การเตรียมฟิล์มพอลิเอทิลีนเทเรฟแทเลตที่อัดซ้อนแบบปราศจากกาวโดยการดัดแปรด้วยพลาสมา

นางสาวอรุณศรี งามอรุณโชติ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ภาควิชาวัสดุศาสตร์
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PREPARATION OF ADHESIVE FREE LAMINATED POLY(ETHYLENE TEREPHTHALATE) FILMS BY PLASMA MODIFICATION

Miss Aroonsri Ngamaroonchote

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Applied Polymer Science and Textile Technology
Department of Materials Science
Faculty of Science
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Thesis Title	Preparation of Adhesive Free Laminated Poly(ethylene terephthalate) Films By Plasma Modification
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Field of Study	Applied Polymer Science and Textile Technology
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อรุณศรี งามอรุณโชติ : การเตรียมฟิล์มพอลิเอทิลีนเทเรฟแทเลตที่อัดซ้อนแบบปราศจากกาวโดยการดัดแปรด้วยพลาสมา. (PREPARATION OF ADHESIVE FREE LAMINATED POLY(ETHYLENE TEREPHTHALATE) FILMS BY PLASMA MODIFICATION) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.วิมลวรรณ พิมพ์พันธุ์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร.รัฐชาติ มงคลนาวิน, 95 หน้า.

งานวิจัยนี้เป็นการเตรียมฟิล์มพอลิเอทิลีนเทเรฟแทเลต (เพ็ต) ที่อัดซ้อนแบบปราศจากกาวโดยการดัดแปรฟิล์มเพ็ตด้วยพลาสมาแบบห้วงที่กำเนิดจากเครื่องทีตาพินช์ ก่อนนำไปขึ้นรูปด้วยการอัดแบบกับฟิล์มเพ็ตเมทัลไลซ์ที่อุณหภูมิ 220°C โดยมีการศึกษาหาภาวะที่เหมาะสมในการดัดแปร ด้วยการปรับเปลี่ยนจำนวนครั้งในการยิงพลาสมาเป็น 5 10 15 และ 20 ครั้ง รวมทั้งใช้แก๊สในการดัดแปร 3 ชนิด คือ ไนโตรเจน ออกซิเจน และอาร์กอน จากผลการทดลอง พบว่า ค่ามุมสัมผัสของน้ำของฟิล์มที่ผ่านการดัดแปร มีค่าต่ำกว่าของฟิล์มที่ไม่ได้ผ่านการดัดแปร (ต่ำกว่า 72 องศา) แสดงว่ามีสมบัติชอบน้ำเพิ่มขึ้นอันเนื่องมาจากการเกิดหมู่ฟังก์ชันที่ชอบน้ำขึ้นบนพื้นผิวของฟิล์ม ซึ่งสามารถยืนยันได้จากเทคนิคเอทีอาร์-เอฟทีไออาร์สเปกโทรสโกปี อย่างไรก็ตาม พบว่า เมื่อเก็บฟิล์มไว้เป็นระยะเวลา 7 และ 14 วัน ค่ามุมสัมผัสกลับมีค่าเพิ่มขึ้น นอกจากนี้ ยังพบว่าการดัดแปรด้วยพลาสมาไม่ส่งผลต่อค่าความขุ่นของฟิล์ม สำหรับผลการวิเคราะห์ด้วยเทคนิคอะตอมมิกฟอร์ซไมโครสโกปี แสดงให้เห็นว่า พื้นผิวฟิล์มภายหลังการดัดแปรมีค่าเฉลี่ยความขรุขระลดลง นอกจากนี้ ฟิล์มที่ผ่านการดัดแปรด้วยพลาสมาไนโตรเจนมีความทนแรงดึงไม่ต่างจากฟิล์มที่ไม่ได้ผ่านการดัดแปร ในขณะที่ฟิล์มที่ผ่านการดัดแปรด้วยพลาสมาออกซิเจนและพลาสมาอาร์กอนมีความทนแรงดึงลดลงเล็กน้อย สำหรับฟิล์มอัดซ้อนที่เตรียมจากฟิล์มที่ผ่านการดัดแปรนั้นมีสมบัติด้านแรงดึงและด้านการยึดติดสูงกว่าฟิล์มอัดซ้อนที่เตรียมจากฟิล์มที่ไม่ได้ผ่านการดัดแปร โดยภาวะที่เหมาะสมที่สุดในการดัดแปรคือ การใช้พลาสมาออกซิเจน ที่จำนวนครั้งในการยิง 5 ครั้ง ซึ่งจะทำให้ได้ฟิล์มอัดซ้อนที่มีสมบัติเชิงกลโดยรวมดีกว่าการใช้ภาวะอื่น

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต...
สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์
และเทคโนโลยีสิ่งทอ ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก...........................
ปีการศึกษา 2552 ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์ร่วม.......................

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KEYWORDS : PULSED PLASMA / POLY(ETHYLENE TEREPHTHALATE) / ADHESION / LAMINATE / THETA-PINCH

AROONSRI NGAMAROONCHOTE : PREPARATION OF ADHESIVE FREE LAMINATED POLY(ETHYLENE TEREPHTHALATE) FILMS BY PLASMA MODIFICATION. THESIS ADVISOR : ASSOC.PROF.VIMOLVAN PIMPAN, Ph.D. THESIS CO-ADVISOR : ASST.PROF.RATTACHAT MONGKOLNAVIN, Ph.D., 95 pp.

In this research, adhesion free laminated poly(ethylene terephthalate) or PET films were prepared by surface modification of PET film using high temperature pulsed plasma generated from theta-pinch device before compression with metallized PET film at 220°C. In order to determine the optimum condition for the treatment, the number of plasma shot were varied as 5, 10, 15 and 20 shots. In addition, three types of gas including nitrogen, oxygen and argon were used. It was found that the water contact angles of the treated films were lower than 72° of the untreated PET film. Increasing wettability of treated film indicated the formation of hydrophilic groups on the film surface as confirmed by ATR-FTIR. However, when the films were stored for 7 and 14 days, the contact angle increased. Furthermore, plasma treatment did not significantly affect the haze of the films. AFM analysis revealed that after plasma treatment, average roughness of the film surface slightly decreased. It was also found that tensile strength of nitrogen plasma-treated PET films was comparable to that of the untreated film, while those of oxygen and argon plasma-treated PET films slightly decreased. Tensile properties and adhesion strength of plasma-treated laminated films were higher than those of laminated film prepared from the untreated one. Optimum condition for the treatment was to use oxygen plasma at 5 shots in order to achieve the laminated film having overall mechanical properties better than using other conditions.

Department: Materials Science Student's Signature………………...
Field of Study: Applied Polymer Science and
Textile Technology Advisor's Signature………………...
Academic Year: 2009 Co-Advisor's Signature……………

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CHAPTER I

INTRODUCTION

Laminated films have been increasingly used in many industries especially in packaging applications due to their specific properties derived from each type of materials presented in each layer. All layers can be adhered together by several methods such as using an adhesive or surface-activation by chemical and physical processes. In the former case, because most adhesives used generally consist of organic solvents as one of the main ingredients, these solvents are needed to evaporate for solidification of the adhesive causing the toxicity in the environment. On the other hand, surface-activation by chemical process can generate great amounts of wastes while some physical treatments can lead to the degradation of polymers. Therefore, new method such as plasma treatment is currently in the focus for substituting conventional lamination process.

Plasma treatment has been increasingly employed in surface modification of many polymers since it is environmental friendly process and it can modify the surface of these polymers without changing their bulk properties in a short period of time using inert gas or monomer in gas form. The surface energy of a polymer film can be increased by selecting a suitable treatment condition. This can lead to better adhesion of the treated film.

Poly(ethylene terephthalate) generally known as “PET” is one of the commercial polymers widely used in laminated films for packaging. This is because PET has many excellent properties such as barrier property, mechanical properties, optical property and thermal properties. However, due to its low surface energy, it is difficult to laminate PET film with the films having higher surface energy such as metallized PET film. Therefore, the improvement of surface adhesion of PET film by plasma treatment in order to prepare adhesive free laminated PET film is the aim of this research. Previously, surface modifications of polymers by plasma treatment mostly emphasize on using continuous plasma generating processes [1-3]. On the contrary, in this research, a new approach for surface modification of PET film by high temperature pulsed plasma generated from theta-pinch device is used instead. Since the plasma is generated in pulse, it is easier to control plasma exposure on the polymer surface than using conventional continuous plasma. The type of gases and the number of plasma shots are varied in order to determine the optimum condition for plasma treatment. All plasma-treated PET films are laminated with metallized PET film by compression molding. Chemical structures of plasma-treated PET films are characterized by Attenuated total reflection/Fourier transform infrared spectroscopy (ATR/FT-IR). Atomic force microscopy (AFM) is employed in order to study the morphology of plasma-treated PET film. Wettability and Haze are investigated by water contact angle and haze measurement, respectively. Moreover, adhesion property of laminated films is studied by tensile test and adhesion test.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Laminated films

The performance requirements include product protection, speed and ease of packing and sealing, together with printing, handling and storage requirements are necessary for packaging applications. An individual polymer cannot meet all these requirements; therefore, multilayer films based on more than one type of polymers have been prepared by extrusion of selected layers onto the existing films or adhering the existing films together. This process is called lamination. Most of the layers are polymers, but a metal foil (usually aluminium) may be used. Paper or paperboard is frequently used as a substrate for lamination. A textile layer may be used, but the products are mainly classified separately from laminated films [4].

A basic requirement but very important for a laminated film is good adhesion between the layers. The materials used to make these layers are often chemically different in order to provide the diversity of properties; however, the adhesion may not be suitable. In such cases, a separated adhesive layer must be applied between the functional layers. This adhesive layer acts in the same way as a compatibiliser in polymer blends. A copolymer is often used, where each of the component monomers contributes to the adhesion with one of the adjacent layers. Some multilayer films are produced with the adhesion component included as a blend with a functional layer. In this way, the number of individual layer is reduced, simplifying the lamination process [4].

The separated layers of the film may consist of the same polymer but in different forms. A layer could be mineral-filled, pigmented, foamed, oriented, radiated or chemically crosslinked, filled with antioxidant or ultraviolet stabilizers, printed or otherwise modified. A further protective layer may then be placed over the modified layer, or the modified layer may be the protective layer [4].

The laminated film often have superior gloss such as when polypropylene is laminated onto printed paper substrates. Surface spreading by the coating layer and film thickness is easier to control by laminating than by solution coating.

2.2 Lamination process

The method that combines sheets or films by bonding them together are called lamination process [5]. This process is widely used for food packaging where paper or paperboard, plastic films, cellophane, and aluminum foil are combined with one another. The bonding is usually accomplished by thermal or chemical methods with adhesives and curing systems, facilitated by pretreatment such as corona discharge.

2.2.1 Thermal and hot melt lamination

Thermal lamination process [5] as shown in Figure 2.1 employs two sheets or films, one of which is pretreated with a thermoplastic adhesive. Adhesives most commonly used is ethylene vinyl acetate (EVA) which has good thermal stability and good adhesion. The sheets or films are heated before pressing them together using two nip rolls which provides the force needed to establish intimate contact required for bonding. After cooling, the adhesive solidifies resulting in a permanent bonding between the layers of laminated sheets or films.

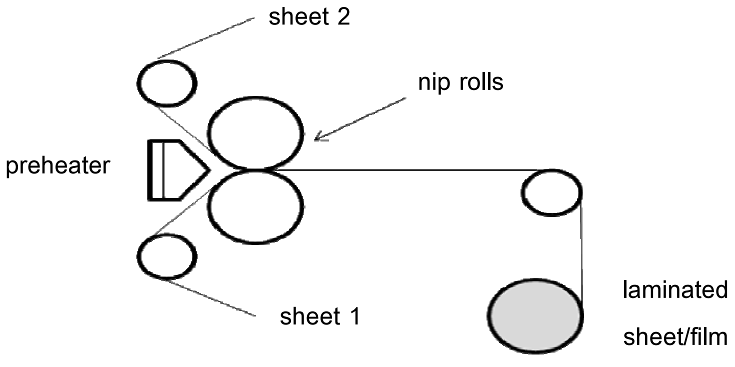


Figure 2.1 Thermal lamination process

Conditions for thermal lamination are determined by the composition and thermal properties of the sheets or films to be joined and the properties of the adhesive.

Common pairs of sheets or films for thermal lamination include plastic films, and aluminum foil to be joined with heat seal coated film, cellophane or paper.

2.2.2 Wet bond and dry bond laminations

In wet bond lamination [5], water or organic solvent-based adhesive is used. Adhesive is still wet at the time of joining and dried later, thus one of the sheets or films must be porous in order to allow evaporation of water or solvent in adhesive. The examples of the porous sheet are paper and non-woven fabric. As shown in Figure 2.2, first sheet such as plastic film or foil is coated with an adhesive and then joined under pressure with second porous sheet. The sheets are pressed by two nip rolls and dried.

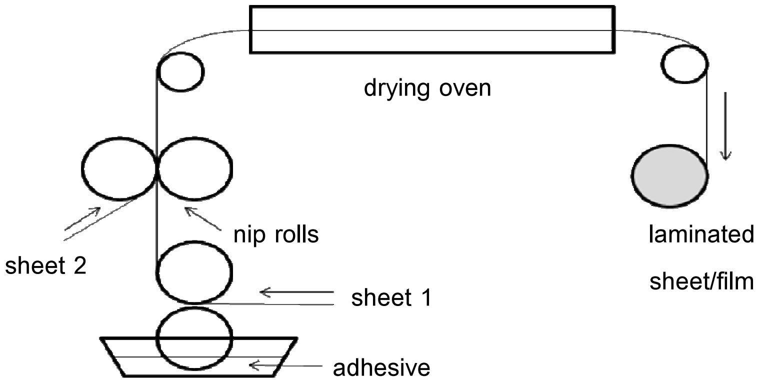


Figure 2.2 Wet bond lamination process

In dry bond lamination, as shown in Figure 2.3, a solvent-based adhesive is coated onto one of the sheets or films by a roller system, and then coated sheet or film is entered drying oven in order to remove solvent in adhesive before joining under pressure of this sheet and second sheet via two nip rolls.

Dry bond lamination can be used with wider range of substrates because the sheet is not needed to be porous unlike in wet bond process. However, the use of organic solvent-based adhesives has been abandon due to legal limitation in releasing volatile component.

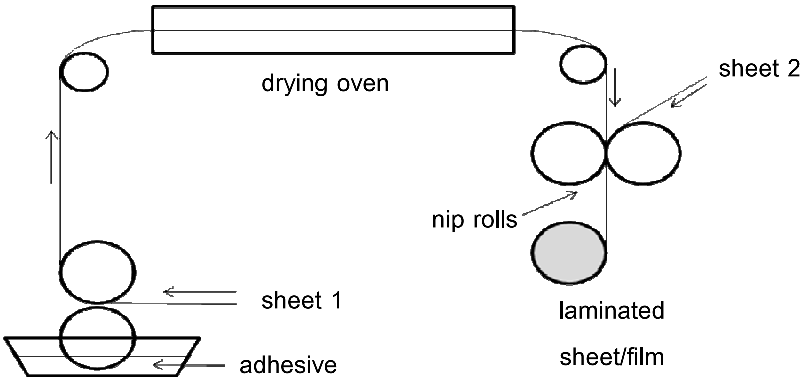


Figure 2.3 Dry bond lamination process

2.2.3 Solventless lamination

Solventless lamination [5] is a process which bonds together two sheets or films by curing in the absence of any solvent. It has been developed rapidly and now becomes important lamination method in commercial use.

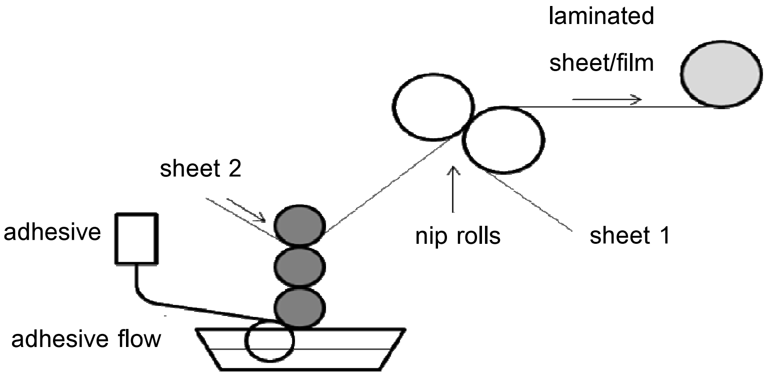


Figure 2.4 Solventless lamination process

A reactive chemical system either single or two-component is used to cure the adhesive. Because the adhesive layer is formed by curing (polymerization), it releases neither solvents nor water, although small amount of carbon dioxide gas may be emitted as a by-product, making their use in laminating high barrier films difficult since the gas interferes with bonding [6].

Single-component urethanes are the most widely-used systems. In these systems, water is needed to complete the reaction. Water reacts with polyester isocyanate prepolymers to produce first an amine and carbon dioxide.

Isocyanate + water → *amine + carbon dioxide* ↑

The amine reacts further with another isocyanate group to produce a polyurea which reacts with more isocyanate thereby increasing the molecular weight.

Solventless system for laminating of film-to-film, foil or paper is shown in Figure 2.4. Adhesive is applied to sheet 2 and brought into join with sheet 1 by pressing them together through two nip rolls. Adhesives may be heated to high temperatures, e.g. 104°C, to bring viscosities into an acceptable range of 500-2000 centipoise (0.5-2.0 Pa•s). A smooth-roll metering system, the four-roll stack reduces the adhesive into successively thinner layers prior to application. Rolls in the stack are alternately steel and rubber. Their function is to control with great accuracy the thickness of adhesive film produced. Since this process no have solvents to remove, drying is not necessary.

2.3 Poly(ethylene terephthalate) film

Poly(ethylene terephthalate) or PET is formed by condensation polymerization of ethylene glycol and terephthalic acid or dimethyl terephthalate. Its chemical structure and the polycondensation stage of PET production [7] are shown in Figures 2.5 and 2.6, respectively.

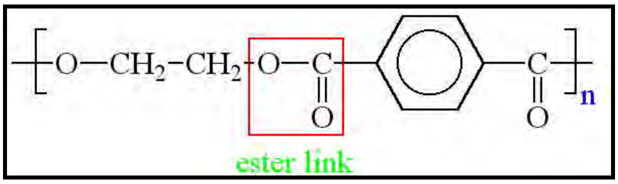


Figure 2.5 Chemical structure of PET

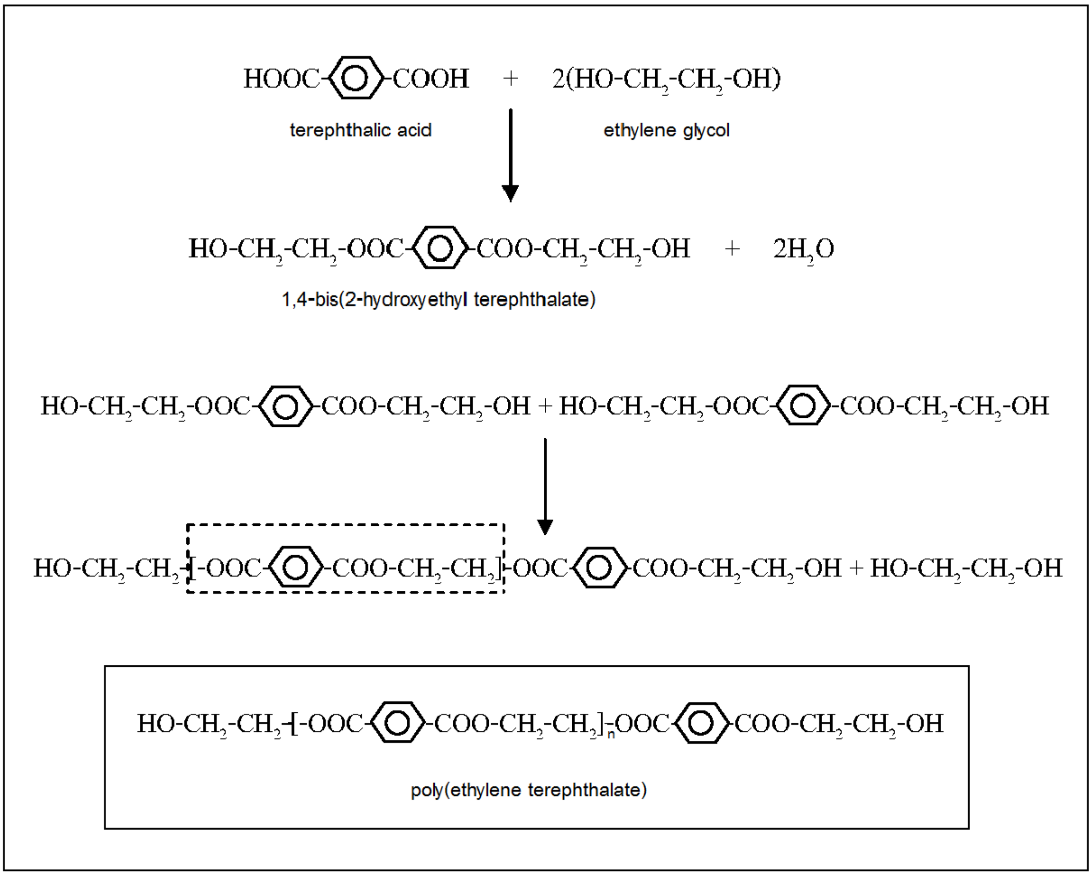


Figure 2.6 The polycondensation stage of PET production

2.3.1 Properties of PET films

The properties that make PET film popular for many applications are as follows [7]:

- Excellent mechanical properties such as high tensile strength, tear, flexure and abrasion resistance
- Thermal stability; dimensional stability over a very wide range of temperatures and humidity, ability to take printing at high ink drying temperatures
- Excellent barrier to both oxygen and water vapor to extend shelf- life
- Resistance to attack by moisture and many chemicals such as weak acids, bases and many solvents

- Brilliantly clear nature, haze resistances, very smooth and glossy surface
- Surface treatable for adhesion to a variety of materials and printable surfaces
- Electrical resistance

These properties are significantly enhanced when the film is oriented, and most commercial PET film is biaxially oriented (called BOPET film). Some properties are listed in Table 2.1 [8]. Commercial PET resin melts at about 248°C while highly crystalline resin melt up to 4°C higher. General purpose PET film can be used continuously at temperatures ranging from -60°C to about 148°C, considerably lower than its melting point of 248-271°C. However, PET films have relatively poor ultraviolet (UV) resistance and poor heat sealability, so some applications often use multilayer films of PET films and other polymer films.

Table 2.1 Typical properties of PET films [4]

Properties	PET films	
	Unoriented	Oriented
T_g (°C)	73-80	73-80
T_m (°C)	245-265	245-265
Heat distortion temperature, at 455 kPa (°C)	38-129	
Density (g/cm^3)	1.29-1.40	1.40
Tensile modulus (GPa)	2.8-4.1	
Tensile Strength (MPa)	48-72	220-270
Elongation (%)	30-3,000	70-110
WVTR, at 37.8°C and 90% RH (g μm/m^2 d)	390-510	440
O_2 permeability, at 25°C (103 cm^3 μm/m^2 d atm)	1.2-2.4	1.1

2.3.2 Applications of PET films

Major applications, primarily for BOPET films, include x-ray and photographic films, magnetic recording tape and disks, printing sheets, electrical insulation, and food packaging for retortable pouches. Much industrial strapping is made from PET. Unoriented, amorphous PET film and sheet have been used where strength is not as important, for example in blister packs, and in multilayer trays, cups, and other thermoformed containers.

a. Packaging [7]

PET film is used in many types of packaging applications ranging from food and drugs to industrial and consumer goods. It is an excellent laminating substrate for flexible packaging structures, i.e. stand-up pouches, offering excellent flex and puncture resistance. Moreover, it maintains its strength at both freezer and oven temperatures, for leak-resistant wraps, lidding, and peelable seals in a wide range of food and nonfood applications. Copolyester film is laminated to metal for can applications. Metallized PET film is used for high barrier, decoration, and embossed holographic applications. In addition, lightly metallized PET film is used in microwave susceptor constructions for cooking food in microwave ovens.

b. Industrial & specialties [7]

PET film is used in the Industrial & Specialties applications such as hot stamping foil, release films, photo resist films, metallic yarns, adhesive tapes, plastic cards (including "smart" cards), labels, lamination films, brightness enhancement films (computer screens), solar/safety window films, medical test strips, and miscellaneous uses.

c. Electrical [7]

PET film is used as an electrical insulator. It is also used as a laminate with other substrates, such as non-woven polyester matt (DMD), and organic and inorganic papers, such as aramid paper, silica paper, and mica paper. Moreover, it is used as motor wire and cable, transformer insulation films, capacitors, thermal printing tapes, membrane touch switches (computer and calculator keyboards), and flexible printed circuit films.

In motor applications, PET film is used for ground insulation as slot liners and wedges, as well as phase insulation. In transformer and high-voltage distribution equipment applications, PET film is used to wrap the conductors.

d. Imaging [7]

Some of the imaging applications include x-ray films, photographic, printing, microfilm, photoresist/phototool, overhead projection transparencies, and drafting/reprographics. Currently, these applications account for about 30% of the total PET film consumption.

e. Magnetics [7]

PET film is used in a variety of magnetic media, including video, camcorder and audio cassette tapes, and data storage applications such as floppy disks and computer tapes. For all magnetics applications, the base film is further coated with a magnetically receptive coating layer.

2.4 Surface modification of polymer for adhesion promotion

Improvement of interfacial bonding between two substrates is based on the following adhesion mechanisms.

a. Mechanical interlocking [8]

Mechanical interlocking of adhesive into the pores and cavities of the solid surface is the major factor in determining adhesion strength. In most cases, the enhancement of adhesion by mechanical interlocking can be attributed to an increase in interfacial area due to surface roughness. Improvement of adhesion does not necessarily result from a mechanical interlocking mechanism but surface roughening can play a significant part in adhesion by increasing the total contact area between the adhesive and the subsurface.

b. Electrostatic theory [8]

In electronic theory, adhesion take place due to electrostatic effects between adhesive and substrate. An electron transfer mechanism occurs between substrate and adhesive having different electronic band structures. Electrostatic forces in the form of an electrical double layer are formed at the adhesive-substrate interface. Adhesion strength results from these forces.

c. Wetting theory [8]

In wetting theory, adhesion is a result of the molecular contact between two materials and the surface forces that develop among them. The process of establishing continuous contact between the adhesive and substrate is called wetting. For an adhesive to wet a solid substrate surface, the adhesive should have a lower surface tension than the critical surface tension of the solid. Many solid organic substrates have surface tensions lower than those of common adhesives, thus increasing surface energy of a plastic substrate is necessary in order to allow wetting.

d. Chemical bonding [8]

Chemical bonds formed across the adhesive-substrate interface can greatly enhance adhesion between two materials. The formation of chemical bonds depends on the reactivity of both the adhesive and the substrate. In general, there are four types of interations that take place during chemical bonding: covalent bonds, hydrogen bonds, Lifshitz-van der Waals forces, and acid-base interactions. The exact nature of the interactions for a given adhesive bond depends on the chemical composition of the interface.

Since most polymer films have low surface free energy, chemical inertness and smooth surface, so they require pretreatment before using in the application which surface adhesion is needed. Surface treatments must focus on the addition of active species, increasing surface energy and the generation of certain surface roughness to improve adhesive efficiency. Various methods are used for the surface treatment of polymers, which have relevance to adhesion enhancement; such as chemical, physical and electrical treatment.

2.4.1 Chemical treatment

a) Chemical etching [9]

Chemical etching is usually used for irregular and, in particular, large substance when other treatment methods are not applicable. It involves immersion of the substance in an etchant solution such as chromic acid, permanganate, sulfuric acid or chlorosulfonic acid.

Sulfuric acid-dichromate is the most commonly applied chemical etching treatment for many plastics. Chromic acid removes amorphous regions of polymer morphology, leading to the formation of complex cavities on the plastic surfaces rather than the polarity surface. Sodium etching is an extreme treatment that is suitable for surface that are very difficult to treat. Examples include fluoropolymes and thermoplastic polyesters.

Bag, DS., et al. [10] modified surface of polyethylene. LDPE and a blend of LDPE and LLDPE (50/50) films were etched by hot fuming nitric acid to introduce polar group on the film surface. The presences of polar groups, mainly –COOH, >C=O, NO_2 and NO, were confirmed by IR studies. Deconvolution of the ESCA peak also supported the generation of active polar groups. Mechanical interlocking due to surface roughening was observed by scanning electron microscopy. Tensile properties testing indicated better adhesion between these active films with epoxy and hence better mechanical performance of their laminates.

b) Chemical grafting [8]

Chemical grafting is using chemical such as ceric ammonium nitrate, potassium persulphate, benzoyl peroxide, etc. for initiation of free radicals on surface of polymers, after that vinyl monomer is grafted onto polymeric materials. This technique can be used in order to improve adhesion between materials having different polarity, It can be performed by appropriate selection of monomer.

Funasaka, T., et al. [11] studied adhesive ability and solvent solubility of propylene-butene copolymers (PPB) modified with maleic anhydride. PPB was grafted with maleic anhydride (MAH) in solution system. The adhesive ability of PPB-g-MAH between oriented polypropylene film (OPP)/Aluminum substrates was investigated from the viewpoint of surface chemistry. T-peel strength increased with the polar component of the surface free energy of PPB-g-MAH. When the degree of grafting was 4.1%, the heat-seal strength revealed the maximum value of 1200 g/in, which was 30 times larger when compared with the control in this system. X-ray photoelectron spectroscopy and atomic force microscopy analysis of peeled surface showed that partial cohesive failure of PPB-g-MAH took place near the aluminum side along with intefacial destruction. The solubility of this polymer increased with the grafting amount of MAH. Though PPB itself can only be dissolved into toluene and cyclohexane, PPB-g-MAH can be dissolved in more than 10 kinds of solvents such as ethyl acetate and tetrahydrofuran at room temperature.

2.4.2 Physical treatment

a) Ultraviolet irradiation (UV) [12]

UV irradiation produces surface modification, which improves the wettability and bondability of the plastics. Photons, usually those with low wavelength, are energetic species which are used to activate many chemical reactions. A typical example of UV action on polymer surfaces is their degradation by the sun exposure.

In most cases, the modification is carried out by introducing functional groups to the material surface, applying UV light to oxidize the material surface, allowing the material to contact a gas or sensitizer to cause a photochemical reaction, allowing UV irradiation graft polymerization to occur at the material surface.

Even though UV treatment shows an improvement in adhesion but the time taken for the treatment is high; thus for commercial purpose, this treatment is infeasible. Moreover, this technique perhaps lead into the degradation of the polymers.

Landete-Ruiz, MD. and Martin-Martinez, JM. [13] improved adhesion between a polychloroprene adhesive and an ethylene vinyl acetate copolymer containing 12 wt% vinyl acetate (EVA12) by treatment with UV radiation. Changes in the EVA12 surface due to UV radiation treatment were assessed using contact angle measurements, ATR-IR spectroscopy, XPS, SEM and T-peel tests. Adhesion was evaluated from T-peel tests of treated EVA12/polychloroprene adhesive +5wt% polyisocyanate. Treatment of EVA12 with UV radiation increased its wettability, carbon–oxygen polar moieties were produced and roughness was created. As a consequence, adhesion of EVA12 to polychloroprene adhesive +5wt% polyisocyanate was enhanced by treatment with UV radiation longer than 5 min. A mixed failure (mainly cohesive failure in EVA12) was obtained.

b) Flame treatment [12]

Flame treatment is widely used for surface modification of polyolefin surfaces mainly to improve printability or paintability. Basically, the process consists of applying heat to the outer surface of polyolefin. The surface should be hot enough to suffer modification while the body remains at much lower temperature. For sheets having thickness lower than 0.6 mm is usually treated by corona discharge while flame treatment is used for heavier sheets. The flaming techniques are very popular and used extensively for treating in blow molding prior to printing, labeling, or the application of other decorative matter.

Flame contains excited species of O, NO, OH, and NH, which can remove hydrogen from the surface. The oxidation that follows is propagated by a free radical mechanism. Equations for the reactions, which can occur during simple thermal oxidation of hydrocarbon, happens in three steps: Initiation, Propagation and Termination. Surface of the polymer has a great effect to oxidation, that is highly branched polymers oxidise at a much more rapid rate than a linear polymer such as polyethylene, unless the branches are sufficiently bulky to sterically hinder oxidation. If the polymer contains both aliphatic and aromatic moieties, only the aliphatic portion is oxidised.

Flame treatment is not suitable for moulded three dimensional objects where the distance between the flame and the substrate can vary. Sheets having thickness less than 0.6 mm are not suitable for flame treatment. Also treatment cannot be used for films due to high shrinkage in films. Melting occurs if the flame is too close. Open flame, particularly in near a painting operation is usually forbidden for safety reasons.

2.4.3 Electrical treatment

a) Corona treatment [12]

Corona discharge treatment is the most widely used method for improving the adhesion properties of the plastic films such as polyolefin films prior to lamination. This treatment is used for various polymers such as polyolefins, polyfluorocarbons, polyesters, polyvinylchloride, silicone, nylon and others. Corona discharge treatment incorporates various functional groups such as carbonyl groups at the polymer surface.

Greater level of treatment increases the blocking tendency of the film. Contact of Corona discharge treated film and metal should be avoided because it erases the treatment on the surface. Additives such as slip additives and other processing aids reduces the treatment over time since these additives migrate to the surface and partially mask the polar groups formed during the treatment, thus the corona discharge treatment should be carried out just before the printing operations.

b) Plasma treatment [12]

Plasma treatment is a very efficient method for modifying polymer surfaces. It has been developed into a commercial important method for difficult surface treatments. It is used in the industry to improve the painting performance of plastic, adhesion of materials and the printability of films.

Sanchis, R., et al. [14] improved the adhesion of low-density polyethylene (LDPE) films to polyolefin foams for automotive industry using low-pressure discharge plasma. The results showed a remarkable increase in T-peel strength of the adhesive joints. Furthermore, the evaluation of the durability of the adhesive joints (in terms of storage conditions: temperature and relative humidity) showed that the T-peel strength of adhesive joints was subjected to an aging process that slightly decreased their mechanical performance, but did not restrict the use of these laminates in automotive uses.

Louis Joseph Dugur, I. and Mermilliod, N. [15] studied the improvement of polypropylene (PP) film adhesion in multilayers by various surface modification, such as grafting of poly(acrylic acid) after either irradiation by y-rays or activation by argon plasma, acrylic acid plasma polymerization and nitrogen plasma treatment. A first evaluation of their efficiency was made by measuring the adhesion energy of a two-layer complex containing the modified PP film and an acrylic adhesive tape. Grafting of poly(acrylic acid) either by pre-irradiation or by argon plasma treatment did not give a satisfactory improvement of the adhesion. On the contrary, the treatments by nitrogen plasma as well as acrylic acid plasma induced a peeling energy that was up to 10 times higher than the value obtained for an untreated PP film towards the acrylic adhesive tape. The adhesion of PP films was also tested on bilayer laminates with (a) an extrusion-oxidized polyethylene film and (b) a terpolymer film of ethylene, acrylic acid and acrylate. Good adhesion was achieved between nitrogen-plasma-treated PP film and the oxidized polyethylene film (600 J m^{-2}) as well as the terpolymer film (427 J m^{-2}). However, the poly(acrylic acid) plasma-deposited layer induced an improvement of the adhesion only with the preoxidized polyethylene film (390 J m^{-2}).

2.5 Surface modification by plasma treatment

2.5.1 Plasma state [16]

Plasma is a gas in which a certain portion of the particles are ionized. It is the fourth state of the matter containing both charged and neutral species, including free electrons, positive and/or negative ions, atoms, and molecules. Overall, plasma is electrically neutral, the densities of positive and negative charges in any sizeable region are equal, a property which is known as quasi-neutrality.

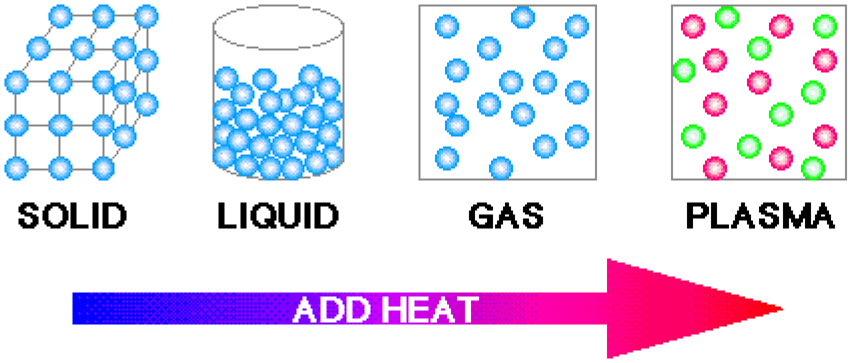


Figure 2.7 States of Matter [17]

The classification as a state of matter is justified by the fact that more than 99% of the universe is in the plasma state. As shown in Figure 2.7, when solid is heated above a critical value temperature, it melts and becomes a liquid. When liquid is heated above a second critical temperature, it is transformed into a gas. The temperature is kept raising, the electron and the nucleus constituent of an atom cannot stay together, the atoms are stripped of their electrons and plasma is formed [17].

Plasma state can be divided in two main categories: hot plasma and cold plasma. Cold or non-thermal plasma is also partially-ionized with a low fractional ionization. It contains very hot free electrons of several eV (1eV = 11600 K), which generate high chemical reactivity while neutrals and ions remain near room temperature (0.025 eV). On the other hand, hot or thermal equilibrium plasma is nearly fully ionized (100%). It contains electrons and the heavy particles at the same temperature so the heat content and overall temperature is high (>10000 K, close to 1eV) [18].

The examples of hot plasma include electrical arcs, plasma focus, plasma jets of rocket engines, nuclear fusion generated by thermonuclear reaction. In the case of plasmas produced by low pressure direct current (DC) and radio frequency (RF) 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. They are called cold plasma because the electron temperature is much higher than the gas temperature [19].

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 [20]. However, its generating system involves continuous processes; therefore, the exposure of the material surfaces to the plasma is difficult to control [21], it is often that the polymers are over exposed and this results in polymer degradation.

Hot plasma discontinuously generated in pulse from theta-pinch and plasma focus devices have been utilized to modify the surface of textile materials [22-23]. Since pulsed-plasma treatment does not require lengthy treatment period to achieve desired effects and can easily control plasma exposure [24]; thus, this process can modify most textile/polymeric materials having low heat resistance.

2.5.2 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 different interactions with the polymer surface [18]. The possible mechanisms for plasma-substrate interactions are illustrated in Figure 2.8.

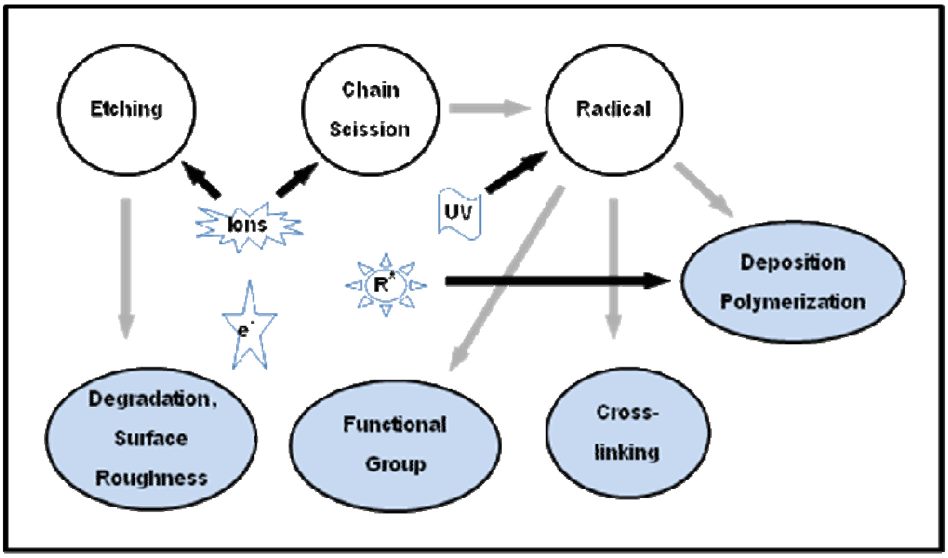


Figure 2.8 Mechanisms of plasma-substrate interaction

When a polymer is exposed to plasma of non-polymerizable gases (Ar, He, O, N_2, CO_2, etc.), ions and neutral species in plasma will collid with the molecules on the substrate surface resulting in roughness of polymer surface. This phenomena is called etching. Moreover, this reactive species bring about the breaking of the long molecular chains into short ones; it is called chain scission. Radicals obtained by chain scission mechanism would leads to chemical interaction with the surface of the molecules, including new functional groups formation and inducing cross-linking generation on the uppermost few mono-layers of polymer. Furthermore, plasma polymerization can be achieved using plasma of polymerizable gases such as methane and tetrafluoroethylene [20].

2.5.3 Physical phenomena in plasma surface modification

2.5.3.1 Plasma cleaning

Plasma cleaning [25] involves the removal of impurities and contaminants from surfaces through the use of an energetic plasma created from gaseous species. Gases such as argon and oxygen, as well as mixtures such as air and hydrogen/nitrogen are used.

Activated species in plasma comprise atoms, molecules, ions, electrons, free radicals, metastables, and photons in the short wave length of ultraviolet (vacuum UV or VUV) range. If the gas used is oxygen, the plasma is an effective, economical, environmentally safe method for critical cleaning. The VUV energy is very effective in the breaking of most organic bonds (i.e., C-H, C-C, C=C, C-O, and C-N) of surface contaminants. This helps to break apart high molecular weight contaminants. A second cleaning action is carried out by the oxygen species created in the plasma (O_2^+, O_2^-, O_3, O, O^+, O^-, ionised ozone, metastably-excited oxygen, and free electrons). These species react with organic contaminants to form H_2O, CO, CO_2, and lower molecular weight hydrocarbons. These compounds have relatively high vapour pressures and are evacuated from the chamber during processing. The resulting surface is ultra-cleaned [25].

If the part to be treated consists of easily oxidised materials such as silver or copper, inert gases such as argon or helium are used instead. The plasma activated atoms and ions behave like a molecular sandblast and can break down organic contaminants. These contaminants are vapourised and evacuated from the chamber during processing. If an organic contaminant is present, the water contact angle is high. After the removal of the contaminant, the water contact angle is reduced to that of pure substrate [25].

2.5.3.2 Plasma etching

Plasma etching is a physical removing process of a material on the surface of a substrate. Roughening of the surface can participate a significant part in adhesion by increasing the total contact area between the adhesive and the substrate. Etching is a result from gas selection or the length of time which the surface is exposed to the plasma [26]. However, etching in plasma treatment has no unfavorable effect on the physical properties of substrate because only few hundred Å layers are etched away. Surface morphology and micro-roughness are achieved by etching process, preferring to removing amorphous region: that is, selective etching. However, the particles etched can re-deposite on substrate surface again, and provide undesirable results on etching processing. Solid particles can be generated in the plasma when the concentration of particles coming off substrate surface is dense enough to interact with molecules on substrate surface or the wall of the plasma reactor or chamber [27].

Etching and deposition rates are dependent on the ion energy flux and deposition species. 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 [18].

2.5.4 Chemical phenomena in plasma surface modification

2.5.4.1 Surface activation

Plasma surface activation [28] used gases, such as oxygen, nitrogen, hydrogen, and ammonia. When substrate is exposed to the plasma, the plasma species (ions, electrons, radicals, UV-radiation, neutrons, etc.) react with the surface. The active species would collide with the molecule substrate which lead to the radical formation by chain scission of molecules and abstraction (taking-off of atoms on molecular chain). Free radicals generated in the plasma treatment on polymeric materials play an important role in surface modification, creating different chemical functional groups on the surface. The new functional groups have strong chemical bonds with the bulk material and have the capability to further bond with adhesives to promote better adhesion. The functional groups also increase the surface area available for the adhesive and thus distribute the load over a larger area resulting in improved adhesive strength. Gas selection and surface type determine the functional group formed on the surface. For an oxygen plasma, it 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. Nitrogen plasma and nitrogen-containing plasma are widely used to introduce nitrogen functionalities on polymer surfaces such as amino, amine, imine and amide.

2.5.4.2 Plasma deposition

a) Plasma polymerization

In plasma polymerization [29], polymerization of monomers into polymers occurs via initiation by plasma species such as electrons, ions, and radicals. Plasma polymerization is chemically different from conventional polymerization involving radicals and ions. In many cases, polymers formed by plasma polymerization have different chemical compositions and physical properties compared to conventional polymerization. This uniqueness results from the reaction mechanism of the polymer-forming process. Polymer formation in plasma polymerization includes plasma activation of monomers to radicals, recombination of the formed radicals, and reactivation of the recombined molecules. Polymers obtained from plasma polymerization do not comprise repeating monomer units, but instead complicated units containing crosslinked, fragmented, and rearranged units from the monomers. In most cases, these polymers have higher elastic modulus and do not exhibit distinct glass transition temperature. Hydrocarbons such as methane, ethane, ethylene, acetylene, and benzene are widely used in the synthesis of plasma polymerized hydrogenated carbon films. The enhanced microhardness, optical refractive index, and impermeability result in good abrasion resistance. Plasmas of fluorine-containing inorganic gases, such as fluorine, hydrogen fluoride, nitrogen trifluoride, bromine trifluoride, sulfur tetrafluoride, and sulfur hexafluoride monomers are used to produce hydrophobic polymers. Polymers fabricated by plasma polymerization using organo-silicon monomers have excellent thermal and chemical resistance and outstanding electrical, optical, and biomedical properties. The common organo-silicon precursors include silane, disilane (SiSi), disiloxane (SiOSi), disilazane (SiNHSi), and disilthiane (SiSSi) [29].

b) Plasma grafting copolymerization

When polymeric materials are exposed to plasma, radicals are created in the polymer chains. These radicals can initiate polymerization reactions when put in contact with monomers in the liquid or gas phase. As a result, grafted copolymers are formed on the surface. In plasma grafting copolymerization [30], polymers are first exposed to the plasma to create radicals on the surface. Inelastic collisions between the electrons in the plasma and polymer surface produce radicals in the polymer chains. Afterwards, the polymers are exposed to a vapor of the monomer or an aqueous or organic solution of the monomer. Since the plasma produces radicals only close to the surface of the polymers, plasma grafting copolymerization is restricted to the near surface. Plasma grafting copolymerization is often employed to alter the surface hydrophilicity of polymers [31]. It is usually conducted by first exposing a polymer to plasma such as argon, helium, or nitrogen for a short time (a few seconds). The process introduces many radicals to the surface of the polymer and experimental results [30] reveal that these radicals can survive for several days. Afterwards, the polymer is brought into contact with the vapor of a monomer at an elevated temperature for a period of time. Oxygen in the monomer vapor or dissolved in the monomer solution inhibit the reactions and should be avoided [31].

2.5.4.3 Crosslinking

It is well-known that the radical formation is strongly related to ion bombardment and UV-radiation. Crosslinking 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 crosslinking is dominated in the subsurface [32]. 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.

Crosslinking 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.

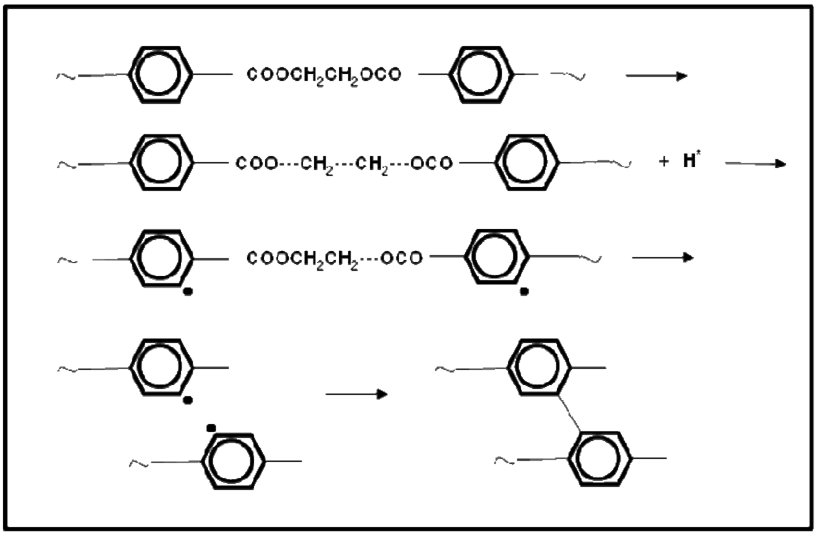


Figure 2.9 Crosslinking by recombination of two aryl radicals obtained by hydrogen abstraction from benzene ring in PET.

As shown in Figure 2.9, crosslinking 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, crosslinking 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 [33].

Singh, N.L., et al. [34] modified the surfaces of polyethylene terephthalate (PET) films by reactive gas (N_2) plasma to determine the effects of low-energy ions on the surface modification of PET. It was observed that the hardness of the film increased significantly as the fluence increases. The bulk hardness of the film was measured at loads greater than 400 mN. The increase followed a linear trend with fluence and has been explained in terms of cross-linking as observed from FTIR spectra. AFM showed that the average roughness (Ra) of the film surface decreased from 51–6 nm after plasma treatment as fluence increases. DSC thermograms indicated changes in the melting properties of the system.

Yang, L., et al. [1] improved poly(ethylene terephthalate) (PET) surface properties for technical applications using low-pressure air plasma. The results showed a considerable improvement in surface wettability and the surface free energy values even for short exposure times in the different discharge areas (discharge area, afterglow area and remote area), as observed by a remarkable decrease in contact angle values. Change of chemical composition made the polymer surfaces to be highly hydrophilic, which mainly depends on the increase in oxygen-containing groups. In addition to, the surface activation and AFM analyses showed obvious changes in surface topography as a consequence of the plasma-etching mechanism.

Pandiyaraj, N., et al. [2] studied effect of glow discharge air plasma on the surface properties of poly(ethylene terephthalate) film. It was found that the plasma treatment modified the surfaces both in chemical composition and morphology. Change of chemical composition made the polymer surfaces to be highly hydrophilic, which mainly depends on the increase in oxygen-containing groups. The AFM and XRD observation showed that the surface roughness and crystallinity of the PET film increased due to plasma treatment.

2.6 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) [35].

This device has been utilized in various applications, for instance, the deposition of thin films, including amorphous carbon 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 [35].

The dynamic process of Theta-pinch device is shown in Figure 2.10. After switch is closed, discharges through a single-turn coil and driving a current in the coil. The discharge current produces an axial magnetic field in the coil-encircled area (Figure 2.11). The rapidly increasing magnetic field induces an electric field opposite to the direction of the discharge current in the coil. The electric field in tube produces a plasma current sheath near the tube wall. The force exerts the plasma current sheath and rapidly compresses it toward the tube axis. Meanwhile, the plasma particles pass the surface of fibers and escape from the tube end (end loss). The plasma experiences shocks wave heating, adiabatic compression heating, and others. [35]

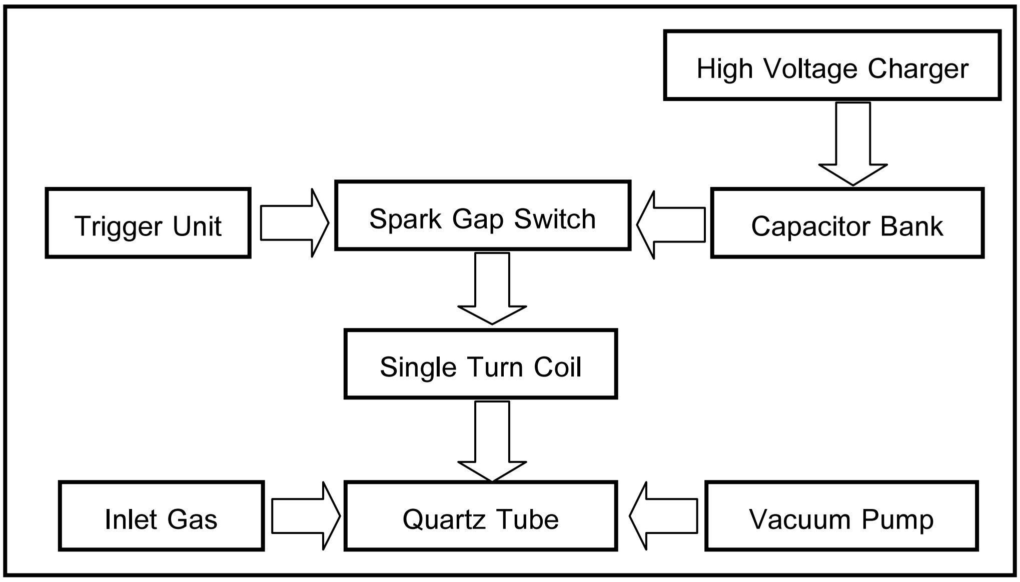


Figure 2.10 The dynamic process of Theta-pinch device [35]

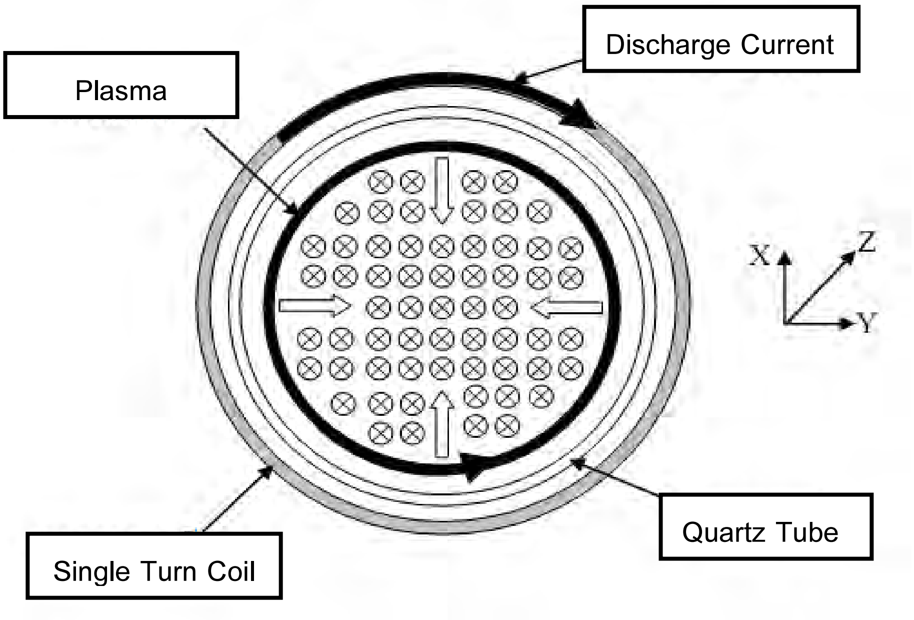


Figure 2.11 Dynamic process of Theta-pinch discharge [35]

Chuenchon, S., et al. [22] 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 plasmas generated at different number of plasma shots caused and increased the roughness of the fiber surface. Because of this, tensile properties, linear densities and diameters 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.

Khaymapanya, P., et al. [36] modified polyester, nylon, silk and cotton fabrics using 20 and 40 shots of oxygen and nitrogen plasmas generated from a theta-pinch device. The morphology and wetting times of treated fabrics were investigated. 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

CHAPTER III

EXPERIMENT

3.1 Experimental scope

Poly(ethylene terephthalate) films were treated by oxygen, nitrogen and argon plasma generated from Theta-pinch device. The chemical structures, morphology and properties of untreated and plasma-treated films were characterized and compared. Then untreated and plasma-treated films were laminated with metallized poly(ethylene terephthalate) films by compression molding. The mechanical properties of laminated films obtained from lamination process were investigated. The flow chart of the entirely experimental procedure is shown in Figure 3.1

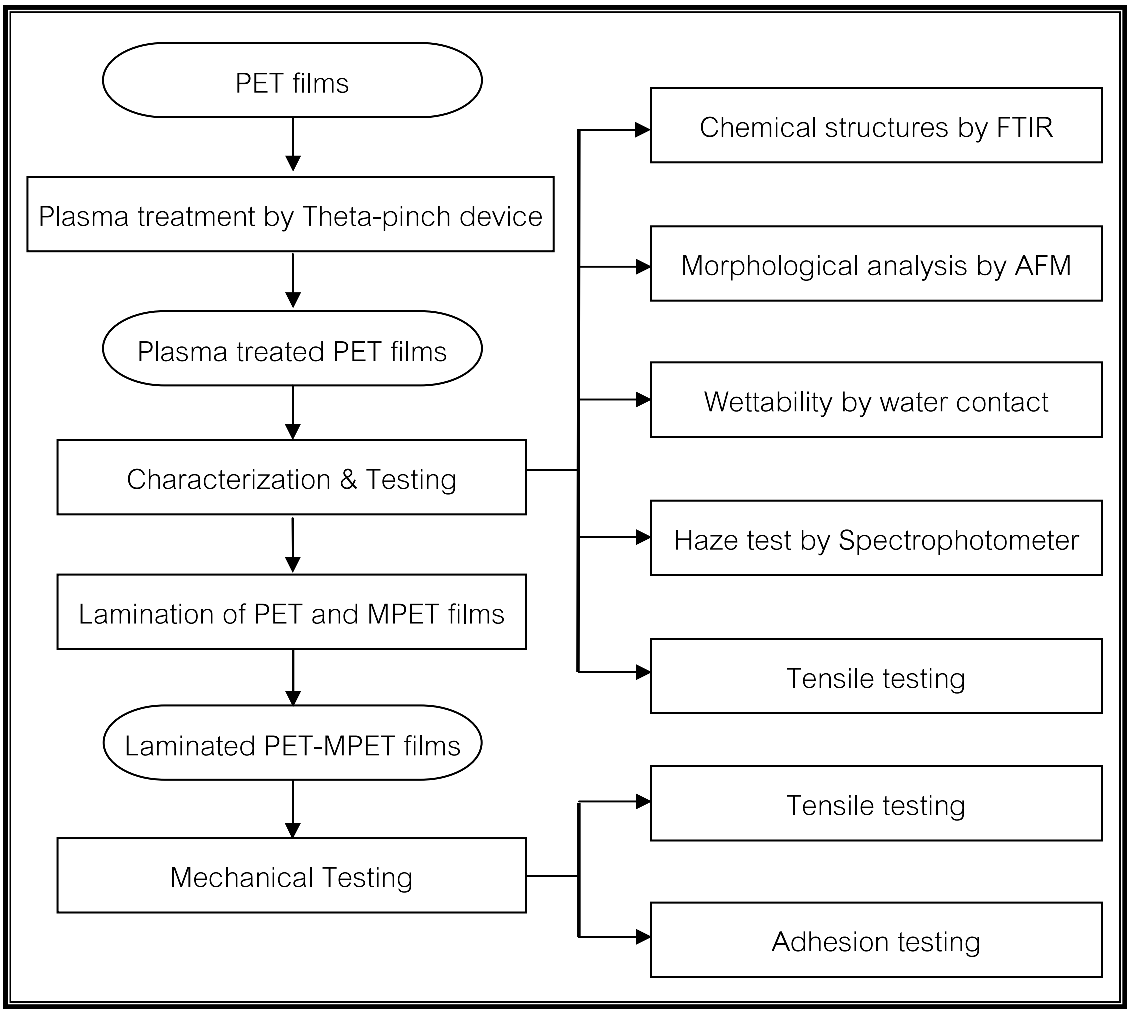


Figure 3.1 The flow chart of experimental procedure

3.2 Materials

1. Biaxial orientation poly(ethylene terephthalate); BOPET film (plain) was supported by AJ plast public Co., Ltd.

Thickness : 12 microns

Dimensions : 21×29.7 cm (A4)

2. Metallized poly(ethylene terephthalate); MPET film was supported by AJ plast public Co., Ltd.

Thickness : 12 micron

Dimensions : 21×29.7 cm (A4)

Optical density : 2.2

3. Oxygen gas was purchased from Thai Industrial Gases public Co., Ltd.

Purity : 99.5%

4. Nitrogen gas was purchased from Thai Industrial Gases public Co., Ltd.

Purity : 99.9%

5. Argon gas was purchased from Thai Industrial Gases public Co., Ltd.

Purity : 99.9%

3.3 Machines and equipments

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

3.3.2 Compression molding machine : Labtech V508-18-CX

3.3.3 Atomic force microscope (AFM) : Veeco, Nanoscope IV, USA

3.3.4 ATR/FT-IR spectrophotometer : Thermo Nicolet Nexus 670

3.3.5 Contact angle meter : Cam-Plus Tantac.

3.3.6 Spectrophotometer : Macbeth Color-Eye 7000

3.3.7 Universal Testing Machine : A LLOYD Model LR 100K

3.4 Procedure

3.4.1 Surface modification of PET film using Theta-pinch device

PET film was surface-modified using Theta-pinch device as shown in Figure 3.2. The film having dimensions of 21×29.7 cm was wound around a sample holder. A sample film was placed in the middle of reaction chamber of theta-pinch device as shown in Figure 3.3. 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, selected gas was introduced into this chamber. The plasma treatment was operated using a voltage of 20 kV, a pressure of 2 pascal and a current intensity of 125 kA. The number of plasma shots and the type of gas were varied according to Table 3.1. After treatment process completed, the film was removed from the chamber and was further characterized, tested properties and introduced to lamination process.

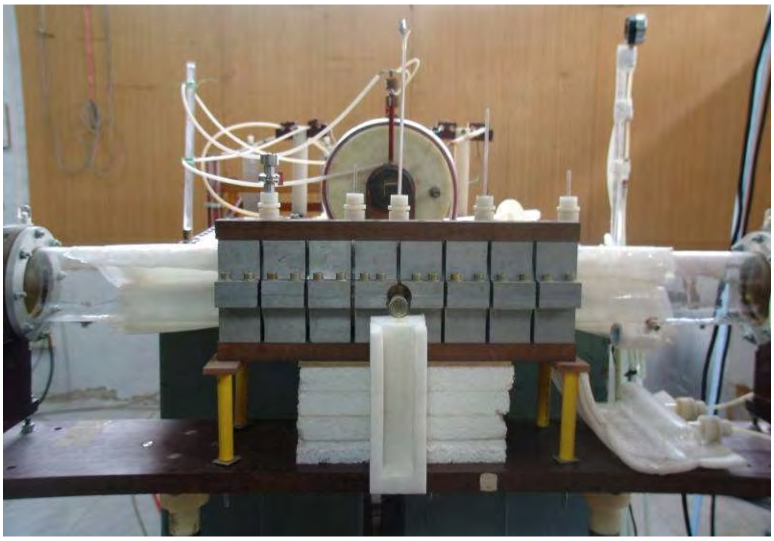


Figure 3.2 AAAPT Theta-pinch device

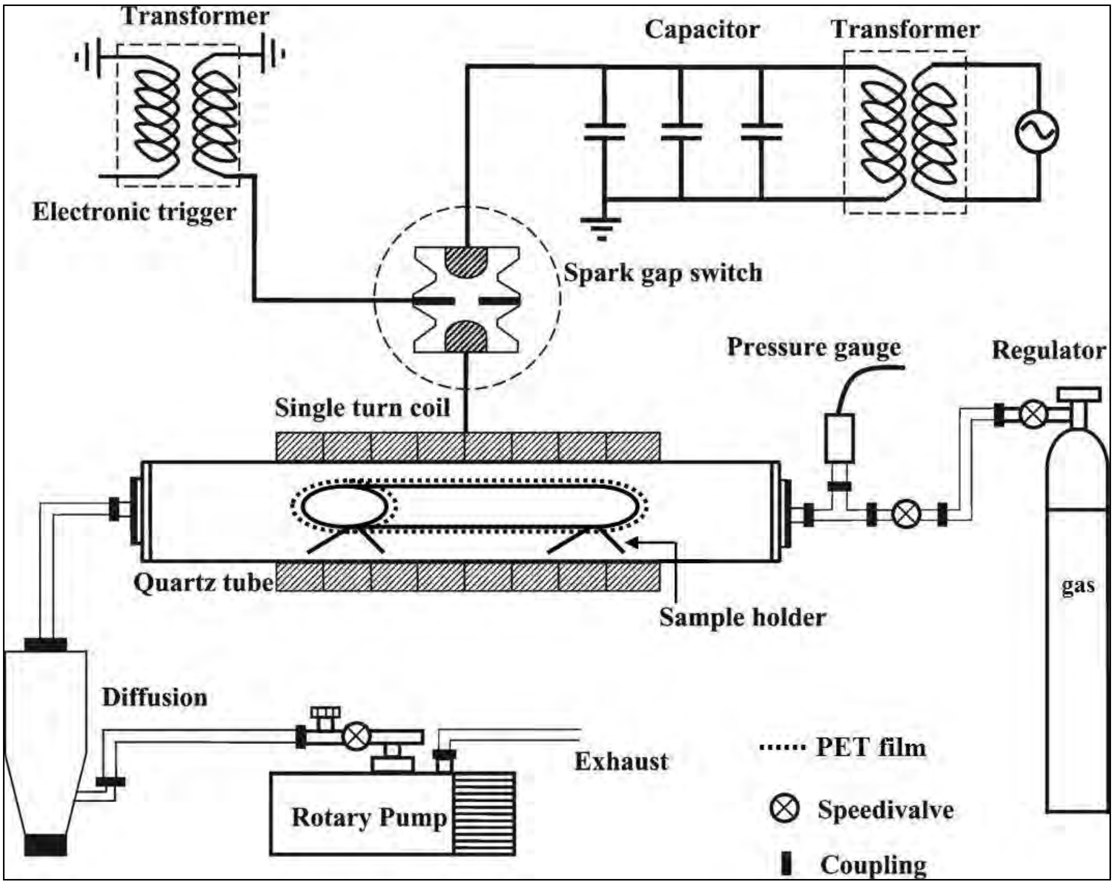


Figure 3.3 Schematic diagram and position of the sample film in chamber of theta-pinch device

Table 3.1 The number of plasma shots and the type of gas

Type of gas	Number of Plasma Shots			
Oxygen	5	10	15	20
Nitrogen	5	10	15	20
Argon	5	10	15	20

3.4.2 Preparation of laminated PET-MPET films

Plasma-treated and untreated PET films were laminated with MPET films using compression molding machine (V508-18-CX) as shown in Figure 3.4. PET and MPET films were preheated at 220°C for 5 minutes. Then they were compressed at the same temperature using a pressure of 1000 psi for 5 minutes. Afterward, they were cooled down to 40°C and laminated PET-MPET films were obtained.

Figure 3.4 Labtech V508-18-CX Compression molding machine

3.5 Characterization and testing

3.5.1 Analysis of chemical structure

The chemical structure of the film samples surface was characterized by Attenuated total reflection/Fourier transform infrared spectroscopy (ATR/FT-IR) (Thermo Nicolet Nexus 670 spectrophotometer) as shown in Figure 3.5. The samples were scanned at the frequency range of 4000-600 cm^{-1} with 300 consecutive scans and 4 cm^{-1} resolution.

Figure 3.5 Thermo Nicolet Nexus 670 spectrophotometer

3.5.2 Morphological analysis

Atomic force microscopy (AFM) was used to determine surface topography and roughness of the plasma-treated films. AFM analysis was performed on a Multimode AFM microscope (Veeco, USA) with a Nanoscope IV as shown in Figure 3.7. A silicon probe (Tip-soft) was used to work on tapping mode. The root mean square roughness (RMS) and the absolute surface roughness (Ra) of the films were obtained using images with scan sizes of 5 × 5 μm and a scan rate of 1.197 Hz.

Ra is defined as the average absolute deviation of the roughness irregularities from the mean line over one sampling length as shown in Figure 3.6. RMS represents the standard deviation of the distribution of surface heights. Two roughness parameters are calculated by equation following [37]:

$$\text{Ra} = \frac{1}{n}\sum_{i=1}^{n}|y_i|$$

$$\text{RMS} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}{y_i}^2}$$

y_i = the ordinate of the profile curve

n = number of intersections of the profile at the mean line

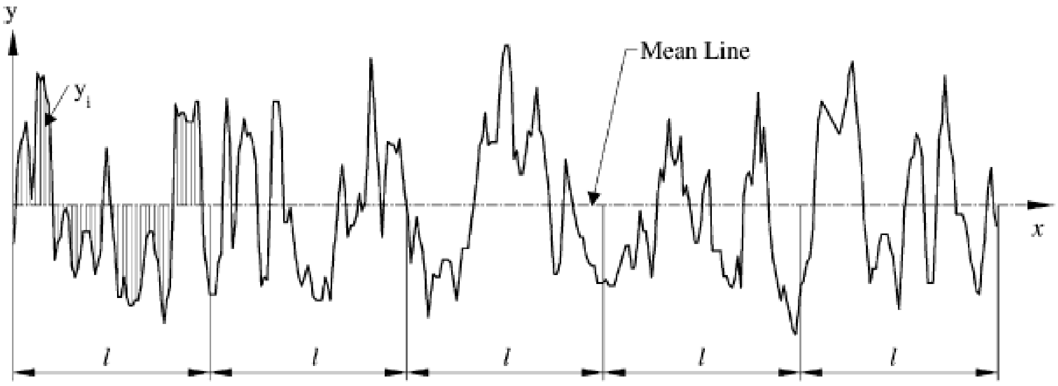


Figure 3.6 Surface roughness profile [38]

Figure 3.7 Veeco Atomic force microscope

3.5.3 Determination of physical properties

3.5.3.1 Wettability measurement

In order to investigate the wettability of untreated and treated films, the water contact angles of samples were measured using CAM-PLUS Tentec contact angle meter (Dataphysics, Germany) as shown in Figure 3.8 at room temperature.

The five microlitres of distilled water droplet were dropped at five different positions of sample. The measured contact angles were averaged as the contact angle of the sample. Moreover, in order to study the effect of storage time on wettability of plasma-treated films, the water contact angles of samples were measured after they were stored for 7 and 14 days in auto dessicator.

Figure 3.8 CAM-PLUS Tentec contact angle meter

3.5.3.2 Haze test

In order to study effect of plasma treatment on the haze of film samples, the haze of plasma-treated films were measured using Spectrophotometer (Macbeth Color-Eye 7000) as shown in Figure 3.9 according to ASTM D1003.

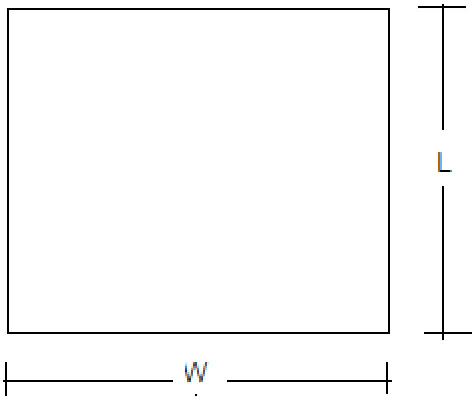
Figure 3.9 Macbeth Color-Eye 7000 Spectrophotometer

Haze test conditions were as follows:

Temperature: ±25°C

Relative humidity ±50%

The specimens were prepared in square shape as shown in Figure 3.10.



L = Length: 50 mm W = Width: 50 mm

Figure 3.10 Schemetic of haze test specimen

3.5.4 Mechanical tests

3.5.4.1 Tensile test

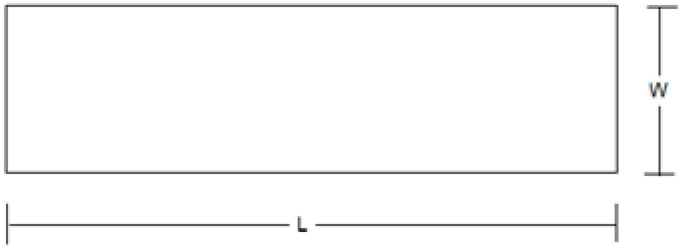
Tensile properties of each film including tensile strength, % strain at maximum load and Young's modulus were determined using Universal Testing Machine (LLOYD LR 100K) as shown in Figure 3.11 according to ASTM D882.

Figure 3.11 LLOYD Universal testing machine (LR 100K)

The tensile testing conditions were as follows:

Temperature:	±25°C
Relative humidity	±50%
Load cell	100 N
Speed of testing	50 mm/min
Initial distance between grips	100 mm

The specimens were prepared in rectangular shape as shown in Figure 3.12.



L = Length: 200 mm W = Width: 20 mm

Figure 3.12 Schemetic of tensile test specimen

3.5.4.2 Adhesion test

The adhesion strength of each film was determined using Universal Testing Machine (LLOYD LR 100K) as shown in Figure 3.11 according to ASTM D1876.

The adhesion testing conditions were as follows:

Temperature:	±25°C
Relative humidity	±50%
Load cell	100 N
Speed of testing	254 mm/min
Initial distance between grips	50 mm

The specimens were prepared in T-peel shape as shown in Figure 3.13.

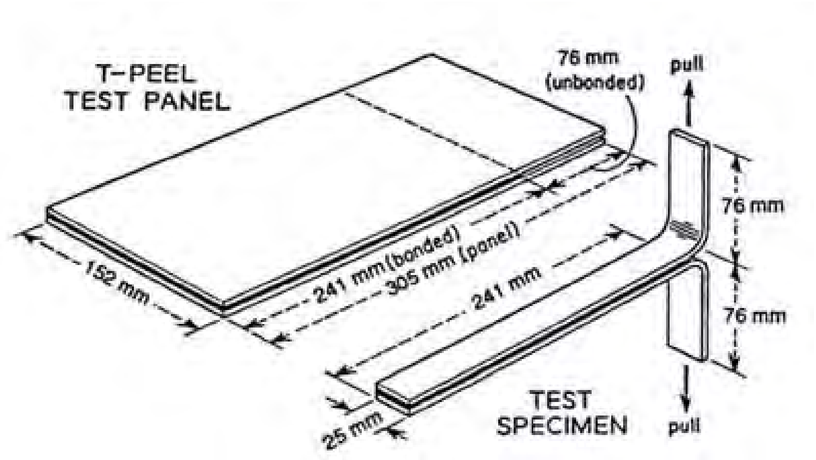


Figure 3.13 Schemetic of adhesion test specimen

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Properties and morphology of untreated and treated PET films

4.1.1 Surface chemical structure

Attenuated total reflection infrared spectroscopic (ATR/FT-IR) studies of untreated and treated PET films were performed to assess any structural changes, the introduction of any new functional groups, or the alteration of existing groups on the surface of the films as a result of plasma treatment using theta-pinch device

After treatment with oxygen, nitrogen and argon plasma, Figure 4.1 shows that there is no change in overall structure of the polymer, but a minor change at some wavenumbers is observed. The intensities of the peak corresponding to O-H stretching of hydroxyl group (OH) at wavenumber of 3500-3600 cm^{-1} slightly increase, while the intensities of the peak attributed to C-H bending of C-H bond at wavenumber of 1340 cm^{-1} distinctly decrease. This might be due to the scission of few bonds as well as the formation of few functional groups on PET surface. The interpretation of all spectra is summarized in Table 4.1.

Table 4.1 The interpretation of ATR/FT-IR spectra of untreated and plasma-treated PET

Wavenumber (cm^{-1})	Interpretation
3500-3600 cm^{-1}	O-H stretching of hydroxyl group
2800-3000 cm^{-1}	C-H stretching of ethylene group
1600-1800 cm^{-1}	C=O stretching of the ester carbonyl group
1200-1400 cm^{-1}	ester C-O-C asymmetric and symmetric stretching vibrations
1000-1100 cm^{-1}	C-O-C stretching vibrations
700-800 cm^{-1}	aromatic

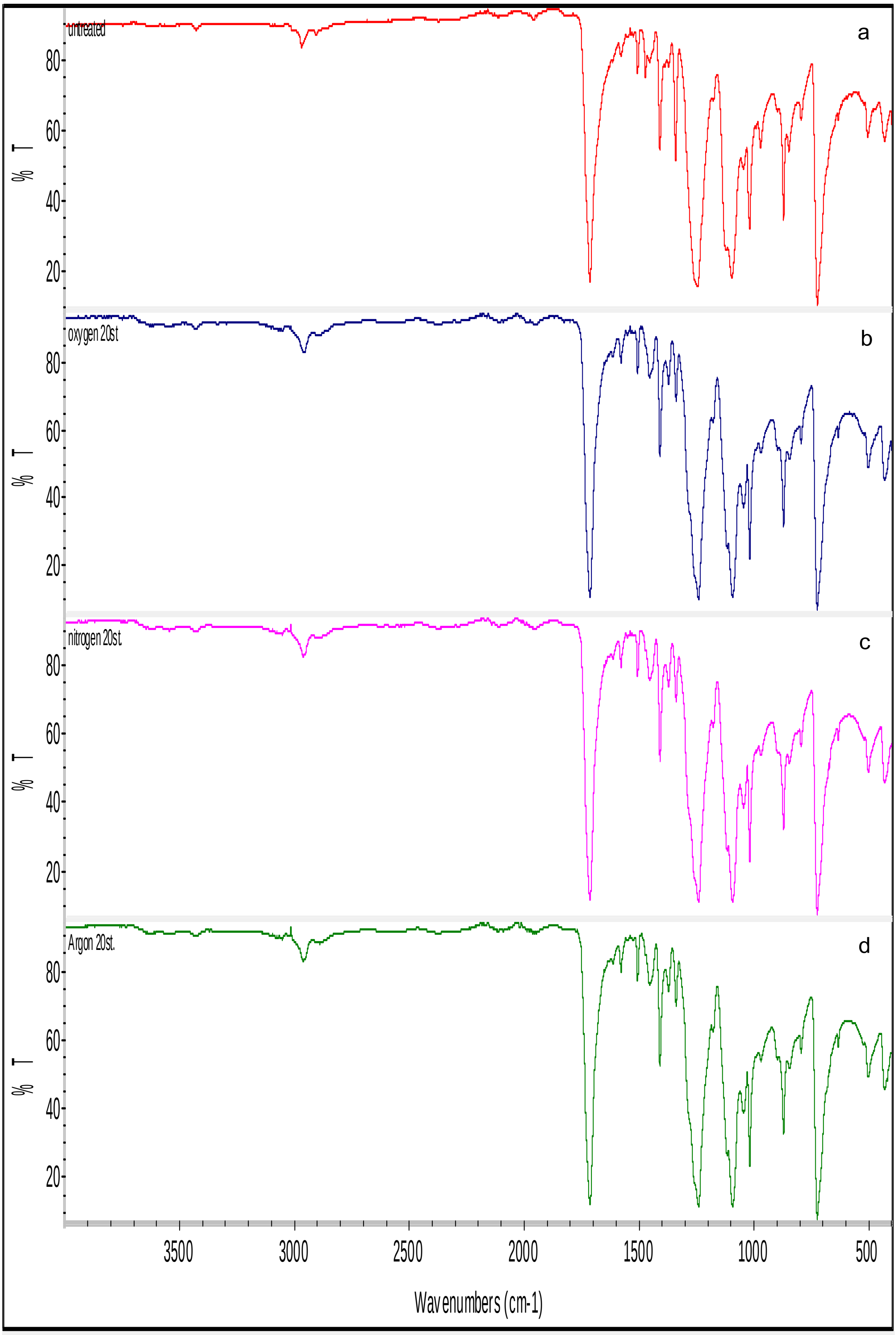


Figure 4.1 ATR/FT-IR spectra of (a) untreated PET film and PET films treated with (b) oxygen, (c) nitrogen, (d) argon plasma at 20 shots.

Moreover, it can be seen that the spectrum of nitrogen plasma treated film exhibited the peak corresponding to N-H stretching at wavenumber of 3400-3500 cm^{-1}. This result suggests the formation of amine group (NH_2) on PET surface. However, the observation is not clearly seen due to low amount of NH_2 groups was formed.

In the case of argon plasma-treated film, the peak corresponding to O-H stretching of hydroxyl group (OH) at wavenumber of 3500-3600 cm^{-1} is also observed. Although, argon plasma does not usually react with the polymer but it can cause chain scission of polymer molecules. The scission segments can react with the polymer surface and form the functional groups.

4.1.2 Morphology

The surface topography of a plasma treated PET film was investigated by atomic force microscopy (AFM). As seen in Figure 4.2a, the surface of untreated PET film was rough. After plasma treatment, the film surface became smoother while the size of the protuberances on the surface increased as shown in Figures 4.2b–4.2g. The root mean square roughness (RMS) and the absolute surface roughness (Ra) of untreated and plasma-treated PET films are shown in Figures 4.3 and 4.4, respectively.

As the number of plasma shots increases, surface roughness decreases. This is due to etching effect induced by the plasma treatment. However, it is clearly seen from Figures 4.3 and 4.4 that nitrogen plasma treatment has lowest etching effect compared to oxygen and argon plasma treatments.

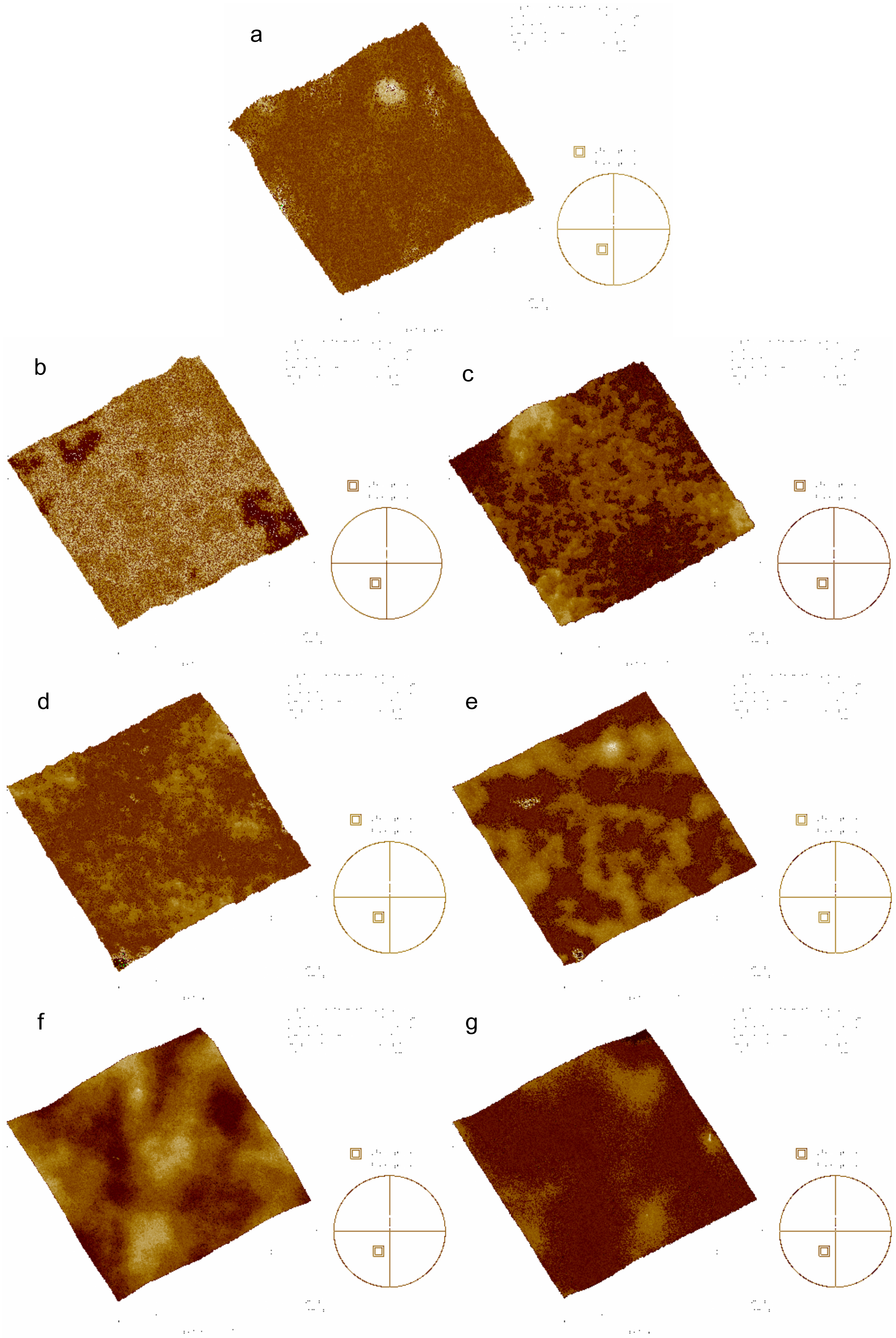


Figure 4.2 AFM images of (a) untreated PET film and PET films treated with (b) oxygen, (c) nitrogen, (d) argon plasma at 5 shots, (e) oxygen, (f) nitrogen, (g) argon plasma at 20 shots.

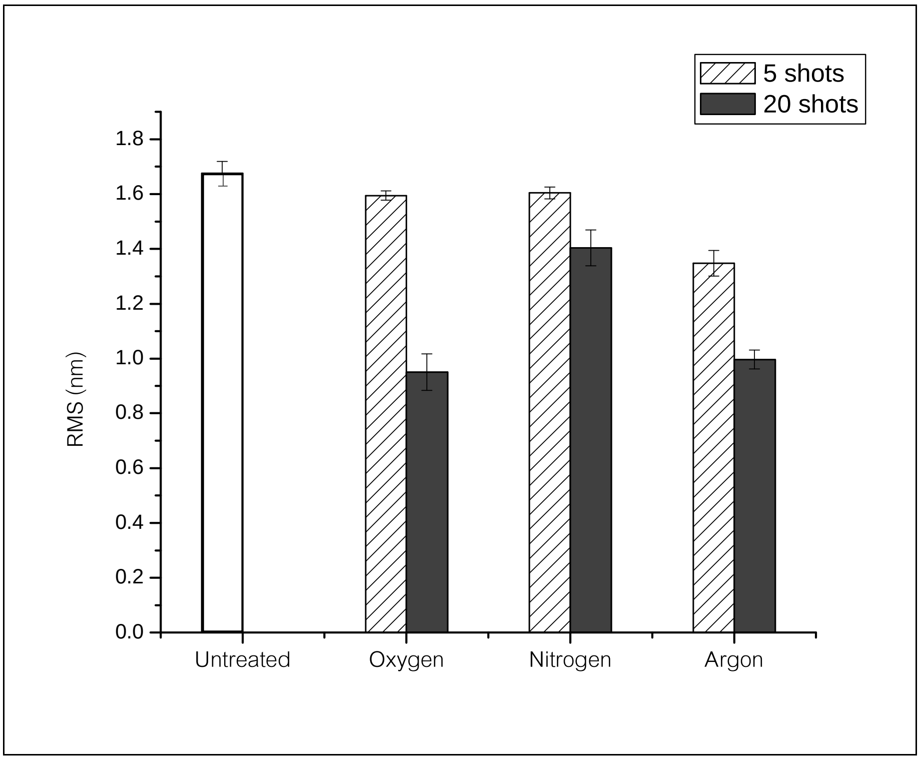


Figure 4.3 RMS of untreated and plasma-treated PET films

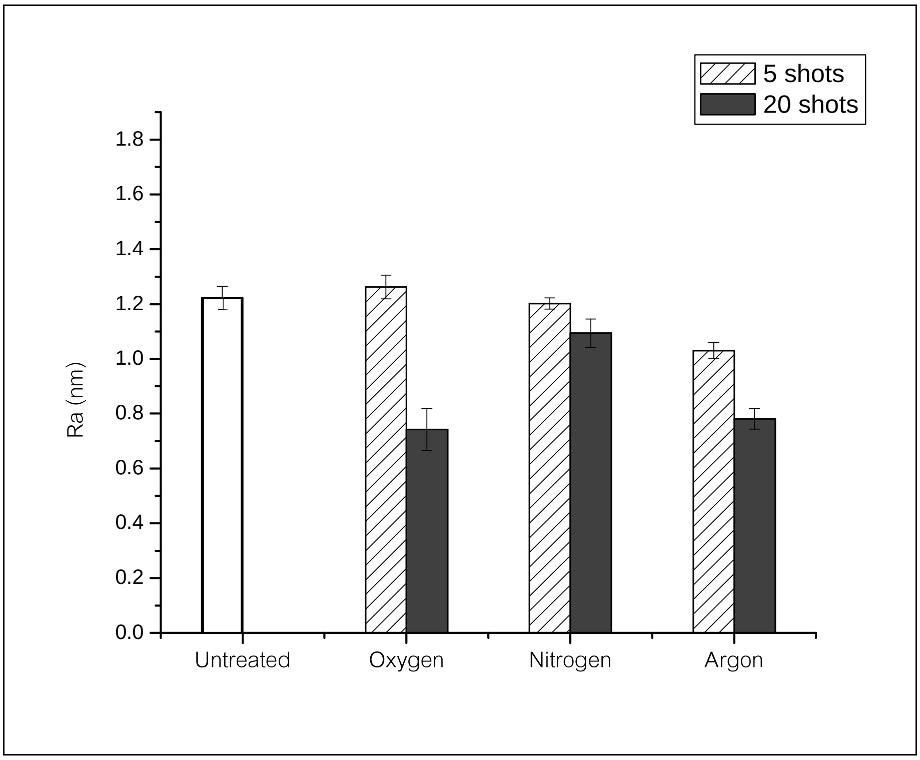


Figure 4.4 Ra of untreated and plasma-treated PET films

4.1.3 Wettability

The results shown in Figure 4.5 indicate that high temperature pulsed plasma treatment of PET films improved their surface wettability. Figure 4.5 shows the water contact angles of the PET films measured immediately after plasma treatment using various numbers of plasma shots and different types of gas. It was observed that the contact angles of the treated films were reduced to 25-37° when compared to that of the untreated one. Furthermore, it can also be seen that as the number of plasma shot increased, the water contact angle decreased. While oxygen-plasma treated films exhibited lowest contact angles, argon-plasma treated films showed highest contact angles. These results suggest that the formation of hydrophilic functional groups on PET films depends on the gas type. Using more reactive gas can yield more hydrophilic functional groups. After storing the samples for 7 days and 14 days, the contact angles increase as shown in Figures 4.6 and 4.7 considerably possibly resulting from the molecular rearrangement [38].

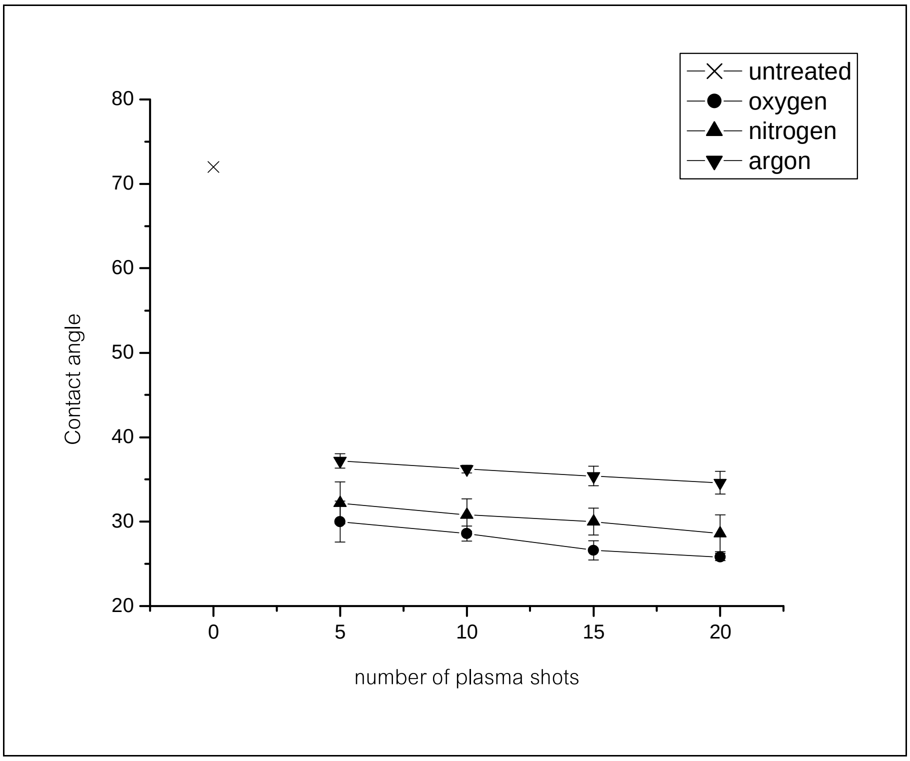


Figure 4.5 The water contact angles of untreated and plasma-treated PET films obtained immediately after plasma treatment

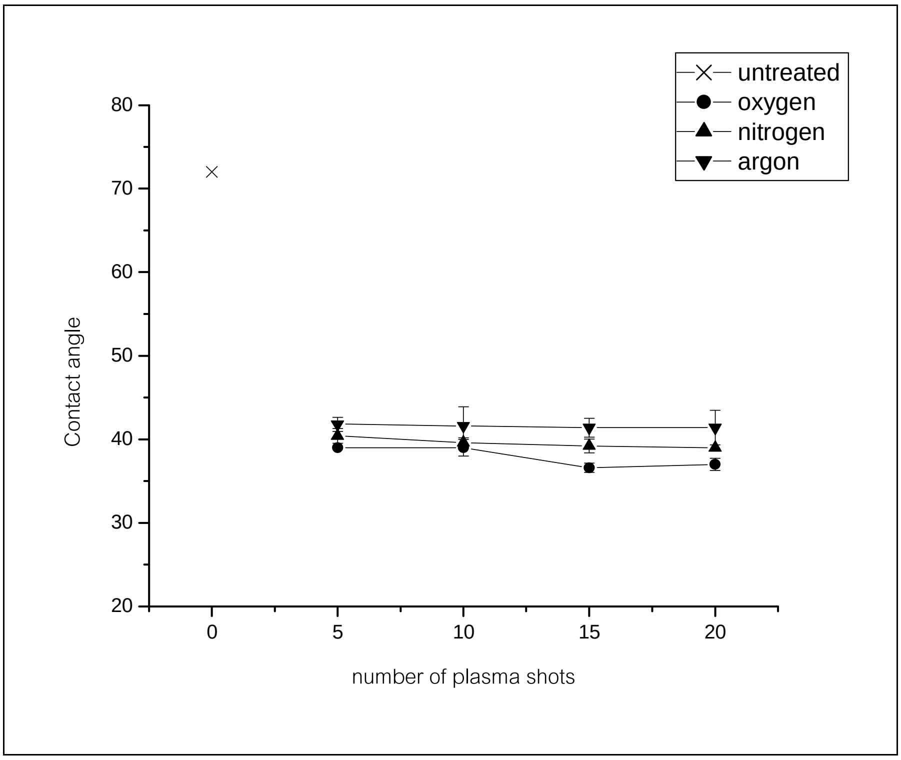


Figure 4.6 The water contact angles of untreated and plasma-treated PET films after 7 days storage

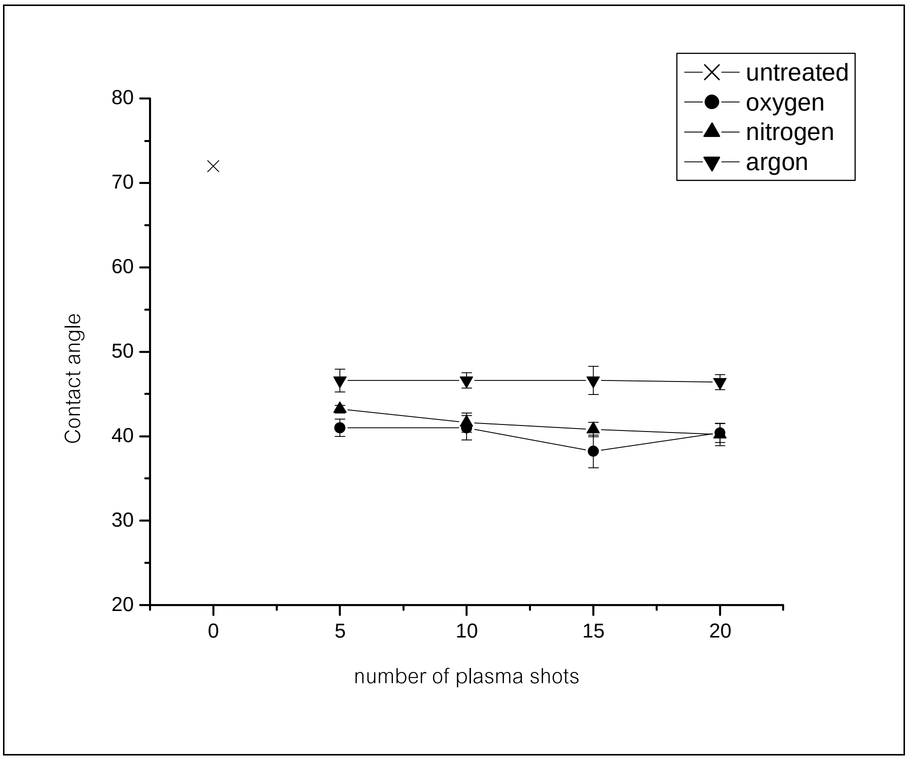


Figure 4.7 The water contact angles of untreated and plasma-treated PET films after 14 days storage

4.1.4 Haze

It can be seen from Figure 4.8 and in Appendix A (Table A-4) that haze of these films are similar. From Figures 4.9-4.12, it is also seen that all films are transparent. These results suggest that high temperature pulsed plasma treatment has no significant effects on film appearance.

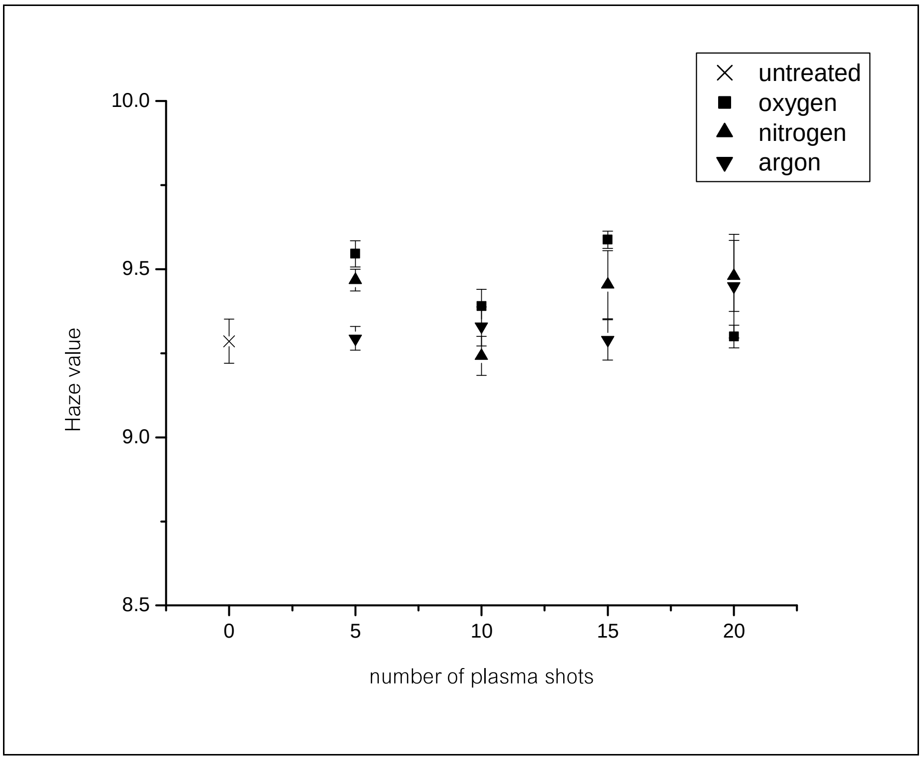


Figure 4.8 Haze of untreated and plasma-treated PET films

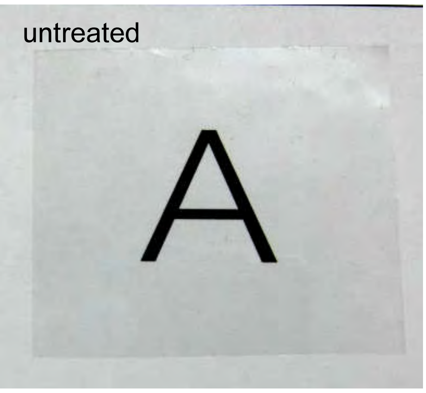


Figure 4.9 Appearances of untreated PET films

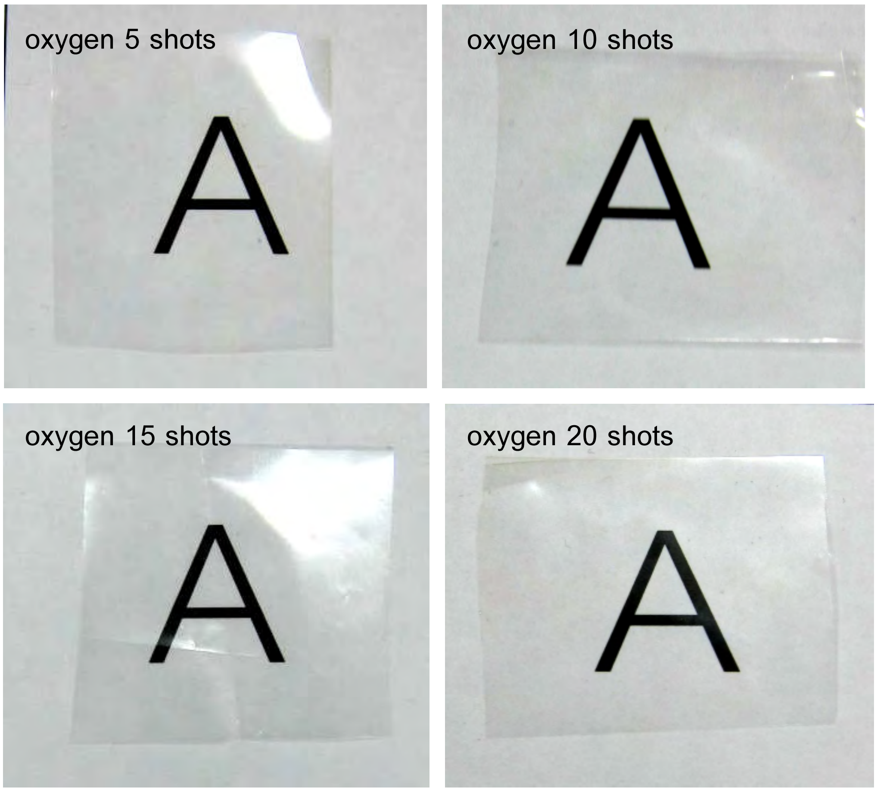


Figure 4.10 Appearances of PET films treated with oxygen plasma

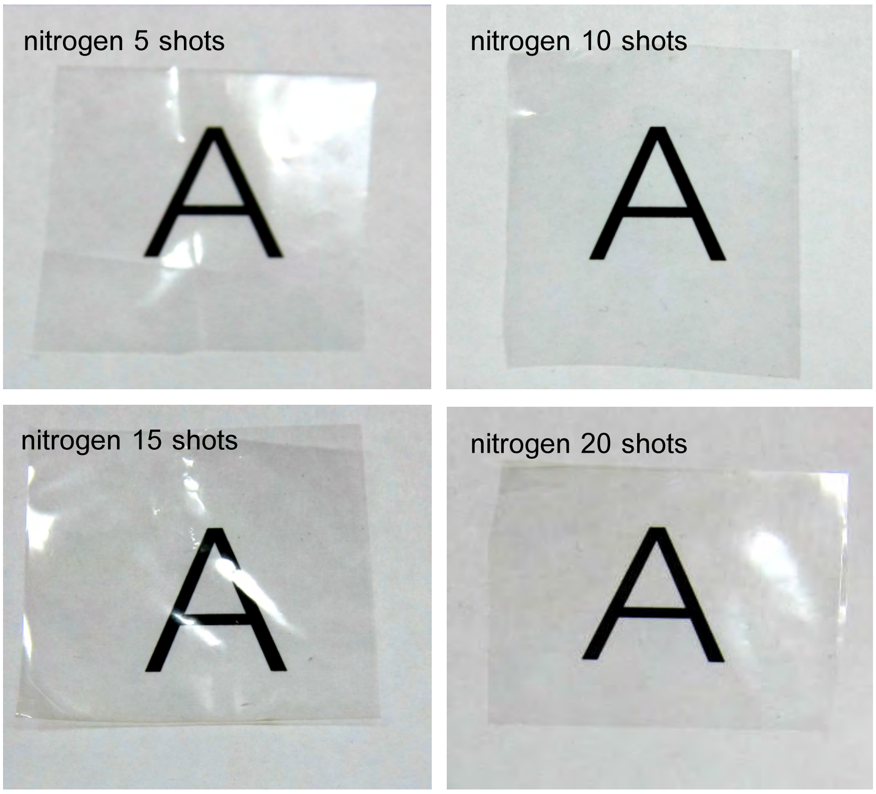


Figure 4.11 Appearances of PET films treated with nitrogen plasma

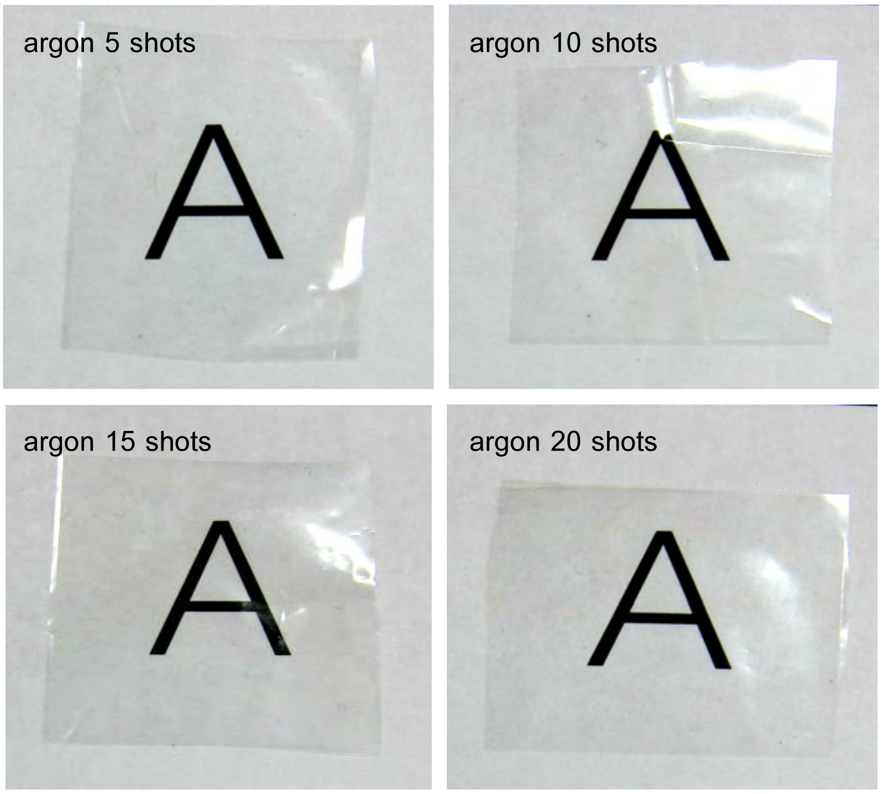


Figure 4.12 Appearances of PET films treated with argon plasma

4.1.5 Tensile properties

From Figure 4.13, it can be seen that tensile strength of plasma-treated PET films at every condition was comparable to that of the untreated film. Since etching effect was lowest in the case of nitrogen plasma-treated films as previously mentioned, tensile strength of these films was slightly higher than those of oxygen and argon plasma treated films. In case of oxygen and argon plasma treatments, tensile strength of treated films slightly decreased when compared to that of the untreated one. This result is also inconclusive with AFM analysis.

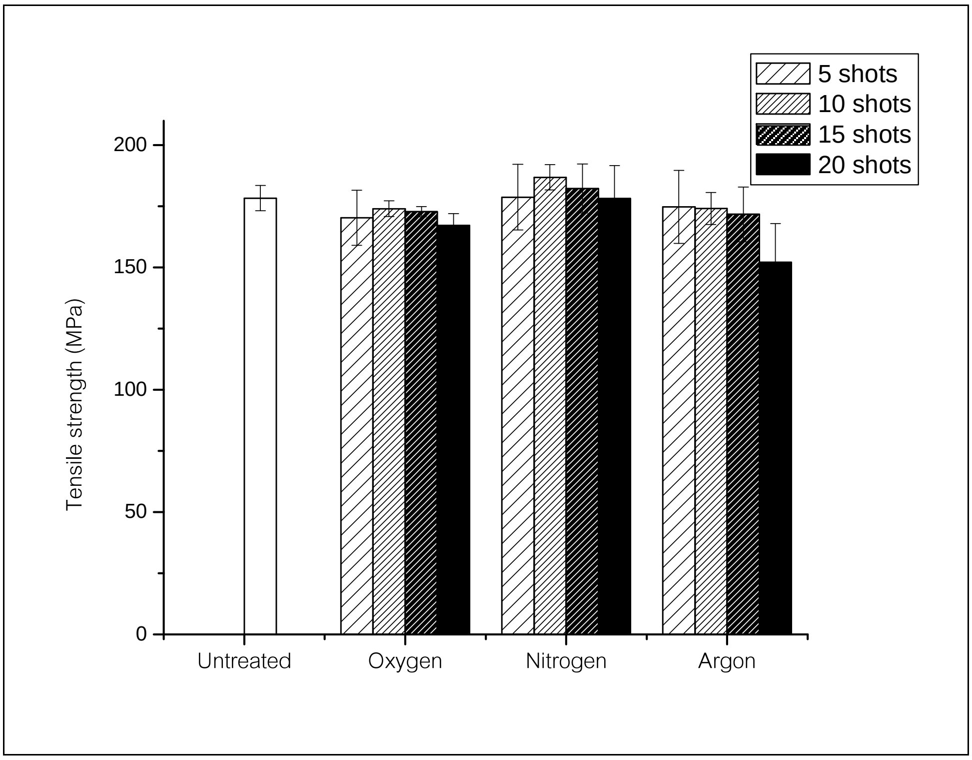


Figure 4.13 Tensile strength of untreated and treated PET films

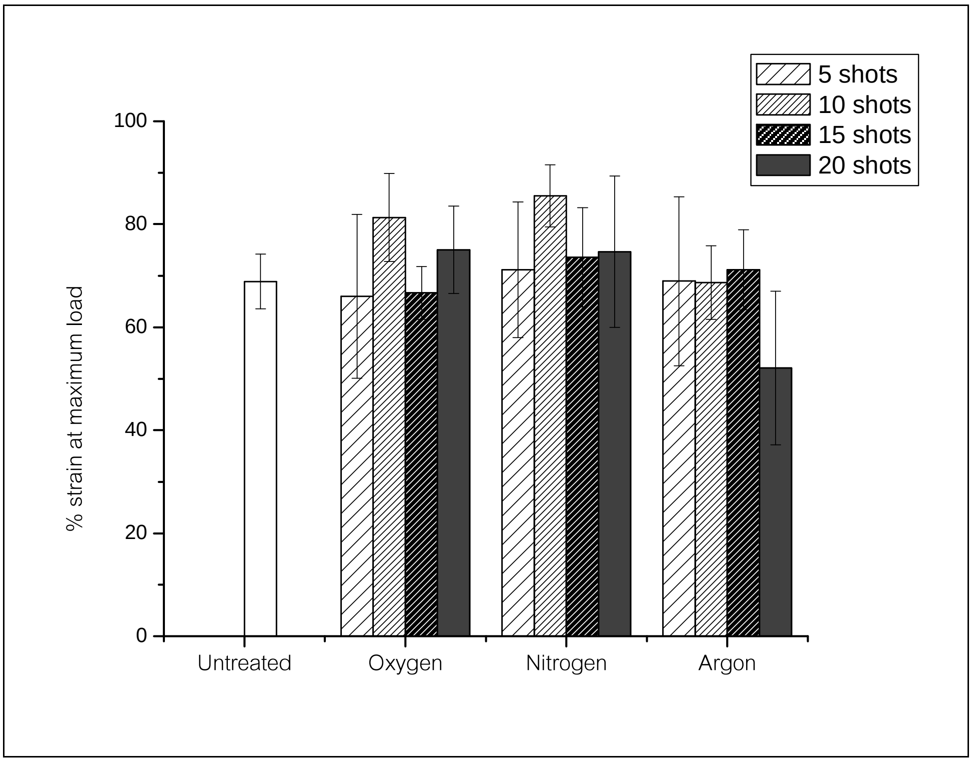


Figure 4.14 % strain at maximum load of untreated and untreated PET films

When considering the effect of plasma treatment on % strain at maximum load, as seen in Figure 4.14, it was found that variation of number of plasma shots and type of gas results in an alteration of percentage strain at maximum load. since the movement of polymer molecules after plasma treatment. Moreover, the type of gas shows slightly effect on this property of plasma treated PET films. Oxygen and nitrogen plasma treated films have slightly higher % strain at maximum load than argon plasma treated films. This may possibly be because oxygen and nitrogen plasma treatment result in the formation of more hydrophilic functional groups than argon plasma treatment, these hydrophilic groups can attract and absorb more moisture. The moisture molecules can facilitate the movement of polymer molecules [39], so the above results were observed.

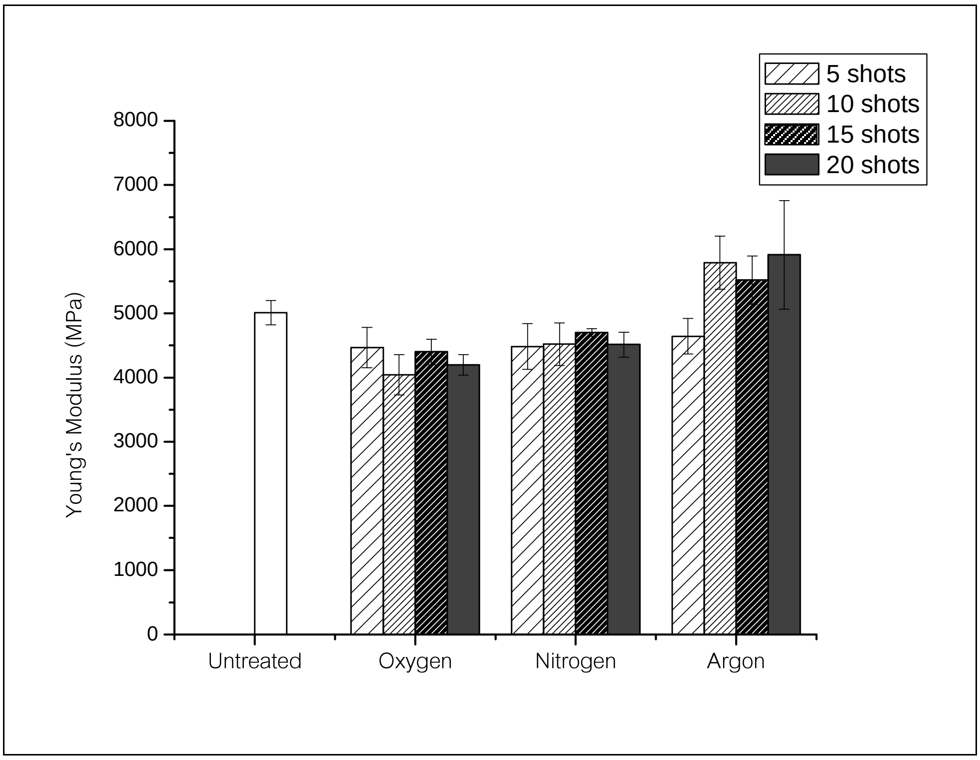


Figure 4.15 Young's modulus of untreated and treated PET films

As shown in Figure 4.15, when considering the number of plasma shots, it can be assumed that the does not significantly affect Young's modulus of oxygen and nitrogen plasma treated films since their Young's modulus is comparable. However, since the movement of polymer molecules in oxygen and nirogen plasma treated films is easier than that of those in argon plasma treated films as previously discussed; thus Young's modulus of the formers is lower than that of the latter.

The results of tensile test as also shown in Appendix A suggested that there was no change in bulk properties of the treated films.

4.2 Properties of laminated PET-MPET films

4.2.1 Tensile properties

Tensile strength of laminated PET-MPET films prepared from untreated and plasma treated films shown in Figure 4.16. It was observed that tensile strength of laminated films prepared from oxygen-plasma treated films was slightly higher than those of oxygen and argon plasma treated films due to the best increasing surface energy after oxygen plasma treatment on PET surface as previously mentioned, resulting in higher interaction between PET and MPET film and an increase in adhered area on PET surface. When considering the number of plasma shot found that it affect to tensile strength of PET film more than after nitrogen and argon plasma treatment. At 10 and 15 shots of plasma treatment, tensile strength of treated PET film distinctly decreased. It can be assumed that adhesion improvement depends on surface energy and etching effect. Although, plasma treatment results in increasing surface energy but overabundantly etching effect may cause the degradation of surface polymer film, thus tensile strength of those laminated films decreased.

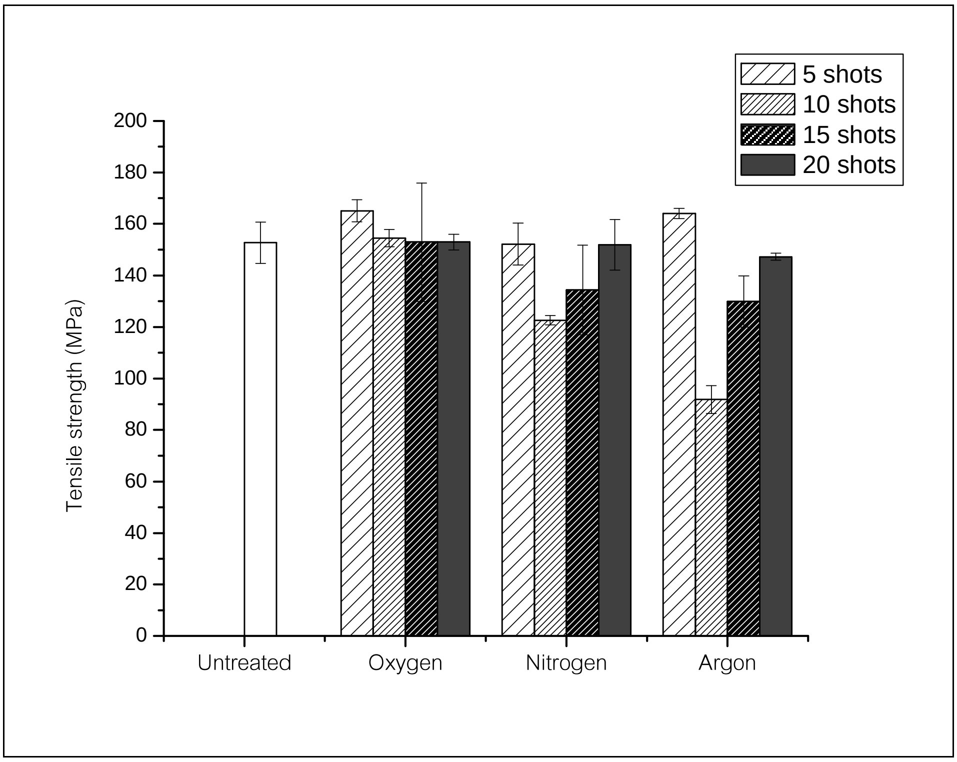


Figure 4.16 Tensile strength of laminated PET-MPET films

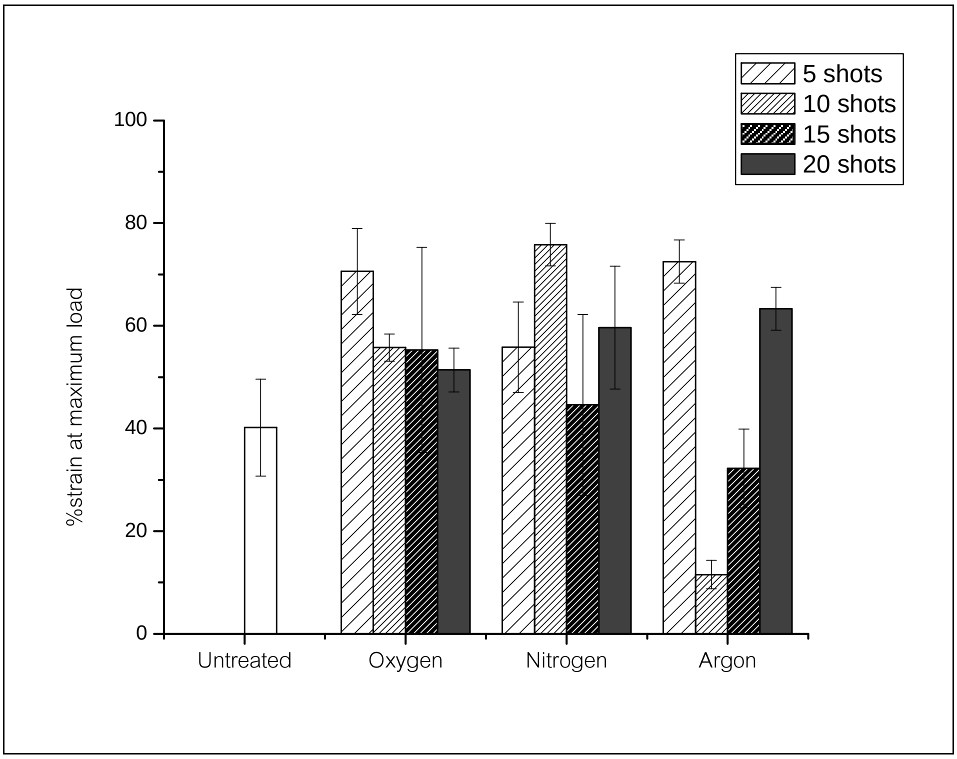


Figure 4.17 %strain at maximum load of laminated PET-MPET films

From Figure 4.17, it was found that at 5 shots of oxygen and argon plasma treatment, and 10 shots of nitrogen plasma treatment, % strains at maximum load of these laminated films are high when compared to that of laminated film prepared from the untreated PET film. Since main application of laminated PET-MPET film is the packaging where the elongation of polymer film is significant in production process, so percentage strain at maximum load of film should be high.

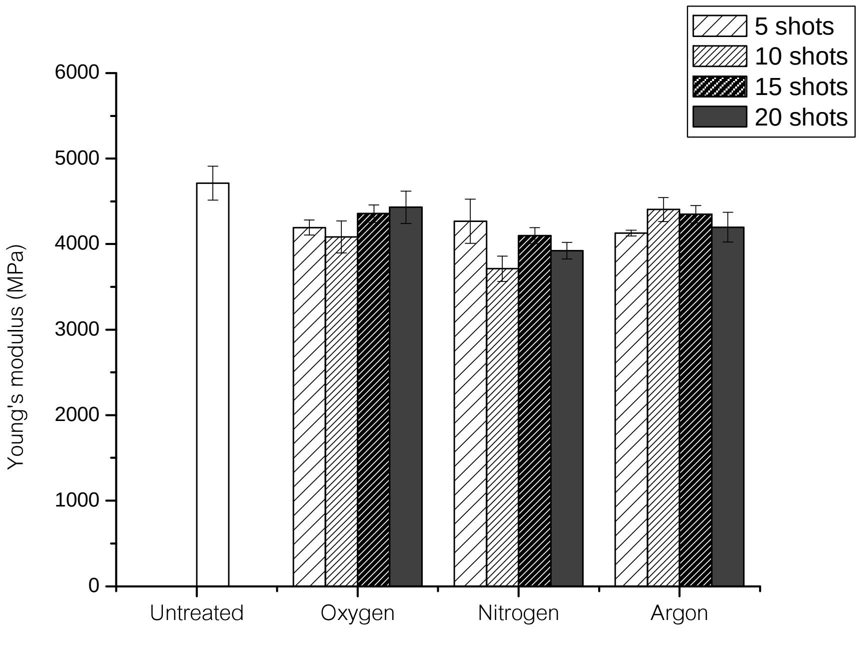


Figure 4.18 Young's modulus of laminated PET-MPET films

Fom Figure 4.18, it was found that Young's modulus of these films was comparable but slighly lower than that prepared from the untreated film. This indicated that plasma treatment does not significantly affect Young's modulus of laminated PET films.

4.2.2 Adhesion strength

As shown in Figure 4.19, when in case of the same gas but different number of plasma shots was considered, in using nitrogen gas exhibited the best of adhesion strength of laminated film at 10 shots, and the lowest at 5 and 20 shots. In case of 20 plasma shots have a cause from highly etching effect of plasma treatment result in decreasing adhesion strength. Even though at 5 plasma shots have less etching effect but lower surface energy, so it did not shown good adhesion strength in laminated film. For using argon gas give a result likewise. On the other hand, oxygen plasma treatment shown the best adhesion at 20 shots due to highest surface energy of treated film. However, at 5, 10 and 15 oxygen plasma shots give a result like in case of nitrogen and argon plasma treatment. Comparing with untreated film, even though laminated films prepared after plasma treatment have less surface roughness but its surface energy is higher, so adhesion strength of those films is higher.

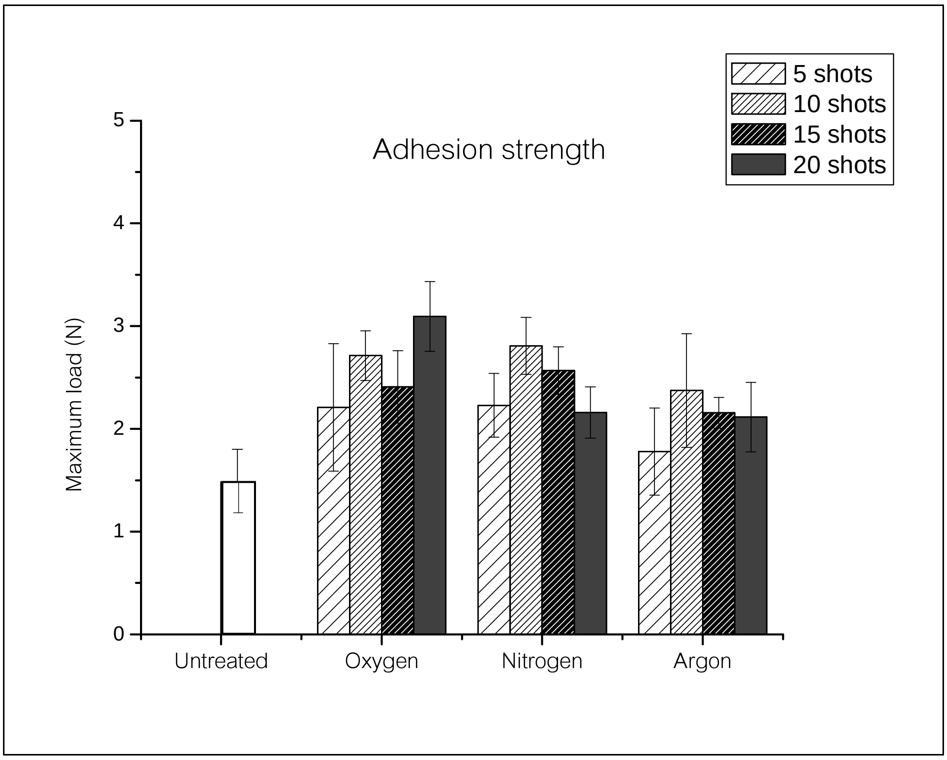


Figure 4.19 Adhesion strength of laminated PET-MPET films

When considering the type of gas, all plasma shots, adhesion strength of laminated films prepared from argon plasma treated films is lowest. This is supported by the result of water contact angle and AFM analysis that argon plasma treatment result in lowest surface energy and low surface roughness.

From the results of t ensile test and adhesion test, It can be concluded that the optimum condition for plasma treatment is to use oxygen plasma at 5 shots due to the following reasons. At this condition, the obtained film exhibits highest tensile strength, high elongation and good adhesion strength. Moreover, oxygen gas is less expensive than argon gas as well as use less energy in the treatment because of lower plasma shot

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In this research, the surface of PET film was modified by high temperature pulsed plasma generated from Theta-pinch device using various conditions. Chemical structure, morphology, physical properties and tensile properties of plasma-treated films were studied. After that plasma-treated PET film was compressed with metalized PET film to prepare laminated PET-MPET films. The mechanical properties of these laminated PET films were investigated in order to determine optimum condition for the treatment. The results can be concluded as follows:

1. FTIR spectra of plasma-treated PET films confirmed formation of hydrophilic functional group on surface films.

2. All plasma-treated PET films exhibited decreasing surface roughness resulted from etching effect.

3. Wettability of plasma-treated PET films is higher than that of the untreated film indicating higher surface energy. The surface free energy of the film can be altered by varying the number of plasma shot and the gas type.

4. There was no change in the bulk properties of the PET film after plasma treatment

5. Most of laminated films prepared from plasma treated PET films exhibited better tensile properties and adhesion strength than that prepared from the untreated PET film.

6. Optimum condition for treatment is to use oxygen plasma at 5 shots.

5.2 Recommendation

The effects of charging voltage and pressure used in plasma treatment on the characteristics of PET film and laminated PET films should be studied.

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APPENDICES

APPENDIX A

Physical and Mechanical properties

Water contact angle of PET film

Table A-1 The water contact angles of PET films obtained immediately after plasma treatment.

Type of gas	No. of plasma shots	Contact angle						
		1	2	3	4	5	Mean	SD
Untreated	0	72	72	72	72	72	72.0	0.00
Oxygen	5	30	28	28	30	34	30.0	2.45
	10	28	29	28	28	30	28.6	0.89
	15	25	27	28	26	27	26.6	1.14
	20	26	26	26	25	26	25.8	0.45
Nitrogen	5	30	30	36	33	32	32.2	2.49
	10	31	33	32	30	28	30.8	1.92
	15	30	29	32	31	28	30.0	1.58
	20	30	30	28	25	30	28.6	2.19
Argon	5	37	37	36	38	38	37.2	0.84
	10	37	36	36	36	36	36.2	0.45
	15	35	35	37	36	34	35.4	1.14
	20	34	34	36	36	33	34.6	1.34

Table A-2 The water contact angles of PET films obtained 7 days after storage

Type of gas	No. of plasma shots	Contact angle						
		1	2	3	4	5	Mean	SD
Untreated	0	72	72	72	72	72	72.0	0.00
Oxygen	5	39	39	39	39	39	39.0	0.00
	10	39	38	40	40	38	39.0	1.00
	15	37	37	37	36	36	36.6	0.55
	20	37	37	36	38	37	37.0	0.71
Nitrogen	5	40	40	40	40	42	40.4	0.89
	10	39	39	40	40	40	39.6	0.55
	15	40	38	40	39	39	39.2	0.84
	20	39	39	39	39	39	39.0	0.00
Argon	5	41	43	42	42	41	41.8	0.84
	10	40	45	43	40	40	41.6	2.30
	15	40	41	41	42	43	41.4	1.14
	20	38	42	43	41	43	41.4	2.07

Table A-3 The water contact angles of PET films obtained 14 days after storage

Type of gas	No. of plasma shots	Contact angle						
		1	2	3	4	5	Mean	SD
Untreated	0	72	72	72	72	72	72.0	0.00
Oxygen	5	40	41	42	42	40	41.0	1.00
	10	40	42	40	43	40	41.0	1.41
	15	39	37	41	38	36	38.2	1.92
	20	42	41	40	39	40	40.4	1.14
Nitrogen	5	43	44	43	43	43	43.2	0.45
	10	40	42	41	42	43	41.6	1.14
	15	40	40	41	41	42	40.8	0.84
	20	41	39	42	40	39	40.2	1.30
Argon	5	45	48	46	46	48	46.6	1.34
	10	48	46	47	46	46	46.6	0.89
	15	47	48	46	48	44	46.6	1.67
	20	46	48	46	46	46	46.4	0.89

Haze of PET films

Table A-4 Haze value of untreated and plasma treated PET films

Type of gas	No. of plasma shots	Haze value						
		1	2	3	4	5	Mean	SD
Untreated	0	9.32	9.23	9.30	9.21	9.37	9.286	0.0658
Oxygen	5	9.50	9.52	9.54	9.59	9.58	9.546	0.0385
	10	9.43	9.44	9.32	9.36	9.40	9.390	0.0500
	15	9.62	9.58	9.59	9.55	9.60	9.588	0.0259
	20	9.29	9.25	9.34	9.30	9.32	9.300	0.0339
Nitrogen	5	9.48	9.43	9.48	9.51	9.44	9.468	0.0327
	10	9.19	9.27	9.22	9.33	9.20	9.242	0.0581
	15	9.45	9.52	9.58	9.40	9.32	9.454	0.1014
	20	9.36	9.62	9.51	9.52	9.39	9.480	0.1056
Argon	5	9.31	9.27	9.34	9.25	9.30	9.294	0.0351
	10	9.34	9.26	9.29	9.35	9.41	9.330	0.0579
	15	9.30	9.33	9.21	9.25	9.36	9.290	0.0604
	20	9.56	9.31	9.40	9.66	9.32	9.450	0.1543

Tensile properties of PET films

Table A-5 Tensile properties of untreated PET films.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	174.97	61.40	5108.80
2	175.39	70.03	4754.00
3	180.88	74.55	4873.20
4	174.21	65.82	5112.80
5	186.12	72.59	5208.60
Mean	178.31	68.88	5011.48
SD.	5.10	5.30	189.74

Table A-6 Tensile properties of PET films obtained after oxygen plasma treatment at 5 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	155.63	48.32	4582.50
2	184.18	86.96	4503.20
3	177.29	77.04	3922.50
4	171.00	63.06	4608.50
5	163.20	54.57	4714.00
Mean	170.26	65.99	4466.14
SD.	11.27	15.91	313.11

Table A-7 Tensile properties of PET films obtained after oxygen plasma treatment at 10 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	172.79	76.28	4155.20
2	175.37	68.81	4508.70
3	169.62	84.72	3947.50
4	173.78	87.54	3650.00
5	178.36	89.10	3953.30
Mean	173.98	81.29	4042.94
SD.	3.22	8.55	316.65

Table A-8 Tensile properties of PET films obtained after oxygen plasma treatment at 15 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	171.01	58.19	4570.50
2	171.46	70.15	4134.80
3	172.37	70.48	4242.60
4	176.34	69.09	4563.50
5	172.63	65.40	4480.80
Mean	172.76	66.66	4398.44
SD.	2.11	5.15	198.38

Table A-9 Tensile properties of PET films obtained after oxygen plasma treatment at 20 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	171.93	85.32	4002.20
2	167.06	72.34	4178.00
3	172.02	82.56	4108.00
4	161.96	68.48	4286.10
5	162.43	66.48	4417.60
Mean	167.08	75.04	4198.38
SD.	4.89	8.45	160.33

Table A-10 Tensile properties of PET films obtained after nitrogen plasma treatment at 5 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	190.44	75.35	4881.10
2	192.45	60.35	4344.30
3	178.86	70.39	4449.70
4	171.39	58.59	4762.90
5	160.27	91.09	3979.50
Mean	178.68	71.15	4483.50
SD.	13.42	13.14	357.31

Table A-11 Tensile properties of PET films obtained after nitrogen plasma treatment at 10 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	181.19	79.63	4272.50
2	184.52	84.20	4090.80
3	193.25	95.71	4599.80
4	191.32	84.19	4907.30
5	183.78	83.97	4718.50
Mean	186.81	85.54	4517.78
SD.	5.19	6.01	332.12

Table A-12 Tensile properties of PET films obtained after nitrogen plasma treatment at 15 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	196.10	83.68	4685.60
2	188.96	84.59	4613.90
3	174.43	66.83	4771.00
4	178.54	66.20	4733.60
5	172.91	66.62	4703.50
Mean	182.19	73.58	4701.52
SD.	9.99	9.64	58.72

Table A-13 Tensile properties of PET films obtained after nitrogen plasma treatment at 20 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	179.28	80.74	4763.30
2	187.14	87.76	4307.60
3	158.74	53.82	4433.20
4	187.31	76.32	4549.50
Mean	178.12	74.66	4513.40
SD.	13.45	14.67	193.68

Table A-14 Tensile properties of PET films obtained after argon plasma treatment at 5 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	153.76	48.02	4498.60
2	169.76	62.52	4300.20
3	195.05	90.08	4748.40
4	176.01	64.05	5038.40
5	178.90	80.19	4639.40
Mean	174.70	68.97	4645.00
SD.	14.97	16.40	276.50

Table A-15 Tensile properties of PET films obtained after argon plasma treatment at 10 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	174.63	72.21	5395.50
2	183.15	77.28	5742.90
3	169.82	61.66	5443.30
4	176.33	71.45	5949.30
5	166.22	60.90	6402.30
Mean	174.03	68.70	5786.66
SD.	6.47	7.14	411.79

Table A-16 Tensile properties of PET films obtained after argon plasma treatment at 15 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	186.90	81.71	5031.20
2	172.99	69.96	5581.20
3	163.06	62.93	5951.80
4	163.51	69.97	5504.40
Mean	171.62	71.14	5517.15
SD.	11.17	7.79	378.30

Table A-17 Tensile properties of PET films obtained after argon plasma treatment at 5 shots.

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	160.30	65.18	6167.40
2	149.70	48.16	4644.90
3	174.53	70.08	5503.90
4	140.99	40.55	6538.60
5	134.69	36.54	6695.70
Mean	152.04	52.10	5910.10
SD.	15.83	14.88	843.22

Mechanical properties of laminated PET-MPET films

1. Tensile properties of laminated PET-MPET films

Table A-18 Tensile properties of laminated PET-MPET films

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	163.41	53.63	4576.19
2	153.80	39.23	4609.90
3	150.96	39.84	4601.73
4	141.09	27.03	5054.88
5	154.35	41.20	4710.84
Mean	152.72	40.18	4710.71
SD.	8.01	9.43	199.11

Table A-19 Tensile properties of laminated PET-MPET films obtained after oxygen plasma treatment at 5 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	167.75	76.69	4299.37
2	160.49	61.66	4081.39
3	160.94	61.41	4256.68
4	170.15	74.57	4192.01
5	166.30	78.52	4137.81
Mean	165.13	70.57	4193.45
SD.	4.26	8.37	87.85

Table A-20 Tensile properties of laminated PET-MPET films obtained after oxygen plasma treatment at 10 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	156.03	55.24	3977.94
2	151.46	56.10	3823.26
3	159.60	59.50	4252.18
4	152.19	55.74	4098.87
5	153.13	52.13	4257.75
Mean	154.48	55.74	4082.00
SD.	3.35	2.62	185.68

Table A-21 Tensile properties of laminated PET-MPET films obtained after oxygen plasma treatment at 15 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	162.10	64.82	4343.16
2	148.08	47.41	4186.98
3	157.20	59.66	4383.15
4	179.71	78.79	4467.15
5	117.46	25.74	4389.37
Mean	152.91	55.28	4353.96
SD.	22.92	19.99	103.58

Table A-22 Tensile properties of laminated PET-MPET films obtained after oxygen plasma treatment at 20 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	152.13	51.43	4543.72
2	149.13	44.31	4566.20
3	152.97	54.48	4230.60
4	152.55	51.74	4217.69
5	157.72	54.99	4591.63
Mean	152.90	51.39	4429.97
SD.	3.09	4.26	188.71

Table A-23 Tensile properties of laminated PET-MPET films obtained after nitrogen plasma treatment at 5 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	155.10	63.74	3975.63
2	160.93	61.82	4380.09
3	141.82	44.46	4644.77
4	157.55	60.86	4133.15
5	145.38	48.16	4196.49
Mean	152.16	55.81	4266.02
SD.	8.18	8.83	256.56

Table A-24 Tensile properties of laminated PET-MPET films obtained after nitrogen plasma treatment at 10 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	120.42	74.67	3704.74
2	121.35	69.32	3947.70
3	124.62	77.84	3721.93
4	124.20	76.88	3646.01
5	122.54	80.37	3548.40
Mean	122.63	75.82	3713.75
SD.	1.80	4.17	147.32

Table A-25 Tensile properties of laminated PET-MPET films obtained after nitrogen plasma treatment at 15 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	112.53	24.91	4027.01
2	134.47	42.00	4143.32
3	122.79	31.86	3996.70
4	146.83	55.84	4091.41
5	155.38	68.34	4230.38
Mean	134.40	44.59	4097.76
SD.	17.38	17.65	93.44

Table A-26 Tensile properties of laminated PET-MPET films obtained after nitrogen plasma treatment at 20 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	157.53	69.27	4016.12
2	158.15	70.05	3800.42
3	138.56	43.86	3840.96
4	144.27	49.97	4000.14
5	160.83	65.13	3950.46
Mean	151.87	59.66	3921.62
SD.	9.83	11.97	96.34

Table A-27 Tensile properties of laminated PET-MPET films obtained after argon plasma treatment at 5 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	160.87	68.96	4159.22
2	164.14	71.83	4100.39
3	164.86	70.37	4169.52
4	164.48	71.54	4093.01
5	166.00	79.76	4126.15
Mean	164.07	72.49	4129.66
SD.	1.92	4.22	34.18

Table A-28 Tensile properties of laminated PET-MPET films obtained after argon plasma treatment at 10 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	85.07	8.73	4374.51
2	94.71	13.05	4202.38
3	89.67	9.69	4427.31
4	99.20	15.58	4594.06
5	90.52	10.59	4418.67
Mean	91.83	11.53	4403.39
SD.	5.36	2.77	140.00

Table A-29 Tensile properties of laminated PET-MPET films obtained after argon plasma treatment at 15 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	116.77	22.28	4265.90
2	143.17	43.65	4258.81
3	129.96	32.75	4319.86
4	125.07	30.01	4404.33
5	134.77	32.49	4497.91
Mean	129.95	32.24	4349.36
SD.	9.94	7.66	101.40

Table A-30 Tensile properties of laminated PET-MPET films obtained after argon plasma treatment at 20 shots

Sample	Tensile Strength (MPa)	% Strain at Maximum Load	Young's Modulus (MPa)
1	145.84	62.97	4138.20
2	145.93	57.79	4250.16
3	147.50	60.96	4476.81
4	148.51	68.08	4047.87
5	148.62	66.67	4078.06
Mean	147.28	63.29	4198.22
SD.	1.35	4.19	173.90

2. Adhesion strength of laminated PET-MPET films

Table A-31 Adhesion strength of laminated PET-MPET films

Sample	Maximum load (N)
1	1.84
2	1.74
3	1.10
4	1.49
5	1.24
Mean	1.48
SD.	0.32

Table A-32 Adhesion strength of laminated PET-MPET films obtained after oxygen plasma treatment at 5 shots

Sample	Maximum load (N)
1	2.57
2	1.49
3	2.57
4	2.000
5	2.300
Mean	2.21
SD.	0.62

Table A-33 Adhesion strength of laminated PET-MPET films obtained after oxygen plasma treatment at 10 shots

Sample	Maximum load (N)
1	2.51
2	2.98
3	2.41
4	2.85
5	2.82
Mean	2.71
SD.	0.24

Table A-34 Adhesion strength of laminated PET-MPET films obtained after oxygen plasma treatment at 15 shots

Sample	Maximum load (N)
1	2.06
2	2.64
3	2.25
4	2.91
5	2.19
Mean	2.41
SD.	0.35

Table A-35 Adhesion strength of laminated PET-MPET films obtained after oxygen plasma treatment at 20 shots

Sample	Maximum load (N)
1	3.11
2	2.97
3	3.17
4	3.58
5	2.64
Mean	3.09
SD.	0.34

Table A-36 Adhesion strength of laminated PET-MPET films obtained after nitrogen plasma treatment at 5 shots

Sample	Maximum load (N)
1	2.28
2	2.00
3	2.06
4	2.75
5	2.05
Mean	2.23
SD.	0.31

Table A-37 Adhesion strength of laminated PET-MPET films obtained after nitrogen plasma treatment at 10 shots

Sample	Maximum load (N)
1	3.05
2	3.13
3	2.46
4	2.68
5	2.72
Mean	2.81
SD.	0.28

Table A-38 Adhesion strength of laminated PET-MPET films obtained after nitrogen plasma treatment at 15 shots

Sample	Maximum load (N)
1	2.41
2	2.69
3	2.63
4	2.26
5	2.85
Mean	2.57
SD.	0.23

Table A-39 Adhesion strength of laminated PET-MPET films obtained after nitrogen plasma treatment at 20 shots

Sample	Maximum load (N)
1	1.79
2	2.32
3	2.20
4	2.06
5	2.43
Mean	2.16
SD.	0.25

Table A-40 Adhesion strength of laminated PET-MPET films obtained after argon plasma treatment at 5 shots

Sample	Maximum load (N)
1	2.23
2	1.18
3	2.04
4	1.52
5	1.92
Mean	1.78
SD.	0.43

Table A-41 Adhesion strength of laminated PET-MPET films obtained after argon plasma treatment at 10 shots

Sample	Maximum load (N)
1	2.01
2	1.75
3	2.40
4	3.20
5	2.49
Mean	2.37
SD.	0.55

Table A-42 Adhesion strength of laminated PET-MPET films obtained after argon plasma treatment at 15 shots

Sample	Maximum load (N)
1	2.22
2	1.94
3	2.27
4	2.28
5	2.06
Mean	2.15
SD.	0.15

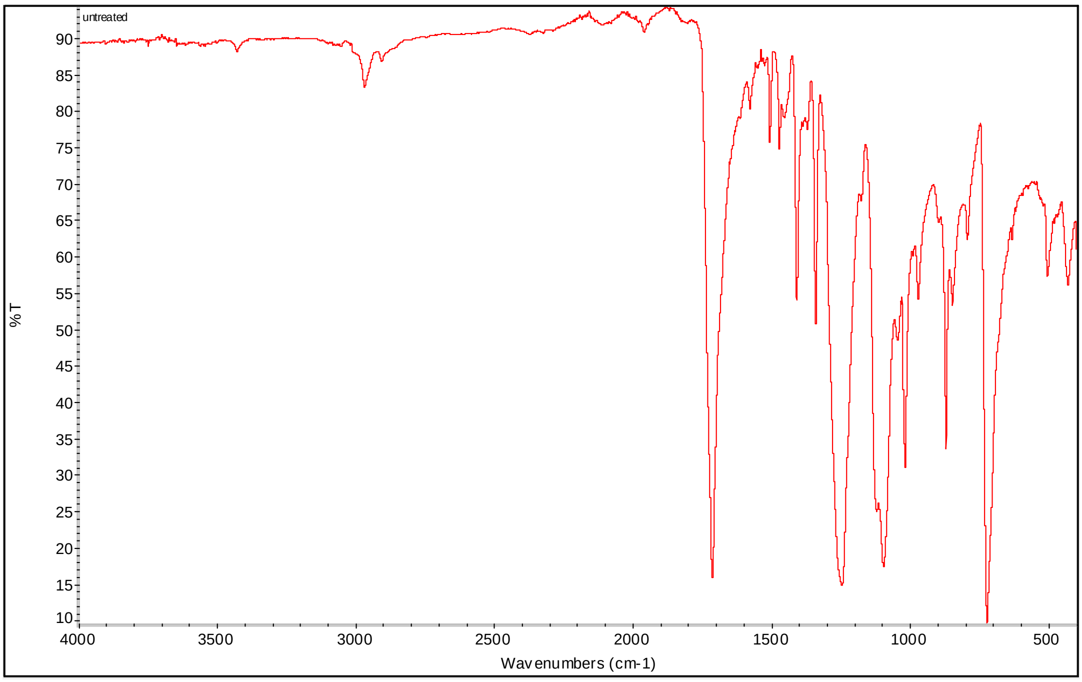
Table A-43 Adhesion strength of laminated PET-MPET films obtained after argon plasma treatment at 20 shots

Sample	Maximum load (N)
1	2.24
2	2.40
3	2.09
4	1.54
5	2.30
Mean	2.11
SD.	0.34

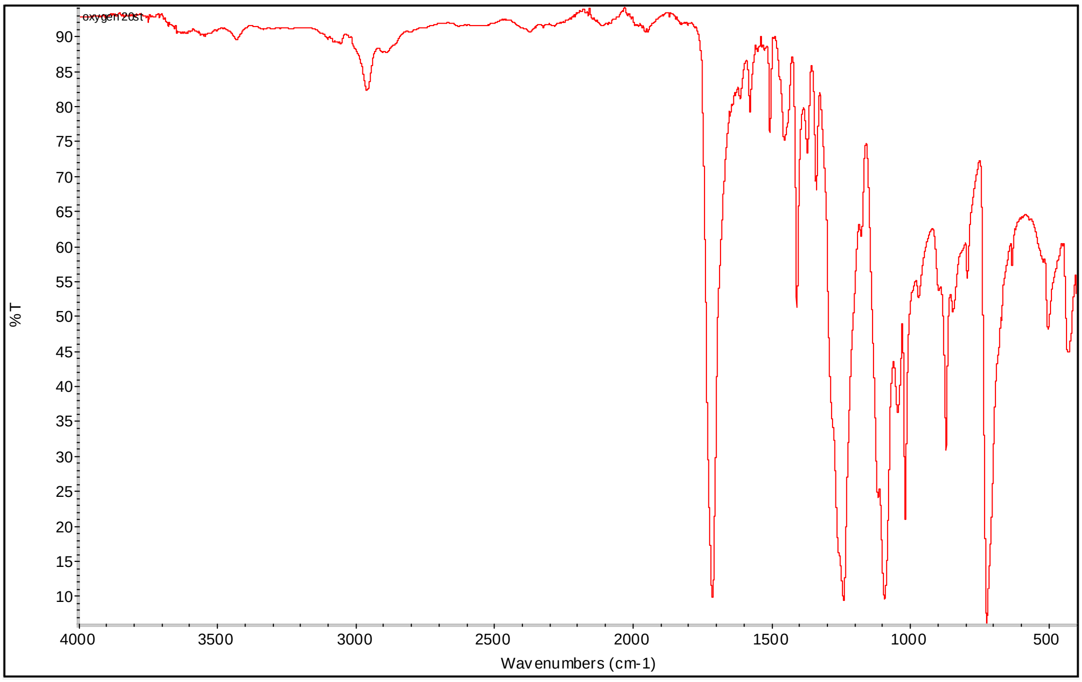
APPENDIX B

ATR-FTIR Spectra

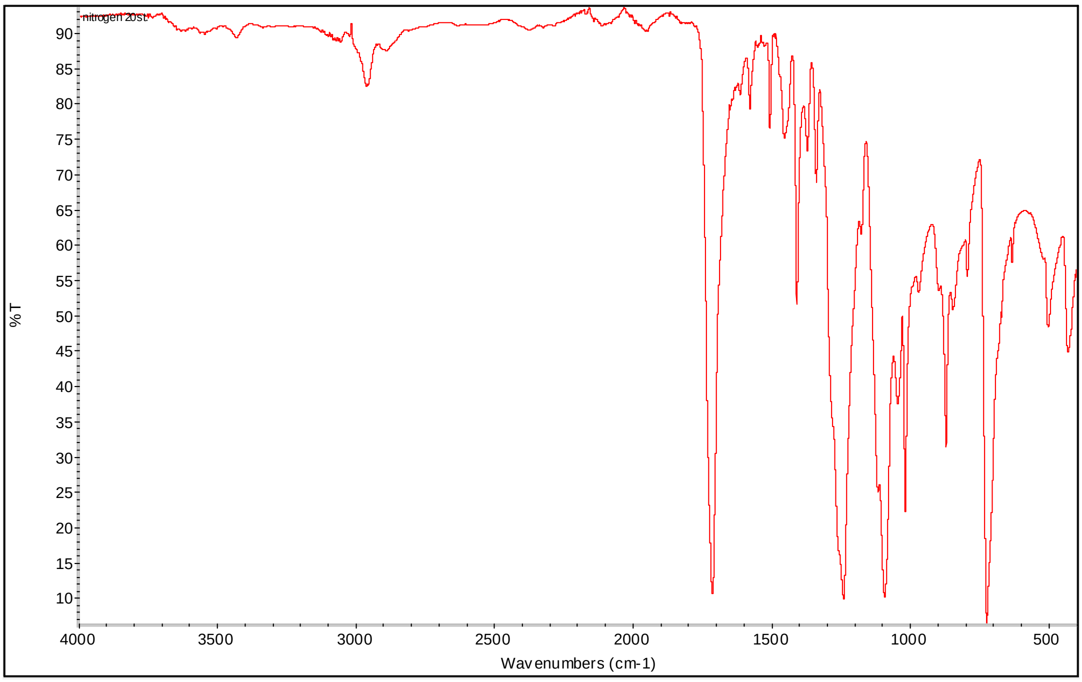
ATR/FT-IR Spectrum of untreated PET film



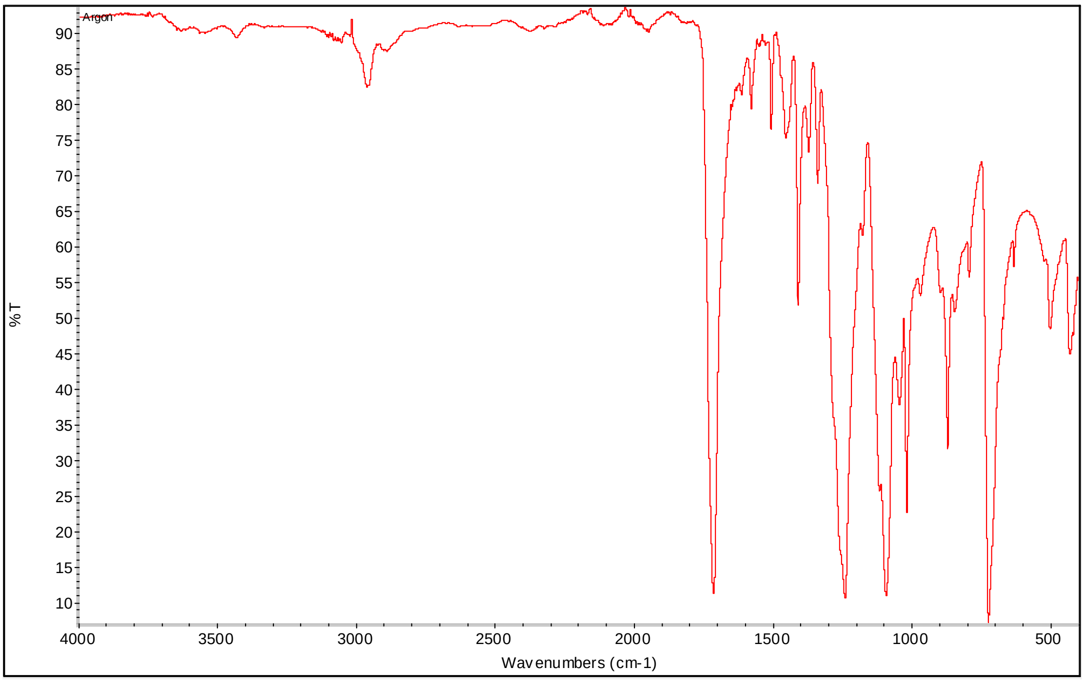
ATR/FT-IR Spectrum of PET film treated by oxygen plasma at 20 shots



ATR/FT-IR Spectrum of PET film treated by nitrogen plasma at 20 shots



ATR/FT-IR Spectrum of PET film treated by argon plasma at 20 shots



APPENDIX C

Morphology

Surface roughness of PET film

Table C-1 RMS of untreated and plasma-treated PET films

Type of gas	No. of plasma shots	RMS (nm)				
		1	2	3	Mean	SD
Untreated	0	1.697	1.627	1.703	1.676	0.042
Oxygen	5	1.576	1.600	1.608	1.595	0.017
	20	1.014	0.955	0.882	0.950	0.066
Nitrogen	5	1.593	1.629	1.591	1.604	0.021
	20	1.353	1.478	1.379	1.403	0.066
Argon	5	1.356	1.297	1.389	1.347	0.047
	20	1.021	1.012	0.956	0.996	0.035

Table C-2 Ra of untreated and plasma-treated PET films

Type of gas	No. of plasma shots	Ra (nm)				
		1	2	3	Mean	SD
Untreated	0	1.246	1.173	1.248	1.222	0.043
Oxygen	5	1.217	1.267	1.302	1.262	0.043
	20	0.799	0.771	0.657	0.742	0.075
Nitrogen	5	1.197	1.184	1.225	1.202	0.021
	20	1.120	1.127	1.034	1.094	0.052
Argon	5	1.065	1.017	1.009	1.030	0.030
	20	0.821	0.773	0.748	0.781	0.037

BIOGRAPHY

Miss. Aroonsri Ngamaroonchote was born in Bangkok, Thailand on January 6, 1985. She received the Degree of the Bachelor of Science in Materials Science Major from Faculty of Science, Chulalongkorn University in 2007. Then, she continued her post graduate study in Applied Polymer Science and Textile Technology Major at the Department of Materials Science, Faculty of Science, Chulalongkorn University and ultimately completed the Degree of the Master of Science in Applied Polymer Science and Textile Technology in May 2010.