CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Flammability & Flame retardants

Flammability is a characteristic of a material that pertain to its relative ease of ignition and relative ability to sustain combustion

Natural and synthetic polymers can ignite on exposure to heat. Ignition occurs either spontaneously or results from an external source such as a spark or flame. If the heat evolved by the flame is sufficient to keep the decomposition rate of the polymer above that required to maintain the evolved combustibles within the flammability limits, then a self-sustaining combustion cycle is established.

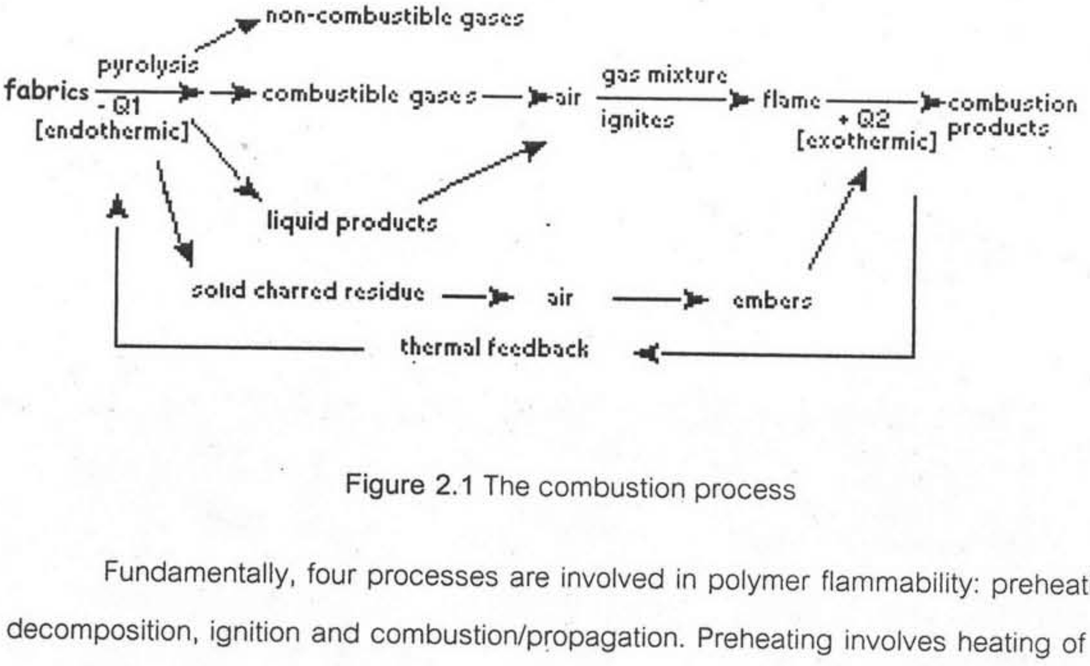

Figure 2.1 The combustion process

Fundamentally, four processes are involved in polymer flammability: preheating, decomposition, ignition and combustion/propagation. Preheating involves heating of the material by means of an external source, which raises the temperature of the material at a rate dependent upon the thermal intensity of the ignition source, the thermal conductivity, the specific heat, and the latent heat of fusion and vaporization of the material. When sufficiently heated, the material begins to degrade, i.e., it loses its original properties as the weakest bonds begin to break. Gaseous combustion products are formed, the rate being dependent upon such factors as intensity of external heat, temperature required for decomposition, and rate of decomposition. The concentration of flammable gases increases until it reaches a level that allows sustained oxidation in the presence of the ignition source. The ignition characteristics of the gas and the availability of oxygen are two important variables in any ignition process. After ignition and removal of the ignition source, combustion becomes self-propagating if sufficient heat is generated and is radiated back to the material to continue the decomposition process. The combustion process is governed by such variables as rate of heat generation, rate of heat transfer to the surface, surface area, and rates of decomposition. Flame retardancy, therefore, can be achieved by eliminating (or improved by retarding) any one of these variables. A flame retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, i.e. during heating, decomposition, ignition or flame spread.

2.1.1 Types of flame retardants [8-9]

A distinction is made between reactive and additive flame retardants. Reactive flame retardants are reactive components chemically built into a polymer molecule. Additive flame retardants are incorporated into the polymer either prior to, during or (most frequently) following polymerization.

In finishing process, some chemicals are used as flame retardant, and they classified into four types as follows;

2.1.1.1 Inorganic flame retardants

Metal hydroxides are the largest class of all flame retardants used commercially today and are employed alone or in combination with other flame retardants to achieve necessary improvements in flame retardancy. Antimony compounds are used as synergistic co-additives in combination with halogen compounds, facilitating the reduction in total flame retardant levels needed to achieve a desired level of flame retardancy. To a limited extent, compounds of other metals also act as synergists with halogen compounds. They may be used alone but are most commonly used with antimony trioxide to enhance other characteristics, such as smoke reduction or afterglow suppression. Ionic compounds have a very long history as flame retardants for wool- or cellulose-based products. Inorganic phosphorus compounds are primarily used in polyamides and phenolic resins, or as components in intumescent formulations.

a) Metal hydroxides

Metal hydroxides function in both condensed and gas phases of a fire by absorbing heat and decomposing to release water by hydration. These make the polymer cool and the flame and dilute the flammable gas mixture. Very high concentrations (50 to 80%) required to impart flame retardancy often adversely affect the mechanical properties of the polymer into which they are incorporated.

Aluminium hydroxide, also known as alumina trihydrate (ATH) is most widely used flame retardants. It decomposes when exposed to temperatures over 200°C, which limits the polymers in which it can be incorporated. Magnesium hydroxide is stable to temperatures above 300°C and can be processed into several polymers.

b) Antimony compounds

Antimony trioxide is not a flame retardant, but it is used as a synergist. It is utilized in plastics, rubbers, textiles, paper and paints, typically 2-10% by weight, with organochlorine and organobromine compounds to diminish the flammability of a wide range of plastics and textiles.

Antimony oxides and antimonates must be converted to volatile species. This is usually accomplished by releasing halogen acids. Halogen acids react with antimony-containing materials to form antimony trihalide and/or antimony halide oxide. These materials act both in the substrate (condensed phase) and in the flame to suppress flame propagation. In the condensed phase, they promote char formation, which acts as a physical barrier to flame and inhibits the volatilization of flammable materials. In the flame, antimony halides and halide oxides, generated in sufficient volume, provide an inert gas blanket over the substrate, thus excluding oxygen and preventing flame spread. These compounds alter the chemical reactions occurring in the flame, thus reducing the ease with which oxygen can combine with the volatile products. It is also suggested that antimony oxychloride or trichloride reduces the rate at which the halogen leaves the flame zone, thus increasing the probability of reaction with the reactive species. Antimony trichloride probably evolves heavy vapors which form a layer over the condensed phase, stop oxygen attack and thus choke the flame. It is also assumed that the liquid and solid antimony trichloride particles contained in the gas phase reduce the energy content of the flames by wall or surface effects.

Other antimony compounds include antimony pentoxide, available primarily as a stable colloid or as a redispersible powder. It is designed primarily for highly specialized applications, although manufacturers suggest it has potential use in fiber and fabric treatment.

Sodium antimonate is recommended for formulations in which deep tone colors are required or where antimony trioxide may promote unwanted chemical reactions.

c) Boron compounds

Within the class of boron compounds, by far the most widely used is boric acid. Boric acid (H_3BO_3) and sodium borate (borax) ($Na_2B_4O_7 \cdot 10H_2O$) are the two flame retardants with the longest history, and are used primarily with cellulosic materials, e.g., cotton and paper. Both products are effective, but their use is limited to products for which non-durable flame retardancy is acceptable since both are very water-soluble.

Zinc borate, however, is water-insoluble and is mostly used in plastics and rubber products. It is used either as a complete or partial replacement for antimony oxide in PVC, nylon, polyolefin, epoxy, EPDM, etc. In most systems, it displays synergism with antimony oxide. Zinc borate can function as a flame retardant, smoke suppressant and anti-arcing agent in the condensed phase. Recently, zinc borate has also been used in halogen-free, fire-retardant polymers.

d) Other metal compounds

Molybdenum compounds have been used as flame retardants in cellulosic materials for many years and more recently with other polymers, mainly as smoke suppressants. They appear to function as the condensed-phase flame retardants. Titanium and zirconium compounds are used for textiles, especially wool.

Zinc compounds, such as zinc stannate and zinc hydroxy-stannate, are also used as synergists and as partial replacements for antimony trioxide.

e) Phosphorus compounds

Red phosphorus was first investigated in polyurethane foams and found to be very effective as a flame retardant. It is now used particularly for polyamides and phenolic applications. The flame-retarding effect is due, in all probability, to the oxidation of elemental phosphorus during the combustion process to phosphoric acid or phosphorus pentoxide. The latter acts by the formation of a carbonaceous layer in the condensed phase. The formation of the fragments that act by interrupting the radical chain mechanism is also likely.

Ammonium polyphosphate is mainly applied in intumescent coatings and paints. Intumescent systems puff up to produce foams. Because of this characteristic, they are used to protect materials such as wood and plastics that are combustible and those like steel that lose their strength when exposed to high temperatures. Intumescent agents have been available commercially for many years and are used mainly as fire-protective coatings. They are now used as flame-retardant systems for plastics by incorporating the intumescent components in the polymer matrix, mainly polyolefins, particularly polypropylene.

f) Other inorganic flame retardants

Other inorganic flame retardants, including ammonium sulfamate (NH_4SONH_2) and ammonium bromide (NH_4Br), are used primarily with cellulose-based products and in forest fire-fighting.

2.1.1.2 Halogenated organic flame retardants

Halogenated flame retardants can be divided into three classes: aromatic, aliphatic and cycloaliphatic. Bromine and chlorine compounds are the only halogen compounds having commercial significance as flame-retardant chemicals. Fluorine compounds are expensive and, except in special cases, are ineffective because the C-F bond is too strong. Iodine compounds, although effective, are expensive and too unstable to be useful. Brominated flame retardants are much more numerous than the chlorinated types because of their higher efficacy.

With respect to processability, halogenated flame retardants vary in their thermal stability. In general, aromatic brominated flame retardants are more thermally stable than chlorinated aliphatics, which are more thermally stable than brominated aliphatics. Brominated aromatic compounds can be used in thermoplastics at fairly high temperatures without the use of stabilizers and at very high temperatures with stabilizers.

Halogenated flame retardants are either added to or reacted with the base polymer. Additive flame retardants are those that do not react in the application designated. There are a few compounds that can be used as an additive in one application and as a reactive in another; tetrabromobisphenol A is the most notable example. Reactive flame retardants become a part of the polymer either by becoming a part of the backbone or by grafting onto the backbone. The choice of a reactive flame retardant is more complex than the choice of an additive type. The development of systems based on reactive flame retardants is more expensive for the manufacturer, who in effect has to develop novel co-polymers with the desired chemical, physical and mechanical properties, as well as the appropriate degree of flame retardance. Synergists such as antimony oxides are frequently used with halogenated flame retardants [19].

a) Brominated flame retardants

Bromine-based flame retardants are commonly brominated organic compounds with a relative molecular mass ranging from 200 to that of large molecule polymers. They usually contain 50 to 85% (by weight) of bromine.

Brominated flame retardants most widely used are tetrabromobisphenol A (TBBPA) followed by decabromodiphenyl ether (DeBDE). Both flame retardants are aromatic compounds. The primary use of TBBPA is as a reactive intermediate in the production of flame-retarded epoxy resins used in printed circuit boards. A secondary use for TBBPA is as an additive flame retardant in ABS. DeBDE is used solely as an additive. The greatest use (by volume) of DeBDE is in high-impact polystyrene, which is primarily used to produce television cabinets. Secondary uses include ABS, engineering thermoplastics, polyolefins, thermosets, PVC and elastomers. DeBDE is also widely used in textile applications as a flame retardant in latex-based back coatings.

Hexabromocyclododecane (HBCD), a major brominated cycloaliphatic flame retardant, is primarily used in polystyrene foam. It is also used as a flame retardant for textiles.

b) Chlorinated flame retardants

Chlorine-containing flame retardants belong to three chemical groups: aliphatic, cycloaliphatic and aromatic compounds. Chlorinated paraffins are by far the most widely used aliphatic chlorine-containing flame retardants. They have applications in plastics, fabrics, paints and coatings.

Bis(hexachlorocyclopentadieno)cyclo-octane is a flame retardant having unusually good thermal stability for a chlorinated cycloaliphatic. In fact, this compound is comparable in thermal stability to brominated aromatics in some applications. It is used in several polymers, especially polyamides and polyolefins for wire and cable applications. Its principal drawback is the relatively high use levels required, compared to some brominated flame retardants.

Aromatic chlorinated flame retardants are not used as a flame retardants for polymers.

2.1.1.3 Organophosphorus flame retardants

Principal classes of organophosphorus flame retardants used in plastics and textiles are that of phosphorus, phosphorus-nitrogen and phosphorus-halogen compounds. Phosphate esters, with or without halogen, are the predominant phosphorus-based flame retardants in use.

For textiles, phosphorus-containing materials are by far the most important class of compounds used to impart durable flame resistance to cellulose. These textiles flame retardant finishes usually also contain nitrogen or halogen, or sometimes both.

a) Non-halogenated compounds

Although many phosphorus derivatives have flame-retardant properties, the number of those with commercial importance is limited. Some are additive types and some reactive types. The major groups of additive organophosphorus compounds are phosphate esters, polyols, phosphonium derivatives and phosphonates. The phosphate esters include trialkyl derivatives such as triethyl or trioctyl phosphate, triaryl derivatives such as triphenyl phosphate and aryl-alkyl derivatives such as 2-ethylhexyl-diphenyl phosphate.

The flame retardancy of cellulosic products can be improved through the application of phosphonium salts. The flame-retardant treatments attained by phosphorylation of cellulose in the presence of a nitrogen compound are also of importance

Plasticizers are mixed into polymers to increase flexibility and workability. The esters formed by the reaction of three functional groups of phosphoric acid with alcohols or phenols are excellent plasticizers. Phosphoric acid esters are also remarkable flame retardants, and for this reason are extensively used in plastics.

Aryl phosphate plasticizers are used in PVC-based products. They are also used as lubricants for industrial air compressors and gas turbines. Miscellaneous uses of aryl phosphates are as pigment dispersants and peroxide carriers, and as additives in adhesives, lacquer coatings and wood preservatives.

b) Halogenated phosphates

In addition to the above types, flame retardants containing both chlorine and phosphorus or bromine and phosphorus are used widely. Halogenated phosphorus flame retardants combine the flame-retardant properties of both the halogen and the phosphorus groups. In addition, the halogens reduce the vapour pressure and water solubility of the flame retardant, thereby contributing to the retention of the flame retardant in the polymer.

One of the largest selling members of this group, tris(1-chloro-2-propyl) phosphate (TCPP) is used in polyurethane foam. Tris(2-chloroethyl) phosphate is used in the manufacture of polyester resins, polyacrylates, polyurethanes and cellulose derivatives.

The most widely used bromine- and phosphorus-containing flame retardant used to be tris(2,3-dibromopropyl)phosphate, but it was withdrawn from use in many countries due to carcinogenic properties in animals.

2.1.1.4 Nitrogen-based flame retardants

Nitrogen-based compounds can be employed in flame-retardant systems or form part of intumescent flame-retardant formulations. Nitrogen-based flame retardants are used primarily in nitrogen-containing polymers such as polyurethanes and polyamides. They are also utilized in PVC and polyolefins and in the formulation of intumescent paint systems.

Melamine, melamine cyanurate, other melamine salts and guanidine compounds are currently the most used groups of nitrogen-containing flame retardants. Melamine is used as a flame retardant additive for polypropylene and polyethylene. Melamine cyanurate is employed commercially as a flame retardant for polyamides and terephthalates (PET/PBT) and is being developed for use in epoxy and polyurethane resins. Melamine phosphate is also used as a flame retardant for terephthalates (PET/PBT) and is currently being developed for use in epoxy and polyurethane flame retardant formulations. Also in the development stages for use as flame-retardant additives are melamine salts and melamine formaldehyde for their applications in thermoset resins [25, 61].

2.1.2 Retardation mechanism of flame retardants [10]

2.1.2.1 Physical action

There are several ways in which the combustion process can be retarded by physical action.

a) By cooling.

Endothermic processes triggered by additives cool the substrate to a temperature below that required to sustain the combustion process.

b) By formation of a protective layer (coating).

The condensed combustible layer can be shielded from the gaseous phase with a solid or gaseous protective layer. The condensed phase is thus cooled, smaller quantities of pyrolysis gases are evolved, the oxygen necessary for the combustion process is excluded and heat transfer is impeded.

c) By dilution.

The incorporation of inert substances (e.g., fillers) and additives that evolve inert gases on decomposition dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded.

2.1.2.2 Chemical action

The most significant chemical reactions interfering with the combustion process take place in the solid and gas phases.

a) Reaction in the gas phase.

The free radical mechanism of the combustion process which takes place in the gas phase is interrupted by the flame retardant. The exothermic processes are thus stopped, the system cools down, and the supply of flammable gases is reduced and eventually completely suppressed.

b) Reaction in the solid phase.

Here two types of reaction can take place. Firstly, breakdown of the polymer can be accelerated by the flame retardant, causing pronounced flow of the polymer and, hence, its withdrawal from the sphere of influence of the flame, which breaks away. Secondly, the flame retardant can cause a layer of carbon to form on the polymer surface. This can occur, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer. These form the carbonaceous layer by cyclizing and cross-linking.

2.2 Textile Materials

Textiles are flexible materials comprised of a network of natural or artificial fibers often referred to as thread or yarn. They are formed by weaving, knitting, crocheting, knotting, or pressing fibers together.

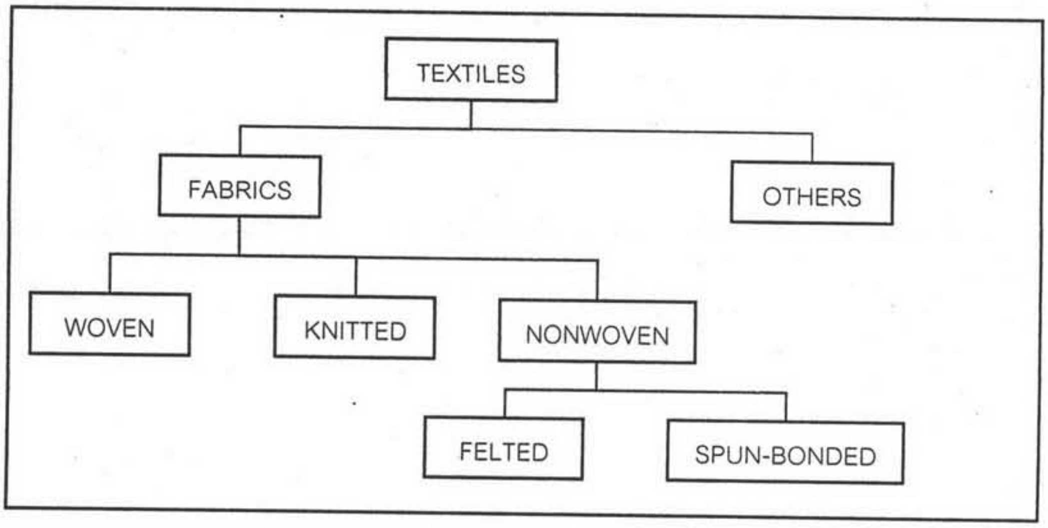

Figure 2.2 Classification of textiles produced based on the methods of assembling the fibers into the textiles [11].

2.2.1 Classification of fiber [11-12].

Fibers used in garments and other domestic purposes can be classified based on their origins into either *natural* or *man-made* that's summarized in Figure 2.3. The natural fibers are subdivided into those of animal origin, which contain protein, and those of plant origin, which contain cellulose. Examples of *protein-based natural fibers* include wool and silk and examples of *cellulose-based natural fibers* include cotton, linen, and hemp.

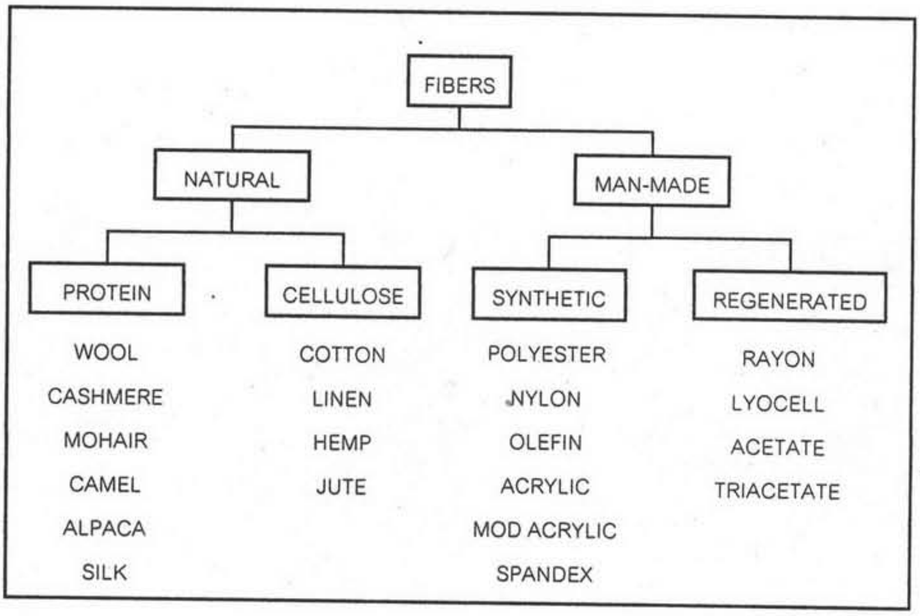

Figure 2.3 Classification of fibers used based on their origin [11].

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

In this research,one type from each fiber class was selected for plasma treatment. In the case of natural fiber, a cellulosic fiber in the form of cotton fiber was used while polyester fiber made from synthetic fiber was used. In addition, polyester and cotton blended fabric was also treated by plasma in order to study the possibility of using this method for blended fabric.

2.2.2 Cotton [11-13].

Cotton, the principal clothing in the world, is a plant fiber. It is cool, soft, and comfortable. When ignited, it burns with a steady flame and smells like burning leaves. The ash left is easily crumbled. Its production is one of the major factors in world prosperity and economic stability.

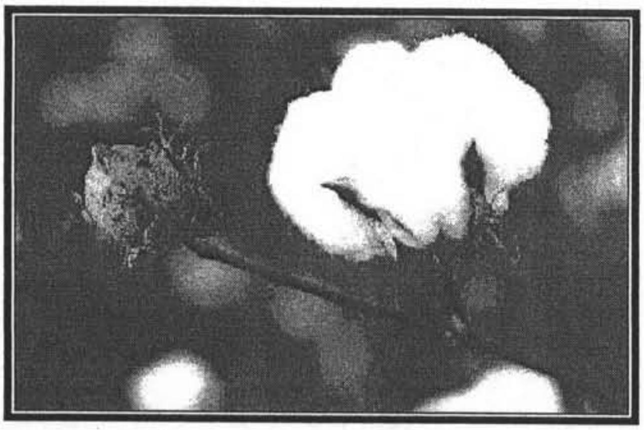

Figure 2.4 Cotton seed in nature [14].

a) Molecular Structure

Cotton is the most widely used textile fiber, composing basically of a substance called *cellulose*. Cellulose is the most abundant of all naturally occurring organic polymers. It is a pure plant cell material consisting of macromolecules of at least several hundreds to several thousands of anhydroglucose units. Cellulose is a polymer of β-D-glucopyranosyl units which are linked together by 1,4-β-D glycosidic bond, with the elimination of water, to form chains of 2,000-4,000 units, as shown in Figure 2.5.

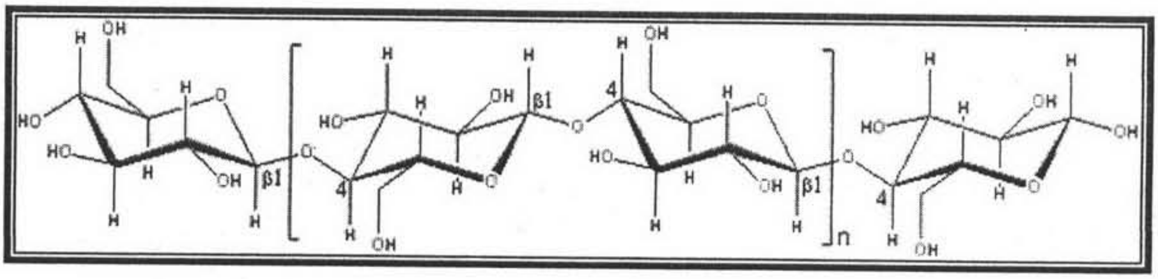

Figure 2.5 Molecular structure of cellulose[15].

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

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

b) Microscopic Properties

The diameter of cotton fiber narrows at the tip. The fiber is hollow in the center and, under a microscope looks like a twisted ribbon. The lumen may appear as a shaded area or as striations; this is more obvious in immature fibers, as illustrated in Figure 2.6.

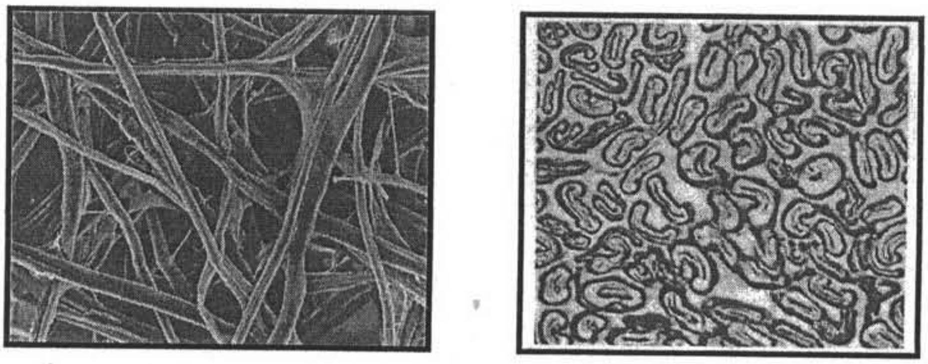

Figure 2.6 SEM and optical photographs of raw cotton fiber In a cross section (right) and a longitudinal view (left) [12].

c) Physical Properties

Color The color of cotton fiber is generally white or yellowish.

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

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

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

Cotton is 10 to 20 percent stronger when wet than dry. Its strength can be increased by a process called mercerization in which yarns or fabrics held under tension are treated with controlled solutions of sodium hydroxide. The alkali causes the fiber to swell, straighten out, and to become more lustrous and stronger.

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

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

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

Dimensional Stability The ability of a fabric to hang easily and fall into graceful shape and folds indicates its drapability. Cotton fibers exhibit neither shrinkage or stretching in their natural state. Woven or knitting cotton fabrics may shrink in the first few launderings because the laundering releases the tension created during weaving or knitting. The relaxation of this tension may cause change in the fabric dimensions.

d) Chemical Properties

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

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

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

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

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

e) Thermal Properties

Effect of Heat Cotton is not thermoplastic so it does not melt. When subjected to high temperature. Long exposure to dry heat above 149°C causes the fiber to decompose gradually, and temperatures greater than 246°C cause rapid deterioration. Excessively high ironing temperatures cause cotton to scorch or turn yellow. Cotton is combustible. It burns upon exposure to a flame and continues to burn when the flame has been removed. It has glow temperature, fire point and auto ignition temperature at 205°C, 210°C and 407°C, respectively. Burning cotton fabric smells like burning paper, and a fluffy, gray ash residue remains. It is not possible to distinguish cotton from other cellulosic fibers by burning.

f) Biological Properties

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

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

2.2.3 Polyester [11-13].

Polyester is one of the most famous fibers. It has many desirable properties such as relatively high tenacity, low creep, good resistance to strain and deformation, high glass transition temperature, good resistance to acid and oxidizing agents, and melts at medium to high temperatures. These physical, chemical, and mechanical attributes to make it excellent candidates not only for apparel and textile products but also for industrial and composite applications.

Polyester is manufactured in many weights including fiber-fill used in pillows and upholstery. Threads spun from polyester fibers are strong, wear exceptionally well, and are used extensively in home sewing and manufactured sewing.

a) Poly(ethylene terephthalate)

poly(ethylene terephthalate) or PET is the majority of the polyester fibe rsproduced and consumed globally. It is the most common fiber-forming polyester. The concept for forming the polyester from diols and diacids was first described by Carothers in 1931 and was developed into a patent on PET by Whinfield and Dickson in 1941. The International Standard Organization (ISO) defines polyester fibers as those from polymers based on a diol and a terephthalic acid. The Federal Trade Commission (FTC) defines them as those which contain at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted terephthalic units and para-substituted hydroxybenzoate units.

b) Molecular Structure

PET is a polycondensation product of ethylene glycol and terephthalic acid or dimethyl terephthalate. Its chemical structure was shown in Figure 2.7.

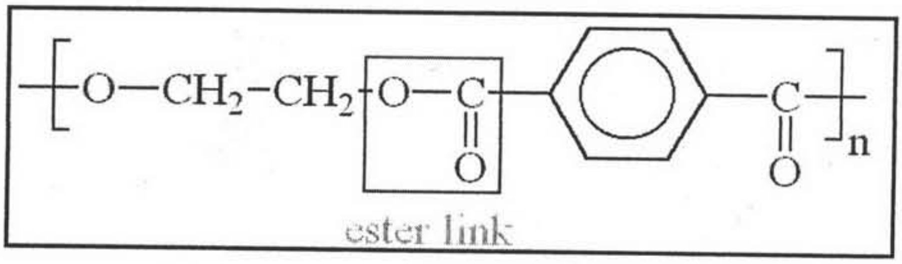

Figure 2.7 The repeating unit of PET.[16]

Dimethyl terephthalate is more frequently used than terephtalic acid, because it is easier to obtain in pure form. The resulting polymer is of superior quality. The polycondensation stage of PET production is shown in Figure 2.8. Methanol is a by-product of this reaction.

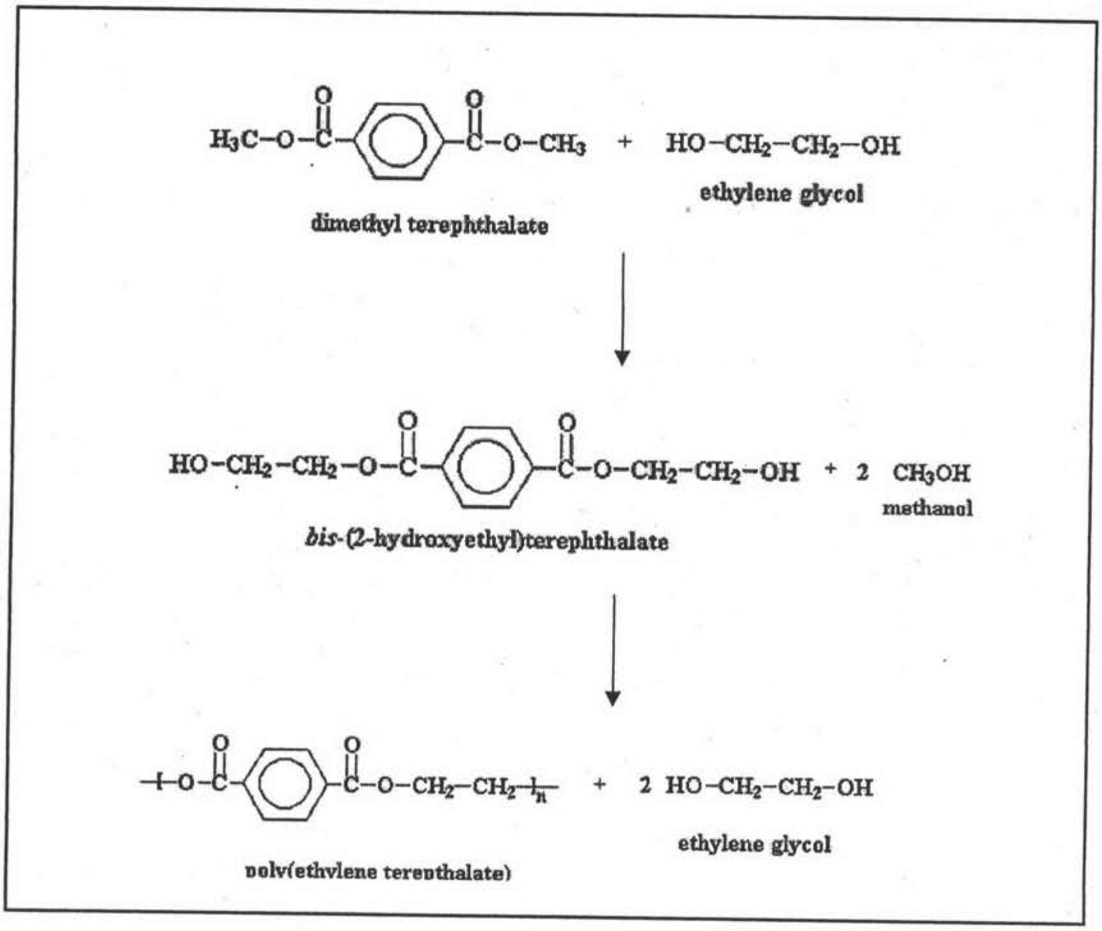

Figure 2.8 The polycondensation stage of PET production [17].

c) Microscopic Properties

PET are manufactured in a variety of cross sections, including round, trilobal, and pentalobal. Under the microscope, round fibers appear as long, smooth rods with spots of pigment as shown in Figure 2.9. This pigmented appearance decreases the luster or brightness of polyesters. Longitudinally, multilobal fibers appear striated.

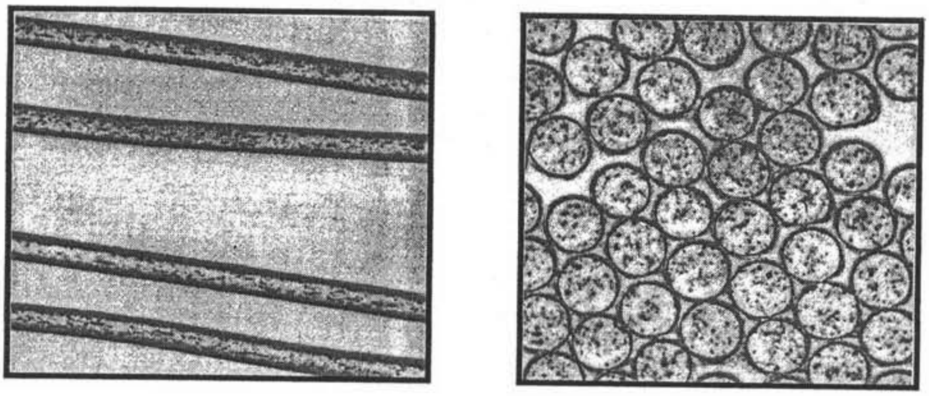

Figure 2.9 Photomicrographs of regular polyester fiber, cross-section (right) and longitudinal view (left).[11].

d) Physical Properties

Shape and Appearance Except for the multilobal varieties, polyesters are generally round and uniform. They can be of any length or diameter as required by fiber producers and yarn and fabric manufacturers. The fiber is partially transparent and white of slightly off-white in color. Optical brighteners are frequently added to produce clear, bright white polyester fibers.

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

Elasticity and Resilience Polyester fibers do not have a high degree of elasticity. In general, polyester fiber is characterized as having a high degree of stretching resistance, which means that polyester fabrics are not likely to stretch out of shape too easily. Polyester fiber has a high degree of resilience. Not only does a polyester fabric resist wrinkling when dry, it also resists wrinkling when wet.

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

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

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

e) Chemical Properties

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

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

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

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

Affinity for Dyes Polyester can be dyed with appropriate disperse and developed dyes at high temperatures. The dyeing of polyester fiber and fabric with disperse dyes is a complex phenomenon and is often a challenge to the dyers and the absence of chemically reactive groups in the molecular chain.

f) Thermal Properties

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

g) Biological Properties

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

2.2.4 Polyester/cotton blended fabric [13]

For satisfactory wash and wear purposes, fabrics for rainwear, tailored clothing, dress shirts, and sport shirts usually have a blend of at least 65 percent polyester with the cotton. Polyester will provide wrinkle resistance and shape retention. Cotton will provide absorbency and consequent comfort. However, unless properly constructed and properly care for, a fabric of a polyester and cotton blend may pucker and lose it shape if the cotton should shrink or if cotton thread is used in sewing. Polyester and cotton blends are well suited for fabrics to be given a permanent press resin finish. The polyester not only contributed its own inherent shape-retentive qualities but also retains its strength, thereby reducing the total potential strength loss from resin finishing that an all-cotton fabric would have.

Where greater absorbency and softer hand are desired, a 50/50 blend is preferable, but there will be a corresponding strength loss of as much as20 percent as well as a slight loss in resilience. A 50/50 blend of polyester and cotton is also satisfactory for effective permanent press finishes.

On the other hand, blends of as much as 80/20 of polyester and cotton, respectively, will have a somewhat stiffer, slicker hand. Strength, wrinkle resistance, and shape retention will be increased but absorbency will be reduced.

2.3 Textile Modification

The modification of woven, knitted, and nonwoven textiles consists of a wide variety of treatments and special processes that give to the fabric desired characteristics needed to enhance its aesthetic and performance properties The modification results in either physical or chemical changes of the fiber or fabric which can be achieved through various techniques, both chemical and physicochemical [18].

2.3.1 Chemical Processes

In general, chemical modification is defined by direct chemical reaction with a given solvent or by the covalent bonding of suitable macromolecular chains to the substrate surface. Chemical process usually involves the development of specified chemical solutions, which exploit specific liquid-polymer interactions [19].

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

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

In addition to alterations in the aesthetics and mechanical properties of chemically modified textiles, there are other disadvantages to this form of processing. These disadvantages include the use of large amounts of chemicals, high temperature treatments, increased cost, and environmental concerns. Environmental problems arise from both air born particulate emission during processing, and water pollution caused by the discharge of untreated effluents. These concerns and limitations have led to the further development of alternative physicochemical processing methods [18].

2.3.2 Physicochemical Processes

Physicochemical techniques have become more commercially attractive and have begun. to supercede conventional wet chemical methods for properties modification. These techniques involve the alteration of the fiber/fabric surface by high energy and coating. Fabric coating processes are direct, indirect, or transfer coating which form a composite material consisting of fiber and matrix phases[20]. This technique provides a fabric with a construction that combines the beneficial properties of a textile material with those of a polymer. High-energy treatments including corona discharge, flame treatments, UV irradiation, hot or cold gaseous plasmas, are much more diverse in applications.

The formation of high-energy electromagnetic fields close to charged thin wires with consequent ionization in their proximity, can lead to an electical-corona discharge [19]. It is known that the corona discharge is not exactly plasma. It generates electrons and ions via ionization. Electrons, ions, excited neutrals, and photons occured by the discharge react with the polymer surface to create surface radicals. Then, these surface free radicals rearrange to form functional groups, thus physicochemical modification of the surface can be achieved. Generally, surface modification by oxidation reaction can lead to enhanced wettability and adhesion. However, there are many problems occuring with this treatment, including non-uniformity, the creation of "pinholes", and difficulty in property control [21]. The variations in electron and ion energies, and their respective randomization, are the main reasons for non-uniformity of treated surfaces. Pinholes are essentially due to the impact of corona, i.e. small arcs, on the surface causing localized heat and penetration into the surface. Due to corona discharges modification can be generated at atmospheric pressure; therefore, it has been widely used for surface modification of textile materials.

The polymer/fabric surface can also be oxidized by flame treatments, a process much similar to corona discharge in providing oxidation. Due to high heat activation of radicals, ions, and molecules in excited states, this form of modification can be accomplished [19]. Flame treatment is commonly used for enhanced adhesion. Variables that must be controlled for property optimization include air-to-gas ratio, flow rate, distance of the flame from the sample, and exposure time [21].

UV exposure to polymeric surfaces has been used to promote photon-activated cross-links and fragmentation of coatings [19]. Wettability and adhesion, as well as antistatic characteristics can be enhanced by UV irradiation in the presence of oxygen leading to photo-oxidation of the surface. Additionally, by conducting UV irradiation in the presence of polymerizable organic vapors, surface polymerization is also possible by creating a thin polymeric film layer on the surface [22]. Like most high-energy sources, UV exposure may result in the deterioration of physical properties and promotes photo-degradation [23].

In light of environmental regulations and concerns, the textile industry has become more interested in plasma applications as a novel finishing technology that significantly reduces toxic-chemical pollution [24]. Plasma technology received enormous attention as a solution for environmental problems in textiles, and there has been rapid development and commercialization of plasma technology over the past decade. Due to plasma treatment is a dry process; therefore, it does not require water or wet chemicals. Additionally, plasma is able to change properties of the surface (such as micro-roughness and functionalization) without affecting bulk properties over the large areas.

2.4 Surface Modification by Plasma Treatment

2.4.1 Definition of Plasma

The term "Plasma" was first used by Irving Langmuir in 1926 to describe the inner region of an electrical discharge [25]. Later definition was broadened by Crookes in 1879, to define a gaseous state of matter (the "4th stated of matter) [1,24]. Plasma may be defined as an ionized gas containing both charged and neutral species, including free electrons, positive and/or negative ions, atoms, and molecules. Ions and radical formation results from electron and ion impact [21]. Electron impact, defined as collisional processes in plasma, is the impact of electrons on other plasma species, including non-ionized neutrals (atoms and molecules). In order to form and sustain plasma, an energy source capable of producing the required degree of ionization must be used. Either direct current (dc) or alternating current (ac) power supplies may be used to generate the electric field required for plasma generation [26]. For many industrial types of plasma, radio frequency (RF) power supplies are used, usually at a standard frequency of 13.56 MHz. Plasma generation may also be performed at various pressures including low (vacuum), atmospheric, or high pressure .

Plasma can be found easily in the universe, including solar coronas, lightening bolts, and nuclear fusion. Plasma also appear in man-made devices such as fluorescent lamps, neon tubes, welding arcs and gas lasers [24]. Plasma technology plays a prominent role in various industrial areas, especially in the electronics industry, such as production or modification of computer chips, semiconductors, aircraft and automobile parts, machine tools, medical implants, and integrated circuits. Recently, plasma techniques are utilized in lighting and large-screen television.

Many types of plasma can be used for industrial processing. They are different in the way they are formed and the range of their characteristics after they are produced. Generally, all plasma are characterized by the same basic parameters no matter the system to which they are coupled. These parameters can be categorized as either internal (qualities of the plasma itself) or external (qualities of the operating control parameters). The main internal parameters of concern are plasma temperature (the average individual temperature of the electrons or ions in the plasma), plasma density (the number of activated species in a plasma), and plasma frequency and collision frequency. The external parameters are the potential (or voltage between the electrodes), distance between the plates, chamber pressure, power, operating frequency, and the type of gas used [27].

2.4.2 Classification of Plasma

Plasma may be classified as "hot" or "cold". Plasma temperature is expressed in units of electronvolts "eV' (1eV = 11600 K). Cold or non-thermal plasma contains very hot free electrons of several eV, which generate high chemical reactivity while neutrals and ions remain near room temperature (0.025 eV). Cold plasma is also partially-ionized with a low fractional ionization. On the other hand, hot or thermal equilibrium plasma contains constituents, which are all at approximately the same temperature so that the heat content, and therefore overall temperature, is high (>10000 K, close to 1eV) and they are close to maximal degrees of ionization (100%). Solar coronas and nuclear fusion generated by thermonuclear reaction are the examples of hot plasma [24]. In the case of a glow discharge, the temperature of the ions and molecules is roughly ambient, while that of the electrons is higher by a factor of 10 to 100. Consequently, plasma produced by glow discharge are called cold plasma because the electron temperature is much higher than the gas temperature [1].

Cold or hot plasma can be used for surface treatment. Due to low heat resistance of most textile/polymeric materials, hot plasma treatment has little to no applicability in surface modification. Cold plasma conducted under low pressure or atmospheric pressure has been used in a wide variety of applications such as surface etching and material processing [24]. However, its generating system involves continuous processes; therefore, the exposure of the material surfaces to the plasma is difficult to control [11, 28].

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

2.4.3 Plasma-Substrate Interactions

The reactive species (positive and negative ions, neutral species, atoms, metastables and free radicals) in plasma bulk are generated by ionization, fragmentation and excitation. They lead to chemical and physical interactions between plasma and substrate surface, depending on plasma conditions such as gas, power, pressure, and exposure time. Different plasma species exhibit very different interaction ranges with the polymer surface. The possible mechanisms for plasma-substrate interaction are illustrated in Figure 2.10.

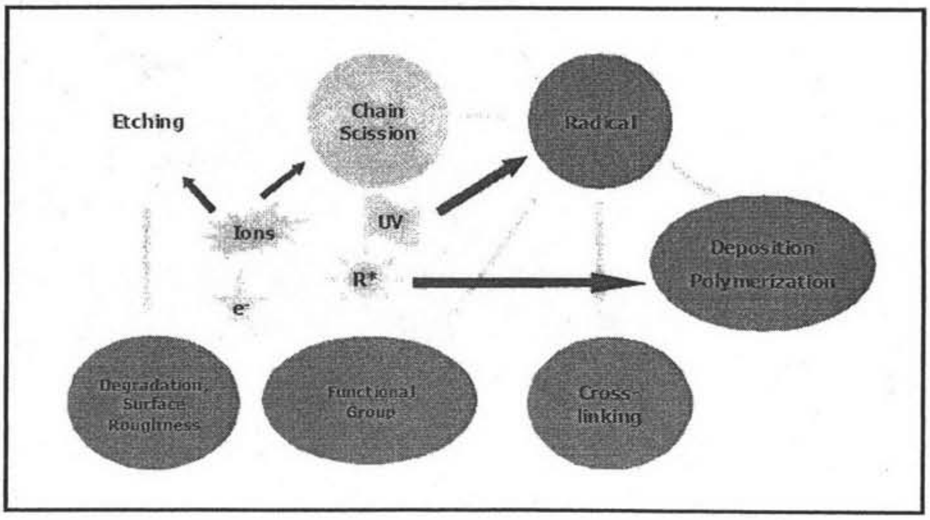

Figure 2.10 Mechanisms of Plasma-Substrate Interaction [24].

When a polymer is exposed to plasma of non-polymerizable gases (Ar, He, O_2, N_2, CO_2, etc.),surface morphology of the polymer changed. As a result, the surface of modified polymer becomes rough. Ions and neutral species in plasma play an important role in colliding with the molecules on the substrate surface and physically etch the surface. This phenomena is well-known as etching effect. In addition, this reactive species bring about the breaking of the long molecular chains into short ones namely chain scission. This leads to chemical interaction with the surface of the molecules, generating new functional groups (functionalization) and radicals. Radicals obtained by chain scission mechanism and oxidation reaction would lead to chemical interaction with surface molecules, including new functional groups (functionalization) formation and inducing cross-linking generation on the uppermost few mono-layers of polymer. Besides, hydrocarbon and fluorocarbon gases can be been used to achieve deposition, and plasma polymerization can be obtained by using a polymerizable [24].

2.4.3.1 Physical Phenomena in Plasma Surface Modifications

2.4.3.1.1 Effects of Plasma Etching

Plasma etching is a physical removing process of a material on the surface of a substrate. This process is dependent on the chemical combination of the solid surface being etched and the active gaseous species produced in the discharge. Molecular weight of the resulting etched material decreases due to the topmost layer is stripped. Etching in plasma treatment has no unfavorable effect on the physical properties of substrate because only few hundred Å layers are etched away [29].

It is well known that etching process results in surface morphology and micro-roughness, preferring to removing amorphous region: that is, selective etching. The etched particles, however, would be re-deposited on substrate surface again, and lead to undesirable results on etching processing [30].

a) Etching and Re-deposition Mechanism

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

b) Effects of Plasma Parameters on Etching

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

The effect of gas on etching process includes both gas type and its flow rate. The different forms and degrees of etching can be achieved by altering either parameter. Specifically, the gas type can determine whether the treatment will induce a higher or lower degree of etching, as well as promote etching in favor of deposition/polymerization. Reactive gases such as O_2 and CF_4, can have a much greater etching effect. However, the composition of these reactive gases must be balanced in order to optimize the etching and/or polymerization balance [18].

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

Pressure can also play an important role in etching mechanism. As pressure is lowered below 0.1 Torr, as in most vacuum plasma systems, the sheath potential is dramatically increased. Given that the pressure is inversely proportional to the mean-free path, this rise in potential translates into a higher energy ion flux [31]. As a result, the ion bombardment promotes etching by physical sputtering or damage-induced mechanisms versus those of chemical etching [32].

2.4.3.1.2 Changes in Surface Morphology and Roughness

As already mentioned, plasma etching of polymer surfaces can lead to morphological and topographical changes. Since most polymers are semi-crystalline; that is to say, they contain both crystalline and amorphous regions. Thus, morphology changes due to selective etching can be occurred [18].

Poletti, G., et al.[33] investigated the morphology changed, mainly root mean square (rms) surface roughness and surface area, of the surface of poly(ethylene terephthalate) (PET) fabrics after cold plasma treatments, using Atomic force microscopy (AFM). The morphology changes were measured as a function of treatment time and as a function of gas pressure. The changes in morphology in the cases of air, He and Ar gases seemed to be due mainly to etching effects. The situation was different for SF_6 and CF_4 gases where reorganization of the surface, possibly due to fluorine atoms grafting, seemed to be effective.

Chen Y.Y., et al.[34] studied the structure, morphology and properties of degummed *Bombyx mori* silk treated by low temperature oxygen plasma. The results showed that slight flutes appeared on the surface of *B. mori* silk fiber and that its surface structure changed after plasma treatment. Because of etching, the weight of the fiber decreased but the breaking strength slightly changed little after short-time treatment. In addition, its conformation changed and its degree of crystallinity decreased as well.

2.4.3.1.3 Chain Scission of Molecules on Polymer Surface

Chain-scission is defined as any event that leads to the breakage of one polymer molecule into two or more parts [35]. This can be occurred through a direct rearrangement of the backbone into two separate entities, or by the loss of side groups and consequent rearrangement, which results inherently in molecular division. Both processes can be occurred because of etching via plasma exposure. The first interaction involves ion bombardment which is a main reason to break off molecular chains on substrate surface, resulting in functionalization. Additionally, chain scission is strongly related to etching effects on polymer surface, leading to weight loss and reduction of molecular weight.

Ward et al [36] suggested the mechanisms of cellulose chain breakage by RF plasma treatment, based on radical formation process. Mainly, the chain breakages of cellulose molecules occured at oxygen of glycosidic bond. Another possibility of chain scission would be ring-opening.

2.4.3.2 Chemical Phenomena in Plasma Surface Modifications

2.4.3.2.1 Radical Formation

In addition to physical modifications, plasma exposure results in changing of the elemental composition of the polymer surface. The active species would collide with the molecules on substrate surface. UV-radiation and the collisions bring about the radical formation by chain scission of molecules and abstraction (taking-off of atoms on molecular chain) [37]. The formation of radical sites occurs through ionization or excitation of the polymers through electrostatic interaction between fast moving electrons and the orbital electrons in the polymers [18]. The consequent ionization leads to molecular fragmentation and the formation of a free radical. In the same way, excitation results in dissociation of the excited polymers, also forming free radicals.

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

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

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

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

Free radicals generated during plasma treatment on polymeric materials play an important role in surface modification. Radical species would react with the radicals on substrate molecules, and then new functional groups are generated. Moreover, these active radicals can also induce the chain cross-linking by re-combination between radicals and initiate graft polymerization of vinyl monomers[38] After plasma treatment on the substrate, unstable free radicals would recombine rapidly with other active species while stable free radicals remain as living radicals [39].

Wilken, R. and Wakida, T. [40,41] found that the free radical intensity of plasma treated fibers was related to plasma parameters (gas, pressure, and exposure time), fiber structures and chemical composition of fibers. The intensity of free radical increased in the following order: cotton>wool>silk>nylon 6 = PET.

2.4.3.2.2 Grafting

Plasma grafting, often referred to as plasma graft-copolymerization, can occur through either of the following two mechanisms [42]. One is the creation of active species on the polymer surface, followed by reaction with a monomer as shown in Figure 2.11. In this mechanism, free radicals are formed on the polymer surface as a result of inert gas plasma treatment. These radicals can either directly initiate grafting or be converted into peroxide or hydroperoxides by the inclusion of an oxidative gas. These activated peroxides also initiate grafting in the presence of the monomer species [43].

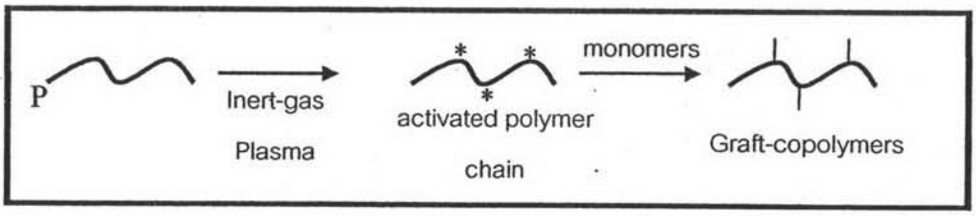

Figure 2.11 The mechanism of plasma grafting through active species created by plasma [42].

The other is direct grafting of the polymer with common or unconventional monomers under monomer-plasma conditions as illustrated in Figure 2.12. Unlike the previous method, this involves a combined plasma and monomer exposure in one step by the use of gaseous monomers in the working gas mixture. Both of these techniques have shown great advantages over conventional grafting by offering a large range of chemical compounds to be used as monomers, varying thickness of monomer layers, and limited destruction [44].

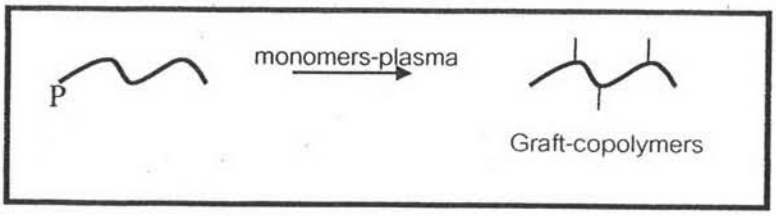

Figure 2.12 The mechanism of plasma grafting through gaseous monomers in the working gas mixture [43].

Man, W. H., and et al [45] prepared chitosan-grafted poly(ethylene terephthalate) using plasma glow discharge. PET texture was exposed to oxygen plasma glow discharge to produce peroxides on its surface . These peroxides were then used as initiator for the polymerization of acrylic acid (AA) in order to prepare a carboxylic and acid group introduced PET (PET-A). Chitosan and quaternized chitosan (QC) were then coupled with the carboxylic groups on the PET-A to obtain chitosan-grafted PET and QC-grafted PET, respectively.

2.4.3.2.3 Cross-linking Formation

It is well-known that the radical formation is strongly related to ion bombardment and UV-radiation. Cross-linking can be achieved by recombination of molecular radicals, resulting in increasing molecular weight of the molecules, while chain scission lead to a decrease in molecular weight. Furthermore, chain scission occurs at the surface while cross-linking Is dominated in the subsurface [46]. 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.

Cross-linking results in an improvement of mechanical properties, a decrease in solubility, elimination of melting point, and resistance to corrosive attack, all of which are desirable properties.

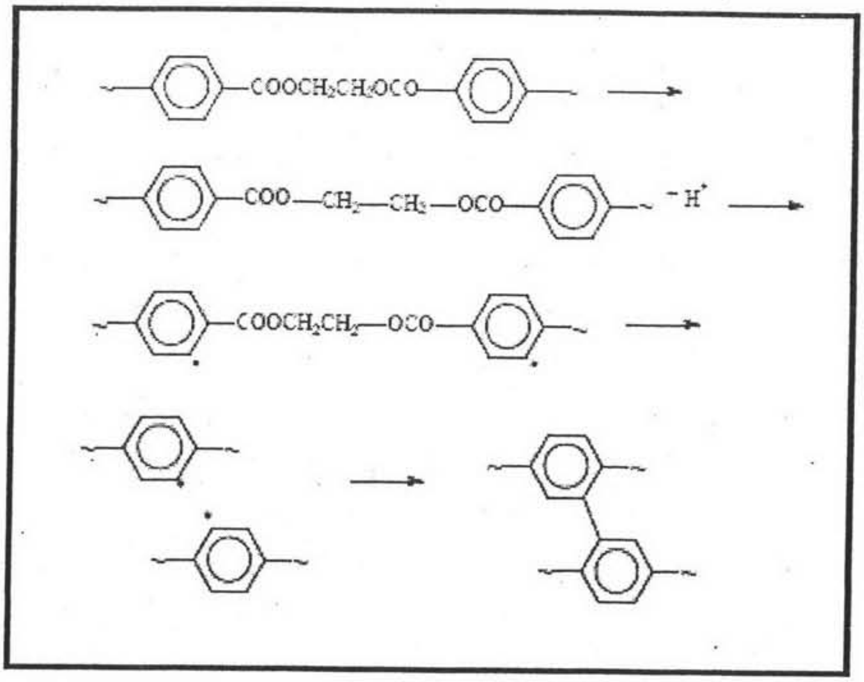

Figure 2.13 Cross-linking by recombination of two aryl radicals obtained by hydrogen abstraction from benzene ring in PET [47].

As shown in Figure 2.13, cross linking of PET results from the recombination of two benzene ring radicals obtained by hydrogen abstraction from the benzene ring. In PET film treated by oxygen plasma, cross-linking reactions are expected from the destruction of benzene ring and ester groups, the combination of ethylene units and benzene ring, and the formation of peroxide [47].

2.4.3.2.4 Functionalization on Polymer Surface

a) Hydrophilic Functionalization

Oxygen and oxygen-containing plasmas are most commonly employed to modify polymer surfaces. In addition, they are very effective at increasing the surface energy of polymers. It has been reported that oxygen plasma can react with a wide range of polymers to introduce a variety of oxygen functional groups, including C-O, C=O, O-C=O, C-O-O, and CO_3 at the surface. For an oxygen plasma, it is well-known that two processes occur simultaneously: etching of the polymer surface through the reactions of atomic oxygen with the surface carbon atoms, giving volatile reaction products; and the formation of oxygen functional groups at the polymer surface through the reactions between the active species from the plasma and the surface atoms. Depending on operation parameters of a given experiment, the balance of these two processes can be achieved [1].

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

Nitrogen and nitrogen-containing plasmas are widely used to introduce nitrogen functionalities on polymer surfaces such as amino, amine, imine and amide. Different nitrogen-containing plasmas have been shown to produce different nitrogen functional groups on a polymer surface [1].

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

In 2004, Chuenchon, S. and et al [6] 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.

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

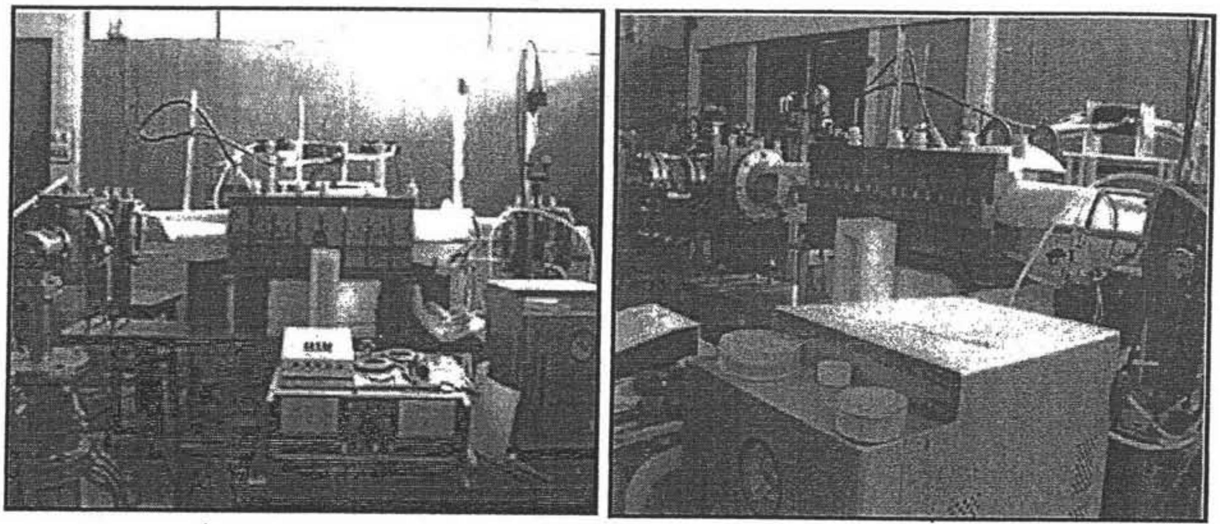

Figure 2.14 Front view (left) and side view (right view) of theta-pinch device used in this research [7].

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

Figure 2.15 shows the basic dynamic process of theta-pinch discharge. This process begins when the capacitor bank is charged to a voltage of a few ten KVs by the charger, The switching of the spark gap controlled by a triggering unit is closed, resulting in discharging to a single turn coil. Because of this, the rapidly increasing axial magnetic field that accompanies the current in the coil induce an electric field. The maximum electric field usually occurs near the wall of quartz tube, and ionizes the neutral gas there most likely; consequently, a plasma current sheath is initiated, which flows opposite to the direction of the discharge current in the coil. Subsequently, the force rapidly compresses the plasma current sheath toward the tube axis, and the neutral gas is simultaneously ionized by the confliction of the sheath. At last, the plasma density and temperature are simultaneously enhanced [48].

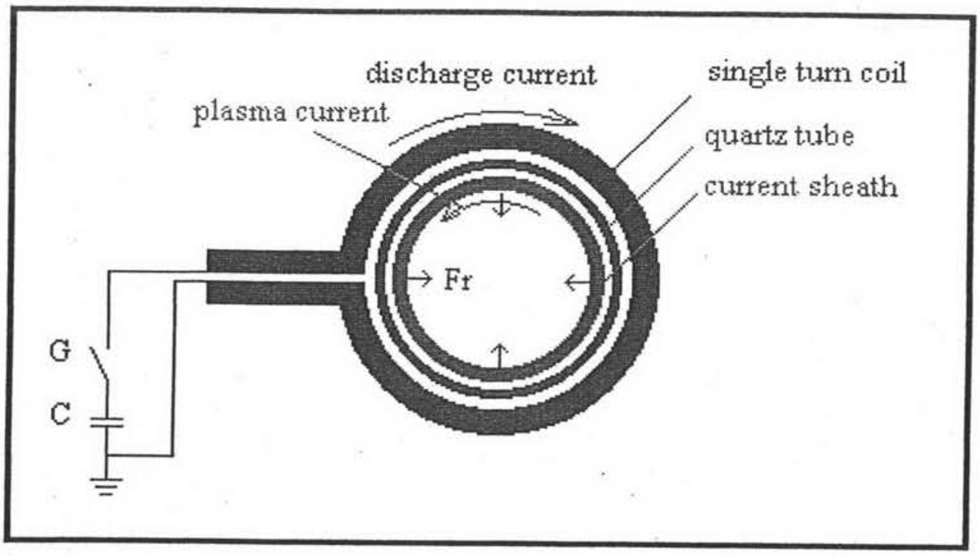

Figure 2.15 Dynamic process of theta-pinch discharge.

b) Hydrophobic Functionalization

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

Surface reactions in a fluorine-containing plasma, including, etching, plasma polymerization, and functionalization can carry out simultaneously. The domination of these reactions in a system depends on gas feed and operating parameters [1]. In tetrafluoromethane (CF_4) plasma, the functionalization on the surface can be generated by competition, etching, and deposition. Etching can increase crystallinity rate and roughness on the polymer surface, while deposition result in functionalization, leading to hydrophobicity on the polymer surface.

Chaivan, P., and et al [49] applied SF_6 low temperature plasma to improve hydrophobic property of Thai silk. The treated samples reached the limit of the absorption times at 180 min and their contact angle increased to 130-140°. These results showed a significant increase in the hydrophobic property compared with the untreated one.

c) Aging Effect

The functional groups generated on the polymer surface by plasma treatment are not stable and have higher mobility than in polymer bulk. In order to become stable after plasma treatment, the surface is likely to be reoriented by the migration of short chain oxidized molecules and the diffusion of oxidized functional groups into polymer bulk [50,51].

The aging effect of functional groups on plasma treated polymer surface can be reduced at low storage temperature and in oxygen atmosphere [52, 53]. The lower storage temperature could lead to slower aging by reduction of the polymer chain mobility [54]. Yasuda, H., et al [55]. found that the decay of wettability was related to degree of cross-linking on polymer treated by oxygen plasma. Aging mechanisms of plasma treated polymers depending on molecular structure of the polymer are shown in Figure 2.16.

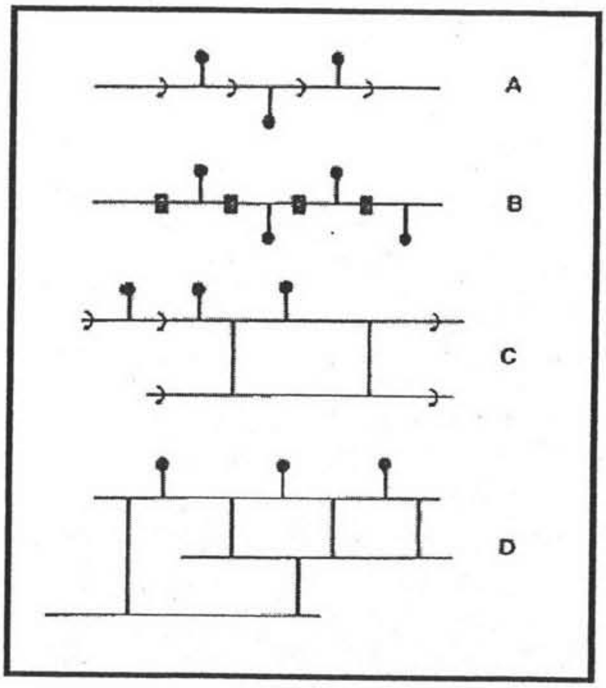

Figure 2.16 Models of molecular mobility on polymer surface by Yasuda [55].

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

Nakamatsu, K. J., et al [56]. studied the aging of plasma surface modification of polytetrafluoroethylene (PTFE) surfaces by keeping the samples in four different environments, some samples were immersed in water at room temperature and at 90°C, and others kept in air at room temperature (20-22°C) and an oven at 100°C. The results showed that the wettability decreased with time due to molecular movement in the polymer and this aging process was reversible since the character of the treated surface changes when the environment changes (i.e., from water to air).

2.5 Plasma Application in Textiles

2.5.1 Wettability Enhancement

The most probably important surface-energy-related characteristic is wettability, which is a requirement for other important functional characteristics of surface. Wettability is the ability to absorb a liquid on a solid surface, or to absorb the liquid in the bulk of fibrous materials such as fabrics. Wettability implies a high surface energy (50-70 dynes/cm) and a low contact angle [57].

Ricky, K. Y., et al [58]. altered the surface properties of Nylon 6 by modifying the molecular structure using oxygen/nitrogen plasma immersion ion implantation (PIII). The observed improvement in the wettability was due to the oxygenated and nitrogen (amine) functional groups created on the polymer surface by the plasma treatment. X-ray photoelectron spectroscopy (XPS) results showed that nitrogen and oxygen plasma implantation resulted in C-C bond breaking to form the imine and amine groups as well as alcohol and/or carbonyl groups on the surface. The water contact angle results revealed that more polar groups (alcohol > amine > amide) gave rise to better wetting properties.

Carmen Almazan-Almazan, M., et al.[59] studied the textural appearance and chemical structure of PET treated by oxygen and carbon dioxide plasmas. The surface-modified samples were characterized by infrared spectroscopy, atomic force microscopy, and inverse gas-solid chromatography. The main difference between the effects of oxygen and carbon dioxide plasmas was mainly related to the time scale of the surface degradation, which was considerably faster for the former. Aggregate globular features revealed by AFM were produced by different treatments due to chain scission and further recombination of evolved products; as a consequence, the specific component of the surface free energy was clearly observed to increase after these long treatments.

Sun, D. and Stylios, G.K., et al [60]. studied the effect of low temperature plasma treatment on the scouring and dyeing of natural fabrics. The contact angles of treated fabrics decreased considerably after O_2 plasma treatment compared to those of untreated cotton samples in both scouring and dyeing bath. This indicated that the surface free energy increased for the plasma-treated fabrics. Morphology changes produced by this modification was small. Plasma oxidation reactions produced oxygen-containing functional groups, which attached to the polymer surface. These functional groups formed and played an important role in increasing hydrophilic properties of the fabrics.

Wrobel, A. M., et al [31] treated PET by plasma initiated in various gases: nitrogen, oxygen, air, carbon dioxide and ammonia. Plasma-treated fabric showed a considerable change in surface structure and wettability. It was observed that the change in the surface structure of polyester fiber was closely dependent on the gas type and treatment conditions. The wetting time of plasma treated fabric considerably dropped in comparison to that of untreated fabric and the best results were obtained by treatment in nitrogen, oxygen and air plasmas. A good correlation existed between change in the surface structure of the fabric and its wettability. Infrared ATR spectroscopy showed some differences in the spectra of plasma treated fabrics but these changes were only moderately dependent on the gas type and plasma conditions.

2.5.2 Water Repellent Finishing

Fluorocarbon, hydrocarbon and mixtures of fluorocarbon and hydrocarbon gases have been used to increase hydrophobicity of polymer substrates in plasma. Compared to oxygen and air plasma treatment, plasma of fluorocarbon and mixtures of fluorocarbon and hydrocarbon gases plasma showed higher durability in air exposure [61, 62].

Mccord M.G., et al [63] treated cotton fabrics by radio-frequency induced plasma of tetrafluoromethane (CF_4) and hexafluoropropene (C_3F_6) gases under different exposure times, pressures, and power levels. The hydrophobicity and water repellency were analyzed with measurements of the cosine of the contact angle ($\cos \Theta$) and wet-out time. The hydrophobicity was enhanced with treatments of both gases. X-ray photoelectron spectroscopy (XPS) revealed increases in the fluorine content of 1-2% for CF_4 plasma and of 2.3-7.8% for C_3F_6 plasma. The relative chemical composition of the C1s spectra after CF_4 and C_3F_6 plasma treatments showed an increase in the relative amounts of –C-O-C- and fluorocarbon groups, whereas peak areas for –COH and –COOH decreased. The hydrophobicity was enhanced by an increase in the fluorine content and fluorocarbon groups.

Iriyama Y., et al [64] studied the water-repellency of nylon fabrics treated in several fluorocarbon plasmas (CF_4, C_2F_4, C_3F_6 and C_6F_{14}). The durability of water-repellency after 30 mins. washing was better for the fabrics treated with saturated fluorocarbon plasmas than those treated with the unsaturated ones. The saturated fluorocarbon plasma introduced longer chains of the polymer on fabric surface, leading to better hydrophobicity and durability.

Regardless of good results from previous research works, fluorocarbon plasma treatments have not been used commercially to improve water-repellency or oil repellency of textile materials. First, fluorocarbon plasma can generate a Teflon-like film not only on the substrate surface, but also on the inside of the plasma chamber. The fluorocarbon coating on the chamber, which is hard to remove, can block gas nozzles and contaminate inside of the plasma chamber. Therefore, use of fluorocarbon plasma for industrial scaled-low-pressure plasma system is not recommended [45]. Secondly, the durability against washing was not well. In order to overcome these issues against fluorocarbon plasma applications, it is suggested that a new plasma system design, plasma conditioning and pre-treatment of fabrics should be considered to optimize durability of washing for textile industrial requirement [24].

2.5.3 Dyeability Enhancement

Dyeability is the ability of a porous or fibrous material such as a fabric to be dyed in bulk. It requires both a high degree of surface adsorptivity and bulk absorptivity. Dyeing affects the surfaces of all fibers throughout a fabric, and may involve chemical reactions with the bulk material of the fibers as well. Dyeing is most effectively done if the fabric to be dyes is wettable and wickable to dyeing solution [57] .

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

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

Antonio R. A., et al [65]. investigated the chemical and topography of PET fabric after treating with air radio frequency (RF) plasma of both a reactive and an inert gas under different operating condition, to correlate them to the plasma-induced variation of the dyeing properties of PET fabrics. The increasing in color depth upon dyeing was obtained after treating PET fabrics with two gases used. This may be easily related to optical effects connected to plasma-induced surface roughness. Additionally, an increase of surface area and the introduction of hydrophilic groups increased water swelling capability and affinity of PET fibers for dyes containing polar groups.

In 2005, Khaymapanya P., et al [7] 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.

Some studies, however, showed that plasma treatment did not increase dyeability of cotton. Kubota et al. [66] found that dyeability of reactive and direct dyes on cotton decreased after argon plasma treatment. The reduction of dyeability resulted from etching away of dyeable amorphous regions, although water absorption of the cotton fiber increased after plasma treatment because of the capillary effect and hydrophilic group formation on the fiber surface. In addition, cross-linking could play important roles in deteriorating dyeability of cotton fabric [32]. Enzyme treatment and enzyme plus plasma treatment have been shown to increase dyeability of cotton fabrics at higher dyeing rate [67-68]. Enhancement of dyeability for PET fibers by air plasma treatment could be derived from a modification of microstructure on the fiber surface resulting in a disintegration of the diffusion barrier [69].

Okuno, T., et al [70]. observed that the increasing in crystallinity of PET fiber resulted in the reduction of dyeability. Etching of plasma treatment was dominant in amorphous region, a dyeable domain, and led to an increasing in crystallinity of PET fiber.

Wakida, T., et al [71-73] extensively investigated the effect of plasma treatment on dyeing properties of nylon 6 fibers. Compared to acid dyes, oxygen plasma treatment enhanced the dye uptake, dyeing rate and dye exhaustion for nylon fibers dyed with basic dyes. Oxygen plasma treatment incorporated –OH and –COOH functional groups on the nylon fiber surface, leading to electronegativity on the fiber surface. Thus, the adsorption of basic dye can be higher than that of acid dye for oxygen plasma treated nylon fibers.

Byrne, G., et al [74]. showed that plasma-induced graft polymerization with acrylic acid improved dyeability of PET fabric using basic dye, as well as anti-soiling and soil release.

Park, J., et al [75]. explained that the formation of carboxylic acid groups (-COOH) on PET surface could result in dyeability enhancement. When acrylic acid was grafted on PET fabric during plasma treatment, higher wettability was observed due to formation of hydrophilic functional groups, such as carboxylic acid groups. This increased the interaction with basic dye, resulting in enhancement of dyeability.

Seto, F., et al [76] and Park, S., et al [77] confirmed that the concentration of carboxylic acid generated by acrylic acid grafting had a significant relationship to an increase of dyeability. This was resulted in the acid-base intermolecular interaction between acidic functional groups and basic dyes.

2.5.4 Altering Electrical Characteristics

Many polymeric fabrics are capable of strongly retaining surface static charge. Their utility for carpeting, upholstery, and clothing is greatly enhanced if the static charge drains off quickly. This can be accomplished through an increase in surface electrical conductivity induced by, for example, bonding copper compounds to plasma-treated fibers to produce conductive fabrics [57].

Kyung, W.O., et al [78]. investigated the effect of plasma treatment on surface characteristics and electrical conductivity of polyaniline-nylon 6 composites fabrics. Oxygen plasma-treated nylon fabric retained the highest conductivity and polyaniline deposit. The surface of nylon 6 fiber was strongly etched by oxygen plasma treatment, and various functional groups such as COOH and C=O could be produced on nylon 6 surface, which was confirmed by XPS. Oxygen was revealed as the most aggressive and effective plasma gas compared with ammonia and argon plasmas in this system. The conductivity of oxygen plasma-treated polyaniline-nylon 6 fabric was more stable with repeated washing and abrasion cycles than polyaniline-nylon 6 fabric without plasma pretreatment [24].

2.5.5 Altering Flame Retardant Property

Most of all fabrics that made from natural and synthetic fibers are polymers that have poor flame retardation. It means that they are easy to burn when they set on fire. There are two main reactions known as oxidation and combustion which occur and sustain the fire. The materials are oxidized in the condense phase to form both solid and gaseous products and the combustion is usually occur in a gas phase. The way to improve flame retardancy of fabrics are to add flame retardant component or to induce the polymerization of the flame retardant monomer on their surface [57].

Shi L. [79] investigated an approach to flame retardation and smoke suppression of ethylene–vinyl acetate copolymer by plasma-induce grafting of acrylamide. It was found that the ignition time of the grafted sample was extended. The limiting oxygen index and char residue were increased. The side groups in the grafted layer not only can be charred in the thermal degradation stage, but can also promote charring of the substrate polymer. The smoke density was lowered after EVA copolymer was grafted with acrylamide.

Quede A. et al [80]. studied the elaboration of fire retardant coatings on polyamide-6 using a cold plasma polymerization process. A cold remote nitrogen plasma process is involved to induce the polymerization of the 1,1,3,3-tetramethyldisiloxane (TMDS) monomer mixed with oxygen. The deposits were efficient fire retardant coatings. The rate of heat release of coated PA-6 decreased by approximately 30% in comparison to PA-6.

Errifai I. et al [81] investigated graft copolymerization of fluorinated acrylate monomer 1,1,2,2-tetrahydroperfluorodecyl acrylate (AC8) onto the PA-6 using a low-pressure microwave plasma process. It was found that the rate of heat released of coated PA-6 was decreased by approximately 50% in comparison to the virgin PA-6.

Tsafack M.J. et al [82] investigated argon plasma-induced graft copolymerization of four acrylate monomers containing phosphorus, diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl)phosphonate (DEAMP) and dimethyl (acryloyloxymethyl)phosphonate (DMAMP) on the cotton and polyacrylonitrile fabrics.