REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

SYNTHESIS OF PHOSPHORUS CONTAINING FLAME RETARDANTS AND INVESTIGATION FLAME RETARDANT BEHAVIOUR ON THE TEXTILE APPLICATIONS

MUHAMMED KANAT

MSc. THESIS
DEPARTMENT OF CHEMISTRY
PHYSICAL CHEMISTRY

ADVISOR
PROF. DR. TARIK EREN

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A thesis submitted by Muhammed KANAT in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** is approved by the committee on 20.10.2017 in Department of Chemistry, Physical Chemistry.

Thesis Advisor

Prof. Dr. Tarık Eren

Yıldız Technical University

Approved By the Examining Committee

Prof. Dr. Tarık Eren

Yıldız Technical University _____

Prof. Dr. M. Kasım Şener, Member

Yıldız Technical University _____

Assoc. Prof. Dr. Bülent AKGÜN, Member

Boğaziçi University _____

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Muhammed KANAT

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LIST OF SYMBOLS

%	Percent
µm	Micrometer
ppm	Parts per Million
h	Hour
s	Second
eV	Electronvolt
w/w	Weight/weight
BL	Bilayer
^{o}C	Centigrade Degree
kJ	Kilojoule
kg	Kilogram
g	Gram
mL	Milliliter
mm	Millimeter

LIST OF ABBREVIATIONS

APP	Ammonium Polyphosphate
APTES	3-aminopropyl Triethoxysilane
ASTM	American Section of the International Association for Testing Materials
ATH	Aluminium Trihydroxide
BS	British Standard
COST	European Cooperation in Science and Technology
DAP	Diammonium phosphate
Deca-BDE	Decabromodiphenyl Ether
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
DOPO	9, 10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide
EDX	Energy-dispersive X-ray spectroscopy
EFRA	The European Flame Retardants Association
EtOH	Ethanol
HBCD	Hexabromocyclododecane
HCI	Hydrogen Chloride
HCN	Hydrogen Cyanide
IPA	Isopropyl Alcohol
ITA	Itaconic Acid
LOI	Limiting Oxygen Index
MAH	Maleic Anhydride
MCC	Micro-scale Combustion Calorimeter
MDH	Magnesium Hydroxide
NASA	National Aeronautics and Space Administration
NH_3	Ammonia

NMR	Nuclear Magnetic Resonance Spectroscopy
Octa-BDE	Octabromodiphenyl Ether
PA	Phosphoric Acid
PCP	Pyrovatex CP
PDMS	Polydimethylsiloxane
Penta-BDE	Pentabromodiphenyl Ether
PFRs	Phosphorus Containing Flame Retardants
Sb_2O_3	Antimony (III) oxide
SEM	Scanning Electron Microscopy
SIPs	Smart Inorganic Polymers
TAEP	Tris(acryloyloxyethyl) Phosphate
TAP	Triallyl Phosphate
TBBPA	Tetrabromobisphenol A
TBP	Tributyl Phosphate
TCEP	Tris(2-carboxyethyl) phosphine
TCPP	Tris(chloroisopropyl) phosphate
TDCP	Tris(1,3-dichloroisopropyl) phosphate
TGA	Thermogravimetric Analysis
TGICA	Triglycidyl Isocyanurate Acrylate
THF	Tetrahydrofuran
THPX	Tetrakis(hydroxymethyl) Phosphonium Salt
TPT	Triallyl Phosphoric Triamide
TUBITAK	The Scientific and Technological Research Council of Turkey
UL	Underwriters Laboratories
UV	Ultraviolet
XPS	X-ray Photoelectron Spectroscopy
YTU	Yıldız Technical University

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ABSTRACT

SYNTHESIS OF PHOSPHORUS CONTAINING FLAME RETARDANTS AND INVESTIGATION FLAME RETARDANT BEHAVIOUR ON THE TEXTILE APPLICATIONS

Muhammed KANAT

Department of Chemistry

MSc. Thesis

Advisor: Prof. Dr. Tarık Eren

Cotton fabrics have been one of the most widely used bio-based textiles all over the world. They have been widely applied in both civilian and military fields due to their excellent properties, such as hydrophilicity, air permeability, softness, comfort and so on. However, their flammability is an important weakness and badly limited the production of high performance flame retardant textile products.

Many people constantly use halogen-free phosphorus compounds as flame retardants for cotton textiles. They are cheap to manufacture, are less volatile and toxic, have good thermal stability and promote char formation during the burning process. Phosphorus compounds can catalyze char formation and reduce the flammability of cotton textiles.

In this study, we have synthesized two types of reactive phosphorus containing flame retardants (MKT-1 and MKT-2) that can be covalently attached to the textile surface. MKT-1 possess anhydride and acid functionality that can react with cellulose -OH functionality. Besides that, MKT-2 has silanol groups that can react with hydroxy group present on cellulose fiber.

The structures of reactive flame retardants (MKT-1 and MKT-2) were characterized by 13C- and 31P NMR. Thermal properties of the cotton fabrics were investigated by thermogravimetric analysis (TGA), surface characterization was done by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy, standard test method for flammability of blankets (BS 5852) was also applied to characterize fire retardancy.

It was observed that cellulose coated with 30% MKT-2 didn't burn after the propane burner was held for 20 seconds. It also produced the highest char yield (36%) at 500 oC.

Furthermore, it also indicated that covalently attached flame retardant materials are durable and do not hydrolyze under washing process.

Key words: Flame retardancy, cotton fabrics, phosphorus

ÖZET

FOSFOR İÇEREN ALEV GECİKTİRİCİLERİN SENTEZİ VE TEKSTİL UYGULAMALARINDAKİ ALEV GECİKTİRİCİ ÖZELLİĞİNİN İNCELENMESİ

Muhammed KANAT

Kimya Anabilim Dalı

Yüksek Lisans Tezi

Tez Danışmanı: Prof. Dr. Tarık EREN

Pamuklu kumaşlar dünyanın her yerinde en çok kullanılan biyo esaslı tekstilden biridir. Hidrofiliklik, hava geçirgenliği, yumuşaklık ve rahatlık gibi mükemmel özelliklerinden dolayı hem sivil hem de askeri alanda yaygın bir şekilde uygulanmaktadır. Fakat yanıcılık özelliği dezavantajlılık gösterip yüksek performansa sahip alev geciktirici tekstil ürünlerinin üretimini kötü bir şekilde sınırlandırmıştır.

Genellikle pamuklu tekstiller için alev geciktirici olarak halojensiz fosfor bileşikleri kullanılır. Üretimleri ucuz, daha az uçucu ve toksik, iyi termal kararlılığa sahiptir ve yanma sürecinde kül oluşumunu desteklerler. Fosfor bileşiklerinin kül oluşumunu kataliz edebileceğini ve pamuklu kumaşların alevlenebilirliğini azaltabileceğini göstermiştir.

Bu çalışmada, tekstil yüzeyine kovalent olarak bağlanabilen reaktif fosfor içeren alev geciktiriciler sentezlenmiştir. MKT-1, selüloz -OH ile reaksiyona girebilen anhidrit ve asit yapısına sahiptir. Bunun yanında, MKT-2 selülozdaki -OH yapısıyla reaksiyona girebilen silanol gruplar içerir.

Reaktif alev geciktiricilerinin (MKT-1 ve MKT-2) yapısı 13C- ve 31P NMR ile karakterize edildi. Tekstil ürünlerinin termal özellikleri, termogravimetrik analiz (TGA), yüzey karakterizasyonu taramalı elektron mikroskobu (SEM) ve x-ray fotoelektron spektrometrisi (XPS) yapılmış, battaniyenin alevlenebilirliği için olan standart test yöntemi (BS 5852) ile ayrıca alev geciktiriciliği karakterize edilmiştir.

30% MKT-2 kaplanmış olan kumaşın, ateş kaynağı ile 20 saniye tutulmasından yanmadığı ve de en yüksek kömürleşme verimini (36%) verdiği gözlenmiştir. Ayrıca,

kovalent bağlanmış alev geciktirici materyallerin dayanıklı olduğu ve yıkama işlemi altında hidrolize olmadığı da belirtilmiştir

Anahtar Kelimeler: Alev geciktirici, pamuklu kumaşlar, fosfor

CHAPTER 1

INTRODUCTION

Cotton fabrics due to their excellent properties of biodegradability, biocompatibility, air permeability, hydrophilicity, mechanical strength, softness and comfort have many applications in both civilian and military fields [1–2]. However, its weakness against ignition and rapid flammability properties desperately limited its used in the fields which needed textile products. In the past years, ignition and combustion of household textiles were one of the main reasons for residential fires [3].

Both our homes and offices contain a critical potential "fire load" of flammable materials due to electrical and electronic equipment that we use, and rising levels of comfort (furniture, carpets, toys, and papers etc). The potential also gave rise of fire tendency, especially in electronic equipment but at the same time, result in a concentration of energy and an increase in risks of overheating or many other electrical fire risks. Flame retardants can prevent an increase in fire risk from the growing number of consumer and electronic goods in homes and offices.

According to results, shown in Table 1.1, residential fires caused many people to die between 2002-2013, USA report. However, residential fires decreased proportionally relating with using flame retardants on materials.

Table 1.1 Residential fires happened between 2002-2013

Year	Fires	Civilian Deaths	Civilian Injuries
2002	401,000	2,695	14,050
2003	402,000	3,165	14,075
2004	410,500	3,225	14,175
2011	386,000	2,550	14,360
2013	387,000	2,785	12,575

In recent years, many flame retardants are widely used in many fields due to their resistance against fires. Therefore, instead of halogenated flame retardants, low-toxic phosphorus flame retardants have been developed for environmental protection and public safety [4-5].

1.1 Literature Review

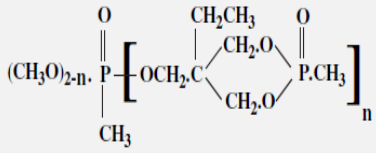
Flame retardants, first developed during the Second World War to be used in both military and civilian applications for which the personal safety is the most important priority. Major earlier improvements were in between 1950- 1980 which was called as ‘’A Golden Period’’ [6].

Giving an example, the risks caused by the flammability of cotton children’s nightwear were frequently realized during the 1950-1980 period in both the UK and USA [7]. Regulations was developed during the 1960s to keep at minimum deaths and injuries to children by the UK Nightwear Safety legislation of 1967 [8]. Therefore, young girl’s nightdresses needed to have a minimum level of flammability due to the fire safety risks.

The first patents were in the 1950s and gave rise to the flame retardants based on cross-linked tetrakis(hydroxymethyl) phosphonium salt adducts (often called THPX chemistry) and N-alkylsubstituted phosphonopropionamide derivatives [6,9].

The need for synthetic fiber industry was to produce types of flame retardants by developing the fire resistance based on polymers which include aromatic groups as shown in Table 1.2. Aramids and the poly(meta-aramid) fibers Nomex (Du Pont) are the main examples of the latter in the 1960 period as a fiber for niche products, such as in racing car driver overalls. In the late 1960s, the poly(para-aramid) fiber Kevlar (Du Pont) was carried out as a high modulus fiber. In 1970, There was a major push to send a human to the moon also after improving of synthetic fibers having very high thermal resistance since 1960. Nomex was identified by NASA in 1971 for using in aerospace personnel’s overalls [10]. However, according to properties of the products used in these fields were quite toxic in fact. Small amounts of risky gases such as carbon monoxide, carbon dioxide, nitrogen oxides, hydrogen cyanide, ammonia or other toxic gases can be produced via combustion of Nomex relating with the burning conditions [11,12].

Table 1.2 Main examples of flame retardant for textiles in 1950-1980

Substrate textile fibre(s)	Generic formula	Comments
Cellulose (cotton, viscose and cotton-rich blends)		
Non-durable	Ammonium phosphates and mixtures with other salts, e.g. ammonium bromide and sulphamate Ammonium polyphosphates Guanidine phosphates Organophosphorus oxyanion salt Organic nitrogen-containing compounds Organic N- and P-containing compounds Borax Combinations of the above	Available as proprietary formulations; semi-durability may be developed by post-curing to achieve cellulose phosphorylation; addition of resins
Durable	Tetrakis (hydroxymethyl) phosphonium salt (THPX) adduct condensates N-methylol and N,N′-dimethylol dialkyl phosphonopropionamides and derivatives	Typified by the ammonia-cured Proban® (Rhodia) Exemplifed by Pyrovatex® (Ciba/Huntsman) its variations and equivalents. Requires presence of cross-linking resins
Back-coatings (application to most textile substrates)	Halo-organic-antimony III oxide (ATO) formulations (e.g. decaBDE/HBCD) Intumescent-based systems for back-coatings	Durability is determined by resin choice
Wool: durable to dry cleaning	Zirconium and titanium hexafluoride complexes Tetrabromophthalic anhydride (TBPA)	Typified by Zirpro® May be used alone or with Zirpro® to reduce afterflame times
Polyester: durable	Cyclic organophosphonate 	Based on Antiblaze 19 (formerly Mobil) and subsequently Antiblaze or Amgard CU (Rhodia) applied by thermofixation
Polyamide: durable	N- and S-containing polycondensates typically based on thiourea derivative- formaldehyde formulations	Find application in technical fabrics
Acrylics and multifibre blends and composites (e.g. furnishing fabrics)	Back-coatings based on halogen-ATO formulations	The only commercial alternatives to using modacrylic fibres, e.g. Kanecaron

Race of treatments of flame retardant was industry's main issue in order to produce preferable flame retardant versions since the 1950 period. After being focused on this field, many flame retardant versions were cited in the literature, as listed in Table 1.2. Properties of modacrylics showed that they formed a residual char and they may be blended with other char-forming such as the aramids.

In this period, many significant researches had been worked in order to improve phosphorus containing flame retardants for the commercial race. After 1980 till 2000, very little new research was approved and cited in the main progress.

Flame retardants might show different chemical structures. They might contain halogens (bromine and chlorine), phosphorus, nitrogen, boron, or other groups [13]. In Europe, 465,000 tonnes of flame retardants were consumed in 2006, and the total consumption of flame retardants in Asia, Europe, and the US was around 1.8 million tonnes in 2007. It is anticipated evaluation of flame retardants that consumed all over the world will reach 2.8 million tonnes in 2018 [14].

1.1.1 Studies of Flame Retardancy on Textile Application in Literature

Yuan Hu studied the flame retardancy of cotton textiles based on UV-curable flame retardant coatings that were prepared using tri(acryloyloxyethyl) phosphate (TAEP) and triglycidyl isocyanurate acrylate (TGICA) [15]. The synthetic routes of TAEP were shown in Figure 1.1 and Figure 1.2.

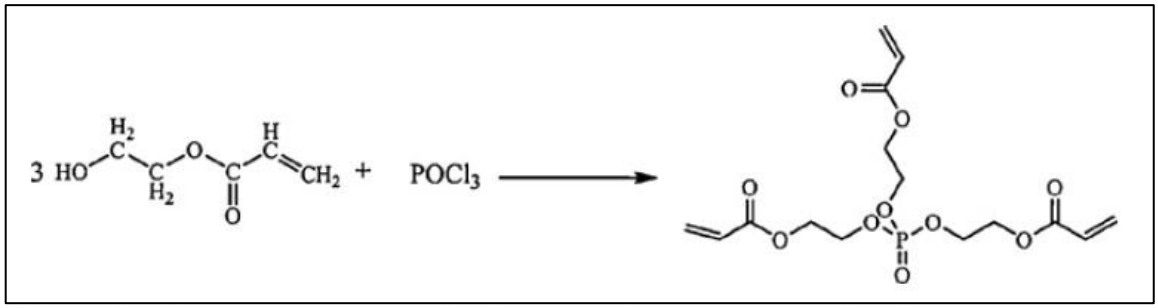


Figure 1.1 The synthetic route of TAEP

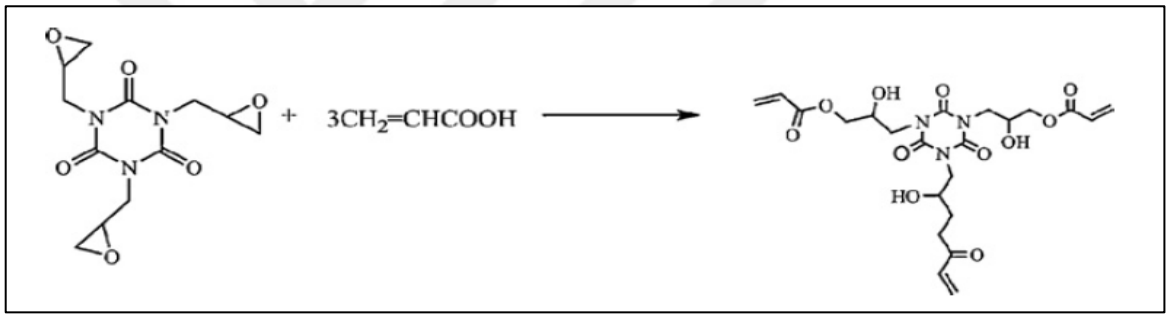


Figure 1.2 The synthetic route of TGICA

Scanning Electron Microscopy (SEM) and Micro-scale Combustion Calorimeter (MCC) results of their study showed that the flame retardant effect correlated with the concentration of the monomer. Figure 1.3 shows the SEM images of char after MCC test.

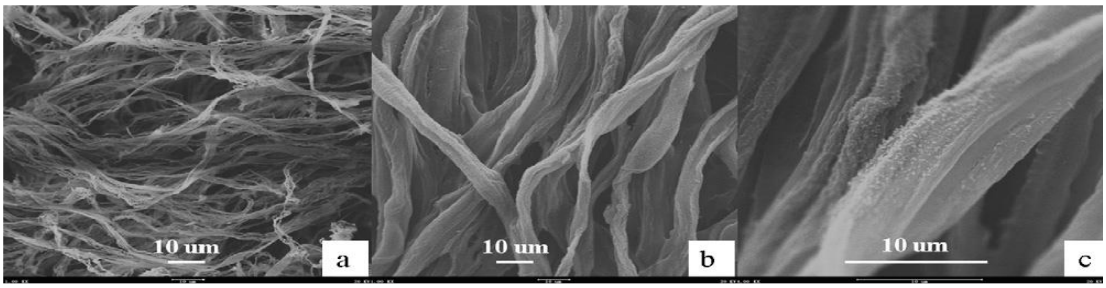


Figure 1.3 SEM images of char left after MCC test: the virgin cotton (a); treated cottons (b, c)

These results suggest that tri(acryloyloxyethyl) phosphate (TAEP) and triglycidyl isocyanurate acrylate (TGICA) monomers under UV radiation were easily polymerized and showed flame resistance on cotton textile. Cotton fabric coated with 20% (w/w) flame retardant produced the highest char yield in air (7.7%) and (31.1%) at 700 ºC under N_2.

In the research of flame retardant properties of cottons done by Yun Liu and his group, their flame retardant was prepared based on 3-aminopropyl triethoxysilane (APTES) and sodium phytate through layer-by-layer assembly as indicated in Figure 1.4 [16].

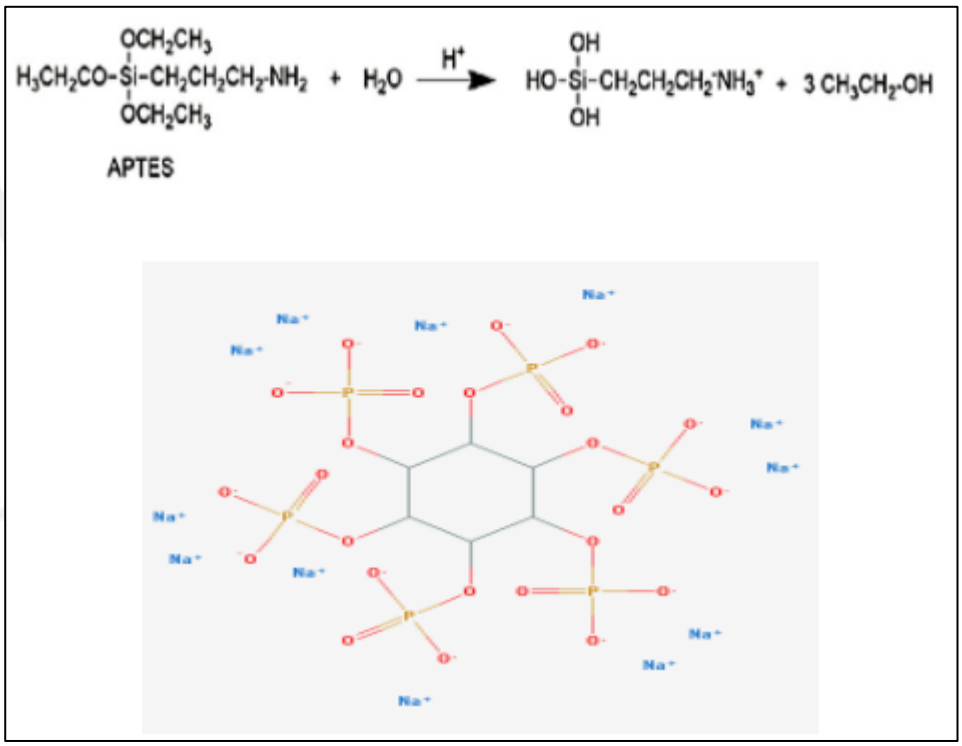


Figure 1.4 APTES hydrolysis and structure of sodium phytate

SEM and the Standard for Safety of Flammability of Plastic Materials (UL 94) results showed that the product of APTES hydrolysis and sodium phytate coated on the surface of cotton textile. According to results, the phosphorus element from sodium phytate had catalyzed the cellulose and remained char formation on the surface. Silicon dioxide formed from APTES hydrolysis during the burning process has also remained residual char and prevent the cotton textile from futher flames. Figure 1.5 shows the UL 94 test of coated fibers.

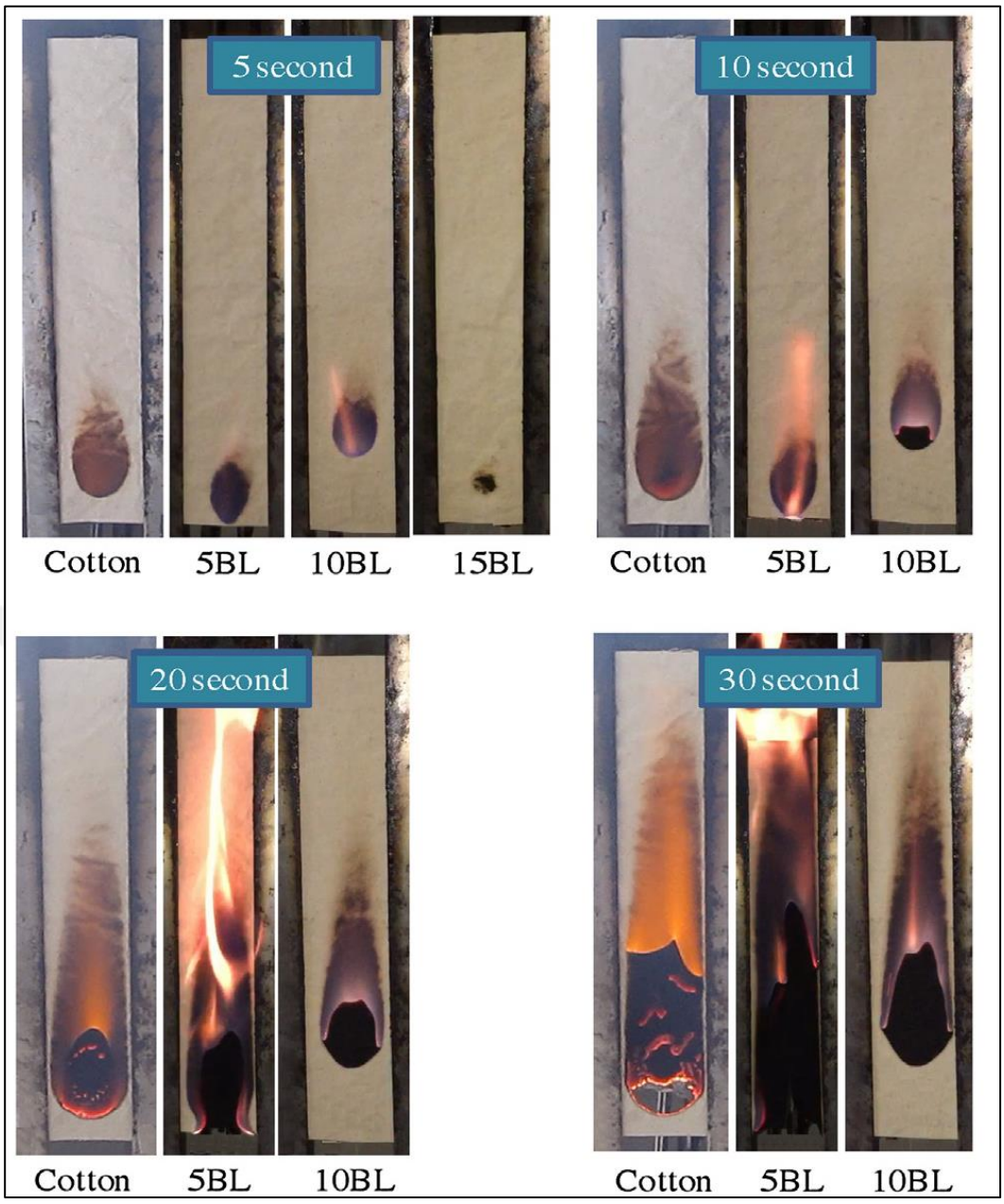


Figure 1.5 Vertical burning test of uncoated and coated cotton fabrics recorded at 5, 10, 20 and 30 s

The results mentioned above showed that the APTES and sodium phytate coating system improved the fire retardant behaviors on cotton textiles.

In the another study, De-Yi Wang and his research group demonstrated that a type of new inorganic–organic hybrid containing phosphorus, silicon and nitrogen was successfully synthesized via a sol–gel process to develop the flame resistance as shown in Figure 1.6. Flammabilities and surface morphology were investigated by SEM, UL 94, TGA and MCC analysis [17].

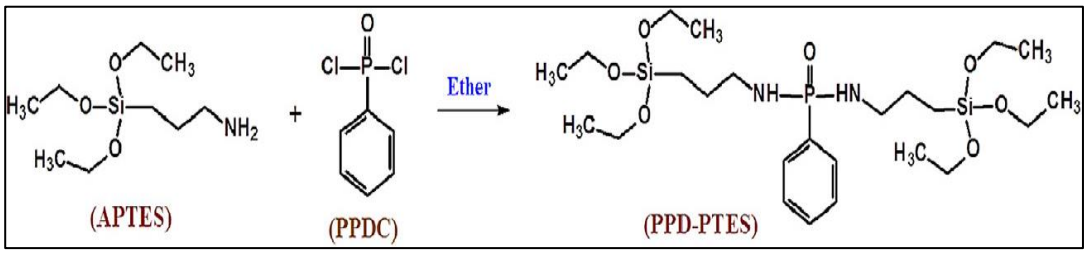


Figure 1.6 Synthetic path of the flame retardant hybrid coating

In his work, they have proven that the synergistic effect of nitrogen and silicon coating increased the flame retardant properties of the cotton fabrics. The hybrid coating provided residual chars on cotton fabrics, which prevented further ignition and release of flammable gases during the thermal degradation process. Cotton fabric coated with flame retardant for 30 minutes produced the highest char yield (38.4%) at 700 ^{o}C. Their research demonstrated that the sol–gel technique is a very effective method to embed flame retardants into cotton or to coat flame retardants on cotton. Figure 1.7 shows the UL 94 test results and SEM images of coated fabrics.

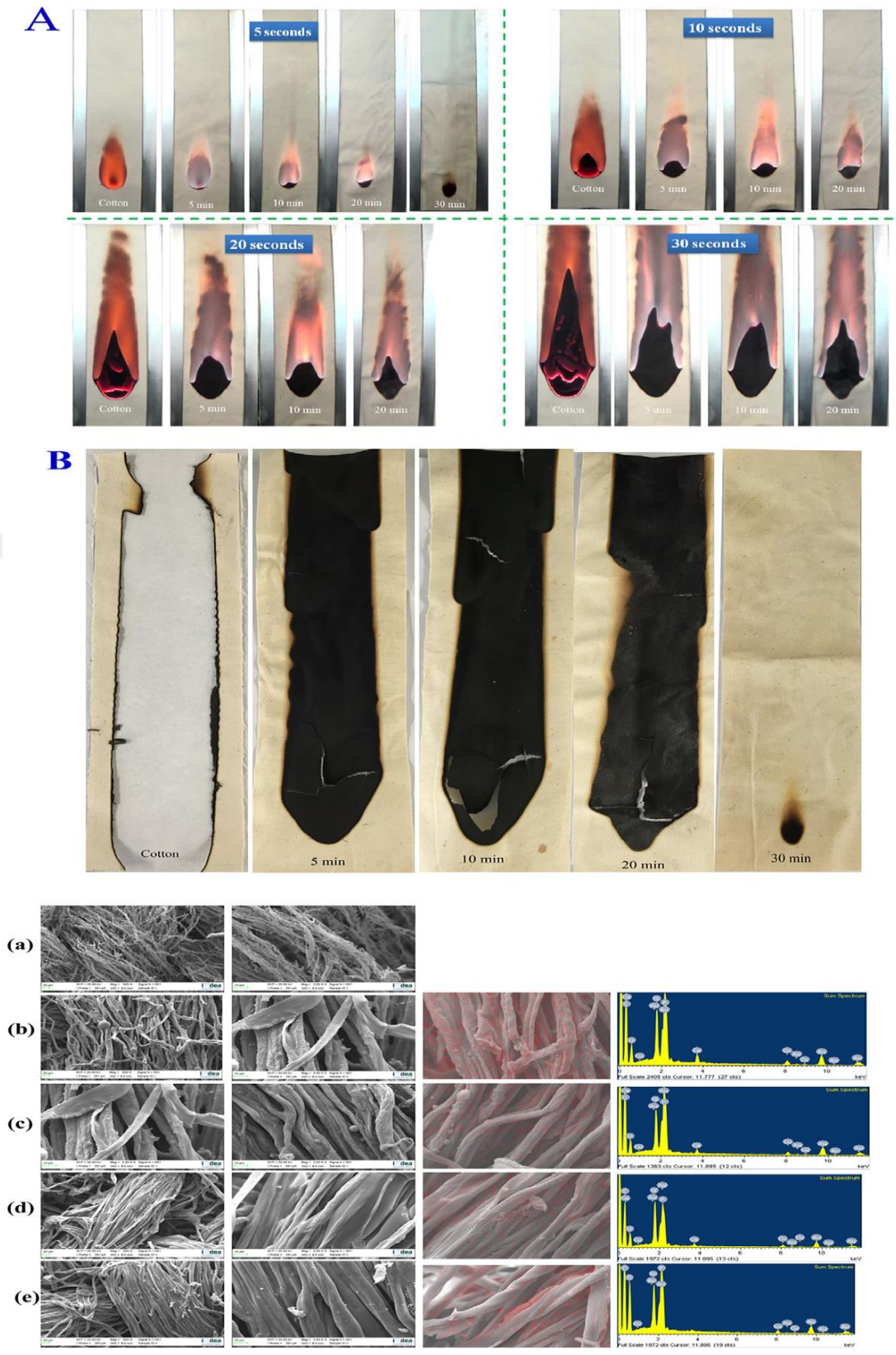


Figure 1.7 Vertical burning test of uncoated and coated cotton fabrics recorded at 5, 10, 20 and 30 s, and SEM images and EDX spectra after burning process

Gang Sun and his research group studied flame retardant behaviours of organophosphorus compounds such as phosphoric acid (PA), triallyl phosphate (TAP), diammonium phosphate (DAP), triallyl phosphoric triamide (TPT), pyrovatex CP (PCP) and tributyl phosphate (TBP) on cotton fabrics. Thermal properties of flame retardants were investigated by SEM and Limiting Oxygen Index (LOI) analysis [18]. Results are given in Figure 1.8.

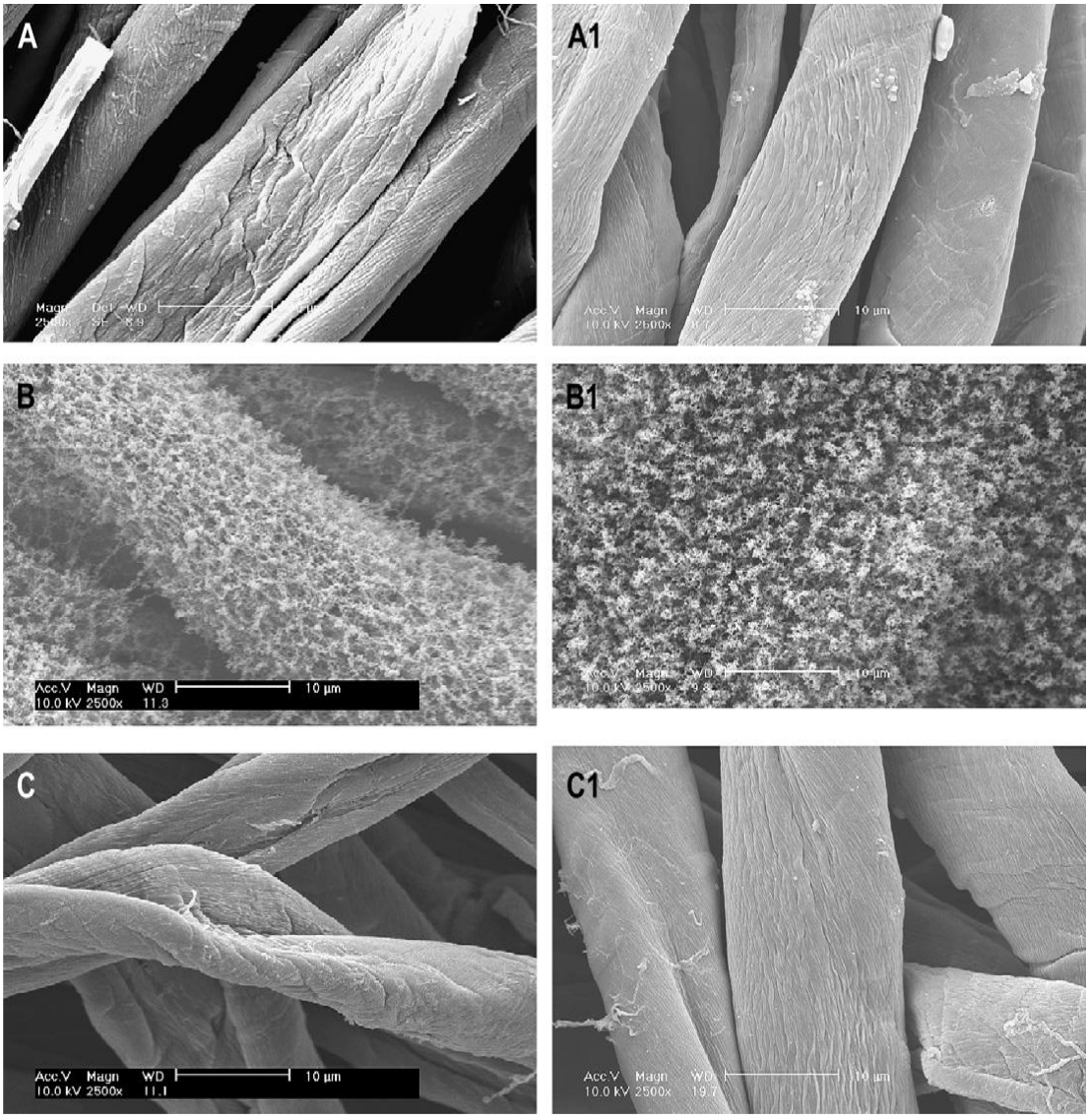


Figure 1.8 SEM images of resudial chars after LOI tests: (A) coated cotton fabric with PA (2% P), (A1) coated cotton with PA (4% P), (B) coated cotton fabric with TBP (2% P), (B1) coated cotton fabric with TBP (4% P), (C) coated cotton fabric with DAP (2% P), (C1) coated cotton fabric with DAP (4% P)

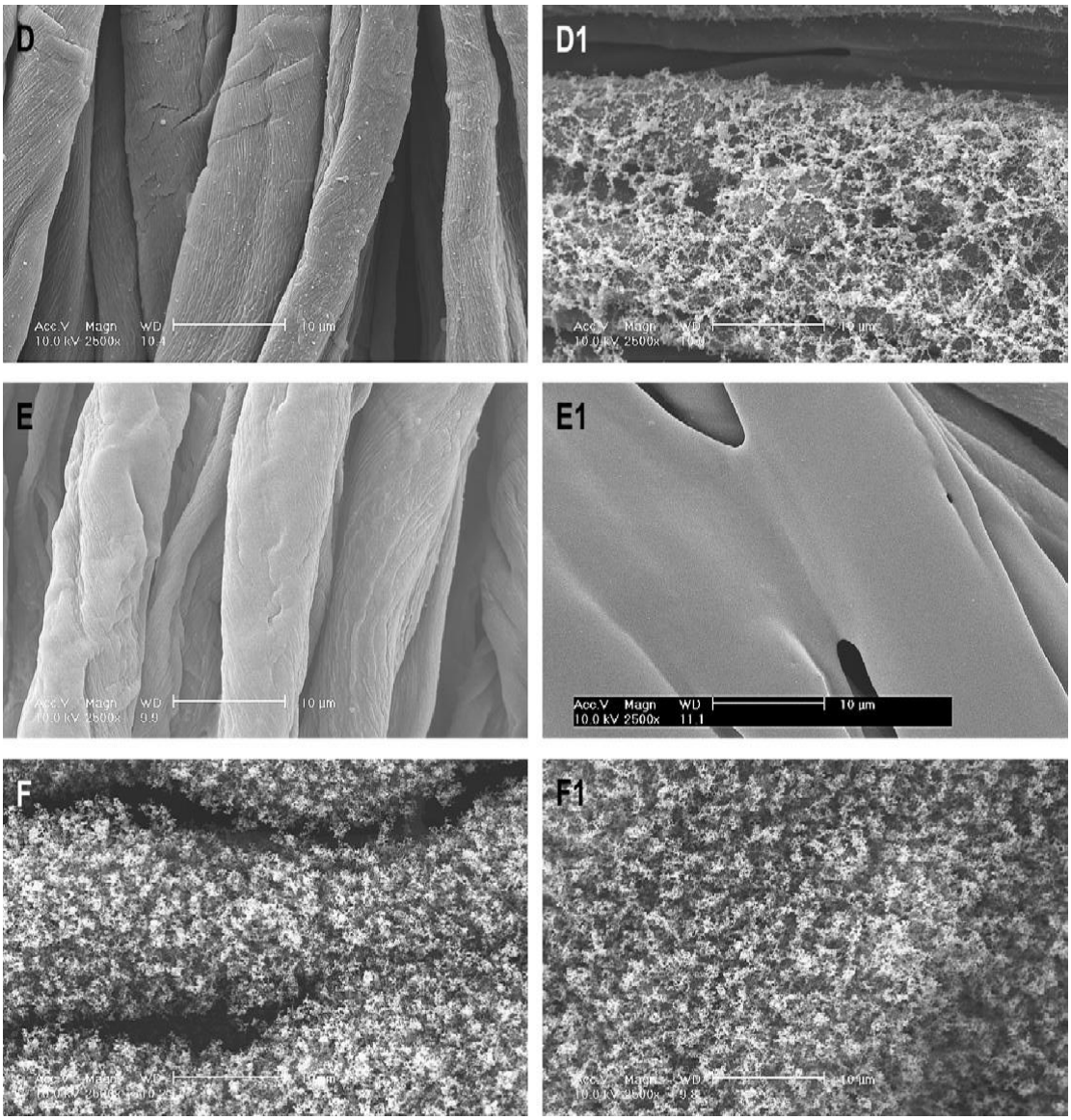


Figure 1.9 SEM images of residual chars after LOI tests: (D) coated cotton fabric with TPT (2% P), (D1) coated cotton fabric with TPT (4% P), (E) coated cotton fabric with PCP (2% P), (E1) coated cotton fabric with PCP (4% P), (F) coated cotton fabric with TAP (2% P), (F1) coated cotton fabric with TAP (4% P)

According to SEM images (Figure 1.9) of coated cotton fabrics with six organophosphorus compounds, it was investigated that flame retardants were dispersed and coated well on the surface of cotton fabrics.

LOI results of cotton fabrics coated with six different organophosphorus compounds were shown in Table 1.3. The LOI of untreated cotton fabric was 18.5. With increase of phosphorus quantity the LOI values increase for all coated cotton fabrics. LOI results showed that PA, PCP and DAP had a higher LOI (31.0, 31.0 and 35.5) compared with

TBP, TPT and TAP (25.0, 26.0 and 25.0). The DAP coated samples provided the highest LOI values (35.5) among all samples at the same phosphorus quantity.

Table 1.3 LOI results of coated fabrics

% Phosphorus (P) on fabric	Limiting oxygen index of treated cotton (LOI) %					
	PA	TBP	DAP	TPT	PCP	TAP
1	24.0	22.5	24.5	21.5	23.5	21.5
2	27.0	23.5	28.5	23.5	26.0	23.5
4	31.0	25.0	35.5	26.0	31.0	25.0

NOTE: the residual chars obtained from 2% and 4% P coated fabrics after LOI tests were done by using SEM

1.2 Aim of the Study

In this study, reactive flame retardants were synthesized based on phosphorus and 3-aminopropyl triethoxysilane (APTES) that can be covalently attached to the textile surface after the dip coating process. As it is shown in Figure 1.10, first reactive (MKT-1) can make a strong ester bonding on the textile surface via both carboxylic acid and anhydride groups. It has phosphorus groups which catalyze the cellulose and produce more residual char. On the other hand, silicon and phosphorus play a major role in MKT-2. These groups act as a good char former and show properties of char formation. It can be attached to the textile surface and made an ester bonding via hydroxyl group. Beside that ethoxysilane groups can also covalently bond to the surface of the cotton. Covalent attachment to the surface is one of the most important parameter that effect the washing cycle on cotton textiles.

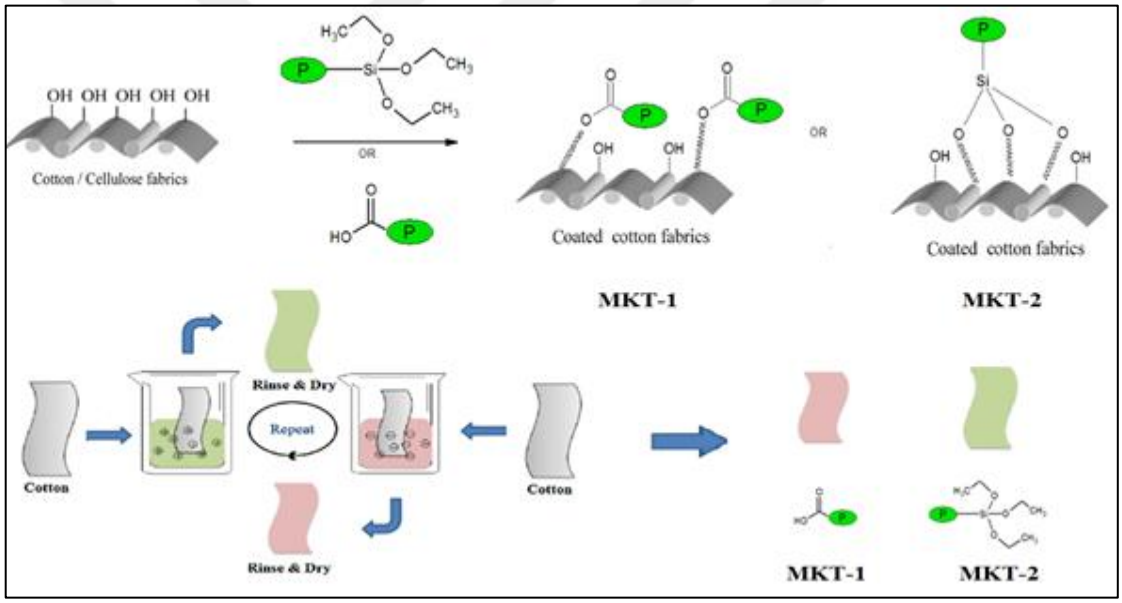


Figure 1.10 Dip coating process of the product of MKT-1 and MKT-2 on cotton fabrics

In this study, we have estimated that MKT-1 and MKT-2 can be covalently attached to textile surface and produce more residual char by catalyzing the cellulose. What is more, coated cotton with MKT-2 might form silicon dioxide, and these with synergistic effect of nitrogen and phosphorus caused more residual char on the surface. Covalent attachment of flame retardants on textile also enchance the durability and long-term flame retardancy.

1.3 Hypothesis

Most of flame retardants are made of halogens and phosphodies. Main examples of halogenated flame retardants include chlorine and bromine flame retardants. Although brominated and chlorinated flame retardants are widely used and effective, they have been banned by the European Union due to their high toxicity (the formation of carcinogenic furan and dioxin) during the fire [19].

In recent years, many scientists have focused on non-halogenated flame retardants. Flame retardants containing phosphorus are getting more important than halogenated flame retardants due to their toxic gas potential during burning.

Many of equipments such as television set, sofa, mattress and other things are generally made from plastics. It may get a fire via a short circuit or cigarette in a few minutes. For example, a TV set contains its flammable materials. It means that the TV set may get burned easily when any small combustion appears on the surface. Flame retardants can be applied on most of the combustible material surfaces in order to prevent its flames or to delay spread of flames on surfaces. Flame retardants are needed for the fire safety on flammable materials. On the other hand, using non-combustible materials may provide fire safety but these materials have many disadvantages which are given below;

- Although using metals for electrical equipment provide fire safety, may cause electrical risks, they are more expensive and less flexible than plastics.
- Using plastic in planes, train or cars provides lower weight but flame retardants are needed for fire safety.
- Mineral fibers are used for insulation of buldings and they are not combustible, but using mineral fibers may not provide a good energy performance, organic properties or mechanic properties.

The main anxieties against flame retardants are that they may be persistance in the environment. In addition, there are worries about harmful decomposition products in case of any fire.

In scientific risk assessment, it is estimated that toxicological properties are individually evaluated. European Flame Retardants Association (EFRA) significantly cares of these risk assessments and also supports studies relating with this issue. Table 1.4 shows the possible risk assessments used common flame retardant in industry.

Table 1.4 An Overview of the Flame Retardants Covered in Risk Assessments

Flame Retardant	Status	Next Steps	Risks Identified	Conclusions	Classification
Penta-BDE	Concluded	---	Risk Assessment Unfavorable	Banned in EU as of Aug 2004	---
Octa-BDE	Concluded	---	Some risks identified	Banned in EU as of Aug 2004	---
Deca-BDE	Concluded	Additional tests, monitoring, and emissions control in progress	None	- Safe for continued use - Emissions control program active	None
TBBPA	ENV: Finalized HH: Finalized	None	ENV: risk identified at one additive user plant only HH: None	- Not restricted for any applications - Authorities have emission requirements - Emissions control program active	R50/53
HBCD	ENV: Finalized HH: Finalized	On the SVHC Candidate List	Classified a PBT Risks identified, PBT status debate – new science	Transferred to REACH - on the SVHC Candidate List	R50/53
TCEP	ENV: finalized HH: finalized	On the SVHC Candidate List	Reprotox + chronic tox + Carc, several exposure scenarios	Transferred to REACH - on the SVHC Candidate List	T, N, R51/53, R22, R60, R40
TCPP	ENV: finalized HH: finalized	REACH registration, C& L decision	Reprotox, dermal, production	TCPP will be sold with the same existing labels	Xn, R22
TDCP	ENV: Finalized HH: Finalized	REACH registration, C& L decision	Chronic tox + Carc, dermal, production & flexible PU foam manufacturing	TDCP will be sold with the same existing labels	N, R51/53, R40
V-6	ENV: Finalized HH: Finalized	Antiblaze® TL-10 successfully completed REACH registration	None	Antiblaze® TL-10 successfully completed registration (REACH Registration # 01-2119419991-33-0000	None
(Sb_2O_3)	ENV: finalized HH: finalized	Risk Assessment transferred to REACH	ENV: risks identified for sediments at a few plants HH: no risks identified at current stage –discussions in progress	Transferred to the REACH	R38, R40

Here, we aim to produce non-halogenated flame retardants, phosphorus based, that can covalently be attached to the surface of textile. These will increase the durability and so long lasting flame retardancy and non-leaching properties from the surface.

CHAPTER 2

FLAME RETARDANTS

Flame retardants are used for flammable materials to provide more resistance against fire during burning. Using flame retardants reduce the fire risks when the materials get burned by a short circuit, cigarette or other flammable reasons in time. The flame retardants provide a residual char on the surface and prevent materials' surface by delaying the spread of flames. Flame retardants may be used in different combinations due to materials' nature and structural properties. Giving an example, mechanical or thermal properties of plastics refer a different flammable behaviour.

Flame retardants are needed to ensure the fire safety on the surface of materials such as plastics, furniture, sofa, natural and man-made products as shown in Figure 2.1. These materials are commonly used in construction, electrical equipments, trains, cars, and airplanes.

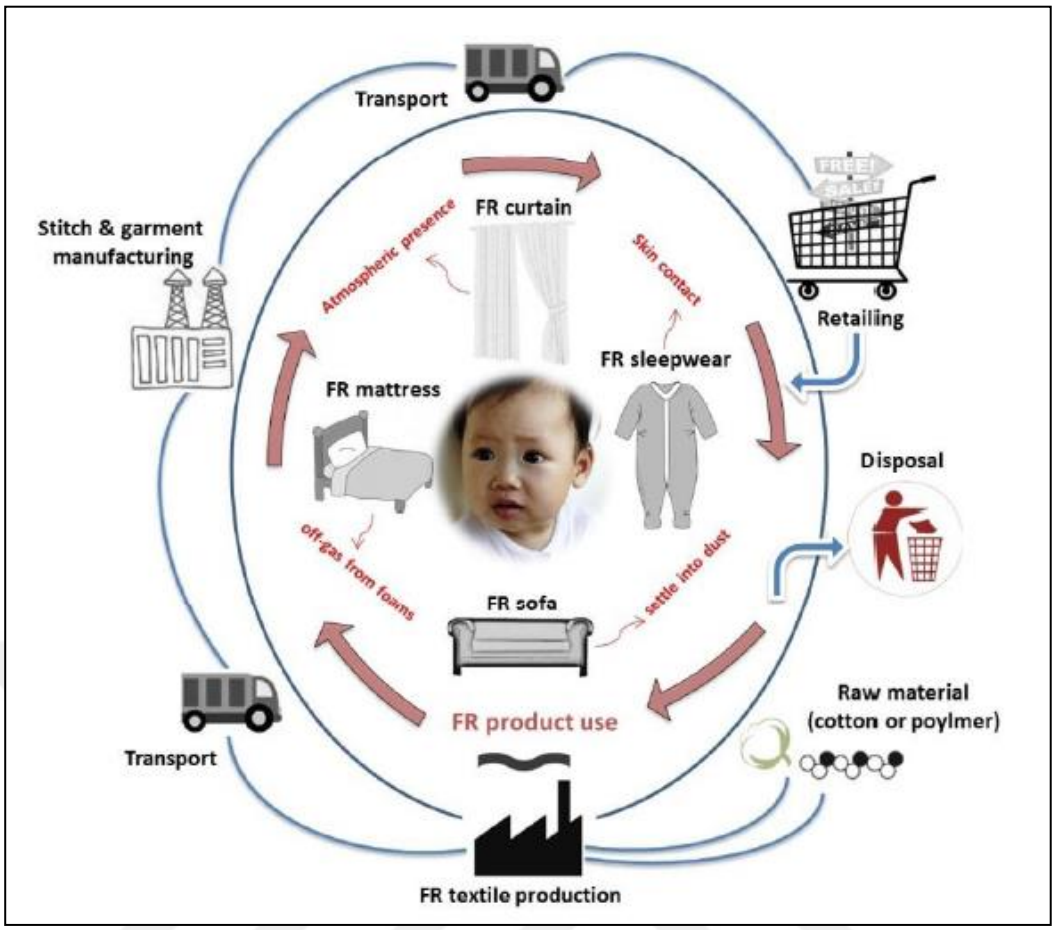


Figure 2.1 Life cycles of flame retardant (FR) on textile products

2.1 Mechanism of Fire

Flame retardants form a char formation on the material's surface and make a layer which lowers thermal conductivity properties. When the coated materials with flame retardants get burned, a residual char is occurred on the surface of the material and prevent the fire from further risks. By this way, thermal resistance of the surface is increased by the char formation. In addition, when the materials are burned, flammable gases are appeared and flame retardants reduce the gas formation on the surface. As a result, materials behave as self-extinguishing. In order to understand how flame retardants behave as a retardant, understanding the mechanism of the fire plays a major role. Fire is such as a gas-phase reaction as shown in Figure 2.2.

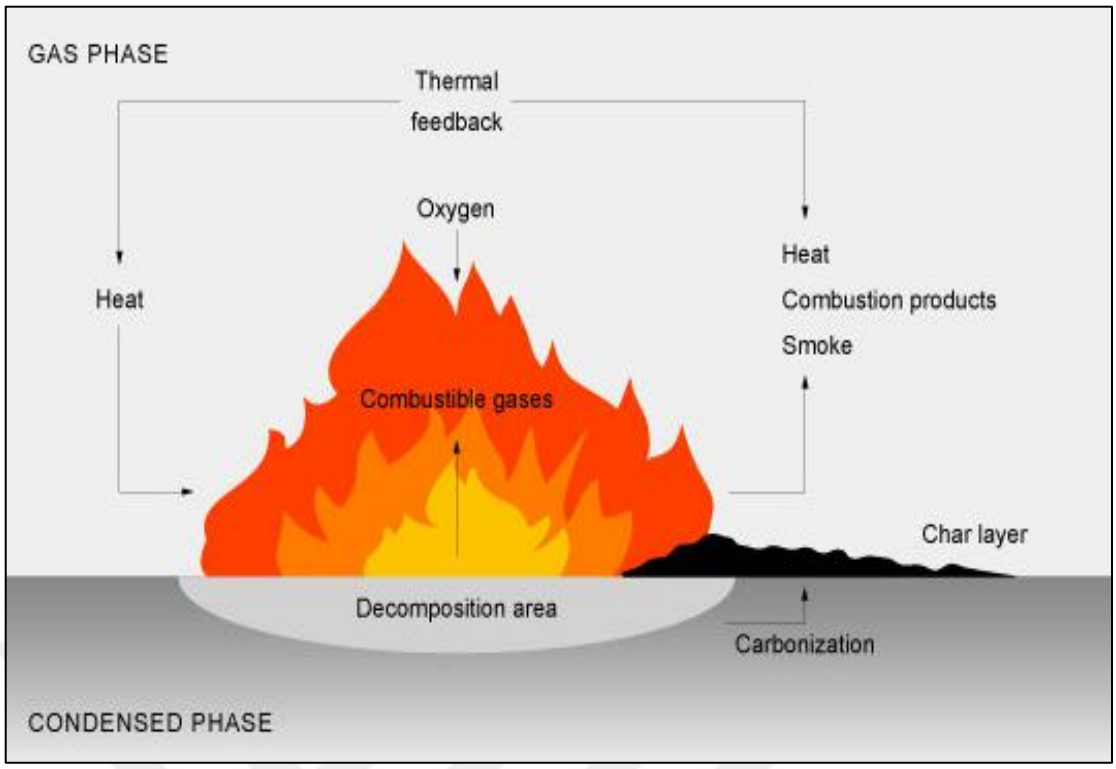


Figure 2.2 The combustion process

Therefore, a gas is needed for the materials to get burned. Flame does not have an oxygen in itself. When materials are burned, some gaps are occurred on the surface. The flame meets with oxygen inside of these gaps. After that the flame reacts with water and carbon dioxide in order to produce carbon monoxide.

Natural and synthetic polymers can get burned when there is a heat in environment. Fire occurs either itself or results from any spark appeared on surface of materials.

2.2 Toxic Gases in Fire

Most of gases in fire are toxic and risky. Because these toxic gasses are formed when the incomplete organic materials like plastics, rubber, textiles, wood, and paper get burned. Carbon monoxide (CO) plays a major role among these toxic gases, and more than 80 % of people die by fire gases. 17 fire deaths due to CO poisoning in the Düsseldorf Airport fire in 1996 is one of the stunning examples. By forming a char formation on the surface, flame retardants cause of delaying the flammable gases and lower the propagation of toxic gases.

Although carbon monoxide (CO) plays a major role, other toxic gases such as hydrogen chloride (HCl) or hydrogen cyanide (HCN) from plastics or natural products may be

formed in a fire. As a result, the other toxic gases except carbon monoxide (CO) play a minor role. Examples of toxic gases in fire are shown in Figure 2.3.



Figure 2.3 Toxic gases in fire

Besides these volatile gases, different complex products like polycyclic aromatic hydrocarbons (PAHs) or halogenated dioxins and furans (PXDD/F) may be formed. However long term health effects may be caused by these products although these products are formed in much lower quantities due to their higher molecular weight. As a results, many scientists focused on this issue although the toxic effects of these products are much risky compared with other gases [20].

2.3 Main Families of Flame Retardants

Flame retardants for textile products such as in blankets, baby clothing, car seats, pushchairs, are used for reducing their flammability. All these textile products are coated by flame retardants-containing chemicals. These materials are coated with chemicals which delay the flames and prevent the spread of fire. These flame retardants may be shown in 5 major categories as it's given below,

- Halogenated (Bromine and Chlorine) Flame Retardants
- Minerals (based on aluminium and magnesium)

- Nitrogen
- Phosphorus
- Others (like Borax, Sb_2O_3, nanocomposites)

2.3.1 Halogenated (Bromine and Chlorine) Flame Retardants

Some examples of brominated and chlorinated flame retardants are shown in Figure 2.4 are very commonly used in industry due to their effective properties. Among these flame retardants, brominated flame retardants (BRFs) are well-known ones. They are generally used in electrical equipment. Fire can be occurred in short circuits and electrical malfunctions. Also, BFRs are used in insulation of wires and cables. What is more, they're also applied in fabrics such as curtains, seating and furniture in transportation and public buildings. Halogen-containing flame retardants may work in the vapor phase or in the condensed phase [21].

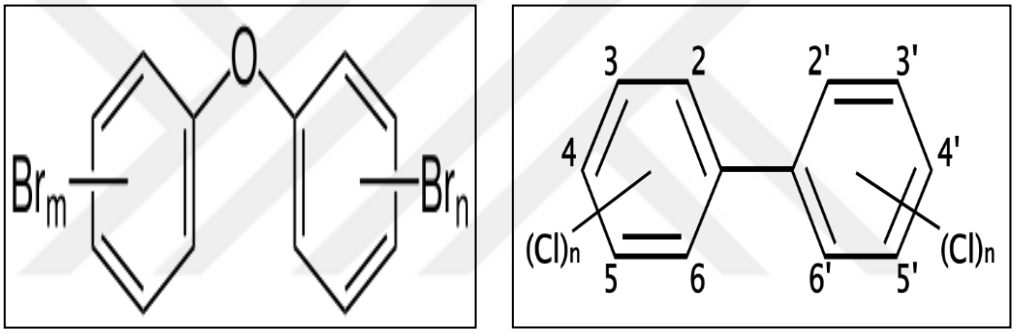


Figure 2.4 Examples of Halogenated Flame Retardants

75 different commercial BFRs are used and separated from each other by their thermal properties and toxicological behaviour. However, these materials which contain bromine and chlorine have been banned periodically due to their carcinogenic effects and contribution to the formation of toxic gas [22]. The most important BFRs are given in Table 2.1.

Table 2.1 Examples of major BFR products

Chemical Name	Typical Products
Pentabromodiphenyl ether (Penta-BDE, PBDE, or Penta)	Polyurethane foams: mattresses, seat cushions, other upholstered furniture and foam packaging. Also: carpet padding, imitation wood, paints, sound insulation panels, small electronic parts, fabric coatings, epoxy resins, conveyor belts
Octabromodiphenyl ether (Octa-BDE, OBDE, or Octa)	Acrylonitrile -butadiene - styrene (ABS) plastic: housings for fax machines, computers and other electronics. Also: automobile trim, telephone handsets, kitchen appliance casings, small electronics parts, audio/video equipment, remote control products
Decabromodiphenyl ether (Deca-BDE, DBDE or Deca)	High-impact polystyrene (HIPS) plastic: housings for televisions, computers, stereos and other small electronics. Also: mobile phones
	Various plastics: polycarbonates, polyester resins, polyamides, polyvinyl chloride, polypropylenes, terephthalates (PBT and PET), and rubber. Also: upholstery textiles (sofas, office chairs, backcoating), paints, rubber cables, lighting (panels, lamp sockets), smoke detectors, electrical equipment (connectors, wires, cables, fuses, housings, boxes, switches), stadium seats
Tetrabromobisphenol A (TBBPA)	Reactive flame retardant: epoxy and polycarbonate resins. Also: printed circuit boards in electronics (96%), office equipment housings
	Additive flame retardant: various plastics, paper and textiles. Also: housings of computers, monitors, TV, office equipment, adhesive coatings in paper and textiles
Hexabromocyclododecane (HBCD)	Various plastics: Polystyrene (EPS, XPS), HIPS, polypropylene. Also: textiles and carpet backing, television and computer housings, textiles in automobiles, building materials (insulation panels, construction blocks, thermal insulation, roofs), upholstered foam, latex binders

2.3.2 Mineral Containing Flame Retardants

Aluminium trihydroxide (ATH) is mostly one of used flame retardant in this group. It is cheap but the quantity of ATH must be more than 60% in polymer. Because its mechanism is based on the release of water by cooling and diluting the flame. Magnesium hydroxide (MDH) is applied in polymers. ATH and MDH (<2 μm) are used in thermoplastics like cable PVC or polyolefins.

Using in cable, ATH and MDH are applied with natural products to develop their relevancy with the polymer.

When the aluminum hydroxide is heated as shown in Figure 2.5, an endothermic reaction is occurred and it separates to form water and alumina. When the water is formed, it transfers to the vapor phase and causes the reduction of heat transfer during combustion. Mineral containing flame retardants are generally applied in thermosets for electrical equipments, seats, vehicles, and panels.

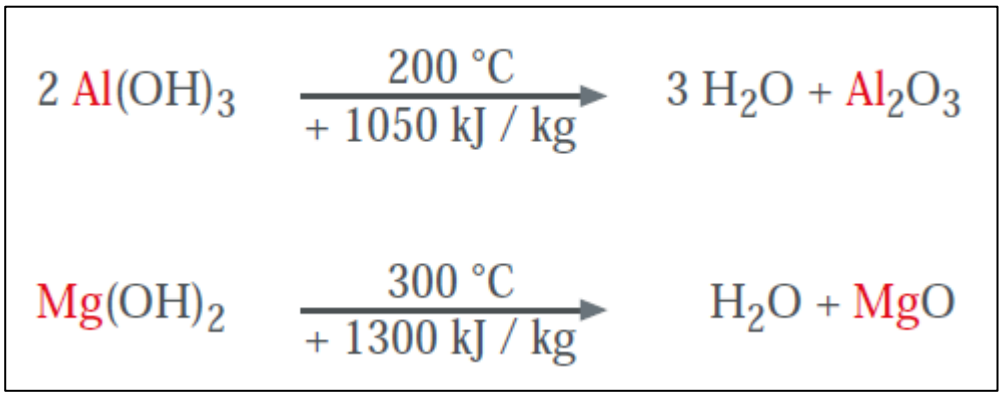


Figure 2.5 Chemical reactions of ATH and MDH

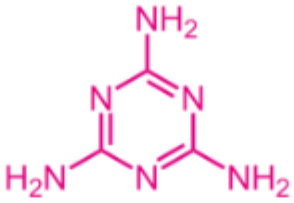
2.3.3 Nitrogen-Containing Flame Retardants

Nitrogen-containing flame retardants essentially provide inert gas release to the environment during combustion by reducing the oxygen concentration in the gas phase and slowing down the combustion process. Nitrogen containing natural polymers such as wool, silk, leather, etc. provide a fire resistance. Thus, some nitrogen-containing organic compounds are used in polymers as additives to show fire resistance properties [23].

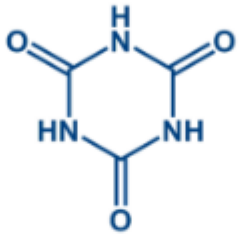
Melamine is commonly used for flexible polyurethane foams in furnitures and upholstery in transport vehicles. In addition, melamine cyanurate (MC) is used in Polyamide 6 and Polyamide 6,6. Morever, zinc or aluminum containing melamine polyphosphates are used in cables. Common nitrogen-containing flame retardants used in industry are shown in Table 2.2.

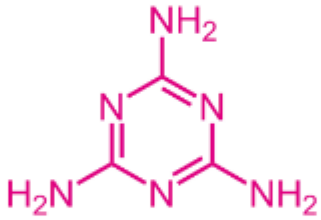
Table 2.2 Examples of nitrogen-containing flame retardants

Melamine

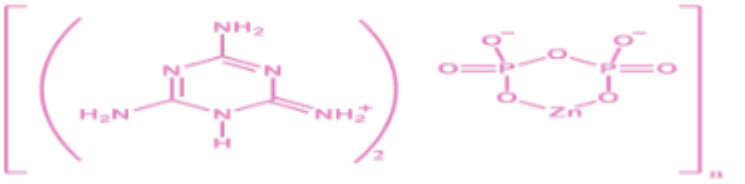


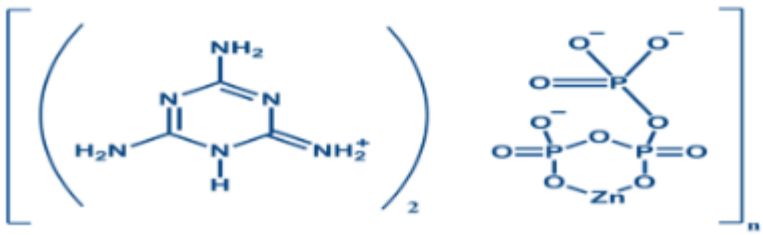
Melamine cyanurate (MC)





Zinc or aluminum containing melamine polyphosphates





2.3.4 Other Flame Retardants, Antimony, Silicon or Boron Containing

Antimony oxide may not act as a flame retardant by itself. It may act as a flame retardant by the reaction with halogen acids emitted from other flame retardant materials during combustion. They can be applied in plastic, textiles, paper and dye by 2-10% (w/w).

Antimony oxide and antimony shown in Figure 2.6 must be converted to volatile species in order to exhibit flame retardant properties. This can usually be achieved by halogen acids released at high temperatures. Halogen acids react with antimony containing materials to form antimony halide or antimony trihalide.

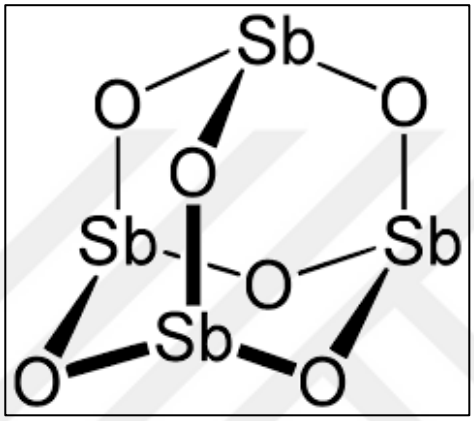


Figure 2.6 Antimony Trioxide

The resulting antimony halide and the antimony trihalide cover both the flammable material and the fire to form a layer and prevent flame splashing. We can also say that since it reduces the toxic gases emitted by the atmosphere, it also reduces the toxic effect released in burning process [24]. Antimony trioxide is used together with bromine or chlorine flame retardants in PVC [25].

Silicon-containing flame retardants may be considered environmentally friendly compared to other flame retardant materials [26]. Although it slows the increase of temperature, its use is not as common as it has no specific effect on the combustion.

The most commonly used as a silicon-containing flame retardant is polydimethylsiloxane (PDMS) as shown in Figure 2.7. Studies have shown that the addition of small amounts of silicone components to polymer materials significantly improves the incombustibility of materials [27].

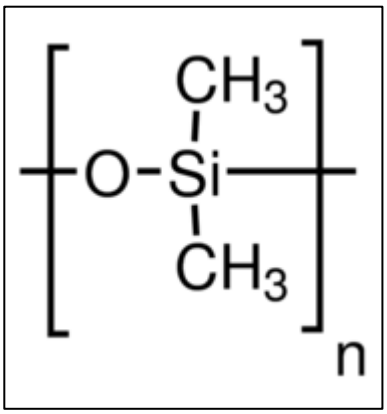


Figure 2.7 Polydimethylsiloxane (PDMS)

Boron-containing flame retardants which contain borate and boric acid are used as additives in polymers with combination of halogen-based flame retardant materials. The boron compounds only produce a carbon formation and prevent carbon dioxide and carbon monoxide during decomposition process. At the same time, they form a resudial char on the surface to prevent the oxidation of oxygen.

Borate based flame retardants are mostly used in wool and cotton products. Borax and boric acid are commonly used together [28]. One of the reasons why boron-containing additives are used as flame retardants is that they undergo endothermic dehydration and water is released after this action. Among the boron-containing compounds, zinc borates are the most commonly used as shown in Figure 2.8.

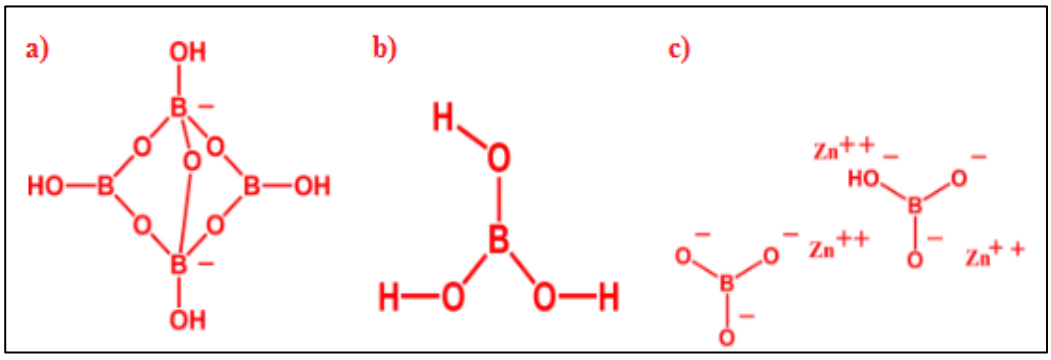


Figure 2.8 Structure of borax (a), boric acid (b) and zinc borate (c)

2.3.5 Phosphorus Containing Flame Retardants (PFRs)

Both organic and inorganic phosphorus compounds provide flame retardant properties for many polymers. These compounds are actively used in the industry as a reactant and additive. Flame retardant mechanisms of phosphorus containing compounds [29] are shown in Figure 2.9.

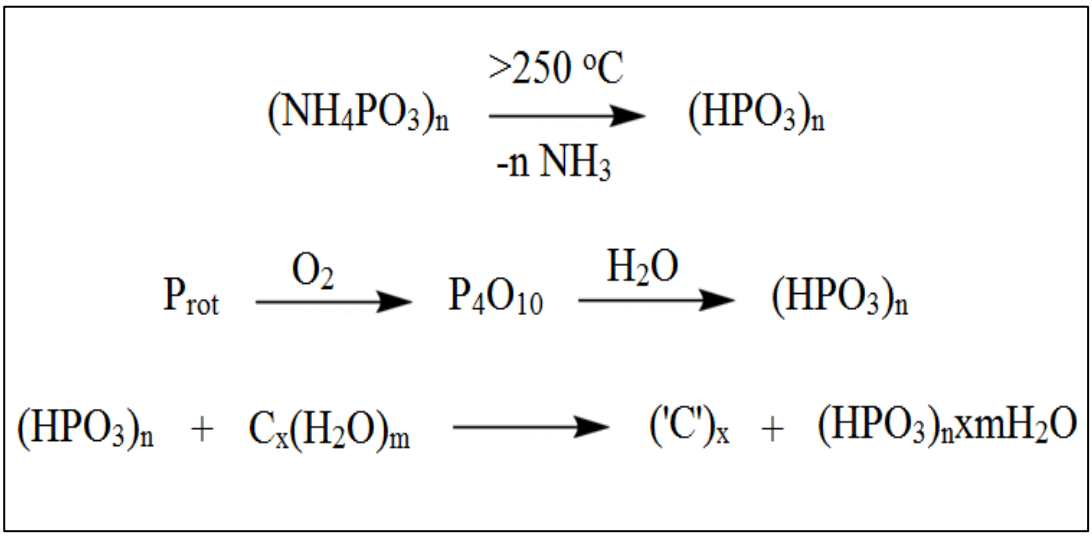


Figure 2.9 Flame retardant mechanisms of phosphorus containing compounds (ammonium phosphates)

In addition, certain flame retardants based on specific phosphorus, such as metal phosphinates, may have negative effects on burning, forming phosphorus and phosphate radicals in the gas layer. Phosphorus containing flame retardants are mostly used in plastics, textiles, thermosets, coatings and other applications. They have a wide application field, and a good fire safety performance. Mode of action of phosphorus containing flame retardants is shown in Figure 2.10.

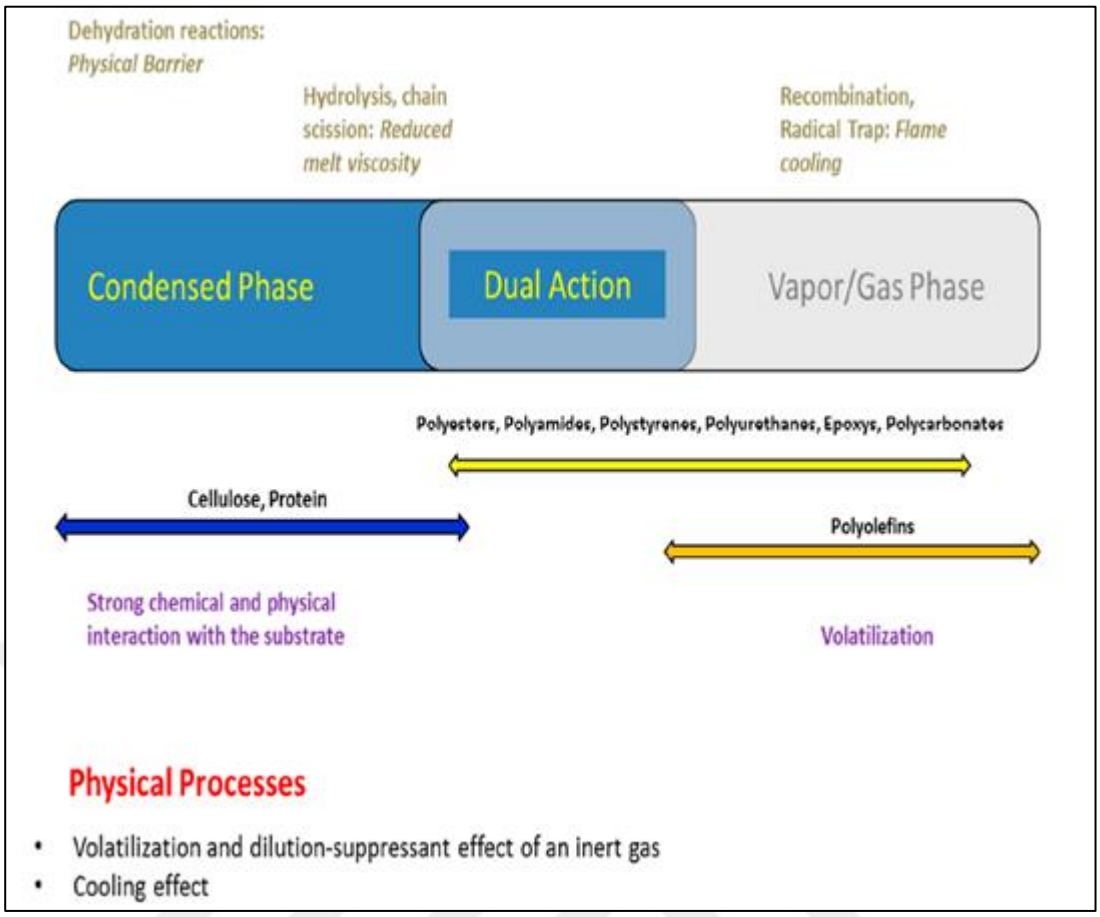


Figure 2.10 Mode of action of phosphorus containing flame retardants

As shown in Figure 2.10, dual action is observed in polyesters, polyamides and polystyrenes. Furthermore, vapor/gas phase is seen in polycarbonates. Chemical and physical interactions with the substrate or volatilization show an alteration relating with condensed phase and vapor/gas phase. Condensation of phosphoric acid also produce pyrophosphate (a char residue) and water to cool the environment as shown in Figure 2.11.

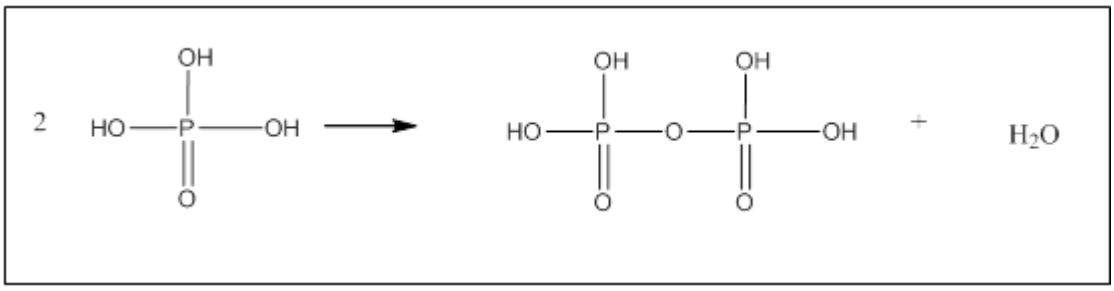
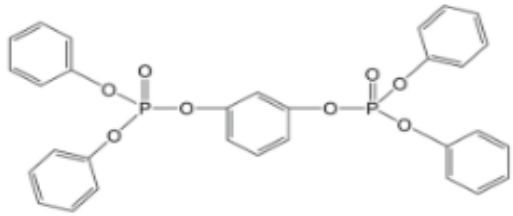


Figure 2.11 The pyrophosphate structure resulting from the condensation of phosphoric acid

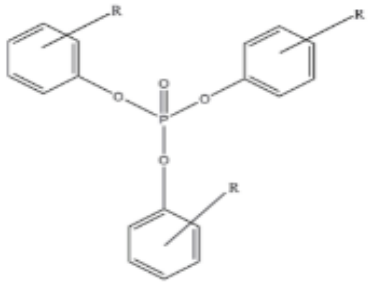
Phosphorus containing flame retardants are widely used in the industry. Therefore, non-halogenated phosphorus containing flame retardants are mostly focused due to their less toxic properties on the materials. For example; TRPs in PC / ABS parts, triaryl phosphate in the applications of thermoplastics, metal phosphinates in glass fiber reinforced polyamides and polybutylene terephthalate, 9,10-dihydro-9-oxa-10-phosphahenanthrene-10-oxide (DOPO) on printed circuit boards and polyester fibers, trichloropropyl phosphate (TCCP) mostly in flexible polyurethane foams, ammonium polyphosphate (APP) and red phosphorus in polyamide are especially applied as shown in Table 2.3.

Table 2.3 Phosphorus containing flame retardants

TRP



Triaryl phosphate



Metal phosphinates

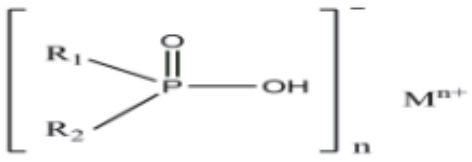
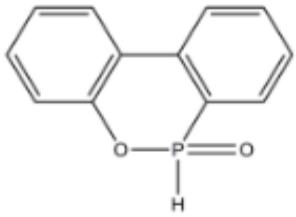
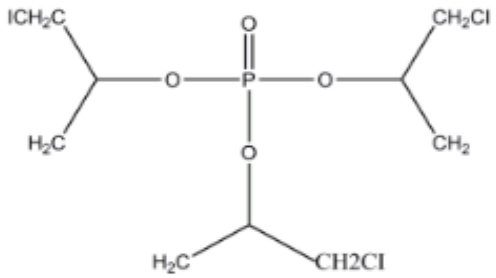


Table 2.3 (cont'd)

9,10-dihydro-9-oxa-10-phosphahenanthrene-10-oxide (DOPO)



Trichloropropyl phosphate (TCCP)



Ammonium polyphosphate (APP)

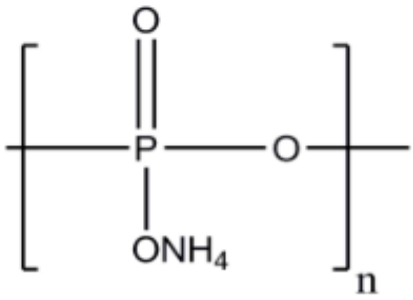
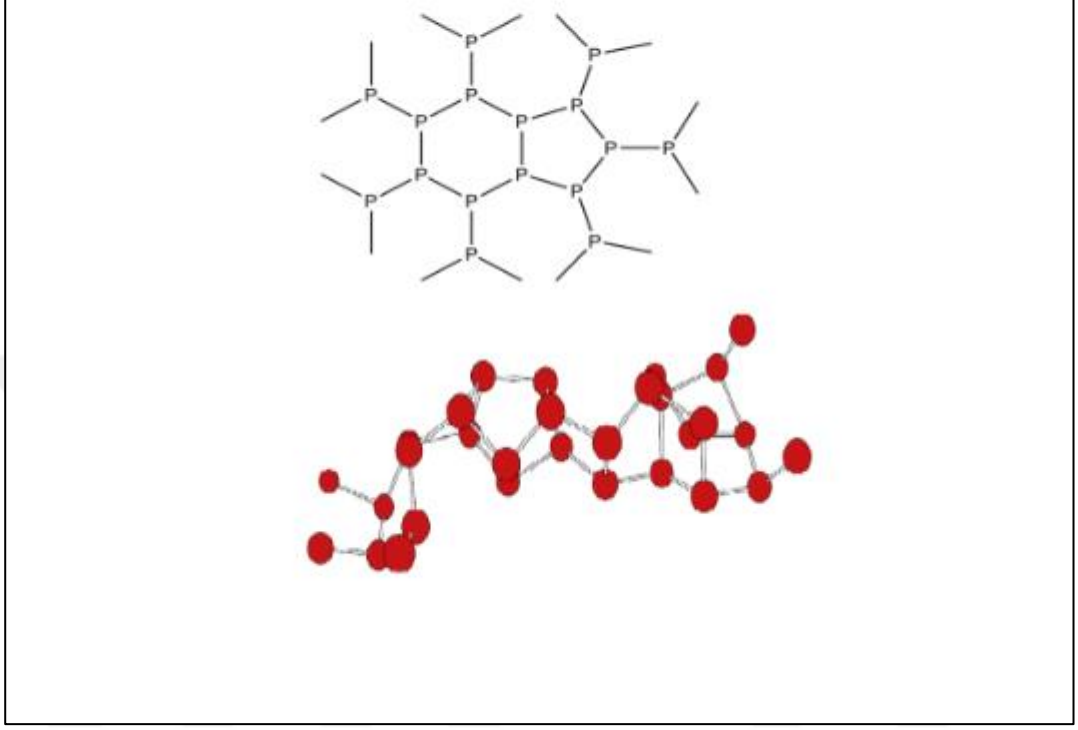


Table 2.3 (cont'd)

Red phosphorus



CHAPTER 3

FLAME TEST FOR TEXTILE APPLICATIONS

Flame tests on textile products are one of the most important parameters in industry. Because it provides important safety performances against a fire. Textile products are classified relating with their test results according to European Fire Standards such as British Standards (BS) [30]. There are some of main BS standards relating with textile applications such as BS 5852, BS 7177, ASTM D-4151 and others. ASTM D-4151 standard test is mainly used in the USA.

3.1 BS 5852 Fire Test Standards (Test Methods for Assessment of the Ignitability of Upholstered Seating by Smouldering and Flaming Ignition Sources)

BS 5852 Standard Test is applied for many fields in the textile industry. This standard has a wide application field comparing with other standard tests. Main areas that BS 5852 are applied are shown below;

- Furnishings
- Beds, bolsters, mattress material
- Upholstery fabrics
- Sofa and seats
- Sheets
- Curtains
- Carpets

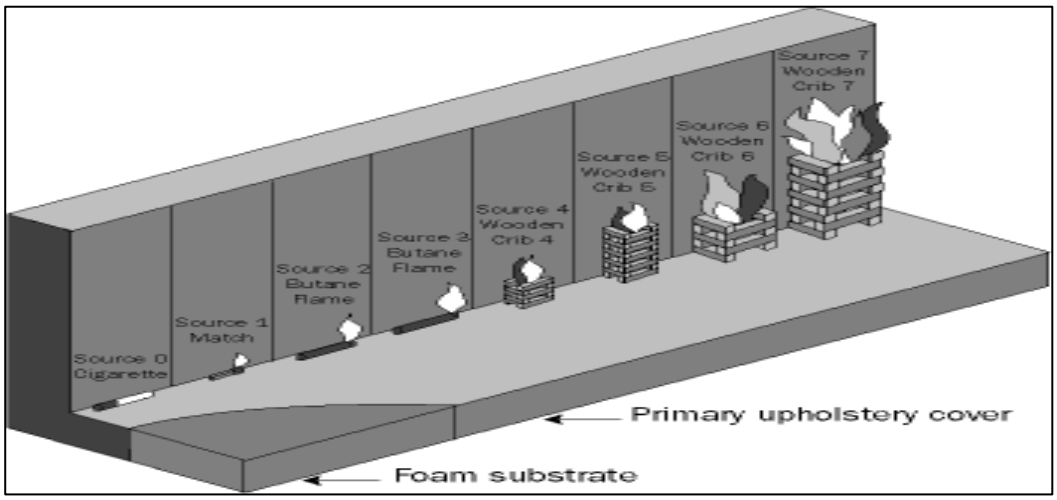


Figure 3.1 BS 5852 Standard Test with different flaming ignition sources

This test determines the effects of a smouldering cigarette, or other flaming ignition sources as shown in Figure 3.1. This standard can be used to define the potential flammability rate of materials. In this test, a propane burner is used to perpendicularly ignite the cotton fabric for 20 s from the profile at room temperature. The method of BS 5852 test in 1979 and 1982 is shown in Table 3.1.

Table 3.1 Method of BS 5852 test

	Definition of the ignition source	Ignition time	Flame	weight
BS 5852 part 1; 1979				
smouldering cigarette	0	12 +/- 3 min / 50 mm	-	-
gas flame	1	20sec	35 mm	
BS 5852 part 2; 1982				
gas flame	2	40 sec	145 mm	
gas flame	3	70 sec	240 mm	
wooden crib	4			8,5 g
wooden crib	5			17 g
wooden crib	6			60 g
wooden crib	7			126 g

After removing the burner (the gas flame) at 20 s, the cotton fabric is observed if the ignition is disappeared till 2 min. If the cotton fabric is self-extinguishing at that time, the material passes the test according to standards as shown in Table 3.1 [31].

3.2 BS 7177 Fire Test Standards (Test Methods for Assessment of the Ignitability of Mattresses, Divans and Beds)

This fire test is applied in mattresses, divans and bed to determine the resistance against ignition on surfaces [31]. According to BS 7177 standards, the test may not define categorically the ignition resistance necessity in different materials as shown in Table 3.2.

Table 3.2 BS 7177 Hazard categories, ignition needs and tests [32]

Hazard category	Ignition resistance requirements	Test method
Low Hazard	Resistant to ignition source: smouldering cigarette – IS0 flame source 1 (match equivalent) – IS1	BS EN 597-1 BS EN 597-2
Medium Hazard	Resistant to ignition source: smouldering cigarette – IS0 flame source 1 (match equivalent) – IS1 flame source 5 – IS5	BS EN 597-1 BS EN 597-2 BS 6807 Clause 9
High Hazard	Resistant to ignition source: smouldering cigarette – IS0 flame source 1 (match equivalent) – IS1 flame source 7 – IS7	BS EN 597-1 BS EN 597-2 BS 6807 Clause 9
Very High Hazard	Resistant to ignition source: smouldering cigarette – IS0 flame source 1 (match equivalent) – IS1 flame source 7 – IS7 additional requirements at the discretion of the specifier with High Hazard requirements as a minimum	BS EN 597-1 BS EN 597-2 BS 6807 Clause 9

Note: IS = Ignition Source

The ignition resistance needs in Table 3.2 must be satisfied by each products. Tests on materials must regularly be repeated in time. This repeating cycle is shown in Table 3.3.

Table 3.3 BS 7177 Frequency of test [33]

No of units produced per month	No of units tested
More than 2400	1 per month
Between 400 and 2,400	1 per 2,400
Less than 400	1 every 6 months

Hazard levels are differently labelled according to BS 7177 Standards. Some examples of BS 7177 labels for low and medium hazard are shown in Figure 3.2 [33].



Figure 3.2 BS 7177 labels for low and medium hazard

3.3 ASTM D-4151 Fire Test Standards (Test Methods for Assessment for Flammability of Blankets)

This test method benefits to identify blanket fabrics which get burned easily and propagate the surface. It specifies the procedures described in the "Voluntary Blanket Flammability Standard" which has been used by the blanket industry in the United States since 1972. Figure 3.3 shows the used equipment for this test.



Figure 3.3 ASTM D-4151 Standard Test Method for Flammability of Blankets

This method should be used to measure and describe the flammability properties of the materials relating with the fire hazard or fire risk of materials. However, results of this test may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular. This standard does not propose to address all of the safety problems. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use [33].

Standard procedure is given below;

i. After preparing the apparatus, remove a mounted specimen from the desiccator and place it in position on the rack in the chamber of the apparatus. Expose the specimen to the flame within 30 s of the time it is removed from the desiccator.

ii. Close the door of the apparatus. Set the timer at zero. Conduct the test in a draft-free room with the apparatus at room temperature.

iii. Activate the timing mechanism to apply the flame to the specimen for a period of 1 ± 0.05 s.

iv. When the burner combustion has stopped, as evidenced by the absence of flame and afterglow, remove the mounted specimen from the cabinet, place it on a flat surface, and determine whether or not ignition has occurred.

v. Ignition is considered to have occurred if the paper monitor is burned, charred, or discolored at any point.

vi. Test ten specimens, five on the face side and five on the back side for each laboratory sample unit.

3.4 UL 94 Flammability Test (Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances)

The UL 94 combustion test was developed by Underwriters Laboratories in the United States to test the combustion properties of the plastic parts of the device and materials. UL 94 is a highly used test that examines the combustion and flame spreading properties of a polymer exposed by a small flame source [34].

3.4.1 UL 94-V (Vertical) Flammability Test

This method is used to determine the UL 94 V-0, V-1 and V-2 flammability ratings as shown in Table 3.4. It evaluates both the burning and afterglow times after repeated flame application and dripping of the burning test specimen [35].

Table 3.4 UL 94 Vertical Flammability Rating

Flammability rating UL 94	V-0	V-1	V-2
Burning time after flame application (s)	≤10	≤30	≤30
Total burning time (s) (10 flame applications)	≤50	≤250	≤250
Burning and afterglow times of specimens after second flame application (s)	≤30	≤60	≤60
Dripping of burning specimens (ignition of cotton batting)	no	no	yes
Specimens completely burned	no	no	no

The UL 94 vertical burn test is used to examine the flammability behavior of polymer specimens which is specifically 120 mm ± 5 mm in length and 13 mm ± 0.5 mm in width. The material is exposed to fire at intervals of 10 seconds and It is removed periodically from the source material.

During this disassembly, the melted parts of the material will show cotton dripping and cotton burning. The UL94-V Flammability Test is included among the standard test methods ASTM D3801–10 [36]. Figure 3.4 shows the UL 94 vertical burning test system.

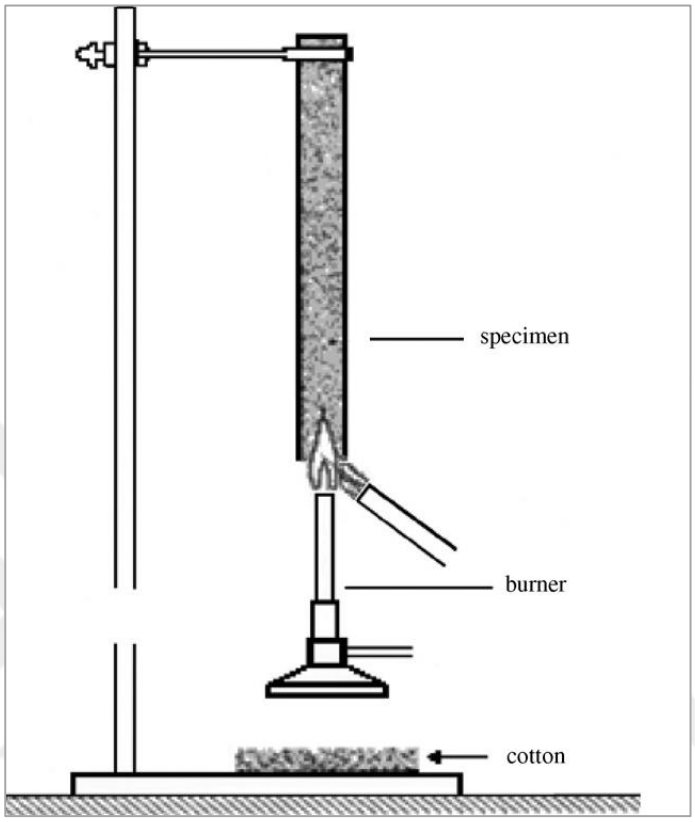


Figure 3.4 Schematic view of the UL 94 vertical burning test

3.4.2 UL 94-HB (Horizontal Burn) Flammability Test

A specimen less than 3 mm thick is tested in a horizontal orientation. It must burn at a rate of less than 76 mm/min. The UL94-HB Flammability Test is included among the standard test methods ASTM D3801-10 and ASTM D635-10 [37]. Figure 3.5 shows UL 94 horizontal burning test.

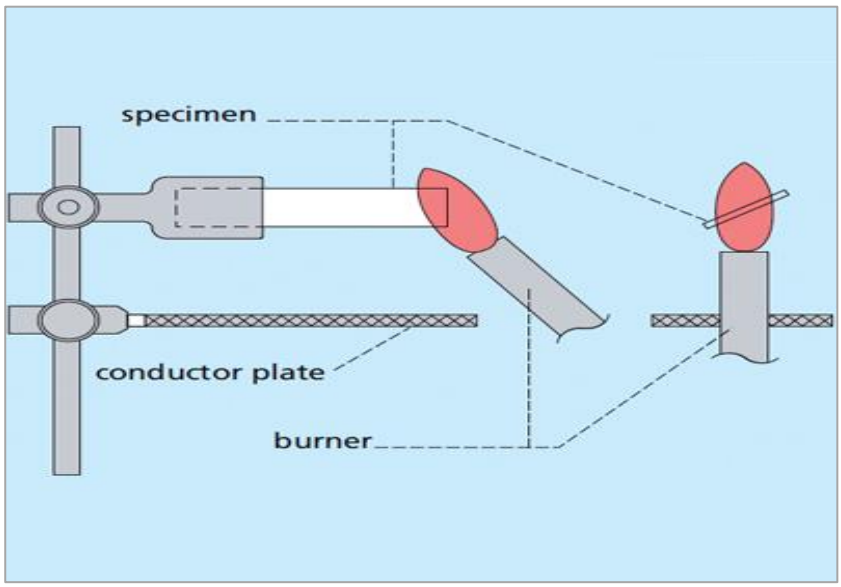


Figure 3.5 UL 94-HB (Horizontal Burn) Burning Test

3.4.3 UL 94-5V Flammability Test

This method is used to determine the UL 94-5VA and -5VB flammability ratings as shown in Table 3.5. It evaluates both the burning and afterglow times and any holes that are formed as well as dripping of the burning test specimen. The UL94-5V Flammability Test is included among the standard test methods ASTM D5048-09 [38].

Table 3.5 UL 94-5V Flammability Rating

Flammability rating UL 94		
Test criteria (test specimens)	5 VA	5 VB
Burning and afterglow times of specimens after fifth flame application	≤60 s	≤60 s
Dripping of burning specimens	no	no

As seen in Figure 3.6, the material is suspended vertically and the flame source which makes the angle at 20 degrees with the floor is periodically applied to the material five times at intervals of five seconds.

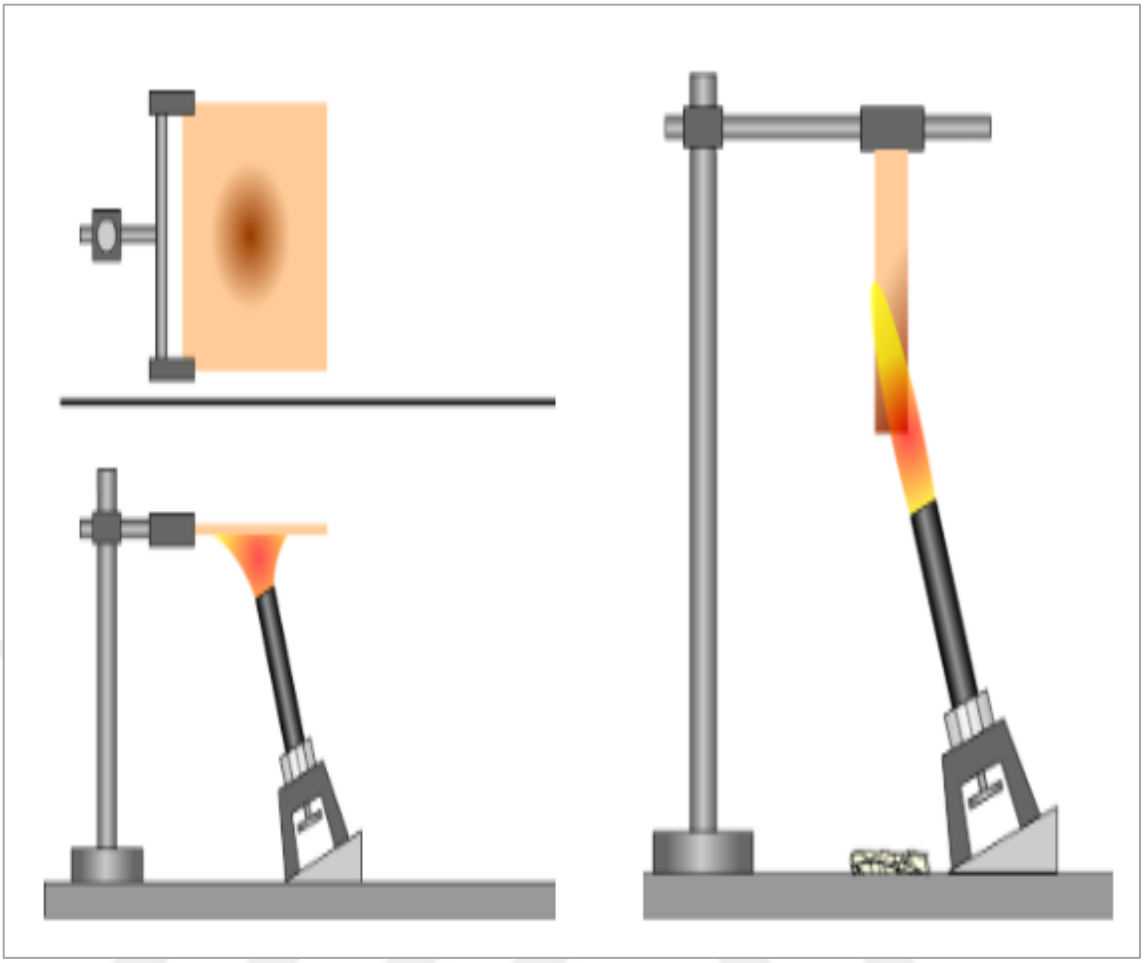


Figure 3.6 UL 94-5V Flammability Test

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Materials

Cotton fabric (260 g/m^2) was provided by Organic Chemistry Chemical Industry in Kemerburgaz. 9,10-dihydro-9-oxa-10-phosphahenanthrene-10-oxide (DOPO), maleic anhydride (MAH), itaconic acid (ITA), 3-Aminopropyl triethoxysilane (APTES), xylene, tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and diethyl ether were supplied by Sigma–Aldrich, and used as received.

4.2 Analysis Equipments

^{13}C- and ^{31}P-nuclear magnetic resonance were used to characterize the structure of flame retardants at Yildiz Technical University NMR Laboratory. Thermogravimetric analysis for thermal degradation and scanning electron microscopy for the surface images were carried out at Yildiz Technical University Central Laboratory. Vertical Burning Test was used to analyze flammability and thermal degradation properties of the untreated and coated cottons at Organic Chemistry Industrial Company in Kemerburgaz. X-ray photoelectron spectroscopy was applied for the surface characterization at Koc University Surface Science and Technology Center.

4.3 Synthesis of MD-1 and DOPO-MAH

These compounds were synthesized according to the literature [39, 40].

4.3.1 Synthesis of MD-1

DOPO (43.2 g) and ITA (26 g) were added in xylene (100 mL) by using a 100 mL one-necked flask, which had its reflux system under N_2. The reaction of DOPO and ITA was at 150 ^{o}C for 4 h. The reaction was stirred in a bot oil-bath and precipitated as a

white solid in 4 h and then washed with acetone (3x100 mL) by using a sonicator. The first compound was obtained with 96.8% yield.

4.3.2 Synthesis of DOPO-MAH

DOPO-MAH was synthesized from the reaction between DOPO and MAH in reflux system under N_2. DOPO (108 g) and MAH (49 g) were added in mixture of xylene and THF (350 mL) by using a 500 mL one-necked flask, which was putted into a hot oil-bath. The reaction was stirred at 80 ^{0}C for 2 d. The reaction of clear mixture of DOPO and MAH was completed after 2 d as understood from white precipitation. After that, DOPO-MAH was collected as a white powder. The resulting powder washed with mixture of diethylether and xylene (3x100 mL). The final white solid was acquired with 80.8% yield.

4.4 Synthesis of Flame Retardants (MKT-1 and MKT-2)

4.4.1 Synthesis of MKT-1

DOPO-MAH (40.9 g) and MD-1 (22.5 g) were added into dimethyl sulfoxide (DMSO) (230 mL) in a 500 mL one-necked flask, which had its reflux system. Subsequently, it was maintained the reaction at 100 ^{o}C for 8 h. The resulting liquid was precipitated in 10% HCI solution and then was washed and filtered with diethyl ether by vacuum filtration. The first flame retardant, which was named MKT-1 was acquired with 67% yield and stored at room temperature.

4.4.2. Synthesis of MKT-2

MKT-2 was synthesized from the reaction between DOPO-MAH and APTES in reflux system. DOPO-MAH (20 g) was first dissolved in DMF (100 mL) inside a 500 mL two-necked flask, which was putted into a hot oil-bath. Subsequently, APTES (16.9 g) was added dropwise in 30 minutes, and maintained the reaction under N_2 at 65 ^{0}C for 4 h. And then the resulting brown liquid was excessively washed with diethylether in sonicator. The final viscous amber product, which was named MKT-2 was acquired with 75.8% and stored at room temperature.

4.5 Preparation of the Treated Cotton Fabrics via Dip Coating Technique

MKT-1 and MKT-2 were introduced into a DMF solution to obtain 10,20, and 30 wt% solution. A piece of cotton fabrics was immersed into the obtained 10, 20, 30 wt% MKT-1 and MKT-2 solution for 30 min, respectively. The obtained samples were

squeezed after the dip coating in the solution to eliminate the excess of MKT-1 and MKT-2. They washed once with a water, and then dried in an oven at 100 ºC for 2 h. Thus, a series of flame retardant treated cotton fabrics were obtained. Non-flame retardant (bare textile) was also coated as a blank sample. Figure 1.10 shows the schematic representation for the coating process.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Synthesis and Characterization of MKT-1 and MKT-2

In order to obtain flame retardants, first compounds (MD-1 and DOPO-MAH) were synthesized according to reactions as shown in Figure 5.1. Yields of compounds were 96.8% and 80.8%, sequentially.

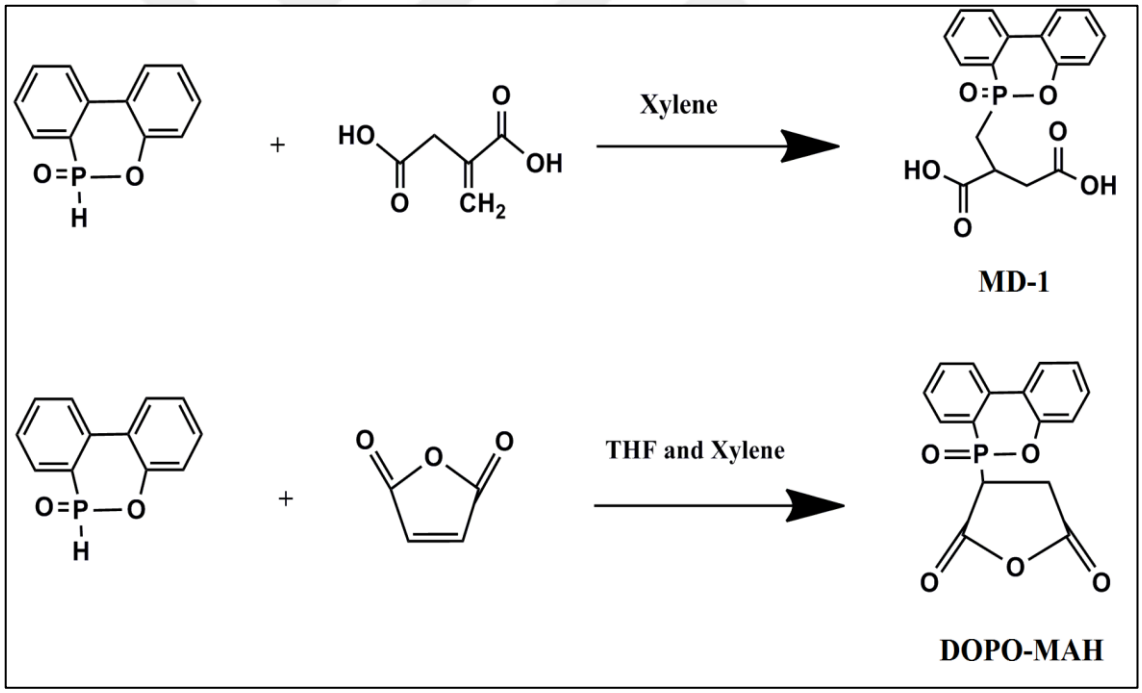


Figure 5.1 Synthesis of Compounds

We have succesfully synthesized our phosphorus containing flame retardant (MKT-1 and MKT-2) by the condensation reaction by DOPO-MAH and MD-1; 3-aminopropyl triethoxysilane (APTES) with DOPO-MAH. Yields of MKT-1 and MKT-2 were 67% and 75.8%, sequentially.

Figure 5.2 shows the synthesis of MKT-1 and MKT-2 additives. Solubility of MKT-1 and MKT-2 in different solvent mixture was given in Table 5.1.

Table 5.1 Solubility of MKT-1 and MKT-2

ADDITIVES	**NH_3-EtOH-H_2O** (1:3:2) (45 ^oC)	**NH_3-EtOH** (2:5) (45 ^oC)	**NH_3-IPA-H_2O** (3:3:1)
MKT-1	+	-	+
MKT-2	-	+	-

Synthesis of MKT-1 and MKT-2 was applied by condensation process by DOPO-MAH and MD-1; aminosilane with DOPO-MAH as indicated in Figure 5.2.

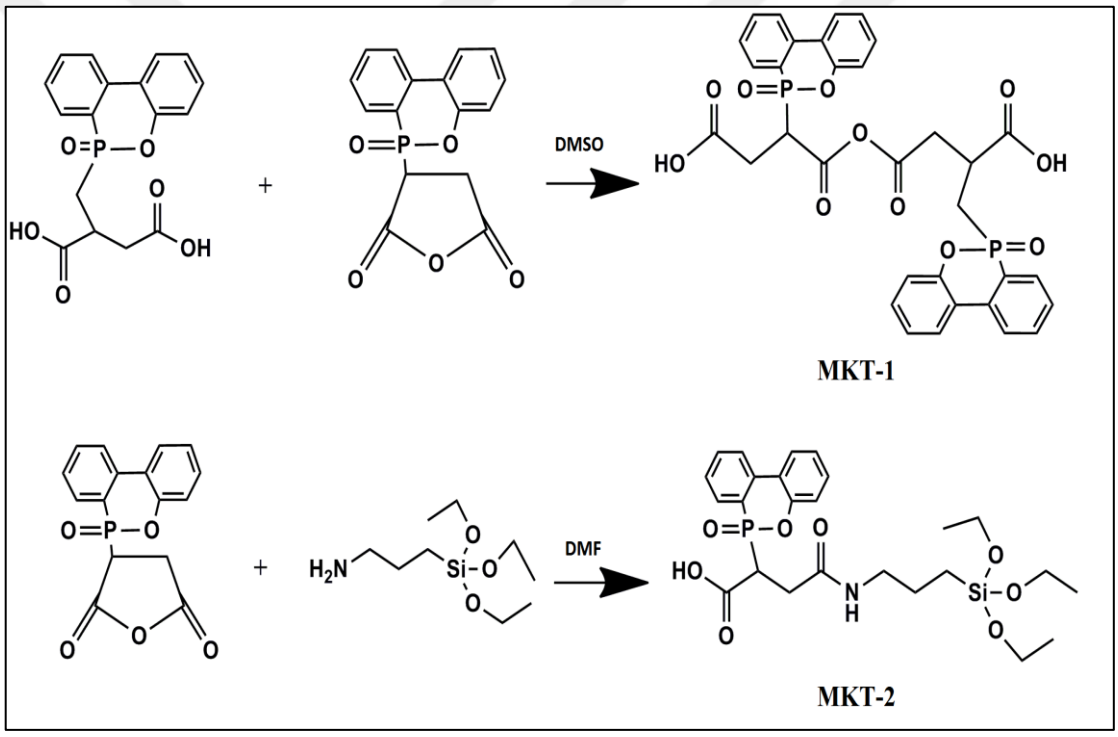


Figure 5.2 Synthesis of MKT-1 and MKT-2 Additives

MKT-1 was obtained via condensation at 100 ^oC and the brown product was purified by excess washing with diethyl ether in vacuum filtration. MKT-2 was obtained by using 3-aminopropyl triethoxysilane (APTES) at 65 ^0C for 4 h under N_2. Afterwards, the resulting brown liquid was excessively washed with diethylether in sonicator and the final viscous amber product acquired. In order to characterize synthesis of MKT-1 and MKT-2, ^{13}C- measurements was done, as shown in Figure 5.3.

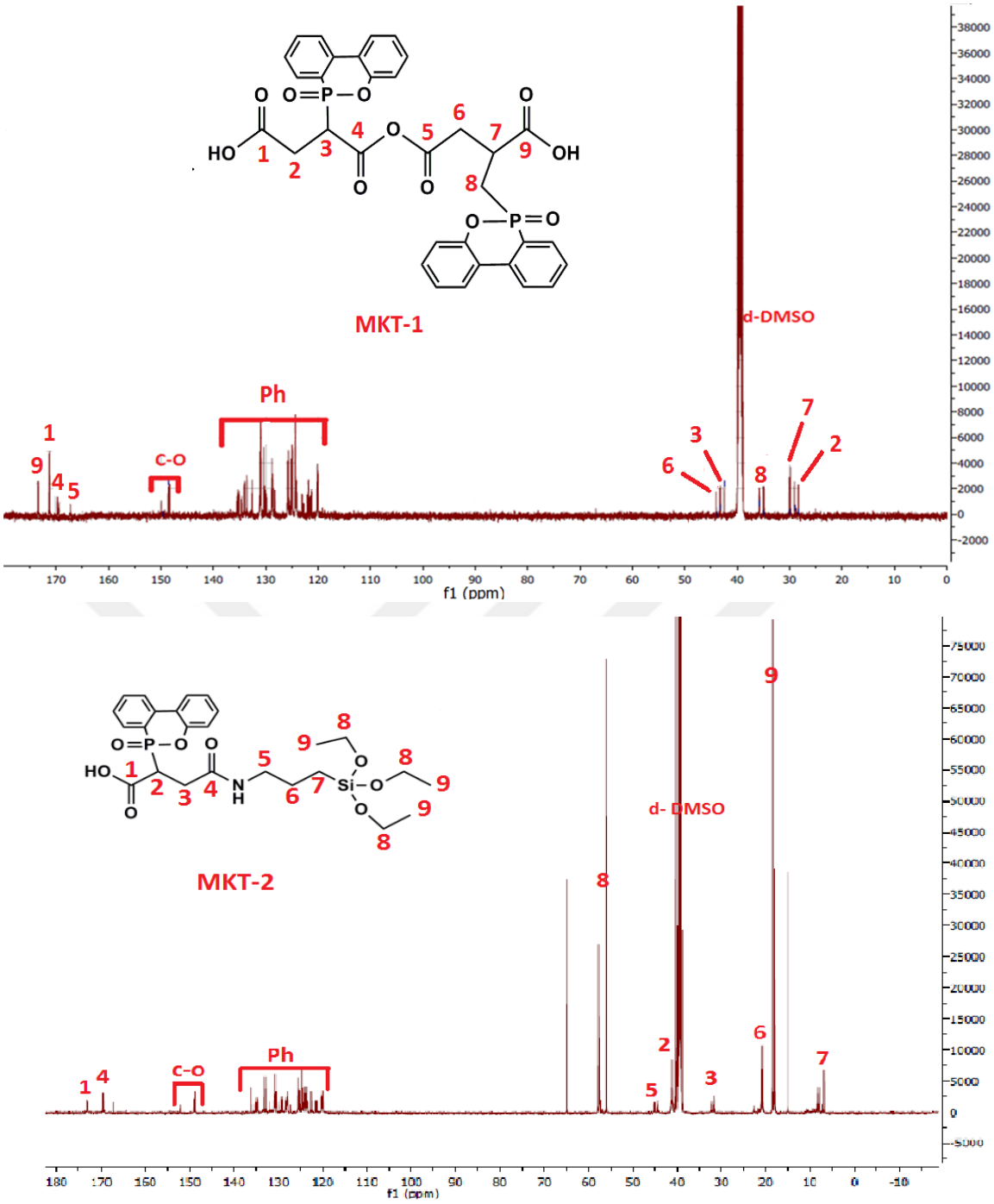


Figure 5.3 ^{13}C NMR spectra of MKT-1 and MKT-2

In the case of ^{13}C NMR spectra, the structure of MKT-1 was carried out by aspect of ^{13}C NMR peaks between 116.21 to 137.62 ppm and 149.62 ppm come via carbons of benzene rings and C-O bondings of DOPO-MAH and MD-1. Corresponding to carboxylic acids (-COOH) belong to carbon number of 9 and 1 at 172.30 and 174.13 ppm were refered to carbons of carboxyl groups. Additionally, peaks at 168.42 and 170.01 ppm were attributed to carbons of anhyride group, which demonstrated the successful reaction between DOPO-MAH and MD-1. In the ^{13}C NMR spectra of MKT-

2, ^{13}C NMR peaks at 7.38, 18.66, 21.03, 44.47 and 57.75 ppm (labeled 7, 9, 6, 5 and 8, respectively) were referred to the carbons from APTES unit; the peaks between 119.94 to 136.21 ppm and 149.36 were assigned to the carbons from benzene ring and C-O bonding. Corresponding to 4 and 1 peaks at 169.64 and 172.96 ppm come via carbons of amide (-HNCO-) and carboxyl groups (-COOH). This results reffers the successful reaction of MKT-2.

The signals in the ^{31}P NMR spectra as shown in Figure 5.4 also matched with the structure of MKT-1 and MKT-2. Furthermore, some of the peaks in both ^{31}P NMR belong to unreacted compounds (DOPO-MAH or MD-1).

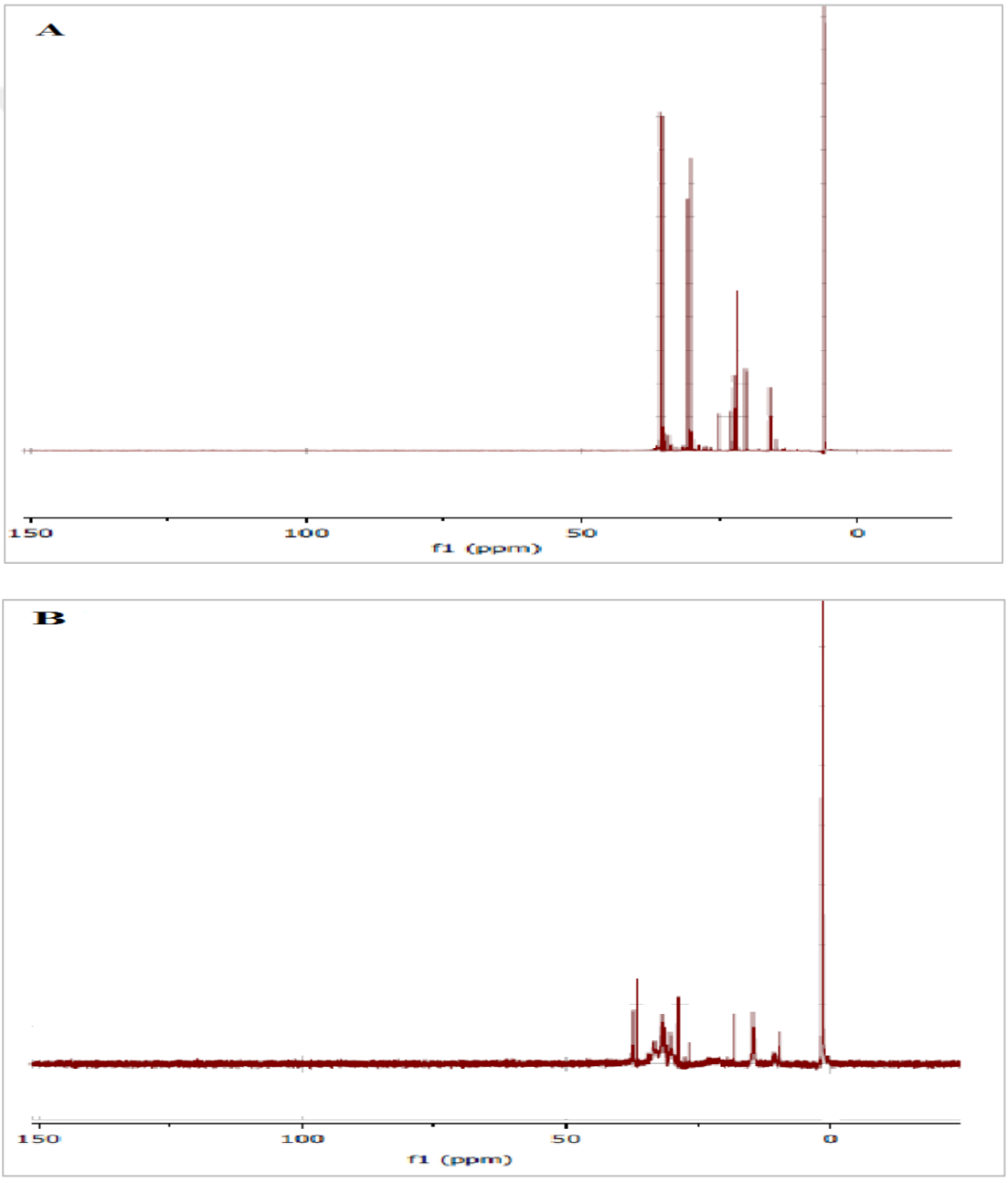


Figure 5.4 ^{31}P NMR spectra of MKT-1 (A) and MKT-2 (B)

5.2 Surface Morphology of Untreated and Coated Cotton Fabrics before Burning Test

In order to analyze the surface morphology, 10, 20, 30% quantities of MKT-1 and MKT-2 were firstly prepared for the surface treatment. Cotton fabrics were soaked in different quantities of MKT-1 and MKT-2 samples for 30 minutes and then washed with water. After washing treated cotton fabrics, they were dried in an oven at 100 ^{o}C for 2 h. Figure 5.5A provided the SEM images of uncoated and coated cotton fabrics and EDX spectra of 30% MKT-1 and MKT-2. The cotton fabrics showed a smooth surface, and It was clearly understood that uncoated and coated cotton fibers showed different morphological properties when the quantities were increased from 10 to 30%.

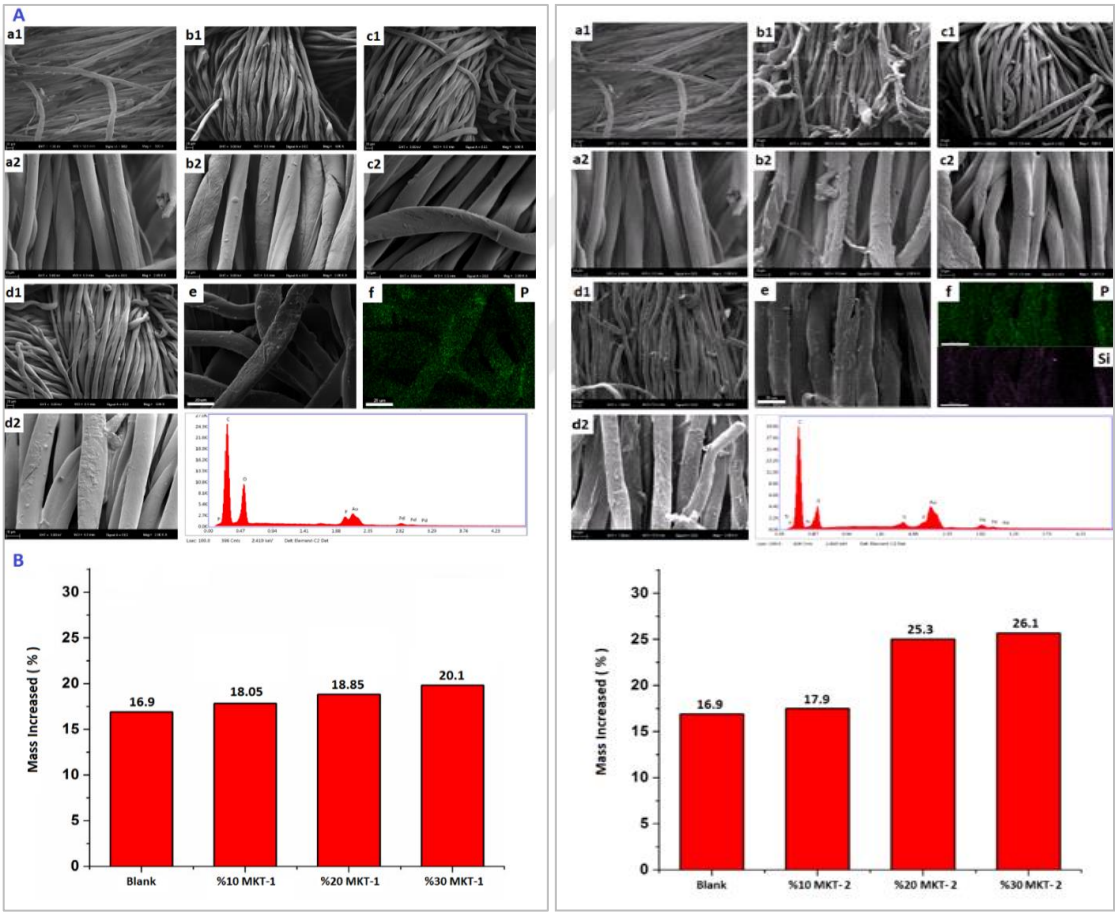


Fig. 5.5 (A) SEM images of uncoated (a1) and coated fabrics for 10% cotton (b1), 20% cotton (c1), 30% cotton (d1), P and Si mapping (f) and EDX spectra of 30% of MKT-1 and MKT-2, at different magnification (500, 2000, respectively) before burning and (B) increased mass of treated cotton fabrics at 30 minutes

When the quantity was increased to 10% and 30% of samples, a lot of cotton fibers were connected together and the gaps among cotton fibers were gradually disappeared due to the increased amount of coatings. Therefore the cotton fiber for 20% and 30% MKT-1 and MKT-2 showed more rough surfaces observed from the higher magnification. These results suggested that MKT-1 and MKT-2 have been successfully coated on the surface of cotton fibers. In order to further confirm the successful deposition and dispersion of MKT-1 and MKT-2 on the surface of cotton fibers, EDX tests were carried out in cottons 30% amounts. It is observed that both phosphorus and silicon were dispersed uniformly on the surface of cotton. These results mentioned above demonstrated the successful deposition and uniform dispersion of MKT-1 and MKT-2 on the surface of cotton.

According to dip coating results as shown in Figure 5.5B, it was noted that the add-on of coated cotton increased with the quantity. The add-ons of untreated and treated cottons with 10%, 20%, 30% MKT-1 were 16.9%, 18.05%, 18.85% and 20.1%, respectively. As a results of 10%, 20%, 30% MKT-2 were 16.9%, 17.9%, 25.3% and 26.1%, respectively. The increased weight of the coated cotton fabrics also indicated the successful deposition of MKT-1 and MKT-2 on the surface of coated cotton fibers.

It was observed that the cotton fabrics coated with 30% MKT-1 and MKT-2 still contained phosphorus on the surface after washing 5 times as it was seen in Figure 5.6. The cotton fabrics coated with 30% MKT-1 and MKT-2 were immersed into the water solution and waited for 15 min in the sondicator five times. The washed cotton fabrics were dried in an oven at 100 ^{o}C for 30 minutes. Thus, 5 times washed treated cotton fabrics were obtained via washing process. SEM and EDX results demonstrated that the colavent attachment of MKT-1 and MKT-2 on cotton surface enhanced the durability.

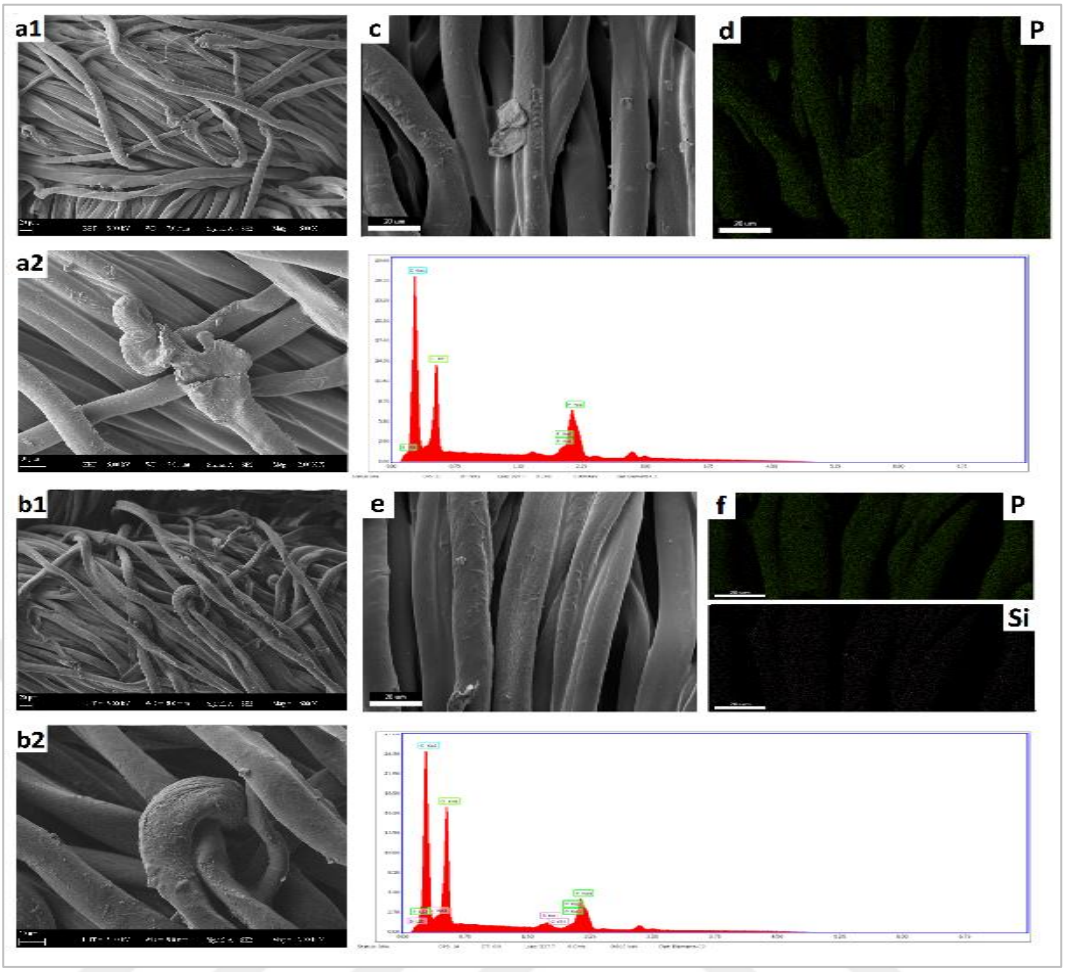
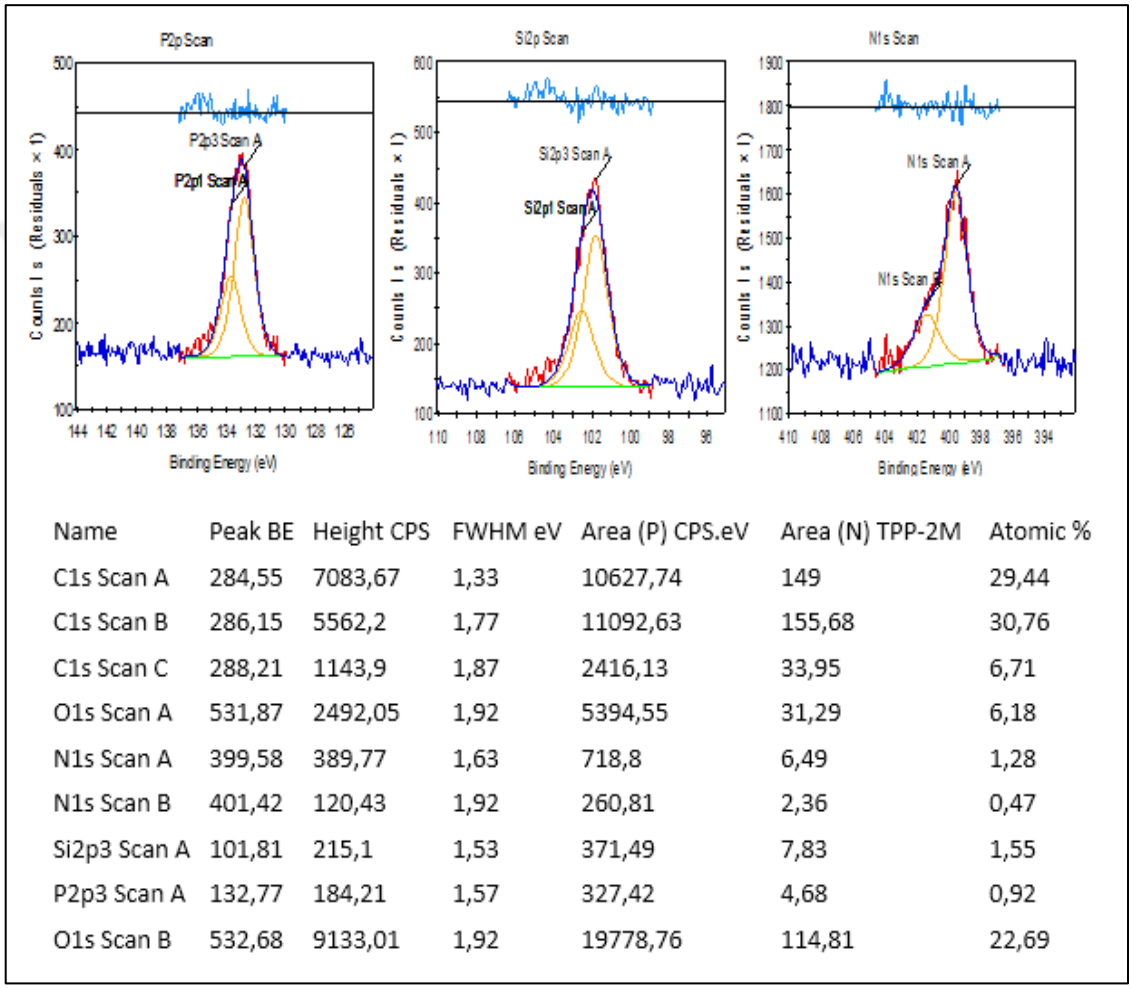


Fig. 5.6 SEM images of unburned coated fabrics with 30% MKT-1 (a1, a2), 30% MKT-2 (b1, b2), P mapping of MKT-1 (d) and P-Si mapping of MKT-2 (f) and EDX spectra of 30% of MKT-1 and MKT-2, at different magnification (500, 2000, respectively) after washing 5 times

XPS technique was carried out in order to investigate the surface modification of cotton fabrics. This technique is used to understand which elements exist on the material's surface. Spectrum peaks in XPS analysis appear from atoms by emitting electrons of a particular characteristic energy. The intensities and energies of the spectrum peaks identify quantities of all the elements on the surface (except H_2).

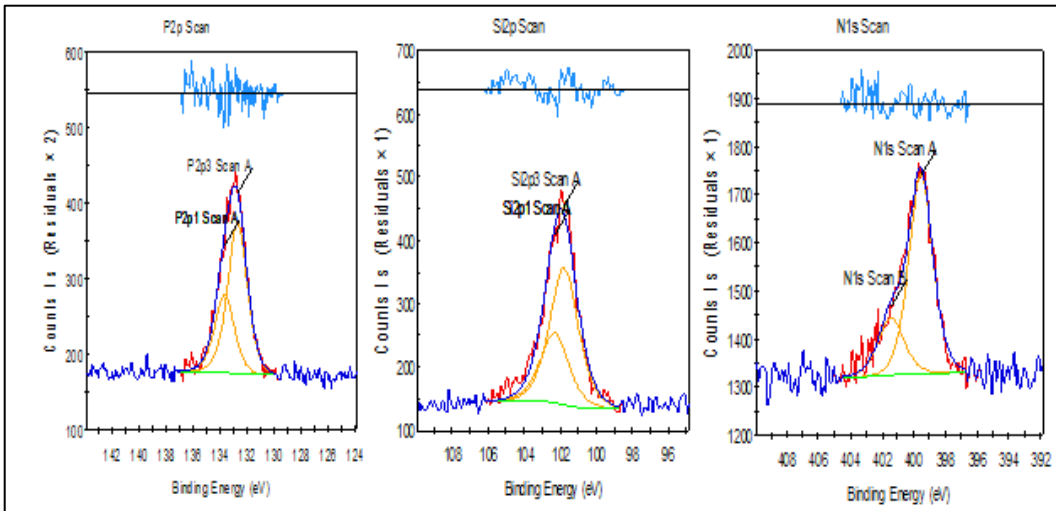
For more accurate surface information of coated cotton surface XPS measurements were performed and correspoing results are presented in Figure 5.7 and Figure 5.8 for MKT-2, Figure 5.9 and Figure 5.10 for MKT-1, sequentially. In the spectrum of MKT-2 coated cotton (Figure 5.7) there exist mainly three major elements; P, Si and N. Detailed description of the chemical bonding of the coated cotton and after washing cycle could be inferred from the respective P, Si and N signals. The N1s spectrum of MKT-2 30% coated cotton has only one strong peak originating from the silane

coupling agent N-C bonds observed at 401.4 eV. Moreover, silane coupling agents have also C-Si bonding. The peak at 101.8 eV represents Si-O bonding. P_{2p} spectrum also indicated 132.7 eV represent phosphorus groups on the cotton surface. Before the washing cycle, percentage of the N, Si, P on the cotton were obtained as 1.28%, 1.55% and 0.9%. After washing cycle, it was observed that 1.47%, 1.89% and 1.08% as shown in Figure 5.8 and this indicates that the MKT-2 is durable and do not leach from the surface after washing.



Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %
C1s Scan A	284,55	7083,67	1,33	10627,74	149	29,44
C1s Scan B	286,15	5562,2	1,77	11092,63	155,68	30,76
C1s Scan C	288,21	1143,9	1,87	2416,13	33,95	6,71
O1s Scan A	531,87	2492,05	1,92	5394,55	31,29	6,18
N1s Scan A	399,58	389,77	1,63	718,8	6,49	1,28
N1s Scan B	401,42	120,43	1,92	260,81	2,36	0,47
Si2p3 Scan A	101,81	215,1	1,53	371,49	7,83	1,55
P2p3 Scan A	132,77	184,21	1,57	327,42	4,68	0,92
O1s Scan B	532,68	9133,01	1,92	19778,76	114,81	22,69

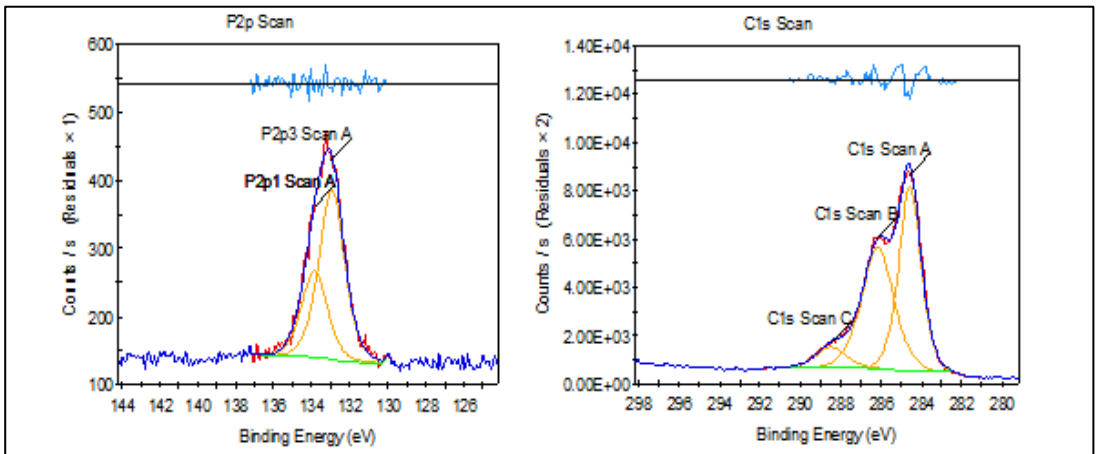
Figure 5.7 XPS spectrum of MKT-2 30% coated cotton before washing



Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %
C1s Scan A	284,48	7912,67	1,4	12495,95	175,19	34,51
C1s Scan B	286,02	4688,19	1,92	10152,92	142,48	28,07
C1s Scan C	288,13	1175,71	1,92	2546,16	35,78	7,05
O1s Scan A	531,82	4575,95	1,89	9787,27	56,77	11,18
O1s Scan B	532,91	5763,3	1,92	12481,22	72,46	14,28
N1s Scan A	399,55	418,32	1,75	828,14	7,48	1,47
N1s Scan B	401,43	121,58	1,92	263,29	2,38	0,47
Si2p3 Scan A	101,8	215,77	1,86	453,94	9,57	1,89
P2p3 Scan A	132,72	200,45	1,69	383,58	5,48	1,08

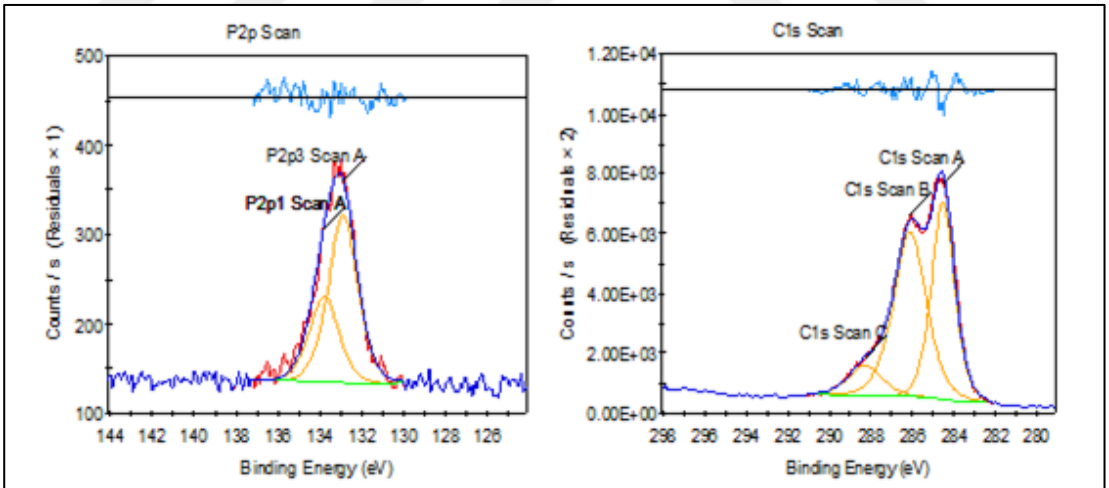
Figure 5.8 XPS spectrum of MKT-2 30% coated cotton after washing

According to XPS spectrum of MKT-1 (Figure 5.9), a major element P is mainly observed on the MKT-1 coated cotton. Detailed description of the chemical bonding of the coated cotton and after washing cycle could be signified from the respective C, O and P signals. The peaks of C1s spectrums of MKT-1 30% coated cotton at 284.5 eV, 286.1 eV and 288.4 eV sequentially represent C-O from DOPO units, C=O/O-C-O from carbonyl and anhydride bonding and lastly -COO from carboxyl groups. P_{2p} spectrum also indicated 132.9 eV represent phosphorus groups on the cotton surface. Before the washing cycle, percentage of the P on the cotton was obtained as 1.35%. After washing cycle, it was observed that 1.03% as shown in Figure 5.10 and this indicates that the MKT-1 is durable and do not leach from the surface after washing. These results mentioned above demonstrated that MKT-1 with 1.35% has more phosphorus component than MKT-2 with 0.92%.



Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %
C1s Scan A	284,56	7682,15	1,28	11068,1	155,18	33,16
C1s Scan B	286,16	5066,05	1,83	10491,66	147,25	31,47
C1s Scan C	288,46	881,34	1,73	1723,87	24,23	5,18
O1s Scan A	532,64	9943,96	1,92	21534,98	125	26,71
P2p3 Scan A	132,95	250,07	1,57	442,6	6,32	1,35

Figure 5.9 XPS spectrum of MKT-1 30% coated cotton before washing



Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) TPP-2M	Atomic %
C1s Scan A	284,51	6606,24	1,3	9682,84	135,75	28,39
C1s Scan B	286,11	5517,65	1,85	11533,13	161,86	33,85
C1s Scan C	288,27	961,81	1,91	2071,34	29,11	6,09
O1s Scan A	532,6	11097,51	1,92	24033,17	139,5	29,18
P2p3 Scan A	132,88	187,98	1,62	344,36	4,92	1,03

Figure 5.10 XPS spectrum of MKT-1 30% coated cotton after washing

5.3 Thermal Degradation Properties of Untreated And Coated Cottons

Thermogravimetric analysis (TGA) and heating crucible test were used to investigate thermal degradation properties of the untreated and coated cotton fabrics. TGA curves of coated cotton fabrics with MKT-1 and MKT-2, and their char residual percentages at 500 ^{o}C under nitrogen were presented in Figure 5.11. TGA results indicated that the main mass loss stage of MKT-1 and MKT-2 were at the temperature ranges from 300 to 500 ^{o}C and 100 to 500 ^{o}C, respectively. Then the thermal degradation rate reduced with the increasing of temperature, while the char residual amount decreased slowly. As shown in Table 5.2, MKT-1 has more phosphorus elements with 9.38% than MKT-2 with 5.78% on the cotton surface. The cotton fibers coated with MKT-1 and MKT-2 for 30 min showed a higher degradation temperature with 14% and 20% char yields, compared with untreated cotton fabric.

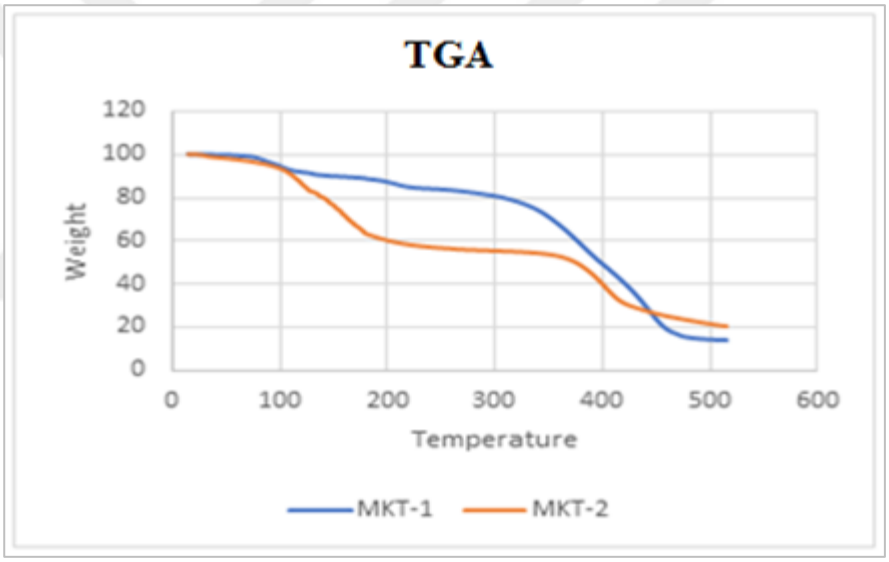


Figure 5.11 TGA curves of MKT-1 and MKT-2 samples at 500 ^{o}C

In the heating crucible test, the mass losses of each samples were compared with uncoated cotton fabric. The temperature was increased to 500 ^{o}C in the oven and 1 g of the coated cotton samples were examined after 15 minutes. The cotton fabrics coated with 30% MKT-1 and MKT-2 provided higher char yields (20.2% and 36.1%) compared with the char yield of uncoated cotton fabric (2.1%) as it was shown in Table 5.2.

Table 5.2 Char yields of coated cotton fabrics in crucibles after heating at 500 ºC and TGA results

Quantities of coated cotton fabrics	BLANK	MKT-1	MKT-2
	2.1 %	-	-
10% (W/V)	-	7%	19.04%
20% (W/V)	-	14.3%	32.43%
30% (W/V)	-	20.2%	36.1%
30% Durability (W/V)	-	19.6%	33.3 %

Additives	Char Yield (%)	P (%)
MKT-1	14%	9.38%
MKT-2	20%	5.78%

The char residual amounts for MKT-1 and MKT-2 at 500 ºC were increased significantly as shown in Table 5.2, from 2.1% (uncoated cotton fabrics) to about 7% and 19,04% (cotton-10% coated), 14.3% and 32.43% (cotton-20% coated), 20.2% and 36.1% (cotton-30% coated) and 19.6% and 33.3% (cotton-30% coated for durability), respectively.

5.4 Flammability of Uncoated and Coated Cotton Fabrics

5.4.1 BS 5852 Standard (Test Methods for Assessment of the Ignitability of Upholstered Seating by Smouldering and Flaming Ignition Sources)

The flame retardancy of the uncoated and coated cotton fabrics were examined by BS 5852 and the photos during the burning test were taken and presented in Figure 5.12, and the SEM images of untreated and coated cotton fabrics with MKT-1 and MKT-2 after burning were shown in Figure 5.13A and Figure 5.13B. The untreated cotton fabrics burned very ferociously at 10 s after the ignition.

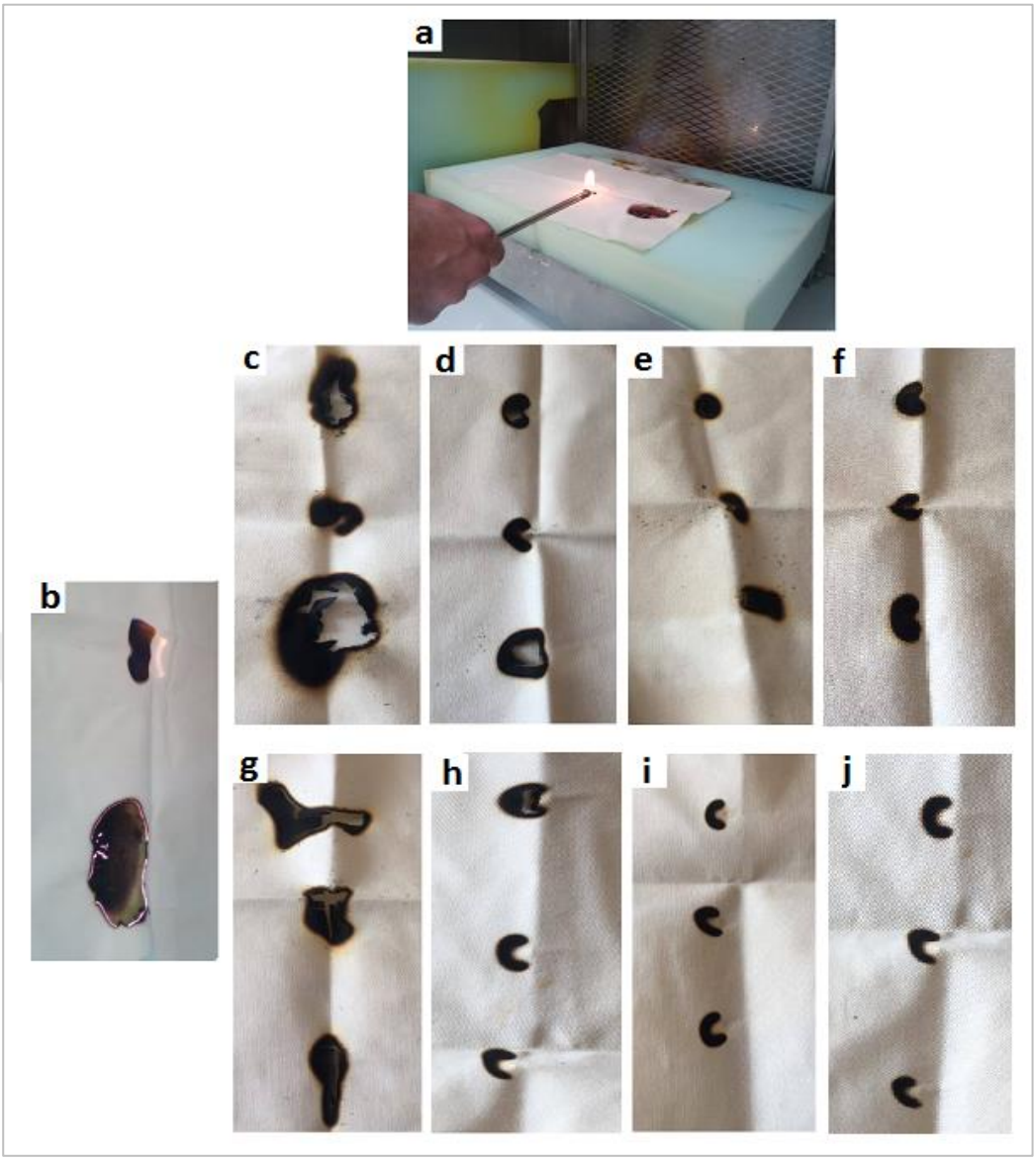


Figure 5.12 BS 5852 Test (a), the digital photos of uncoated (b) and cotton fabrics coated with 10, 20, 30% and 30% washed MKT-1 and MKT-2 (labeled c, d, e, f for MKT-1 and g, h, i, j for MKT-2, respectively) after burning

Although the cotton fabric coated with 30% MKT-1 was extinguished at 5 seconds after the ignition, other cotton fabrics coated with 20% and 30% MKT-2 showed highest resistance against the fire. They were immediately extinguished after the burner was removed. Only black marks on the surface were observed after burning. This indicated the residual chars in cottons coated with 20% and 30% MKT-2 were enough to prevent the cotton from any flames.

SEM images and EDX spectra of the samples after burning test were shown in Figure 5.13. It was noted that the untreated cotton fabric showed a lowest residue after burning and there were many holes among the fibers. Heat and O_2 easily penetrated through

these holes, and this easily caused a fire on the untreated cotton fabric's surface. Fibers in the cotton-10% and cotton-20% of MKT-1 showed less resistance against flames. They were sequentially extinguished at 50 and 42 seconds after the ignition. The surface of the cotton-10% and cotton-20% of MKT-1 were seen rough, and there were some gaps between cotton fibers. Fibers in the cotton-30% of MKT-1 were seen smooth and showed a higher resistance against the fire. In the surface of the residual fibers in the cotton-20% and cotton-30% of MKT-1 were seen very smooth and there were no holes between fibers. This resulted that cotton fabrics coated with 20% and 30% MKT-2 provided the highest flame resistances and synergistic effect of nitrogen and silicon increased the flame retardant properties of the cotton fabrics.

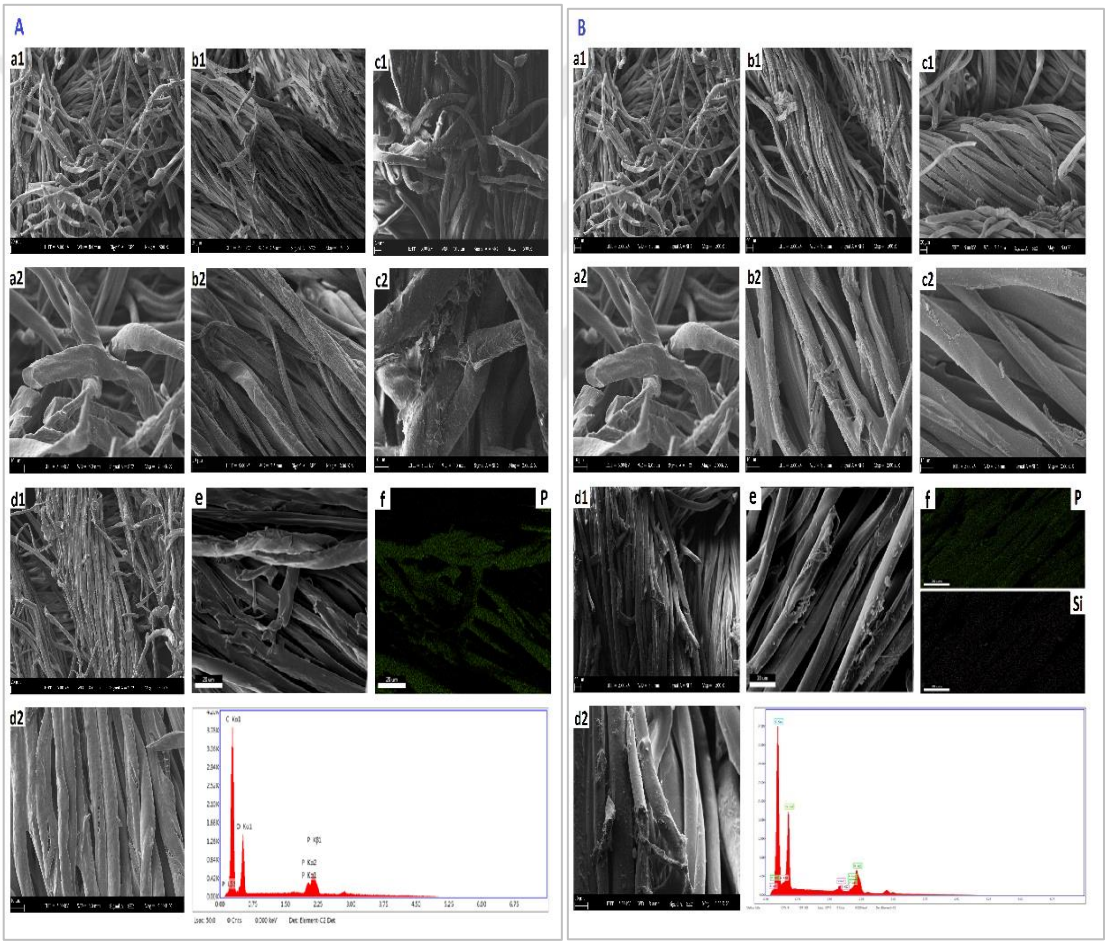


Figure 5.13 (A) SEM images of uncoated (a1, a2) and coated cotton fabrics for 10% cotton (b1, b2), 20% cotton (c1, c2), 30% cotton (d1, d2) of MKT-1, P mapping (f) and EDX spectra of 30% of MKT-1, and (B) SEM images of uncoated (a1, a2) and coated cotton fabrics for 10% cotton (b1, b2), 20% cotton (c1, c2), 30% cotton (d1, d2) of MKT-2, P and Si mapping and EDX spectra of 30% of MKT-2 at different magnification (500, 2000, respectively) after burning

In order to investigate that silicon and phosphorus elements existed on the surface, EDX test was carried out. From Figure 5.13A and 5.13B, it was clearly understood that silicon and phosphorus elements were still on the cotton surface.

The SEM images of coated cotton fabrics with 30% MKT-1 and MKT-2 after washing 5 times were shown in Figure 5.14. The washed cotton fabric coated with 30% MKT-1 was extinguished at 10 seconds after the ignition. The surface of coated cotton was seen smooth and there were few gaps between fibers. The washed cotton fabric coated with 30% MKT-2 showed the same behaviour with unwashed 30% MKT-2. It was observed that the cotton fabrics coated with 30% MKT-1 and MKT-2 still contained phosphorus elements on the surface after washing 5 times as it was seen on EDX spectra in Figure 5.14. This demonstrated that the colavent attachment of MKT-1 and MKT-2 on cotton surface was stable enough to prevent the fire.

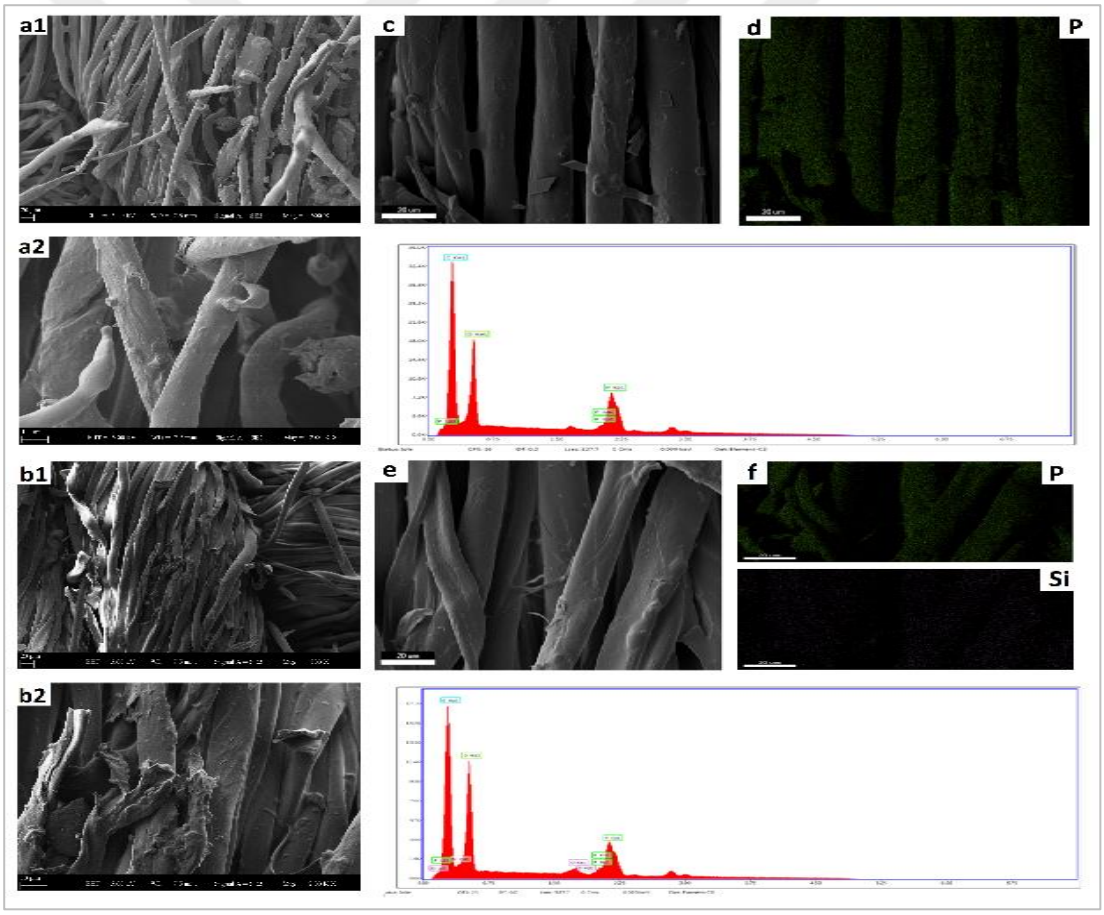


Figure 5.14 SEM images of burned coated fabrics with 30% MKT-1 (a1, a2), 30% MKT-2 (b1, b2), P mapping of MKT-1 (d) and P-Si mapping of MKT-2 (f) and EDX spectra of 30% of MKT-1 and MKT-2, at different magnification (500, 2000, respectively) after washing 5 times

CHAPTER 6

CONCLUSION

This study has shown that new phosphorus containing flame retardant additives (MKT-1 and MKT-2) have been synthesized. MKT-1 contains carboxylic acid and acid anhydride functionality with phosphorus units. MKT-2 contains nitrogen, carboxylic acid and silanol group functionality with phosphorus units. Surface coated cotton with MKT-1 and MKT-2 was applied for thermal analysis to investigate flame retardancy of coated fabric. TGA analysis of samples showed that char yields of coated cotton fabrics with 30% MKT-1 and MKT-2 are 20.2% and 36.1%, sequently. SEM and EDX results showed that MKT-1 and MKT-2 dispersed well on the surface of cotton fabrics. Especially, compared to coated cotton fabrics with MKT-1, coated cotton fabrics with 20% and 30% MKT-2 provided the highest flame resistance against the fire due to synergistic effect of N and Si. XPS analysis showed that phosphorus, nitrogen and silicon elements exist and MKT-1 and MKT-2 additives were covalently attached to the cotton surface. This demonstrated that durability of cotton fabric was successfully increased due to the covalent attachment of MKT-1 and MKT-2 on the cotton surface. Durability test also showed that coated fabric is stable under washing conditions. A new phosphorus containing reactive functional group processing flame retardant have been synthesized. Application of these new additives to polyurethane and polyester formulation are under study.

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CURRICULUM VITAE

PERSONAL INFORMATION

Name Surname : MUHAMMED KANAT

Date of Birth and Place : 01.09.1990 Kiraz/Izmir

Foreign Languages **:** English, Greek

E-mail **:** mkanat@materials.uoc.gr

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Undergraduate	Chemistry	Dumlupinar University	12.06.2014
High School	Mustafa Usdu High School		15.06.2009

WORK EXPERIENCE

Year	**Corporation/Institute**	**Enrollment**
2016	Eren Research Group/YTU	Researcher in Polymer
2016	Yildiz Technical University	Teaching Assistant

PUBLISHMENTS

Conference Papers

1. Synthesis of Phosphorus Containing Flame Retardants and Investigation Flame Retardant Behavior on Textile Applications at the EWPC 14th/2017 (European Workshop on Phosphorus Chemistry) in Romania.

AWARDS

1. 2013 May First Prize, Universal Science Competition - Group Leader in Chemistry at Dumlupinar University in Turkey. The title of the competition was preparing of the best quality soap with low-cost (solid, liquid, or foam). Our experiment was based on the antibacterial foam soap.