ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF FLAME RETARDANT POLYURETHANE FILM CONTAINING PHOSPHINE OXIDE AND NITROGEN

M.Sc. THESIS

Hanife Elif GÜRSEL

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2018

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF FLAME RETARDANT POLYURETHANE FILM CONTAINING PHOSPHINE OXIDE AND NITROGEN

M.Sc. THESIS

Hanife Elif GÜRSEL
(515151012)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. İ. Ersin SERHATLI

JANUARY 2018

ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FOSFİN OKSİT VE AZOT İÇEREN YANMAZLIK KATKILI POLİÜRETAN FİLM SENTEZİ

YÜKSEK LİSANS TEZİ

Hanife Elif GÜRSEL
(515151012)

Polimer Bilimi ve Teknolojisi Anabilim Dalı

Polimer Bilimi ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. İ. Ersin SERHATLI

OCAK 2018

Hanife Elif Gürsel, a M.Sc student of **ITU Polymer Science and Technology Programme** student ID **515151012**, successfully defended the thesis/dissertation entitled "**SYNTHESIS OF FLAME RETARDANT POLYURETHANE FILM CONTAINING PHOSPHINE OXIDE AND NITROGEN**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. İ. Ersin SERHATLI** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. F. Seniha GÜNER** İstanbul Technical University	.....
	Prof. Dr. M. Vezir KAHRAMAN Marmara University	.....

Date of Submission : 2 January 2018
Date of Defense : 11 January 2018

To my family,

FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Material Research Group), Faculty of Science and Letters, Istanbul Technical University.

First of all, I would like to sincerely thank my advisor, Prof. Dr. İ. Ersin SERHATLI for sharing his knowledge and experience with me and for his encouragement and guidance.

I would also like to give my sincere thanks to my supervisor, Dr. Tuba ÇAKIR ÇANAK for sharing her invaluable knowledge, advice, support and encouragement with me throughout this study.

I would like to thank Prof. Dr. Ayşen ÖNEN for her support and positive energy.

I am also very grateful to Dr. Müfide KARAHASANOĞLU for her comments, suggestions and positive energy.

Finally, I would like to offer the most gratitude to my family for their love, patience, support and encouragement during all stages of my life.

January 2018

Hanife Elif GÜRSEL
(Chemical Engineer)

TABLE OF CONTENTS

Page

ABBREVIATIONS

PU	**:** Polyurethane
PPU	**:** Phosphorus-containing Polyurethane
BHAPPO	**:** Bis(3-hydroxy aminophenyl)phenylphosphine oxide
PPG	**:** Poly(propylene glycol)
IPDI	**:** Isophorone Diisocyanate
DBTDL	**:** Dibutyltin Dilaurate
LOI	**:** Limiting Oxygen Index
FT-IR	**:** Fourier Transform Infrared
^{1}H-NMR	**:** Hydrogen Nuclear Magnetic Resonance
^{31}P-NMR	**:** Phosphorus-31 Nuclear Magnetic Resonance
TGA	**:** Thermogravimetric Analysis
DMSO-d_6	**:** Deuterated dimethyl sulfoxide
ATH	**:** Alumina trihydrate
ABS	**:** Acrylonitrile-butadiene-styrene copolymer

LIST OF TABLES

Page

LIST OF FIGURES

Page

SYTNHESIS OF FLAME RETARDANT POLYURETHANE FILM CONTAINING PHOSPHINE OXIDE AND NITROGEN

SUMMARY

Polyurethanes have a wide range of application areas due to their various advantages such as their excellent abrasion resistance, high toughness, chemical resistance, flexibility and low film-forming temperatures. They have been widely used in coating, foam, adhesives and composites.

Phosphorus and nitrogen elements give excellent flame retardant properties to polymers. Moreover, polymers containing phosphine oxide moieties have many other advantages such as high thermal and oxidative stability, solubility in organic solvents, good adhesion to other compounds and miscibility. In addition to phosphorus-based reactive-type flame retardants, phosphorus-nitrogen flame-retardant synergism system was reported in many literature and exhibited better flame-retardant efficiency than those only containing phosphorus, due to the synergistic effect between phosphorus and nitrogen.

Over the past decades, additive-type flame-retardants have been used to improve the flame retardancy of polyurethanes (PU). However, the use of the additive-type flame-retardants in PUs has many disadvantages such as poor compatibility, easy leaching and decreasing mechanical properties. Therefore, studies on developing reactive-type flame retardants are emphasized on in order to incorporate the flame retardants into the PU structure. In general, the reactive-type flame-retardants containing phosphorus element were incorporated into the PU backbone to improve the flame retardancy by chemical reaction. A number of studies confirmed that phosphorus element incorporated into the PU backbone increases thermal stability of the material.

This thesis is separated into three sections. In the first section, bis(3-hydroxy aminophenyl)phenylphosphine oxide (BHAPPO) was synthesized by the reaction between 3-aminophenol and P,P-dichlorophenylphosphine oxide producing BHAPPO compound and hydrochloric acid as byproduct.

In the second section of the thesis, BHAPPO which contains both phosphine oxide and nitrogen groups for flame retardancy and two phenol groups, was used as a diol in the polyurethane prepolymer synthesis. In PU film synthesis, different concentrations of BHAPPO and poly(propylene glycol) (PPG) was reacted with isophorone diisocyanate (IPDI). Different diisocyanate/diol and BHAPPO/PPG ratios were used in order to determine the optimum ratios for film forming, flame retardancy and mechanical properties.

In the third section, polyurethane prepolymer was applied on surfaces such as teflon, silicone, plexiglass and glass to observe its behavior on different surfaces. Different curing methods such as curing in oven, curing in vacuum oven and curing at room temperature were performed in order to determine the optimum curing conditions. After curing, the free films were separated from the surfaces and various properties

such as limiting oxygen index, gloss, gel content, chemical resistance, water absorption, pendulum and pencil hardness, thermogravimetric analysis and mechanical measurements (tensile strength, elastic modulus, elongation at break and stress-strain) were investigated.

FOSFİN OKSİT VE AZOT İÇEREN YANMAZLIK KATKILI POLİÜRETAN FİLM SENTEZİ

ÖZET

Poliüretanlar termoset veya termoplastik özellikte olabilen, ana zincirinde üretan bağları içeren polimerlerdir. Poliüretanlar kolaylıkla gerdirilebilmelerinden dolayı elastomerlere benzer. Çizilmeye, yırtılmaya ve darbeye dayanıklıdır, sıkıdır fakat çok iyi darbe absorplama özelliklerine sahiptir. Organik solventlere, asitlere ve yağlara dayanıklıdır.

Poliüretanlar, poliol ve izosiyanatların katalizörlü ve aktifleyici bileşiğin eşliğinde kondenzasyon polimerizasyonuyla elde edilir. Poliüretanlar kauçuk gibi elastik, metaller gibi dayanıklı ve uzun ömürlü plastiklerdir. Poliüretanların çoğu çapraz bağlıdır ve ısıtıldıklarında termoset plastikler elde edilir. Çapraz bağı olmayan bazı poliüretan polimerler de vardır, bunlar doğrusal moleküler düzendedirler ve termoplastiklerdir.

Termoset poliüretanlar yumuşak köpük, sert köpük gibi çeşitli biçimlerde olabilir. Yumuşak köpükler yatak, yorgan ve paketleme malzemeleri üretiminde, sert köpükler ise genellikle izolasyon malzemesi olarak kullanılırlar.

Termoplastik poliüretanlar doğrusal ve kristalinite dereceleri yüksek moleküllerden oluşur, bunlardan aşınmaya dayanıklı malzemeler yapılır. Bu malzemelere örnek olarak ayakabı tabanları, araba çamurluğu, kapı panelleri, araç dış lastiği, conta, tampon ve sentetik deri verilebilir.

Poliüretan malzemeler mükemmel aşınma direnci, yüksek tokluk, kimyasal direnç, esneklik ve düşük film oluşturma sıcaklıkları gibi avantajları sayesinde çok farklı alanlarda kullanılabilmektedir. Kaplama, köpük, yapıştırıcı ve kompozit olarak geniş bir kullanım alanına sahiptir.

Ticari amaçlı poliüretanların üretiminde kullanılan izosiyanatlar genellikle aromatik yapılıdır. Üretimde kullanılan izosiyanatın türü, elde edilen poliüretanın özelliklerini, kürleme sistemini ve işleme sistemini doğrudan etkiler. Bir izosiyanatın en önemli özelliği fonsiyonalitesidir, yani her bir molekülde bulunan izosiyanat gruplarının sayısıdır. Çapraz bağlı poliüretanların üretiminde uygun izosiyanatlar 2'den fazla fonksiyonel grup içermelidir. Difonksiyonlu bir izosiyanat (diizosiyanat) difonksiyonlu bir poliolle (diol) reaksiyona girdiğinde uzun, doğrusal poliüretan molekülü meydana gelir.

Poliüretan endüstrisinde polieter ve polyester tipte olmak üzere başlıca iki tür poliol kullanılır. Polyester polioller etilen glikol gibi bir diol ile bir dikarboksilik asidin kondenzasyon reaksiyonuyla elde edilir. Polieter polioller genellikle düşük molekül ağırlıklıdır, propilen oksit ve etilen oksitten elde edilir. Bu tür poliollerde temel bileşen propilen oksittir; etilen oksit poliolün özelliklerini modifiye etmek için az miktarda kullanılır. Poli(etilen adipat) tipik bir polyester poliol, poli(tetrametilen eter) de tipik bir polieter polioldür.

Poliüretan esaslı malzemeler yüksek ısılara ya da aleve maruz kaldıklarında kolaylıklar tutuşup yanabilen malzemelerdir. Poliüretan malzemeler içerdikleri poliol ve izosiyanatların özelliklerine bağlı olarak ön tutuşma, tutuşma, yanma ve yanmanın genişleme safhalarında ortama ısı, duman, zehirli gazlar ve korozyona sebep olan

bileşikler çıkarabilmektedir. Bu durum ise yangınlarda hem ısıl hem de ısıl olmayan problemlere sebep olmaktadır.

Geçen yıllarda, poliüretanların alev geciktiriciliğini arttırmak için katkı-tipi alev geciktiriciler kullanılmıştır. Katkı maddeleri genellikle dolgu maddeleri olarak kullanılır, reaktif bileşenlerin aksine diğer bileşenlerle reaksiyona girmez. Ayrıca katkı-tipi alev geciktiricilerin kullanımı zayıf uyumluluk, kolay süzülme ve mekanik özelliklerinin azalması gibi bir çok dezavantaja sahiptir. Bu nedenle alev geciktiricileri poliüretan yapısına entegre etmek için reaktif-tipi alev geciktiricilerin geliştirilmesine yönelik çalışmalar üzerinde durulmaktadır.

Genel olarak, alev geciktiriciliği arttırmak için fosfor içeren reaktif-tipi alev geciktiriciler kimyasal reaksiyon ile poliüretan ana zincirine dahil edilmiştir. Yapılan çalışmalar poliüretan ana zincirine dahil edilen fosfor elementinin malzemenin termal kararlılığını arttırdığını doğrulamıştır.

Fosfor ve azot elementleri polimerlere yüksek alev geciktirici özellik katar. Ayrıca, fosfin oksit içeren polimerler yüksek termal ve oksidasyon kararlılığı, organik çözücülerde çözünürlük, diğer bileşiklere iyi yapışma ve karışabilirlik gibi birçok avantaja sahiptir.

Fosfor-bazlı reaktif-tipi alev geciktiricilere ek olarak, fosfor-azot alev geciktirici sinerjizmi literatürde belirtilmiş ve fosfor ile azot elementleri arasındaki sinerjik etkiden dolayı sadece fosfor içeren alev geciktiricilere nazaran daha iyi alev geciktirici özellik sergilemiştir.

Bu tez 3 bölümden oluşmaktadır. İlk bölümde 3-aminofenol ile P,P-diklorofenilfosfin oksit reaksiyonundan bis(3-hidroksi aminofenil)fenilfosfin oksit (BHAPPO) sentezlenmiştir. P,P-diklorofenilfosfin oksitteki klor elementleri ile 3-aminofenolün amin grubundaki bir hidrojen atomu reaksiyona girerek BHAPPO bileşiği ve yan ürün olarak ise hidroklorik asit oluşturmuştur. BHAPPO bileşiği içerdiği fosfin oksit ve azot gruplarının sinerjik etkisinden dolayı yüksek alev geciktirici özelliğine sahip bir bileşiktir.

Tezin ikinci bölümünde, alev geciktiricilik için fosfin oksit ve azot gruplarını birlikte içeren BHAPPO bileşiği, poliüretan prepolimer sentezinde diol olarak kullanılmıştır, böylelikle alev geciktirici gruplar kimyasal reaksiyon ile poliüretanın yapısına entegre edilmiştir. Tamamen azot gazı atmosferi altında gerçekleşen poliüretan prepolimer sentezinde farklı konsantrasyonlardaki BHAPPO ve poli(propilen glikol) (PPG) yeterli miktarda asetonda çözülmüştür. Yine asetonda çözülen isoforon diizosiyanat (IPDI) damla damla reaksiyon sistemine eklenmiştir. Reaksiyonun hızlı bir şekilde gerçekleşmesi amacıyla katalizör olarak dibütiltin dilorat (DBTDL) kullanılmıştır. Reaksiyon azot gazı atmosferi altında 65°C'de gerçekleştirilmiştir.

Reaksiyon sırasında numuneler alınarak FT-IR analizi yapılmış ve izosiyanat piki kontrol edilerek polimerleşmenin gerçekleştiği gözlenmiştir.

Film oluşturma, alev geciktiricilik ve mekanik özellikler için optimum oranları belirlemek adına farklı diizosiyanat/diol ve BHAPPO/diol mol oranları kullanılmıştır. Diizosiyanat/diol mol oranları 1 ila 4 arasında denenmiş ve film oluşturma açısından en uygun değer 4 olarak belirlenmiştir. Bu tezdeki bütün çalışmalar diizosiyanat/diol mol oranı 4 olan numuneler üzerinde gerçekleştirilmiştir.

Alev geciktiricilik ve mekanik özelliklerinin karşılaştırılması amacıyla toplam diol üzerinden BHAPPO bileşiğinden molce yüzde olarak 0, 20, 40 ve 60 oranında

kullanılmıştır ve BHAPPO bileşiğinin miktarının poliüretan film üzerindeki etkileri belirlenmiştir.

Üçüncü bölümde, poliüretan prepolimer teflon, silikon, pleksiglas ve cam gibi farklı yüzeyler üzerine metal bir aplikatörün yardımıyla uygulanmış ve farklı kürleme yöntemleri kullanılarak en uygun kürleme koşulları 24 saat oda sıcaklığında ve 24 saat de 75°C etüvde termal kürleme olarak belirlenmiştir.

Kürlemeden sonra serbest filmler plakalardan ayrılmış ve kısıtlayıcı oksijen imleci, parlaklık, jel içeriği, kimyasal direnci, su absorpsiyonu, sarkaç ve kalem sertliği, termogravimetrik analiz ve mekanik ölçümler (çekme direnci, elastik modülü, kopma uzaması ve stres-gerilme) gibi özellikleri incelenmiştir.

Sentezlenen alev geciktirici BHAPPO bileşiğinin kimyasal yapısı FT-IR, ^{1}H-NMR ve ^{31}P-NMR ile karakterize edilmiştir.

BHAPPO konsantrasyonu arttıkça, akma sınırındaki gerilme direnci ve kopma anındaki gerilme direnci kısmen artmış ve kopma uzaması BHAPPO konsantrasyonuyla orantılı bir şekilde azalmıştır. Elastik modülü %40 BHAPPO konsantrasyonuna kadar kısmen artmış, %40'tan sonra aniden artmıştır. Mekanik özelliklere bakıldığında BHAPPO eklenmesi, poliüretan filmlerin elastikiyetini azaltmıştır ve daha sert filmler elde edilmesine sebep olmuştur.

Jel içeriği analizi sonuçlarına göre poliüretan filmin içerdiği BHAPPO konsantrasyonu arttıkça polimer zincirlerinin çapraz bağlanma oranı artmaktadır.

Su absorpsiyonu değerleri BHAPPO konsantrasyonu arttıkça kısmen artmaktadır.

BHAPPO konsantrasyonu arttıkça poliüretan filmlerin parlaklık değeri orantılı olarak azalmakta ve sarkaç sertliği değerleri artmaktadır.

Termogravimetrik analiz, adezyon ve kalem sertliği değerlerinde fazla bir değişim gözlenmemektedir.

Filmlerin kimyasal direnci %10'luk HCl çözeltisinde artmakta, %10'luk asetik asit çözeltisinde sabit kalmakta ve %10'luk NaOH çözeltisinde ise azalmaktadır.

Öngörülenin aksine kısıtlayıcı oksijen imleci (LOI) değerleri azalmaktadır. Poliüretan film içeriğindeki BHAPPO konsantrasyonu arttıkça filmlerin yanma karşısındaki davranışı değişmiş ve eriyik haldeki viskozitesi azalmıştır. Maddenin yanma esnasında erime ve damlama davranışı alevin yayılmasına sebep olmuş ve böylece kısıtlayıcı oksijen imleci değerlerinde azalma gözlenmiştir.

1. INTRODUCTION

Polyurethanes are versatile polymeric material with various advantages such as their excellent abrasion resistance, high toughness, chemical resistance, flexibility and low film-forming temperatures. They have been widely used in coating, foam, adhesives and composites [1-4].

Phosphorus element gives excellent flame retardant properties to polymers. In addition, polymers containing phosphine oxide moieties have many other advantages such as high thermal and oxidative stability, solubility in organic solvents, good adhesion to other compounds and miscibility [1-3].

Over the past decades, additive-type flame-retardants have been used to improve the flame retardancy of polyurethanes (PU). However, the use of the additive-type flame-retardants in PUs has many disadvantages such as poor compatibility, easy leaching and decreasing mechanical properties. Therefore, studies on developing reactive-type flame retardants are emphasized on in order to incorporate the flame retardants into the PU structure. In general, the reactive-type flame-retardants containing phosphorus element were incorporated into the PU backbone to improve the flame retardancy by chemical reaction. A number of studies confirmed that phosphorus element incorporated into the PU backbone increases thermal stability of the material. Zhang L. et al. [5] synthesized a polyol containing phosphorus unit from castor oil and used it in polyurethane foam synthesis. Chiu S. et al. [6] also synthesized flame retardant containing phosphorus and used in polyurethane prepolymer synthesis. Both studies showed a significance increase in limiting oxygen index (LOI) values even with low concentration of the flame-retardant molecule.

In addition to phosphorus-based reactive-type flame retardants, phosphorus-nitrogen flame-retardant synergism system was reported in many literature and exhibited better flame-retardant efficiency than those only containing phosphorus, due to the synergistic effect between phosphorus and nitrogen. Ding H. et al. [7] have synthesized a flame-retardant polyurethane prepolymer containing phosphorus and

nitrogen and this prepolymer was used as a curing agent and reactive-type flame retardant in PU sealant synthesis. This study demonstrated significant enhancements in thermal properties, flame retardancy and combustion properties due to the synergistic effect of phosphorus and nitrogen elements. Zhang M. Et al. [8] have synthesized a reactive-type flame retardant containing phosphorus and nitrogen in order to use in rigid polyurethane foam synthesis which showed high physical and thermal stability and flame retardancy. Limiting oxygen index (LOI) of the material has significantly increased when synthesized with the small concentration (20%) of the phosphorus and nitrogen based flame retardant.

1.1 Purpose of Thesis

This thesis is separated into three sections. In the first section, bis(3-hydroxy aminophenyl)phenylphosphine oxide (BHAPPO) was synthesized by the reaction between 3-aminophenol and P,P-dichlorophenylphosphine oxide. Chlorine elements in P,P-dichlorophenylphosphine oxide reacted with a hydrogen atom in amine group of 3-aminophenol, producing BHAPPO compound and hydrochloric acid as byproduct.

In the second section of the thesis, BHAPPO which contains both phosphine oxide and nitrogen groups for flame retardancy and two phenol groups, was used as a diol in the polyurethane prepolymer synthesis. In PU film synthesis, different concentrations of BHAPPO and poly(propylene glycol) (PPG) was reacted with isophorone diisocyanate (IPDI). Different diisocyanate/diol and BHAPPO/PPG ratios were used in order to determine the optimum ratios for film forming, flame retardancy and mechanical properties.

In the third section, polyurethane prepolymer was applied on surfaces such as teflon, silicone, plexiglass and glass to observe its behavior on different surfaces. Different curing methods such as curing in oven, curing in vacuum oven and curing at room temperature were performed in order to determine the optimum curing conditions. After curing, the free films were separated from the surfaces and various properties such as limiting oxygen index, gloss, gel content, chemical resistance, water absorption, pendulum and pencil hardness, thermogravimetric analysis and mechanical measurements (tensile strength, elastic modulus, elongation at break and stress-strain) were investigated.

2. THEORETICAL PART

2.1 Flame Retardants

Polymeric materials are being used in wide application areas to increase the quality of modern life. However, one of the most important problems arising with their use is that these materials are organic and therefore highly flammable. To increase the performance of polymers against fire, flame-retardants are used. The purpose of the flame retardant is to change the polymer formulation by interfering with the chemistry or the physics of the combustion process in order to make it less flammable [9-12].

2.1.1 History of flame retardants

The interest in the flame-retardants goes back to the discovery of highly flammable cellulose nitrate and celluloid in the 19th century. Since that time, different approaches have been made to overcome high flammability of polymers. These approaches include incorporating nonflammable fillers, compounds that decompose endothermically, substances that provoke char formation and materials that liberate gases acting as radical traps in the gas phase during fire. The halogenated compounds can be given as an example to the last mentioned group. These compounds evolve into hydrogen halides when heated. The incorporation of halogen-based compounds was the most commonly used method for increasing the flame retardancy of polymers, as the mechanical properties of the resulting material do not decrease and due to their low cost. However, concerns about using halogen-based compounds as flame-retardants have been raised since toxic dioxins and furans were formed during the combustion of halogens that were harmful to environment and humans. Since then, the market trend has been changed to usage of halogen-free flame-retardants. However, halogen-free compounds have also some disadvantages including their inefficiency at low concentrations, higher cost and deterioration of mechanical properties of polymer [13-15].

2.1.2 Polymer combustion

Due to their chemical structure, polymers are generally highly combustible. When exposed to sufficient heat, they decompose and generate combustible gases that mix with the oxygen of the air to form an ignitable blend. Ignition can occur either impulsively at autoignition temperature (defined as the temperature at which the activation energy of the combustion reaction is achieved) or at a lower temperature called flash point due to the presence of an external ignition source such as flame or spark. After combustion, a part of the combustion heat is transferred to the substrate causing further decomposition. If the heat evolved is enough to keep the decomposition rate of the polymer above that required to maintain the concentration of the volatiles within the flammability limits, then a self-sustaining combustion cycle is established (Figure 2.1). In order to establish the fire triangle, which is necessary for a sustained fire, three elements should be present: fuel (combustible volatiles generated from a thermally degrading carbon rich substance), heat (supplied by an external source or by the exothermic oxidative decomposition of the fuel) and oxygen (provided by the air) [16-17].

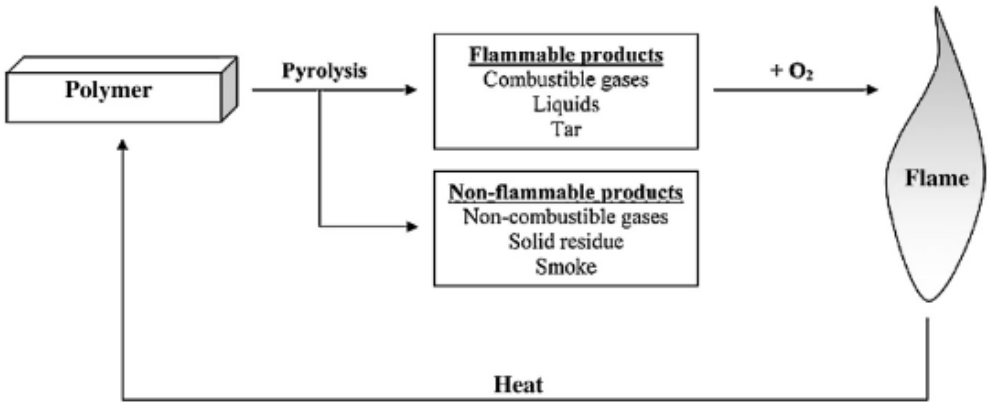

Figure 2.1 : The combustion cycle of polymers [17]

Physical characteristics of the polymer determine the amount of heat needed to initiate combustion. In particular, ignitability basically depends on the rate that the surface of the polymeric material reaches the temperature required for ignition. Therefore, the energy stored by the polymer during its exposure to a heat source is associated with its heat-storage capacity, enthalpy of fusion and degree of

crystallinity. For example, heating thermosetting polymeric materials does not lead to simple phase changes therefore they do not melt; thus, heating them leads directly to decomposition. Amorphous thermoplastics behave the same way in the case of heating due to the absence of melting point. Semicrystalline thermoplastics, on the other hand, they become soft on heating, they melt and drip, removing a part of the heat from the polymer surface. This behavior increases the fire retardancy of polymers that do not char upon combustion. Despite this, these types of polymers may ignite easier at a higher heat exposure as ignition may occur before the surface is heated to adequate depth for the melted material to drip [16-18].

Whereas ignition is mainly related to the initial temperature of polymer decomposition, steady combustion is typically connected to the tendency of the polymer to yield char at the expense of combustible volatiles. Therefore, when designing the strategy of flame retardancy enhancement of the polymers, the degradation pathway of the material is significant. The most important mechanisms of polymer thermal decomposition are the following: (1) random chain scission, in which the polymer chains split at random locations into smaller fragments; (2) chain-end scission, where individual monomer units are successively removed from the chain ends; (3) chain stripping, during which elimination of atoms not part of the polymer chain or pendant groups are cleaved without the breaking of the backbone; and (4) cross-linking, in which bonds are created between polymer chains. In most cases, the thermal decomposition of a polymer involves more than one of these reaction mechanisms [18-20].

Generally, the combination of the effects of both heat and oxygen determines the degradation pathway of a polymeric material. Degradation can be therefore classified into nonoxidizing thermal degradation and oxidizing thermal degradation. In the first case, chain scission takes place due to the individual effect of temperature, leading to varying degrees of material depolymerization. The main factors effecting initial scission include the presence of oxygen atoms in the polymer backbone, the existence of catalyst residues, and/or former residues of oxidation, and the presence of the chemical defects (e.g. weak bonds) in the polymer chains. In oxidizing conditions, the polymer reacts with the oxygen of the air, generating low molecular weight products (carboxylic acids, alcohols, aldehydes, etc.), and/or very reactive

species, (H• and OH• , which confer a high velocity on the flame front resulting in rapid flame spread). Through recombination reactions of the macromolecular radicals, oxidative thermal degradation can lead also to cross-linking. In terms of flammability, polymers undergoing random scission and depolymerization are usually more flammable than polymers, which experience cross-linking or pendant group elimination upon heating. The latter two mechanisms (cross-linking and pendant group removal) result in the production of species, which acting as precursors of char, reduce flammability. The char development proceeds basically through four stages: (1) cross-linking, (2) aromatization, (3) fusion of aromatics, and (4) graphitization. The tendency of a polymer to form char during heating depends principally on its structure. For instance, polymers with short flexible bonds between aromatic rings are inclined to cross-linking and, thus, charring. Nonetheless, polymers, without inherent inclination to cross-link, can undergo charring through the addition of specific flame retardants [21,22].

2.1.3 Strategies of flame retardancy

Successful strategies to improve the fire performance of a polymeric material includes interrupting the combustion process at one or more of its complex stages, with the purpose of inhibiting ignition, decreasing the burning rate and/or changing the combustion mechanism. In essence, the main goal is to eliminate one of the three required factors of fire: (1) the combustible substance or fuel, (2) the heat supplied either externally or from the combustion process itself or (3) the oxidizing gas (primarily oxygen).

In practice, this is accomplished either (1) by the mechanical blending of a suitable flame-retardant compound with the polymeric material during the transformation process or (2) by the chemical incorporation of the flame retardant into the polymer during synthesis (by copolymerization) or through chemical modification of the preformed polymer (chemical grafting using a reactive component). The first category of flame-retardants are called additive flame retardants and they are designed not to react with the polymer at the stage of blending but only at higher temperatures, at the beginning of a fire. On the other hand, reactive flame-retardants, which comprise the second category of flame-retardants, are integrated in the polymer chains by covalent bonds. This is why they offer several advantages over

additives types. More specifically, due to the fact that their incorporation takes place at the time of polymerization, they can be homogeneously dispersed preventing the formation of separate phase, which causes problems during the processing of the polymer into final plastic product. Additionally, since “mixing” occurs at the molecular level, reactive flame retardants are inherently immobile within the polymer, being thus less prone to loss through migration to the polymer surface (called blooming) or due to solvent leaching. Moreover, lower concentrations are needed to achieve the desired level of flame retardancy; therefore, the overall properties of the polymer are less likely to be adversely affected. Despite these merits of the reactive ones, the additive flame-retardants are more commonly used; the reasons behind their popularity are wider applicability and lower cost. More particularly, the reactive modification of chain-growth polymers is less readily accomplished than for step-growth polymers. Furthermore, extensive reactive modification of a partly crystalline polymer is likely to result in a considerable reduction of crystallinity (additive flame retardants end up in the amorphous phase). Besides, reactively modifying polymers for which commercially well-established methods for manufacturing already exist would lead to a significant increase of expenses [23-25].

Regardless of their type (additive or reactive), flame retardants, depending on their nature, interfere with the combustion cycle through physical or chemical modes of action (Figure 2.2). The main underlying physical mechanisms for hindering combustion are the following:

• Promotion of endothermic reactions (heat sink), which cool the substrate to a temperature below that required to maintain combustion.

• Generation of inert gases, which dilute the oxygen supply at the surface of the burning polymer, resulting in flame snuffing because of lack of oxidizing agent.

• Formation of a protective impermeable coating, which decreases the amount of heat transferred to the polymer, hampers the diffusion of oxygen to the area of decomposition, and impedes the escape of volatile flammable gases generated during polymer decomposition.

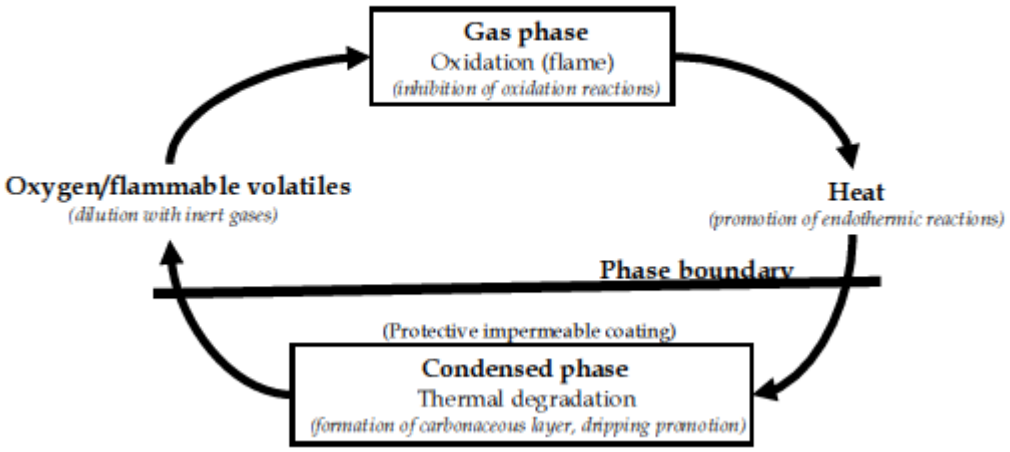

Figure 2.2 : Combustion/flame retardation cycle [9]

On the other hand, the following are the chemical modes of action by which flame-retardants operate:

• Inhibition of the oxidation reactions, which occur in the gas phase, through trapping of free-radical species (especially, H• and OH•) evolved as a consequence of polymer degradation. Hydrogen radicals are responsible for the chain-branching reaction which propagates the combustion of fuel ($H• + O_2 \rightarrow OH• + O•$) while hydroxyl radicals is involved with the most exothermic reaction ($OH• + CO \rightarrow H• + CO_2$) of polymer decomposition, which provides most of the energy needed to preserve the flame. These highly reactive species react with specific radicals released by the flame-retardants to form less reactive or even inert molecules.

• Formation of a carbonaceous (or vitreous) layer on the polymer surface by promoting low-energy solid-state reactions, which lead to the carbonization of the polymer at the expense of volatiles production. This layer acts as a physical insulating barrier between the gas phase and the condensed phase.

• Acceleration of polymer degradation, causing pronounced dripping and, thus, the withdrawal of the fuel from the flame source. Additives operating through this mode of action are usually not preferable; they can be used however for the qualification of a polymeric material under the UL94 protocol [26-29].

Generally, the abovementioned mechanisms do not take place separately but in combination. Therefore, the way in which a flame retardant acts is usually a complex process consisting of individual stages, among which one is the dominating. The criteria for selecting a suitable additive for each case are based on a variety of factors, the most important of which are the following:

• The effectiveness of the flame retardant in the particular polymer matrix.

• The stability of the flame retardant in the processing conditions of the polymer.

• The compatibility and the ability of the additive to protect the physical properties of the polymer (mechanical properties, electrical performance, color, etc.).

• The cost efficiency.

• The toxicity of the flame retardant together with its tendency to migrate and/or to cause corrosion [21,24].

Speaking about toxicity, the public concern and the (increasingly) prohibitive legislation with regard to the persistent, bioaccumulative and toxic nature of several halogen-based compounds have divided flame retardants into two categories: halogenated and nonhalogenated. The class of halogen-free compounds is further disintegrated into smaller categories; the most frequently referred in literature are phosphorus-based flame-retardants, nitrogen compounds, intumescent systems, mineral flame-retardants (metal hydroxides and born compounds), silicon-based additives, and nanoparticles. Even though intumescent systems usually contain phosphorous and nitrogen substances, they perform differently than their individual counterparts; therefore, they comprise a separate class of flame-retardants.

2.1.3.1 Phosphorus-based flame retardants

The phosphorus-containing substances comprise, value-wise, one of the most commonly used groups and probably the fastest growing segment of flame-retardants due to their versatility and the increasing environmental awareness of the problems arising from the use of halogen-based additives. Since the element exists in several oxidation states, the range of phosphorus-containing flame-retardants is extremely broad, allowing a wide variety of applications. Phosphorus-based chemicals are employed for enhancing the fire performance of thermoplastics, thermosets, textiles, paper, coatings, and mastics. They can be added in the polymer by simple blending or they may be incorporated into the polymer chains through homopolymerization, or copolymerization. Their flame-retardant mechanism depends on the type of phosphorus compound, the chemical structure of the polymer, and the fire exposure conditions. Phosphorous compounds can function through various mechanisms, in the condensed polymer or in the gas phase, and possibly in both phases concurrently. Regarding the operation in the condensed phase, it is generally accepted that

phosphorus flame-retardants are notably more efficient in oxygen- or nitrogen-containing polymers, which could be either heterochain polymers or polymers with these elements in pendant groups. By generating anhydrides of phosphoric and related acids, which act as dehydrating agents, phosphorous compounds react with these polymers promoting char formation (dehydration reactions lead to the formation of double bonds, which at elevated temperatures result in cross-linked or carbonized structures). In general, the chemical reactions involved in the decomposition of the matrix are redirected in favor of those yielding carbon rather than CO or CO_2. The charring mode of action of phosphorus can be exploited even in the case of poor char forming polymers, such as polyolefins and styrenics, through the introduction of a char forming additive. The acids evolved during the degradation of phosphorous-based chemicals can also form a thin glassy or liquid protective coating on the condensed phase, lowering thus the oxygen diffusion, as well as the heat and mass transfer between the gas and the condensed phase.

This glassy residue may also coat the char making it more strong and cohesive, thus delaying its collapse. Even if the char does undergo oxidation (usually by smoldering), the presence of a phosphorus compound tends to inhibit complete oxidation of the carbon to carbon dioxide, thus decreasing the exothermic heat of combustion (heat sink). In some cases, phosphorus compounds have been reported to act under fire-exposure conditions by evolving acids, which catalyze the thermal degradation of the polymer matrix. Hence, the melt viscosity is reduced and the flow (dripping) of the molten polymer away from the fire zone is facilitated, withdrawing the fuel that feeds the flame [17,30-32].

Besides retarding the progress of fire in the condensed phase, phosphorus additives may well perform in the gas phase exhibiting free-radical trapping properties. Volatile phosphorus compounds are among the most efficient inhibitors of combustion. They liberate species that cause the hydrogen atom concentration in the flame to be reduced, thus quenching the flame. The step in the flame chemistry, which is inhibited, is the same step hampered by the scavenging effect of halogens: the rate controlling branching step involving the reaction of a hydrogen atom with an oxygen molecule to yield a hydroxyl radical and an oxygen atom. In fact, phosphorus is, at the same molar concentration, much more effective radical scavenger than bromine and chlorine. Some key reactions, of the hundreds possible, that have been

proposed as the ones governing the gas phase action of phosphorous-based additives are the following:

$$PO\bullet + H\bullet \rightarrow HPO$$

$$PO\bullet + OH\bullet \rightarrow HPO_2$$

$$HPO + H\bullet \rightarrow H_2 + PO\bullet$$

$$OH\bullet + H_2 + PO\bullet \rightarrow H_2O + HPO$$

$$HPO_2\bullet + H\bullet \rightarrow H_2O + PO$$

$$HPO_2\bullet + H\bullet \rightarrow H_2 + PO_2$$

$$HPO_2\bullet + OH\bullet \rightarrow H_2O + PO_2$$

In spite of the fact that there is a scarcity of detailed investigations in the flame zone identifying the intermediate products and monitoring the concentrations of the different species generated, the main principle seems to have been understood: it is believed that the PO radical plays the major role. However, the vapor-phase action of phosphorous compounds does not necessarily have to involve flame chemistry. Flame inhibition via a physical means of action, based on heat capacity and heat of vaporization, and, probably, endothermic dissociation in the gas phase, may also be important during the flame retarding process. In particular, it has been shown that in certain cases phosphorus compounds, besides their modes of action mentioned above, result in flame retardation also by virtue of their heat of vaporization and heat capacity [33-36].

Phosphorous-based flame-retardants can be either inorganic or organic. The most commonly used inorganic compounds are red phosphorous and ammonium polyphosphate. The latter is mainly employed in intumescent formulations. Red phosphorus, typically manufactured as a red black powder, is the simplest and most concentrated source of phosphorus for flame retardancy. Added just in small quantities, it is very effective in a wide range of polymeric systems including polyolefins, polyamides, polyesters, and thermosetting resins. In Europe, it is used in electrical parts (e.g. electrical switches) molded from glass-filled nylon. Red phosphorous is believed to act principally in the solid phase through the formation of phosphoric acid, although some evidence also suggests free-radical scavenging.

Except its red color that impairs the optical homogeneity of the polymer matrix, the main disadvantage of red phosphorus is its propensity (attributed to its poor thermal stability) to react with water (moisture) during melt compounding, releasing the highly toxic phosphine (PH_3). An efficient route of minimizing the trace amounts of phosphine involves the incorporation of metal oxides (such as copper oxide, cadmium oxide, or zinc oxide), which transform phosphine into phosphoric acid. Alternatively, prior to use, red phosphorus can be coated with a resin [30].

The organic phosphorus-containing compounds exhibiting flame-retarding characteristics are numerous, yet only few of them have met commercial success. Three are the major groups of organic phosphorus fillers that are commonly used: (1) phosphinates, (2) phosphonates, and (3) phosphate esters (Figure 2.3).

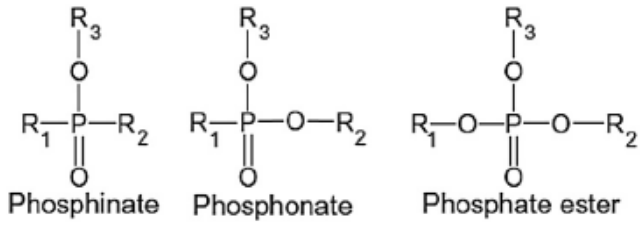

Figure 2.3 : Chemical structures of commonly used organic phosphorus flame retardants

Triethyl phosphate is an organic phosphate used in practice for enhancing the flame retardancy of polyester laminates and in cellulosics. Cycloaliphatic phosphates, such as pentaerythritol phosphates, which take advantage of the char forming ability of the pentaerythritol structure, are also employed. Aryl phosphates comprise an additional group of organic phosphates. Triphenyl phosphate is a representative of this group; it is used as a flame-retardant additive for engineering thermoplastics such as polyphenylene oxide-high impact polystyrene and acrylonitrile butadiene styrene(ABS)-polycarbonate blends. The improvement of the flame retardancy of ABS-polycarbonate blends (as well as of thermoplastic polyesters, polyamides, and polycarbonates) can be achieved also with a member of the “aromatic diphosphates” family, precisely tetraphenyl resorcinol diphosphate. Turning to phosphonates, dimethyl methylphosphonate has been employed as a flame retardant in aluminum trihydroxide (ATH)-filled polyester resins. On the other hand, aluminum diethylphosphinate, belonging to the class of phosphinates, has been used in combination with a melamine for improving the fire performance of polyamides,

PBT, and epoxies. Apart from the abovementioned compounds, halogenated phosphorous flame-retardants constitute a broadly used group, since they combine the properties of both the halogen and the phosphorus components. Two examples of compounds of this category are tris(chloropropyl)phosphate and tris(2-chloroethyl)phosphate. The phosphorous flame-retardants, as mentioned, can be incorporated in the polymer either as additives or as reactive (co-)monomers. Simple reactive phosphate monomers, linear polyphosphazenes, and aromatic cyclic phosphazenes have attracted most attention as reactive flame retardants; however, none of them has been commercially exploited [13,31,37].

2.1.3.2 Nitrogen-based flame retardants

Nitrogen-containing compounds comprise one of the most environmentally benign classes of flame-retardants, producing low amounts of smoke, and no dioxin and/or halogen by-products during combustion. They also present several very important advantages over halogen-based compounds and red phosphorus owing to their chemistry, which is very similar to that of most polymers themselves. In addition, polymeric materials including nitrogen-based flame retardant have been shown to be suitable for recycling. Nitrogen compounds of principal interest as flame-retardants are melamine, melamine derivatives, and related heterocyclic compounds. Nitrogen-containing flame-retardants have been used for enhancing the fire performance primarily of polyamides and secondarily of polyolefins (and polyurethanes), but usually they are not very effective in other polymers alone [38].

Melamine (2,4,6-triamino-1,3,5-triazine, $C_3N_6H_6$) is a thermally stable crystalline product, produced by urea. Like cyanamide, it contains 67% nitrogen by mass and it is characterized by a melting point as high as 345 °C. The flame retardant actions of this inexpensive solid originates from the ability of melamine to sublimate (melt with vaporization) at about 350 °C, absorbing a significant amount of heat, thus decreasing the temperature of the degrading polymer's surface exposed to fire. At high temperature (or if evaporation is constrained), melamine decomposes evolving ammonia (which dilutes oxygen and combustible gases) and leads to the formation of the thermally stable condensates melem (2,5,8-triamino-1,3,4,6,7,9,9b-heptaazaphenalene), melam ((N-4,6-diamino-1,3,5-triazin-2-yl)-1,3,5-triazine-2,4,6-triamine), and melon (Poly(8-amino-1,3,4,6,7,9,9b-heptaazaphenalene-2,5-diyl)imino). The evolution of melam, melem, and melon is accompanied by the

generation of residues in the condensed phase, resulting in the occurrence of endothermic processes, also effective for flame retardancy. Melamine is occasionally used by itself as a flame retardant (at levels of 3-20 phr, it has been found to endow nylon 6, 6.6, and 6/6.6 blends with V0 rated performance), but more often it is employed as a blowing agent and flame-retardant adjuvant in intumescent coatings, elastomers, and plastic formulations as well as in flexible polyurethane foams [23,39].

Melamine is a weak base, which can form well-defined, thermally stable salts, with both organic and inorganic acids. The salts, having been found to possess flame retardant characteristics, and for that reason, commonly used in practice for improving polymer fire behavior, are melamine cyanurate, melamine phosphate, and melamine pyrophosphate. The latter two operate as intumescent compounds during combustion, and their mode of action is discussed in the following section. Melamine cyanurate (salt of melamine and cyanuric acid), the chemical structure of which is shown in Figure 2.4, on the other hand, has been reported to act in a completely different manner.

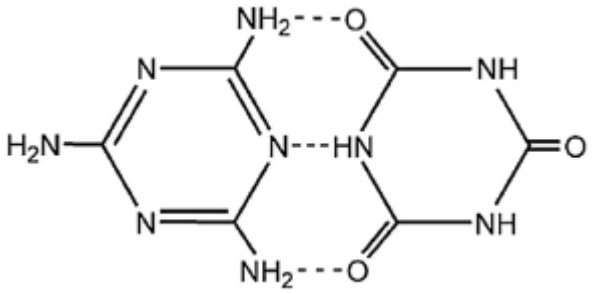

Figure 2.4 : Chemical structure of melamine cyanurate

In particular, it has been demonstrated that melamine cyanurate degrades polyamides at burning conditions promoting enhanced noncombustible flow dripping; hence, the polymer is withdrawn from the flame source not providing fuel to feed the fire. It also interferes with the combustion cycle in a physical manner, functioning as a heat sink and as an inert gas source. More specifically, its initial endothermic dissociation followed by the sublimation of the produced melamine and the subsequent degradation of melamine vapors absorb the generated heat, cooling the substrate. Furthermore, the inert gases produced contribute additionally to flame retardancy by diluting the oxygen and the flammable gases. Similar action to that of melamine cyanurate has been reported also in the case of melamine oxalate and melamine

phthalate. However, melamine cyanurate is the leading flame retardant for unfilled PA6 and PA6,6, being quite more efficient (lower quantity of the flame retardant is needed) in the case of the PA6,6. This difference is associated to the degradation mechanisms of these two polymers: the degradation products of PA66 (cyclopentanone) may cross-link with the decomposition products (mainly NH_3) of melamine cyanurate, yielding in less flammable high molecular weight structures. On the contrary, PA6 decomposed to less reactive compounds that do not cross-link. Though efficient for nonreinforced polymers, melamine cyanurate is relatively ineffective for filled compositions like glass-fiber-reinforced polymeric materials; glass fibers act as a "wick" and retard melt flow thus holding the polymer in place to fuel the flame [40-42].

The majority of melamine salts operate in the condensed phase. A rather different mode of action was found by using N-alkoxy or cycloalkoxy derivatives as flame-retardants forming radical species during decomposition. These compounds are effective for enhancing the performance against fire mainly of polypropylene and polyethylene films, and in several cases of polypropylene moldings, polyurethane adhesives and polystyrene. This novel family of nitrogen-based flame-retardants was discovered by the inventors of Ciba Specialty Chemicals (now BASF), who were the first that realized that alkoxyamines can individually act as flame-retardants without the assistance of other additives (synergists). Alkoxyamines are typically synthesized from the corresponding sterically hindered piperidine via the nitroxyl intermediate through reaction with a hydrocarbon; to facilitate this reaction, the presence of an organic peroxide (e.g. peracetic acid), a hydrogen peroxide, molybdenum oxide or iodide is needed. They were first introduced as UV stabilizers for providing protection against oxidation in automotive coatings and agricultural films. However, it was unexpectedly found that they do not only improve the UV stability of these materials but they also contribute to their fire performance, even when solely added. Their activity is based on the thermolysis of nitroxyl ethers, during which either alkoxy and aminyl radicals or alkyl and nitroxyl radicals are formed interfering with the free radical chemical reactions taking place during the combustion process. Alkoxyamines have also been reported to synergize with conventional flame-retardants, including brominated, phosphorus, and inorganic compounds, enhancing further their flame retarding action. The first commercial product exploiting the fire retarding characteristics of alkoxyamines was put on the market in 2000 by Ciba

under the trade name Flamestab NOR 116 (its structure includes an N-cyclohexyloxy-2,2,6,6-tetramethylpiperidinyl group attached to an oligomeric polymer chain). Since then, further research has been focused on a series of different Nalkoxy hindered amines as well as on nitrogen compounds able to generate free radicals during combustion like azoalkanes [43-45].

Another nitrogen-containing formulation, exhibiting flame retardant properties, is the oxazene resin; it can be used either as homopolymer or as a reactive additive in epoxies, presenting, compared to brominated epoxy resins, superior mechanical and electrical properties, good processing characteristics, and low toxicity and corrosiveness, in addition to elevated flame retardancy. Poly(isocyanurate)s (PICs) also present inherent flame retardancy, owing to their cyclic structure. Nevertheless, it is especially effective when combined with phosphorus containing epoxy resins. Epoxy resins generally exhibit an LOI of 20; quite recently, a route for producing phosphazene-triazine formulations achieving LOI between 32 and 38 was reported. These polymers, through a condense-phase mode of action, develop a charred coating on their surface during combustion preventing the substrate from further degradation. Formulations, produced via the polycondensation of macrocyclic chloric cyanure chloride with aromatic diamines or diols, have also been proposed to possess promising fire properties. It has been, accordingly, shown that the inclusion of -NH- linkages in the polymer chain comprises an effective means of enhancing polymer flame retardancy. Moreover, the co-presence of metals (Cu, Co, and Ni) results in further increase of thermal stability [13,46,47].

2.1.3.3 Interactions between phosphorus and nitrogen containing flame retardants

Phosphorus-nitrogen synergistic behavior plays an important role in the flame retardancy of polymeric material. Nitrogen-containing additives such as urea, cyanamides, dicyandiamide, guanidine salts, melamine and its derivatives have limited flame retardancy when used separately however, they synergistically improve the flame retardancy behavior of phosphorus-containing flame-retardants when used together [48].

Several theories have been proposed for the phosphorus-nitrogen synergism on polymeric materials. One theory hypothesized that the nitrogen-containing species

react with fire retardant phosphorus species to form reactive P-N bonds that could phosphoxylate polymer more efficiently. The formation of P-N bonds is an undeniable fact, as it was observed from the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrum of charred flame retardant cotton, but the higher the reactivity of P-N bonds with cellulose may not be true. The flame retardant efficacy of phosphoramidates (triethylphosphoric triamidate, m.p. 60°C, b.p. 240°C; tri-n-butylphosphoric triamidate, m.p. 65°C, b.p. 340°C) may be attributed to their higher boiling points than the analogous phosphates (phosphoric acir triethyl ester, b.p. 216°C; phosphoric acir tripropyl ester, b.p 252°C; phosphoric acid tributyl ester, b.p. 289°C). Higher boiling points of phosphoramidates make them more likely to be retained in cellulose during the combustion process and thus exhibit better a condensed-phase mechanism. Also the presence of nitrogen additives like urea, guanidine carbonate and melamine formaldehyde would result in alkaline media during the combustion process, in which the P-N bond is more difficult to be hydrolyzed than the P-O bond. The PN bond is easier to hydrolyze under acidic conditions. The decomposition of nitrogen additives like urea, guanidine salts and melamine derivatives leads to production of bases like ammonia. The presence of nitrogen additives improves char content and phosphorus retention on the substrate during the combustion process [49].

2.1.4 Challenges posed by replacing halogen-containing flame retardants

The challenges finding alternative halogen-free flame-retardants are comprised of overcoming their possible low flame retardant efficiency, high cost, serious melt-dripping behaviors and deterioration in mechanical properties.

• *Lower flame-retardant efficiency:* Acrylonitrile-butadiene-styrene copolymer (ABS) can reach an acceptable flame-retardant value with the addition of 60 wt% of a halogen-free flame retardant called alumina trihydrate (ATH) although with only 20 wt% or less of halogen-containing flame retardants can achieve the same results.

• *Deterioration in mechanical properties:* The need for usage of halogen-free flame-retardants in high amounts gives rise to deterioration of mechanical properties of polymers. For the ABS with 60 wt% ATH example, the impact and tensile strengths of the ABS decrease more than 50%.

• *Increased product cost:* For some low-cost flame-retardants, high loadings are necessary in order to obtain good flame retardancy, which leads to increased cost.

• *More serious melt-dripping behaviors:* Melt dripping is a common phenomenon for most of melting-processed polymeric materials such as polyethylene, polypropylene, polyethylene terephtalate and so on [50]. We will discuss this subject more detailed in the next title.

2.1.5 Melt-dripping behavior of polymers

The melting and flaming drops can either remove the polymer fuel from the burning region and hence stop further burning or can become secondary source of ignition. Generally, resolution of the melt-dripping problem is more difficult than improving their flame retardancy. In polymers, a conflict often exists between reducing both melt dripping and polymer flame retardancy together since promotion of melt dripping increases energy removal from the flame zone and confers a physical flame retarding effect [50].

It is accepted that there are four mechanisms by which polymers undergo thermal degradation: chain scission, end chain scission, chain stripping and cross-linking. Polymers pyrolysing through random chain scission such as polyethylene, are reported to form small size drips, whereas those pyrolysing by unzipping reactions, such as poly(methyl methacrylate) result in large size drips in fires. It is believed that the critical material parameter for melt dripping is viscosity. As the temperature rises, the viscosity of a thermoplastic polymer decreases both by increased mobility of the polymer molecules and degradation of the polymer due to breaking of bonds and leaving shorter polymer chains. Hence, viscosity is a function of both temperature and molecular weight. The addition of flame retardant or other additives influences the viscosity of the pyrolysing melt and hence, the melt dripping behavior of the polymer [51].

2.2 Polyurethanes

Polyurethanes include polymers containing a significant number of urethane groups, regardless of the composition of the rest of the molecule. For instance, a typical polyurethane may contain, in addition to urethane groups, aliphatic and aromatic hydrocarbon, ester, ether, amide, and urea groups.

Polyurethanes are the most versatile of all polymers. Their applications include diverse types of foams, (soft and rigid), coatings, adhesives, sealants, and elastomers. Although the number of chemicals is small, the molecular weight of the reactants and the method of polymer formation can be varied widely to meet the desired properties of the final product.

There are four basic reactions that chemists employ to make polyurethanes. The reaction of isocyanates with hydroxyl groups to produce urethane is the primary reaction. The reaction of isocyanates with amines yields urea; and the reactions of isocyanates with urea and urethane produce biurets and allophanates, respectively [52].

2.2.1 Reaction of isocyanates with alcohols

Isocyanate groups react with polyfunctional active hydrogen compounds to give high molecular weight polyurethane products. One of the most important reactions of isocyanate compounds is with di- or polyfunctional hydroxyl compounds, e.g. hydroxyl terminated polyesters or polyethers (Figure 2.5). The functionality of the hydroxyl-containing compound as well as of the isocyanates can be increased to three or more to form branched or cross-linked polymers. Different degrees of reactivity are expected from different compounds. This is also affected by the steric hindrance of either the isocyanate or the active hydrogen compounds.

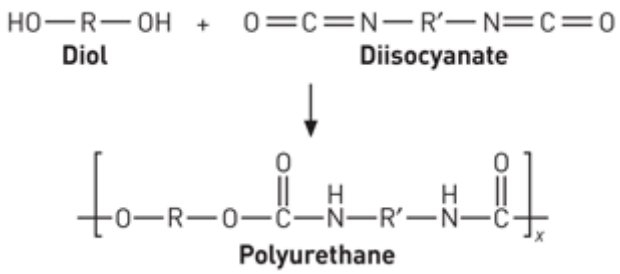

Figure 2.5 : Reaction of diisocyanates with diols

The reaction proceeds at ambient temperatures without the use of catalysts. Reactivity is higher for primary alcohols, decreasing for secondary, tertiary, and aromatic alcohols [52].

A polymer is rarely isolated in this form due to the isocyanate functionalities as end groups. Regardless of the process, these end groups must continue to react (by the addition of water and/or a catalyst) to complete the process. This is called

prepolymer. It is reacted with catalysts to complete the formation of a true polyurethane via several methods. The first is based on the fact that isocyanate groups will, in time, react with one another. Thus, even the most carefully controlled prepolymer has a shelf life. Water, acid, and temperature must all be kept to a minimum to extend the useful life of a prepolymer.

Normally, however, you will want to continue the reaction in a controlled manner. The conduct of that reaction will depend on the composition of the prepolymer and the intent of the device under study. If a prepolymer is hydrophilic (the polyol being polyethylene glycol), curing might be done by the addition of water. The nature of a hydrophilic prepolymer permits the addition of large amounts of water. The isocyanate reacts with the water to abstract CO_2. The amine that also results from the reaction then reacts with an isocyanate group to produce a urea linkage. The reaction continues until the water or the isocyanates are consumed. If provisions are made to trap the CO_2 in the mass, a foam is produced. If such provisions are not made, the CO_2 will bubble away, leaving behind a low gel-strength hydrogel. Careful examination of the resultant molecule might cause one to rename it a polyurethane/polyurea.

2.2.2 Diisocyanates

It was not until the 1930s that the work of Caruthers in the U.S. and Bayer in Germany led to the development of polymers based on diisocyanates and triisocyanates. The first polymers were based on diamines; the technology quickly shifted toward polyethers and polyesters. Isocyanate development after the 1930s has focused on aromatic isocyanates, more specifically on two molecules and close variations. The molecules are toluene diisocyanate (TDI) and its isomers and methylene-bis-diphenyl diisocyanate (MDI) in monomeric and polymeric forms (see Figure 2.6). As a general rule, TDI makes flexible polyurethanes and MDI produces stiffer polymers.

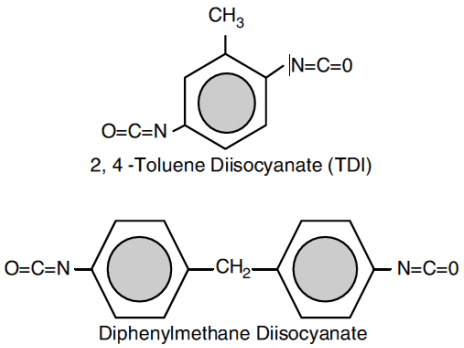

Figure 2.6 : Most common commercial diisocyanates

MDI offers a number of advantages. First, it is somewhat safe to use based on its much lower vapor pressure and is available in convenient forms. It is produced by the reaction of an amine and phosgene. The result is a mixture of multi-ring isocyanates. The isomer is recovered by distillation. What is left behind is the so-called polymeric MDI that is sold commercially.

As a general rule, the isocyanates are hard segments that impart rigidity to the polymer. The polyol is the so-called soft segment. The various molecular weights (more correctly equivalent weights available in the form of polymeric MDIs) provide certain advantages. Table 2.1 lists a few commercially available polyisocyanates and their physical properties.

Table 2.1 : Commercially available diisocyanates

Designation	Formula	Molecular Weight	Melting Point
2,4-Toluene diisocyanate (TDI)	$C_9H_6O_2N_2$	174.2	21.8
Diphenylmethane-4,4′-diisocyanate (MDI)	$C_{15}H_{10}O_2N_2$	250.3	39.5
1,6- Hexane diisocyanate (HDI)	$C_8H_{12}O_2N_2$	168.2	–67
Hydrogenated MDI	$C_{15}H_{18}O_2N_2$	258.3	30
Isopherone diisocyanate (IPDI)	$C_{12}H_{18}O_2N_2$		–60
Naphthalene diisocyanate (NDI)	$C_{12}H_6O_2N_2$		127

2.2.3 Polyols

Since the early days of polyurethane discovery, the technology has focused on isocyanate reactions with polyesters or polyethers. The polyesters of interest to polyurethane chemists terminate in hydroxyl groups and are therefore polyols produced by the polycondensation of dicarboxylic acids and polyols.

The polyethers are more easily designed when the polarity of the backbone is important. For instance, one can use polyethers to construct polyurethanes that are

hydrophilic or hydrophobic or react to water at all levels between these extremes. Polyethers permit the development of biocompatible and hemocompatible devices. Lastly, they are more hydrolytically stable and so are more appropriate for environmental studies.

Polyethers are typically products of base-catalyzed reactions of the oxides of simple alkenes. More often than not, ethylene oxides or propylene oxides and block copolymers of the oxides are used. A polypropylene oxide-based polymer is built and then capped with polyethylene oxides. An interesting aspect of this chemistry is the use of initiators. For instance, if a small amount of a trifunctional alcohol is added to the reactor, the alkylene oxide chains grow from the three alcohol end groups of the initiator. Suitable initiators are trimethylol propane, glycerol or 1,2,6 hexanetriol. The initiator is critical if one is to make a polyether foam.

Propylene- and ethylene-based polyols are produced for physical reasons and will serve as the backbone. The scope of polyethers and polyesters is much broader when willing to sacrifice some physical strength to gain a chemical advantage. For example, castor oil was a common polyol for the production of polyurethanes. It was replaced by less expensive and more predictable polyols in commercial production. Mixed polyols can be used to advantage.

The use of polyethers in polyurethanes is relatively recent. The first reports were based on experiments with copolymers of ethylene oxide (EO) and propylene oxide (PO). This discussion of polyols is important because polyols provide us with opportunities for chemical designs. Polymerized polyethylene glycol could be used as a solvent extraction medium. In this sense, the isocyanate is simply a means to an end. If other immobilization techniques were as cost effective and simple, they would serve as well [53].

3. EXPERIMENTAL PART

3.1 Materials

3-Aminophenol (M_w = 109.13 g/mol) is purchased from Sigma Aldrich. Chemical structure of 3-aminophenol is shown in Figure 3.1.

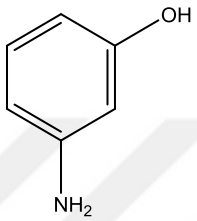

Figure 3.1 : 3-Aminophenol

P,P-Dichlorophenylphosphine oxide (M_w = 194.98 g/mol, density = 1.375 g/ml) was purchased from Merck. Chemical structure of P,P-dichlorophenylphosphine oxide is shown in Figure 3.2.

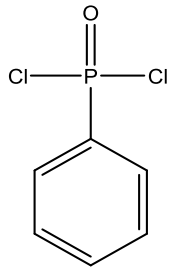

Figure 3.2 : Dichlorophenylphosphine Oxide

Poly(propylene glycol) (M_w = 2000 g/mol, density = 1.01 g/ml) was purchased from Arcol. Chemical structure of poly(propylene glycol) is shown in Figure 3.3.

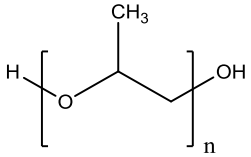

Figure 3.3 : Poly(propylene glycol)

Isophorone diisocyanate (M_w = 222.288 g/mol, density = 1.056 g/ml) was purchased from Bayer. Chemical structure of isophorone diisocyanate is shown in Figure 3.4.

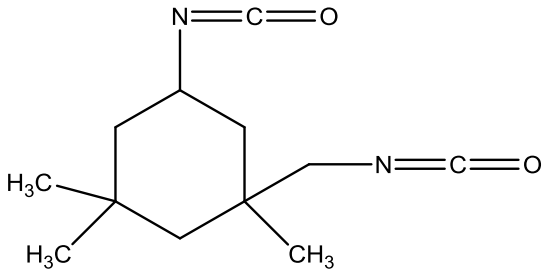

Figure 3.4 : Isophorone diisocyanate

Pyridine (M_w = 79.10 g/mol, density = 0.978 g/ml), ethyl alcohol and acetone (purity ≥ 99.8%) were purchased from Merck. Tetrahydrofuran was purchased from VWR Chemicals. Dibutyltin dilaurate (DBTDL) was used as a catalyst during polymerization. All the products were used without further purification or drying.

Teflon, silicone and plexiglass plates were used for producing films with a metal applicator that has 120μm film thickness.

3.2 Characterization

3.2.1 FT-IR analysis

Room temperature infrared spectrum of bis(3-hydroxy aminophenyl)phenylphosphine oxide (BHAPPO) and uncured polyurethane (PPU) prepolymer samples during the polymerization process were taken with Thermo Scientific Nicolet FT-IT IS 10 Spectrometer with a resolution mode of 4 cm^{-1}. The average of sixteen scans is used for each sample in the range of 4000-600 cm^{-1}.

3.2.2 Nuclear magnetic resonance (NMR)

^{1}H-NMR spectrum of BHAPPO in deuterated dimethyl sulfoxide (DMSO-d_6) solvent were recorded using an Agilent VNMRS 500 MHz spectrometer to characterize the chemical composition of the materials. ^{31}P-NMR spectrum of the raw material P,P-dichlorophenylphosphine oxide and BHAPPO was also taken for further inspection.

3.2.3 Thermogravimetic analysis (TGA)

Thermogravimetric analysis of cured PPU film samples were performed with TA Q50 instrument. Film samples ranging from 10-15 mg were placed in a platinum pan and heated from room temperature to 900 °C with a heating rate of 20 °C/min under nitrogen atmosphere. Weight loss (%) were recorded as a function of temperature. 5% weight loss temperature, 50% weight loss temperature and residual char yield of the samples were recorded.

3.2.4 Gel content

Cured PPU film samples were weighed (m_1) and added in the Soxhlet extractor with xylene as extraction agent for 8 hours. The films were dried in vacuum oven at 60 °C until its weight remains constant (m_2). Gel content of the film was calculated according to the equation (3.1);

$$\text{Gel content (\%)} = (m_2 / m_1) \times 100 \qquad (3.1)$$

where m_1 is the weight of the cured PPU film sample; m_2 is the residual weight of the cured PPU film sample after the extraction.

3.2.5 Chemical resistance

Cured PPU film samples were weighed accurately and immersed in various chemicals at room temperature for 24 hours. The weight losses of the samples were calculated according to the equation (3.2).

$$\text{Weight loss (\%)} = ((m_s - m_d) / m_d) \times 100 \qquad (3.2)$$

where m_s and m_d are the weights of a swollen and dry sample, respectively.

Materials used for chemical resistance are 10% NaOH, 10% acetic acid and 10% HCl.

3.2.6 Water absorption

Cured PPU film samples were weighed accurately and immersed in distilled water at room temperature for 24 hours. Samples were dried with lint-free wipes and weighed. The water absorption value of the samples were calculated according to the equation (3.3)

$$\text{Water absorption (\%)} = ((w_{ht}-w_d) / w_d) \times 100 \quad (3.3)$$

where w_{ht} and w_d are the weights of a humid and dry sample, respectively.

3.2.7 Specular gloss

Gloss is the ability of a surface to reflect light in specular directions. The factors that effect gloss are the refractive index of the material, the angle of incident light and the surface topography.

Specular gloss analysis of the PPU films was performed with a BYK Gardner micro-tri-glossmeter according to the ASTM D 523. Coated plexiglass samples were measured at angles of 20°, 60° and 85°.

3.2.8 Pendulum hardness

König pendulum hardness test was applied to coated plexiglass plates of each sample. The procedure is based on the measurement of the damping of a pendulum oscillating on the coated plate. The amplitude of the oscillations increases on harder coatings, which give better scratch resistance. Two important factors that effects pendulum hardness value of a sample are chain flexibility and crosslinking degree.

The pendulum hardness test of the PPU films was performed with a BYK Gardner pendulum hardness tester according to the ASTM D 4366 (pendulum weight = 200±0.2 g, amplitude limitation angle (deflection) = 6-3°, oscillation period = 1.4 s, starting position 6° König). Five points were tested on the coated plexiglass sample of the each specimen and average value was calculated.

3.2.9 Pencil hardness

This test was performed in order to measure the hardness values against pointy tips of the films in addition to pendulum hardness.

The pencil hardness of the cured PPU films was measured according to ASTM D 3363. The test was applied on coated plexiglass samples of the each specimen.

3.2.10 Cross-cut adhesion

Cross-cut adhesion test measures the resistance of coatings to separation from substrates. A right angle lattice pattern was made on the coating by a cutting tool and brushed diagonally for 5 times. If the edges of the cuts are completely smooth, an adhesive tape is taped on the lattice pattern and removed rapidly in the direction of the diagonal.

The cross-cut adhesion of the cured PPU films was measured according to ASTM F 2296. The test was applied on coated plexiglass samples of the each specimen.

3.2.11 Stress-strain analysis

Stress-strain analysis was performed with an Instron 3345 testing machine at room temperature in order to measure the tensile strength at yield and at break, elasticity modulus and elongation at break. Elasticity modulus, also known as Young's modulus is obtained from the slope in the elastic region of the stress-strain diagram. Tensile strength at yield is the tensile stress level at which the rise in the stress-strain curve equals to zero for the first time. Tensile strength at break is the maximum strength before the fraction. Elongation at break is the maximum elongation value before the material breaks.

Five film samples of each specimen, prepared in dimensions 50x20x0.8 mm were measured and the values were averaged.

3.2.12 Limiting oxygen index (LOI)

Limiting oxygen index was performed on a sample in order to measure its material flammability. LOI is defined as the minimum level of oxygen, expressed as volume percent, in a flowing mixture of oxygen and nitrogen that will just support candle like flaming combustion of a material at room temperature. The schematic of the device is shown in Figure 3.5. Device is comprised of a glass test column with 75 mm diameter and 450 mm length that is open to the atmosphere at the top. A gas control and metering system supplies the oxygen/nitrogen ratio from the bottom and a specimen holder to keep specimen vertical. Oxygen and nitrogen mixture is passed through the column at different ratios and the sample is observed to determine whether the material burns or extinguishes. High LOI values indicate that the material is less easily ignited therefore it is less flammable [54-55].

Limiting oxygen index analysis of the samples was performed with Fire Testing Technology instrument. The oxygen ratio of the oxygen-nitrogen gas mixture were set at 20% at first and for each gas mixture concentration, the samples were ignited 3 times. If the flame extinguishes, then gas mixture concentration were increased by 0.5% and the process was repeated until the flame does not extinguish for 180 seconds.

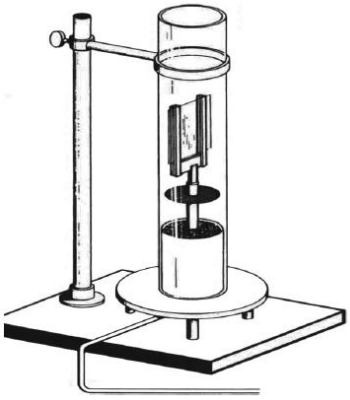

Figure 3.5 : The schematic of the LOI device for film type samples [56]

3.3 Synthesis of bis(3-hydroxy aminophenyl)phenylphosphine oxide (BHAPPO)

A round-bottom 3-necked reaction flask equipped with a nitrogen inlet, a silicone septa and a calcium chloride tube was placed on a magnetic stirrer. The system was flushed with nitrogen gas at least for 3 minutes. 6 g (0.055 mol) 3-aminophenol and 20 ml tetrahydrofuran was added and stirred until 3-aminophenol was completely dissolved. Then 5 ml (0.062 mol) pyridine was added to the solution and stirred until completely homogeneous. With a syringe, 3.6 ml (0.025 mol) P,P-dichlorophenylphosphine oxide was added to the solution dropwise over a period of 3 hours and stirred. Reaction continued until the magnetic stirrer movement is ceased due to the dense layer that formed at the bottom of the flask. Then, the solution on top was decanted and the dense layer was dissolved in ethyl alcohol. This solution of the dense layer was precipitated into 800 ml of cold distilled water and filtered with a vacuum pump to obtain BHAPPO sediment. The sediment was dried in a vacuum oven at 55 °C. According to the ^{1}H-NMR results, the dissolution and precipitation processes were repeated until the impurity peaks disappear. The reaction takes place according to the Figure 3.6.

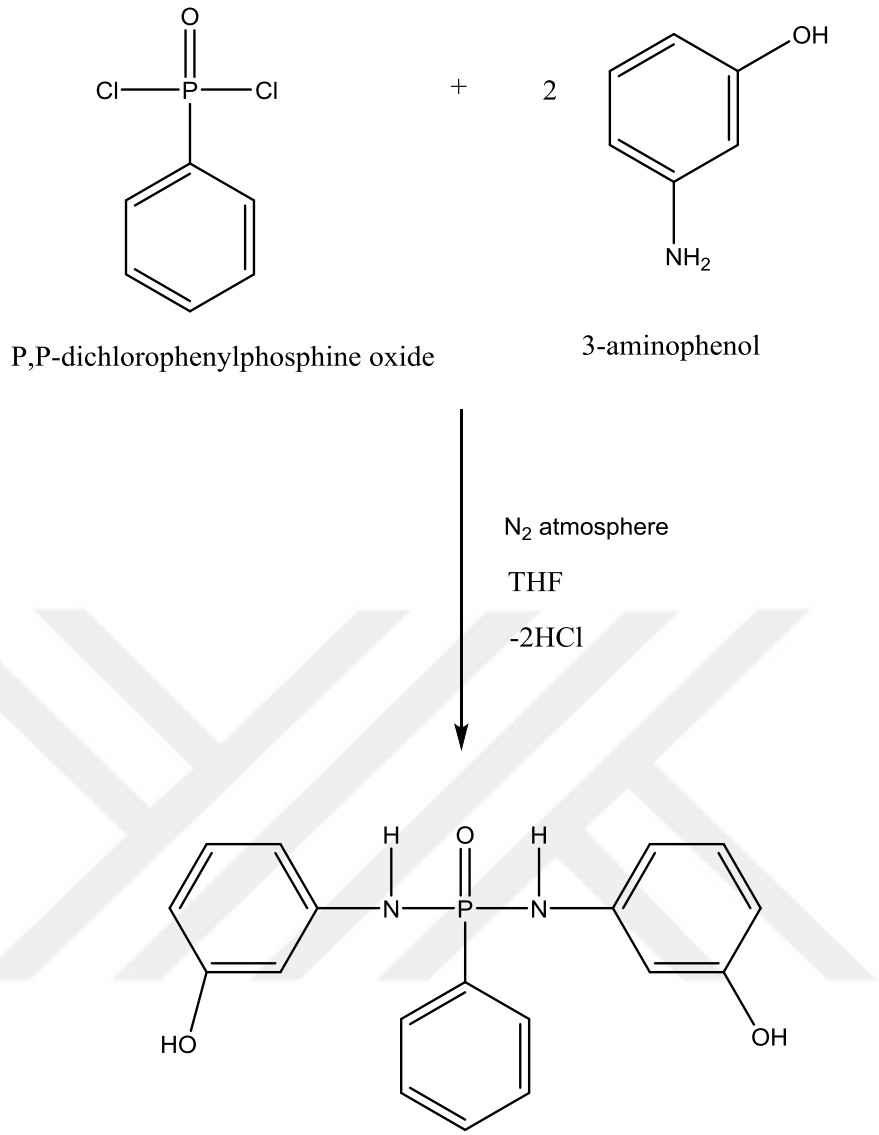

Figure 3.6 : Synthesis of bis(3-hydroxy aminophenyl)phenylphosphine oxide (BHAPPO)

3.4 Synthesis of polyurethane prepolymer

Polyurethane prepolymer was prepared by condensation polymerization of diisocyanate/polyol with molar ratio of 4:1. The used materials were isophorone diisocyanate (IPDI) with different concentrations of poly(propylene glycol) (PPG) and bis(3-hydroxy aminophenyl)phenylphosphine oxide (BHAPPO) mixture as polyol. The ratios of different formulations prepared are given at Table 3.1. A round-bottom 3-necked reaction flask equipped with a nitrogen inlet, reflux condenser, a calcium chloride tube and a dropping

funnel was placed in an oil bath on a magnetic stirrer. The system was flushed with nitrogen gas for at least 3 minutes. PPG and BHAPPO dissolved in acetone were added to the flask. When completely dissolved, IPDI dissolved in 10 ml of acetone was added to the dropping funnel, added to the solution dropwise over a period of 30 minutes and stirred. FT-IR measurement was performed when the solution was completely homogeneous. After then, 25 drops of dibutyltin dilaurate (DBTDL) were added to the solution as a catalyst and the reaction temperature was increased to 65 °C. The reaction mechanism is shown in Figure 3.7. Every 30 minutes, the NCO peak of the FT-IR spectrum at 2270 cm^{-1} was checked and reaction was continued until the depth of the peak remains constant. The final solution was taken out of oil bath, cooled at room temperature and acetone was evaporated in a rotary evaporator. The viscous prepolymer solution obtained after the evaporation was placed in a refrigerator overnight.

Table 3.1 : Molar ratios of PPU formulations.

Sample Code	IPDI	PPG	BHAPPO
PPU0	4	1	0
PPU20	4	0.8	0.2
PPU40	4	0.6	0.4
PPU60	4	0.4	0.6

IPDI: Isophorone diisocyanate
PPG: Poly(propylene glycol)
BHAPPO: Bis-(3-hydroxy aminophenyl)phenylphosphine oxide

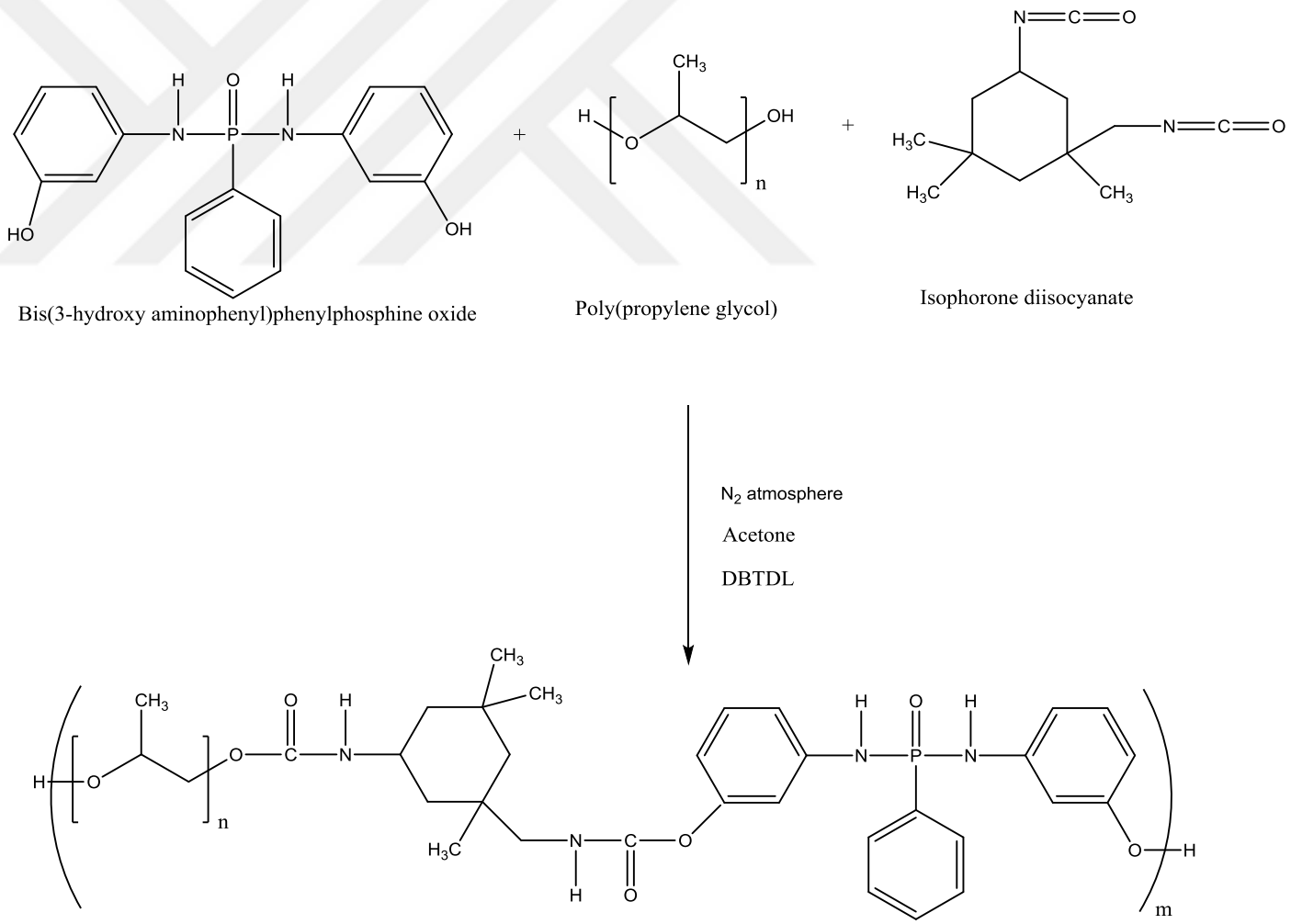

Figure 3.7 : Synthesis of Polyurethane Prepolymer

3.5 Application of the polyurethane films

The prepolymer solution was taken out of the refrigator the next day and it was applied on teflon, plexiglass and silicone plates with a metal applicator. Coated surfaces were kept at room temperature for 24 hours and in an oven at 75 °C for another 24 hours. The films were freed from the teflon and silicone surfaces with flat surface of a metal spatula.

4. RESULTS AND DISCUSSION

4.1 Characterization

4.1.1 ^{1}H- NMR spectrum of BHAPPO

Bis(3-hydroxy aminophenyl)phenylphosphine oxide (BHAPPO) was synthesized according to the procedure mentioned in section 3.3.

Figure 4.1 shows the ^{1}H-NMR spectrum of BHAPPO taken in DMSO-d_6. The broad peak at 9.2 ppm was observed due to hydroxyl groups. The singlet peak at 6.7 ppm was due to NH groups. The peaks at the 7.8 and 7.5 ppm were due to CH protons in the phenyl group bonding with the phosphorus atom. The peaks at the far right side of the graph that are located at the 6.2, 6.5 and 6.9 ppm belong to the protons in the phenol. This ^{1}H-NMR spectrum proves the formation of BHAPPO.

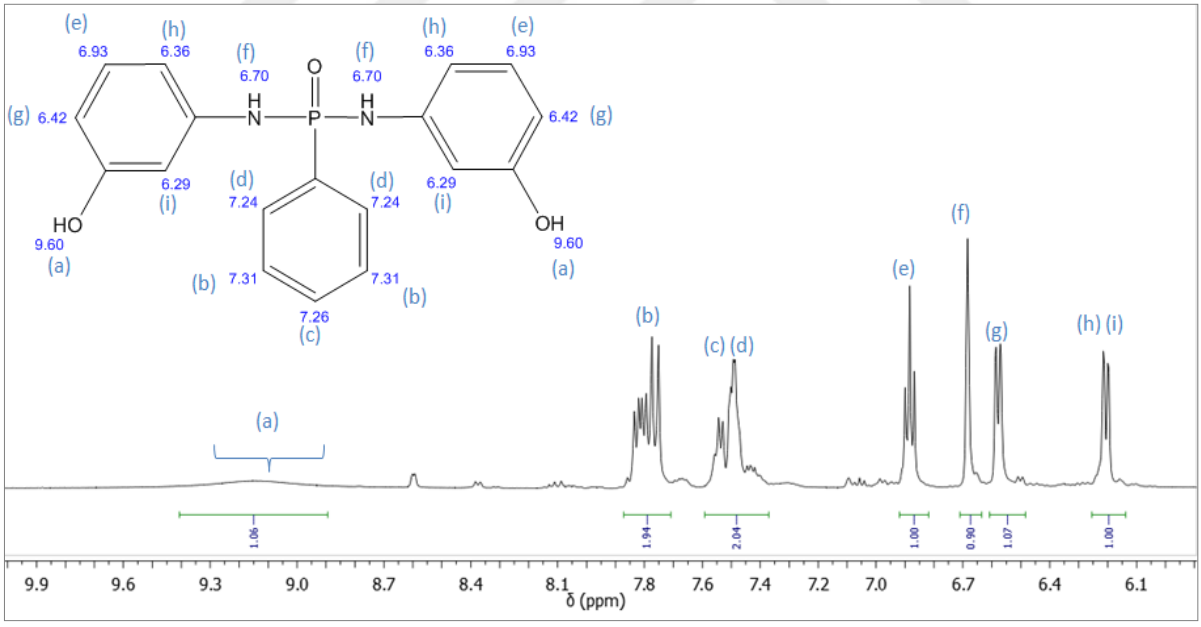

Figure 4.1 : ^{1}H-NMR spectrum of BHAPPO

4.1.2 ^{31}P- NMR spectrum of BHAPPO

Figure 4.2 and 4.3 shows the ^{31}P-NMR spectrum of P,P-dichlorophenylphosphine oxide and BHAPPO respectively. The peak located at 14.4 ppm in Figure 4.2 has disappeared and a new peak at 8.27 ppm has been formed therefore the disappereance of P-Cl bonds in P,P-dichlorophenylphosphine oxide and the formation of BHAPPO structure has been observed in this spectrum.

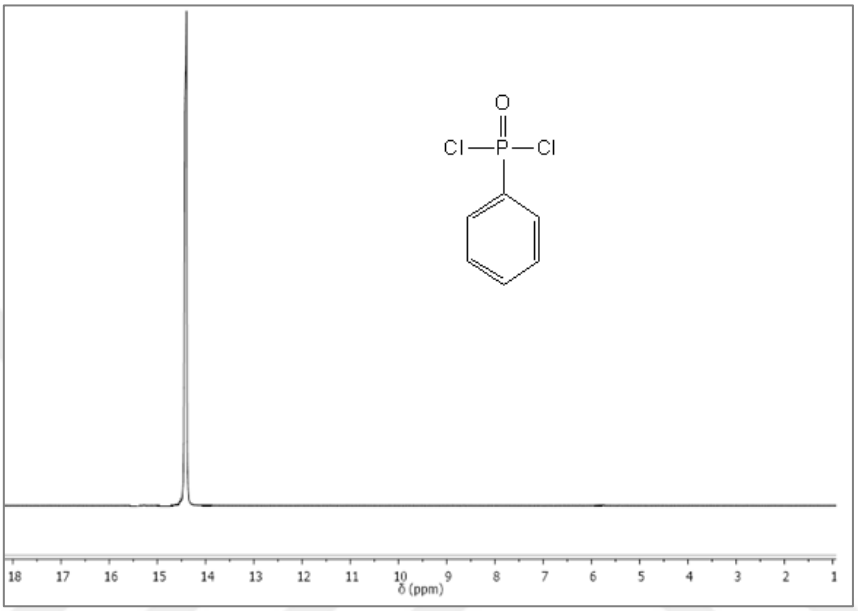

Figure 4.2 : ^{31}P-NMR spectrum of P,P-diclorophenylphosphine oxide

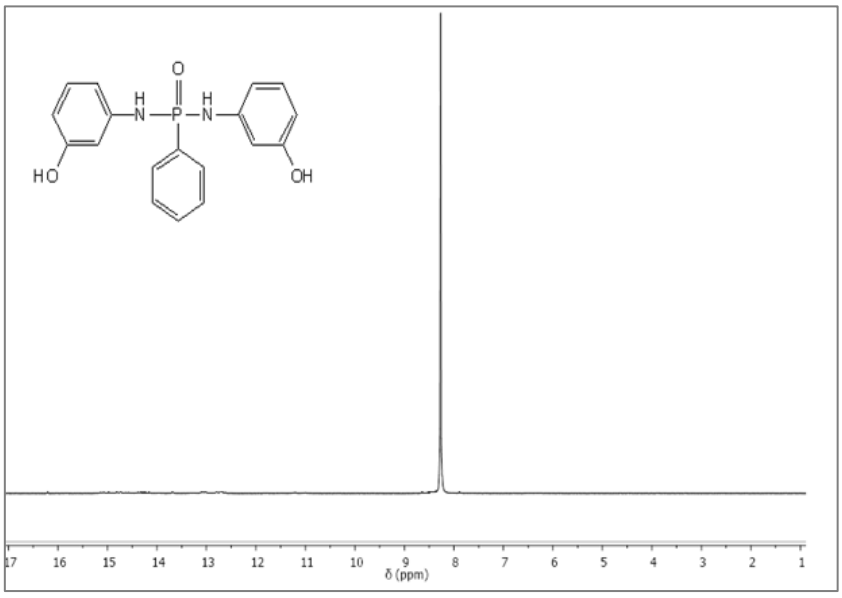

Figure 4.3 : ^{31}P-NMR spectrum of BHAPPO

4.1.3 FT-IR spectrum of BHAPPO

Figure 4.4 displays the FT-IR spectrum of BHAPPO. The apperance of the P-N bond at 900 cm^{-1} proves the formation of BHAPPO. The broad absorption signal at wavelength 3200 cm^{-1} represents the O-H bonding and the reason for its broadness is due to the hydrogen bonding that may occur between two molecules. On this peak, the characteristic signals of N-H (3300 cm^{-1}) and C-H (3100 cm^{-1}) aromatic stretching bands are also observed. In the spectrum, there are also characteristic peak of C-O group at 1100 cm^{-1}. Other peak at 1200 cm^{-1} represents the P=O presence in the molecule.

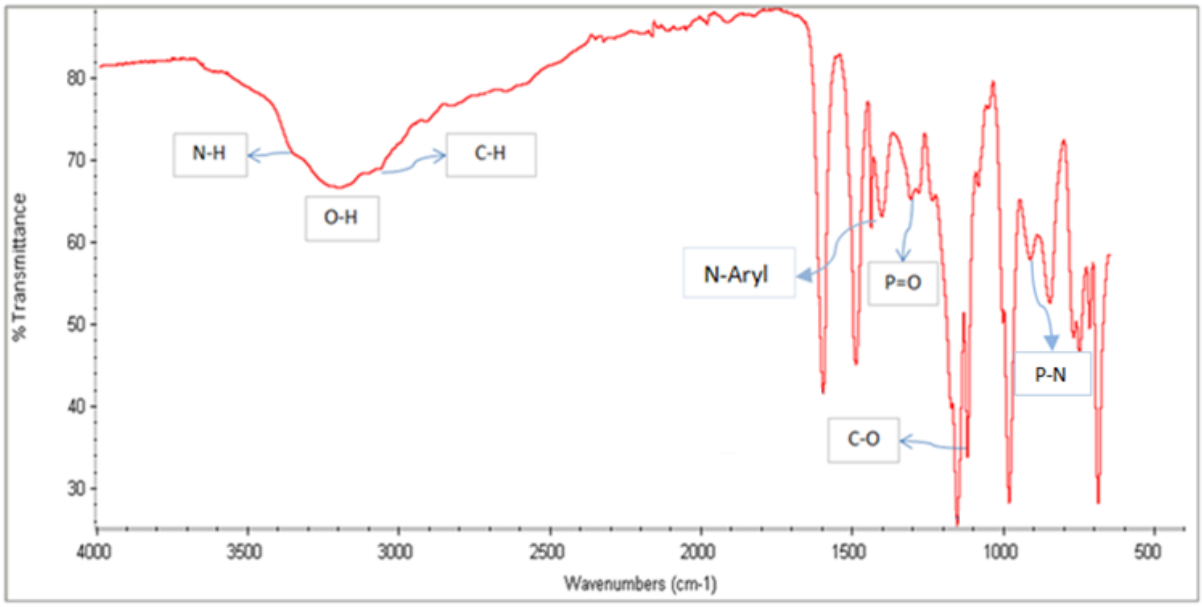

Figure 4.4 : FT-IR spectrum of BHAPPO

4.1.4 FT-IR spectrum of polyurethane prepolymer

Initial and final FT-IR spectrums of polyurethane prepolymer were recorded during polymerization and were listed in Figure 4.5 and 4.6. Initial and final FT-IR spectrums of PPU prepolymer corresponds to the spectrums taken before and after polymerization process. As can be seen in the Figures 4.5 and 4.6, the depth of the NCO peak, which is located at 2260 cm^{-1} wavelength has decreased which signifies that the polymerization process has taken place and NCO concentration has decreased. Stocchiometrically excessive amount of

diisocyanate was used in the reaction due to film formation properties. Since diisocyanate/diol ratio is 4:1, NCO peak in the FT-IR spectrum has not reached zero.

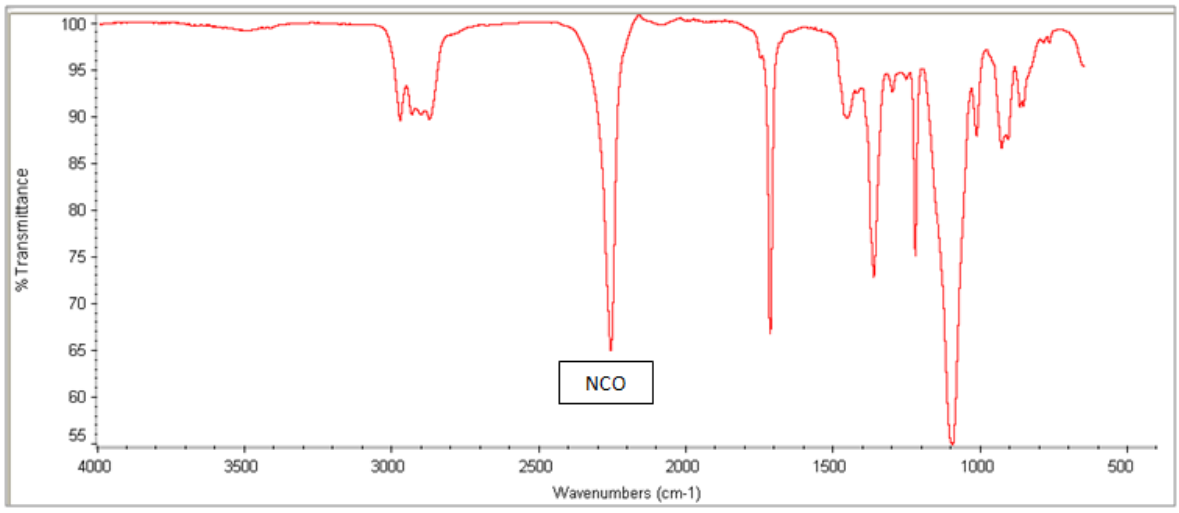

Figure 4.5 : Initial FT-IR spectrum of PPU prepolymer

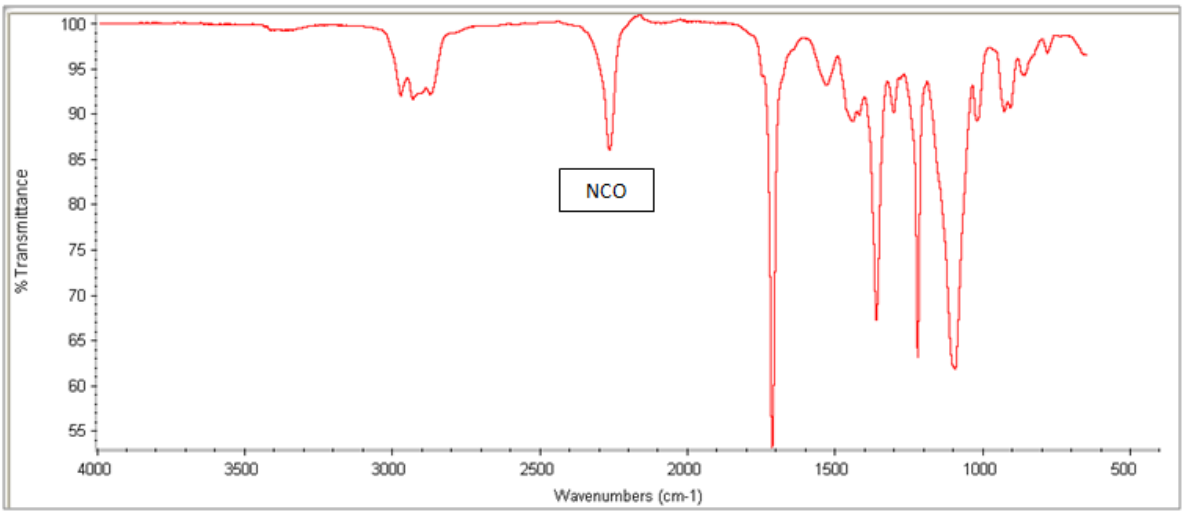

Figure 4.6 : Final FT-IR spectrum of PPU prepolymer

4.1.5 Specular gloss

Plexiglass plates were coated for the specular gloss test. The gloss value was measured with a micro-tri gloss meter for 20°, 60° and 85° used in order to measure high gloss, medium gloss and matte surfaces respectively.

The average gloss values of polyurethane films (PPU) at 20° and 60° angles are shown in Table 4.1. The addition of the fire-retardant BHAPPO containing phosphine oxide and

nitrogen to polyurethane films caused an almost linear decrease of the gloss value, proportional to the BHAPPO concentration as seen in Figure 4.7. This could due to the fact that the integration of BHAPPO into the PU structure caused cross-linking of the material. Cross-linking increased the viscosity of the PPU prepolymer therefore application of the film became harder and surface topography has changed. The free PPU films became more opaque and their surfaces became rougher which leads to the decrease in gloss properties.

The gloss values for 20° were between 145-165 for PPU0, 133-141 for PPU20, 93-108 for PPU40 and 62-99 for PPU60. The gloss values for 60° were between 146-162 for PPU0, 138-146 for PPU20, 106-128 for PPU40 and 86-115 for PPU60. 85° angle is applied when the specimens have 60° gloss values lower than 10 so 85° gloss values were neglected.

Table 4.1 : Average gloss values of PPU films

Sample Code	20°	60°
PPU0	154	152
PPU20	138	142
PPU40	103	121
PPU60	85	102

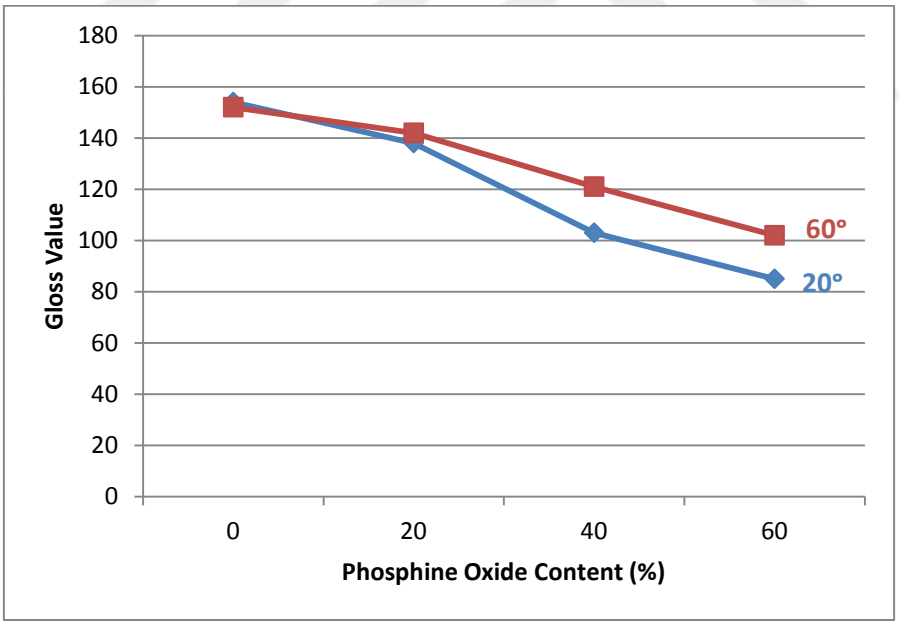

Figure 4.7 : 20° and 60° gloss values of PPU films

4.1.6 Water absorption

PPU film samples were immersed in distilled water at room temperature for 24 hours according to the ASTM D570 standard. The measurements were performed after drying the wet samples with lint-free wipe. Water absorption values were calculated according to the equation 3.3.

The water absorption results are listed in Table 4.2. Incorporation of BHAPPO into the polyurethane film structure slightly decreased the water absorption value. Due to the cross-linking, free volume between the polymer chains became smaller therefore less water was absorbed by the films. Overall it stayed under 4%, therefore it can be concluded that PPU films are water resistant.

4.1.7 Gel content

Gel content analysis was performed according to the method mentioned in section 3.2.4. This test was performed in order to measure the polymerization and cross-linking degree of PPU films.

The gel content results are listed in Table 4.2. The cross-linking degree increased up to 92.6% with the increasing BHAPPO concentration incorporated into the film structure whereas the polyurethane film synthesized with only PPG has 72.7% cross-linked structure. Hydroxyl groups located at the ends of the polymer chains may have formed strong hydrogen bonds between the chains thus acting as a cross-linking agent.

Table 4.2 : Water absorption and gel content of PPU films

Sample Code	Water absorption (%)	Gel Content (%)
PPU0	4.1	72.7
PPU20	1.9	84.2
PPU40	1.4	90.6
PPU60	1.0	92.6

4.1.8 Chemical resistance

Cured films were weighed and immersed in 10% HCl, 10% acetic acid and 10% NaOH for 24 h at room temperature, wiped with a lint-free wipe and weighed again. The weight losses of

the samples were calculated according to the equation (3.2). The results of chemical resistance are listed in Table 4.3.

The weight loss values in chemicals were less than 0.5% for each sample. This indicates that chemical resistances of PPU's with different concentrations were very high. As the BHAPPO concentration increases, HCl resistance of the films increases and acetic acid and NaOH resistance decreases slightly. The appearance of the samples were good except PPU60 became brittle and broken in 10% NaOH solution.

Table 4.3 : Chemical Resistance of PPU films

Sample Code	10% HCl		10% Acetic Acid		10% NaOH	
	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance
PPU0	0,33	Good	0,02	Good	0,17	Good
PPU20	0,20	Good	0,02	Good	0,21	Good
PPU40	0,014	Good	0,05	Good	0,25	Good
PPU60	0,09	Good	0,06	Good	0,34	Broken

4.1.9 Pendulum hardness

The pendulum hardness values of coated plexiglass plates are given in Table 4.4. The test was applied on 5 different locations for each plate and the average value is calculated. The pendulum hardness values were between 23-24 for PPU0, 24-26 for PPU20, 32-49 for PPU40 and 69-87 for PPU60. The pendulum hardness values of the films increased gradually with the increasing BHAPPO content in the PPU's backbone as seen in Figure 4.8. Hard phenyl groups in the PPU structure and cross-linking degree caused an increase of the film hardness.

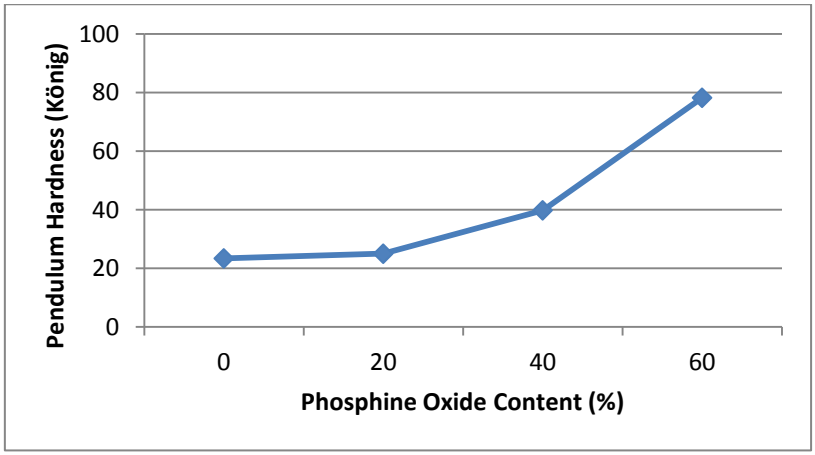

Figure 4.8 : Pendulum hardness values of PPU films

4.1.10 Pencil hardness

Pencil hardness test was applied to coated plexiglass plates of each sample with application of pencils with different hardness values from HB to 7H.

The pencil hardness values are listed in Table 4.4. As the content of the BHAPPO was increased in PPU films, the pencil hardness values were decreased slightly.

4.1.11 Adhesion tests

Cross-cut test was applied on the coated plexiglass plate of each sample according to the ASTM F 2296.

Adhesion test results are listed in Table 4.4. The edges of the cuts were completely smooth and none of the squares of the lattice was detached for each sample. This proves that PPU films have excellent adhesion property.

Table 4.4 : Pendulum hardness, pencil hardness and adhesion test results of PPU films

Sample Code	Pendulum Hardness	Pencil Hardness	Adhesion Test	
			ISO Class	ASTM Class
PPU0	23	3H	0	5B
PPU20	25	3H	0	5B
PPU40	40	2H	0	5B
PPU60	78	2H	0	5B

4.1.12 Thermogravimetric analysis (TGA)

The thermal stability of the samples were measured in the temperature range of 25 °C to 900 °C by TGA under nitrogen atmosphere at a heating rate of 20 °C/min.

The influence of phosphine oxide content on 5% weight loss temperature, 50% weight loss temperature and residual char yield are shown in Table 4.5. As the phosphine oxide content increases, 5% weight loss temperature slightly increases but it does not have a significant effect on 50% weight loss temperature and residual char yield. The overlapped TGA diagrams of all PPU film samples are shown in Figure 4.9. These results prove that the decomposition behavior of the PPU films are very similar and does not change with increasing concentration of BHAPPO.

Table 4.5 : Thermal properties of cured PPU films

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Residual Char Yield (%)
PPU0	252	347	0.53
PPU20	255	349	0.87
PPU40	278	355	0.03
PPU60	270	343	0.03

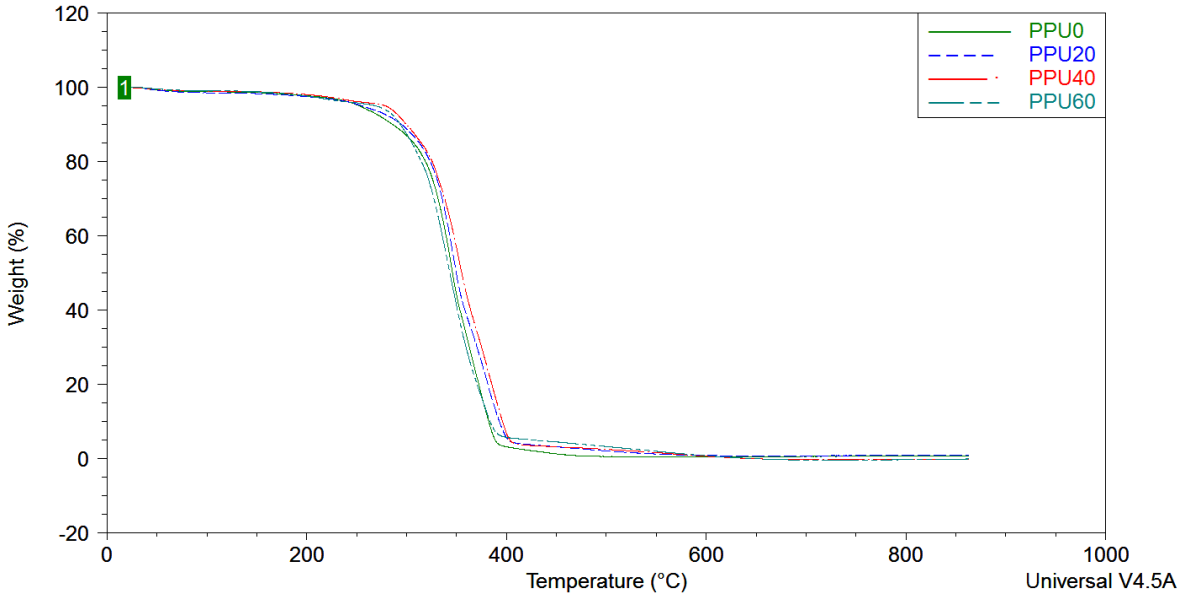

Figure 4.9 : Overlapped TGA graphs of PPU films

4.1.13 Limiting oxygen index (LOI)

LOI values of the samples are listed in Table 4.6. LOI values of the PPU films decreased as the BHAPPO concentration increases. This is the opposite behavior to the expected results. Integration of the flame retardant containing phosphorus and nitrogen elements changed the fire mechanism in an unexpected way. While PPU0 forms a char layer and extinguish itself, the integration of BHAPPO increased the melting and dripping behavior of the film, these behavior provide an additional ignition source therefore, flame retardancy of the PPU films decreased instead of increasing.

There may be physical and chemical effects causing the increase in the melt flow. The TGA thermograms of PPU films show that the decomposition behavior of the PPU films does not change with increasing concentration of BHAPPO. Therefore, physical effects play the major role in this behavior. As the BHAPPO concentration increases in the material, the viscosity of the material decreases to a point that it starts dripping at the same temperature. PPU0 also melts but its melt viscosity is so high that the molten part does not flow and forms a layer that prevents the contact of the flame with air therefore it extinguishes itself. PPU60 has low melt viscosity therefore molten part drips, carries and spreads the flame.

Table 4.6 : Limiting oxygen index (LOI) values of PPU films

Sample Code	LOI value
PPU0	30
PPU20	28
PPU40	26
PPU60	23

4.1.14 Tensile stress-strain test

Mechanical properties of the films were determined by tensile stress-strain tests in order to measure the tensile strength, elastic modulus and elongation at break. The mechanical specifications of the free films prepared at 50x20x0.8mm dimensions are made with the measurement of stress-strain values.

Mechanical properties such as elastic modulus, tensile strength at yield and at break and elongation at break values are listed in Table 4.7. Tensile strength at yield, tensile strength at break, elongation at break and e-modulus values versus phosphine oxide concentration in PPU structure diagrams are shown in Figure 4.10, 4.11, 4.12 and 4.13 respectively.

Tensile strength at yield and tensile strength at break values increased only slightly with increasing concentration of BHAPPO. Elongation at break values decreased proportionally with the increasing concentration of BHAPPO. Elastic modulus of the material remains almost constant until 40% of BHAPPO and then a sudden increase is observed.

It can be concluded that the incorporation of reactive-type flame-retardants into the PPU structure increased rigidity of the films due to the rigid aromatic groups present in BHAPPO structure.

Table 4.7 : Mechanical properties of cured PPU films

Sample Code	E-Modulus (MPa)	Tensile Strength at Yield (MPa)	Tensile Strength at Break (MPa)	Elongation at Break (mm)
PPU0	1.69	3.79	3.39	223
PPU20	2.81	3.90	3.77	170
PPU40	9.68	5.31	5.41	100
PPU60	204	7.35	8.04	20

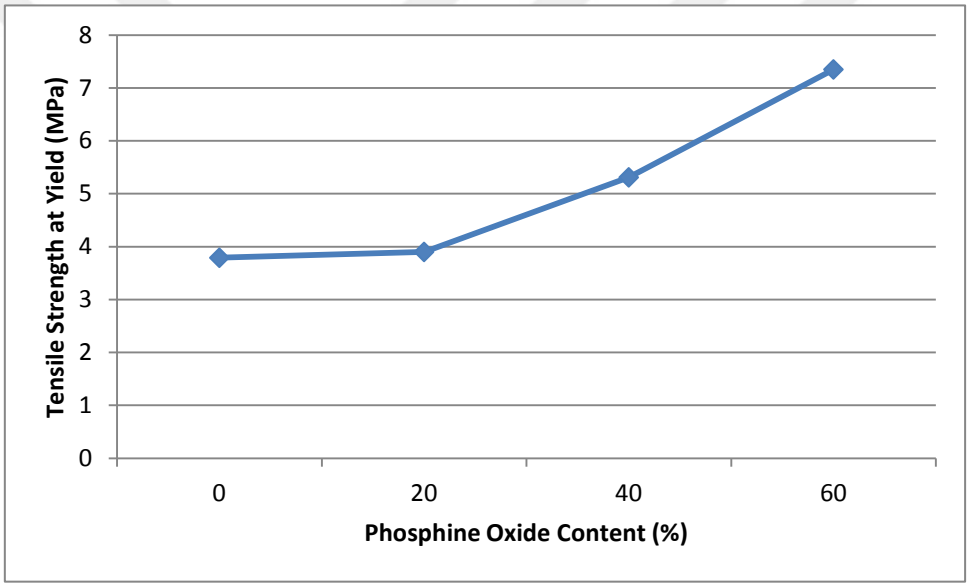

Figure 4.10 : Tensile strength at yield values of PPU films

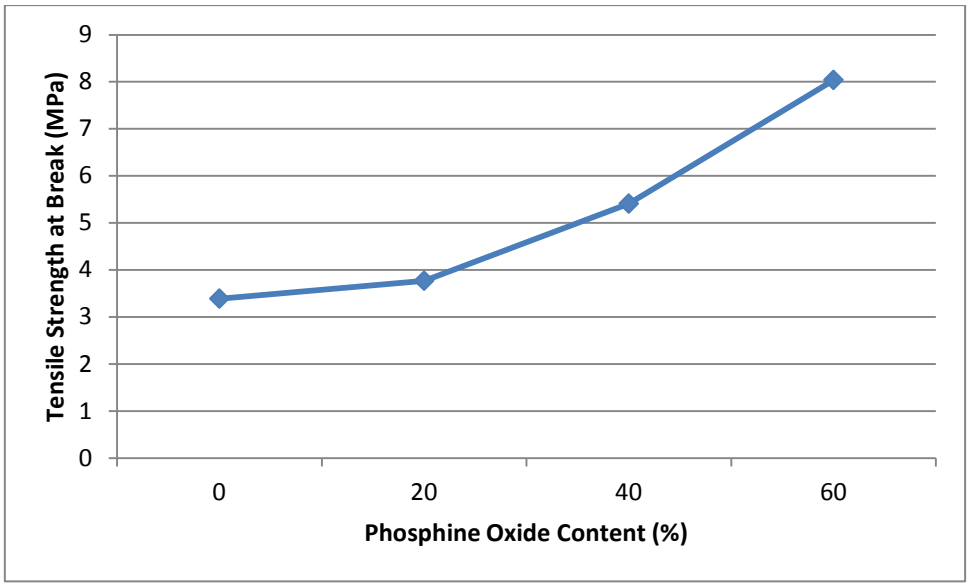

Figure 4.11 : Tensile strength at break values of PPU films

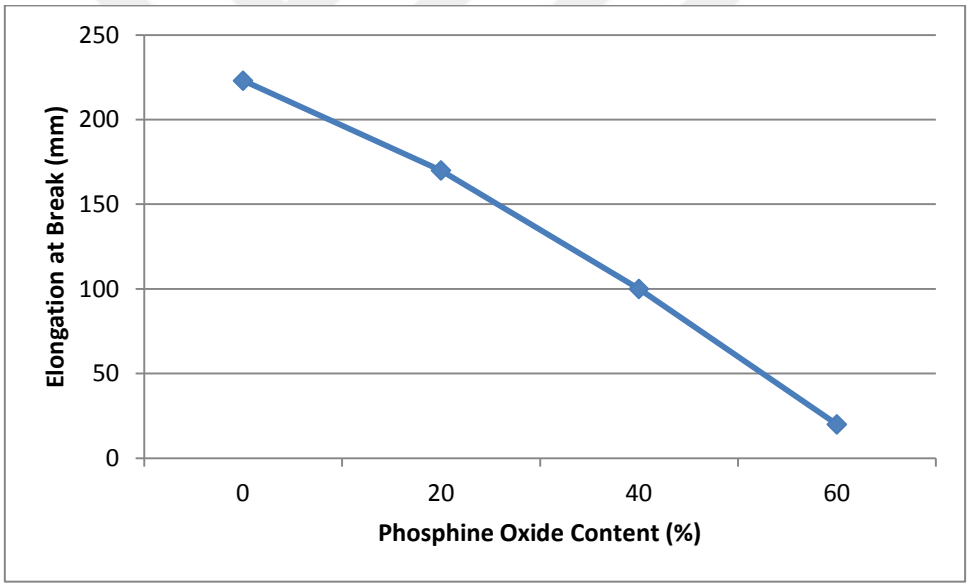

Figure 4.12 : Elongation at break values of PPU films

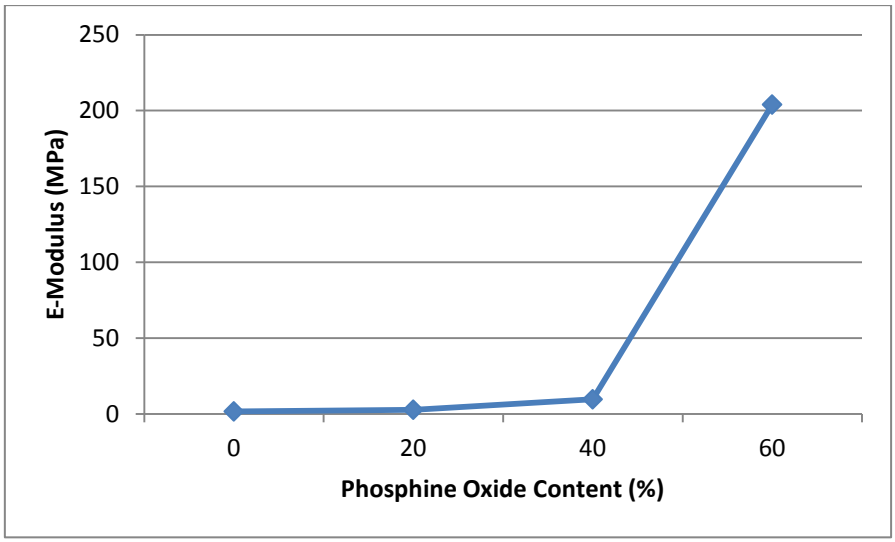

Figure 4.13 : E-Modulus values of PPU films

5. CONCLUSION

Phosphine oxide and nitrogen containing flame retardant diol (BHAPPO) was synthesized and its chemical structure was proven by FT-IR, ^{1}H-NMR and ^{31}P-NMR analysis. BHAPPO was used in the synthesis of PPU prepolymer with different molar concentrations (0, 20%, 40% 60% of the total diol amount) along with PPG incorporating the flame retardant elements into its structure by chemical reaction.

As the concentration of BHAPPO increases, tensile strength at yield and tensile strength at break values increased slightly and elongation at break values decreased proportionally with phosphine oxide content. Elastic modulus values increased slightly until 40% of BHAPPO and then a sudden increase is observed. It can be concluded that aromatic groups in BHAPPO provides rigidity to PPU films.

It was found that the integration of BHAPPO in the PPU structure lead to cross-linking of the materials by strong hydrogen bonds as investigated by gel content analysis. Gel content values increased from 72.7% for PPU0 to 92.6% for PPU60.

Gloss values of the material decreased proportionally with the increasing phosphine oxide content. The cross-linking of the material caused rigidity and an increase in viscosity of the material, therefore application of the film became harder and its surface became rougher. Pendulum hardness values are also increased due to the same reason.

Water absorption values decreased as the free volume decreased due to the cross-linking of the material.

There is no significant change in TGA, adhesion tests and pencil hardness values.

Chemical resistance of the films in 10% HCl is increased, in 10% NaOH is decreased and in 10% acetic acid remained almost constant.

Incorporation of flame retardant phosphine oxide and nitrogen elements into the PPU backbone decreased the LOI values contrary to the expected. Flame-retardants caused a significant decrease in the melt viscosity of the PPU film. This case of melting and dripping of the material caused further propagation of the flame, therefore decreasing its LOI value.

REFERENCES

[1] Turel, B., Serhatli, I. E. (2013). *Synthesis and characterization of phosphine oxide and sulfone containing polyurethanes.* (Ph. D. Thesis). ISTANBUL Technical University, Graduate School of Science Engineering and Technology, ISTANBUL

[2] Çanak, T. Ç., Celioğlu, S., Erbay, B. T., Serhatlı, İ. E. (2015). Synthesis and characterization of sulfone containing polymethylmethacrylate via atom transfer radical polymerization. *J Polym Mater, 32,* 113-126.

[3] Erbay, B. T., Serhatlı, İ. E. (2013). Synthesis of bis[(4-hydroxyethoxy)phenyl]sulfone containing urethane acrylates and their applications. *Progress in Organic Coatings, 76,* 1-10.

[4] Zhang, C. (2014). *Polyurethane films, foams and nanocomposites prepared from vegetable oil-based polyols.* (Ph. D. Thesis). IOWA State University, Material Science and Engineering, IOWA

[5] Zhang, L., Zhang, M., Hu, L., Zhou, Y. (2014). Synthesis of rigid polyurethane foams with castor oil-based flame retardant polyols. *Industrial Crops and Products, 52,* 380-388.

[6] Chiu, S., Wu, C., Lee, H., Gu, J., Suen, M. (2016). Synthesis and characterization of novel flame retardant polyurethanes containing designed phosphorus units. *J Polym Res, 23,* 205. doi:10.1007/s10965-016-1098-y

[7] Ding, H., Xia, C., Wang, J., Wang, C., Chu, F. (2016). Inherently flame-retardant flexible bio-based polyurethane sealant with phosphorus and nitrogen-containing polyurethane prepolymer. *J Mater Sci., 51,* 5008-5018. doi:10.1007/s10853-016-9805-y

[8] Zhang, M., Luo, Z., Zhang, J., Chen, S., Zhou, Y. (2015). Effects of a novel phosphorus-nitrogen flame retardant on rosin-based rigid polyurethane foams. *Polymer Degradation and Stability* (Vol. 120, pp.427-434)

[9] Constantine, D. P., Pantelis, K. (2014). *Polymer Green Flame Retardants*. Elsevier.

[10] Tesoro, G. C. (1978). Chemical modification of polymers with flame-retardant compounds. *J Polym Sci Macromol Rev*, 13:283-353, doi:10.1002/pol.1978.230130106

[11] Hilado, C. (1998). *Flammability handbook for plastics.* Pennsylvania, USA: Technomic Publishing Company.

[12] Landrock, A. H. (2002). *Hanbbook of plastics flammability and combustion toxicology.* New Jersey, USA.: Noyes Publications.

[13] Lu, S. Y., Hamerton, I. (1983). Recent developments in the chemistry of halogen-free flame retardant polymers. *Progr Polym Sci*, 27:1661-712.

[14] Lomakin, S. M., Haslam, E. (1999). *Ecological aspects of polymer flame retardancy (new concepts in polymer science).* Leiden, The Netherlands: Brill Academic Publishers.

[15] Crummett, W. B. (2002). *Decades of dioxin.* Princeton, NJ: Xlibris Corp.

[16] Price, D., Anthony, G., Carty, P. (2001). *Introduction: polymer combustion, condensed phase pyrolysis and smoke formation.* Cambridge, UK: Woodhead Publishing Ltd.

[17] Kiliaris, P., Papaspyrides, C. D. (2010). Polymer/layered silicate (clay) nanocomposites: an overview of flame retardancy. *Progr Polym Sci*, 35:902-58.

[18] Hirschler, M. M. (2000). *Chemical aspects of thermal decomposition of polymeric materials.* New York, USA: Marcel Dekker Inc.

[19] Bilingham, N. C. (2005). *Encyclopedia of polymer science and technology, Vol. 6.* New Jersey, USA: John Wiley & Sons Inc.

[20] Pielichowski, K., Njuguna, J. (2005). *Thermal degradation of polymeric materials.* Shropshire, UK: Rapra Technology Limited.

[21] Levchik, S. V., Wilkie, C. A. (2000). *Fire retardancy of polymeric materials.* New York, USA: Marcel Dekker Inc.

[22] Wilkie, C. A., Levchik, S. V., Levchik, G. F. (2001). *Specialty polymer additives: principles and application.* Oxford, UK: Blackwell Science.

[23] Laoutid, F., Bonnaud, L., Alexandre M., Lopez-Cuesta, J. M., Dubois, P. (2009). New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. *Mater Sci Eng R*, 63:100-25.

[24] Sutker, B. J. (2002). *Ullman's encyclopedia of industrial chemistry Vol. 14.* Weinheim, Germany: Wiley-VCH Verslag.

[25] Joseph, P., Tretsiakova-Mcnally, S. (2011). Reactive modifications of some chain- and step-growth polymers with phosphorus containing compounds: effects on flame retardance- a review. *Polym Adv Technol*, 22:395-406.

[26] Camino, G., Costa, L., Luda di Cortemiglia, M. P. (1991). Overview of fire retardant mechanisms. *Polym Degrad Stab*, 33:131-54.

[27] Focke, W. W., Strydom, C. A., Barti, N. (1997). Thermal analysis of commercial inorganic flame retardants. *SA J Chem Eng*, 9:41-51.

[28] Skinner, G. A. (1998). *Flame retardancy: the approaches available.* London, UK: Chapman and Hall.

[29] Bourbigot, S., Le Bras, M. (2004). *Fundamentals: flame retardants in plastics.* Munich, Germany: Hanser Publishers/Hanser Gardner Publications.

[30] Levchik, S. V., Weil, E. D. (2000). Combustion and fire retardancy of aliphatic nylons. *Polymer Int*, 49:1033-73.

[31] Green, J. (2000). *Phosphorus containing flame retardants.* New York, USA: Marcel Dekker Inc.

[32] Schmitt, E. (2007). Phosphorus-based flame retardants for thermoplastics. *Plast Addit Compd*, 9:26-30.

[33] Lewin, M., Weil, E. D. (2001). *Mechanisms and mode of action in flame retardancy of polymers.* Cambridge, UK: Woodhead Publishing Ltd.

[34] Green, J. (1996). Mechanism for flame retardancy and smoke suppression-a review. *J Fire Sci*, 14:426-42.

[35] Babushok V., Tsang, W. (2000). Inhibitor rankings for alkane combustion. *J Combust Flame*, 124:488-506.

[36] Schartel B. (2010). Phosphorus-based flame retardancy mechanisms – old hat or a starting point for future development. *Materials*, 3:4710-45.

[37] Van der Veen I., De Boer, J. (2012). Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*, 88:1119-53.

[38] Levchik, S. V., Weil, E. D. (2008). New developments in flame retardancy of styrene thermoplastics and foams. *Polym Int*, 57:431-48.

[39] Crew, G. M., Ripperger, W., Kersebohm, D. B., Seeholzer, J., Güthne, T. (2002). *Melamine and guanamines.* Weinheim, Germany: Wiley-VCH Verslag.

[40] Gijsman, P. M., Steenbakkers, R., Furst, C., Kersjes, J. (2001). Differences in the flame retardant mechanism of melamine cyanurate in polyamide 6 and polyamide 66. *Polym Degrad Stab*, 78:219-24.

[41] Weil, E. D., Levchik, S. (2002). Current practice and recent commercial developments in flame retardancy of polyamides. *J Fire Sci*, 22:251-64.

[42] Kiliaris, P., Papaspyrides, C. D., Pfaendner, R. (2008). Polyamide 6 filled with melamine cyanurate and layered silicates: evaluation of flame retardancy and physical properties. *Macromol Mater Eng*, 293:740-51.

[43] Pfaendner, R. (2006). Nitroxyl radicals and nitroxylethers beyond stabilization: radical generator for efficient polymer modification. *CR Chim*, 9:1338-44.

[44] Nicolas, R. C., Wilen, C. E., Roth, M., Pfaendner, R., King III, R. E. (2006). Azoalkanes: a novel class of flame retardants. *Macromol Rapid Commun*, 27:976-81.

[45] Pfaendner, R. (2006). How will additives shape the future of plastics. *Polym Degrad Stab*, 91:2249-56.

[46] Schreiber, H., Saur, W. (1993). New fire retardant halogen free polymers. *Makromol Chem Macromol Symp*, 74:165-71.

[47] Aseeva, R. M., Zaikov, G. E. (1993). Flammability of macrocyclic polymers and their complexes with metals. *Makromol Chem Macromol Symp*, 74:335-8.

[48] Gaan, S., Sun, G., Hutches, K., Engelhard, M. (2008). Flame retardancy of cellulosic fabrics: Interactions between nitrogen additives and phosphorus-containing flame-retardants. *Fire Retardancy of Polymers: New Strategies and Mechanisms,* 5008-5018. doi:10.1039/9781847559210-00294

[49] Granzow, A. (1978). *Acc. Chem. Res., 11,* 177.

[50] Wang, Y. Z. (1978). *Halogen-free flame-retardants*. Sichuan University, China

[51] Kandola, B. K., Price, D., Milnes, G. J., Da Silva, A. (2013). Development of a novel experimental technique for quantitative study of melt dripping of thermoplastic polymers. *Polymer Degradation and Stability*, 98:52-63.

[52] Segura, D. M., Nurse, A. D., McCourt, A., Phelps, R., Segura, A. (2005). *Handbook of adhesives and sealants.* Leicestershire, UK: Elsevier Ltd.

[53] Thomson, T. (2005). *Polyurethanes as specialty chemicals: principles and applications.* Florida, USA: CRC Press LLC.

[54] Oxygen Index. Acces: 09 November 2017, https://www.uclan.ac.uk/

[55] Kumar, A., S. T'ien, J. (2012). *Numerical modeling of limiting oxygen index apparatus for film type fuels.* International journal of spray and combustion dynamics (Vol. 4, Number 4, pp.299-322) . New York : Wiley.

[56] ASTM (2013). *Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)* (ASTM D2863-12). Retrieved from https://compass.astm.org

CURRICULUM VITAE

Name Surname **:** Hanife Elif Gürsel

Place and Date of Birth **:** İstanbul, 25.12.1986

E-Mail **:** elifgursel@gmail.com

EDUCATION **:**

- **B.Sc.** **:** 2012, Marmara University, Engineering Faculty, Chemical Engineering Department

PROFESSIONAL EXPERIENCE AND REWARDS:

- VSY Biotechnology-R&D Assistant Specialist (01.2015-08.2016)
- Vitra Karo-Internship (07.2011-08.2011)