กราฟต์โคพอลิเมอไรเซชันเหนี่ยวนำด้วยพลาสมาของมอนอเมอร์ที่มีฟอสฟอรัสหน่วงไฟบนผ้า

นางสาวปิยรัตน์ เจิมสุจริต

PLASMA-INDUCED GRAFT COPOLYMERIZATION OF FLAME-RETARDANT
PHOSPHORUS-CONTAINING MONOMER ONTO FABRICS

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งานวิจัยนี้ศึกษาเกี่ยวกับการปรับปรุงสมบัติด้านการหน่วงไฟของผ้าฝ้ายและผ้าไหมโดยใช้
กระบวนการกราฟต์โคพอลิเมอไรเซชันเหนี่ยวนำด้วยพลาสมาโดยใช้คลื่นความถี่วิทยุ ของมอนอ
เมอร์หน่วงไฟที่มีฟอสฟอรัสเป็นองค์ประกอบที่มีชื่อว่า 2-เมทาคริโลอิลออกซีเอทิลไดเฟนิล
ฟอสเฟต) และ 2-เมทาคริโลอิลออกซีเอทิลเฟนิลเบนซีนฟอสโฟเนต มอนอเมอร์จะถูกพอลิเมอไรซ์
และกราฟต์ลงบนพื้นผิวของผ้าฝ้ายและผ้าไหมโดยอาร์กอนพลาสมาที่อุณหภูมิและความดันต่ำ
ผลการทดสอบแสดงให้เห็นว่า เมื่อเพิ่มความเข้มข้นของมอนอเมอร์นำไปสู่เปอร์เซ็นต์การกราฟต์
บนผืนผ้ามากขึ้น สิ่งนี้เป็นผลทำให้เกิดการปรับปรุงค่า LOI (ค่า LOI สูงสุด=28%) เมื่อ
เปรียบเทียบกับผ้าที่ไม่ได้ผ่านการกราฟต์ นอกจากนี้น้ำหนักของสารที่เหลือจากการวิเคราะห์
การสลายตัวทางความร้อนของผ้าที่ผ่านการกราฟต์จะมีค่าสูงกว่าผ้าที่ไม่ผ่านการกราฟต์ ที่
ภาวะที่เหมาะสมสมบัติทางกายภาพของผ้าที่ผ่านการกราฟต์มีการเปลี่ยนแปลงเพียงเล็กน้อย แต่
สมบัติเชิงกลของผ้าที่ผ่านการกราฟต์แล้วไม่ถูกทำลาย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
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PIYARAT JERMSUTJARIT: PLASMA-INDUCED GRAFT COPOLYMERIZATION OF FLAME-RETARDANT PHOSPHORUS-CONTAINING MONOMER ONTO FABRICS. ADVISOR: ASST. PROF. BOONCHOAT PAOSAWATYANYONG, Ph.D., CO-ADVISOR: ASST. PROF. WORAWAN BHANTHUMNAVIN, Ph.D., 80 pp.

This thesis studied on the improving of fire resistance of cotton and silk fabrics which were carried out by radio frequency inductively couple plasma induced graft copolymerization of phosphorus-containing monomer, namely 2-methacryloyloxyethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP). The monomers were polymerized and grafted onto surface of cotton and silk fabrics by argon plasma at low temperature and pressure. The surface investigation revealed that the increase in monomer concentration led to an increase in percentage of grafting on the fabrics. This resulted in an improvement of LOI values (the highest LOI value = 28%) compared to that of the non-grafted fabric. Moreover, the weight residues from thermogravimetric analysis of grafted fabrics were higher than that obtained from the non-grafted fabrics. At the optimized condition, the physical property of grafted fabrics was slightly changed but the mechanical property was not damaged.

Field of Study : Petrochemistry and Polymer Science   Student's Signature :

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CHAPTER I

INTRODUCTION

1.1   Statement of the Problem

Among natural textile fibers, cotton and silk are usually used in domestic applications such as clothing, furniture covering and bedding because of their comfort, soft and aesthetic appearance [1-2]. Hence, one of all important properties is the fire resistances [3] since cotton is the flammable fabric (LOI 18.4%). In case of silk, although silk was low natural flammable material due to the high nitrogen content (15-18%) in the structure (LOI 25%) but in some application it still needs to improve fire resistance to fulfill some commercial requirement. Previously, the flame retardant property was improved by immersing in the mixture of borax and boric acid solution [4] but in this method, the flame retardant property of the fabric is not durable becaues it easily removed by water.

Recently, one of the interesting techniques for durability and resistance to washing of flame retardant finishing fabric is plasma technique [5-6]. Plasma treatment is one particular interesting technique for permanent fire prooving on the surface of treated fabrics although after washing. This cause is the strongly bond between flame retardant and the surface of fabric *via* the covalent bonds. Moreover this process is environmentaly friendly, rapid and the desirable properties of fabric is still retained [6] because in plasma, the effect of the treatment are usually confined to surface layer of 1-10 μm in depth and the effect at the outermost layer are strongest [7].

Plasma technologies have been used in many fields related to polymer such as synthesis of new polymeric structures, plasma induced polymerization processes, surface grafting of polymers and modification of polymers. Flame retardants were devided in many types such as halogen (bromine and chlorine), phosphorus, nitrogen, intumescent systems, minerals (Al and Mg), borax and Sb_2O_3. Among numerous types of fire proving agent which have been tested as fire resistance, and among them phosphorus compounds were found to be suitable for this application [1,4]. A phosphorus containing flame retardant can function in the condensed (polymer) phase,

the gas phase or concurrently in both phases. Some phosphorus compounds decompose in the condensed phase to form phosphoric acids or polyphosphoric acids, these can act as dehydration catalysts in cellulose. For example polyphosphoric acids form a viscous molten surface layer or surface glass. This layer can shield the polymeric substrate from the flame (heat) and oxygen [8]. Phosphate esters are thermally stable, high boiling so they are usually used commercially as flame retardants in many types of materials such as plastics, rubbers and textiles [5,9]. The other advantage of organophosphorus base compound is the less toxicity because the mainly machanism is occur on condensed phase and avoid the release of toxic gas [10].

Therefore, the objective of this research is to improve the fire resistance properties of both natural fibers by radio frequency (RF) plasma induced graft polymerization of vinyl phosphate ester onto their surface at the various conditions. In the first step, the phosphorus-containing monomers as flame retardant compounds were synthesized and characterized. The second step, the grafting and the polymerization of various monomers using argon plasma was carried out. The desired flame retardant properties are achieved by creating covalent bonds between the cotton and silk fabrics and the growing polymer at the surface [5].

1.2   Research Objectives

The objectives of this research are as follows:

1. To synthesize the flame retardant phosphorus-containing monomers namely, 2-methacryloyloxy ethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP).

2. To study on the using of RF plasma induced graft-copolymerization of flame retardant phosphorus-containing monomers onto cotton and silk fabrics.

3. To investigate flame-retardant properties, thermal properties, mechanical properties and physical properties of the fabrics before and after treated with both organophosphorus monomers by argon plasma.

1.3   Scope of the investigation

The stepwise investigation was carried out as follows:

1. Literature survey for related research work of the improving of fire resistance properties of fabrics and phosphorus-containing flame retardants.

2. Synthesis and characterization of two organophosphorus compounds:

    - 2-methacryloyloxyethyl diphenyl phosphate (MEDP)

    - 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP)

3. Optimization of graft-copolymerization conditions by argon plasma

    - Ratio of monomer/cross-linking agent**.**

4. Characterization of fabrics grafted with MEDP and MPBP.

5. Characterization of the thermal properties and flame-retardant properties of treated and untreated fabrics.

6. Characterization of the physical property and mechanical property of treated and untreated fabrics.

7. Discussion of the results and summary.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1   Structure and compositions of cotton

Cotton, the purest form of cellulose found in nature, is the seed hair of plants of the genus *Gossypium*. Many species are grown commercially, but they may be conveniently divided into three types. Type 1 fibers have staple lengths which are average fiber lengths varying from 25 to 60 mm. These are include high-quality fine cottons such as the Egyptian, Sudanese, and Sea Island varieties. Type 2 are coarser species with shorter staple lengths (about 13-33 mm), such as American upland cottons. Type 3 species of still shorter staple lengths (about 9-25 mm), are commonly produced in various Asian countries. Major cotton producers at the present time are the USA, China, India, Pakistan, and the Central Asian republics. Other countries which produce small but not insignificant quantities include Mexico, Turkey, Brazil, Egypt, and Sudan [11].

Cotton fibers have a fibrillar structure. Their morphology, illustrated schematically in Figure 2.1, exhibits three main features: primary wall, secondary wall, and lumen. The primary wall consists of a network of cellulose fibrils covered with an outer layer, or cuticle of pectin, protein, mineral matter and wax. The wax renders the fiber impermeable to water and aqueous solutions unless a wetting agent is present. The secondary wall constituents the bulk of a mature fiber and consists almost entirely of fibrils of cellulose arranged spirally around the fiber axis, the direction of the spiral reversing many times along a single fibril. Reversal points frequently correspond with layers and the spiral angle of the fibrils varies from one layer to the next, from about 20 – 35 degrees.
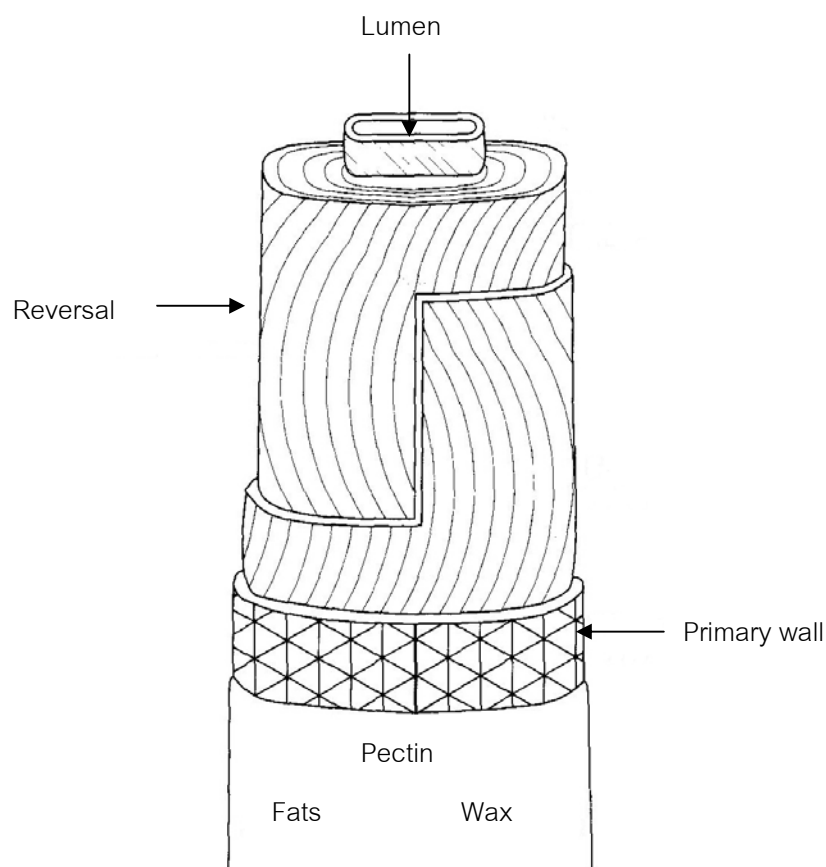
Figure 2.1   Ideal diagram of cotton morphology [11].

The main features of chemical structure of cellulose are well known. It mainly be most conveniently described as a 1,4-β-D glucan, i.e., a condensation polymer of β-D-glucopyranose with 1,4-glycosidic bonds.
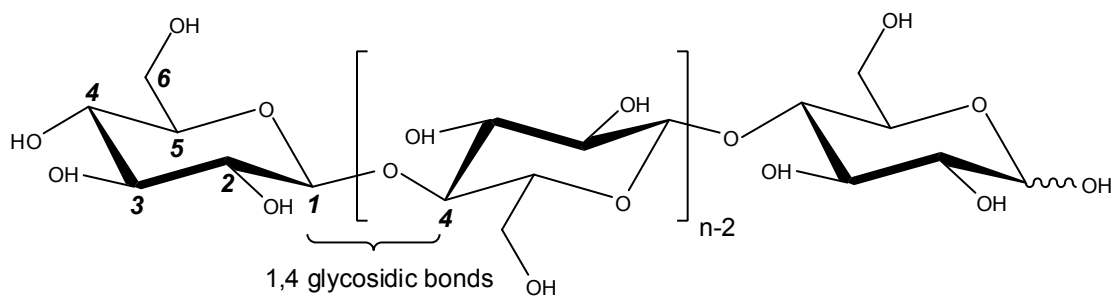
Figure 2.2   Chemical structure of cellulose.

It is instructive to compare the composition of the primary wall with that of the cotton fiber as a whole, since it is the primary wall that becomes disintegrated when preparing cotton for dyeing and printing. Although the primary wall accounts for only 5% by weight of the fiber, it contains most of the non-cellulosic constituents. Table 2.1 gives comparative data for typical cotton composition. The 'other substances' are mostly water-soluble organic acids and sugars. The table illustrates the very high cellulose content of cotton, which surpasses all other natural sources in this respect [11].

Table 2.1   Composition of a typical cotton [11].

Constituent	Proportion of dry weight (%)	
	Whole fiber	Primary wall
Cellulose	94.0	54.0
Protein (%N x 6.25)	1.3	14.0
Pectin	1.2	9.0
Wax	0.6	8.0
Ash	1.2	3.0
Other substances	1.7	12.0

2.2   Structure and compositions of Silk

Silk is protein fibers originated from animals, and is composed of amino acids. Silk contains portions of hydrogen, nitrogen, oxygen, and carbon and are amphoteric, that is it contains both acidic and basic reactive groups which can be attributed to its high nitrogen content (about 15-18%) [4].

Silk is a continuous filament fiber consisting of fibroin protein secreted from two salivary glands in the head (as shown in Figure 2.3) of each larva and a gum called sericin which cements the two filaments together. Silk must be reeled off the cocoon quickly before the pupa begins to rot and taint the thread with unpleasant smells. The cocoon is then softened in hot water to remove the sericin, which frees the silk filament ends for reeling or filature.

White Caterpillar
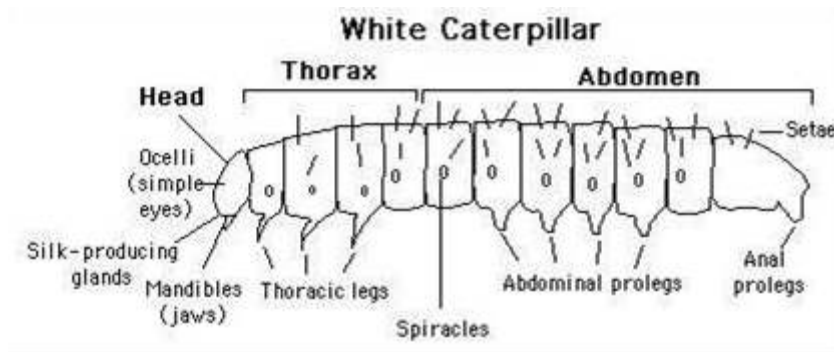
Figure 2.3 The picture of silkworm.

The silk proteins isolated from the cocoon have been characterized more extensively than any of the other silks. A number of groups have reported the amino acid composition of silkworm fibroin as shown in Table 2.2. Generally, domestic silkworm silk heavy chain fibroin contains approximately 87% short chain amino acids (45% glycine, 30% alanine, 12% serine) [12]. Some fibroins contain up to 96% of these three amino acids. The fibroin light chain contains a very different amino acid composition of 15% aspartate, 14% alanine, 11% glycine, 11% serine and a trace of cystine. The consensus peptide crystalline repeat in the heavy chain fibroin is GAGAGSGAAG[SG(AG)$_2$]$_8$Y (G=glycine, A= alanine, S=serine, Y=tyrosine). The amorphous domains are less defined but generally include some of the bulkier side chain amino acids.

Silk filaments are very fine and are much as 300 to 900 meters in length. Silk has a high natural lustre and sheen of a white or cream color; and is one of the strongest fibers at 2.6 to 4.8 grams per denier. When it is dry the elongation (elastic recovery) varies from 10-25% and when wet it will elongate as much as 33-35%. Silk has a relatively high standard moisture regain of 11%. Protein fibers have moderate to high resiliency, that is, they do not wrinkle as easily as cellulosic fabrics and are able to maintain their shape. However unlike cellulosic fabrics, protein fabrics become weaker with excess moisture by silk can lose up to 15% of its original strength. [13]

The silk of *Bombyx mori* is composed of the proteins fibroin and sericin, matter such as fats, wax, sand pigments plus minerals. Fibroin in the *Bombyx mori* comprises a high content of the amino acids glycine and alanine, 42.8 g and 32.4 g respectively as shown in Table 2.2.

Sericin is a complex protein composed of three distinct components as shown in Figure 2.4 (I, II and III) of which sericin III is the interior layer directly adjacent to the

fibroin core. The sericin I outer lay is the most soluble of the three constituents, while sericin III is difficult to dissolve.

Table 2.2   Amino acid composition of fibroin and sericin [14].

Amino acids	% Amino acids in		Amino acids	% Amino acids in	
	Fibroin	Sericin		Fibroin	Sericin
Glycine	42.8	8.8	Glutamic acid	1.7	10.1
Alanine	32.4	4.0	Serine	14.7	30.1
Leucine	0.7	0.9	Threonine	1.2	8.5
Isoleucine	0.9	0.6	Phenylalanine	1.2	0.6
Valine	3.0	3.1	Tyrosine	11.8	4.9
Arginine	0.9	4.2	Proline	0.6	0.5
Histidine	0.3	1.4	Methionine	0.2	0.1
Lysine	0.5	5.5	Tryptophan	0.5	0.5
Aspartic acid	1.9	16.8	Cystine	0.1	0.3

2.3   Decomposition of materials

To understand how flame retardants work it is first necessary to see how materials burn. Solid materials do not burn directly: they must be first decomposed by heat (pyrolysis) as shown in Figure 2.5 to release flammable gases. Visible flames appear when these flammable gases burn with the oxygen (O_2) in the air. If solid materials do not break down into gases, then they will only smolder slowly and often self extinguish, particularly if they "char" and form a stable carbonaceous barrier which prevents access of the flame to the underlying material. However, as we all know, even materials such as wood do in fact burn vigorously, because once ignited the heat generated breaks down long-chain solid molecules into smaller molecules which transpire as gases.
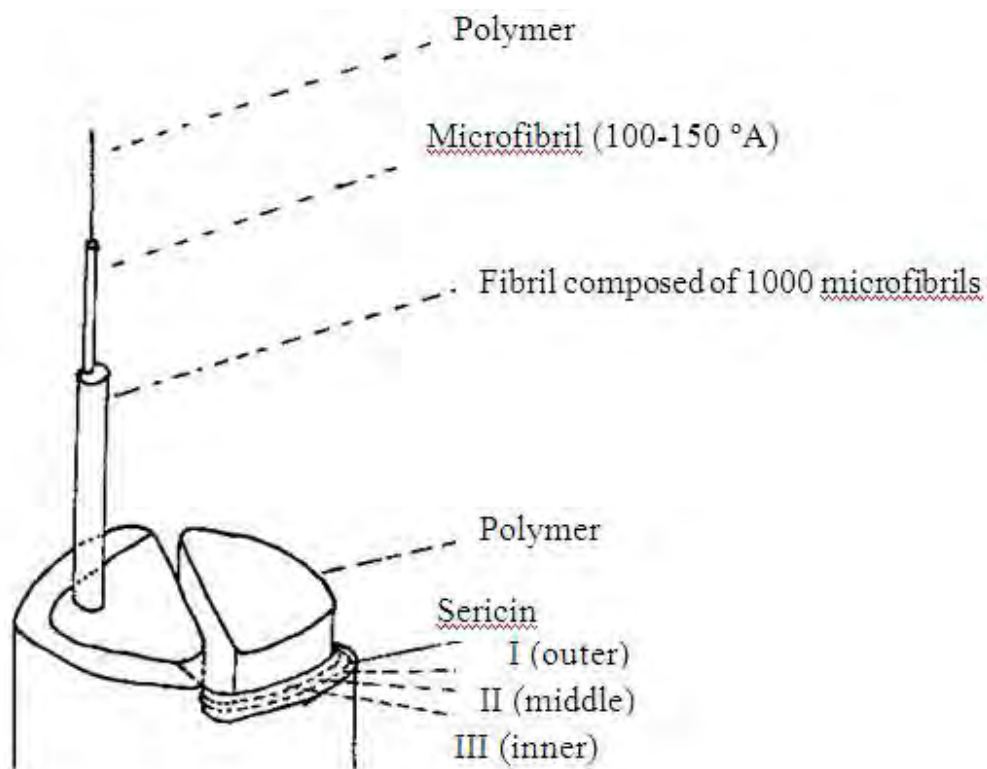
Figure 2.4   The structure of raw silk fiber [15].
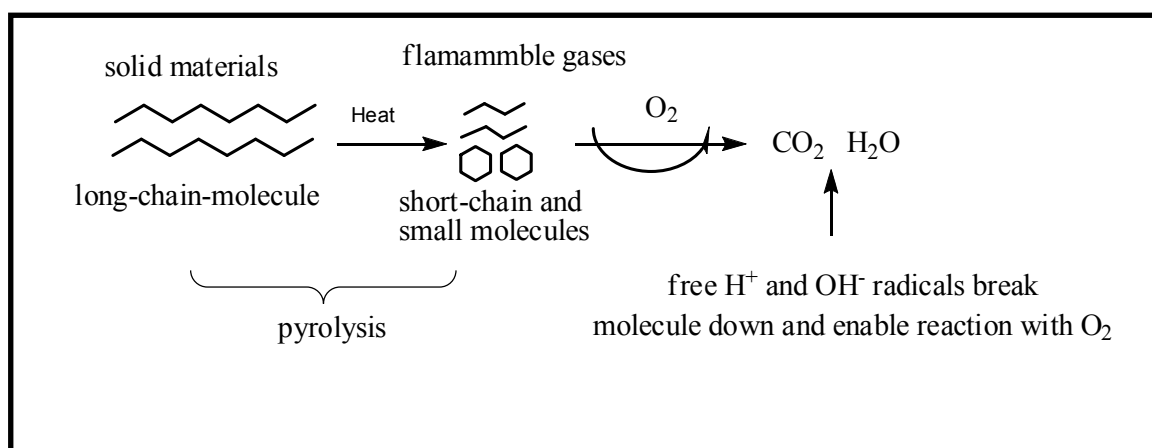
Scheme 2.1   Mechanism of pyrolysis.

2.4 Flame Retardants

Flame retardants are chemicals which are added to combustible materials to render them more resistant to ignition. They are designed to minimize the risk of a fire starting in case of contact with a small heat source such as a cigarette, candle or an electrical fault. If the flame retarded material or an adjacent material has ignited, the flame retardant will slow down combustion and often prevent the fire from spreading to other items. Since the term "flame retardant" describes a function and not a chemical class, there is a wide range of different chemicals which are used for this purpose. Often they are applied in combinations. This variety of products is necessary, because materials and products which are to be rendered fire safety are very different in nature and composition. For example, plastics have a wide range of mechanical and chemical properties and differ in combustion behavior. Therefore, they need to be matched to the appropriate flame retardants in order to retain key material functionalities. Flame retardants are thus necessary to ensure the fire safety of a wide range of materials including plastics, foam and fiber insulation materials, foams in furniture, wood products, natural and man-made textiles. These materials are e.g. used in parts of electrical equipment, cars, airplanes and building components.

2.4.1 Mode of action of flame retardant

By chemical and/or physical action, flame retardants will inhibit or even suppress the combustion process. They interfere with combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread. The amount of flame retardant one has to add to achieve the desired level of fire safety can range from less than one percent for highly effective flame retardants up to more than 50 percent for inorganic fillers. Typical ranges are 5 to 20 percent by weight.

The most effective chemical action may take place by the reaction in the gas phase. The radical gas phase combustion process is interrupted by the flame retardant, resulting in cooling of the system, reducing and eventually suppressing the supply of flammable gaseous. Another is in the solid phase, the flame retardant builds up a char layer and shields the material against oxygen and provides a barrier against the heat source (flame).

The less effective physical action may take place by cooling, energy absorbing (endothermic) processes triggered by additives and/ or the chemical release of water cool the substrate to a temperature below that required for sustaining the combustion process. The other mechanism is the formation of a protective layer (coating), the material is shielded with a solid or gaseous protective layer and protected from heat and oxygen necessary for the combustion process. The last of physical action may take place by the dilution, inert substances (fillers) and additives evolving non-combustible gaseous dilute the fuel in the solid and gaseous phases [8].

2.4.2   Type of flame retardants

2.4.2.1   Halogenated flame retardants

These act by effectively removing the H and OH radicals in the gas flame phase. This considerably slows down or prevents the burning process, thus reducing heat generation and so the production of further gaseous flammable material. In fact, the mechanism is as follows. When exposed to high temperatures, the flame retardant molecule releases bromine (Br) or chlorine (Cl), as free radicals which react with hydrocarbon molecules (flammable gases) to give HBr or HCl. These then react with the high-energy H and OH radicals to give water and the much lower energy Br or Cl radicals, which are then available to begin a new cycle of H and OH radical removal. The effectiveness of halogenated flame retardants thus depends on the quantity of the halogen atoms they contain and also, very strongly, on the control of the halogen release. Because chlorine is released over a wider range of temperatures than bromine, it is then present in the flame zone at lower concentrations, and so is less effective. Bromine is released over a narrow temperature range, thus resulting in optimal concentrations in the flame zone. Many different bromine containing flame retardants have been developed, with bromine atoms bound into different organic molecules. These offer different properties, in terms of how the bromine is bound into the flame retardant molecule (aliphatically, aromatically), and of how the flame retardant molecule interacts with different plastics. Different specific brominated compounds can thus be added to or chemically bound into different plastics without deteriorating their properties (flexibility, durability, color). The many varying brominated products available thus offer high flame retardancy effectiveness solutions for all plastics

currently on the market and for most of their varied applications [16]. Similarly, several chlorinated flame retardants are also available, and are effective flame retardants in standard and technical plastics, thermosets, textiles and rubbers.

2.4.2.2 Antimony trioxide Sb$_2$O$_3$

Antimony trioxide does not have flame retarding properties on its own, but is an effective synergist for halogenated flame retardants. It acts as a catalyst, facilitating the breakdown of halogenated flame retardants to active molecules. It also reacts with the halogens to produce volatile antimony halogen compounds, which are themselves directly effective in removing the high energy H and OH radicals which feed the flame phase of the fire, thus reinforcing the flame suppressing effect of the halogenated flame retardants. When added to PVC, antimony trioxide acts to suppress flames by activating the chlorine present in the plastic itself [17].

2.4.2.3 Nitrogen flame retardants

The mechanisms of nitrogen containing flame retardants are not fully understood, but it is thought that they have several effects such as formation of cross-linked molecular structures in the treated material. These are relatively stable at high temperatures, thus physically inhibiting the decomposition of materials to flammable gases (needed to feed flames) or release of nitrogen gas which dilutes the flammable gase reducing flames. Moreover, synergy with phosphorus containing flame retardants by reinforcing their function to be effective.

Nitrogen based flame retardants are often used in conjunction with other flame retardants, in particular phosphorus based flame retardants. They can be either simply added to plastics, or reacted into the plastic molecules. Melamine-based products are the most widely used type of nitrogen flame retardant today, and are used for example in furniture and building foams, nylons.

2.4.2.4 Intumescent system

Intumescent coatings are fire protection systems which are used to protect materials such as wood or plastic from fire (prevent burning), but also to protect steel and other materials from the high temperatures of fires (thus preventing or retarding structural damage during fires). The coatings are made of a combination of

products, applied to the surface like paint, which are designed to expand to form an insulating and fire-resistant covering when subject to heat [18]. The products involved contain a number of essential interdependent components such as spumific compounds, which (when heated) release large quantities of non-flammable gas (nitrogen, ammonia, CO_2). The other mechanism is a binder, which (when heated) melts to give a thick liquid, thus trapping the released gas in bubbles and producing a thick layer of froth. This mechanism can occur *via* an acid source and a carbon compound. On heating, the acid source releases phosphoric, boric or sulphuric acid which chars the carbon compound (mechanism described under phosphorus flame retardants below), causing the layer of bubbles to harden and producing a fire-resistant barrier. Often the binder can also serve as this carbon compound [17].

2.4.2.5   Phosphorus flame retardants

Phosphorus containing flame retardants take action efficiently in the solid phase of burning materials. When heated, the phosphorus reacts to give a polymeric form of phosphoric acid. This acid causes the material to char, forming a glassy layer, and so inhibiting the pyrolysis process (break down and release of flammable gases) which is necessary to feed flames. By this mode of action the amount of fuel produced is significantly diminished, because char rather than combustible gas is formed. The intumescent char plays particular roles in the flame retardant process. It acts as a two-way barrier, both hindering the passage of the combustible gases and molten polymer towards the flame (as shown in Figure 2.5), and shielding the polymer from the heat of the flame. Furthermore, the amount of fuel available for the fire is significantly diminished, because char rather than combustible gas is formed [8].

A wide range of different phosphorus based flame retardants is available, including elemental red phosphorus (P), which is oxidized to phosphoric acid with heat, ammonium polyphosphate, melamine polyphosphate, phosphonates, phosphinates and phosphate esters. P-containing flame retardants are thus able to offer specific performance properties, depending on the requested fire performance, processing conditions and mechanical properties of the material. Certain products contain both phosphorus and chlorine or nitrogen, thus combining the different flame retarding mechanisms of these elements.
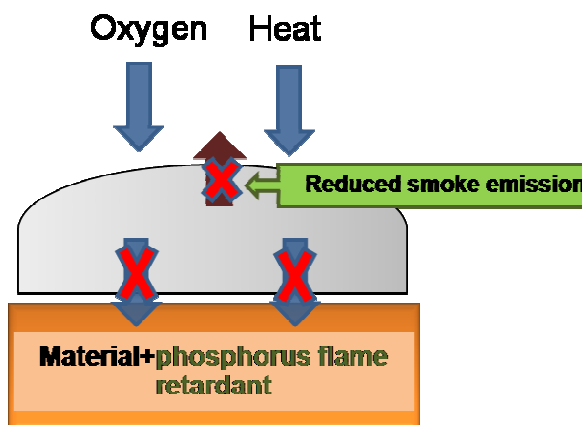
Figure 2.5   Mechanism of phosphorus flame retardant.

Phosphorus-containing flame retardants include inorganic phosphates, insoluble ammonium phosphate, organophosphates and phosphonates, chlorophosphates and phosphonates, bromophosphates, phosphine oxides, and red phosphorous. The mechanism for flame retardancy varies with the phosphorus compound and the polymer/polymer type. A phosphorus-containing flame retardant can function in the condensed (polymer) phase, the gas phase, or concurrently in both phases.

Some phosphorus compounds decompose in the condensed phase to form phosphoric or polyphosphoric acids. These can act as dehydration catalysts, reacting with cellulosics for example, to form a good char. Char yield is also increased with rigid polyurethanes. The polyphosphoric acid also can form a viscous molten surface layer or surface glass. This layer can shield the polymeric substrate from the flame (heat) and oxygen. An intumescence, which requires an acid such as phosphoric acid, results in a dense carbon chars on the polymer surface protecting the substrate form heat and oxygen [19].

Phosphate esters are thermally stable, high boiling (>350 ºC) materials used commercially as flame retardants for polyvinyl chloride (PVC), modified polyphenylene oxide (PPO) and cellulose acetate. In PVC the phosphate ester replaces the flammable organic ester plasticizers such as dioctyl phthalate.

In modified PPO, the preponderance of evidence indicates that the phosphate ester functions in the gas phase by the radical trap mechanism proposed for halogen compounds. The phosphate ester volatilizes without significant decomposition into the flame zone. In another example, pyrolysis studies showed that triphenyl phosphine

oxide and diphenyl phenyl phosphate volatilize quantitatively from polyethylene terphthalate. These are highly effective flame retardants for this polymer.

Flame inhibition reactions similar to the halogen radical trap theory have been proposed.

$$H_3PO_4 \longrightarrow HPO_2 + HPO + PO$$

$$H + PHO \longrightarrow HPO$$

$$H + HPO \longrightarrow H_2 + PO$$

$$OH_2 + PO \longrightarrow HPO + H_2O$$

$$OH + H_2 + PO \longrightarrow HPO + H_2O$$
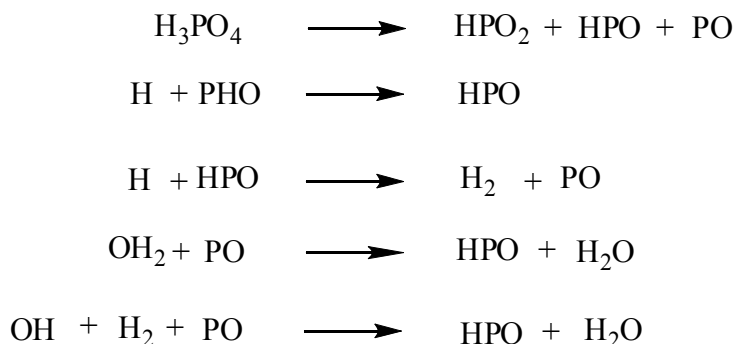
Scheme 2.2   The reaction of PO of phosphorus flame retardants in pyrolysis [8].

PO is generally the most significant species. The PO reactions are particularly important where the flame processes are determined mainly by chain branching reactions such as $H + O_2 \rightarrow OH + O$ [8].

2.5   Graft copolymerization

Graft copolymers are a special type of branched copolymer in which the side chains are structurally distinct from the main chain. However, the individual chains of a graft copolymer may be homopolymers or copolymers. Note that different copolymer sequencing is sufficient to define a structural difference, thus an A-B diblock copolymer with A-B alternating copolymer side chains is properly called a graft copolymer.

Several methods for initiation in graft copolymerization [20]:

- ionizing radiation
- ultraviolet light
- decomposition of chemical initiators
- oxidation of polymers
- plasma treatment

Although, the initiation step of graft-copolymerization was divided in many ways, but sometime they can be incorporated. In 2010, Yu *et at.* [21] studied about the using of photo-induced surface grafting of flame retardant onto PET fabric with glycidyl methacrylate (GMA) as monomer in association with a pad-curing treatment. From this method the highest LOI value reached up 25.9% at 22% of grafting and the heat released was lower than the original sample.

In case of plasma treatment, plasma technology offers a means of achieving of developing novel nanocoatings having the desired thermal shielding effects. In 2006, Shi *et al.* demonstrated that low pressure, radio frequency discharge plasma treatment of a number of polymer surfaces including poly(ethylene terephthalate) in the presence of gaseous (CF_4/CH_4) leaded to flame retardation [22]. Later studies in which ethylene-vinyl acetate copolymer were plasma-exposed for times up to 15 min followed by immersion into acrylamide, gave very high yields of surface graft poly(acrylamide) and LOI values approaching 24 vol% at 47 wt % grafting levels [23].

2.6   Plasma

Plasma is an ionized gas. When solid is heated sufficiently that the thermal motion of the atoms breaks the crystal lattice structure apart, usually a liquid is formed. When a liquid is heated enough that atoms vaporized off the surface faster than they recondense, a gas is formed. When a gas is heated enough that the atoms collide with other and knock their electrons off in the process, plasma is formed. This is so-called fourth state of matter. Exactly when the transition between a very weakly ionized gas and plasma occurs is largely a matter of nomenclature. The important point is that an ionized gas has unique properties. In most materials the dynamics of motion are determined by forces between near-neighbor regions of the material. In plasma, charge separation between ions and electrons gives rise to electric fields. These fields results in action at a distance, and a range of phenomena of startling complexity, of considerable practical utility and sometimes of great beauty. Irving Langmuir, the Nobel laureate who pioneered he scientific study of ionized gases, gave this new state of matter the name 'plasma' [24] .

Plasma is not usually made simply by heating up a container of gas. The problem is that for the most part a container cannot be as hot as a plasma needs to be in

order to be ionized or the container itself would vaporize and become plasma as well. Typically, in the laboratory, a small amount of gas is heated and ionized by driving an electric current through it, or by using the radio frequency waves. Either, the thermal capacity of the container is used to keep it from getting hot enough to melt- let alone ionized-during a short heating pulse or the container is actively cooled for longer-pulse operation. Generally, these means of plasma formation give energy to free electrons in the plasma directly, and then electron-atom collisions liberate more electrons and the process cascades until the desired degree of ionization is achieved. Sometimes the electrons end up quite a bit hotter than ions, since the electrons carry the electrical current or absorb the radio waves.

Generally, there are various forms of an electrical discharge which differ in their external appearance and the temperature, depending on the pressure and the voltage source connected to the gas station. This current flow is brought about by ionization through a gas, whereby the current flow is produced by applying high voltages. For textile fields of application, fundamentally only "cold" plasma and in particular the corona and glow-discharge are of interest. "cold" plasma are unbalance plasma or low temperature plasma. The electron energy is up to 100 times greater than the energy of the gas particles. "Hot plasma" is known from nuclear fusion. The energy of electrons and gas particles is equal.

2.6.1   Generation of plasma and its action

Plasma may be produced by:

(i)   thermal ionization at high temperatures at normal gas pressures or,

(ii)   by using electrical discharges-the frequency of the electrical

energy vary from zero (d.c.) to 10 Hertz (microwaves). These may be subdivided as (a) electrode discharges (glow, plane, point, corona etc.) and (b) electrodeless discharge using radio frequency (RF) at low gas pressures. The use of RF has a further advantage that it can be used to bring about RF heating. Various types of electrode assemblies can be used for initiation plasma.

2.6.2   The interaction of plasma with substrate

The interaction of plasma with materials can be roughly divided into three different classes:

(i)   Reactions due to formation of ions which would lead directly to a new chemical product like formation of NH_3, NO_2, ozonization etc.

(ii)   The second type of plasma reaction is the initiation of polymerization i.e. deposition of thin uniform polymer film on the electrodes. Organic monomers in the vapor phase, like other gaseous, are ionized by bombardment of electrons under the discharge conditions. Such ions when neutralized have energy which leads of rapid polymerization. Films having good stability, insulating properties, free of holes and uniform thickness can be obtained at a rate of few grams per kwh. Continuous movement of textiles, paper etc. through flat plate electrodes (0.1 m separation) for coating is possible. Manufacturing of thin film for capacitors, coating of cans or metal surfaces has been achieved.

(iii)   The third type of plasma reaction is concerned with effects produced at organic polymer surfaces in contact with plasma. This type of reactions forms the basis of major developmental work on textiles. The energic ions from the plasma break organic bonds with the evolution of gaseous products (for e.g. hydrogen from hydrocarbons) and the formation of carbon radicals. These radicals can in turn lead to chemical reactions at the surface of the substrate [15].

2.6.3   Surface modification of fabrics under plasma treatment

To-date, the required surface modification of the fiber is mainly accomplished by wet chemical processes. An appropriate alternative to its conventional techniques is given by pre-treatment of textile fibers with low temperature glow-discharge plasma I air. There is also an increase in patent applications on the latest developments in plasma technology. Physical-chemical method of modifying the surface has been great interest. Particularly in the area of pretreatment of textiles, this technology which is relatively new to the textile industry seems to bring about obvious advantages in relation to the conventional technique.

Conventional wet pre-treatment processes of textiles are generally energy consuming process. Plasma modification of textiles saves large quantity of water,

chemicals, and electrical energy. Ecological and economical constrains which are imposed on the textile industry to an increasing extent, call for the development of environmentally friendly and economic finishing processes. Large savings are possible since the plasma process does not produce large number of waste or toxic by-products.

The plasma-induced surface modification of textile substrates has gained increasing interest over the last few years. The reason for this interest is the intriguing possibility of modifying properties leading to better performance. The range of applications is diverse and modifications of surface of various materials like cotton, wool, silk, polyester have been reported. Plasma treatment generally takes place in dry conditions, thus the fibers are not swollen. The changes in properties induced by plasma treatment are therefore restricted to the surface and any damage to the interior of the fiber is very likely. The physic-chemical nature of the modified fiber surface has a tremendous influence on the following important phenomenon:

i)   Static electricity build up and dissipation.

ii) Moisture transport and comfort.

iii) Oily stain adsorption and release in detergent solution.

iv) Soil deposition, release and redeposition in detergent solutions.

v)   Wettability and adhesion.

vi) Scourability and bleachability of textiles.

vii) Wettability and dyeability.

Form the physical point of view, roughening of fiber surface as seen by atomic force microscopy is responsible for changes in the efficient of friction, top cohesion, spinnability, yarn strength, etc. From the chemical point of view, the oxidation of the fiber surface and interaction with polymer materials are the main factors responsible for improvements in various properties of plasma treated materials.

2.7 Fabric analysis

2.7.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is one of the most widely used techniques to characterize thin film surface morphology. It operates by scanning a focused electron beam over a surface and sensing the secondary electrons emitted from the surface. The electron beam can be focused on a very small and the beam size is the detrimental factor of the microscopy resolution. A basic diagram of an SEM is shown in Figure 2.6. The electron gun produces a beam of electrons that is attracted through the anode and condensed by the condenser lens and then focused as a very fine point on the substrate by the objective lens. A set of small coils are energized by a varying voltage produced by the scan generator and created a magnetic field that deflects the beam of electrons back and forth in a controlled pattern. When the beam of electrons strikes the substrate, a complex series of interactions occurs, resulting in the production of secondary electrons from the sample, which are collected by the detector, converted to a voltage, and amplified. The amplified voltage is then applied to the grid of the cathode-ray tube (CRT) and changes the intensity of the spot of light on the surface.
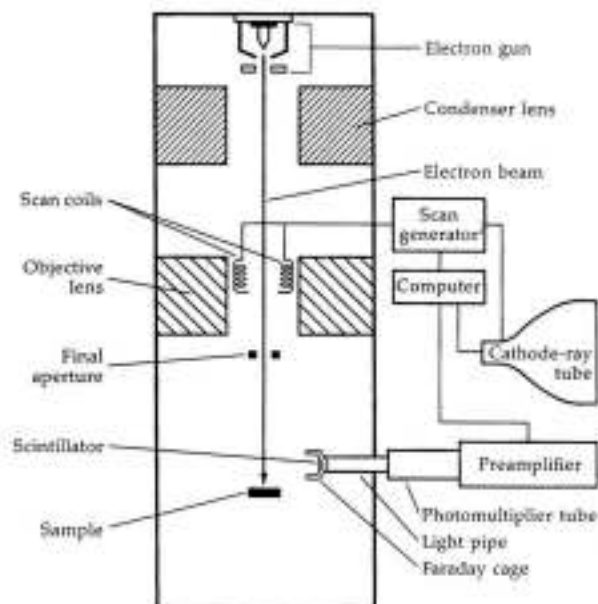
Figure 2.6 A basic diagram of scanning electron microscopy (SEM).

2.7.2   Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

Fourier transform infrared (FT-IR) spectroscopy is a technique based on the determination of absorption of infrared light due to energy resonance with vibrational motions of functional molecular groups, this technique has been applied as an analytical technique in different fields such as geology, material science, polymer science, and many others.

FT-IR sampling technique is generally a transmission technique using KBr pellets [25]. The infrared beam is directly passed through the sample. Since the color of hair sample is usually dark, transmission technique cannot be used. Also a sample thicker than 20 µm cannot be analyzed. Reflectance sampling techniques is therefore utilized. The IR beam is bounced off the sample instead of passing through it. In the conventional attenuated total reflectance (ATR) technique, a good contact between the sample and internal reflection element (IRE) is required [26]. ATR occurs when a sample is brought into contact with an IRE that has a higher refractive index than the sample and is transparent through the mid-infrared radiation. In general, the IRE configuration includes variable-angle hemispherical crystal with single reflection and multiple reflection planar crystal. The IRE is used in internal reflection spectroscopy for establishing the conditions necessary to obtain internal reflection spectra of materials.

In this study, ATR-FTIR was used for identifying functional groups on the surface of untreated fabric and the fabrics were treated with phosphorus containing monomer.

2.7.3   Thermogravimetric analysis (TGA)

Thermal Gravimetric Analysis (TGA) is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can lose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and gain are disruptive processes to the sample material or batch, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods. The characteristics or properties were

measured is drying, structural water release, structural decomposition, carbonates decomposition, gas evolution, sulfur oxidation, fluoride oxidation, and re-hydration.

The sample of the test material is placed into a high alumina cup that is supported on or suspended from an analytical balanced located outside the furnace chamber. The balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis.

2.7.4   Limiting oxygen index (LOI) test

The Oxygen index, n, of a material is the percentage concentration of oxygen in a mixture of oxygen and nitrogen which will maintain equilibrium burning conditions, i.e., the heat produced during combustion just balances the heat lost to the surroundings. Physically, this is the lowest concentration of oxygen which will support sustained combustion of the material, and is calculated from the following equation:

$$n(\%) = \frac{100xO_2}{O_2 + N_2}$$

where O_2 is the oxygen concentration at equilibrium and N_2 is the associated nitrogen concentration.

The important point concerning the Oxygen Index is that it is a numerical measure of a unique property of the material which can be accurately reproduced provided the test equipment and procedures are not changed. This is in direct contrast with many other widely accepted tests where care cannot prevent erratic results. This poor performance in these other tests is usually explained by the fact that the end-points have been set arbitrarily at some time or distance without regard for any physical situation, so numerous unexplained outside influences can affect the results.

The equipment used for this test consists of two sections: the gas metering system and the test column as showed in Figure 2.7. In the gas metering system the volumetric flow of gas in each line is accurately measured before the streams are mixed and fed into the base of the column. A sample of material is placed vertically in the

center of the column and ignited at the top so that it burns or extinguishes at each concentration, it is possible to determine quite accurately the minimum oxygen concentration which supports combustion, i.e., the oxygen Index. It was taken from the latest draft of the ASTM D2683 standard now being developed for the Oxygen Index Test.
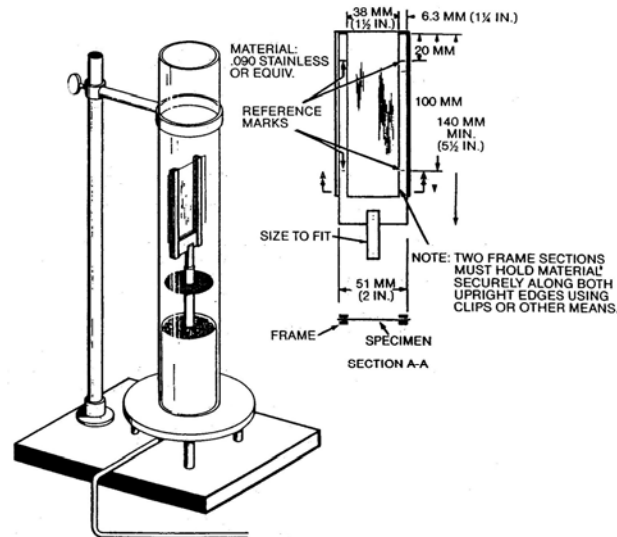
Figure 2.7   Limiting oxygen index apparatus

2.7.5   Tensile properties

Tensile strength is the mechanical property to measure the maximum force that the material can support before rupture. The tensile property can provide valuable insights into the structure of fiber and the level of strength required from a yarn or fabric depends on its end use [BP saville]. In this thesis, the kind of fabric is woven fabric (cotton and silk) and the typical load-extension curve of woven fabric in a tensile strength is present in Figure 2.8. Careful examination of the generalized load-extension curve for woven fabric reveals the present of three distinct regions. Region 1, the initial part of the curve, is dominated by interfiber friction which is usually very small that is the frictional resistance due to thread (yarn) bending. Region 2, a region of lower modulus, is the decrimping region resulting from the straightening of thread set in a direction of application of the load, with the associated increase in crimp in the direction perpendicular. Region 3, the last part of the load extension curve, is due to yarn extension, i.e., tensile loading of threads in the direction of stress. As the crimp is decreased, the magnitudes of the loading force rise very steeply, and as result, the fibers

themselves begin to be extended. In summary, in this final region, the load-extension properties of fabric are basically governed by the load-extension properties of the threads or fibers. This is clearly a region of higher modulus [27].
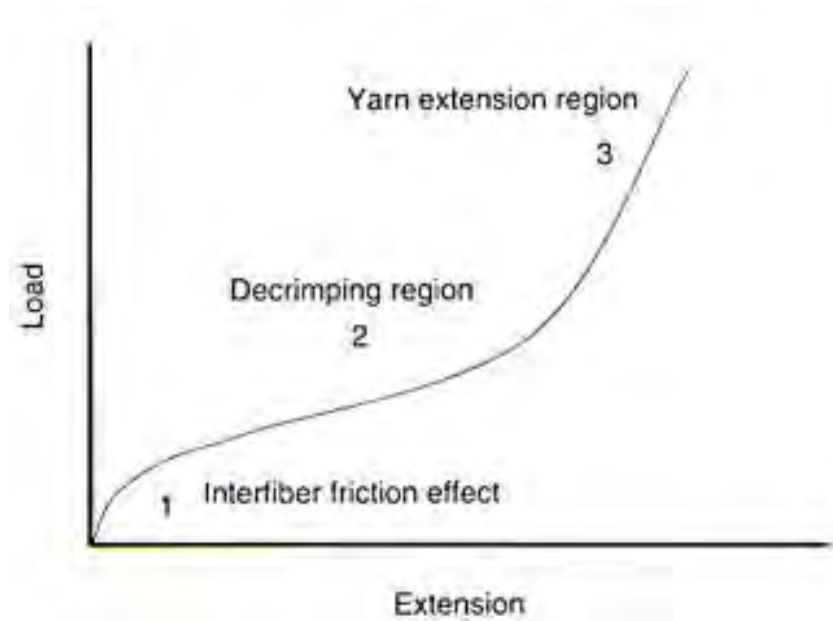
Figure 2.8   A typical load-extension curve for woven fabric [27].

In this thesis, tensile strength of untreated and treated fabrics were tested following by strip test method (ASTM D5035-95)

2.7.6   Color spectroscopy

Color spectroscopy is the technique for determining the color difference between the samples. The color difference or ΔE was analyzed by investigating the L*, a*, b*.

Where

L*=   lightness (or luminance),

a* =   balance between green (−) and red (+)

b* =   balance between blue (−) and yellow (+)

The color difference or ΔE can be calculated by the following equation:

$$\Delta E_{ab}^* = \left[\left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2 + \left(\Delta L^*\right)^2 \right]^{1/2}$$

Where ΔL^* =   the difference of lightness between the samples

Δa^*, Δb^* = the difference of chroma between the samples

Figure 2.9 shows the L^*, a^*, b^* color space. The derived quantities saturatation (chroma) C^* and hue h are also indicated. L^* may have values between 0 and 100. a^* and b^* may have values between around -80 and +80. Colors with no chroma always have the values $a^* = b^* = 0$. Since the opponent color theory is used to develop the transformation, one of the coordinates (a^*) shows the redness or the greenness of the color the other coordinate (b^*) shows the yellowness or the blueness.
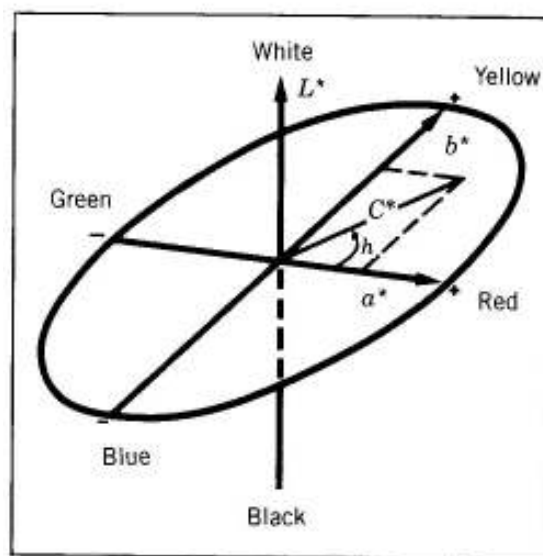
Figure 2.9 CIELAB color space.

2.7.7 Electron probe micro analysis (EPMA)

An electron microprobe is an electron microscope designed for the non-destructive x-ray microanalysis and imaging of solid materials. It is essentially a hybrid instrument combining the capabilities of both the scanning electron microscope (SEM) and x-ray fluorescence spectrometer (XRF), with the added features of fine-spot focusing (~1 micrometer), optical microscope imaging, and precision-automated sample positioning. The analyst makes measurements while observing the sample (with the optical microscope or with a secondary/backscattered electron image) and selecting specific analysis locations (using the precision sample stage), involving scanning electron microscope (SEM) and analytical electron microscope (AEM).

The technique is capable of high spatial resolution (~1um) and relatively high analytical sensitivity (<0.5% for major elements) and detection limits (~100 ppm for trace elements). It cal also acquire digital secondary-electron and backscattered-electron and cathode-luminescence images as well as digital x-ray maps. It is normally equipped with up to 5 wavelength-dispersive spectrometers. EPMA is primarily utilized to determine the elemental composition of various materials on a micro scale. The use of standards and matrix corrections can realize accuracies of typically 3-5% or better which allows the determination of many (inorganic) chemical formulas. The figure of cross-sectional view of EPMA column and X-ray spectrometer was shown in Figure 2.10 [28].
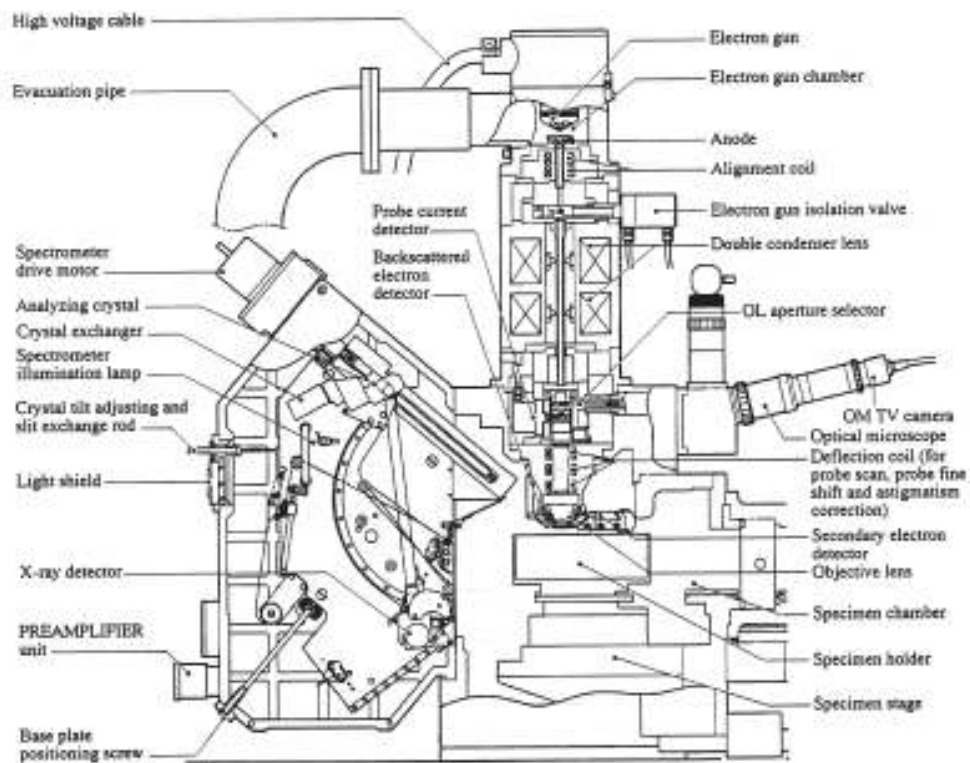
Figure 2.10   Cross-sectional view of EPMA column and X-ray spectrometer [28].

At the present, plasma treatment technique shows the distinct advantages, because it is able to modify the surface properties of inert material such as natural and synthetic fiber or fabrics. On textile surfaces, three main effects can be obtained

depending on the treated conditions: the cleaning effect, the increasing microroughness and production of radical.

In case of cleaning effect, plasma pretreatment was used for degumming process in silk fabric [29]. From this method, the etching effect include bombardments and/or plasma chemical reactions by excited plasma species on sericin layers. The sericin macromolecule chains were broken by plasma, even desquamated sericin layer and/or particle from the fiber resulting in significant improvement of degumming efficiency. This method is more environmentally friendly, water and energy conservation. Moreover, plasma technique was used in many fields for improving and/or finishing the desirable properties of fabric one particular interest is to produce the durable hydrophobic properties on the surface.

C_3F_6 and SF_6 were used to improve the hydrophobicity of the cotton silk and fabric [6,31] by plasma treatment. From this, the contact angles were increased because the replacement of fluorine atom instead of hydrogen atom. This process is initiated by hydrogen abstraction from the polymer surface by very active species generated in the plasma. The mechanical properties were measured by tensile strength, it was found that the tensile strength slightly increased after plasma treatment and the water vapor permeability of treated fabric was not changed.

In some fabrics, the improvment of hydrophilic properties was interested such as polyester and acrylic fabrics. In 2002 [31], Ferrero studied the wettability measurement on plasma treated of polyester and acrylic fabrics by capillary method. The three types of gases were studied (nitrogen, air and oxygen), it was found that on polyester fabric, nitrogen plasma induced higher wettability than air and oxygen, whereas the wettability on acrylic fabric slightly increased in air compared with nitrogen. It was reported that in the presence of =C=N- and =C=O groups lead to polar and probably responsible for the improved surface properties. Besides, grafting of copolymer *via* addition polymerization of vinyl monomer is another way to improve the hydrophobic, hydrophilic or other desirable properties instead of using the fluorine-containing gas.

In 2002 [32], the hydrophobic properties in polyacrylonitrile (PAN) fabrics was improved by grafting of tetrahydroperfluorodecyl acrylate (AC8) at low-pressure microwave plasma process. The grafting and the polymerization process were followed

by weight measurement. The water and oil repellency properties of fabric after treatment came from the creating of covalent bonding between PAN fabrics and fluorinated polymer *via* free radical addition polymerization as showed in Figure 2.11.
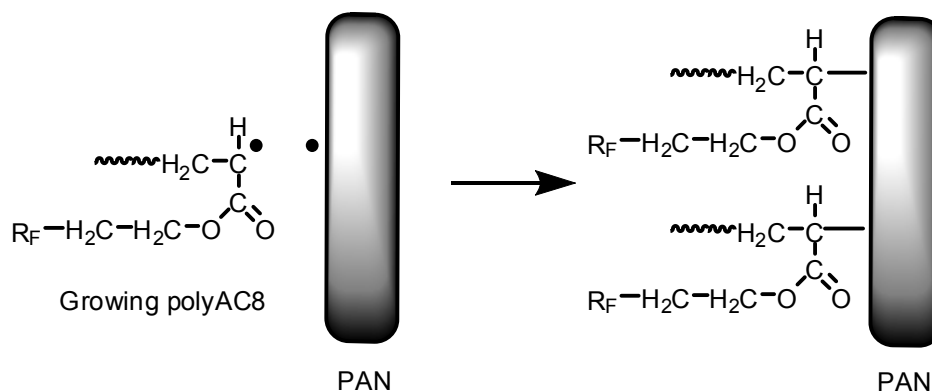
Figure 2.11 Schematic representation of the grafting of growing polyAC8 on the PAN tissue [32].

The improving of hydrophobic and hydrophilic properties, fire resistance property by using plasma induce graft-copolymerization technique are more interesting. Since this technique gave the strong attachment between flame retardant and fabric *via* covalent bond. Therefore, this method is suitable for natural fiber and fabric such as cotton and silk because only surface treatment can be applied.

In 1990, RF plasma technique was used to improve the flame retardant property of polyacrylonitrile (PAN) fabric with organophosphorus compound compared with hexamethyl disiloxane (HMDS) [3]. Normally, siloxane was usually used as anti oxidant and heat resistance in materials. In case of organophosphorus compounds, they were usually used as flame retardant in many materials due to low toxicity. After treatment for 60 minutes by RF plasma, the LOI vales of HMDS treated fabrics were lower than untreated one but in case of organophosphorus compound treated fabrics, the LOI values were raised up to 29%. This result could be explained by char formation of phosphorus compound to protect the combustion materials from volatiles species for the future combustion.

In 2004, Tsafack *et al.* [1] studied about using plasma-induced graft copolymerization of phosphorus-containing flame retardant onto polyacrylonitrile

(PAN) and fabrics. This experiment can be performed in a single work-step in the plasma chamber as showed in Figure 2.12.
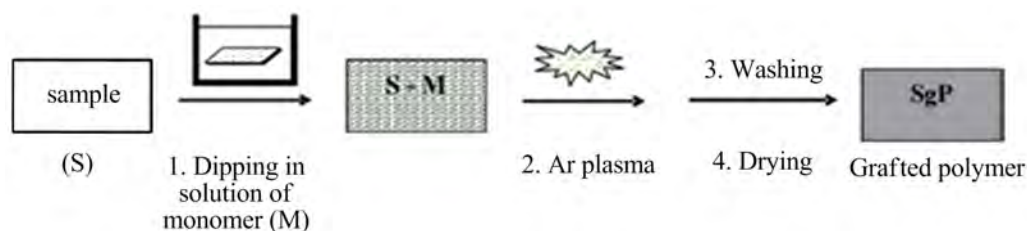
Figure 2.12 Experimental procedure for Ar plasma-induced graft copolymerization of monomer [1].

In this work, four types of monomers were investigated as following, diethyl (acryloyloxyethyl) phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl) phosphate (DEMEP), diethyl (acryloyloxymethyl) phosphonate (DEAMP), and dime- thyl (acryloyloxymethyl) phosphonate (DMAMP) with ethyleneglycol diacrylate (EGDA) as a cross-linking agent with 15 minutes of treatment time. The percentage of grafting was investigated by weight measurement, and it was found that the percentage of grafting increased with increasing of monomer concentration. The highest LOI value obtained far reach 28% compared with untreated one (LOI = 18.5%). Moreover the LOI of treated fabric slightly decreased after washing because the strong attachment between polymer film and the surface of fabrics *via* the covalently bond.

In 2005, halogen free flame retardant was used to improve fire resistance properties of cotton fabric by gamma radiation [33]. This work was divided in three stages. The first stage, the effect of 2,3-epoxypropyl methacrylate (GMA) concentration and dose of gamma ray on the percentage of grafting were studied. It was found that, the percentage of grafting increased with increasing of GMA concentration and dose of gamma ray (at rate of 0.56 kGy/h). LOI value of grafted fabrics in this stage was 20% (untreated LOI=20.4%). The second stage, GMA-g-cotton fabric was grafted with ethylene diamine for 8 hours, and LOI value in this stage was slightly increased (LOI=21.9%). In the last stage, the GMA-g-cotton fabric reacted with ethylene diamine was grafted with orthophosphoric acid at the ambient temperature and LOI in this stage was 35.9%. The LOI value was raised up to 15 units but more than 8 hours of reaction times in each step was used.

In 2008, diethyl-2-(methacryloyloxyethyl) phosphate (DEMEP) was used to improve the flame resistance of silk fabric as well as using potassium persulfate as an

initiator [2]. The polymerization process can be done under 85ºC for 30 minutes in the emulsion solution in the presence of 10% (on the weight of DEMEP monomer) and 1% potassium persulfate (on the weight monomer). After that rinsed for 10 minutes, and then washed with a non-ionic surfactant solution for 20 minutes. After that silk fabrics were soxhlet extraction with acetone for 24 hours to remove the homopolymer on the surface. From the results, the grafted silk fabrics with weight gain above 10.9% have self-extinguish property (LOI > 28%) and the LOI increased with increasing of weight gain.

In 2009, the combination of a hydroxyl-functional organophosphorus oligomer (HFPO) and 1,2,3,4-butanetetracarboxylic acid (BTCA) were used for improving the flame retardant properties of silk fabric by padded dried cured technique [34]. In this work, BTCA was used as a cross-linking agent between silk fiber and HFPO. This technique used 2 minutes for curing time and the temperature was raised up to 170ºC. After grating, the thermal and physical properties were investigated. It was found that the LOI value of grafted fabric was increased to 30% (untreated LOI=22.8%). However, it was found that the increasing the HFPO concentration from 20% to 30% does not show significant improvement in the flame retardant performance of the treated silk. Moreover, the mechanical property was dropped due to the high temperature in curing process.

In 2011, the fire resistance of silk fabric was improved by using of RF plasma induced graft polymerization (PIGP) with the phosphate and phosphoramidate monomers [35]. This work was divided in two parts. The first part, silk fabrics were grafted with diethyl 2-(acryloyloxyethyl) phosphoramidate (DEAEPN) and diethyl 2-(acryloyloxyethyl) phosphate (DEAEP) by argon plasma with ethyleneglycoldimethacrylate (EGDA) and Irgacure 819 was used as the cross-linking agent and photo initiator, respectively. The second part, the grafted fabric were treated with SF_6 for improving the water repellent. After argon plasma treatment, the LOI values were increased to 3-6 unit by the highest LOI = 31% (untreated LOI=25). It was found that phosphoramidate (DEAEPN) gave the higher LOI value than diethyl 2-(acryloyloxyethyl) phosphate (DEAEP) at the same monomers concentrations. This could be attributed by the nitrogen content in the phosphoramidate which contributes to the reduction of the flammability of the fabric *via* the consistent with a P–N synergistic effect. In the second step, the flame retarded fabrics have been exposed to SF_6 plasma.

After 5 minutes of treatment, the fabrics which were originally absorbent became water repellent and exhibited an apparent contact angle of 134°. This property remains even after several weeks of air exposure and the tensile strength was slightly decreased.

It can be seen that, only the few minutes were adequate in plasma technique to complete the reaction, whereas the alternative techniques such as gamma radiation or emulsion solution techniques needed more than 30 minutes. Moreover, in each step, the temperatures were raised up to 85ºC which could damage the mechanical property of fabrics.

CHAPTER III

METHODS AND MATERIALS

This work was divided into three parts. The first part, two target phosphorus-containing flame retardant monomers, 2-methacryloyloxyethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphophate (MPBP) were synthesized. The second part, MEDP and MPBP monomers were grafted onto cotton and silk fabrics by argon plasma. The last part, physical and mechanical properties of grafted fabrics were studied. In an addition, the presence of the polymer film coated on both natural fabrics was determined by scanning electron microscopy (SEM) and attenuated total reflection-fourier transform infrared (ATR-FTIR).

3.1   Materials

3.1.1   Sample and reagents

Cotton fabrics used in this study were supplied by C.R. printing Ltd., Part. Degummed silk fabrics were purchased from Jim Thompson, Co., Ltd.. The reagents (analytical grade): 2-Hydroxyethyl methacrylate (HEMA) (Aldrich, 97%), phenylphosphonic dichloride (PPDC) (Fluka, 95%), phenyl dichlorophosphate (PDCP) (Aldrich, 95%), phenol (Merck), triethylamine (TEA) (Fluka, 98%) were used as received. Tetrahydrofuran (THF) was dried by sodium metal which benzophenone as indicator, the mixture is refluxed under nitrogen asmosphere until the blue color of benzophenone ketyl forms. Ethyl acetate (commercial grade) and *n*-hexanes (commercial grade) were distilled prior to use.

3.2   Instruments

3.2.1   Radio Frequency Inductively Coupled Plasma (RF-ICP) System

In this thesis, the experiments for improving flame retardant property of cotton and silk fabrics by Ar plasma were carried out at low pressure by using a radio-frequency inductively couple (RF-ICP) plasma reactor. A schematic diagram of radio-frequency plasma generation is shown in Figure 3.1. The employed plasma system consists of five main parts, (i) RF generator, (ii) the impedance matching network, (iii)

the vacuum chamber in which the process takes place, (iv) a pumping system and, (v) unit mass flow controllers to regulate the gas flow. The reactor is a cylindrical chamber of stainless steel, which has several ports for feeding gas and plasma diagnostic equipments. The top stainless steel plate has a circular opening of 20 cm. in diameter where a quartz window is mounted to isolate the vacuum and still let the RF field from planar coil place above the quartz plate to couple into the plasma. A flat coil (7 turns) with maximum diameter of 150 mm. is mounted directly on top of the quartz window to induce the plasma at 13.56 MHz. Power source that operates at 50 ohms and delivered up to 1000 watts of power. The matching network is placed inside a perforated aluminum cylinder which acts as a Faraday cage protecting the electronic instruments from the effect of stray RF fields. The power used could be adjusted by a variable capacitance-matching network. Before plasma was generated, the pressure in the chamber was reduced to 4×10^{-2} torr by rotary vane pump. After the base pressure was reached, then Ar gas is allowed to enter the chamber *via* mass flow controller and the operating pressure in this work is at $3.0x10^{-1}$ torr with the power 30 watt in 3 minutes.

3.2.2   Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton (^{1}H) NMR spectra were obtained on Mercury Varian 400 MHz nuclear magnetic resonance (NMR) spectrometer at 400 MHz. at the Faculty of Science, Chulalongkorn University. The samples were analyzed in a solution of chloroform-D (purity 99%, Aldrich). Chemical shifts (δ) are reported in parts per million (ppm) and are relative to that of tetramethylsilane (TMS) or relative to the residual protonated signal of deuterated solvents as a reference.

3.2.3   Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy

The attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) were recorded on a Nicolet iS10 ATR-FTIR spectrometry (Figure 3.2) in the 4000-600 cm^{-1} range. Functional groups present in of MEDP and MPBP phosphorus containing flame retardant monomers, as well as untreated and treated fabrics with flame retardant monomers can be detected by this technique with 32 scans at the resolution of 4 cm^{-1}.
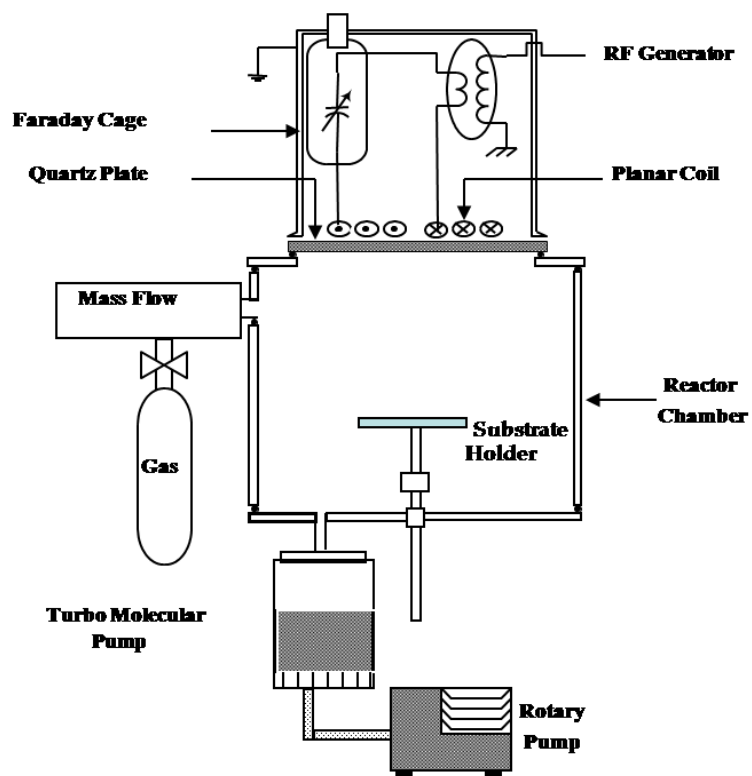
Figure 3.1   Schematic diagram of the radio frequency inductively couple plasma reactor.

Figure 3.2   Photograph of attenuated total reflection fourier transform infrared spectrometer (ATR-FTIR).

3.2.4   Scanning electron microscopy (SEM)

SEM analysis was carried out with a JEOL model JSM-6480LV, at the Faculty of Science, Chulalongkorn University to investigate the morphology of untreated and treated fabrics. The samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimens.

Figure 3.3   Photograph of scanning electron microscope (SEM).

3.2.5   Electron Probe Micro Analysis (EPMA)

In this work, the percentage of phosphorus on treated fabrics were determined by an electron probe micro analyzer with JEOL model JXA-8100/8200 and the photograph as shown in Figure 3.4. The sample were cut into 0.5×0.5 cm^2 size and placed on a sample holder which is located in the center of the chamber. The everage value of phosphorus (P %) came from the bombardment by an electron beam for five times.

3.2.6   Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a Mettler Toledo thermogravimetric analyzer model TGA/SDTA 851. This was carried out to measure continuous weight loss of untreated and treated fabrics. The method starts with placing the sample into an aluminum pan suspended from the arm of a microbalance situated in

the furnace tube. The measurement was carried out in a nitrogen atmosphere at the heating rate of $10^{\circ}Cmin^{-1}$ and the temperature was scanned from 25-600°C.

Figure 3.4   Photograph of an electron probe micro analyzer (EPMA)

3.2.7   Limiting Oxygen Index (LOI) test

The flame retardant properties of untreated and treated fabrics were measured by the limiting oxygen index (LOI) method. The LOI value corresponds to the minimum concentration of oxygen in an oxygen/nitrogen mixture necessary for the combustion of sample during a 3 minute period over a total sample length of 80 mm. according to the ASTM D2863-06a standard. The oxygen index apparatus as shown in figure 3.5 manufactured by laboratory instrument at the faculty of science, Chulalongkorn University.

3.2.8   Tensile properties

In this thesis the strip method, ASTM D5035-95 were used to measure the tensile strength of untreated and treated fabrics which performed on a Universal testing machine. The terms of warp and weft directions are used in reference to textile,

specifically those which are woven. The warp is tightly stretched lengthwise core of fabric, while the weft is woven thread between the warp thread to create various patterns. The test samples were cut into 5×10 cm^2 in both of warp and weft directions with the crosshead speed at 500 mm/min.

Figure 3.5   Limiting oxygen index apparatus

3.3   Synthesis

3.3.1   Synthesis of 2-methacryloyloxyethyl diphenyl phosphate (MEDP)
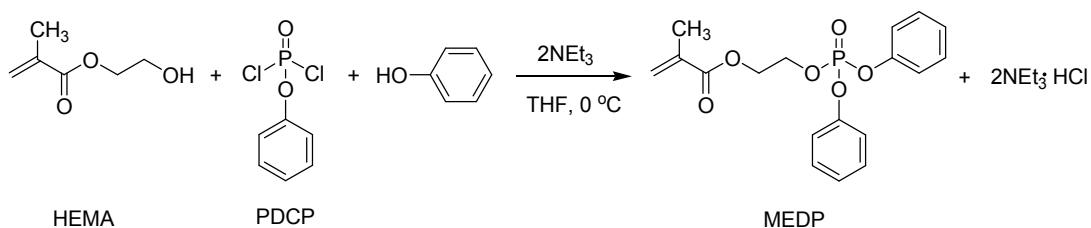
2-Methacryloyloxyethyl diphenyl phosphate (MEDP) was synthesized by the reaction of phenyl dichlorophosphate (PDCP), 2-hydroxyethyl methacrylate (HEMA) and phenol in anhydrous tetrahydrofuran (THF). First, PDCP (31.7 g, 0.5 mol) was dissolved in anhydrous tetrahydrofuran (THF) (120 mL) in a 1000 mL three-necked

round bottom flask equipped with mechanical stirred under N_2 atmosphere. Triethylamine (TEA) (41.7 mL, 1.0 mol) was added to the mixture and the mixture was cooled down in an ice bath and stirred for 30 minutes. The solution of HEMA (19.5 g, 0.5 mol) in anhydrous THF (30 mL) was added dropwise to the mixture and then, the mixture was stirred for 40 minutes. Next, a solution of phenol (14.1 g, 0.5 mol) in anhydrous THF (40 mL) was added dropwise to the mixture and the temperature was kept at 0°C for 4 hours. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the reaction was complete, triethylamine hydrochloride salt was filtered off by suction filtration. The filtrate was placed in a rotary evaporator to remove THF and unreacted starting materials. Finally, the crude mixture was purified by using a flash silica gel chromatography column, and eluted with a 7:3 mixture of *n*-hexanes and ethyl acetate. The product was obtained as a yellowish liquid in 40% yield. ^{1}H NMR (CDCl$_3$, ppm): δ 7.2-7.4 (m, 10H, aromatic protons), 6.15 (d, 1H, J = 6.8 Hz, CH_2=C(CH$_3$)-), 5.59 (d, 1H, J = 6.9 Hz, CH_2=C(CH$_3$)-), 4.40-4.50 (m, 4H, CH_2-CH_2-O-P), 1.90 (s, 3H, CH$_2$=C(CH_3)-); FT-IR (liquid, cm^{-1}): 3063 (aromatic C-H stretching), 2957 and 2932 (C-H stretching, CH$_3$ and CH$_2$), 1730 (C=O stretching), 1635 (C=C stretching), 1600 and 1493 (aromatic C=C stretching), 1265 (P=O stretching), 1161 and 975 (P-O-C stretching, aromatic), 1070 and 928 (P-O-C stretching, aliphatic) [22].

3.3.2 Synthesis of 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP)
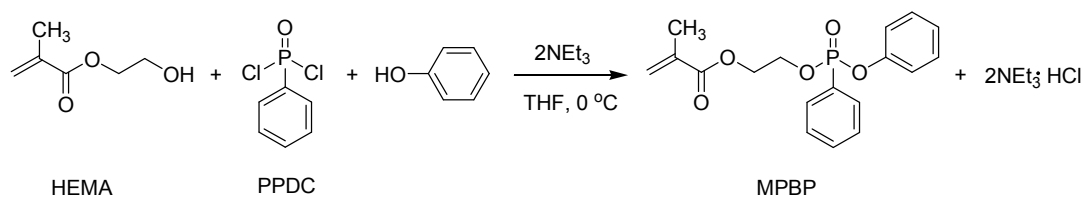
2-Methacryloyloxyethyl phenyl benzenephosphonate (MPBP) was synthesized *via* the same procedure as described for MEDP by using triethylamine (TEA) (34.75 ml, 0.25 mol), HEMA (16.27 g, 0.125 mol) in anhydrous THF (30 mL) and phenylphosphonic dichloride (PPDC) (17.5 mL, 0.125 mol) as a reactant instead of PDCP. The crude mixture was purified by using a flash silica gel chromatography

column, which was eluted with a 7:3 mixture of *n*-hexanes and ethyl acetate. The product was obtained as a yellowish liquid in 53% yield. ^{1}H NMR (CDCl$_3$, ppm): δ 7.10-7.30 (m, 10H, aromatic protons), 6.09 (s, 1H, C*H*$_2$=C(CH$_3$)-), 5.55 (s, 1H, C*H*$_2$=C(CH$_3$)-), 4.20-4.40 (m, 4H, C*H*$_2$-C*H*$_2$-O-P), 1.90 (s, 3H, CH$_2$=C(C*H*$_3$)-); FT-IR (liquid, cm^{-1}): 3063 (aromatic C-H stretching), 2957 and 2932 (C-H stretching of CH$_3$ and CH$_2$), 1730 (C=O stretching), 1635 (C=C stretching), 1600 and 1493 (aromatic C=C stretching), 1440 (P-Ph stretching), 1265 (P=O stretching), 1161 and 975 (P-O-C stretching, aromatic), 1070 and 928 (P-O-C stretching, aliphatic) [22] .

3.3.3 Plasma induced graft-copolymerization of MEDP and MPBP monomers onto the surface of cotton and silk fabrics

All the experiments were run, following the method of Tsafack and co-worker [1]. The schematic diagram of procedure is as shown in Figure 3.6 and the steps of grafting can be explained as follows: (a), pieces of fabrics were cut into a 11×14 cm^2 dimension. The fabric was then immersed in a mixture of a monomer, photoinitiator and cross-linking agent in chloroform at various concentrations of monomer (100-300 g/L, cross-linking agent at 5% and 10% (w/w) in the presence of 5% (w/w) of photo initiator. And then, (b) the solvent was removed by air-dried at room temperature for 30 minutes. Then (c), placed the immersed fabrics onto the sample holder that was located at a distance of 3 cm away from the quartz plate. The chamber was evacuated to a base pressure of 4×10^2 torr before argon gas was purged into the chamber *via* a mass flow controller. The argon plasma was generated at RF power of 30 watt. The operating condition was set at pressure of 0.3 torr and the treatment time was 3 minutes with the argon flow rate at 30 sccm. Next, (c) the treated fabrics were extracted in a soxhlet apparatus with acetone. In the last step (d) acetone was removed by air-dried at room temperature for 12 hours, and kept in the desiccator for future analysis.
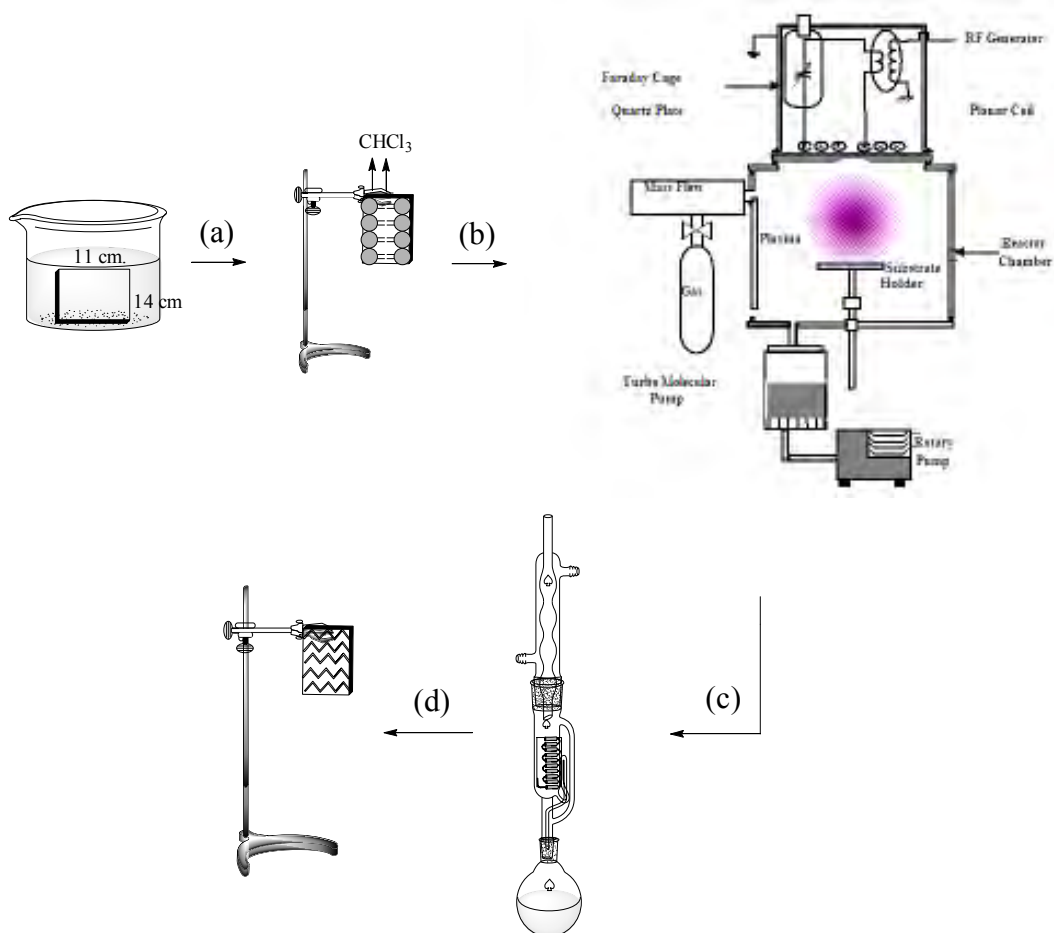
Figure 3.6   Experimental procedure for the Ar plasma-induced graft-polymerization

of monomers (see 3.3.3).

3.3.3.1 Determination of grafting properties of phosphorus-containing flame retardant monomers

Degree of grafting was calculated as the follow equation:

$$\text{Degree of grafting } (G \%) = [(w_g - w_o)/w_o] \times 100$$

Where w_o =   weight of the original fabrics,

w_g =   weight of grafted fabrics.

3.4   Cleaning method

3.4.1   The commercial dry-cleaning testing.

The durability for washing of silk fabric was tested by a the commercial dry-cleaning method. Tetrachloroethylene (C_2Cl_4) was used as a solvent . The fabrics were placed into a washing/extraction chamber which the solvent temperature maintained at 30 ºC. After washing, the solvent was removed and sent to a distillation unit comprising a boiler and condenser.

3.4.2   The commercial laundering procedure for textile fabrics prior to flammability testing

The durability for washing of cotton fabrics were tested followed ISO 10528, textile commercial laundering procedure for textile fabrics prior to flammability testing. Sodium perborate was used as a solvent and the temperature obtained at 30 ºC with line dried. After that, the appearance after washed will be observed.

CHAPTER IV

RESULT AND DISCUSSION

The objectives of this research are to develop the flame retardant property of cotton and silk fabrics by directly incorporating flame retarding agent to the fabrics. This could be carried out by graft copolymerization technique of an organophosphorus flame retarding monomer onto the fabrics. The target monomers include 2-methacryloyloxyethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphophate (MPBP) as shown in Figure 4.1. The results have been divided into 3 parts. The first part focused on the synthesis and characterization of MEDP and MPBP phosphorus-containing monomers. The second part is dedicated to the grafting of the monomers onto cotton fabric by argon plasma. The last part describes the outcome of flame retardant incorporation onto silk fabric.

2-methacryloyloxyethyl diphenyl phosphate
(MEDP)

2-methacryloyloxyethyl phenyl benzenephosphonate
(MPBP)
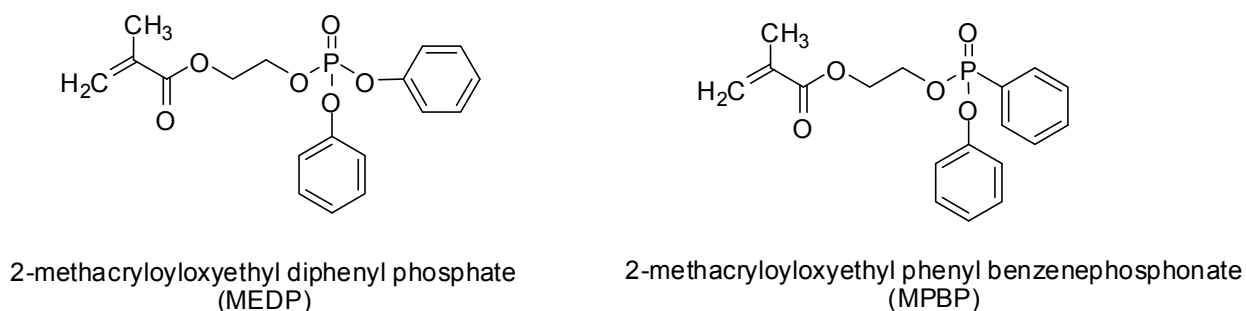
Figure 4.1   Chemical structures of MEDP and MPBP.

4.1   Synthesis and characterization of phosphorus-containing monomers

4.1.1   Synthesis and characterization of 2-methacryloyloxyethyl diphenyl phosphate (MEDP)

Phosphate monomer, 2-methacryloyloxyethyl diphenyl phosphate (MEDP) was synthesized by a reaction of phenyl dichlorophosphate (PDCP), 2-hydroxyethyl methacrylate (HEMA) and phenol in tetrahydrofuran (THF) at 0°C. After workup and column chromatography purification, the product was obtained as a yellow liquid with 48% yield. The chemical structure of MPBP was verified by ^{1}H NMR.

In the ^{1}H NMR of MEDP demonstrated in Figure 4.2, the signals of olefinic vinyl protons were observed as two singlet signals at 5.59 (*cis*) (1H, CH_2=C(CH$_3$)-) and 6.15 (*trans*) ppm (1H, CH_2=C(CH$_3$)-). The signals of methyl (s, 3H, CH$_2$=C(CH_3)-), methylene protons (m, 4H, CH_2-CH_2-O-P), and aromatic protons (m, 10H, aromatic protons) were found at 1.90, 4.40-4.50 and 7.2-7.4 ppm, respectively.
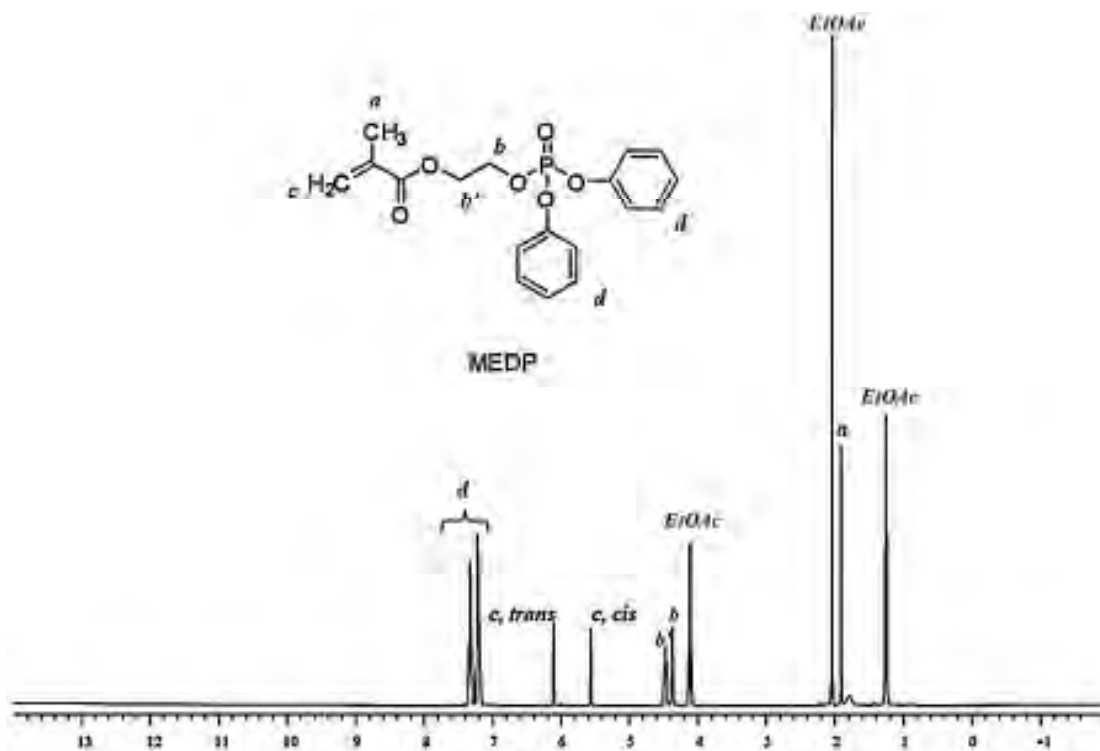
Figure 4.2   ^{1}H NMR of MEDP.

The structure of MEDP was also confirmed by FT-IR analysis as shown in Figure 4.4, (a). FT-IR spectrum showed strong absorption band at 1722 cm^{-1}. This was attributed to the C=O stretching vibration of the flame retardant. The stronger peaks of treated cotton fabric at 1632, 1594 and 1484 cm^{-1} were due to the stretching vibrations of C=C stretching in vinyl and aromatic ring respectively. The absorption band of phosphate structure P=O and P-O stretching were appeared at 1292 and 946 cm^{-1}, respectively [10].

4.1.2 Synthesis and characterization of 2-methacryloyloxyethyl phenyl benzenephosphophate (MPBP)

The second monomer, 2-methacryloyloxyethyl phenyl benzenephosphophate (MPBP), was synthesized by a reaction of phynylphosphonic dichloride (PPDC), 2-hydroxyethyl methacrylate (HEMA) and phenol in tetrahydrofuran (THF) at 0°C. After workup and column chromatography purification, the product was obtained as a yellow liquid with 40% yield. The chemical structure of MPBP was verified by ^{1}H NMR.

In the ^{1}H NMR spectrum of MPBP as showed in Figure 4.3, the signals of olefinic vinyl protons were observed as two singlet signals at 5.55 (*cis*) (1H, CH_2=C(CH$_3$)-) and 6.09 (*trans*) ppm (1H, CH_2=C(CH$_3$)-).The signal of methyl protons appeared at 1.90 ppm (s, 3H, CH$_2$=C(CH_3)-) and the signals of methylene protons were observed at 4.2-4.4 ppm The signal of aromatic protons appeared at 7.1-.7.3 ppm (m, 10H, aromatic protons) corresponding to phosphate aromatic protons (P-OPh) and 7.45-7.90 ppm corresponding to the phosphonate aromatic protons (P-Ph).
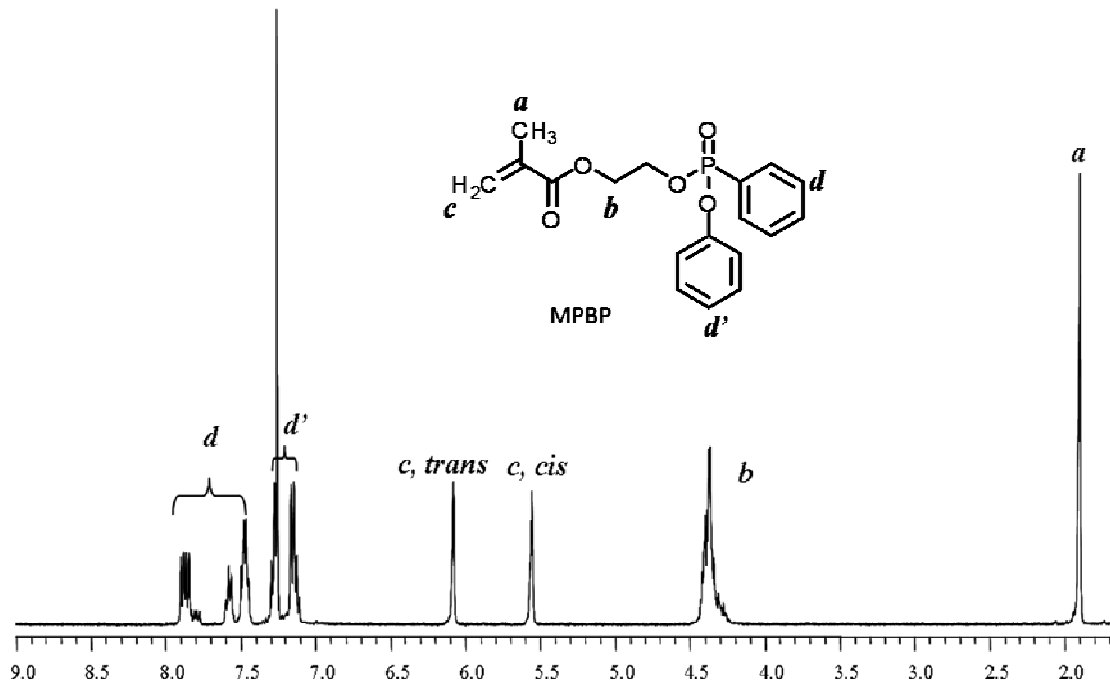
Figure 4.3 ^{1}H NMR of MPBP.
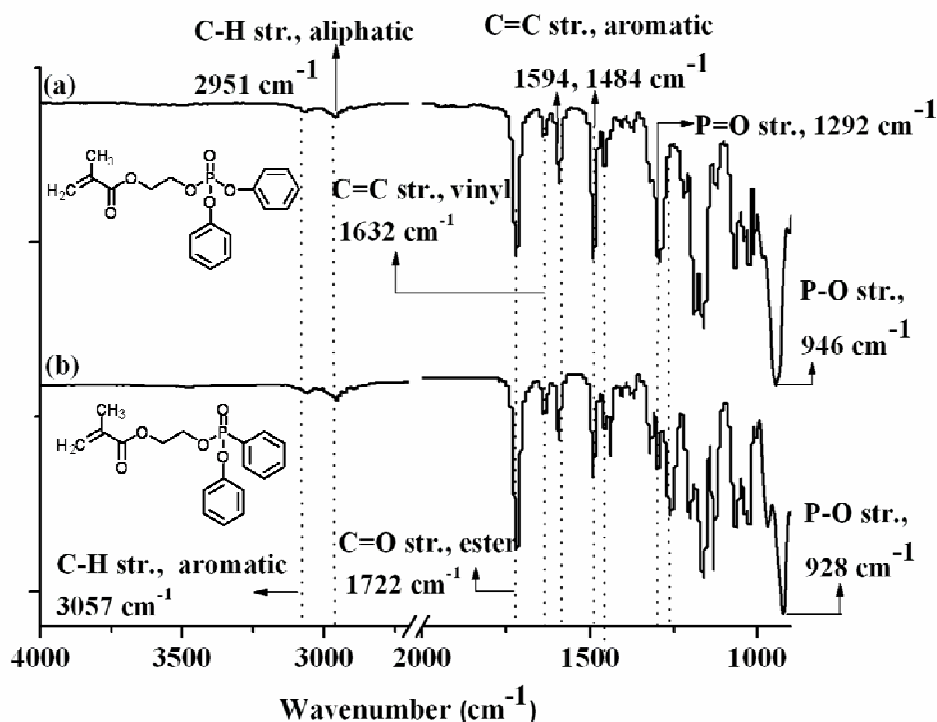
Figure 4.4   FT-IR spectra of (a) MEDP and (b) MPBP.

The structure of MPBP was also confirmed by FT-IR analysis as shown in Figure 4.4, (b). All absorption bands match the result reported by Wang *et al.* [9]. FT-IR spectrum showed strong absorption band at 1722 cm^{-1}. This was attributed to the C=O stretching vibration in ester groups of the flame retardant. The characteristic peak C=C stretching of vinyl was observed at 1632 cm^{-1}. The strong peak absorption bands of C=C of aromatic were observed at 1594 and 1484 cm^{-1}. The important P=O and P-O stretching vibrations appeared at 1292 and 928 cm^{-1}, respectively.

4.2   Surface modification of fabric cotton with MEDP and MPBP

4.2.1   Characterization of polymer thin films grafted onto the surface of cotton fabrics by MEDP and MPBP

The procedure of graft copolymerization induced by argon plasma was described in section 3.2.1, the pieces of fabrics were cut into 11×14 cm^2 then immersed

in the solution with chloroform at the various concentration of monomer between 100 and 300 g/L, cross-linking agent at 5% and 10% (w/w) in the presence of 5% (w/w) of photo initiator then placed the immersed fabrics into the plasma chamber. After that, the surface morphology was characterized by comparing photomicrographs of a virgin fabric with that of treated fabrics. Attenuated total reflection infrared (ATR-IR) spectroscopy was used to characterize existing functional group on the fabric surface. Moreover, physical properties were investigated by tensile strength measurement. The color differences of the untreated and the treated fabrics were investigated by the color spectrophotometer. Thermal properties of treated and untreated fabrics were investigated by thermogravimetric analysis (TGA) and limiting oxygen index (LOI) measurement.

4.2.1.1 Surface morphology

The morphology of untreated and treated cotton fabric with MEDP and MPBP by Ar plasma were characterized by SEM technique. Photomicrographs of untreated cotton, Ar plasma treated cotton, as well as MEDP-treated cotton fabrics are shown in Figure 4.4. Similar comparison in the case of MPBP-treated series is shown in Figure 4.5.

Figure 4.5 showed SEM photomicrograph of (a) untreated cotton, (b) Ar plasma treated cotton in 3 minute at the power of 30 watt, pressure at 0.3 torr and (c) MEDP treated cotton by using argon plasma induced graft-copolymerization respectively. From the results, both (a) and (b) showed that no significance of surface morphology changed after the samples were exposed in RF plasma treatment.
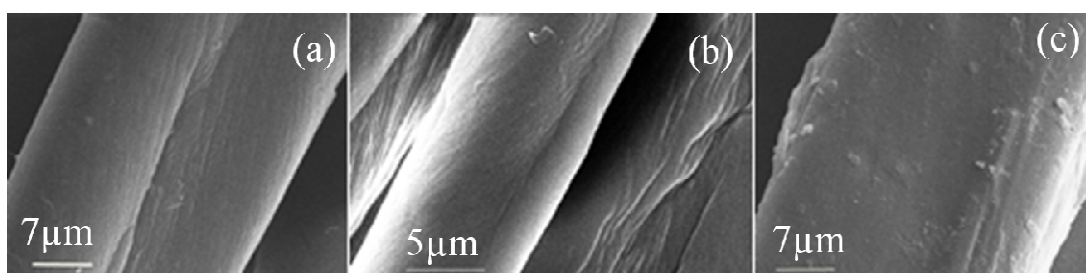
Figure 4.5   SEM images of (a) untreated cotton, (b) Ar plasma treated cotton and (c) MEDP grafted cotton

Differently with (c) Ar plasma treated cotton fabric with MEDP monomer by using argon plasma induce graft-copolymerization at the same condition of (b), we found that the surface morphology of cotton fabric was completely covered with

polymer thin film. In addition, the surface roughness was increased compared with (a) untreated cotton and (b) only Ar plasma treated, so the main cause of increasing of surface roughness came from the deposition of polymer film than etching effect from Ar plasma treatment. The obviously increased of surface roughness after MEDP grafted cotton fabric by plasma treatment showed a good evidence for polymer film that was successfully grafted on the surface of cotton fabric.

The MPBP grafted cotton fabric was shown in Figure 4.6 (a) untreated cotton, (b) Ar plasma treated cotton in 3 minutes at the power of 30 watt, pressure at 0.3 torr and (c) MPBP treated cotton by using argon plasma induced graft-copolymerization respectively. The results could be explained in the same way of MEDP grafted cotton. The surface roughness was obviously increased after grafting with MPBP by Ar plasma treatment. It came from the deposition of MPBP polymer film on the surface of cotton fabric more than etching effect from Ar plasma, which could be found from SEM photomicrograph of (a) untreated cotton and (b) Ar plasma treated cotton in 3 minutes at the power of 30 watt, pressure at 0.3 torr. Both (a) and (b) showed that no significance of surface morphology was changed when compared with (c).
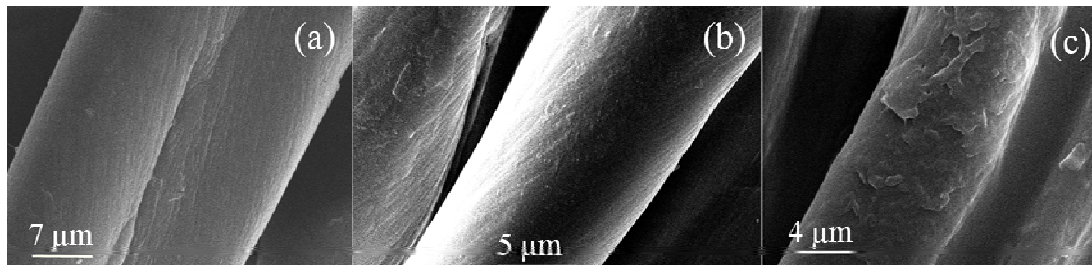
Figure 4.6   SEM images of (a) untreated cotton, (b) Ar plasma treated cotton and (c) MPBP grafted cotton**.**

4.2.1.2   Characterization of functional groups

ATR-FTIR spectroscopic analysis was used to determine the important functional groups presented in the treated fabrics compared to the untreated one. Several different points in the ATR-FTIR spectra between (a) untreated and (b) treated cotton fabrics can be observed in Figure 4.7. The spectrum of the untreated cotton exhibited typical characteristic cellulose peaks at 1000-1200 cm^{-1} were shown C-H wagging at 1316 cm^{-1} and C-O stretching at 1025 cm^{-1}. The other peaks were observed

corresponded to the original characteristic of cellulose, O-H stretching at 3300 cm^{-1}, C-H stretching at 2896 cm^{-1} [22]. In addition to the already existing cellulosic characteristic peaks, the spectrum of the treated cotton fabric showed a new peak at 1734 cm^{-1}. This was attributed to the C=O stretching vibration of ester in MEDP flame retardant. The stronger peaks of treated cotton fabric at 1487 and 1544 cm^{-1} were due to the stretching vibrations of C=C in aromatic rings. O-H bending of absorbed water was observed at 1652 cm^{-1} [36]. From spectrum (b) in Figure 4.7, although after treating with MEDP by Ar plasma, the treated cotton still showed the original characteristics of cellulose at 1000-1200 cm^{-1}. These indicated that the deposition of polymer on the surface of cotton is a very thin layer [1]. This is the advantage of this method because the desirable properties of fabrics were still

In the case of cotton treated with MPBP, ATR-FTIR spectra were shown in Figure 4.8, (a) the spectrum of untreated cotton fabric and (b) MPBP grafted cotton fabric. After the cotton fabric was treated with MPBP, new peaks were appeared at 1725 cm^{-1} and 1253 cm^{-1} which demonstrated of the C=O stretching vibration of ester and P=O stretching of the functional group which are part of MPBP respectively. The P-O-C stretching around 1000-1100 cm^{-1} was covered by the characteristic peaks of cellulose. Moreover, the original characteristic of cellulose, O-H stretching at 3300 cm^{-1} and C-H stretching at 2896 cm^{-1} were still retained as with the case of the cotton treated with MEDP.
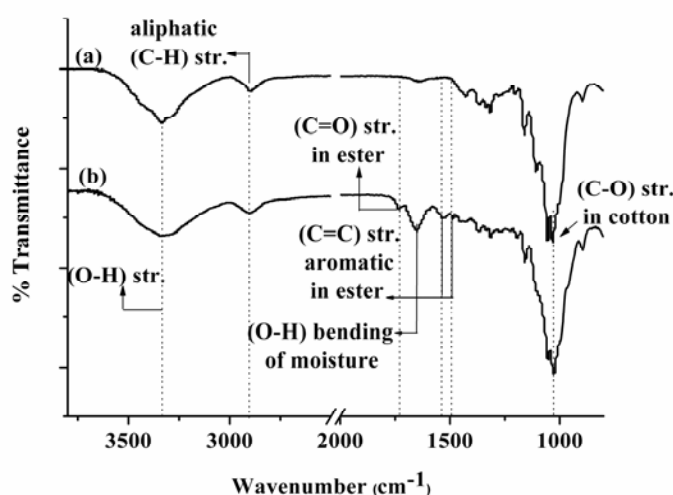
Figure 4.7   ATR–FTIR spectra of (a) untreated and (b) treated cotton fabrics prepared at 200 g/L of MEDP, 10% (w/w) of cross-linking agent, 5% (w/w) of BAPO after washing and air-drying.
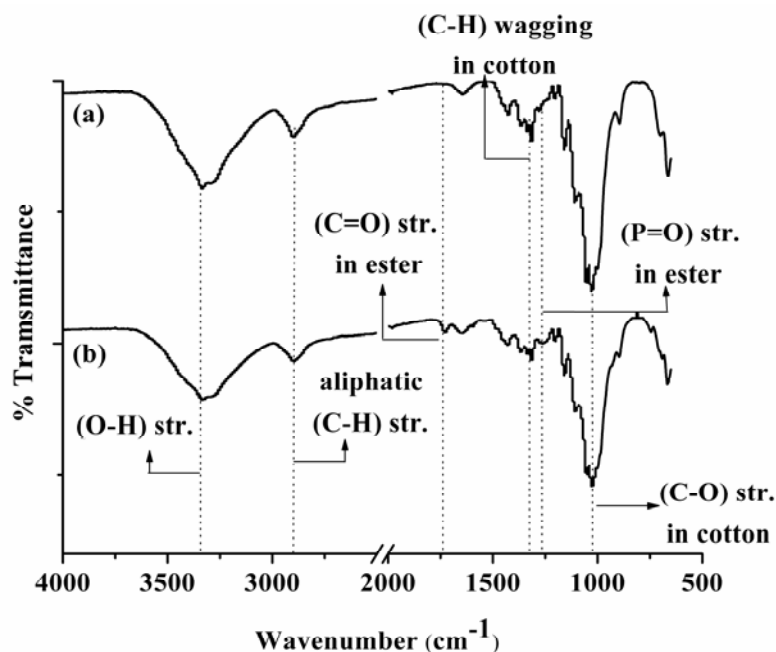
Figure 4.8 ATR–FTIR spectra of (a) untreated and (b) treated cotton fabrics prepared at 200 g/L of MPBP, 10% (w/w) of cross-linking agent, 5% (w/w) of BAPO after washing and air-drying.

4.2.2 Physical properties of cotton fabric treated MEDP and MPBP

4.2.2.1 Effect of MEDP and MPBP treated cotton fabric to the color difference

The color difference between the untreated cotton fabric and treated cotton fabric with phosphorus-containing monomers were investigated by using a color spectrophotometer (X-RITE 530) to determine the color change after treated. The color difference was analyzed by investigating the L*, a*, and b* of the fabric where:

L* = lightness (or luminance),

a* = balance between green (−) and red (+)

b* = balance between blue (−) and yellow (+)

The L*, a*, and b* color difference between untreated cotton fabric and treated cotton fabrics with MEDP and MPBP were measured at three different positions on each piece of fabric along a diagonal of the sample and the color difference or ΔE was calculated from the following equation [6].

$$\Delta E = \sqrt{\left(L_2^* - L_1^*\right)^2 + \left(a_2^* - a_1^*\right)^2 + \left(b_2^* - b_1^*\right)^2}$$

The color change after argon plasma treatment was shown in Tables 4.1 and 4.2. Notably, both MEDP and MPBP were yellowish so the increasing of monomer concentrations led to increase of color intensities of yellowness.

Table 4.1   ΔE of the untreated and MEDP-treated cotton fabric obtained from various conditions.

MEDP (g/L)	Cross-linking agent (%)	L*	a*	b*	ΔE
Untreated	-	92.97	1.89	-3.16	-
100	5	93.04	1.34	-1.13	2.1
	10	92.35	1.08	-0.15	3.2
200	5	92.49	1.29	-0.57	2.7
	10	92.55	1.09	-0.27	3.0
300	5	92.15	1.21	-0.82	2.6
	10	92.23	1.17	-1.29	2.1

with 5% (w/w) and 10% (w/w) of cross-linking agent in the presence of 5% (w/w) of BAPO.

4.2.2.2 The effect of phosphorus-base flame retardants on tensile of cotton fabrics

To investigate the effects of phosphorus-base flame retarding agent graft-copolymerized by radio frequency-induced argon plasma treatment on the mechanical property of cotton fabrics, the tensile strength at break was determined according to the guidelines of ASTM D5035. Mechanical analysis revealed that after the cotton fabric was grafted with MEDP or MPBP monomer by Ar plasma induced-graft copolymerization, the tensile strength of cotton fabrics was not adversely affected.

Table 4.2   ΔE of the untreated and MPBP-treated cotton fabric obtained from various conditions.

MPBP (g/L)	Cross-linking agent (%)	L*	a*	b*	ΔE
Untreated	-	94.16	1.75	-1.31	-
100	5	93.92	1.27	0.36	1.8
	10	94.06	1.34	-0.30	1.1
200	5	93.74	1.33	0.19	1.6
	10	93.75	1.30	0.18	1.6
300	5	93.32	1.25	1.19	2.7
	10	93.65	1.33	0.33	1.8

with 5% (w/w) and 10% (w/w) of cross-linking agent in the presence of 5% (w/w) of BAPO.

The tensile strength values of the untreated and treated of cotton fabrics with MEDP are shown in Table 4.3. The results showed that when the monomer concentration was increased, the tensile strength values were also increased.The highest value of tensile strength obtained when MEDP was used at 300 g/L and the lowest tensile strength values were observed when organophosphorus monomers were used at 100 g/L. From these results, the increasing in the grafting percentage of the flame retardant onto the surface of cotton fabric increased with the monomer concentrations, this part will be explained in the further section (4.2.3.2). This means that amount of deposited polymer film on the surface of fabric also increased. However all of tensile strength values of MEDP treated fabrics were higher than those of untreated ones because the roughness of the fabrics was increased after treated with MEDP monomer. Therefore, the friction was also increased, this factor was the important role in the tensile strength properties of the fabrics [6].

Table 4.4 presents the tensile strengths of untreated and treated cotton fabric with MPBP. In this case the results showed that after grafting MPBP monomer by Ar plasma onto cotton, the tensile strength significantly increased. This is similar to results obtained from the treated fabric with MEDP. The highest value of tensile strength

obtained when MPBP was used at 300 g/L and the lowest tensile strength values were observed when organophosphorus monomers were used at 100 g/L Again, it is also shown here that the increase in the grafting percentage of the flame retardant onto the surface of cotton fabric when the monomer concentrations were increased. Moreover, it was found that the tensile strength values of all fabrics in warp direction were higher than the tensile strength values in weft direction. This result came from the manufacturing process, the yarn or fiber in warp direction must be stronger than the yarn in weft direction to resist the friction from weaving.

Table 4.3   The tensile strength of the untreated and MEDP treated cotton fabrics.

Concentration (g/L)	Grafting (%)	Tensile strength (N)	
		Warp	Weft
-	-	311 ± 1	214 ± 1
100	26.1	498 ± 7	386 ± 11
200	47.5	553 ± 57	438 ± 17
300	65.0	590 ± 26	463 ± 5

*At various MEDP concentrations with 10% (w/w) cross-linking agent, and 5% (w/w) of BAPO

Table 4.4   The tensile strength of the untreated and MPBP treated cotton fabrics.

Concentration (g/L)	Grafting (%)	Tensile strength (N)	
		Warp	Weft
-	-	311 ± 1	214 ± 1
100	22.6	537 ± 12	424 ± 7
200	43.6	629 ± 25	456 ± 30
300	50.0	792 ± 7	479 ± 20

*At various MPBP concentrations with 10% (w/w) cross-linking agent, and 5% (w/w) of BAPO.

4.2.3 Thermal properties of cotton fabric treated with MEDP and MPBP

4.2.3.1 Thermal degradation of the untreated cotton fabric and cotton fabric treated with phosphorus-containing monomers determinated by thermogravimetric analysis (TGA)

The thermal behavior of the untreated cotton fabric and MEDP or MPBP treated cotton fabrics was investigated by thermogravimetric analysis (TGA). The sample was scanned from 50-600 °C at a heating rate of 10 °Cmin^{-1} under nitrogen gas. The results were shown in Figure 4.11, which could be tabulated in Table 4.5 as well.

The thermogram in Figure 4.9 revealed that the range of decomposition of the untreated cotton fabrics appeared as a one-step process which occurred between 318 and 394 °C. In contrast, after grafted with MEDP phosphate monomer, the onset temperatures of thermal decompositions were shifted to the lower temperature. The range of the first step temperatures (T_1) of treated fabrics cotton with MEDP 200 and 300 g/L were between 269-293 °C. These represent the degradation of the phosphate monomer coated on fabric surface which occurred before the decomposition of cotton fabrics in the second step temperature (T_2) at 293-355 °C. From this thermogram, both the onset and the end temperature of grafted fabrics slightly shifted to the lower temperature and the percentage of char residues of treated fabric (26.6%) was up to 10 times higher than that of the untreated fabrics (2.06%). These results revealed that the MEDP-grafted cotton fabrics showed the good property in thermal resistance.The results from Figures 4.9 could be summarized in Tables 4.5.

Table 4.5 TGA results of the untreated and treated cotton fabrics with MEDP.

Cotton (MEDP g/L)	T$_1$ (°C) range	Mass loss in the 1st step (%)	T$_2$ (°C) range	Mass loss in the 2nd step (%)	Char residue (%)
The untreated	318-394	97.9	-	-	2.1
Grafted (100)	275-359	78.7	-	-	21.3
Grafted (200)	269-293	53.3	293-355	22.4	24.3
Grafted (300)	270-293	47.8	293-336	25.6	26.6
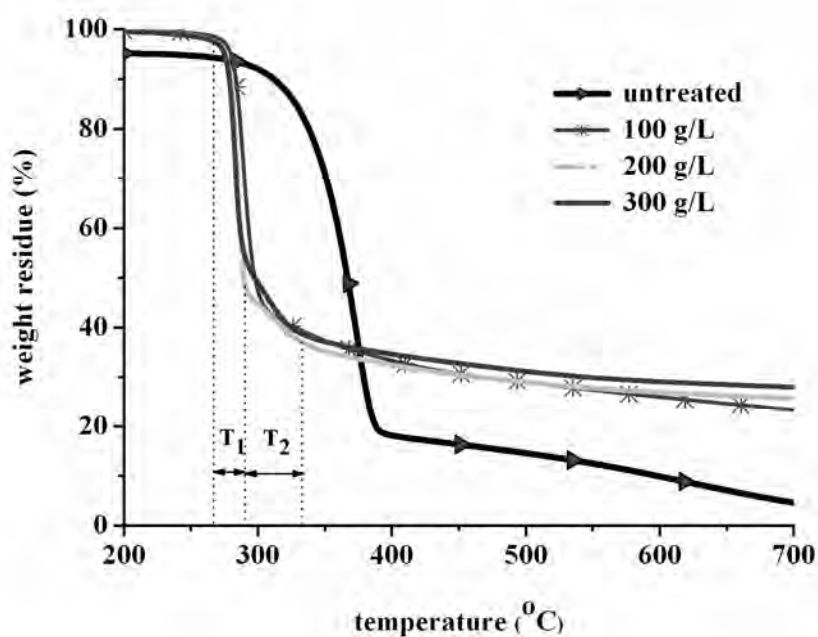
Figure 4.9 TGA thermograms of the treated cotton fabrics with various monomer concentrations of MEDP with 5% (w/w) of cross-linking agent at 5% (w/w) of BAPO and untreated cotton fabrics.
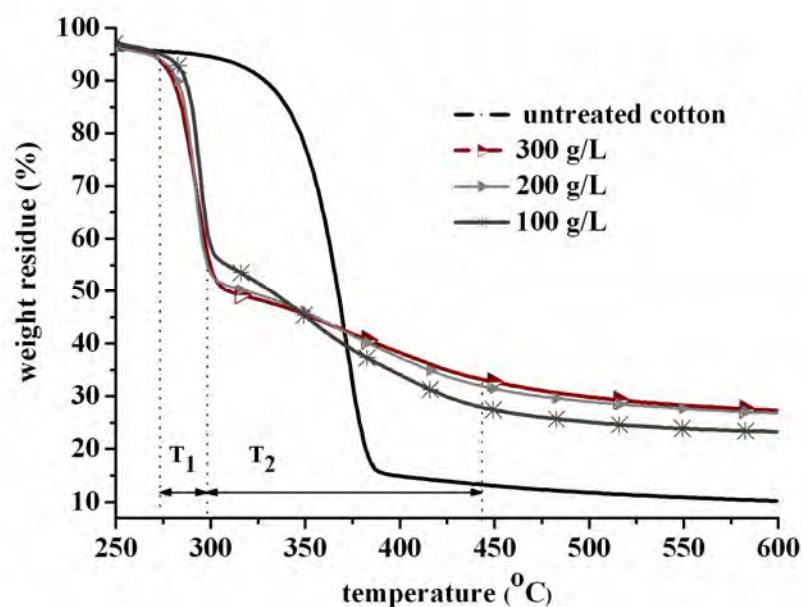
Figure 4.10 TGA thermograms of the treated cotton fabrics with various monomer concentrations of MPBP with 5% (w/w) of cross-linking agent at 5% (w/w) of BAPO and untreated cotton fabrics.

The results from Figures 4.10 could be summarized in Table 4.6

Table 4.6 TGA results of the untreated and treated cotton fabrics with MPBP.

Cotton (MPBP g/L)	T_1 (°C) range	Mass loss in the 1st step (%)	T_2 (°C) range	Mass loss in the 2nd step (%)	Char residue (%)
The untreated	352-388	89.77	-	-	10.23
Grafted (100)	290-300	45.20	300-440	31.57	23.23
Grafted (200)	280-298	49.58	298-442	23.68	26.74
Grafted (300)	281-300	50.65	300-460	22.08	27.27

The TGA thermogram of cotton fabrics treated with MPBP phosphonate was shown in Figure 4.10. The range of decomposition of untreated cotton fabrics were in between 352 and 388 °C with only one step. In contrast, after treatment with MPBP phosphonate monomer, the onset temperatures of thermal decompositions were shifted to the lower temperature. The range of the first step temperatures (T_1) of treated fabrics cotton with MPBP 200 and 300 g/L were between 290-300 °C. The temperatures were

the degradation of the phosphornate monomer coated on fabric surface which occurred before the decomposition of cotton fabrics in the second step temperatures (T_2) at 300-440 °C. From this thermogram, both the onset and the end temperature of treated fabrics slightly shifted to the lower temperature and the percentage of char residues of treated fabric (27.37%) was higher than that of untreated fabrics (10.23%). These results revealed that the treated cotton fabrics with MPBP showed the good property in thermal resistance. In both cases where cotton fabrics were grafted with phosphorus-containing monomer, up to 10 times higher amount of char were observed. This is because of char layer in solid phase of burning fabric. When the treated fabric was heated, the phosphorus reacts to give a polymeric form of phosphoric acid [37]. This acid causes the material to char [17], forming a glassy layer, and so inhibiting the pyrolysis process (break down and release of flammable gases) which is necessary to feed flames.

4.2.3.2 The effect of monomer concentrations on the percentage of grafting and LOI value

The various monomer concentrations were investigated to enhance the percentage of grafting on the cotton fabric. Since cotton fabrics were treated with MEDP monomer at the various concentrations (100-300 g/L) with 5% w/w of cross-linking agent and 5% BAPO at power of 30 W., exposure time of 3 minutes, flow rate of 30 standard cubic centimeters per minute (sccm) and pressure of 0.3 torr. The percentage of grafting and limiting oxygen index (LOI) versus monomer concentration were shown in Figure 4.11 it was found that the percentage of grafting and LOI value increased with increasing monomer concentration since the highest LOI value is 28% at 300 g/L of MEDP. The increasing percentage of grafting brought about an increase in the amount of phosphorus (as shown previously in Table 4.1) so the flame retardant property was improved.

It may be possible to increase the percentage of grafting on cotton fabric with increasing cross-linking agent of 10% w/w, leading to increase LOI value. However, It was found that the LOI values were not increased. This might cause the deposition of excess cross-linking agent instead of MEDP flame retardant monomer so when increasing amount of cross-linking agent, LOI values were not increased (the highest LOI value = 27 at 300 g/L). Anyway all of LOI values from all of monomer

concentrations of treated cotton fabrics were higher than LOI values of the untreated cotton fabric by 5-8 units (LOI of untreated cotton was 19%).

In the case of MPBP as shown in Figure 4.12, the LOI values increased with increasing monomer concentrations. Under various conditions, treating cotton fabrics with a variety of MPBP monomer concentrations in the presence of 5% and 10% (w/w) of cross-linking agent as same as in MEDP, presented that the use of monomer concentration at 300 g/L showed the highest LOI value (24%). Besides, all of the LOI values from all of monomer concentrations of treated cotton fabrics were higher than LOI values of the untreated cotton fabric by 3-5 units (LOI of untreated cotton was 19). These results confirmed that the flame retardant properties of cotton fabrics were improved after treatment with MEDP and MPBP monomer by argon plasma induced grafted copolymerization technique.

In addition, the percentage of grafting was increased to 65%, this might be the partially over crossed of polymer film between inter-fiber which was illustrated in Figure 4.13. The over crossing could cause the increasing of tensile strength because the inter-yarn and inter-fiber friction were increased [6].

Figure 4.11 Effect of MEDP monomer concentrations on percentage of grafting and LOI values of cotton fabrics treated with 5% and 10% (w/w) of cross-linking agent at 5% (w/w) of BAPO in RF argon plasma after washing and air drying.
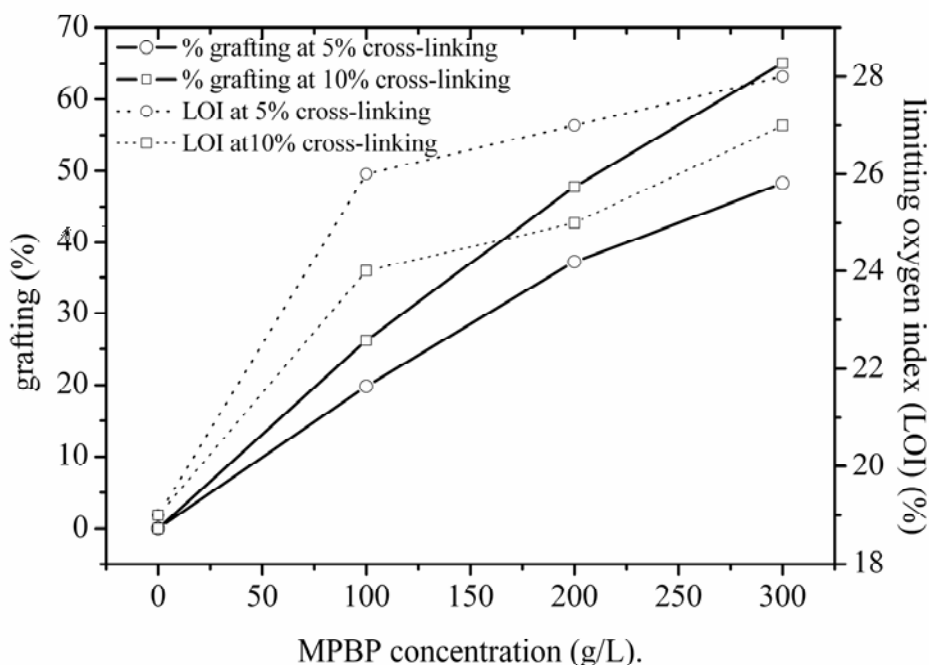
Figure 4.12   Effect of MPBP monomer concentrations on percentage of grafting and LOI values of cotton fabrics treated with 5% and 10% (w/w) of cross-linking agent at 5% (w/w) of BAPO in RF argon plasma after washing and air drying.
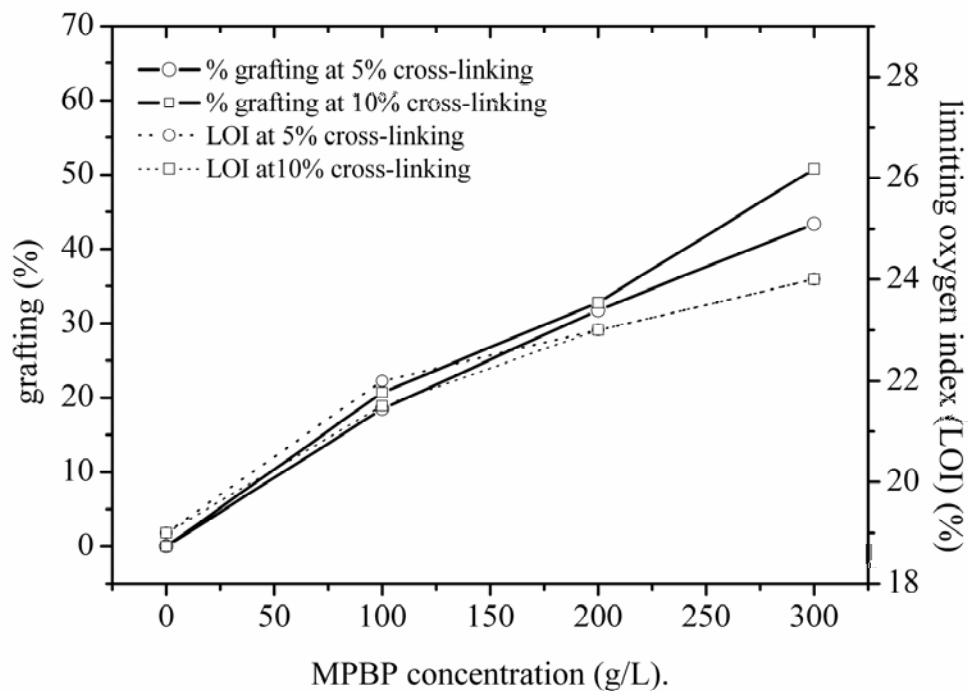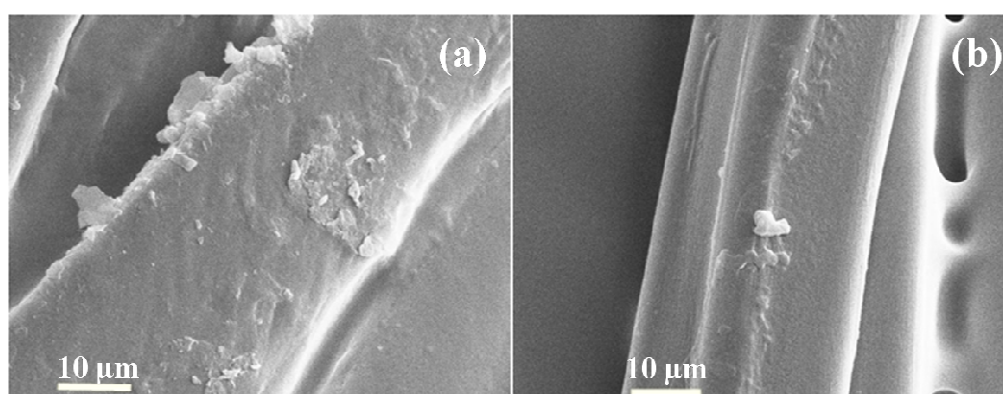

Figure 4.13   SEM images of (a) MEDP grafted cotton, (b) MEDP grafted silk.

4.3 Surface modification of silk fabric with MEDP and MPBP

4.3.1 Characterization of polymer thin films grafted onto the surface of silk fabrics by MEDP and MPBP

Figures 4.14 showed SEM photomicrograph of (a) untreated silk, (b) Ar plasma alone treated silk in 3 minutes at the power of 30 watt, pressure at 0.3 torr. and (c) MEDP treated silk by using argon plasma induced graft-copolymerization, respectively. From the results, both (a) and (b) showe that no significance of surface morphology changed after the sample was exposed in RF plasma treatment. Differently, with (c) Ar plasma treated silk fabric with MEDP monomer by using argon plasma induced graft-copolymerization at the same condition of (b), it was found that the surface morphology of silk fabric was completely covered with polymer thin film. In addition, the surface roughness was increased when compared with (a) the untreated silk and (b) Ar plasma alone treated. Increasing of surface roughness significantly came from the deposition of polymer film.

In case of MPBP grafted silk fabric, the picture was shown in Figure 4.15 (a) untreated silk, (b) Ar plasma alone treated silk in 3 minutes at the power of 30 watt, pressure at 0.3 torr. and (c) MPBP treated silk by using argon plasma induce graft-copolymerization, respectively. The results could be explained in the same way of MEDP grafted silk. The surface roughness was obviously increased after grafting with MPBP by Ar plasma treatment. It came from the deposition of MPBP polymer film on the surface of silk fabric more than etching effect from Ar plasma, which could be found from SEM photomicrographs of (a) untreated cotton and (b) Ar plasma treated cotton in 3 minute at the power of 30 watt, pressure at 0.3 torr. Both (a) and (b) showed that no significant of surface morphology was changed when compared with (c). These exhibit good evidence that grafting occurred on the surface of silk fabrics as same as in the case of cotton.
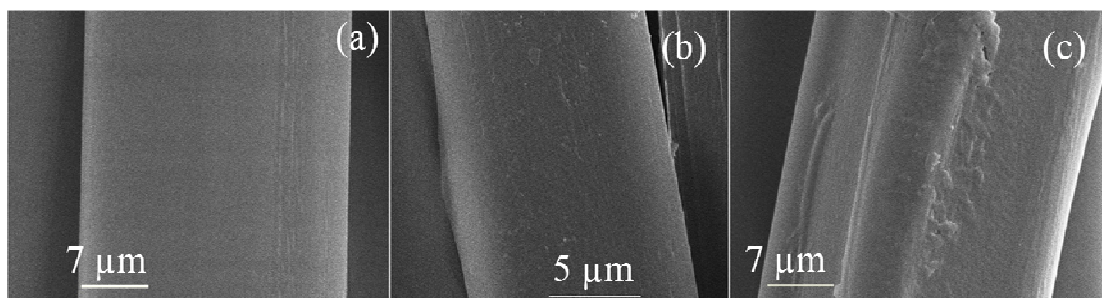
Figure 4.14   SEM images of (a) untreated silk, (b) Ar plasma treated silk and (c) MEDP grafted silk.
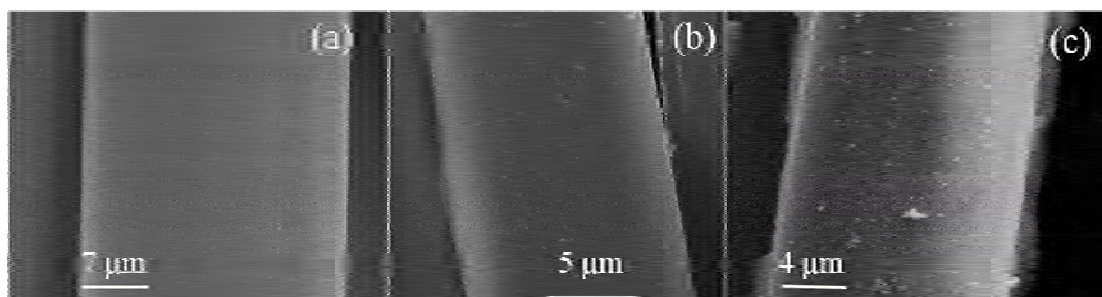
Figure 4.15   SEM images of (a) untreated silk, (b) Ar plasma treated silk and (c) MPBP grafted silk.

ATR-FTIR spectra of (a) the untreated and (b) MEDP treated silk fabrics are illustrated in Figure 4.16. The untreated silk fabric presented a strong peak at 3270 cm^{-1} which is due to the stretching vibration of N-H. Moreover, the peaks at 1600 cm^{-1} and 1500 cm^{-1} corresponded to C=O of amide I and amide II in silk fabric, respectively. In case of the treated silk fabric, a new peak at 1725 cm^{-1}, at 1590 cm^{-1} and 1487 cm^{-1} was observed, this can be attributed to the C=O stretching in ester and C=C stretching vibration in aromatic ring of MEDP, repectively. A strong band at 957 cm^{-1} attributed to the P-O-C vibration in aliphatic. These bands indicated the presence of a MEDP phosphorus containing polymer on the surface of the silk fabric. Note that the stretching vibration of the N-H group of silk fabric is still visible. This indicates that the thickness of the deposited polymer layer is less than 1 μm [1] so the desired properties were still retained.

In case of silk fabric treated with MPBP, the ATR-FTIR spectra was shown in Figure 4.17, (a) the spectrum of the untreated silk fabric and (b) is the silk fabric treated with MPBP monomer by Ar plasma at the same condition of MEDP. It was found that after silk fabric treated with MPBP, the new peak of C=O stretching in ester was appeared at 1734 cm^{-1}, P=O stretching at 1228 cm^{-1}, P-O-C stretching of aromatic ring at 1151 cm^{-1} and 921 cm^{-1} and P-O-C stretching of aliphatic at 921 cm^{-1}. Moreover, the stretching vibration of the N-H group at 3276 cm^{-1} of silk fabric was still retained as same as in case of silk treated with MEDP.
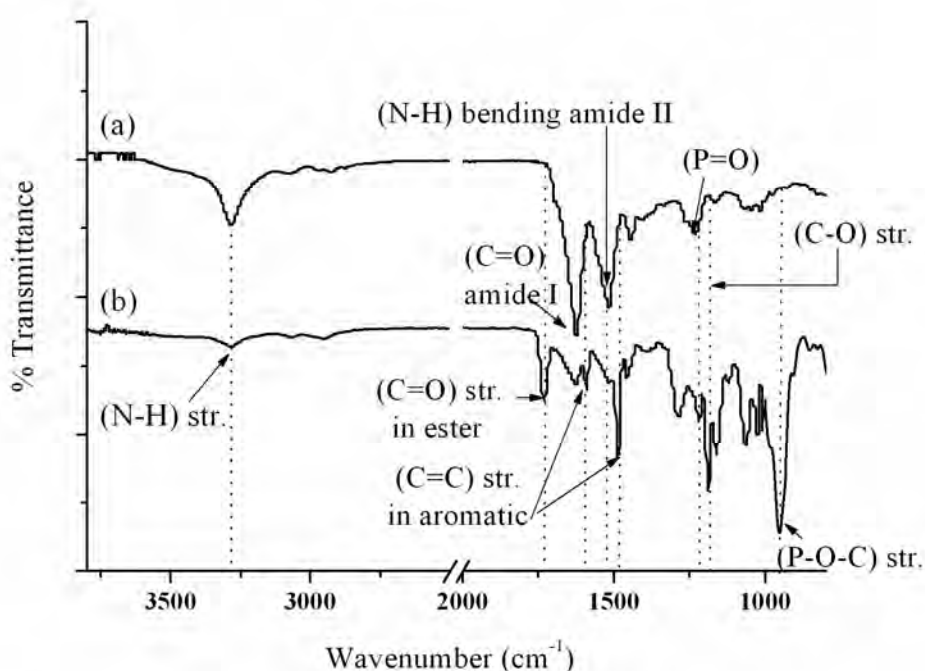
Figure 4.16 ATR–FTIR spectra of (a) untreated and (b) treated of silk fabrics at 200 g/L of MEDP, 10% (w/w) of cross-linking agent, 5% (w/w) of BAPO after washing and air-drying.
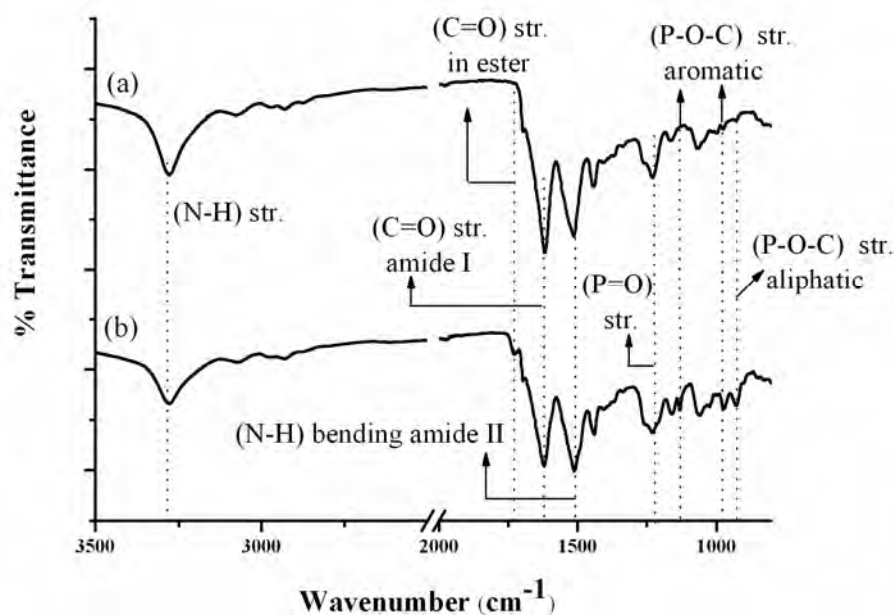
Figure 4.17 ATR–FTIR spectra of (a) untreated and (b) treated silk fabrics at 200 g/L of MPBP, 5% (w/w) of cross-linking agent, 5% (w/w) of BAPO after washing and air-drying.

From ATR-FTIR spectroscopic analysis on surface of both grafted cotton and silk fabrics. The spectra were still shown the original characteristic of each fabric, such as O-H stretching in cotton and N-H stretching in silk. These showed that the range of film thickness was in micron only. Since, the models of grafted fabrics could be assumed as Figure 4.18.

4.3.2 Physical properties of silk fabric treated with MEDP and MPBP

4.3.2.1 Effect of MEDP and MPBP treated silk fabric to the color difference

To investigate the color change of treated and untreated silk fabrics after treatment with argon plasma, color spectrophotometer (X-RITE 530) was used to examine the color change property as same as in the case of cotton fabric. The results were shown in Table 4.7 and Table 4.8 after treatment with both MEDP and MPBP by argon plasma, the color intensities of yellow were increased as same as in case of cotton

fabrics. Besides, the color difference or ΔE of treated silk fabrics were slightly changed compared with MEDP and MPBP treated cotton fabrics because the original color of untreated silk was nearly light yellowness so this technique was not effective to the color change of silk fabrics when compared with solution method [4] which made the yellowness get apparent changing.

(a)

(b)
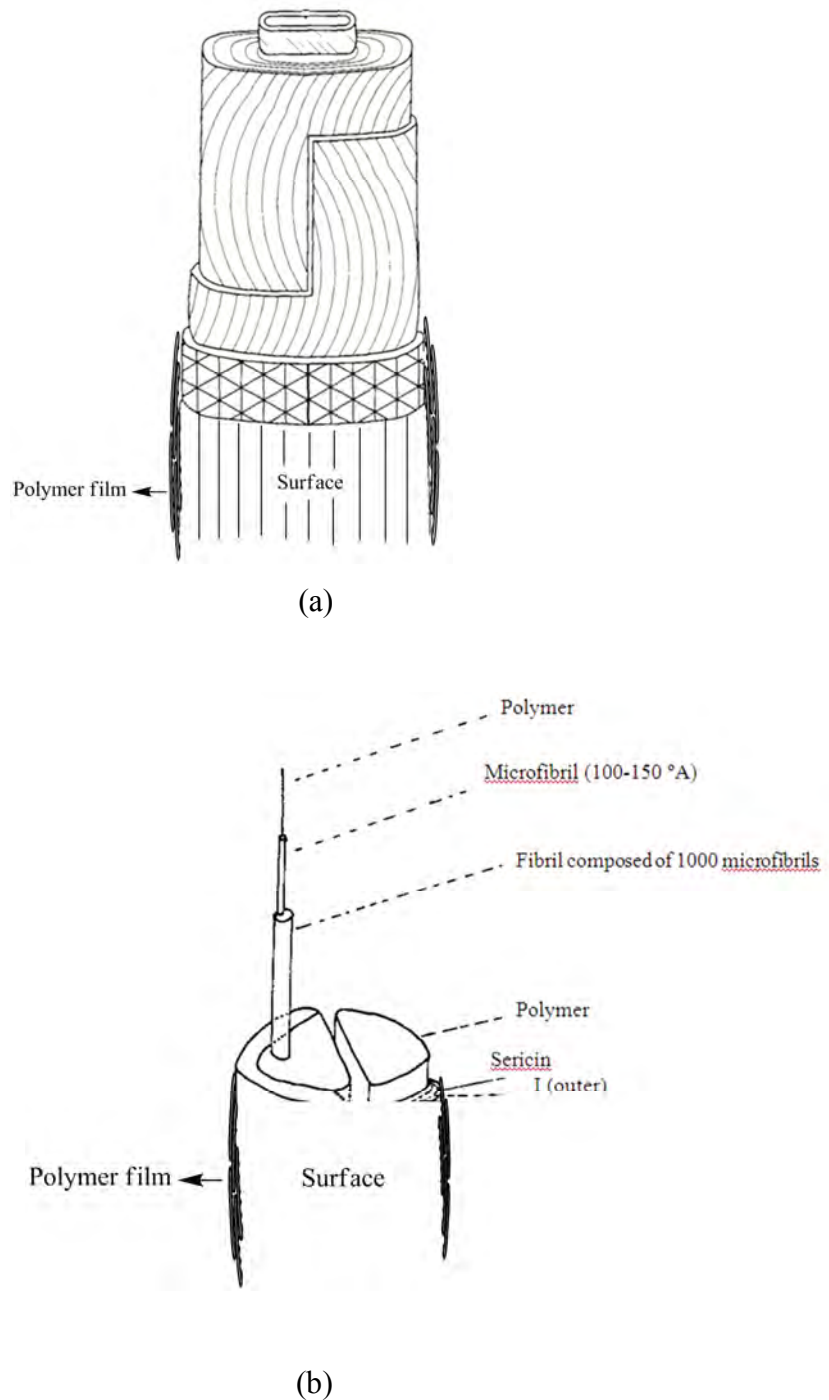
Figure 4.18   Proposed model of (a) grafted cotton fabric and (b) grafted silk fabric

Table 4.7 ΔE of the untreated and MEDP treated silk fabrics at the various concentrations with 10% (w/w) of cross-linking agent in the presence of 5% (w/w) of BAPO.

MEDP conc.	L*	a*	b*	ΔE
untreated	91.33	0.75	4.99	-
200	91.16	1.04	6.33	1.4

Table 4.8 ΔE of the untreated and MPBP treated silk fabric at the various concentrations with 5% (w/w) of cross-linking agent in the presence of 5% (w/w) of BAPO.

MPBP conc.	L*	a*	b*	ΔE
untreated	91.33	0.75	4.99	-
100	90.63	0.77	4.97	0.7
200	91.94	0.69	6.03	1.2
300	91.37	0.92	6.60	1.6

4.3.2.2 The effect of phosphorus-based flame retardants on the tensile strength

Mechanical property of treated and untreated fabrics was investigated *via* the tensile strength according to the guidelines of ASTM D5035. Mechanical analysis revealed that plasma treatment did not adversely affect the tensile strength of silk fabrics as same as the cotton. The tensile strength values of treated and untreated of silk fabrics with MEDP and MPBP were shown in Table 4.9 and Table 4.10. The results showed that the tensile strength values of all treated fabrics were increased. These result from after using argon plasma treatment, the roughness of the treated fabrics was increased so the friction was also increased as the same as the previous results of cotton fabric.

Table 4.9   Tensile strength of the untreated and MEDP treated silk fabrics.

MEDP	Grafting (%)	Tensile strength (N) warp	Tensile strength (N) weft
-	-	379$\pm$ 8	745$\pm$1
200	82.44	441$\pm$ 13	757$\pm$3

*At 200 g/L of MEDP concentration with 10% (w/w) cross-linking agent, and 5% (w/w) of BAPO.

Table 4.10   Tensile strength of the untreated and MPBP treated silk fabric.

MPBP	Grafting (%)	Tensile strength (N) warp	Tensile strength (N) weft
-	-	379$\pm$ 8	745$\pm$3
100	13.9	429$\pm$ 3	731$\pm$3
200	27.8	445$\pm$ 1	669$\pm$10
300	31.5	468$\pm$ 1	723$\pm$12

*At various MPBP concentrations with 5% (w/w) cross-linking agent, and 5% (w/w) of BAPO.

4.3.3 Thermal properties of silk fabric treated MEDP and MPBP

4.3.3.1   Thermal degradation of the untreated silk fabric and silk fabric treated with phosphorus-containing monomers determinated by thermogravimetric analysis (TGA)

In order to have more insights into the flame resistance mechanism, thermogravimetric (TG) and derivative thermal gravimetry (DTG) as shown in Figures 4.18 (a) and (b) respectively have been performed. The initial decomposition temperatures and percent char residue of those silk fabrics were shown in Table 4.11. Upon being exposed to heat, the untreated silk started to decompose at 270-360 ºC and the rate of weight loss accelerated above 270 ºC. At this stage, most of the volatiles species were produced and char residues formed [34]. The second step (270–

600 °C) is assigned to the decomposition of the char of the silk fabric [35]. Its char residue reaches 27.3% at 600 ºC. The decomposition of the treated silk fabrics with the MEDP followed the same pattern with almost the same onset of decomposition temperatures, but the end of decomposition temperature in the first step was lowed by 20 ºC to 340 ºC, and its char residue increased to 32.8 % at 600 ºC. This was the best visible in Figure 4.18 (b).

In case of the treated silk fabrics with MPBP, the thermogravimetric (TG) and derivative thermogravimetry (DTG) curve were shown in Figures 4.19 (a) and (b), respectively. The pyrolysis mechanism of the untreated silk fabric can be explained in the same way as described above, whereas the decomposition of the treated silk fabrics with the MPBP was shown in Figures 4.20 (a) illustrated a distinct weight loss (%) in three decomposition stages. According to TGA curves, the silk fabrics treated with MPBP underwent three main thermal decomposition stages: the first step, slight thermal decomposition of the MPBP flame retardant polymer exhibited at 250 to 290 ºC which occurred before the degradation of silk fiber. The second, abrupt decomposition step from 290 ºC to 370 ºC and the third, from 370 ºC to 470 ºC, these corresponded to the degradation of silk fiber, these could be confirmed by the decomposition stages of untreated silk fabric. The derivative thermogravimetry (DTG) curves as shown in Figure 14.20 (b) support a clear evidence for the three degradation steps.
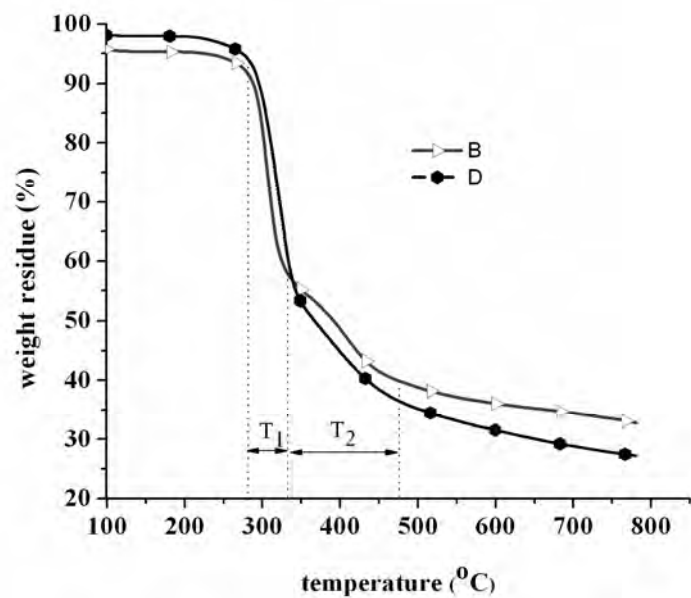
(a)
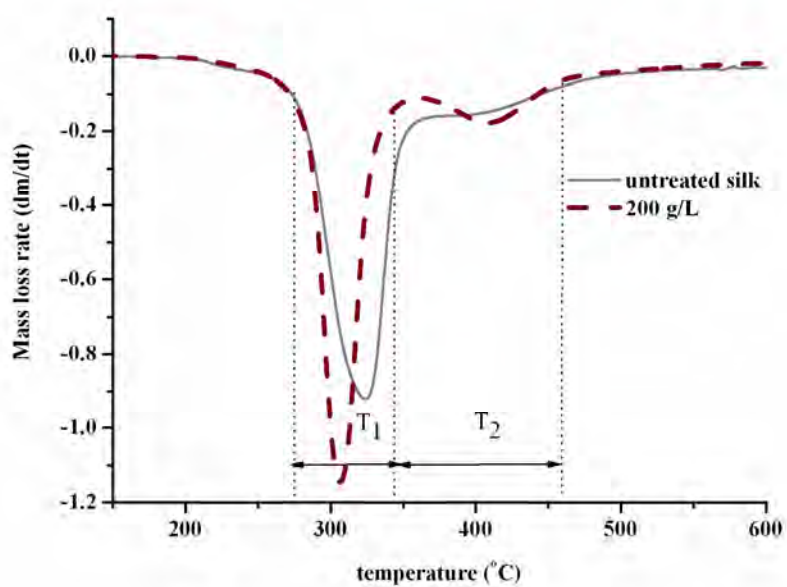
(b)

Figure 4.19　TG (a) and DTG (b) curves in nitrogen of treated silk fabric at 200 g/L of MEDP concentration with 10% (w/w) cross-linking agent at 5% (w/w) of BAPO and untreated silk fabric.

(a)

(b)

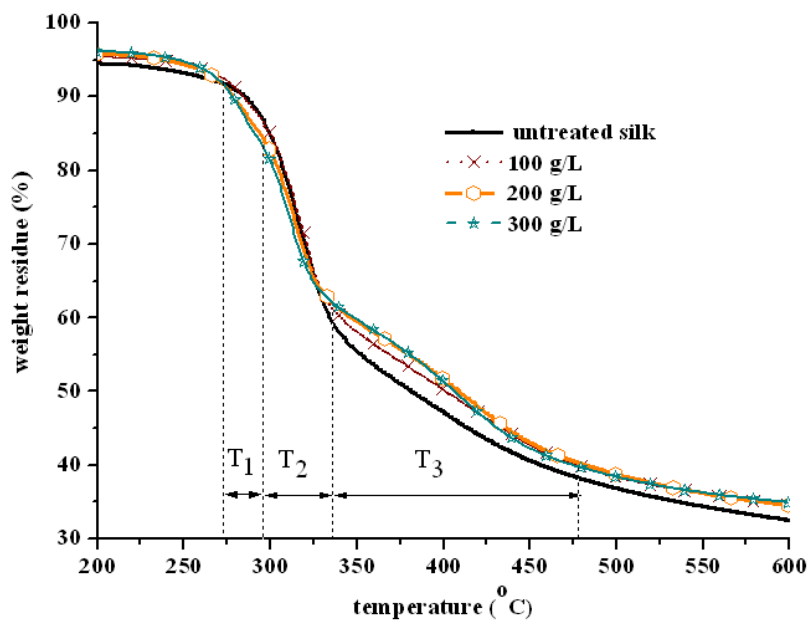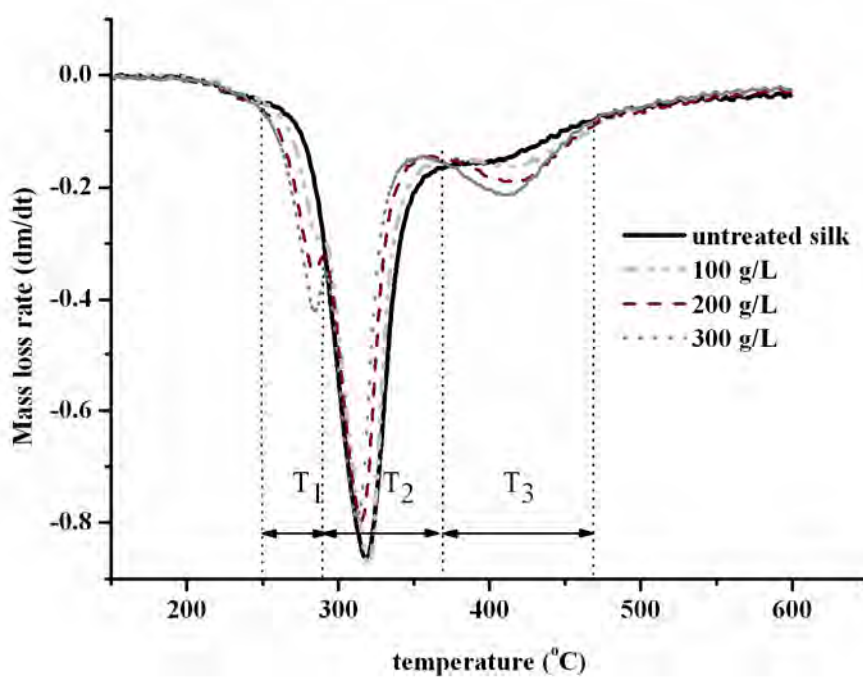**Figure 4.20** TG (a) and DTG (b) curves in nitrogen of treated silk fabric at 200 g/L of MPBP concentration with 5% (w/w) cross-linking agent at 5% (w/w) of BAPO and untreated silk fabric.

The results from Figure 4.19 could be summarized in Table 4.11.

Table 4.11   TGA results of treated and untreated silk fabrics.

Silk (MEDP g/L)	T_1 (°C) range	Mass loss in 1st step (%)	T_2 (°C) range	Mass loss in 2nd step (%)	Char residue (%)
untreated	-	-	288-477	-	27.3
Treated (200)	280-350	41.2	350-470	26	32.8

From the thermal analysis, the silk fabric treated with MEDP and MEDP monomers demonstrated the good thermal resistivity because during the thermal decomposition, phosphorus flame retardants acting in condensed phases form phosphoric acid and polyphosphoric acids which prevented the surface of combustion materials from the volatile gas for the further combustion [17,39].

4.3.3.2   The effect of monomer concentrations on the percentage of grafting and LOI value

In order to investigate percentage of grafting and LOI values of silk fabrics under various of MPBP monomer concentrations, the silk fabrics were treated with MPBP monomer at the various concentrations (100-300 g/L) with 5% w/w of cross-linking agent and 5% BAPO at the power of 30 W., exposure time of 3 minutes., flow rate of 30 standard cubic centimeters per minute (sccm) and pressure of 0.3 torr as same as in the case of treated cotton fabric with MPBP. The percentage of grafting and limiting oxygen index (LOI) versus monomer concentrations were shown in Figure 4.21. It was found that the percentage of grafting and LOI value increased with increasing monomer concentration since LOI values from all of monomer concentrations of treated silk fabrics were higher than LOI values of untreated silk fabric by 1-3 units and the highest LOI value was 28 and the untreated silk was 25. This resulted from the increasing of percentage of grafting brought about an increased in the amount of phosphorus content which forming char layer on the surface of fabric to prevent the volatile gases for the future combustion (as shown in Table 4.12) so the flame retardant property was improved. Anyway, the slightly increased of LOI value in case of treated silk compared with treated cotton might due to in the chemical structure

consisted of a high nitrogen contents in amino acids which showed the good flame retardant properties by themselves [34]. For this reason, the LOI value of the untreated and treated silk fabrics with MEDP was not changed though the MEDP monomer concentrations were increased.
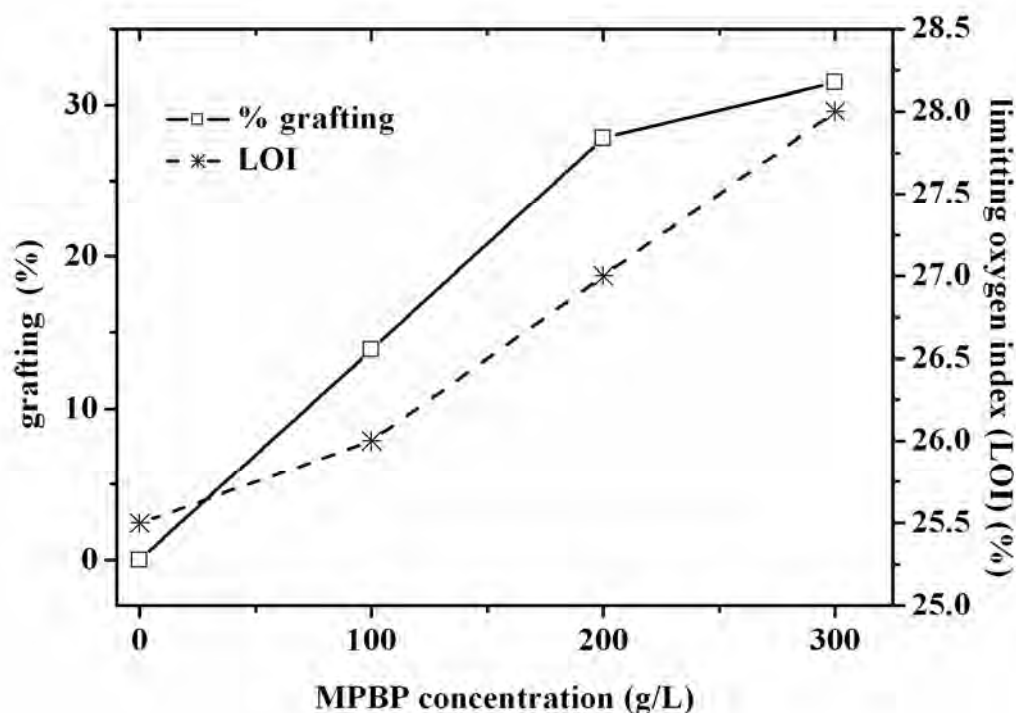
Figure 4.21   Effect of MPBP monomer concentrations on percentage of grafting and LOI values of silk fabrics treated with 5% (w/w) of cross-linking agent at 5% (w/w) of BAPO in RF argon plasma after washing and air drying.

Table 4.12   The percentage of grafting and phosphorus containing at the various of MPBP monomer concentrations with 5% cross linking agent and 5% BAPO on silk fabrics.

	Concentration (g/L)	Grafting (%)	Phosphorus (%)	LOI (%)	Tensile strength warp (N)
MPBP	100	13.87	8.54	26	428
	200	27.84	9.13	27	445
	300	31.51	14.20	27	468

4.4   Durability of treated cotton and silk fabric to washing

The resistance to washing of the MPBP treated cotton and silk fabrics were studied to confirm the strong attachment between polymer film and surface of fabrics. The treated cotton fabrics were subjected to a specified number of commercial laundering procedures for textile fabrics prior to flammability testing with the use of ISO10528 for 3 cycles. Whereas silk fabric treated with MPBP was tested the resistance to dry-cleaning, followed the commercial dry-cleaning method. The results were shown in Table 4.13.

Table 4.13   LOI of treated fabrics before LOI $_1$ and after LOI $_2$ the accelerated laundering method for textile fabrics prior to flammability testing

Fabric	Monomer	W_0	W_1	LOI_0	LOI_1
Cotton	MEDP	3.05	3.05	28	24
	MPBP	3.78	3.78	24	24
Silk	MPBP	2.54	2.54	28	28

[Monomer] = 200 g/L, 5% (w/w) of cross-linking agent, 5% (w/w) BAPO

W_0 = weight of treated fabric before washed

W_1 = weight of treated fabric after washed

The results in Table 4.13, the LOI after washing of the treated cotton and silk fabrics with MEDP and MPBP monomers showed that they were dropped slightly. In case of cotton fabric, this might be due to the effect of sodium perborate detergent. The high concentrations of sodium perborate might also cause a gradual deterioration in fabric flame-retardant performance especially if washing was carried out repeatedly. Moreover, the weight of treated fabrics was not changed although after 3 cycles washing. This demonstrated that the polymers were strongly attached with the surface of fabrics.

CHAPTER V

CONCLUSIONS AND SUGGESSIONS

5.1   Conclusions

In this research, the improving of flame retardant properties of cotton and silk fabrics were successfully performed by using plasma-induced graft copolymerization of 2-methacryloyloxyethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphophate (MPBP) flame retardant monomers. We investigated the effect of these phosphorus-containing monomer concentration to the percentage of grafting and LOI values. Moreover chemical, physical and mechanical properties of untreated and treated fabric were investigated too.

Cotton fabrics showed good flame retardant properties after treatment with MEDP and MPBP monomer. The LOI values obtained so far reached 28% in case of MEDP and 24% in case of MPBP while that of untreated cotton was 19%. Moreover, it was found that the percentage of grafting and LOI values increased with an increase of monomer concentration. ATR-FTIR spectra and SEM micrographs confirmed that the success in the grafting of copolymer on the surface of cotton fabric was occured. The treated cotton fabric showed characteristic IR absorptions of P=O and P-O-C, these bands indicated the presence of phosphorus containing polymer on the fabric. From this result, it can decrease the thermal degradation that was analyzed by using TGA. The weight residue of treated fabric was higher than the untreated fabric. Furthermore, it was found that the tensile properties were slightly increased with the increasing of monomer concentration. The roughness of the treated fabric was increased by the polymer film deposition so the inter fiber friction was also increased. This is the important role in the tensile strength properties of the fabrics. Beside, the color differences, ΔE, of untreated and treated fabric were not significantly changed. The highest value of color difference is about 1-3 units. This value means the noticeable difference in color.

In case of silk, the original silk was classified in the ignition material which has LOI value about 25%. After treating with MPBP monomer, the LOI was raised up and

we found that the percentage of grafting and LOI value increased with increasing monomer concentration since LOI values from all of monomer concentrations of treated silk fabrics were higher than LOI values of untreated silk fabric by 1-3 units by the highest LOI value was 28% and the untreated silk was 25%. This result according to the TGA results by the weight residue from the treated was higher than that from the untreated silk. This showed the good evidence of flame retardant properties was improved after treatment. The slight increase of LOI value in silk compared cotton fabrics might be from the high nitrogen content in the structure of original silk which showed the good flame retardant properties by themselves. To confirm the deposition of flame retardant monomer on the surface of silk fabric, ATR-FTIR and SEM micrograph were used and the results showed the characteristic IR absorption of P=O and P-O-C stretchings, these indicated the presence of phosphorus containing polymer on the surface. The stretching vibration of N-H group of silk was still visible on the treated samples. These demonstrated that the thickness of the covered polymer film was less than 1 μm so the original and desirable properties were still retained. These results confirmed by physical and mechanical properties which measured by the color differences ΔE and tensile strength, respectively. Tensile strength of the treated silk fabric was increased with increasing of monomer concentration due to the higher surface roughness from the polymer deposition. The color differences ΔE of untreated and treated silk were not significant. The highest value of color difference was about 1-2 units, this value means the noticeable difference in color.

From these experiments, it could be concluded that MEDP phosphate and MPBP phosphornate monomers have been successfully grafted onto the surface of cotton and silk fabrics by using plasma-induced graft copolymerization technique. The strong attachment between flame retardant and the surface of fabrics were confirmed by the weight of treated fabrics after 3 washing were not changed and the LOI also higher than the untreated one. Besides, the surface approach was easy to handle and could be applied to the other synthetic or natural fibers/fabrics. Moreover, the desired properties still retained.

5.2   Suggestions for future works

Directions that could be further explored are in the following aspects:

- The Investigation of phosphorus ratio in each monomer to the percentage of grafting and LOI value.

- The investigation of chain length of cross-linking agent to the binding efficiency on grafting and LOI value.

- Comparison of grafting efficiency between using radio frequency (RF) plasma and the other systems such as microwave (MW), direct current (DC) or alternating current (AC) plasma.

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