washing

Table 4.7 K/S values and ΔE after washing of untreated and plasma-treated nylon 6 fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.)

Conditions	Cycles	K/S	L*	a*	b*	ΔE	Color Change
Untreated	0	14.905	30.785	15.795	-46.630	-	-
	10	13.067	34.285	14.040	-48.450	4.320	2.5
	20	10.705	37.640	11.270	-47.920	8.327	1.5
	30	9.102	40.060	9.315	-47.150	11.334	1.5
20 Shots, O_2 Plasma	0	15.503	29.820	14.705	-44.150	-	-
	10	13.122	34.015	12.075	-45.910	5.255	2.5
	20	10.374	37.580	9.080	-44.710	9.603	1.5
	30	8.244	40.720	6.850	-43.395	13.457	1
40 Shots, O_2 Plasma	0	15.572	30.360	15.815	-46.595	-	-
	10	12.868	34.930	12.705	-47.990	5.701	2.5
	20	10.972	37.450	10.845	-47.610	8.718	1.5
	30	9.387	39.845	9.035	-47.030	11.667	1.5
20 Shots, N_2 Plasma	0	15.463	29.885	15.820	-45.710	-	-
	10	13.826	33.415	14.065	-47.930	4.583	2.5
	20	11.487	36.670	11.425	-47.625	8.325	1.5
	30	9.161	39.905	9.250	-46.535	12.019	1.5
40 Shots, N_2 Plasma	0	15.518	30.020	16.080	-46.240	-	-
	10	13.944	33.220	14.005	-47.550	4.053	2.5
	20	11.236	36.815	11.255	-47.270	8.404	1.5
	30	10.089	38.270	10.135	-46.705	10.190	1.5

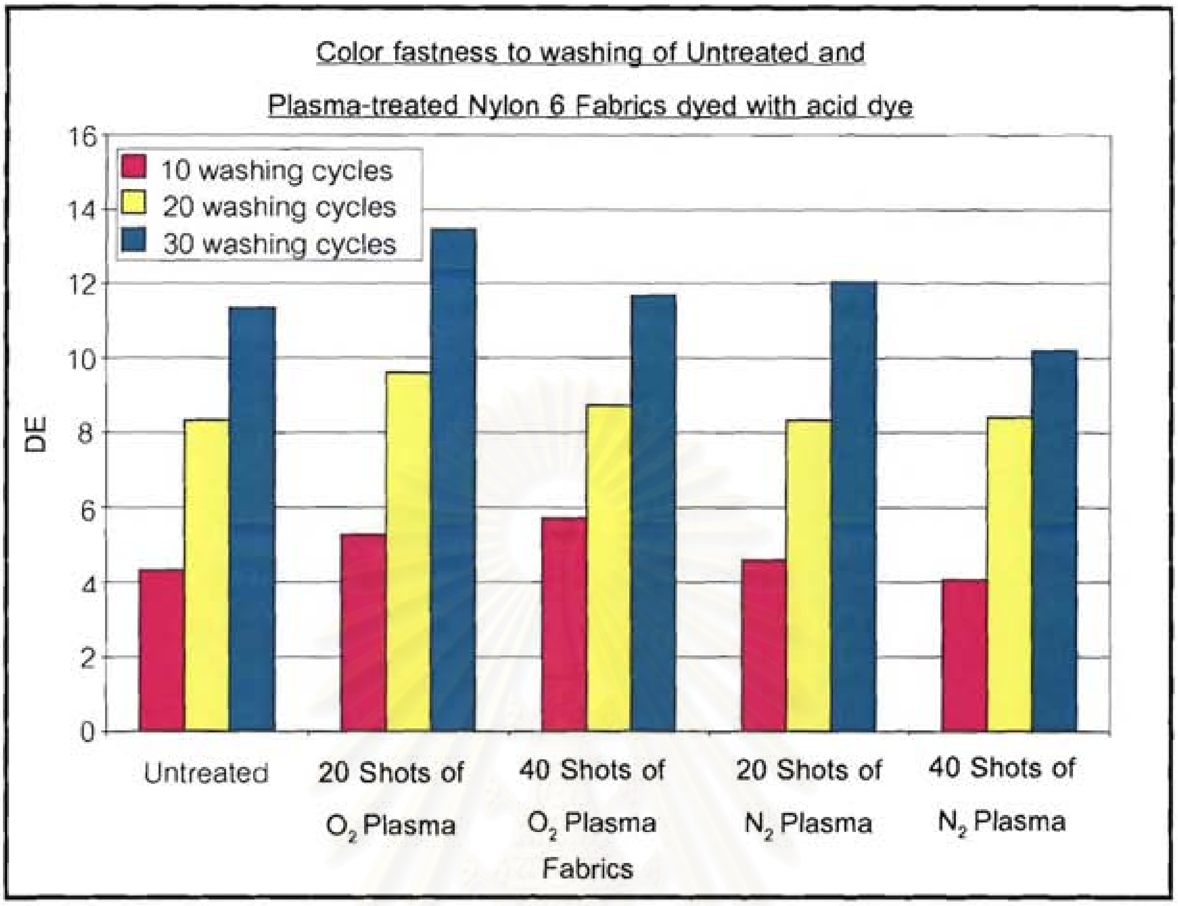

Figure 4.15 DE of untreated and plasma-treated nylon 6 fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.) after washing

The results from Table 4.7 and Figure 4.15 show that dyed nylon 6 fabrics pretreated with 40 shots of nitrogen plasma have better colorfastness to washing than those untreated and treated with other conditions. This may be a result of the difference in type and amount of functional groups formed on the fabric surface.

Additionally, it can be seen that color strength of nylon 6 fabric treated with 40 shots of nitrogen plasma dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.) was clearly improved; therefore, for this selected acid dye, the treatment with 40 shots of nitrogen plasma is suitable for surface modification of nylon 6 fabric.

4.1.2.6 Burning Characteristics

Table 4.8 shows burning characteristics of untreated and plasma-treated nylon 6 fabrics. These results indicate that their characteristics remain unchanged. Therefore, surface modifications by oxygen and nitrogen plasma treatments do not affect burning characteristics of nylon 6 fabrics.

Table 4.8 Burning characteristics of untreated and plasma-treated nylon 6 fabrics

Fabrics **Characteristics**	**Untreated**	**O_2/20**	**O_2/40**	**N_2/20**	**N_2/40**
Approaching Flame	Melted and shrank from flame.	Melted and shrank from flame.	Melted and shrank from flame.	Melted and shrank from flame.	Melted and shrank from flame.
In Flame	Melted and burnt slowly;smoky.	Melted and burnt slowly;smoky.	Melted and burnt slowly;smoky.	Melted and burnt slowly;smoky.	Melted and burnt slowly;smoky.
Out of flame	Burnt slowly; tended to self extinguish.	Burnt slowly; tended to self extinguish.	Burnt slowly; tended to self extinguish.	Burnt slowly; tended to self extinguish.	Burnt slowly; tended to self extinguish.
Odor	Celery	Celery	Celery	Celery	Celery
Residue	Hard, shiny brown or gray bead.	Hard, shiny brown or gray bead.	Hard, shiny brown or gray bead.	Hard, shiny brown or gray bead.	Hard, shiny brown or gray bead.

4.2 Properties and Morphology of Natural-fiber Fabrics

4.2.1 Properties and Morphology of Silk Fabrics

4.2.1.1 Surface Chemical Structure

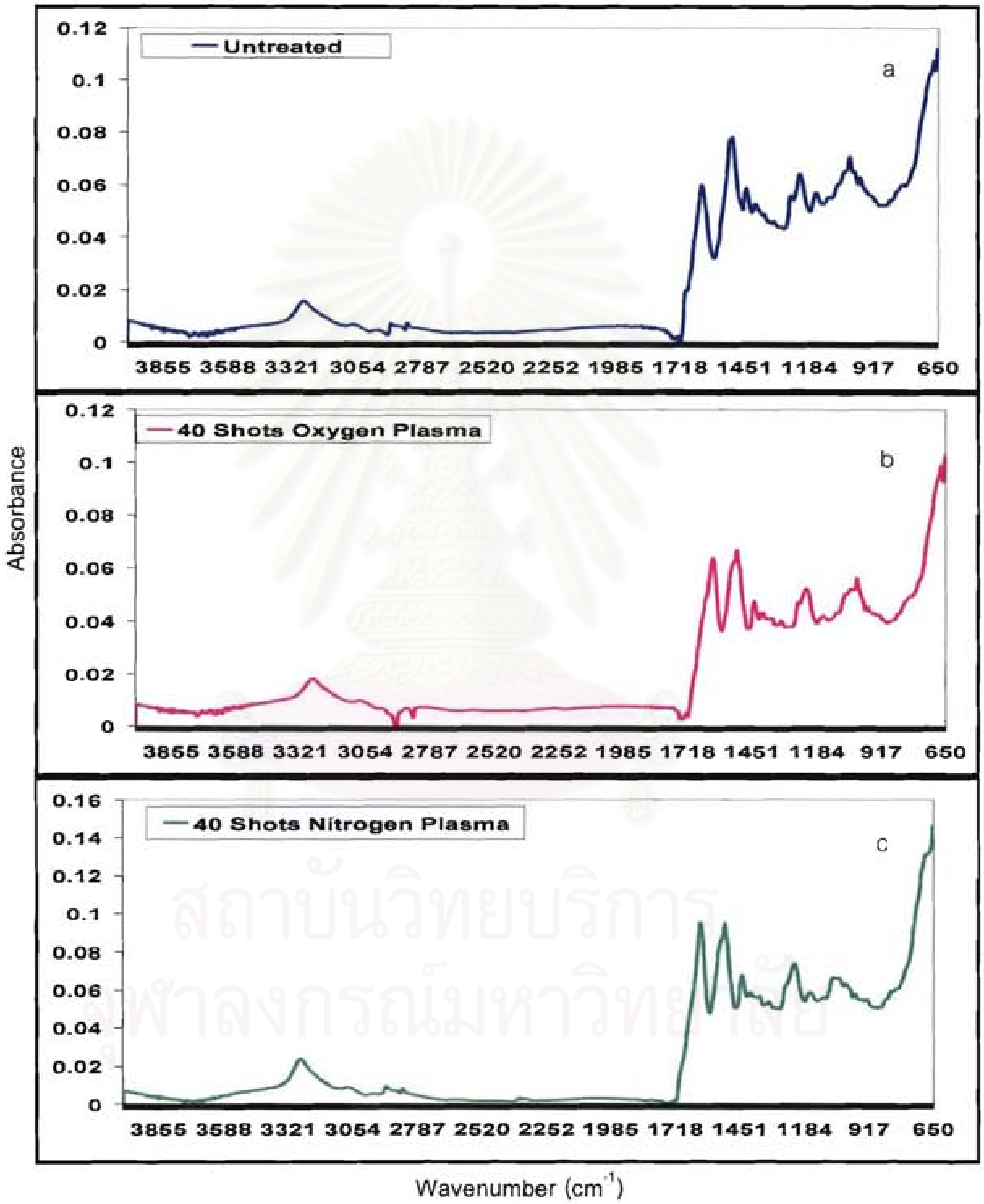

Figure 4.16 ATR-FTIR spectra of untreated silk fabric (a),
silk fabrics treated with 40 shots of O_2 plasma (b) and with 40 shots of N_2 plasma (c)

ATR-FTIR spectra of untreated and plasma-treated silk fabrics are shown in Figure 4.16. Table 4.9 presents the interpretation of these ATR-FTIR spectra. When silk fabric was treated with 40 shots of O_2 plasma, the intensity of the peak at 1614 cm^{-1} which can be assigned to C=O stretching of secondary amide or amine groups increase as seen from Figure 4.16 (b). On the contrary, a decrease in the intensity of the peak corresponding to N-H in plane bending (1513 cm^{-1}) is observed. These results suggest that oxygen containing groups, such as carbonyl groups were attached to silk fabric surface when it was treated with oxygen plasma. In case of silk fabric treated with 40 shot of N_2 plasma, an increase in the intensity of the peak at 1612 cm^{-1} assigned to C=N stretching of imine group is observed as shown in Figure 4.16 (c). This result indicates that nitrogen containing groups, such as imine groups were formed on silk fabric surface after nitrogen plasma treatment.

Table 4.9 The interpretation of ATR-FTIR spectra of untreated and plasma-treated silk fabrics

Wavenumber (cm-1)			Interpretration
Untreated	O_2 plasma	N_2 plasma	
3275	3270	3270 (broadened)	N-H stretching of secondary amide
2915,2846	2915,2846	2916,2847	C-H stretching of methylene groups
1628	1614	1612 (increased)	C=O stretching of secondary amide, and amine
			C=N stretching of imine group
1502	1513	1513 (decreased)	N-H in plane bending of secondary amide, and amine
1442	1441	1440 (increased)	C-H bending of $-CH_2$ and $-CH_3$
1224	1226	1226 (broadened)	C-N stretching of secondary amide, and amine

4.2.1.2 <u>Morphological Analysis</u>

SEM images of morphological changes on untreated and plasma-treated silk fabrics at different number of plasma shots are shown in Figure 4.17 and 4.18. As illustrated in Figure 4.17(a) the original surface of untreated silk is smooth. After treatment with oxygen plasma, an increase in surface roughness was observed as shown in Figure 4.17 (b). Furthermore, with increasing the number of plasma shots, the surface roughness increased as seen in Figure 4.17(c). These results can be attributed to the etching process caused by bombardment of oxygen plasma reactive species on the fabric surface.

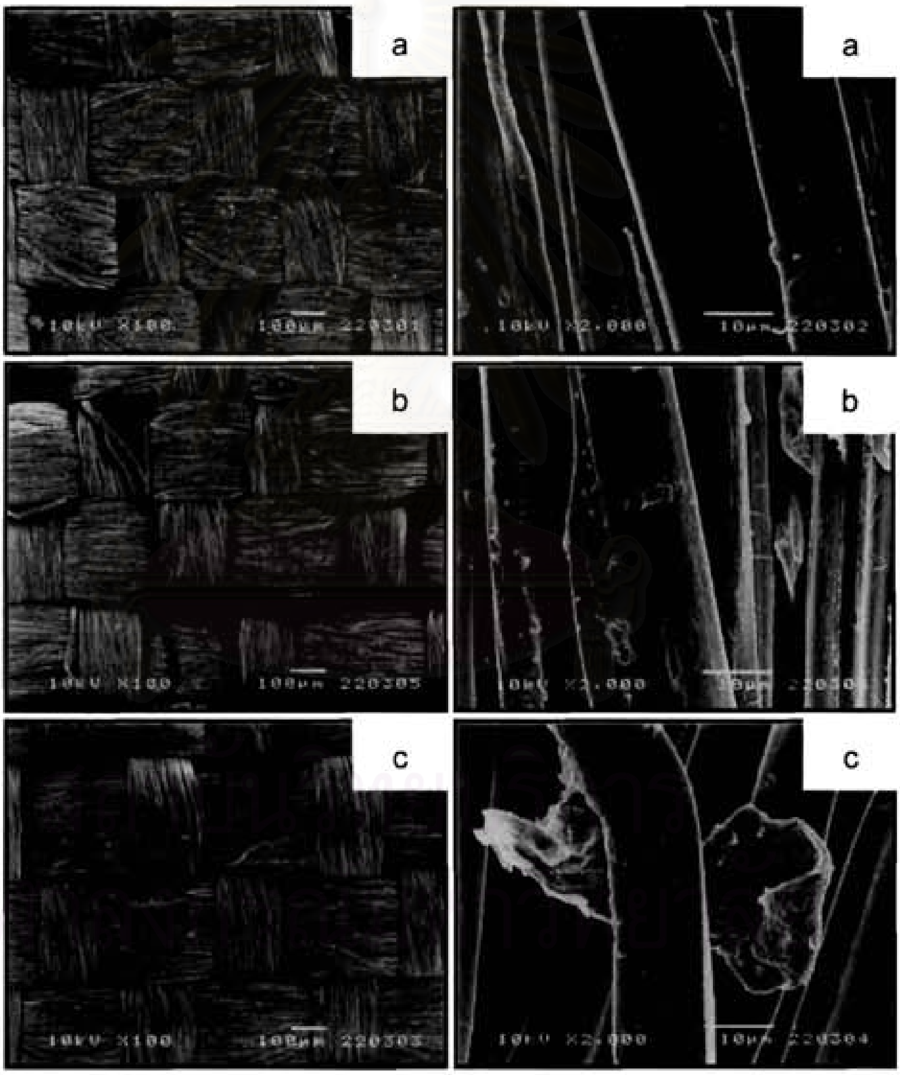

Figure 4.17 SEM photographs at X100 (left) and X2000 (right) of untreated silk fabric (a), silk fabrics treated with 20 (b), and 40 (c) shots of oxygen plasma

Figure 4.18 (b) and (c) shows SEM images of silk fabrics surface treated by nitrogen plasma at 20 and 40 shots, respectively. It can be obviously seen that nitrogen plasma also caused the changes in surface roughness of silk surface similar to oxygen plasma. However, the surface of silk fabric treated with oxygen plasma is rougher that that of treated with nitrogen plasma. 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.

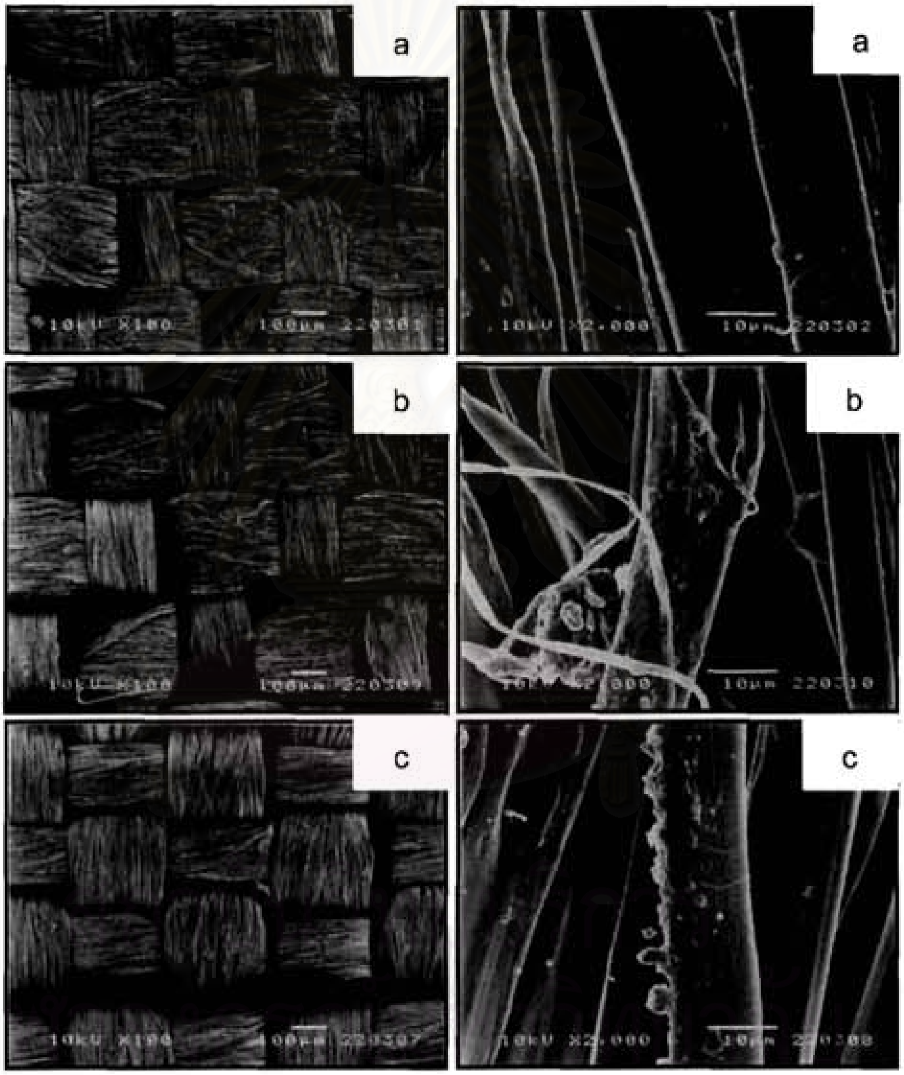

Figure 4.18 SEM photographs at X100 (left) and X2000 (right) of untreated silk fabric (a), silk fabrics treated with 20 (b), and 40 (c) shots of nitrogen plasma

4.2.1.3 Wettability

The surface wettability 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 natural-fiber fabrics were randomly investigated of all fabric area. The wettability of untreated and plasma-treated silk fabrics are shown in Figure 4.19.

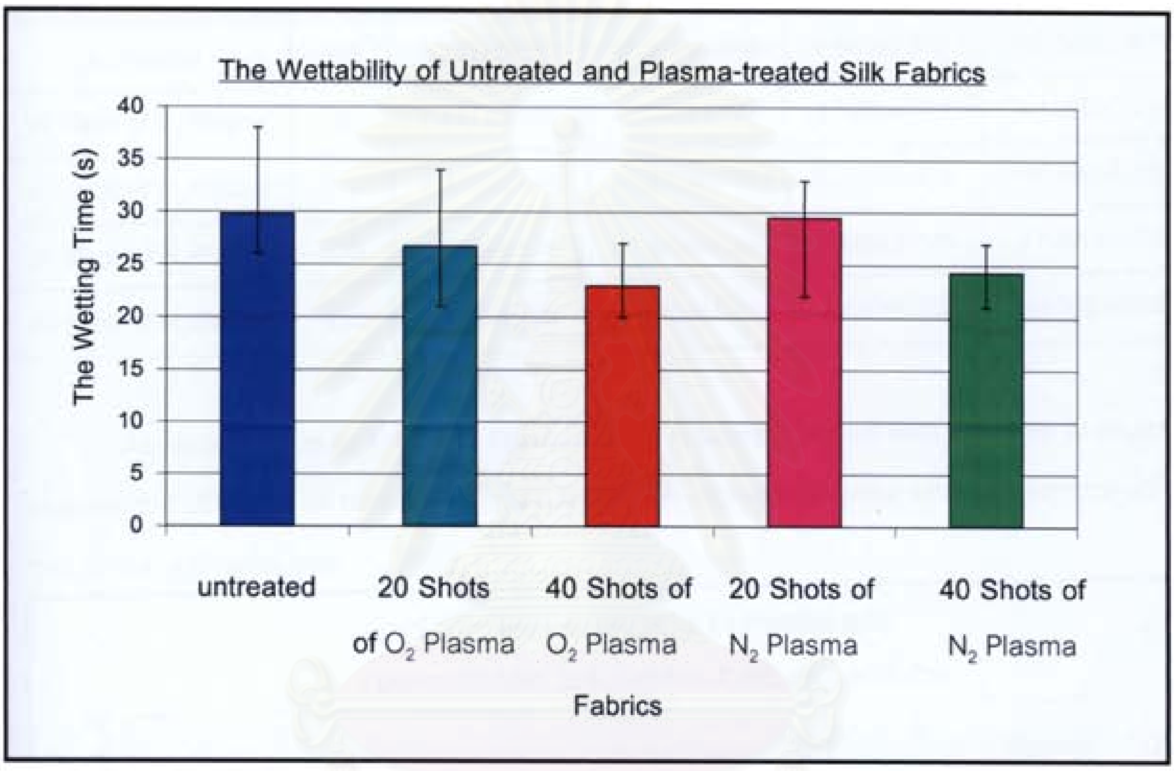

Figure 4.19 The wettability of untreated and plasma-treated silk fabrics

From Figure 4.19, the wetting times of silk fabrics treated with oxygen and nitrogen plasma are lower than that of the untreated fabric. In addition, it was found that oxygen plasma treatment resulted in more effective improvement of the wettability of silk fabric than nitrogen plasma treatment. This is due to the fact that oxygen plasma led to the formation of more hydrophlic functional groups confirmed by ATR-FTIR spectroscopy.

4.2.1.4 Dyeability

Table 4.10 Color measurement of untreated and plasma-treated silk fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.)

Conditions	λ_{max} (nm)	K/S	L*	a*	b*
Untreated	610	8.232±0.631	42.310±0.594	6.895±0.487	-47.560±0.955
20 Shots of O_2 Plasma	620	8.427±0.199	41.890±0.346	5.525±0.177	-45.800±0.014
40 Shots of O_2 Plasma	610	8.210±0.616	42.845±0.757	5.275±0.573	-46.655±0.785
20 Shots of N_2 Plasma	620	8.716±0.079	41.665±0.049	6.605±0.078	-47.100±-0.000
40 Shots of N_2 Plasma	620	6.308±6.308	45.110±45.110	4.430±4.430	-44.610±0.000

As shown in Table 4.10 and Figure 4.20, silk fabrics treated with 20 shots of oxygen plasma and 20 shots of nitrogen plasma exhibit an increase in color strength compared to that of the untreated one.

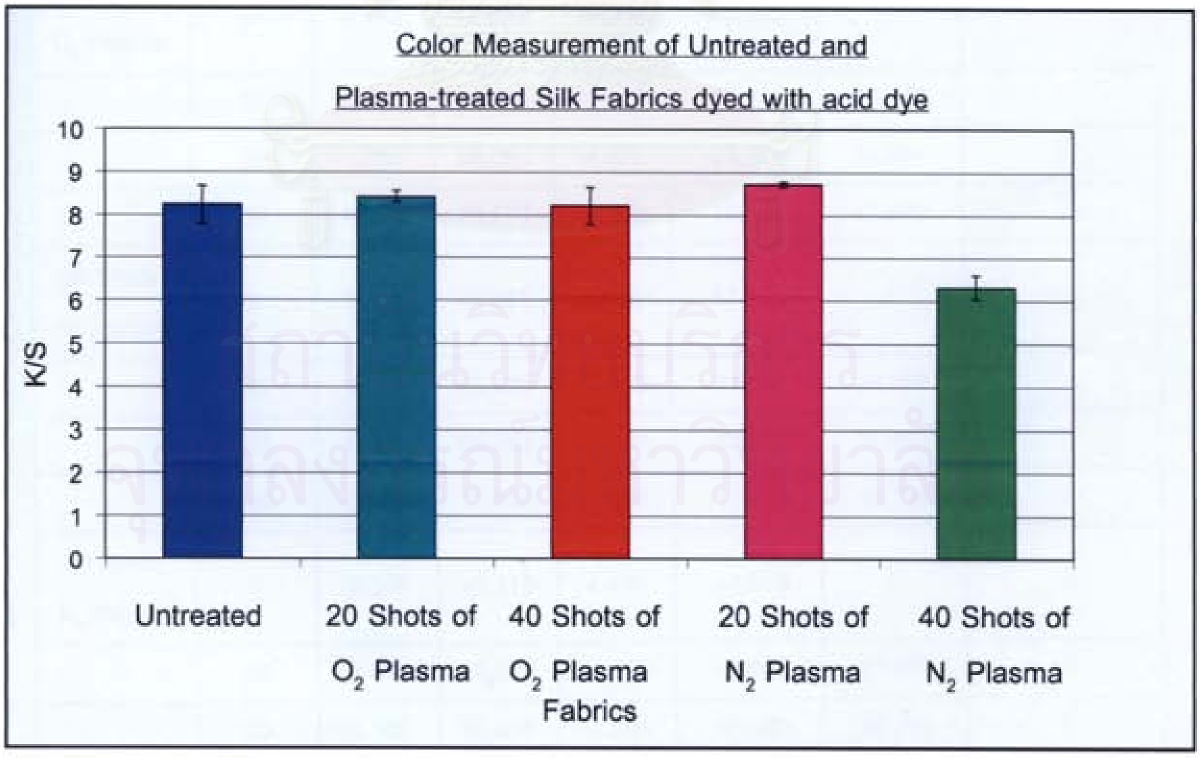

Figure 4.20 K/S values of untreated and plasma-treated silk fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.)

4.2.1.5 Colorfastness to Washing

Table 4.11 K/S values and ΔE after washing of untreated and plasma-treated silk fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.)

Conditions	Cycles	K/S	L^*	a^*	b^*	ΔE	Color Change
Untreated	0	8.232	42.310	6.895	-47.560	-	-
	10	2.212	57.540	-1.350	-33.465	22.330	1
	20	1.188	65.330	-3.665	-26.565	32.898	1
	30	0.763	69.945	-4.425	-20.580	40.246	1
20 Shots, O_2 Plasma	0	8.427	41.890	5.525	-45.800	-	-
	10	2.404	56.715	-1.700	-34.095	20.227	1
	20	1.208	65.010	-4.205	-25.665	32.166	1
	30	0.698	70.850	-4.700	-19.220	40.617	1
40 Shots, O_2 Plasma	0	8.210	42.845	5.275	-46.655	-	-
	10	2.156	57.970	-2.945	-31.530	22.920	1
	20	1.065	66.06o	-4.920	-23.020	34.664	1
	30	0.690	70.725	-5.300	-17.135	41.960	1
20 Shots, N_2 Plasma	0	8.716	41.665	6.605	-47.100	-	-
	10	1.928	59.420	-2.335	-31.945	24.997	1
	20	0.932	68.285	-4.530	-23.225	37.452	1
	30	0.566	72.850	-4.540	-17.040	44.729	1
40 Shots, N_2 Plasma	0	6.308	45.110	4.430	-44.610	-	-
	10	2.370	56.920	-1.790	-33.970	17.070	1
	20	1.160	65.415	-4.005	-25.380	29.225	1
	30	0.710	70.620	-4.620	-19.270	37.078	1

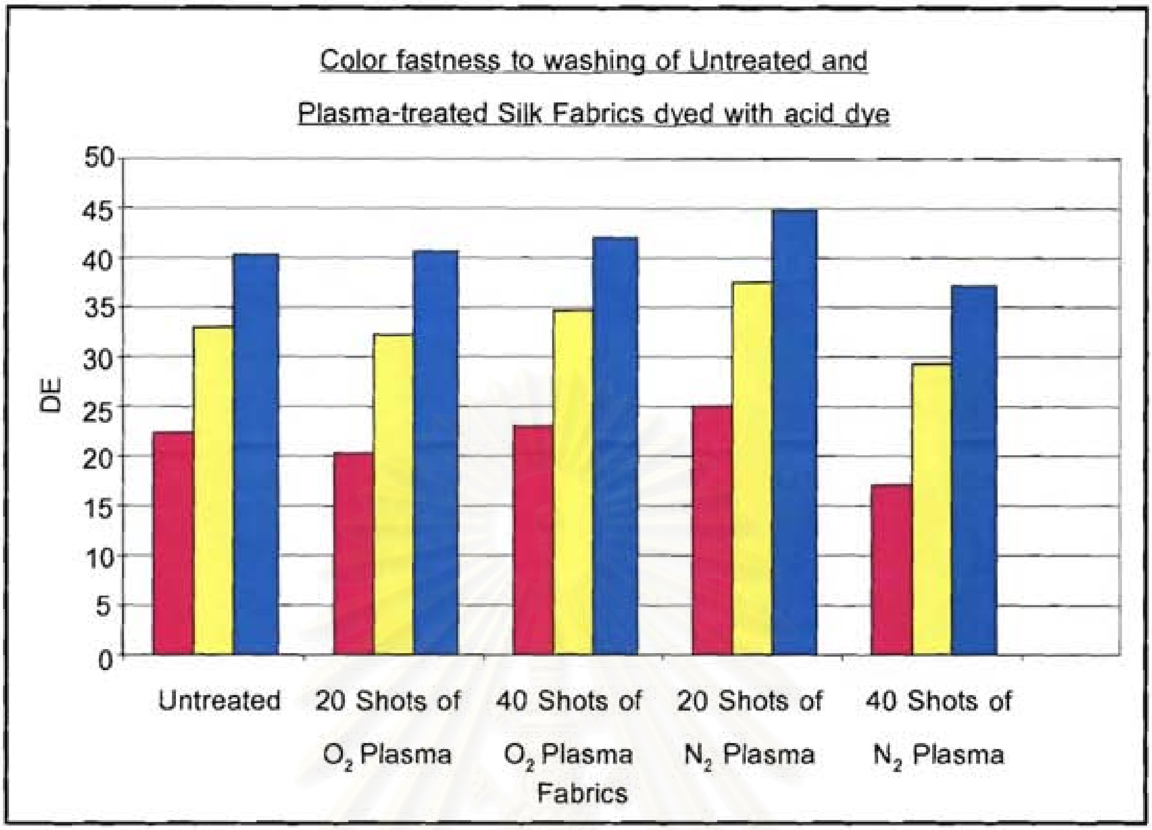

Figure 4.21 DE of untreated and plasma-treated silk fabrics dyed with acid dye (Erionyl Blue A-R, supplied by CIBA Specialty Chemicals Co., Ltd.) after washing

In contrast to dyeability, silk fabric treated with 40 shots of nitrogen plasma has better colorfastness to washing than untreated fabric and those treated with other conditions. This may due to the difference in the type and the amount of hydrophilic functional groups formed after plasma treatment.

The above results suggest that oxygen and nitrogen plasma treatments slightly improve the wetting time and dyeability of silk fabric because the nature of silk is already highly hydrophilic.

4.2.1.6. Burning Characteristics

Table 4.12 shows burning characteristics of untreated and plasma-treated silk fabrics. These results indicate that their characteristics remain unchanged. Therefore, surface modifications by oxygen and nitrogen plasma treatments do not affect burning characteristics of silk fabrics.

Table 4.12 Burning characteristics of untreated and plasma-treated silk fabrics

Fabrics Characteristics	untreated	O_2/20	O_2/40	N_2/20	N_2/40
Approaching Flame	Curls away from flame	Curls away from flame	Curls away from flame	Curls away from flame	Curls away from flame
In Flame	Burns slowly and sputters	Burns slowly and sputters	Burns slowly and sputters	Burns slowly and sputters	Burns slowly and sputters
Out of flame	Self-extinguishing or may burn very slowly	Self-extinguishing or may burn very slowly	Self-extinguishing or may burn very slowly	Self-extinguishing or may burn very slowly	Self-extinguishing or may burn very slowly
Odor	Like singed hair	Like singed hair	Like singed hair	Like singed hair	Like singed hair
Residue	Round, shiny black beads, easily crushed	Round, shiny black beads, easily crushed	Round, shiny black beads, easily crushed	Round, shiny black beads, easily crushed	Round, shiny black beads, easily crushed

4.2.2 Properties and Morphology of Cotton Fabrics

4.2.2.1 Surface Chemical Structure

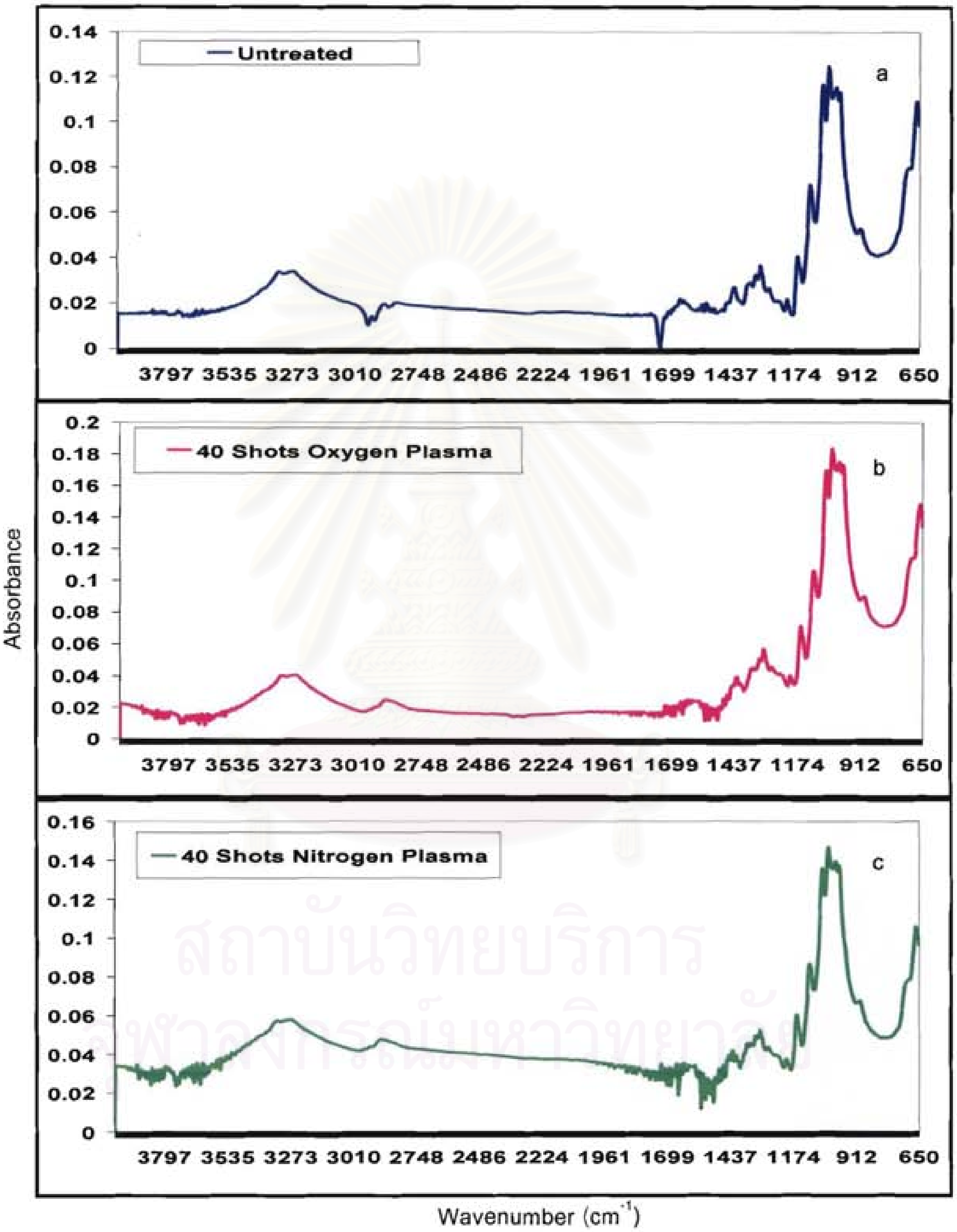

Figure 4.22 ATR-FTIR spectra of untreated cotton fabric (a),

cotton fabrics treated with 40 shots of O_2 plasma (b) and with 40 shots of N_2 plasma (c)

As shown in Figure 4.22, ATR-spectra of cotton fabric treated with oxygen and nitrogen plasmas are similar to that of the untreated one. Changes in surface chemical structure of plasma-treated cotton fabrics cannot be clearly seen of after modifying cotton fabric with plasma treatment.

Table 4.13 The interpretation of ATR-FTIR spectra of untreated and plasma- treated cotton fabrics

Wavenumber (cm-1)			**Interpretation**
Untreated	**O_2 plasma**	**N_2 plasma**	
3320	3320	3320	O-H stretching : intermolecular hydrogen bonding
2887	2891	2894	C-H stretching of -CH_2
1425	1426	1426	C-H bending of –CH_2
1335,1314,1204	1335,1313,1203	1335,1313,1203	O-H in plane bending
1160	1160	1160	Anti-symmetrical bridge C-O-C stretching
1108	1105	1106	C-O stretching of secondary alcohol
1030	1029	1029	Skeleton vibration involved in C-O stretching
662	661	663	O-H out-of-plane bending

4.2.2.2 Morphological Analysis

As shown in Figure 4.23 (a) the original surface of untreated cotton is smooth. When it was exposed to 20 shots of oxygen plasma, its surface was etched, resulting in surface roughness as shown in Figure 4.23 (b). When 40 shots of oxygen plasma were applied, the breaking of the fiber was observed as seen in Figure 4.23 (c). These results can be attributed to the etching process or ablation effect caused by bombardment of oxygen plasma reactive species on the fabric surface.

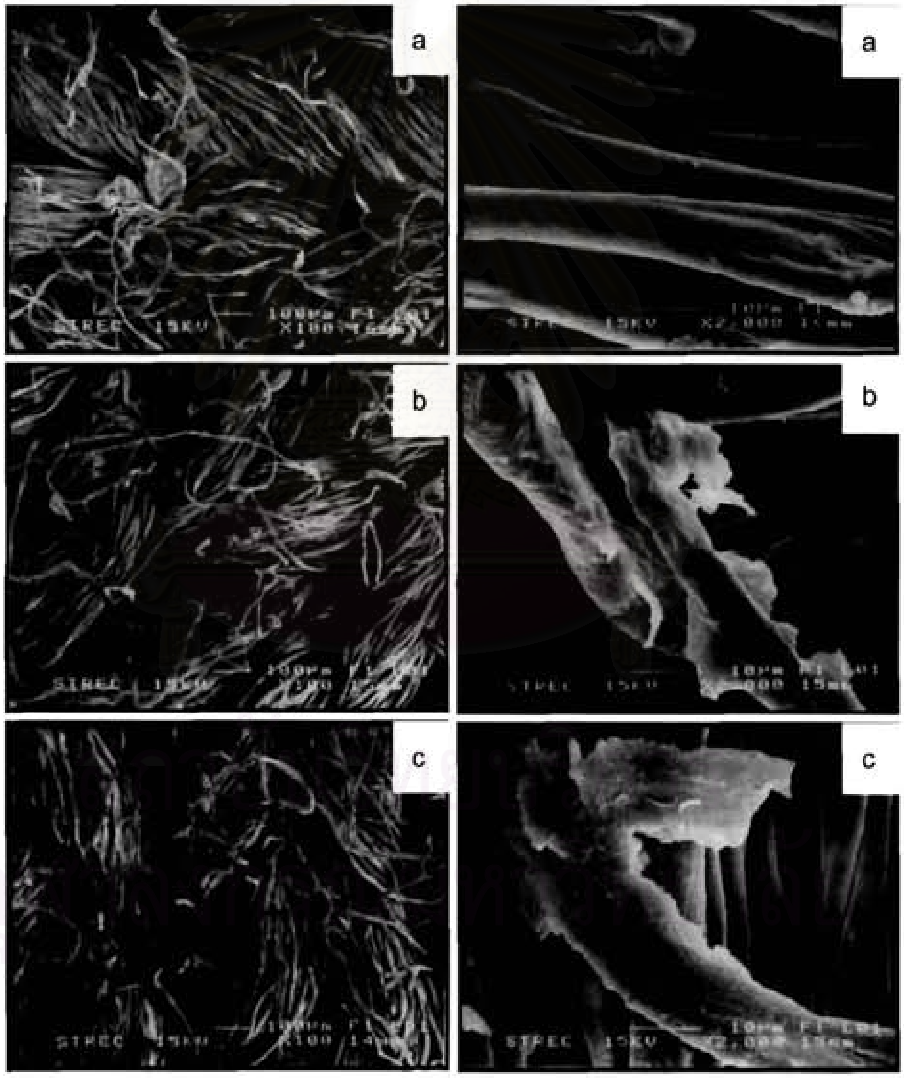

Figure 4.23 SEM photographs at X100 (left) and X2000 (right) of untreated cotton fabric (a), cotton fabrics treated with 20 (b), and 40 (c) shots of oxygen plasma

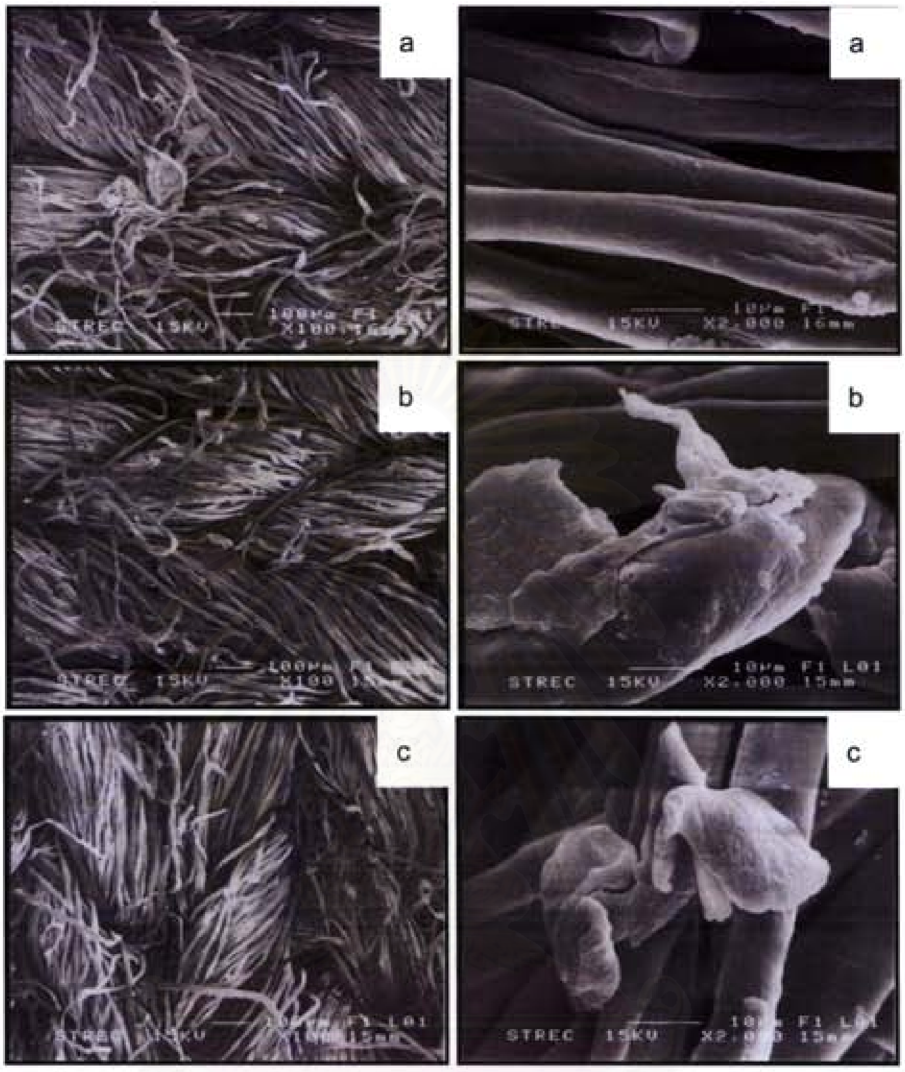

Figure 4.24 SEM photographs at X100 (left) and X2000 (right) of untreated cotton fabric (a), cotton fabrics treated with 20 (b), and 40 (c) shots of nitrogen plasma

Figures 4.24 (b) and (c) show SEM images of cotton fabrics surface treated with nitrogen plasma. It is clearly seen that nitrogen plasma also causes the changes in surface roughness of cotton surface similar to oxygen plasma.

4.2.2.3 Wettability

Figure 4.25 shows the wettability of untreated and plasma-treated cotton fabrics. The wettability of nitrogen and oxygen 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 posseses hydrophilic characteristics.

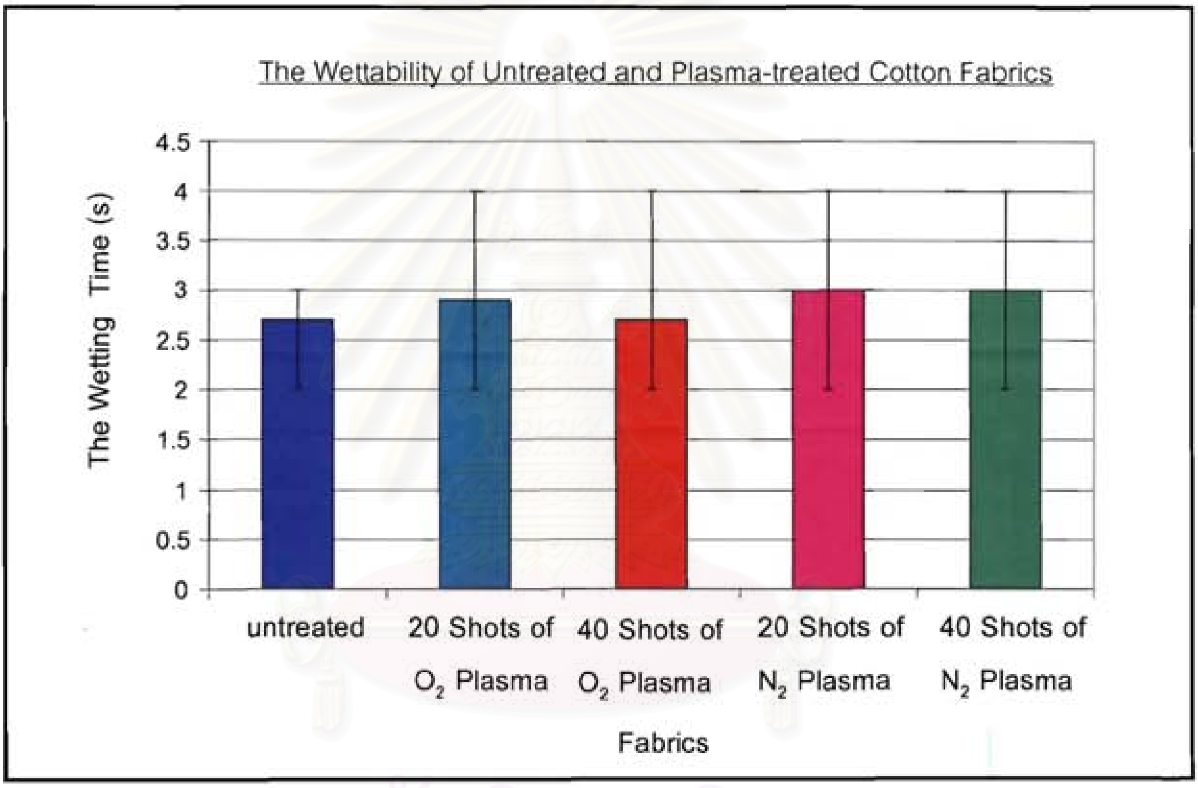

Figure 4.25 The wettability of untreated and plasma-treated cotton fabrics

4.2.2.4 Dyeability

As shown in Table 4.14 and Figure 4.26, oxygen and nitrogen plasma treatments were found to result in no improvement of dyeability. In fact, the treated fabrics tended to have less dye affinity the untreated fibers. 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 [66].

Table 4.14 Color measurement of untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

Conditions	λ_{max} (nm)	K/S	L*	a*	b*
Untreated	610	12.195±0.025	33.365±0.021	-6.420±0.000	-20.440±0.028
20 Shots of O_2 Plasma	620	11.413±0.108	33.905±0.106	-6.615±0.021	-19.440±0.325
40 Shots of O_2 Plasma	610	12.073±0.649	33.240±0.636	-6.530±0.170	-19.775±0.177
20 Shots of N_2 Plasma	620	10.969±0.020	33.445±0.021	-6.645±0.177	-19.950±0.481
40 Shots of N_2 Plasma	620	11.956±0.071	33.430±0.014	-6.670±0.014	-19.750±0.127

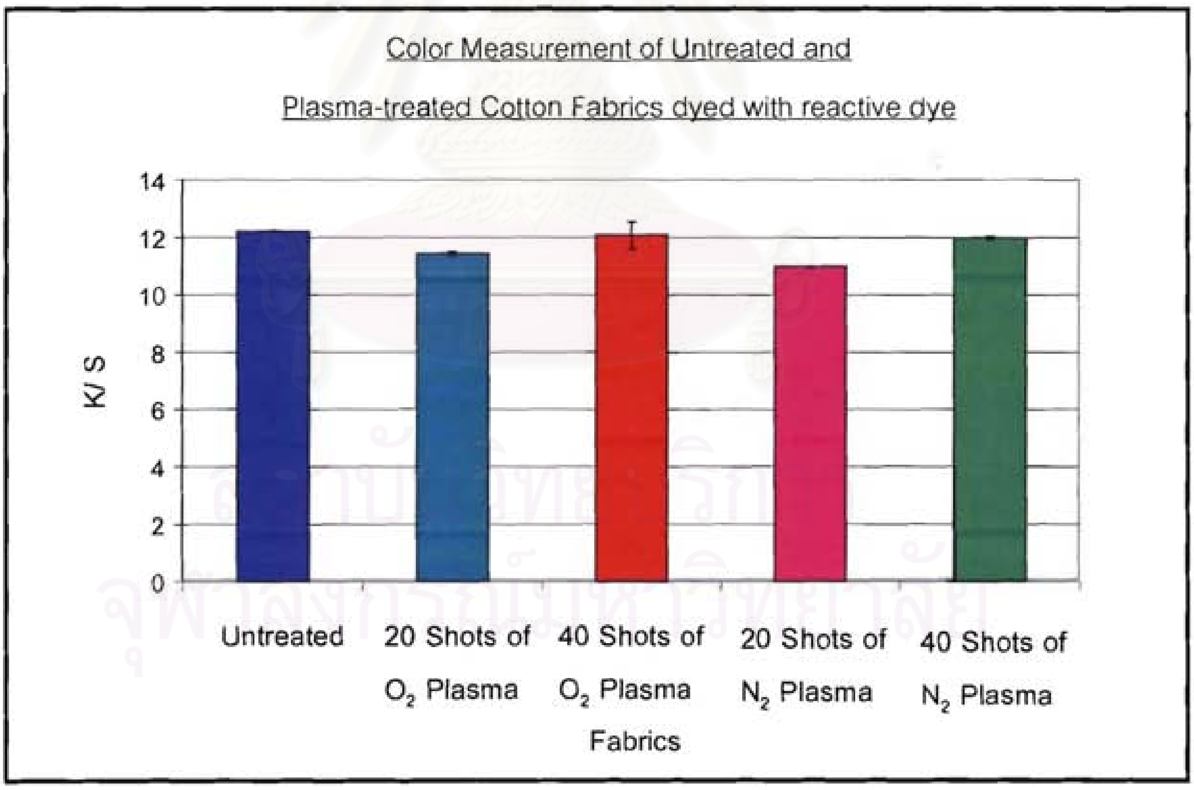

Figure 4.26 K/S values of untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.)

4.2.2.5 Colorfastness to Washing

As shown in Table 4.15 and Figure 4.27, untreated and plasma-treated dyed cotton fabrics have excellent washfastness properties. However, the results indicate that the untreated fabric exhibit slightly better colorfastness to washing than all plasma-treated fabrics.

Table 4.15 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	12.195	33.365	-6.420	-20.440	-	-
	10	11.497	33.265	-6.575	-20.465	0.236	5
	20	11.759	33.695	-6.620	-20.050	0.549	5
	30	11.352	34.075	-6.590	-20.010	0.863	5
20 Shots, O_2 Plasma	0	11.413	33.905	-6.615	-19.440	-	
	10	11.175	34.345	-6.795	-19.825	0.657	5
	20	10.717	34.715	-6.785	-19.725	0.877	5
	30	10.246	35.325	-6.885	-19.625	1.457	4.5
40 Shots, O_2 Plasma	0	12.073	33.240	-6.530	-19.775	-	
	10	11.382	34.210	-6.760	-20.045	1.033	4.5
	20	10.507	34.970	-6.775	-19.780	1.753	4
	30	10.360	35.125	-6.775	-19.675	1.902	4
20 Shots, N_2 Plasma	0	10.969	33.445	-6.645	-19.950	-	
	10	10.622	34.950	-6.725	-19.825	1.513	4.5
	20	10.421	35.080	-6.855	-19.595	1.688	4
	30	10.297	35.115	-6.780	-19.485	1.739	4
40 Shots, N_2 Plasma	0	11.956	33.430	-6.670	-19.750	-	
	10	11.505	33.875	-6.650	-19.780	0.458	5
	20	11.134	34.165	-6.670	-19.605	0.783	5
	30	10.815	34.485	-6.745	-19.500	1.094	4.5

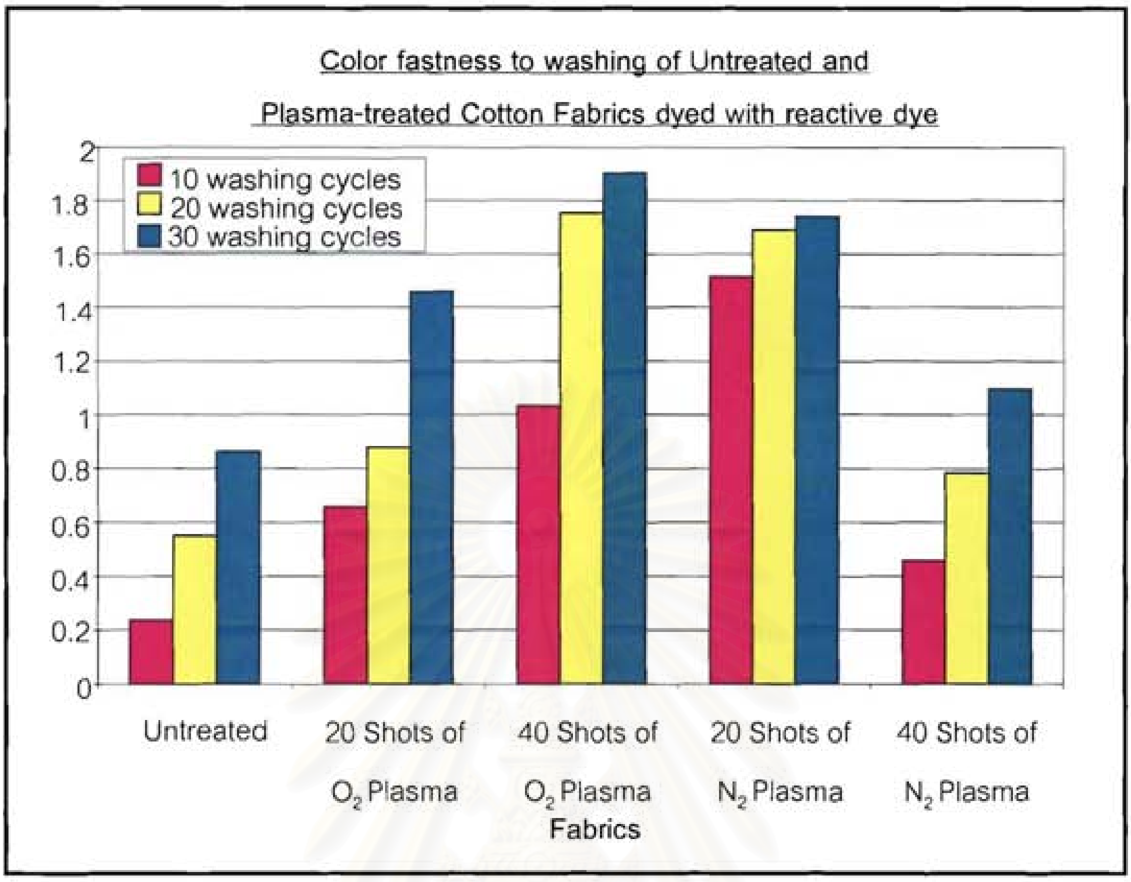

Figure 4.27 DE of untreated and plasma-treated cotton fabrics dyed with reactive dye (Levafix Navy CA gran, supplied by DyStar Thai Ltd.) after washing

The above results suggest that oxygen and nitrogen plasma treatments do not affect wettability and dyeability of cotton fabric since the nature of cotton is already highly hydrophilic. The above results suggest that oxygen and nitrogen plasma treatments do not affect wetting time and dyeability of cotton fabric since the nature of cotton is already highly hydrophilic.

4.2.2.6 Burning Characteristics

Table 4.16 shows the burning characteristics of untreated and plasma-treated cotton fabrics. These results indicate that their characteristics remain unchanged. Therefore, surface modification by oxygen and nitrogen plasma treatments does not affect burning characteristics of cotton fabrics.

Table 4.16 Burning characteristics of untreated and plasma-treated cotton fabrics

Fabrics / Characteristics	untreated	$O_2/20$	$O_2/40$	$N_2/20$	$N_2/40$
Approaching Flame	Ignited readily. Scorched.	Ignited readily. Scorched.	Ignited readily. Scorched.	Ignited readily. Scorched.	Ignited readily. Scorched.
In Flame	Burnt rapidly with yellow flame.	Burnt rapidly with yellow flame.	Burnt rapidly with yellow flame.	Burnt rapidly with yellow flame.	Burnt rapidly with yellow flame.
Out of flame	Continued rapid burning;red afterglow upon extinguishing.	Continued rapid burning;red afterglow upon extinguishing.	Continued rapid burning;red afterglow upon extinguishing.	Continued rapid burning;red afterglow upon extinguishing.	Continued rapid burning;red afterglow upon extinguishing.
Odor	Burning paper	Burning paper	Burning paper	Burning paper	Burning paper
Residue	Light feathery ash,gray to charcoal color.	Light feathery ash,gray to charcoal color.	Light feathery ash,gray to charcoal color.	Light feathery ash,gray to charcoal color.	Light feathery ash,gray to charcoal color.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Surface modification induced on synthetic and natural-fiber fabrics by treatment with high temperature-pulsed plasmas of nitrogen and oxygen gases generated from theta-pinch device using the number of plasma shots of 20 and 40 shots were investigated. From characterizations and testings, surface chemical structure and morphology of all plasma-treated fabrics were influenced by several parameters including the gas types and the number of plasma shots applied. These results can be concluded as follows:

(1) Surface modification of textile fabrics using oxygen and nitrogen plasmas generated from theta-pinch device resulted in the etching of the fabric surface confirmed by SEM photographs and the formation of hydrophilic functional groups on the fabric surface confirmed by ATR-FTIR spectra.

(2) As a consequence of the formation hydrophilic functional groups and an increase in surface roughness caused by etching effect, the enhancement of wettability or hydrophilic characteristic of all plasma-treated fabrics was significantly observed. As the number of plasma shots increased, 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 and colorfastness to washing of plasma-treated fabrics.

(4) Burning characteristics of all plasma-treated fabrics were not affected by oxygen and nitrogen plasma treatments.

(5) When considering all characteristics and properties, the results suggested that 20 shots of nitrogen plasma were suitable for surface modification of PET fabric

while 40 shots of nitrogen plasma were suitable for surface modification of nylon 6 fabric. However, for fabrics which are already highly hydrophilic characteristic such as silk and cotton, oxygen and nitrogen plasma treatments slightly improved or had no effects on the wetting time and dyeability.

5.2 Recommendations

In order to improve other properties of the fabric such as flammability, surface modification of PET, nylon, silk and cotton fabrics using high temperature pulsed-plasma generated from theta-pinch device using other types of gases such as halogen-containing gases should be studied.

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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 PET Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
0	1	690	685	705	690	693	679	683	716	670	690.11	13.72
	2	587	662	706	664	551	699	672	570	649	640.00	56.60
	3	611	674	692	695	560	615	689	667	792	666.11	66.00
	4	610	632	540	668	682	603	550	589	724	622.00	60.95
	5	611	702	686	687	583	620	960	869	721	715.44	123.91
	6	623	525	644	693	555	709	645	555	639	620.89	63.53
	7	677	558	573	669	645	641	681	563	890	655.22	100.92
	Mean	629.86	634.00	649.43	680.86	609.86	652.29	697.14	647.00	726.42		
	S.D.	38.36	67.42	67.43	13.28	61.96	43.01	125.58	114.93	89.36		

Table A2. Data of The Wetting Time of 20 Shots Nitrogen Plasma-treated Polyester Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
20	1	525	660	567	465	369	585	600	684	587	560.22	96.90
	2	304	414	293	456	246	364	449	462	548	392.89	97.92
	3	389	474	474	371	244	353	463	488	498	417.11	84.51
	4	390	580	430	404	290	548	504	549	502	466.33	94.37
	5	360	436	362	354	302	388	491	505	475	408.11	71.19
	6	423	476	449	411	294	387	477	464	347	414.22	62.50
	7	265	361	368	288	209	416	457	392	443	355.44	83.67
	Mean	379.43	485.86	420.43	392.71	279.14	434.43	491.57	506.29	485.71		
	S.D.	84.12	102.20	89.13	61.41	51.94	93.01	51.56	91.79	77.17		

Table A3. Data of The Wetting Time of 40 Shots Nitrogen Plasma-treated Polyester Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
40	1	464	502	520	451	232	498	512	507	518	467.11	91.32
	2	404	448	355	445	198	395	570	391	510	412.89	104.15
	3	414	483	343	326	233	523	406	440	460	403.11	89.43
	4	339	433	427	336	242	240	384	498	490	376.56	95.66
	5	358	359	474	338	292	390	425	422	467	391.67	60.73
	6	232	274	360	340	297	401	312	200	232	294.22	66.31
	7	407	490	372	458	192	288	348	432	346	370.33	91.40
	Mean	374.00	427.00	407.29	384.85	240.86	390.71	422.43	412.86	431.86		
	S.D.	74.54	82.91	68.18	62.45	41.09	101.98	90.63	102.54	105.08		

Table A4. Data of The Wetting Time of 20 Shots Oxygen Plasma-treated Polyester Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
20	1	393	328	350	434	300	459	510	411	418	400.33	66.06
	2	416	464	495	479	258	405	450	466	405	426.44	71.06
	3	412	444	478	515	248	527	515	449	409	444.11	85.74
	4	443	492	554	525	153	418	413	330	368	410.67	120.45
	5	428	455	462	576	176	448	415	456	407	424.78	105.47
	6	551	604	471	523	302	479	512	404	364	467.78	95.49
	7	334	477	567	460	292	475	537	477	541	462.22	92.73
	Mean	425.29	466.29	482.43	501.71	247.00	458.71	478.85	427.57	416.00		
	S.D.	65.53	81.13	71.34	47.49	60.36	40.82	51.64	50.89	59.00		

Table A5. Data of The Wetting Time of 40 Shots Oxygen Plasma-treated Polyester Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
40	1	399	390	393	428	283	343	349	386	358	**369.89**	**42.24**
	2	372	253	348	195	221	257	349	347	416	**306.44**	**76.24**
	3	446	320	360	331	174	338	284	309	362	**324.89**	**72.63**
	4	486	398	372	436	205	308	415	364	449	**381.44**	**84.26**
	5	446	410	326	278	125	318	269	280	352	**311.56**	**92.46**
	6	543	533	417	221	264	275	266	255	282	**339.56**	**124.81**
	7	504	473	469	319	206	338	372	345	439	**385.00**	**95.03**
	Mean	**456.57**	**396.71**	**383.57**	**315.43**	**211.14**	**311.00**	**329.14**	**326.57**	**379.71**		
	S.D.	**59.55**	**92.34**	**47.91**	**93.35**	**53.10**	**33.55**	**57.21**	**47.06**	**58.78**		

Table A6. Data of The Wetting Time of Untreated Nylon Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
0	1	480	500	410	479	460	422	510	525	411	**466.33**	**43.40**
	2	442	443	456	476	491	474	484	443	448	**461.89**	**19.43**
	3	504	404	450	414	423	449	473	431	405	**439.22**	**33.41**
	4	468	445	434	390	410	404	400	414	445	**423.33**	**25.84**
	5	404	497	420	452	441	494	472	408	476	**451.56**	**35.62**
	6	403	454	438	429	471	464	496	440	446	**449.00**	**26.62**
	7	457	466	448	413	470	469	418	416	459	**446.22**	**23.90**
	Mean	**451.14**	**458.43**	**436.57**	**436.14**	**452.29**	**453.71**	**464.71**	**439.57**	**441.43**		
	S.D.	**37.79**	**33.35**	**16.72**	**33.87**	**28.85**	**31.29**	**40.61**	**39.98**	**25.28**		

Table A7. Data of The Wetting Time of 20 Shots Nitrogen Plasma-treated Nylon Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
20	1	262	267	276	246	285	317	261	253	358	280.56	35.76
	2	286	200	233	274	269	201	198	208	277	238.44	37.78
	3	277	208	275	244	257	251	201	322	293	258.67	38.67
	4	324	252	299	293	252	232	205	204	267	258.67	41.55
	5	352	211	279	259	232	214	235	231	251	251.56	43.35
	6	351	270	256	223	277	251	258	223	220	258.78	40.46
	7	286	366	267	223	189	213	288	291	296	268.78	53.53
	Mean	305.43	253.43	269.29	251.71	251.57	239.86	235.14	247.43	280.29		
	S.D.	36.61	57.52	20.63	25.80	32.65	39.07	35.21	44.34	43.06		

Table A8. Data of The Wetting Time of 40 Shots Nitrogen Plasma-treated Nylon Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
40	1	210	252	178	232	181	200	218	219	202	210.22	23.51
	2	116	168	135	125	112	132	161	167	151	140.78	21.63
	3	96	138	195	159	131	182	213	202	189	167.22	38.85
	4	150	172	132	269	97	182	252	153	160	174.11	54.87
	5	87	137	182	200	97	180	194	138	186	155.67	42.51
	6	73	76	155	112	90	133	142	111	196	120.89	40.06
	7	226	166	115	153	96	178	155	146	185	157.78	38.22
	Mean	136.86	158.43	156.00	178.57	114.86	169.57	190.71	162.29	181.29		
	S.D.	60.74	52.85	29.94	57.49	32.29	26.34	39.87	37.39	18.76		

Table A9. Data of The Wetting Time of 20 Shots Oxygen Plasma-treated Nylon Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
20	1	200	245	255	305	285	235	370	298	348	282.33	54.69
	2	220	271	245	244	218	225	225	252	185	231.67	24.70
	3	217	216	193	290	199	195	237	224	212	220.33	29.76
	4	211	265	240	205	255	212	211	324	196	235.44	40.84
	5	203	181	197	169	210	251	204	174	187	197.33	24.59
	6	92	103	135	147	139	113	113	142	182	129.56	27.37
	7	131	97	121	132	89	108	116	120	117	114.56	14.39
	Mean	182.00	196.86	198.00	213.14	199.29	191.29	210.86	219.14	203.86		
	S.D.	49.96	72.87	53.46	68.64	66.72	57.91	86.44	77.60	70.20		

Table A10. Data of The Wetting Time of 40 Shots Oxygen Plasma-treated Nylon Fabrics

Number of plasma shots	Position	Wetting Time (s)										
		I	II	III	IV	Middle	V	VI	VII	VIII	Mean	S.D.
40	1	225	201	227	215	158	218	186	188	245	207	26.44
	2	138	152	156	108	146	148	173	188	138	149.67	22.59
	3	138	108	172	139	125	128	165	145	141	140.11	19.60
	4	154	175	166	176	135	181	72	167	117	149.22	35.73
	5	154	136	115	120	128	138	113	154	124	131.33	15.37
	6	80	139	87	97	75	107	87	127	77	97.33	22.74
	7	122	118	84	95	104	128	98	120	124	110.33	15.44
	Mean	144.43	147.00	143.86	135.71	124.43	149.71	127.71	155.57	138.00		
	S.D.	43.61	32.33	51.63	44.89	27.62	37.75	40.01	27.17	51.66		

Table A11. Data of The Wetting Time of Untreated and Plasma-treated Silk Fabrics

Conditions	The Wetting Time (s)											
	1	2	3	4	5	6	7	8	9	10	**Mean**	**S.D.**
Untreated	29	27	33	38	26	27	26	26	34	32	**29.80**	**4.211**
20 Shots of Oxygen Plasma	22	21	24	32	34	33	27	29	22	23	**26.70**	**4.989**
40 Shots of Oxygen Plasma	20	22	23	24	27	20	26	23	23	22	**23.00**	**2.261**
20 Shots of Nitrogen Plasma	22	28	31	33	32	30	31	26	32	30	**29.50**	**3.410**
40 Shots of Nitrogen Plasma	27	21	22	26	26	23	25	23	24	26	**24.30**	**2.003**

Table A12. 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	2	3	3	3	3	3	3	2	3	2	2.7	0.483
20 Shots of Oxygen Plasma	2	3	3	3	3	3	3	3	2	4	2.9	0.568
40 Shots of Oxygen Plasma	2	2	2	3	3	4	3	2	2	3	2.7	0.675
20 Shots of Nitrogen Plasma	3	3	4	3	3	3	4	2	3	2	3.0	0.667
40 Shots of Nitrogen Plasma	3	3	4	3	3	4	3	2	3	2	3.0	0.667

Appendix B

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

Conditions	Maximum wavelength (nm)	K/S	L*	a*	b*
Untreated	630	4.778	49.020	-0.650	-37.800
	630	4.700	49.540	-1.230	-37.740
	Mean	4.739	49.280	-0.940	-37.770
	S.D.	0.055	0.368	0.410	0.042
20 Shots of Oxygen Plasma	630	2.561	59.950	-4.130	-31.210
	630	3.047	55.120	-3.990	-32.950
	Mean	2.804	57.535	-4.060	-32.080
	S.D.	0.344	3.415	0.099	1.230
40 Shots of Oxygen Plasma	630	4.085	51.260	-4.580	-32.840
	630	4.235	51.620	-4.620	-34.570
	Mean	4.160	51.440	-4.600	-33.705
	S.D.	0.106	0.255	0.028	1.223
20 Shots of Nitrogen Plasma	630	3.189	54.840	-3.800	-34.430
	630	3.568	52.850	-3.340	-33.540
	Mean	3.379	53.845	-3.570	-33.985
	S.D.	0.268	1.407	0.325	0.629
40 Shots of Nitrogen Plasma	630	3.841	52.120	-4.310	-32.990
	630	3.996	51.240	-3.490	-33.400
	Mean	3.919	51.680	-3.900	-33.200
	S.D.	0.237	0.622	0.580	0.290

Table B2. Data of Colorfastness to Washing of Untreated and Plasma-treated PET Fabrics Dyed with Disperse Dyes

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
Untreated	10	1	4.333	50.320	-1.180	-37.220	1.201	4.5
		2	4.406	50.140	-1.160	-37.290	1.009	
		Mean	4.370	50.230	-1.170	-37.255	1.105	
		S.D.	0.052	0.127	0.014	0.049	0.547	
	20	1	3.967	51.180	-1.370	-36.250	2.471	3.5
		2	3.864	51.400	-1.390	-35.990	2.805	
		Mean	3.916	51.290	-1.380	-36.120	2.638	
		S.D.	0.073	0.155	0.014	0.184	0.236	
	30	1	3.788	51.810	-1.440	-36.15	3.046	2.5
		2	3.432	53.410	-2.260	-35.65	4.826	
		Mean	3.610	52.610	-1.850	-35.900	3.936	
		S.D.	0.252	1.131	0.580	0.354	1.259	
20 Shots, O_2 Plasma	10	1	2.692	56.140	-3.000	-32.510	1.804	4.5
		2	2.372	57.620	-3.140	-31.480	1.102	
		Mean	2.532	56.880	-3.070	-31.995	1.453	
		S.D.	0.226	1.046	0.099	0.728	0.909	
	20	1	2.415	57.420	-2.700	-32.240	1.374	4.5
		2	2.540	57.400	-2.940	-32.700	1.287	
		Mean	2.478	57.410	-2.820	-32.470	1.331	
		S.D.	0.088	0.014	0.170	0.325	0.061	
	30	1	2.184	58.900	-3.150	-31.590	1.712	4
		2	2.646	56.700	-2.750	-33.580	2.159	
		Mean	2.415	57.800	-2.950	-32.585	1.936	
		S.D.	0.326	1.555	0.283	1.407	0.316	

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

Conditions	Cycles	Number of Testing	K/S	L^*	a^*	b^*	ΔE	Color Change
40 Shots, O_2 Plasma	10	1	3.254	54.500	-3.870	-33.770	3.147	3.5
		2	3.943	52.470	-3.590	-33.540	1.452	
		Mean	3.599	53.485	-3.730	-33.655	2.299	
		S.D.	0.487	1.435	0.198	0.163	1.198	
	20	1	3.173	54.650	-3.960	-33.180	3.315	3.5
		2	3.718	53.050	-3.260	-35.490	2.752	
		Mean	3.446	53.850	-3.610	-34.355	3.034	
		S.D.	0.385	1.131	0.495	1.633	0.398	
	30	1	3.047	55.350	-3.590	-33.910	4.043	3
		2	3.629	53.490	-3.080	-35.910	3.373	
		Mean	3.338	54.420	-3.335	-34.910	3.708	
		S.D.	0.411	1.315	0.360	1.414	0.474	
20 Shots, N_2 Plasma	10	1	2.964	55.750	-3.350	-34.730	2.057	3.5
		2	3.107	54.850	-2.410	-35.620	2.242	
		Mean	3.036	55.300	-2.880	-35.175	2.145	
		S.D.	0.101	0.636	0.665	0.629	0.131	
	20	1	2.721	56.680	-3.310	-34.090	2.849	3.5
		2	3.153	54.600	-2.210	-35.780	2.375	
		Mean	2.937	55.640	-2.760	-34.935	2.612	
		S.D.	0.305	1.471	0.778	1.195	0.335	
	30	1	2.662	59.980	-3.910	-34.370	6.156	2.5
		2	3.191	54.560	-2.040	-36.270	2.841	
		Mean	2.927	57.270	-2.975	-35.320	4.499	
		S.D.	0.374	3.833	1.322	1.344	2.344	

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

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
40 Shots, N_2 Plasma	10	1	3.050	54.740	-3.220	-32.970	3.143	3
		2	2.854	55.360	-3.110	-33.240	3.764	
		Mean	3.309	53.795	-3.280	-33.255	3.453	
		S.D.	0.366	1.336	0.085	0.403	0.439	
	20	1	2.695	56.140	-3.010	-32.470	4.606	2.5
		2	2.937	55.640	-2.760	-34.935	4.471	
		Mean	2.816	55.890	-2.885	-33.703	4.539	
		S.D.	0.171	0.354	0.177	1.743	0.095	
	30	1	2.927	57.270	-2.975	-35.32	6.050	2.5
		2	2.721	56.680	-3.310	-34.090	5.113	
		Mean	2.824	56.975	-3.143	-34.705	5.581	
		S.D.	0.146	0.417	0.237	0.870	0.662	

Table B5. Data of Color Measurement of Untreated and Plasma-treated Nylon 6 Fabrics Dyed with Acid Dyes

Conditions	Maximum wavelength (nm)	K/S	L*	a*	b*
Untreated	630	15.409	30.160	16.230	-46.530
	630	14.401	31.41	15.360	-46.730
	Mean	14.905	30.785	15.795	-46.63
	S,D.	0.713	0.884	0.615	0.141
20 Shots of Oxygen Plasma	590	15.197	29.880	14.500	-43.980
	590	15.409	29.760	14.910	-44.320
	Mean	15.303	29.820	14.705	-44.150
	S,D.	0.150	0.085	0.290	0.242
40 Shots of Oxygen Plasma	590	15.517	30.410	15.800	-46.620
	590	15.626	30.310	15.830	-46.570
	Mean	15.572	30.36	15.815	-46.595
	S,D.	0.077	0.071	0.021	0.035
20 Shots of Nitrogen Plasma	590	15.355	29.930	15.650	-45.510
	590	15.571	29.840	15.990	-45.900
	Mean	15.463	29.885	15.820	-45.710
	S,D.	0.153	0.064	0.240	0.276
40 Shots of Nitrogen Plasma	590	15.626	29.900	16.290	-46.320
	590	15.409	30.140	15.870	-46.160
	Mean	15.518	30.020	16.080	-46.240
	S,D.	0.153	0.170	0.297	0.113

Table B6. Data of Colorfastness to Washing of Untreated and Plasma-treated Nylon 6 Fabrics Dyed with Acid Dyes

Conditions	Cycles	Number of Testing	K/S	L^*	a^*	b^*	ΔE	Color Change
Untreated	10	1	13.303	33.890	14.340	-48.360	3.841	2.5
		2	12.830	34.680	13.740	-48.540	4.800	
		Mean	13.067	34.285	14.040	-48.450	4.320	
		S.D.	0.344	0.559	0.424	0.127	0.678	
	20	1	11.069	37.230	11.720	-48.270	7.799	1.5
		2	10.334	38.050	10.820	-47.570	8.855	
		Mean	10.705	37.640	11.270	-47.920	8.327	
		S.D.	0.520	0.580	0.636	0.495	0.746	
	30	1	9.355	39.680	9.770	-47.500	10.778	1.5
		2	8.849	40.44	8.860	-46.800	11.889	
		Mean	9.102	40.060	9.315	-47.15	11.334	
		S.D.	0.358	0.537	0.643	0.495	0.785	
20 Shots, O_2 Plasma	10	1	13.142	33.910	12.160	-45.850	5.108	2.5
		2	13.102	34.120	11.990	-45.970	5.401	
		Mean	13.122	34.015	12.075	-45.910	5.255	
		S.D.	0.028	0.1478	0.120	0.085	0.207	
	20	1	10.258	37.740	8.810	-44.530	9.880	1.5
		2	10.490	37.420	9.350	-44.890	9.327	
		Mean	10.374	37.580	9.080	-44.710	9.603	
		S.D.	0.164	0.226	0.382	0.254	0.392	
	30	1	8.303	40.640	6.870	-43.400	13.380	1
		2	8.185	40.800	6.830	-43.390	13.533	
		Mean	8.244	40.720	6.850	-43.395	13.457	
		S.D.	0.083	0.113	0.028	0.007	0.109	

Table B7. Data of Colorfastness to Washing of Untreated and Plasma-treated Nylon Fabrics Dyed with Acid Dyes (Con't)

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
40 Shots, O_2 Plasma	10	1	12.868	34.970	12.720	-48.040	5.738	2.5
		2	12.868	34.890	12.690	-47.940	5.665	
		Mean	12.868	34.930	12.705	-47.990	5.701	
		S.D.	0.000	0.057	0.021	0.071	0.051	
	20	1	10.758	37.720	10.670	-47.540	9.029	1.5
		2	11.186	37.180	11.020	-47.680	8.407	
		Mean	10.972	37.450	10.845	-47.610	8.718	
		S.D.	0.303	0.382	0.247	0.099	0.440	
	30	1	9.355	39.870	9.030	-47.040	11.691	1.5
		2	9.419	39.820	9.040	-47.020	11.643	
		Mean	9.387	39.845	9.035	-47.03	11.667	
		S.D.	0.045	0.035	0.007	0.014	0.033	
20 Shots, N_2 Plasma	10	1	14.307	32.840	14.760	-48.180	3.994	2.5
		2	13.344	33.990	13.370	-47.680	5.171	
		Mean	13.826	33.415	14.065	-47.930	4.583	
		S.D.	0.681	0.814	0.983	0.354	0.832	
	20	1	11.973	36.040	12.060	-47.930	7.547	1.5
		2	10.983	37.300	10.790	-47.320	9.104	
		Mean	11.478	36.670	11.425	-47.625	8.325	
		S.D.	0.700	0.890	0.898	0.431	1.101	
	30	1	9.355	39.840	9.620	-46.890	11.787	1.5
		2	8.966	39.970	8.880	-46.180	12.251	
		Mean	9.161	39.905	9.250	-46.535	12.019	
		S.D.	0.275	0.092	0.523	0.502	0.328	

Table B8. Data of Colorfastness to Washing of Untreated and Plasma-treated Nylon Fabrics Dyed with Acid Dyes (Con't)

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
40 Shots, N_2 Plasma	10	1	14.122	32.980	14.340	-47.700	3.731	2.5
		2	13.766	33.480	13.670	-47.410	4.376	
		Mean	13.944	33.230	14.005	-47.550	4.053	
		S.D.	0.252	0.354	0.474	0.205	0.456	
	20	1	11.489	36.440	11.680	-47.510	7.886	1.5
		2	10.983	37.190	10.830	-47.030	8.921	
		Mean	11.236	36.815	11.255	-47.270	8.404	
		S.D.	0.358	0.530	0.601	0.339	0.732	
	30	1	10.516	37.660	10.750	-47.110	9.356	1.5
		2	9.662	38.880	9.520	-46.300	11.024	
		Mean	10.089	38.27	10.135	-46.705	10.190	
		S.D.	0.604	0.863	0.870	0.573	1.179	

Table B9. Data of Color Measurement of Untreated and Plasma-treated Silk Fabrics Dyed with Acid Dyes

Conditions	Maximum wavelength (nm)	K/S	L*	a*	b*
Untreated	630	8.678	41.890	7.240	-48.230
	630	7.785	42.730	6.550	-46.880
	Mean	8.232	42.310	6.895	-47.560
	S.D.	0.631	0.594	0.487	0.955
20 Shots of Oxygen Plasma	630	8.286	42.130	5.400	-45.790
	630	8.568	41.640	5.650	-45.810
	Mean	8.427	41.890	5.525	-45.800
	S.D.	0.199	0.346	0.177	0.014
40 Shots of Oxygen Plasma	630	8.641	42.310	5.680	-47.210
	630	7.770	43.380	4.870	-46.100
	Mean	8.210	42.845	5.275	-46.655
	S.D.	0.616	0.757	0.573	0.785
20 Shots of Nitrogen Plasma	630	8.772	41.630	6.660	-47.100
	630	8.660	41.700	6.550	-47.100
	Mean	8.716	41.665	6.605	-47.100
	S.D.	0.079	0.049	0.078	0.000
40 Shots of Nitrogen Plasma	630	6.029	45.480	4.430	-44.610
	630	6.586	44.740	4.430	-44.610
	Mean	6.308	45.110	4.430	-44.610
	S.D.	0.394	0.523	0.000	0.000

Table B10. Data of Colorfastness to Washing of Untreated and Plasma-treated Silk Fabrics Dyed with Acid Dyes

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
Untreated	10	1	2.197	57.660	-1.270	-33.570	22.316	1
		2	2.226	57.420	-1.430	-33.360	22.344	
		Mean	2.212	57.540	-1.350	-33.465	22.330	
		S.D.	0.021	0.170	0.113	0.149	0.020	
	20	1	1.204	65.230	-3.710	-26.880	32.712	1
		2	1.172	65.330	-3.620	-26.250	33.085	
		Mean	1.188	65.33	-3.665	-26.565	32.898	
		S.D.	0.023	0.000	0.064	0.445	0.264	
	30	1	0.762	69.920	-4.300	-20.630	40.160	1
		2	0.764	69.970	-4.550	-20.530	40.332	
		Mean	0.763	69.945	-4.425	-20.58	40.246	
		S.D.	0.001	0.035	0.177	0.071	0.121	
20 Shots, O_2 Plasma	10	1	2.495	56.140	-1.630	-34.100	19.777	1
		2	2.313	57.290	-1.770	-34.090	20.676	
		Mean	2.404	56.715	-1.700	-34.095	20.227	
		S.D.	0.129	0.813	0.099	0.007	0.635	
	20	1	1.223	64.870	-4.340	-25.530	32.191	1
		2	1.193	65.150	-4.070	-25.800	32.142	
		Mean	1.208	65.010	-4.205	-25.665	32.166	
		S.D.	0.021	0.198	0.191	0.191	0.035	
	30	1	0.690	71.000	-4.710	-19.150	40.772	1
		2	0.706	70.700	-4.690	-19.290	40.462	
		Mean	0.698	70.850	-4.700	-19.220	40.617	
		S.D.	0.011	0.212	0.014	0.099	0.219	

Table B11. Data of Colorfastness to Washing of Untreated and Plasma-treated Silk Fabrics Dyed with Acid Dyes (Con't)

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
40 Shots, O_2 Plasma	10	1	2.053	58.610	-2.860	-31.470	23.352	1
		2	2.259	57.330	-3.030	-31.590	22.489	
		Mean	2.156	57.970	-2.945	-31.530	22.920	
		S.D.	0.146	0.905	0.120	0.085	0.610	
	20	1	1.115	65.620	-4.880	-22.970	34.392	1
		2	1.054	66.500	-4.960	-23.070	34.937	
		Mean	1.085	66.060	-4.920	-23.020	34.664	
		S.D.	0.043	0.622	0.057	0.071	0.385	
	30	1	0.668	71.030	-5.100	-17.120	42.123	1
		2	0.712	70.420	-5.500	-17.150	41.797	
		Mean	0.690	70.725	-5.300	-17.135	41.960	
		S.D.	0.031	0.431	0.283	0.021	0.230	
20 Shots, N_2 Plasma	10	1	1.884	59.600	-2.180	-31.830	25.140	1
		2	1.972	59.240	-2.490	-32.060	24.855	
		Mean	1.928	59.420	-2.335	-31.945	24.997	
		S.D.	0.062	0.254	0.219	0.163	0.201	
	20	1	0.933	68.090	-4.480	-23.430	37.167	1
		2	0.930	68.480	-4.580	-23.020	37.736	
		Mean	0.932	68.285	-4.530	-23.225	37.452	
		S.D.	0.002	0.276	0.035	0.145	0.201	
	30	1	0.540	73.330	-4.540	-16.670	45.309	1
		2	0.592	72.380	-4.540	-17.410	44.150	
		Mean	0.566	72.850	-4.540	-17.040	44.729	
		S.D.	0.036	0.672	0.000	0.523	0.820	

Table B12. Data of Colorfastness to Washing of Untreated and Plasma-treated Silk Fabrics Dyed with Acid Dyes (Con't)

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
40 Shots, N_2 Plasma	10	1	2.359	57.000	-1.780	-34.010	17.097	1
		2	2.380	56.840	-1.800	-33.930	17.043	
		Mean	2.370	56.920	-1.790	-33.970	17.070	
		S.D.	0.015	0.113	0.014	0.057	0.038	
	20	1	1.161	65.430	-4.020	-25.500	29.146	1
		2	1.159	65.400	-4.090	-25.260	29.304	
		Mean	1.160	65.415	-4.005	-25.380	29.225	
		S.D.	0.001	0.021	0.049	0.170	0.111	
	30	1	0.735	70.230	-4.660	-19.490	36.669	1
		2	0.685	71.010	-4.580	-19.050	37.487	
		Mean	0.710	70.620	-4.620	-19.270	37.078	
		S.D.	0.035	0.551	0.057	0.311	0.578	

Table B13. Data of Color Measurement of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dyes

Conditions	Maximum wavelength (nm)	K/S	L*	a*	b*
Untreated	610	12.177	33.380	-6.420	-20.460
	610	12.212	33.350	-6.420	-20.420
	Means	12.195	33.365	-6.420	-20.440
	S.D.	0.025	0.021	0.000	0.028
20 Shots of Oxygen Plasma	620	11.336	33.980	-6.600	-19.670
	620	11.489	33.830	-6.630	-19.210
	Means	11.413	33.905	-6.615	-19.440
	S.D.	0.108	0.106	0.021	0.325
40 Shots of Oxygen Plasma	610	12.532	32.790	-6.410	-19.900
	610	11.614	33.690	-6.650	-19.650
	Means	12.073	33.240	-6.530	-19.775
	S.D.	0.649	0.636	0.170	0.177
20 Shots of Nitrogen Plasma	620	10.954	33.430	-6.520	-20.290
	620	10.983	33.460	-6.770	-19.610
	Means	10.969	33.445	-6.645	-19.950
	S.D.	0.020	0.021	0.177	0.481
40 Shots of Nitrogen Plasma	620	12.006	33.440	-6.680	-19.840
	620	11.906	33.420	-6.660	-19.660
	Means	11.956	33.430	-6.670	-19.750
	S.D.	0.071	0.014	0.014	0.127

Table B14. Data of Colorfastness to Washing of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dyes

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
Untreated	10	1	11.352	33.410	-6.610	-20.440	0.195	5
		2	11.642	33.120	-6.540	-20.490	0.277	
		Mean	11.497	33.265	-6.575	-20.465	0.236	
		S.D.	0.205	0.205	0.049	0.035	0.058	
	20	1	11.710	33.740	-6.660	-19.970	0.647	5
		2	11.807	33.650	-6.580	-20.130	0.450	
		Mean	11.759	33.695	-6.620	-20.050	0.549	
		S.D.	0.069	0.063	0.057	0.113	0.139	
	30	1	11.458	33.910	-6.540	-19.920	0.763	4.5
		2	11.245	34.240	-6.640	-20.100	0.964	
		Mean	11.352	34.075	-6.590	-20.010	0.863	
		S.D.	0.151	0.233	0.071	0.127	0.142	
20 Shots, O_2 Plasma	10	1	10.954	34.580	-6.860	-19.720	0.771	4.5
		2	11.396	34.110	-6.730	-19.930	0.544	
		Mean	11.175	34.345	-6.795	-19.825	0.657	
		S.D.	0.313	0.332	0.092	0.149	0.161	
	20	1	10.676	34.790	-6.810	-19.690	0.940	4.5
		2	10.758	34.640	-6.760	-19.760	0.815	
		Mean	10.717	34.715	-6.785	-19.725	0.877	
		S.D.	0.058	0.106	0.035	0.049	0.089	
	30	1	10.208	35.420	-6.910	-19.620	1.554	4.5
		2	10.283	35.230	-6.860	-19.630	1.361	
		Mean	10.246	35.325	-6.885	-19.625	1.457	
		S.D.	0.053	0.134	0.035	0.007	0.136	

Table B15. Data of Colorfastness to Washing of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dyes (Con't)

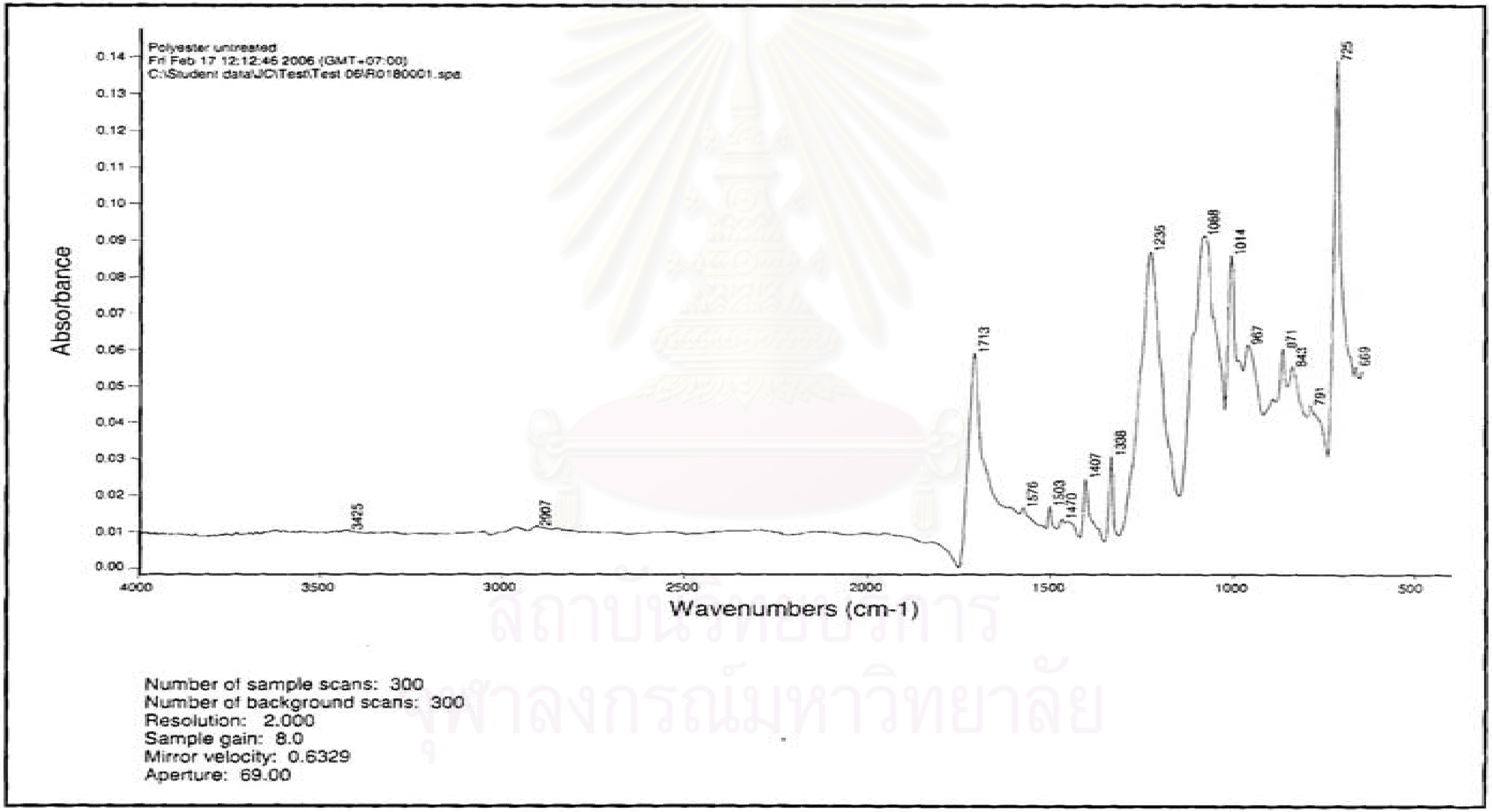
Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
40 Shots, O_2 Plasma	10	1	11.458	34.140	-6.740	-20.050	0.964	4.5
		2	11.305	34.280	-6.780	-20.040	1.102	
		Mean	11.382	34.210	-6.760	-20.045	1.033	
		S.D.	0.108	0.099	0.028	0.007	0.097	
	20	1	10.283	35.140	-6.760	-19.650	1.918	4
		2	10.731	34.800	-6.790	-19.910	1.587	
		Mean	10.507	34.970	-6.775	-19.780	1.753	
		S.D.	0.317	0.240	0.021	0.184	0.234	
	30	1	10.283	35.290	-6.810	-19.620	2.075	4
		2	10.437	34.960	-6.700	-19.730	1.729	
		Mean	10.360	35.125	-6.775	-19.675	1.902	
		S.D.	0.109	0.233	0.078	0.078	0.245	
20 Shots, N_2 Plasma	10	1	10.676	34.950	-6.680	-19.840	1.509	4.5
		2	10.569	34.950	-6.770	-19.81	1.517	
		Mean	10.622	34.950	-6.725	-19.825	1.513	
		S.D.	0.076	0.000	0.064	0.021	0.005	
	20	1	9.684	35.850	-6.890	-19.430	2.473	4
		2	11.157	34.310	-6.820	-19.760	0.903	
		Mean	10.421	35.080	-6.855	-19.595	1.688	
		S.D.	1.042	1.089	0.049	0.233	0.555	
	30	1	10.208	34.980	-6.650	-19.280	1.675	4
		2	10.386	35.25	-6.910	-19.69	1.843	
		Mean	10.297	35.115	-6.780	-19.485	1.759	
		S.D.	0.126	0.191	0.184	0.290	0.119	

Table B16. Data of Colorfastness to Washing of Untreated and Plasma-treated Cotton Fabrics Dyed with Reactive Dyes (Con't)

Conditions	Cycles	Number of Testing	K/S	L*	a*	b*	ΔE	Color Change
40 Shots, N_2 Plasma	10	1	11.427	33.880	-6.630	-19.680	0.457	4.5
		2	11.583	33.870	-6.670	-19.880	0.459	
		Mean	11.505	33.875	-6.650	-19.780	0.458	
		S.D.	0.071	0.014	0.014	0.127	0.001	
	20	1	10.841	34.570	-6.730	-19.720	1.142	4.5
		2	11.427	33.760	-6.610	-19.490	0.424	
		Mean	11.134	34.165	-6.670	-19.605	0.783	
		S.D.	0.141	0.573	0.085	0.163	0.507	
	30	1	10.926	34.260	-6.670	-19.440	0.886	4.5
		2	10.704	34.710	-6.820	-19.560	1.303	
		Mean	10.815	34.485	-6.745	-19.500	1.094	
		S.D.	0.157	0.318	0.106	0.085	0.295	

Appendix C

1. ATR-FTIR Spectra of untreated PET fabric



Polyester untreated
Fri Feb 17 12:12:46 2006 (GMT+07:00)
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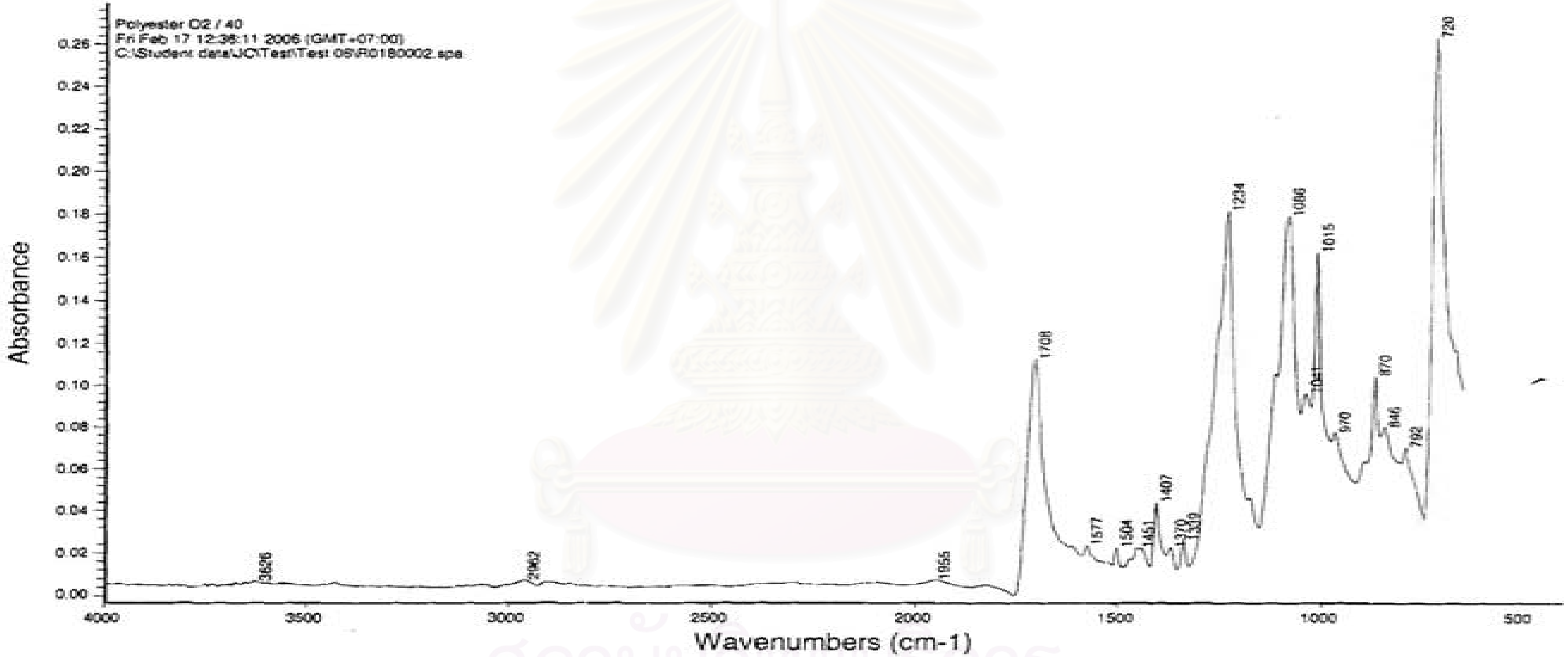
Number of sample scans: 300
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

2. ATR-FTIR Spectra of oxygen plasma-treated PET fabric for 40 shots



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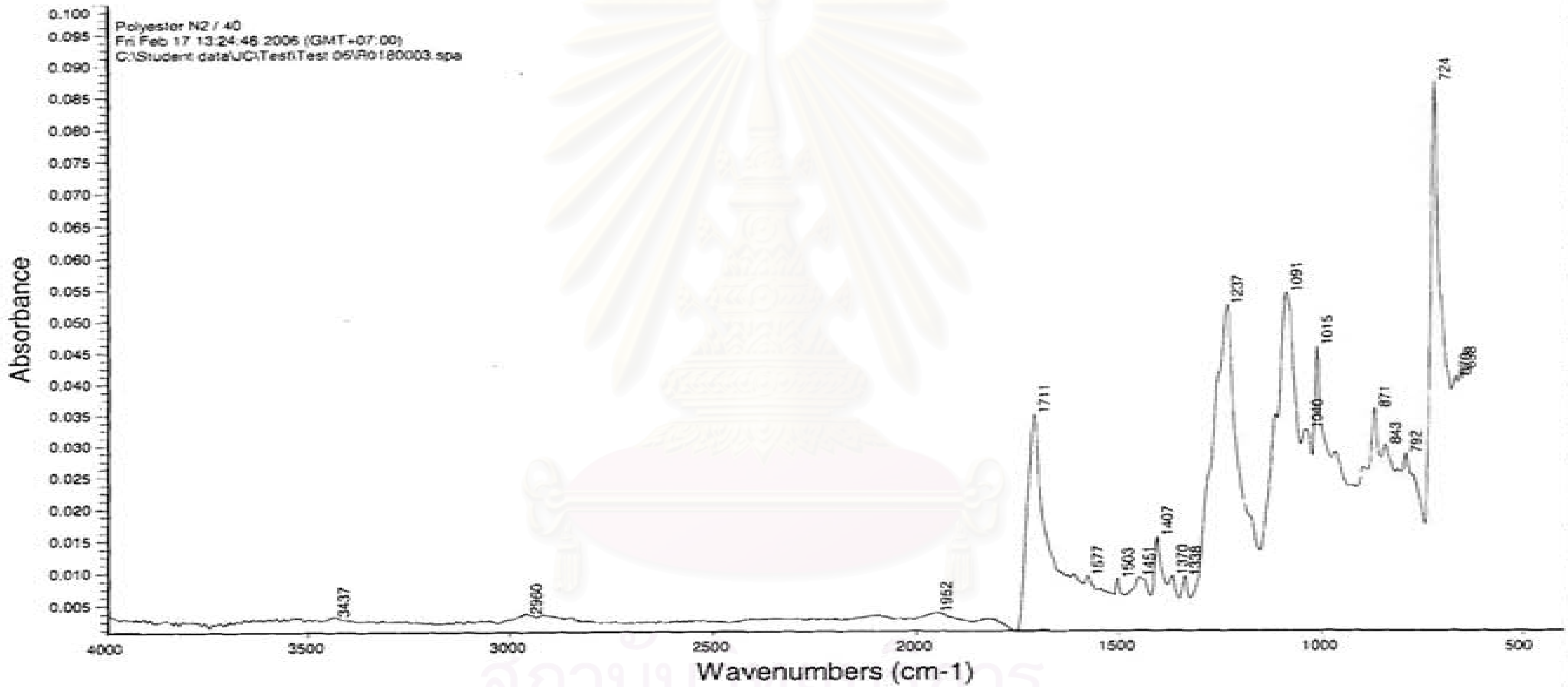
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

3. ATR-FTIR Spectra of nitrogen plasma-treated PET fabric for 40 shots



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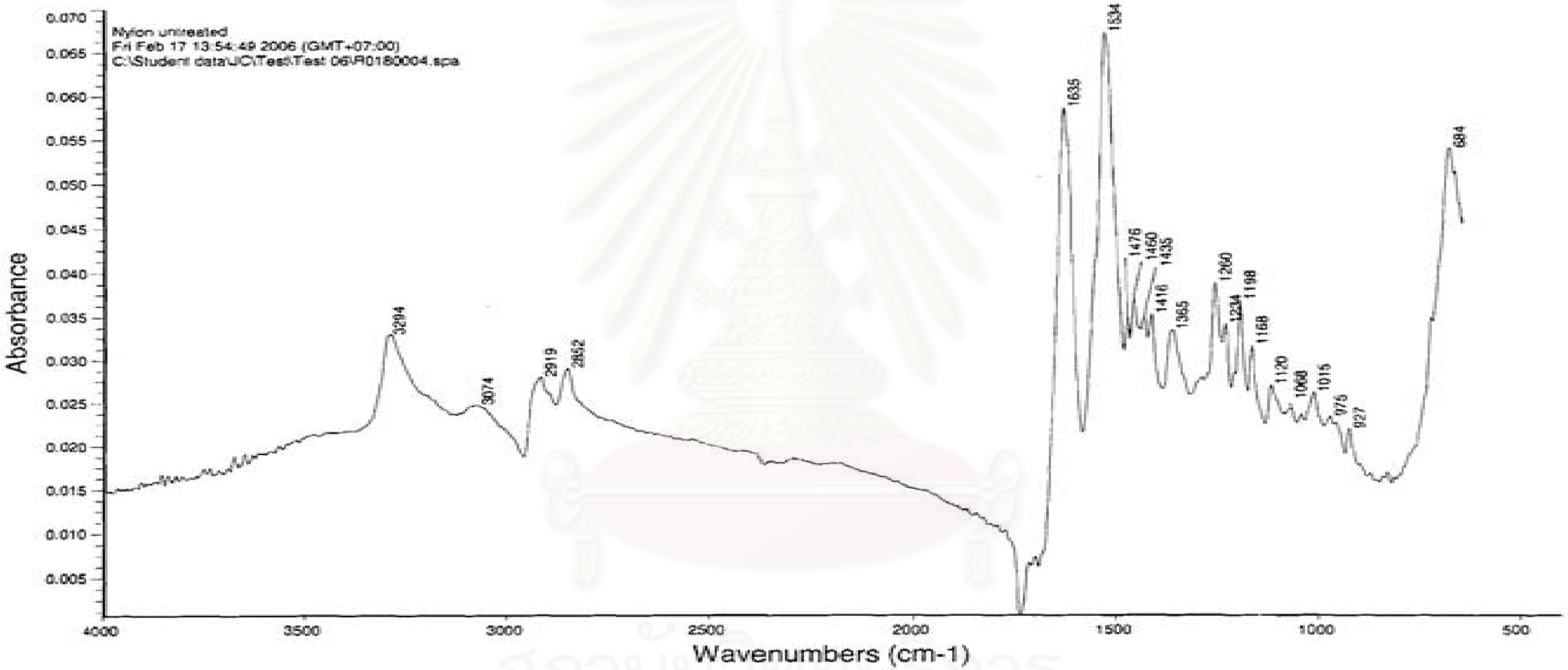
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

4. ATR-FTIR Spectra of untreated nylon 6 fabric



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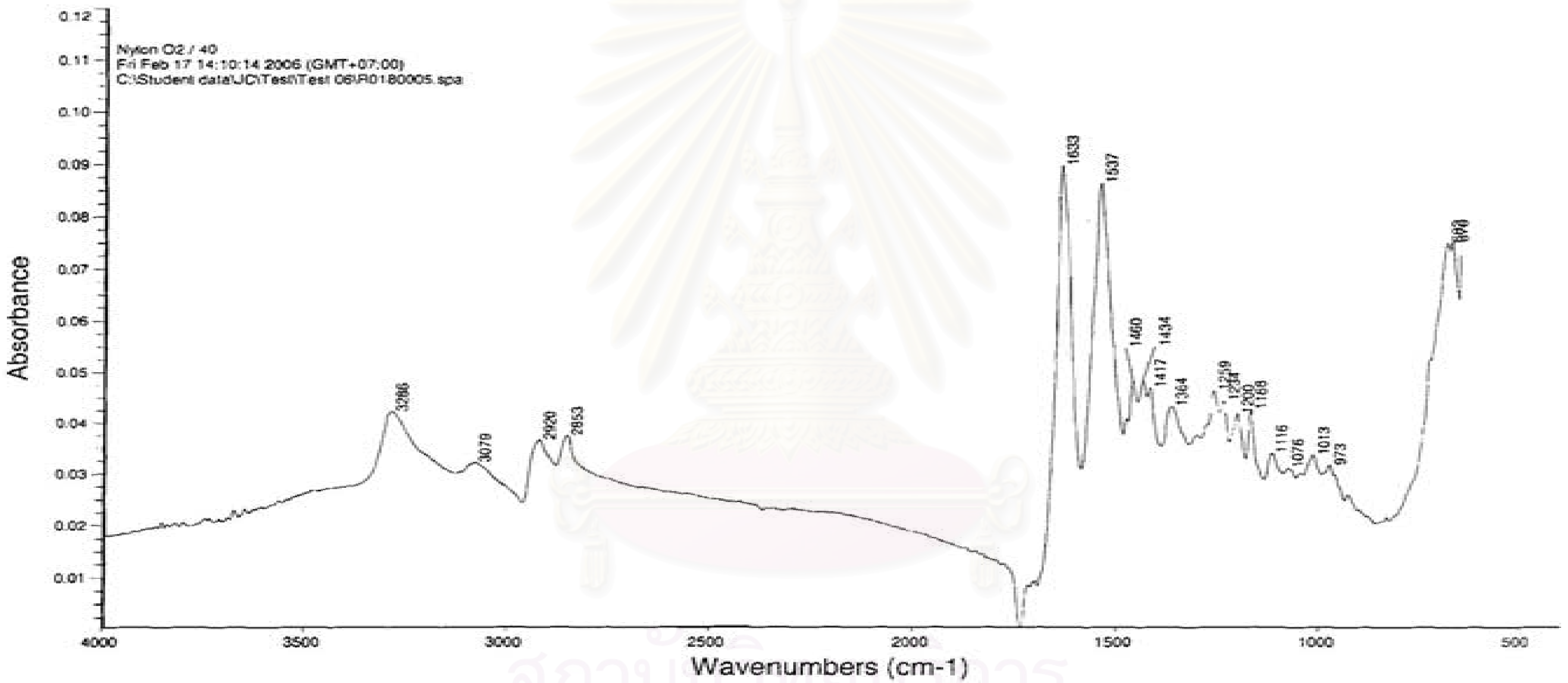
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

5. ATR-FTIR Spectra of oxygen plasma-treated nylon 6 fabric for 40 shots



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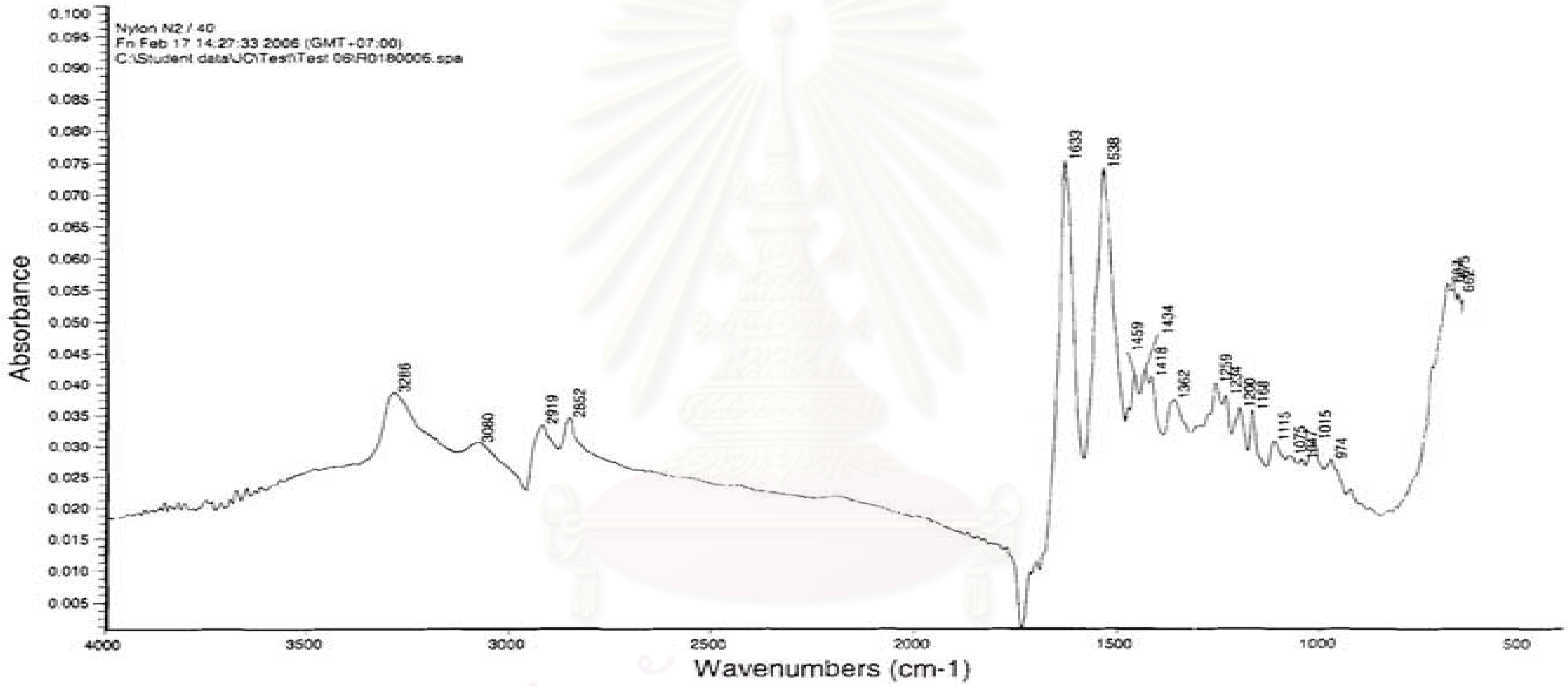
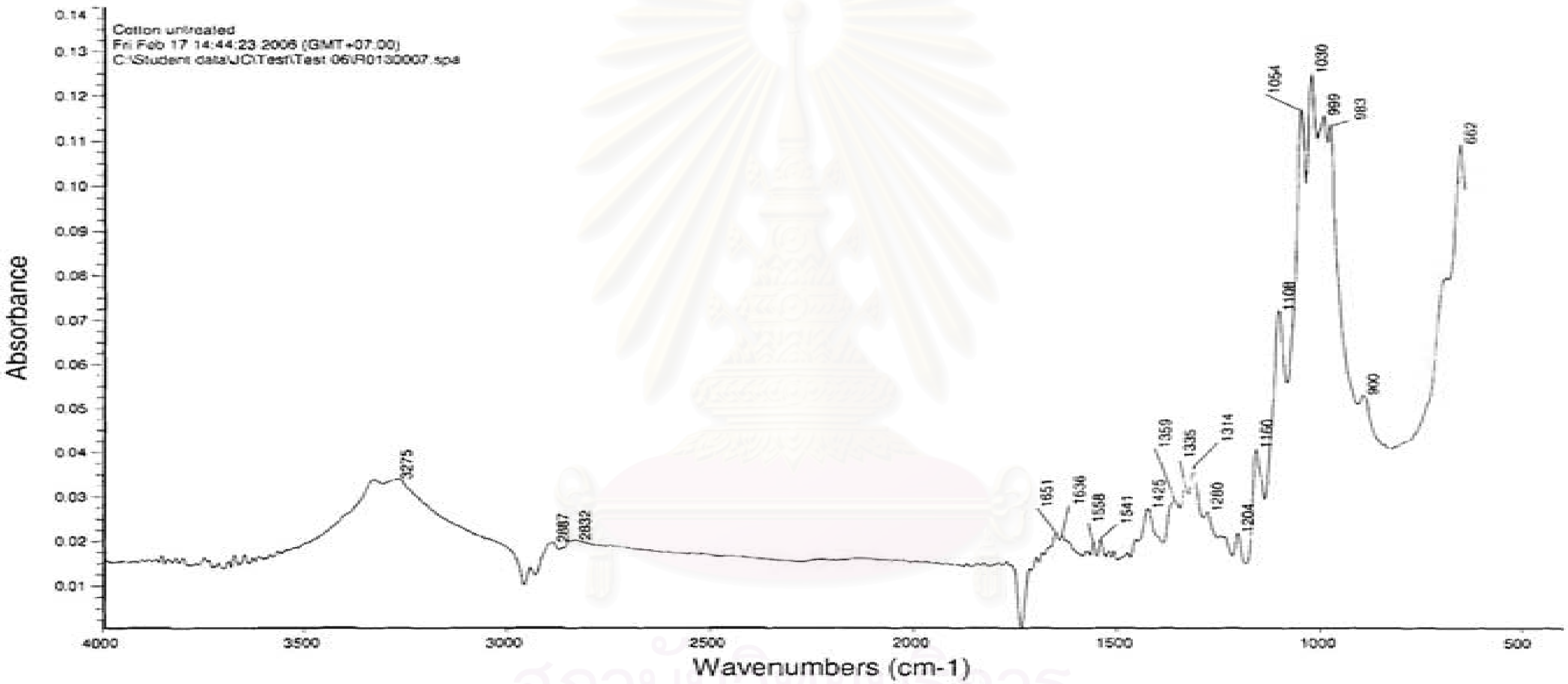
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

6. ATR-FTIR Spectra of nitrogen plasma-treated nylon 6 fabric for 40 shots



Number of sample scans: 300
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

7. ATR-FTIR Spectra of untreated cotton fabric



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Number of background scans:  300
Resolution:   2.000
Sample gain:  8.0
Mirror velocity:  0.6329
Aperture:  69.00
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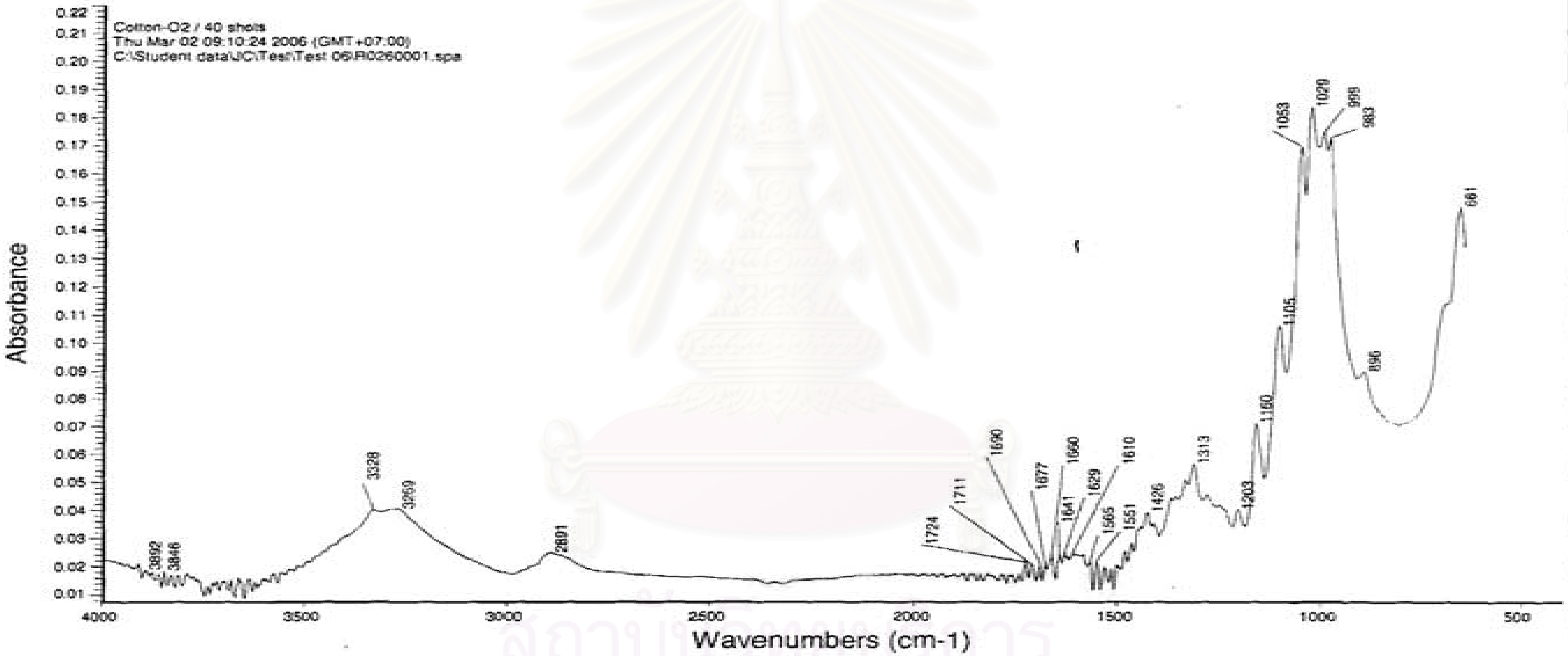
8. ATR-FTIR Spectra of oxygen plasma-treated cotton fabric for 40 shots



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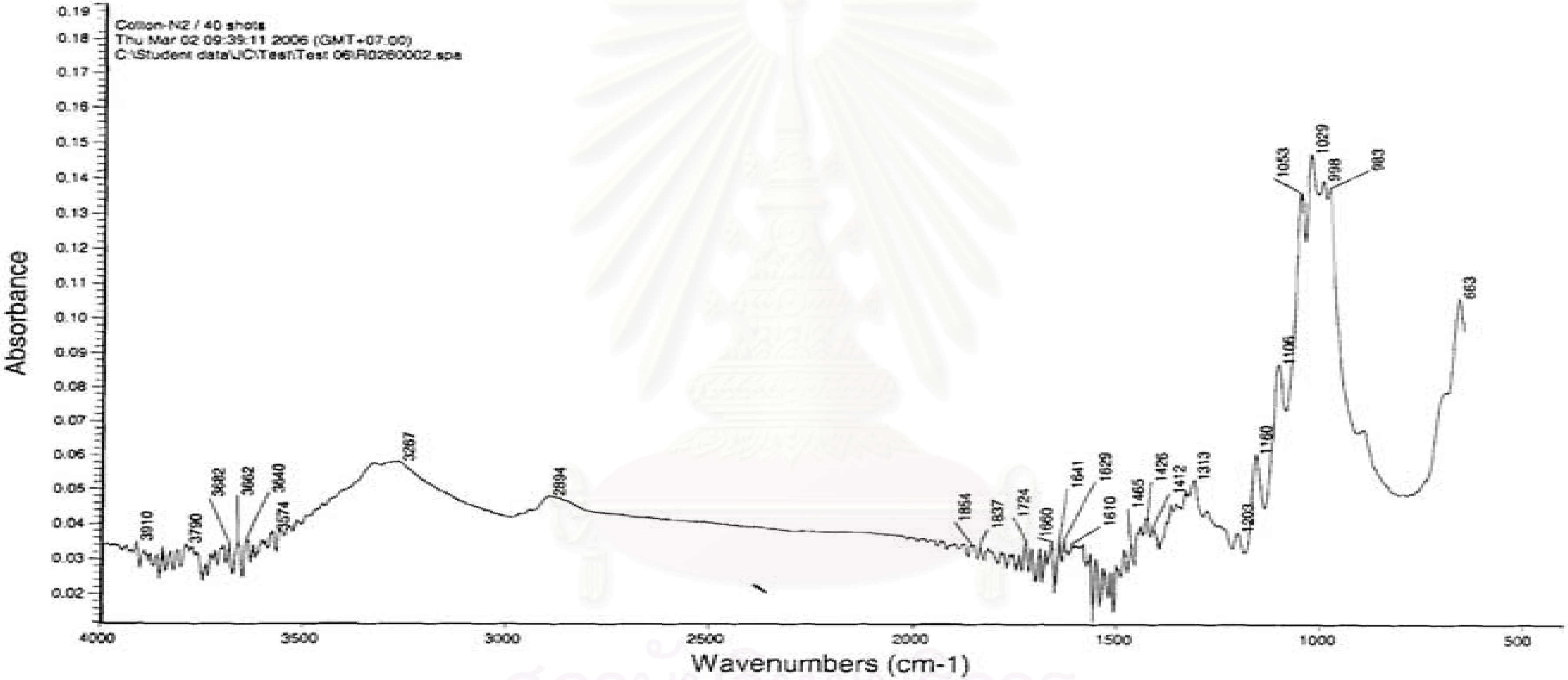
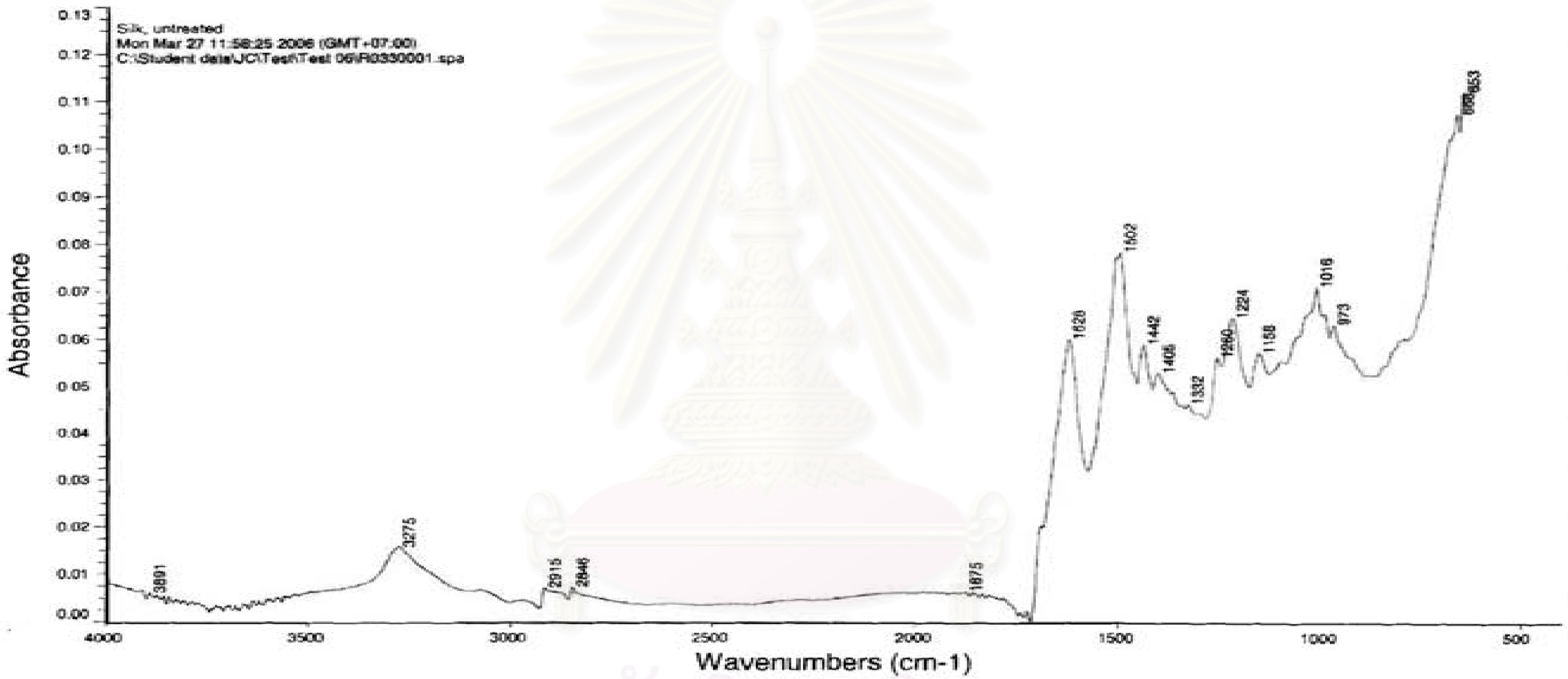
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

9. ATR-FTIR Spectra of nitrogen plasma-treated cotton fabric for 40 shots



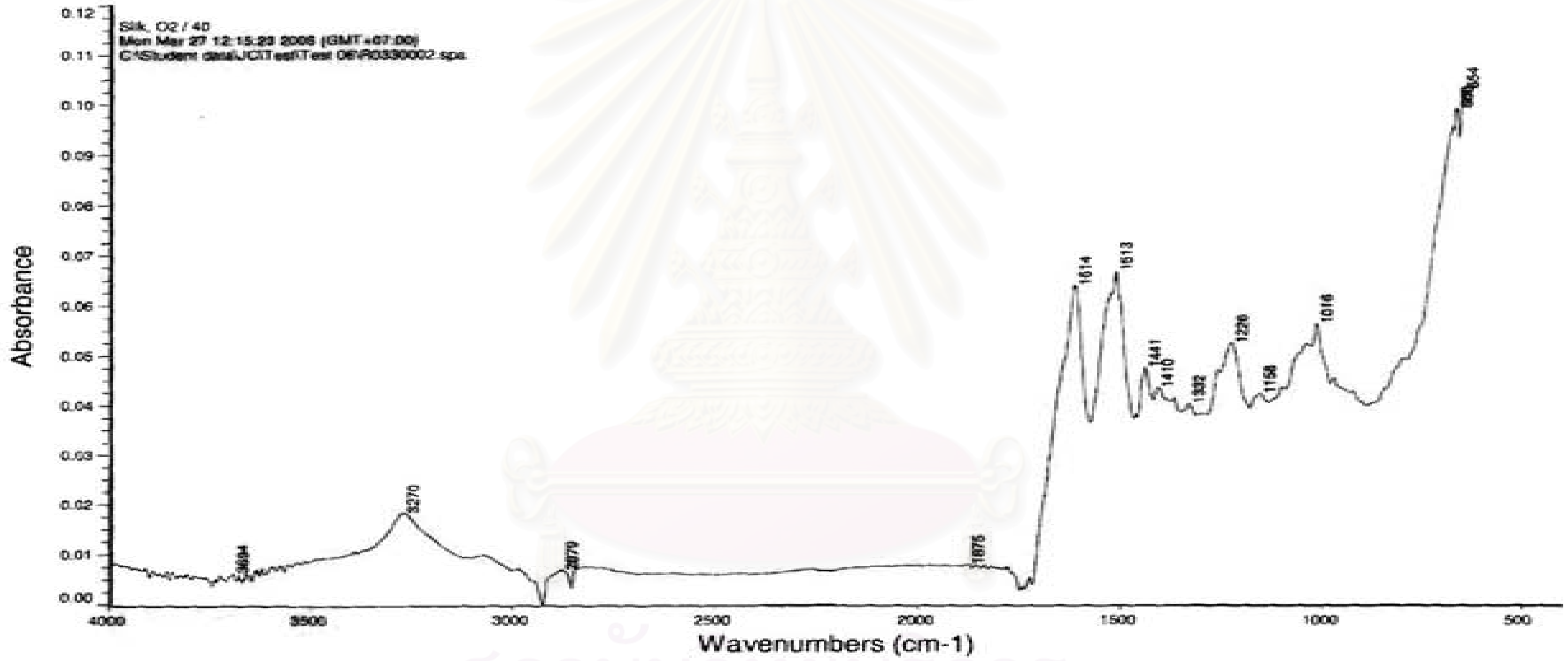
Number of sample scans: 300
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

10. ATR-FTIR Spectra of untreated silk fabric



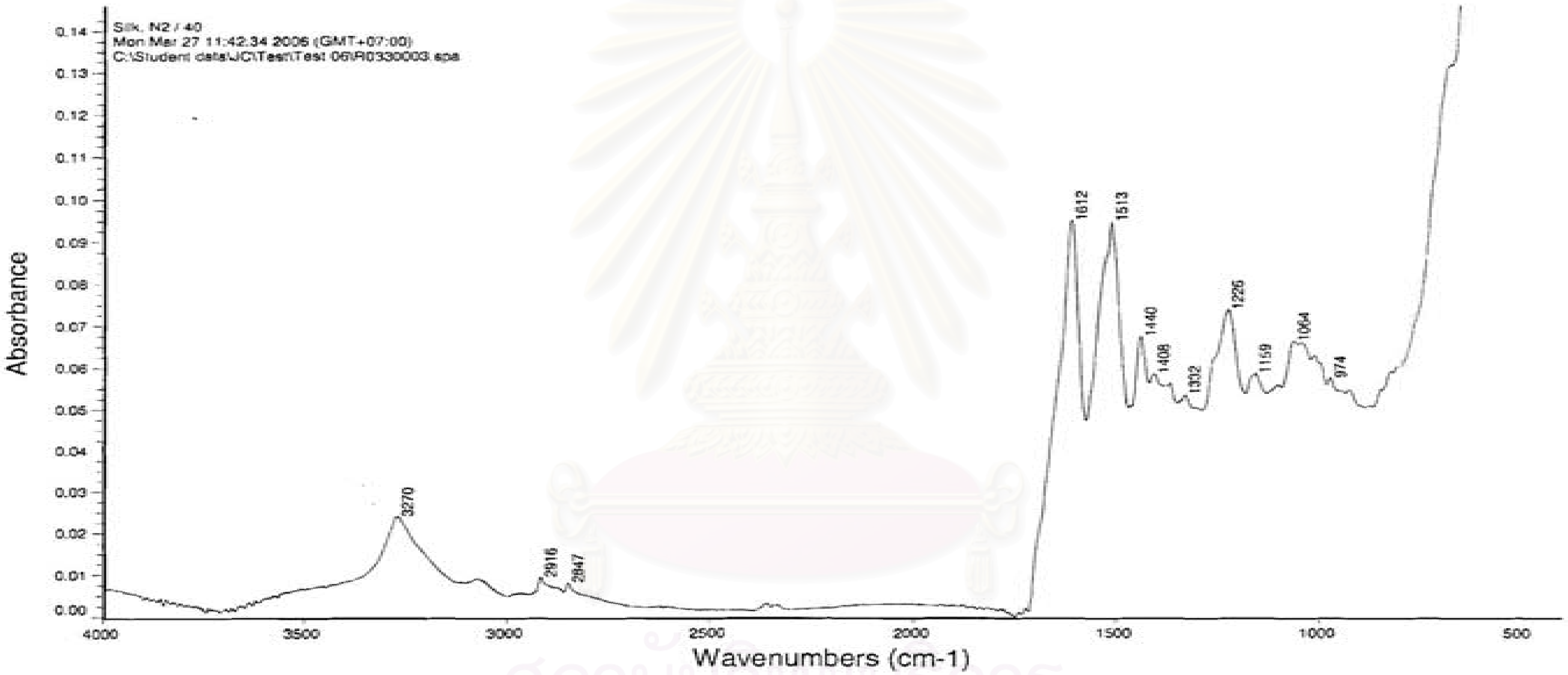
Number of sample scans: 300
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

11. ATR-FTIR Spectra of oxygen plasma-treated silk fabric for 40 shots



Number of sample scans: 300
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

12. ATR-FTIR Spectra of nitrogen plasma-treated silk fabric for 40 shots



Number of sample scans: 300
Number of background scans: 300
Resolution: 2.000
Sample gain: 8.0
Mirror velocity: 0.6329
Aperture: 69.00

VITA

Miss Parnnapa Khaymapanya was born on November 9, 1981 in Chumsaeng, Nakhonsawan, Thailand as a daughter of Tragoon Khaymapanya and Rattana Khaymapanya. She graduated from Chumsaeng Chanutid School in March 2000 and received a Bachelor of Science degree with a major in Industrial Chemistry from King Monkut Institute of Technology Ladkrabang in March 2004. 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 2004.