İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

NEW FUNCTIONAL POLYOLS FOR POLYURETHANES

Ph.D. THESIS

Başar YILDIZ

Department of Polymer Science and Technology

Polymer Science and Technology Programme

MARCH 2016

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Thesis Advisor: Prof. Dr. Ahmet AKAR

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİÜRETANLAR İÇİN YENİ FONKSİYONEL POLİOLLER

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MART 2016

Başar Yıldız, a Ph.D. student of İTU Graduate School of Science Engineering and Technology student ID 515052013, successfully defended the thesis entitled "NEW FUNCTIONAL POLYOLS FOR POLYURETHANES", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my mother Saime YILDIZ and my lovely family,

FOREWORD

I would like to express my deep appreciation and thanks for my advisor Prof. Dr. Ahmet Akar for his endless support and for giving me the opportunity to learn about the field of flame retardants.

I would like to thank Tükek family, my colleagues from Flokser Tekstil ve Tic. Aş; Gökay Gürel, Erhan Mendi, Lale Şen Çetin for helping at experiments and characterization parts.

Last but not least, I cannot thank enough my wife, as none of this would have been possible without her constant support.

February 2016 Başar YILDIZ

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ABBREVIATIONS

PU (PUR) **:** Polyurethane
PTMG **:** Polytetramethylene Glycol
MDI **:** 4,4'-Methylene Diphenyl Diisocyanate
PMDI **:** Polymeric MDI
TDI **:** Toluene Diisocyanate
UV **:** Ultraviolet
PPG **:** Polypropylene Glycol
TPU **:** Thermoplastic Polyurethane
BDO **:** 1,4- Butanediol
MMA **:** Methylmethacrylate
PDMS **:** Polydimethylsiloxane
FR **:** Flame Retardant
DMPP **:** Dimethyl Phosphonate
PIR : Polyısocyanurate
DPP : Diphenyl Phosphite
VPADME : Vinyl Phosphonic Acid Dimethylester
TCPP : Tris (1-Chloro-2 Propyl) Phosphate
LOI : Limiting Oxygen Index
MEK : Methyl Ethyl Ketone
DMF : Dimethylformamide
CF-R : Cyclohexanone-Formaldehyde Resin
MEKF-R : Methyl Ethyl Ketone-Formaldehyde Resin
DEP : Diethyl Phosphite
AF-R : Acetophenone-Foramladehyde Resin
THEIC : Tris (hydroxyethyl) isocyanurate
AA : Adipic Acid
DEG : Diethylene Glycol
PES : Polyester
HBA : 4-Hydroxybutyl Acrylate
DOPO : 9,10-Dihydro-9-Oxy-10-Phosphaphenanthrene-10-Oxide
DMSO : Dimethyl Sulfoxide
FTIR : Fourier Transform Infrared Spectroscopy
^{1}H NMR : Proton Nuclear Magnetic Resonance
C-13 NMR : Carbon-13 Nuclear Magnetic Resonance
P-31 NMR : Phosphorus-31 Nuclear Magnetic Resonance
EA : Ethanolamine
DICAFR : Acetophenone-2,4-Dicholoroacetophenone-Formaldehyde Resin

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NEW FUNCTIONAL POLYOLS FOR POLYURETHANES

SUMMARY

In this work, different polyols have been either synthesized or used to for three fundamental industrial application areas. These application areas are shoe sole, rigid foam (isolation) and artificial leather, respectively.

First, low density requirements in shoe sole applications have been solved by producing polystyrene dispersions in polyester polyol and then styrene graft unsaturated polyols have been utilized to meet the needs in industry. With the help of these dispersions shoe soles with higher amount of open cells have been obtained. In this respect, products with lower density are obtained and comfort and cost advantages provided for end users. Styrene grafted polyester polyols were produced by adding styrene and dibenzoil peroxide into polyol and mixed and heated up to 130-150^{o}C to get styrene grafted polyol. Both saturated and unsaturated polyester polyols were synthesized and used for styrene grafting polymerization. The effect of polymerization temperature, dibenzoil peroxide concentration and styrene concentration were examined and optimum conditions were set up for industrial application. The final polyol product was vacuum distilled to remove residue styrene monomer. Other initiators such as AIBN and t-butyl hydro peroxide were also tried. Highest styrene grafting efficiency was about 12 wt. % based on polyol. The structure of the styrene grafted polyols were proved by using FTIR. Their physical and chemical properties such as viscosity, hydroxyl value, acid value, water content were determined. The polyurethane foam produced from these styrene grafted polyols has better stability and much lower shrinkage value depending on the amount of styrene grafted.

Second application; trichloropropyl phosphate (TCPP) has been widely used as fire retardant in rigid foam applications of polyurethane. However, toxic TCCP migrates out of the foam in time and toxic TCPP accumulate in the atmosphere and unfortunately the fire retardant property of the foam decreases. Due to these disadvantages of TCPP, some new alternative fire retardant agents have been synthesized by reacting TCPP with trihydroxyethyl isocyanurate (THEIC). Mole ratio of TCPP: THEIC were 1:1, 2:1, 3:1, and 5:1 respectively and the physical and chemical properties such as hydroxyl value, FTIR, NMR, TGA, GPC and viscosity of the produced fire retardant compounds were examined. The formed transesterification products have higher molecular weight and contain active primary hydroxyl group. Obtained new products are fire retardants compounds and can be used in the place of TCPP in fire retardant polyurethane formulations. These new products would be chemically bonded to polyurethane foam since they contain active primary OH groups. The covalent bonding eliminates the problem of migration and volatility of the fire retardant compounds. These produced fire retardant compounds were added into polyol component in the range of 5-23 wt. % of polyol and their fire retardant properties were compared using TGA, LOI and UL94 test methods. The fire retardant

efficiency of the new non-volatile and reactive compounds were about the same of TCPP.

Third, similar studies were carried out for the synthesis of transesterification reaction products between THEIC and tri (2-chloroethyl) phosphite. The formed products were added into polymix component in the range of 5-20wt% of polymix and the fire retardant properties of produced rigid polyurethane foams were compared using TGA, LOI, and UL94 test methods. 20 different polyurethane formulation were prepared and the fire retardant effect of the new nonvolatile reaction products were compared and found that their effects were about the same of TCPP.

Fourth, for halogen free and non-toxic fire retardant compounds, modified ketone resins have been synthesized and used as an alternative fire retardant.

The utilized resins were methyl ethyl ketone-formaldehyde resin (MEKF-Resin), cyclohexanone-formaldehyde resin (CF-Resin) and acetophenone-formaldehyde resin (AF-Resin) and they were modified with a mixture of diethylphosphite and ethanol amine and a mixture of diphenylphosphite and ethanol amine by using the Kabachnik-Fields reaction. Increasing reaction time and addition of catalyst such as magnesium perchlorate increase the conversion of carbonyl groups of the ketonic resin. However, conversion yield of carbonyl groups of ketonic resins were in the range of 60-85% thus the modified resins would have phosphorous in the range of 2-6%. The physical properties such as solubility in organic solvents and melting point of modified resins were drastically different than corresponding base ketonic resins. The structures of modified ketonic resins were elucidated by using FTIR, 1H-NMR, 13C-NMR and 31P-NMR spectroscopy and microanalysis. These modified ketonic resins were added into polyol component of the rigid polyurethane foam in the range of 5-25% and fire resistant properties of the foam products were determined using TGA, LOI and UL94 test methods. Polyurethane foams containing about 10 wt. % modified MEKF-Resin, modified CF-Resin and modified AF-Resin showed considerably good fire retardant effect.

Fifth, with the help of the knowledge gained from styrene grafting to polyester polyol grafting of dimethyl vinyl phosphonate to polyol has been studied to develop new polyester polyols with fire retardant property. The effect of polymerization time, the amount of initiator and temperature was studied. The viscosity, hydroxyl value of dimethyl vinyl phosphonate grafted polyol determined and used as polyol component in rigid polyurethane production. This developed polyester polyol containing about 20% dimethyl vinyl phosphonate enhanced the fire retardant property of the polyurethane foam and achieved a 9 cm fire length value in the horizontal test chamber in the UL 94 test.

Sixth, furthermore different additional new polyols have been synthesized and investigated for their fire retardant effect in the end product of rigid polyurethane foam. The Mannich reaction products of isocyanuric acid, diethanolamine and formaldehyde, and trimethylol isocyanurate were among synthesized compounds. Additionally, the reaction product of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with maleic anhydride and melamine modified ketone resin have been synthesized. However, the synthesis of these type of compounds has not been continued without any further research attempts due to low fire retardant property and/or high cost.

Seventh, using bio-based polyols. Nowadays, bio-based product development is one of trend research topic. The world tends to favor the usage of sustainable resources instead of petroleum. International companies make investments and request products.

In this respect, bio-polyol has been supplied from Croda Corporation. By using this polyol, toxic dimethylformamide free polyurethane artificial leather has been synthesized. Dimethyl sulfoxide and toluene have been used as solvent. The obtained product was a bio-based (51% Bio), dimethylformamide free polyurethane artificial leather and its physical properties were similar to conventional polyurethane artificial leather prepared under similar conditions.

POLİÜRETANLAR İÇİN YENİ FONKSİYONEL POLİOLLER

ÖZET

Bu çalışmada, üç farklı temel uygulama alanı için çeşitli polioller sentezlenmiş veya kullanılmıştır. Bu uygulamalar sırasıyla, ayakkabı tabanı, sert köpük(yalıtım için) ve suni deridir.

Ayakkabı tabanı uygulamalarındaki İlk düşük yoğunluk talebi, poliester poliolde polistiren dispersiyonu hazırlayarak çözülmüş ve sonra stiren graft edilmiş doymamış poliol kullanılarak endüstrinin ihtiyacı karşılanmıştır. Bu dispersiyonların yardımıyla, yüksek miktarda açık hücreler içeren ayakkabı tabanlığı elde edilmiştir. Nu şekilde, düşük yoğunluklu ürünler elde edilirken konfor ve maliyet avantajları oluşmuştur. Stiren graftlanmış poliester poliol, poliolün içine stiren ve benzoil peroksidin eklenmesi, karıştırılması ve sıcaklığın 130-150^{o}C çıkarılmasıyla elde edilmiştir. Doymuş ve doymamış poliesterlerin herikiside sentezlenmiş ve stirenin graft edilmesinde kullanılmıştır. Polimerleşme sıcaklığı, benzoil peroksit konsantrasyonu ve stiren konsantrasyonu etkisi araştırılmış ve endüstriyel uygulama için optimum şartlar tespit edilmiştir. Son poliol ürünü, içende kalan stiren monomerini uzaklaştırmak için vakum damıtılması yapılmıştır. Ulaşılan en yüksek stiren graft etkinlik değeri poliol ağırlığının %12'si olmuştur. Ürünün viskozite, hidroksil sayısı, asit sayısı ve su içeriği gibi fiziksel ve kimyasal özellikleri tespit edilmiştir.

Bu stiren graft edilmiş poliolden üretilen poliüretan köpüğün stabilitesi graftlanmış stiren miktarına bağlı olarak daha iyi ve büzülme değerine daha azdır.

İkinci uygulama, trikloropropil fosfat (TCPP), alev geciktirici olarak rijit poliüretan uygulamalarında çok yaygın kullanılmaktadır. Fakat toksik olan TCPP, zamanla migrasyona uğrar ve atmosferde birikir ve maalesef köpüğün alev geciktirici özelliği azalır. TCPP nin bu olumsuzlukları nedeniyle, bazı yeni alternatif alev geciktiriciler, TCPP nin trihidroksietil izosiyanürat (THEIC) ile reaksiyonu ile sentezlenmiştir. TCPP:THEIC mol oranları sırasıyla 1:1, 2:1, 3:1, ve 5:1 alındı ve üretilen alev geciktirici ürünlerin hidroksil sayısı, FTIR, NMR, TGA, GPC and viskozitesi gibi fiziksel ve kimyasal özellikleri iclenmiştir. Oluşan transesterleşme ürünleri daha yüksek mol ağırlığına sahip olup aktif primer hidroksil grubu içerir. Ele geçirilen yeni ürünler alev geciktirici bileşiklerdir ve alev geciktirici poliüretan formülasyonlarında, TCPP yerine kullanılabilir. Bu yeni ürünler aktif primer hidroksil grubu içerdiği için poliüretana kimyasal olarak bağlıdır. Kovalent bağ, alev geciktirici bileşiklerin uçuculuk ve migrasyon problemlerini ortadan kaldırır. Bu üretilen alev geciktirici bileşikler poliol komponenti içine, poliolün ağırlıkça % 5-23 arasında eklenmiştir ve alev geciktirici özellikleri TGA, LOI ve UL94 test yöntemleri kullanarak mukayese edilmiştir. Bu yeni uçucu olmayan ve reaktif bileşiklerin alev geciktirici bileşikleri alev geciktirici etkinliği TCPP'ye aynıdır.

Üçüncü çalışmada, benzer çalışmalar THEIC ve tri(2kloroetil) posfit arasındaki transesterleşme reaksiyonu ile sentezlenecek ürünler için gerçekleştirilmiştir. Oluşan ürünler polimiks komponenti içine, polimiks'in %5-20 kadar eklenir ve oluşan

poliüretan köpüklerin alev geciktirici özellikleri TGA,LOI ve UL94 test yöntemleri kullanarak mukayese edilmiştir. 20 farklı poliüretan formülasyonu hazırlanmış ve alev geciktirici etkileri incelenmiş ve etkilerinin TCPP ile aynı düzeyde olduğu bulunmuştur.

Dördüncüsü, halojen içermeyen ve toksik olmayan alev geciktirici bileşikler olarak modifiye ketonik reçineler sentezlenmiş ve alternatif alev geciktirici olarak kullanılmıştır.

Kullanılan reçineler, metil etil keton- formaldehit reçinesi (MEKF-Resin), siklohekzanon-formaldehit reçinesi (CF-Resin), asetofenon-formaldehit reçinesi (AF-Resin) ve bu reçineler dietil fosfit ve etanolamin karışımı ve difenilfosfit ve etanol amin karışımı ile Kabachnik-Fields reaksiyonu kullanılarak modifiye edilmiştir. Artan reaksiyon zamanı ve magnezyum perklorat gibi kataliz eklenmesi ketonik reçinenin karbonil grubunun dönüşüm verimi arttırmıştır. Fakat, ketonik reçinenin karbonil grubunun dönüşüm verimi %60-85 arasında kalmıştır ve böylece modifiye reçineler %2-6 aralığında fosfor içerikli olmuştur. Modifikasye olmuş ketonik resin'in organik çözücülerde çözünürlüğü ve erime sıcaklığı gibi fiziksel özellikleri, asıl reçinin değerlerinden dramatik bir şekilde farklılaşmıştır. Modifiye ketonic reçinelerin yapıları FTIR, 1H-NMR, 13C-NMR, and 31P-NMR spektroskopisi ve mikroanaliz kullanarak aydınlatılmıştır. Bu modifiye ketonik reçineler, sert poliüretan formülasyonunda kullanılan poliol komponenti içine %5-25 oranında katılmıştır ve poliüretan köpük ürünlerinin alev geciktirici özellikleri TGA, LOI, ve UL94 test yöntemleri kullanarak tayin edilmiştir. Yaklaşık %10 modifiye MEKF-Reçine, modifiye CF-Reçine ve modifiye AF-Reçinesi içeren poliüretan köpükler oldukça iyi alev geciktirici özellik göstermişlerdir.

Beşincisinde ise stiren graft yapımında kazanılan deneyim ile dimetil vinil fosfonat'ın poliole graft yapılması alev geciktirici özellikli yeni poliester polioller geliştirilmesi amacıyla çalışılmıştır. Polimerleşme zamanı,başlatıcı miktarı, ve sıcaklığın polimerleşmeye etkisi çalışılmıştır. Dimetilvinil fosfonat graft edilmiş poliollerin viskozitesi ve hidroksil değerleri tayin edilmiş ve poliol komponenti olarak rijit poliüretan üretiminde kullanılmıştır. Yaklaşık %20 dimetil vinil fosfonat içeren bu geliştirilmiş poliester poliol, poliüretan köpüğün alev geciktirici özelliğini iyileştirmiş ve UL94 yatay test bölmesinde 9 cm lik alev uzunluğu değeri gerçekleştirmiştir.

Altıncı olarak, farklı yeni ek polioller sentezlenmiş ve poliüretan son üründe alev geciktirici etkileri incelenmiştir. İzosiyanürik asit, dietanolamin ve formaldehit arasındaki Mannich reaksiyon ürünü ve trimetiol izosiyanürat sentezlenen bileşikler arasındadır. Buna ek olarak, melamin modifiye ketonik reçine, 9,10-dihidro-9-okza-10-fosfafenantren-10-oksit (DOPO) ile maleik anhidrit reaksiyon ürünü sentezlenmiştir. Fakat, düşük alev geciktirici özelliği ve/veya yüksek maliyeti nedeniyle, bu tür bileşiklerin sentezine daha fazla araştırma denemeleri yapılmadan devam edilmemiştir.

Yedincisi, biyo esaslı poliollerin kullanımı. Günümüzde, biyo esaslı ürün geliştirme, araştırma konularındaki eğilimden birisidir. Dünya, petrol yerine yenilenebilir kaynak kullanımını tercih etmeye meyillidir. Uluslararası firmalar yatırımlar yapmakta ve ürünler talep etmektedir. Bu çerçevede, Croda firması biyo-poliol sunmaktadır. Bu poliolü kullanarak, toksik dimetilformamid içermeyen poliüretan suni deri sentezlenmiştir. Dimetilsülfoksit ve toluen solvent olarak kullanılmıştır. Elde edilen ürün biyo-esaslı(%51), dimetilformamid içermeyen poliüretan suni deridir ve onun

fiziksel özellikleri, aynı koşullarda hazırlanan bilinen poliüretan suni derinin özelliklerine benzerdir.

1. INTRODUCTION

Polyurethanes (PUs) are part of a very functional group of materials which are used in a wide range of domestic and industrial applications. Polyurethanes are widely used in many applications such as paints, artificial leather, foam mattresses, medical implants, rollers, insulation rigid foam, electrical encapsulation, engineering components, shoe soles, seals, and in the mining industry.

Polyurethanes are organic polymers that contain the urethane group in the structure. In general, they are produced by the reaction of a polyol with a diisocyanate. Depending on end use, the reaction may require the addition of additives such as chain extenders, catalysts, and blowing agents. The entire process can be carried out in one step by arrangement of the chemistry. Polyureas are similar in reaction to polyurethanes. They are made from polyamides and not polyols. Instead of urethane groups, they contain urea groups. Figure 1.1 illustrates the differences of the urethane and urea groups.

Urethane Urea

Figure 1.1 : Urethane and Urea Structure.

Polyurethane was first discovered by Otto Bayer and coworkers at I.G. Ferbenindustri, Germany in 1937 (Oertel, 1985). The initial work was the reaction of aliphatic isocyanate with a diamine to form polyurea which was infusible and hydrophilic. Further research on this subject demonstrated the reaction of a glycol with an aliphatic isocyanate to produce new materials with interesting properties. The industrial scale production of PU started in 1940. A noticeable improvement in the elastomeric properties PU was achieved in 1952, when polyisocyanate became commercially available. In 1952–1954, Bayer developed different polyester–polyisocyanate system. In 1958, Schollenberger of BF Goodrich introduced a new virtually crosslinked

thermoplastic PU elastomer. At approximately the same time, Dupont introduced a Spandex fibre called Lycra, which is a PU based on polytetramethylene glycol (PTMG), 4,4-diphenylmethylene diisocyanate (MDI) and ethylene diamine. With the development of low-cost polyether polyols, PU coatings opened the door for automotive applications. Formulations and processing techniques continuously developed as one- and two-pack systems were developed. The PU coating industry has entered a stage of stable progress and advanced technological exploitation. Today, PU coatings can be found on many different materials, to improve their appearance and lifespan. PU coatings give the demanded exterior high gloss, improved color retention, improved scratch and corrosion resistance in automotive industry. Different types of PU coatings are used in construction, where construction components are spray coated to make them more durable against environmental deterioration (Kim, 2003).

The wide applicability of polyurethane is due to functionality in selection of monomeric materials from a wide variety of macrodiols, diisocyanates and chain extender. The chemistry involved in the synthesis of polyurethane is centered on the isocyanate reactions (Szycher, 1999).

Recent trends in polyurethane are:

Renewable compounds, halogen free, non-toxic and smoke suppressant fire retardant polyols.

The main aim of this work is to synthesize variety of polyurethanes by using different special polyols with below properties;

Low density elastic and tough polyurethane for shoe sole;

Polyols for non-combustible and smoke depressed for rigid polyurethane;

Bio based polyurethane for synthetic leather;

Using these polyols polyurethane elastomers, microcellular elastomers, ıntegral skin polyurethanes, rigid polyurethane foams will be synthesized. After these works ındustrial trials and tests will also be carried out.

2. THEORICAL PART

2.1 Polyurethane

Polyurethanes (PUs or PURs) are an extremely versatile class of polymers. A wide variety of raw materials coupled with adaptable synthetic techniques allows the polyurethane chemist to design useful materials for many applications with different functions.

Table 2.1 lists commercially important usage categories for urethanes along with examples of manufacturing methods and physical properties. All of the items shown can be readily achieved by proper choice of starting materials, polymer design, processing conditions, and application technique. While polyurethanes certainly have limitations, it is arguable that no other class of polymers can match their collective versatility, usefulness, and performance.

Urethane polymers are formed by reaction of polyisocyanates and polyols which create the urethane chemical linkage. The general structure or bond that forms the basis of this chemistry is the urethane linkage shown in Figure 2.1.Second level titles must be bold and the first letter of each word in the title must be capital (i.e. 2.1 Process Qualification Analysis).

Polyurethanes are of great significance in a large number of industrial applications. For example they can be use in shoe sole, rigid foam (isolation) and artificial leather industries. These include adhesives, elastomers and foams, as well as raw materials for coatings.

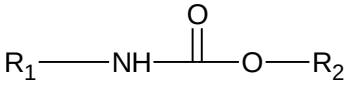


Figure 2.1 : Basic urethane structure.

In Table 2.1 Types of polyurethane applications, their physical states and properties and also their processing methods are summarised.

Table 2.1 : Polyurethanes: Applications, properties and processing methods.

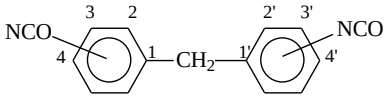
Applications	Physical States and Properties	Processing Methods
Foams	Thermosets	Open-cast molding
Elastomers	Thermoplastics	Fiber spinning
Coatings	Amorphous or	Blow molding
Adhesives/sealants/binders	Microcrystalline	Injection molding
Encapsulants	Hard or soft	Extrusion/pultrusion
Elastomeric fibers	Transparent or opaque	Reaction injection
Films	High or low T_g	Molding
Gels	Aromatic or aliphatic	Spraying/brushing/rolling
Composites	Hydrophilic or	Resin transfer molding
Microcellular elastomers	Hydrophobic	Rotational casting
Rubbers/millable gums	100% Solids/solvent	Rotomolding
	borne/water borne	Thermoforming
	Resilient or energy	Compounding/vulcani-
	Absorbing	Zation
	Polyester/polyether/	Compression molding
	Polyacrylate	Centrifugal molding

2.1.1 Isocyanates

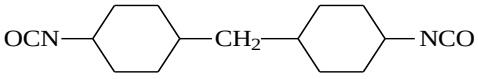
Unlike polyethylene, which is the polymerization product of ethylene, polyurethane is not the result of the polymerization of urethane. Urethane is a specific chemical bond that comprises a very small percentage of the bonds of polyurethane.

There are several ways to categorize isocyanates. However, the broadest picture is aromatic versus aliphatic. Aromatic MDI, PMDI, and TDI constitute by far the largest worldwide volume of isocyanates manufactured. Two characteristics emerge with these compounds. First, their aromaticity causes materials based on them to absorb ultraviolet (UV) radiation, which triggers numerous oxidative side reactions in the presence of atmospheric oxygen and water. These oxidation reactions form colored quinoidal and other delocalized moieties which cause a discoloration to yellow or brown. Discoloration is undesirable in most applications, but usually does not affect bulk physical properties unless its extent is extreme. In coating applications, this sensitivity to light is critical and can cause not only discoloration but also loss of surface gloss, crazing, and many other problems. UV radiation can also penetrate a larger percentage of the material's thickness, affecting not only the surface, but the bulk properties of the material as well, causing embrittlement, cracking, and peeling. It is important to note that although aliphatic urethanes are dramatically less sensitive to light than aromatic formulations, they are still susceptible to UV-induced degradation and are extensively tested accordingly.

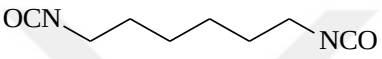
It is important to be aware of the chemical effects of isocyanates. The ratio of the polyols and isocyanates will in part dictate both the physical and chemical properties of the product. As a general rule, the isocyanates are hard segments that impart rigidity to the polymer (Gillis, 1994). There are different types of isoctanates listed in Figure 2.2.



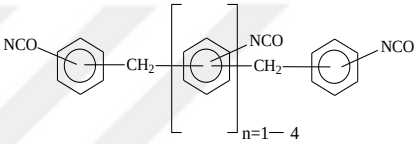
4.4', 2,4' and 2,2' Methylene diphenyl diisocyanate (MDI)



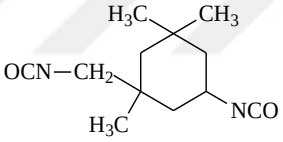
4.4' Dicyclohexylmethane diisocyanate



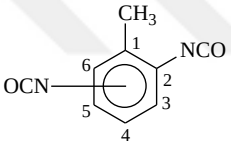
Hexamethylene diisocyanate



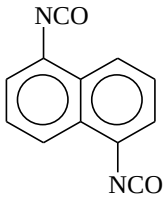
Polymeric MDI (PMDI)



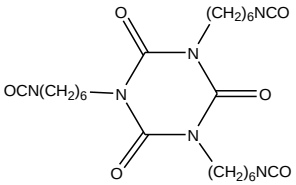
Isophrone diisocyanate (IPDI)



2.4 and 2.6 diisocyanate



Naphtalane diisocyanate



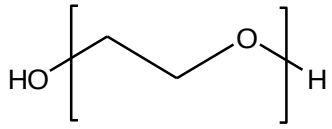
Isocyanurate trimer of HDI

Figure 2.2 : Examples of commercially important isocyanates.

2.1.2 Polyols

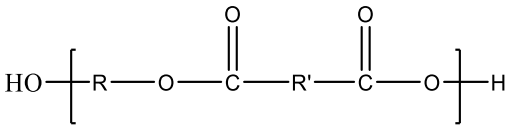
The polyol takes part in defining properties of the finished polymer, including flexibility, softness, low-temperature properties, and processing characteristics.

Figure 2.3 shows representations of common polyol types, distinguished by their backbone structure. (Ionescu, 1998)

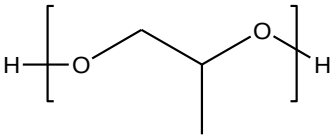


Polyethylene glycol

(C_2 polyether polyol)

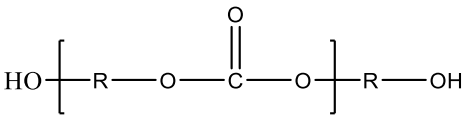


Polyester polyol

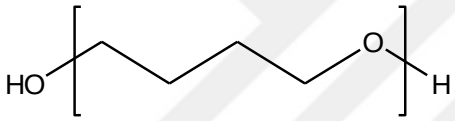


Polypropylene glycol

(C_3 polyether polyol)



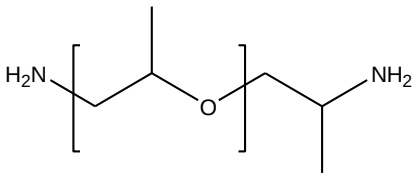
Polycarbonate polyol



Polytetramethylene glycol

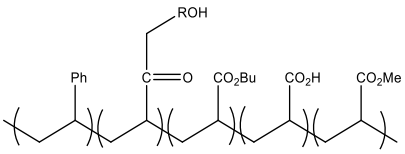
C_4 polyether polyol

Polycaprolactone polyol

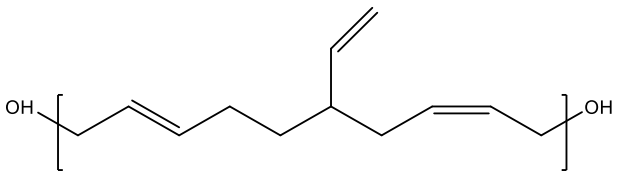


Amine terminated polyether

(ATPE)



Polyacrylate polyol (Acrylic)



Polybutadiene polyol

Figure 2.3 : Common urethane-grade polyol types.

2.1.2.1 Polyether polyol

Polyether diols form a very important segment of the diols used in the manufacture of polyurethanes. The normal route is by addition polymerization of the appropriate monomeric epoxide.

The most important polyethers are polypropylene glycol (C_3) and polytetramethylene glycol (C_4). The manufacturing route is given in Figure 2.4.

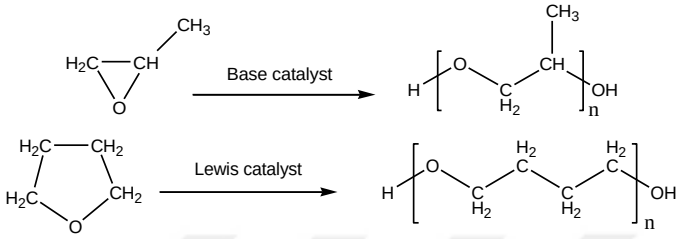


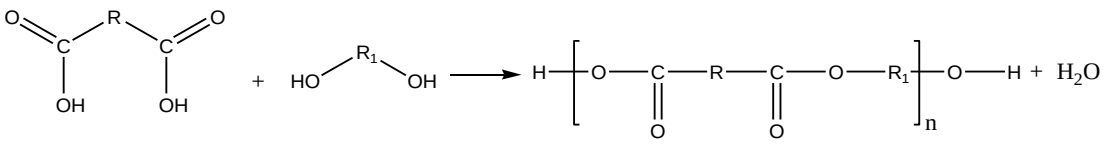
Figure 2.4 : Manufacturing route of PPG and PTMEG.

Polyurethanes produced from polyether glycols are not as strong and tough as the polyester-based polyurethanes, but they have far superior hydrolytic stability. The standard polyol in this group is polytetramethylene glycol (PTMEG), which gives compounds superior physical and mechanical properties to those produced with polypropylene glycol (PPG). The PTMEG provides excellent mechanical properties and very low abrasion loss.

2.1.2.2 Polyester polyol

There are three main classes of polyester polyols: (i) Linear or lightly branched aliphatic or aromatic polyester polyols (mainly adipates or phtalates) with terminal hydroxyl groups, (ii) Polycaprolactones and (iii) Polycarbonate polyols

Ester linkage have inherently better oil resistance but lower hydrolytic stability. The classical-based polyester is made by the reaction of a dibasic acid diol with the formation of a polyester and water, but the water has to be removed. The general reaction equation is shown in Figure 2.5.



Dibasic acid Diol

Figure 2.5 : Polyester polyol reaction.

Polyesters produce strong, tough, oil-resistant materials. The major drawback is absence of hydrolysis resistance. The basic polyester polyols are prepared by the reaction of a dibasic acid (usually adipic, sebacic, or phthalic acid) with a diol such as ethylene glycol, 1,2-propylene glycol, and diethylene glycol.

The polyesterification conditions must be such that only hydroxyl groups form the terminal groupings. The water of condensation formed must be removed to a level of 0.03% for production of good polyurethanes in the next step.

The molecular weight of polyester polyol is determined by the molar ratio of the glycols and adipic acid. Closer the molar ratios to 1:1, higher the degree of polymerization is maintained. The functionality of polyester polyol can be increased by the introduction of triols such as glycerol or trimethylolpropane, which leads to branching of the polyester backbone.

Polyester polyols for elastomeric applications are usually linear or slightly branched, with the latter used mainly for fast curing shoe soling applications. The glycol selection is a decision making between cost, ease of processing and the required level of physical properties. For thermoplastic polyurethane (TPU) applications, adipates based on ethlene glycol, 1,4-butane diol and 1,6-hexane diol are most commonly used

Polycaprolactam polyol is made by the opening of the caprolactam ring.Caprolactam is also used in the production of nylon. Their structure appears to provide a degree of protection from hydrolytic attack. They are formed by the reaction shown in Figure 2.6. Their hydrolytic properties fall between those of PTMEG and other polyesters.

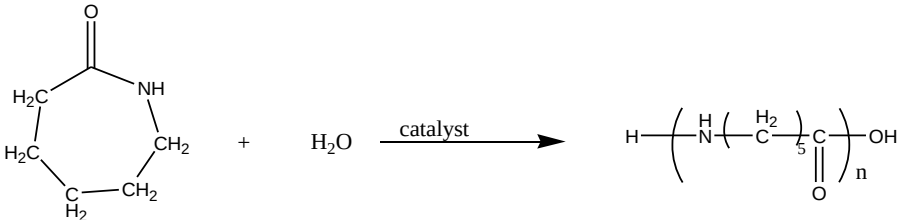


Figure 2.6 : Synthesis of polycaprolactam.

When reacting either ethylene carbonate or propylene carbonate with an aliphatic diamine, a polyurethane can be produced (Figure 2.7). Poly (ethylene ether carbonate) diols produce elastomers that have polyester polyol features when fabricated into polyurethanes using methylene diphenyl diisocyanate and 1,4-butanediol. This was shown using ^{13}C NMR. The structure gives rise to potential for a very high virtual

cross-linking density.These carbonate-derived polyesters have superior hydrolysis resistance compared to the traditional materials.

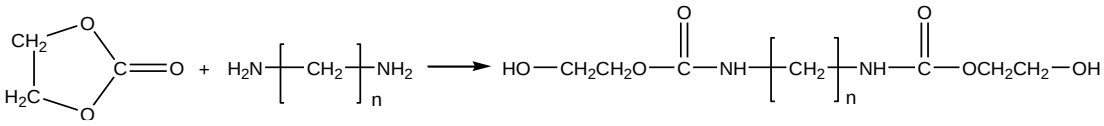


Figure 2.7 : Synthesis of polycarbonate polyol (Buist, 1968; Saunders, 1962).

Polymer containing polyester polyol; Polymer containing polyols consist of dispersions of a solid polymer in the polyols are frequently used in the manufacturing processes for flexible polyurethane foams. The use of such products provides advantages such as an increase in the degree of opening the foam cells and improvement of the mechanical properties, which are derived from an increased hardness, compression strength, tear strength and tensile strength.

This allows a reduction in the polyurethane system density because it is possible to maintain the same properties as obtained with higher densities and conventional polyols, with the financial savings that the process involves.

The most frequent process are the polymerization, by using conventional polyol as medium although there are also references to use of other types of polymers, such as polyureas produced from polyisocyanates and polyamines, always in a polyol.

The reaction is carried out by the in situ polymerization of vinyl monomers, usually either acrylonitrile or mixtures of acrylonitrile and styrene, in a carrier polyol in the presence of free radical catalyst, such as azobisisobutyronitrile or benzyl peroxide at temperatures around 80 to 90 ^{o}C. The choice of carrier polyol is determined by the end application. Apart from free polyol and and dispersed polymer, the polymer polyol contains a third and very important species which is called graft co-polymer. It is made separately, for example by reacting a vinyl monomer onto the polyether backbone.

The reaction conditions should be controlled to obtain stable dispersions with the required particle size distribution, in the range of 0,1 to 5 micron. The introduction of styrene resolved the problems of polyol and foam discoloration. However, it is difficult to make stable polymer polyols as the level of styrene is increased. 80 percent styrene (based on the total vinyl monomers) is the maximum amount found in commercial products. The references are less frequent to the use of hydroxylated polyesters, as is

the case of this work, and among the few known, practically none emphasizes their use in specific applications (Capellades and Maria, 1987).

2.1.2.3 Acrylic polyol

Traditionally, acrylic resins are used in paints and coatings. Acrylic polyols are employed in polyurethane coatings for automotive finish with good chemical resistance and durability. Below these comonomers can be used in acrylic polyol synthesis (Figure 2.8);

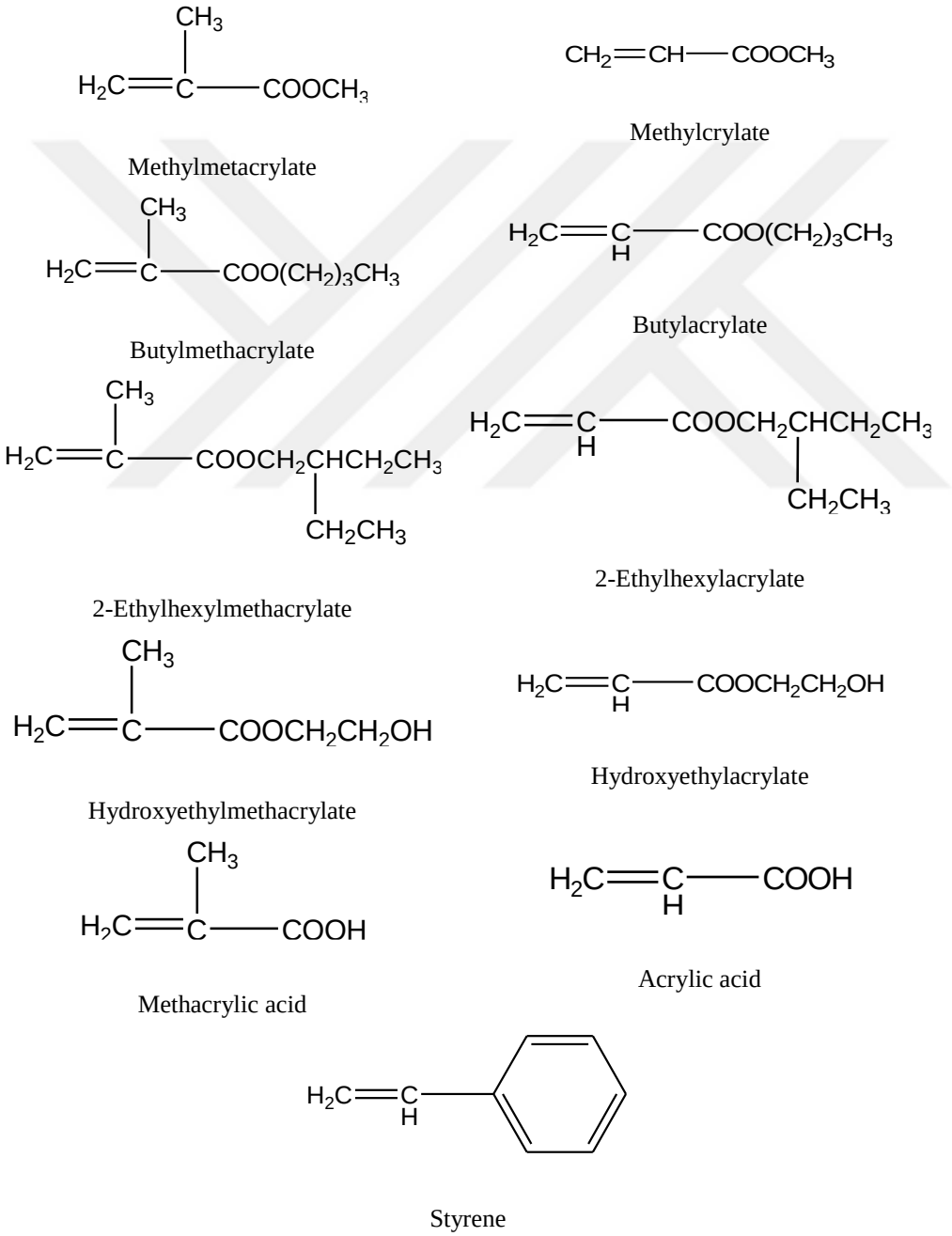


Figure 2.8 : Common monomers for acrylic polyol.

Acrylic polyol based PU coatings depend profoundly on the chemical nature of the monomers used. Example of preparation of acrylic polyol reaction can be seen in Figure 2.9;

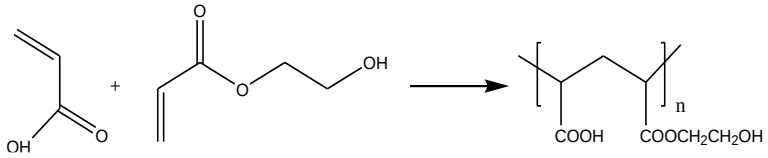


Figure 2.9 : An example for preperation of acrylic polyol.

Thus, methylmethacrylate (MMA) confers exterior durability, excellent light stability, hardness and water resistance. Styrene confers hardness, water stability but, unfortunately, poor light stability. Butyl and 2-ethylhexyl acrylates and methacrylates confer flexibility and acrylic and methacrylic acids confer adhesion to metals and solvent/grease resistance (Lyons, 1970; Ferrigno, 1967).

2.1.2.4 Polysiloxane polyol

Polysiloxane chains display a combination of very interesting properties. These include very low glass transition temperature (T_g) of (T_g = –123 °C), high thermal, UV and oxidative stability, low surface energy, hydrophobicity, high gas permeability, good electrical properties and physiological inertness or biocompatibility (Bruins, 1969).

As a result, it is very meaningful to use these kinds of polymeric chains to build an oligo-polyol structure with terminal hydroxyl groups. The resulting structure called a polysiloxane polyol gives polyurethane (PU) elastomers which conserve their high elasticity at very low temperatures, after reaction with diisocyanates.

The synthesis of some experimental siloxane polyols is based on several reactions developed in two steps:

Step I: Synthesis of a polysiloxane chain of molecular weight (Mw) of 1000-3000 daltons, having terminal -Si-H bonds, by using classic reactions. These kinds of polysiloxanes with terminal -Si-H bonds are available commercially.

Figure 2.10 shows that a method of polysiloxane synthesis by using dimethylchlorosilane and dimethyldichlorosilane in presence of water. The formation of the product can be seen in the step 2.

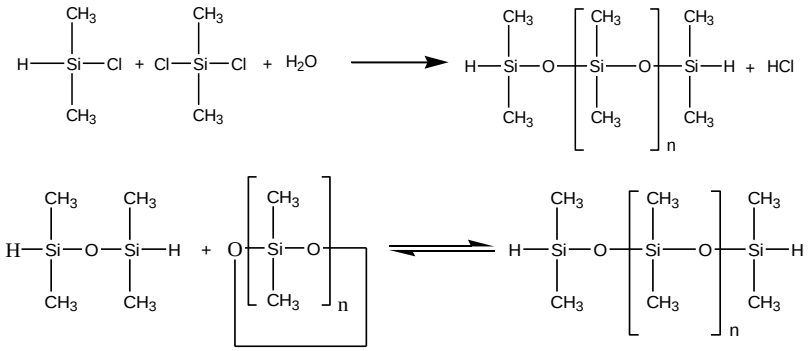


Figure 2.10 : Polysiloxane synthesis methods.

Step II: The addition of the -SiH group to a compound having a double bond and a hydroxyl group (allyl alcohol or allyl alcohol based polyethers). The reaction is catalysed by platinum, palladium or rhodium catalysts as can be seen in Figure 2.11 (for example H_2PtCl_6, platinum complexes or even solid platinum supported catalysts). Hydrolysis resistant -Si-C- bonds are formed" (Lyons, 1970; Ferrigno, 1967).

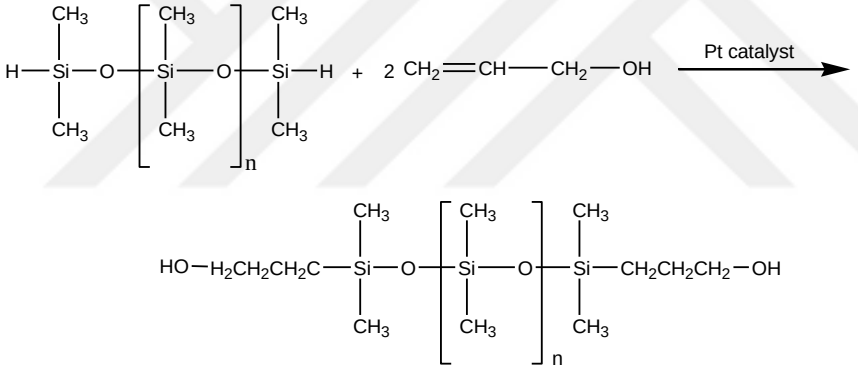


Figure 2.11 : PDMS diol synthesis.

2.1.2.5 Polybutadiene polyol

Polybutadiene diol is especially preferred because of its excellent hydrolysis and chemical stability, and insulating properties. It is obtained by free radical polymerization of butadiene, initiated by hydrogen peroxide and an alcohol as diluents. Figure 2.12 shows synthesis of hydroxyl terminated polybutadiene reaction.

Figure 2.12 : Synthesis of hydroxyl terminated polybutadiene.

Due to its very low glass transition temperature the PUs formed have excellent elastomeric properties at extremely low temperatures. They possess great capacity to

accept fillers as asphalt, aromatic and paraffinic oils, pentanes, plasticizers and carbon black.

Hydroxyl terminated polybutadiene microstructure is 60% of 1,4-trans, 20% of 1,4-cis and 20% of 1,2-vinyl insaturations that turn possible further vulcanization and chemical modifications (Lyons, 1970; Ferrigno, 1967).

2.1.2.6 Chain extender

The two main groups used as chain extenders are diamines and hydroxyl compounds. Triols are also used where some cross-linking is required. The choice of chain extender depends on the properties required and the process conditions. However, diols are the most commonly used hydroxyl compound. They provide good properties and processing speed with MDI-based prepolymers and diamines with TDI-terminated prepolymers.

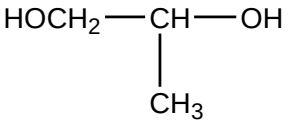
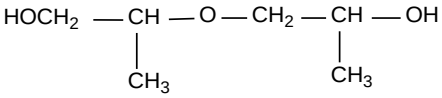
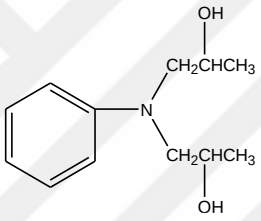
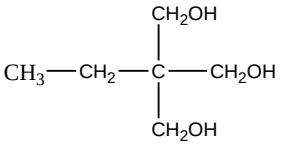
The molecular shapes of the isocyanate and extender molecule often are considered to play a part in the ease of formation of hydrogen bonding. The molecules must be able to come closer to each other for hydrogen bonding to take place.

There must be no steric hindrance to the two chains. Molecules with an even number of carbons allow the hydrogen donor group (NH) to fit more easily to each electron donor group (C=O). If the carbon number is odd, the fit is poor, and many groups cannot participate in hydrogen bonding.

Experimentally it has been shown that the melting points of polyurethanes made with a series of aliphatic diisocyanates with different number of carbons in the chain varied with the number of carbons in the diisocyanate. Polyurethane fabricated with an odd number of carbons in the isocyanate had a lower melting point than those on either side with an even number of carbonatoms in the isocyanate chain (Clemitson, 2008).

Hydroxylated chain extender and crosslinkers are listed in Table 2.2 which interiors chain extenders and crosslinkers' chemical structure, OH funtction number and molecular weight

Table 2.2 : Hydroxylated chain extender and crosslinkers.

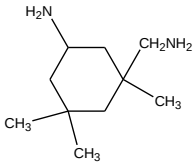
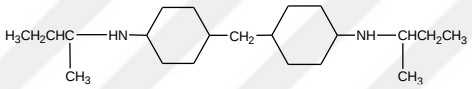
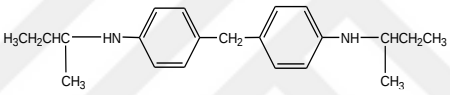
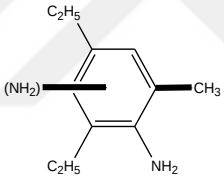
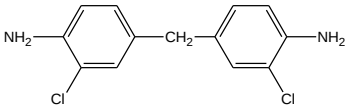
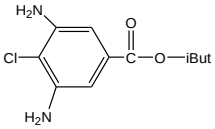
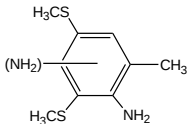
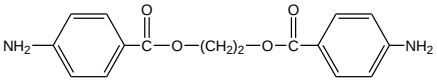
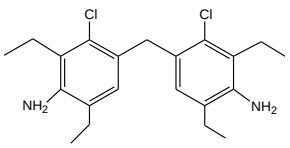
COMPOUND	STRUCTURE	F	M_W
Ethylene glycol	$HOCH_2$-CH_2OH	2	62
Di-ethylene glycol	$HOCH_2$-CH_2-O-CH_2CHOH	2	106
Propylene glycol		2	76
Di-propylene glycol		2	134
1,4 Butane-diol	$HOCH_2$-CH_2-CH_2-CH_2OH	2	90
2-Methyl-1,3-Propylene- diol	$HOCH_2$-$CH(CH_3)$-CH_2OH	2	90
Water	HOH	2	16
N-N'-Bis-(2 hydroxy-propylaniline) (DHPA)		2	221
1,4-Di-(2-hydroxyethyl) hydroquinone (HQEE)		2	198
Diethanol amine	$HOCH_2CH_2NHCH_2CH_2OH$	3	105
Triethanol amine	N-$(CH_2CH_2OH)_3$	3	149
Trimethylol propane		3	134
Glycerine	HOCH-CH_2OH-CH_2OH	3	92

Low molecular weight diamines (Table 2.3) are used as chain extenders in polyurea and polyurethane/urea processes. Compared to their reaction kinetics with polyols, they react much faster with isocyanates.

Due to their longer pot life, the less reactive aromatic diamines are used in cast PU elastomers prepared in two-step processes. Aliphatic and aromatic amines are used as chain extenders in polyurea, RIM processes and spray coatings, where their higher reactivity results in shorter demold times.

The use of more reactive aliphatic or less reactive secondary aromatic diamines makes possible to vary the system reactivity.

Table 2.3 : Diamines used as chain extender.

COMPOUND	STRUCTURE	M_W
Hydrazine	$H_2N\text{-}NH_2$	32
Ethylene daimine	$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$	60
1,4-Cyclohexanediamine		114
Isophorone diamine (IPDA)		170
4,4'-Bis-(sec-butyl amine) dicyclohexylamine. (SBADCHM)		322
4,4'-Bis-(Sec-butil amine) diphenylmethane (SBADFM)		310
Diethyl-toluene diamine (DETDA) isomers 2,4 (80) e 2,6 (20)		178
4,4'-Methylene-bis(2-Chloroaniline) (MOCA)		267
4-Chloro-3,5-diamino-benzoic acid isobutylester (CDABE)		242,5
3,5-Dimethylthio-toluenediamine (DMTDA) - isomers 2,4 (80) e 2,6 (20)		214
Trimethyleneglycol-di-p-aminobenzoate (TMGDAB)		314
4,4'-Methylene-bis-(3-chloro-2,6-diethylaniline) (M-CDEA)		365

2.1.2.7 Reactions of isocyanates

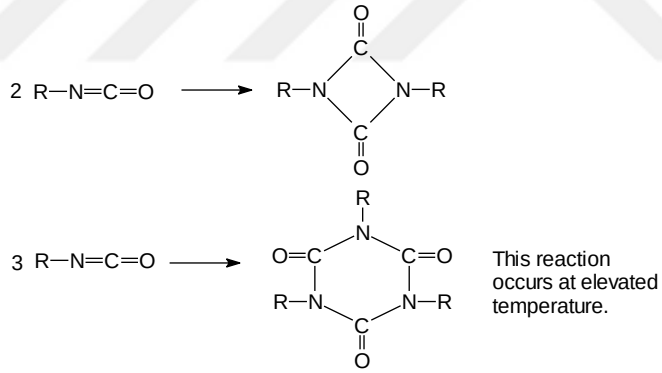
Isocyanates are highly reactive chemicals and create several chemically different products when combined with –OH and –NH functional sub¬stances.

Desired products and side products are formed in different amounts. The basic reactions of isocyanate with different reagents are shown in Figure 2.13.

The high reactivity of isocyanate groups, especially in aromatic systems, toward nucleophilic reagents is mainly due to the positive character of the C atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen. In the isocyanate group, the electronegativity of the oxygen and nitrogen conveys a large electrophilic character to the carbon in the isocyanate group.

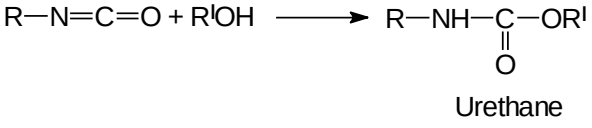
The common reactions of isocyanates can be divided into two main classes: (1) the reaction of isocyanates with compounds containing reactive hydrogen to give addition products, and (2) the polymerization of isocyanates, i.e., self-addition reaction. Isocyanates react with hydroxyl compounds to give urethanes.

Self Reaction (Cyclic dimerization and trimerization)



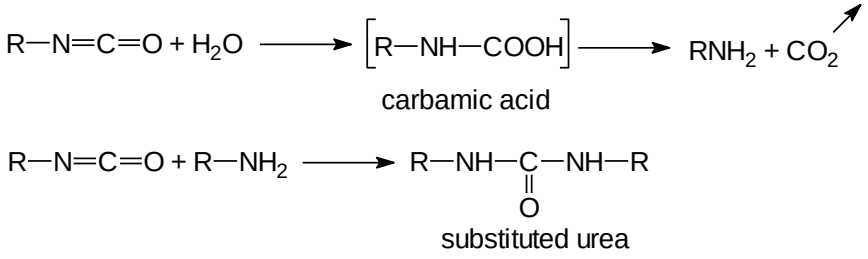
Self Reaction (Carbodiimid formation)

Reaction with alcohols

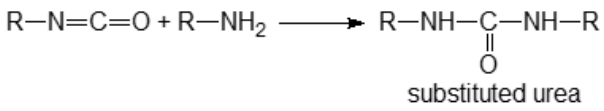


Urethane

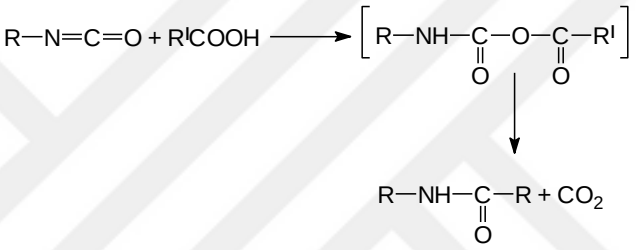
Figure 2.13 : Reactions of isocyanates with different reactants.



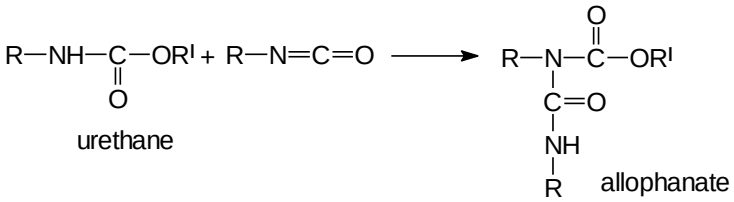
Reaction with amine



Reaction with carboxylic acid



Reaction with urethane (allophanate formation- This reaction occurs at elevated temperature.)



Reaction with substituted urea (Biuret formation)

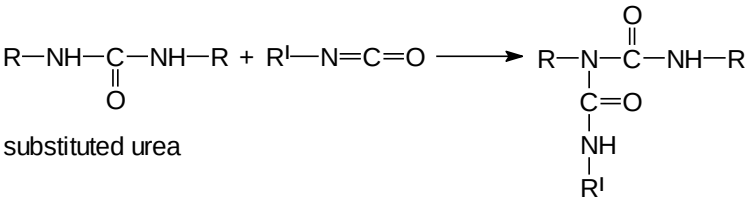


Figure 2.13 (continued) : Reactions of isocyanates with different reactants.

2.1.2.8 Catalyst

In terms of industrial productivity, the isocyanate group reacts rather slowly with alcohols, water and itself in the absence of catalysts. The catalyst choice for PU's

manufacture is usually directed for obtaining an appropriate profile among the several reactions that can occur during PU production processes.

Tertiary amines, organometallics (primarily tin containing compunds) and carboxylic acid salts are used as catalyst in the reaction of isocyanates with water (blowing) and polyols (polymer gelation). The catalyst functions as a controlling agent for the relative reaction rates of the isocyanate with polyol and water.

Amine catalysts are generally considered as blowing catalysts since they tend to catalyse the isocyanate water reaction better than the isocyanate-polyol reaction. However, amines actually catalyse both reactions, with the relative rates of each reaction being dependant on the specific amine catalyst used.

Organametallic catalysts are mainly seen as gelation catalysts although they take partial role in the isocyanate–water blowing reaction. Organotins are the most widely used, but organomercury and organolead catalysts are also used. The mercury catalysts are very good for elastomers because they give a long working time with a rapid cure and very good selectivity towards the gelation. The lead catalysts are often used in rigid spray foams. "Potassium and carboxylic acid salts and quaternary ammonium carboxylic acid salts are used to catalyse the trimerisation reaction and thus are used mainly in isocyanurate foams" (Randall and Lee, 2002). For the tin salts the following mechanism has been proposed Figure 2.14. The isocyanate, polyol and tin catalyst form a ternary complex, which then gives the urethane products. Two routes have been proposed for the complex formation. In the first route, the tin first adds to the polyol then the isocyanate. In the second one, the tin adds to the oxygen of the isocyanate then reacts with the polyol.

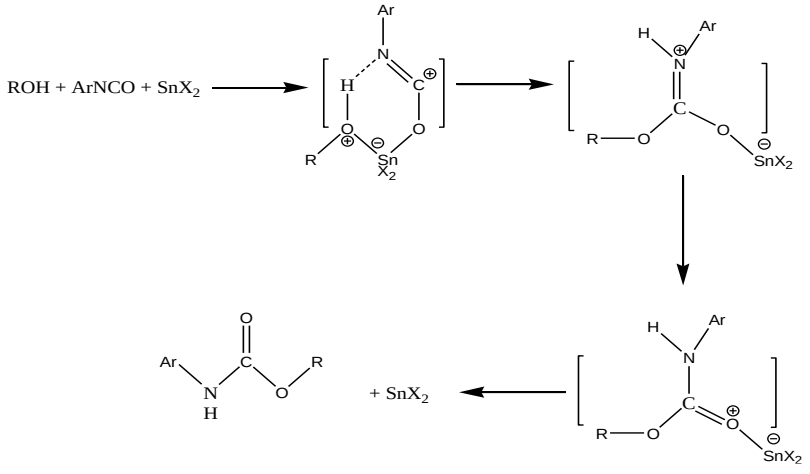


Figure 2.14 : Mechanism for tin (II) salts.

The growing catalyst basicity promotes improved crosslink formation (alophanate and biuret). Generally, with tertiary amines the higher basicity increases the catalytic effect, except in the occurrence of steric hindrance. Triethylene diamine (TEDA) or 1,4-diazo (2,2,2)-bicyclo-octane (DABCO) have a stronger catalytic effect due to the absence of steric hindrance. It is important to state that the catalyst specificity can vary according to the system used. Therefore, attention should be paid for extraction of correlations from studies done in different systems. Basically the catalyst should be sufficiently nucleophilic to stabilize the isocyanate group by resonance, or to activate the active hydrogen atom-containing compound. According to the basic catalysis mechanism given in Figure 2.15, initially formation of a complex between the base and the isocyanate group takes place which activates the NCO group and makes easier the reaction with the non-paired electrons of the alcohol oxygen atom. Afterwards the complex is decomposed, forming PU and regenerating the base.

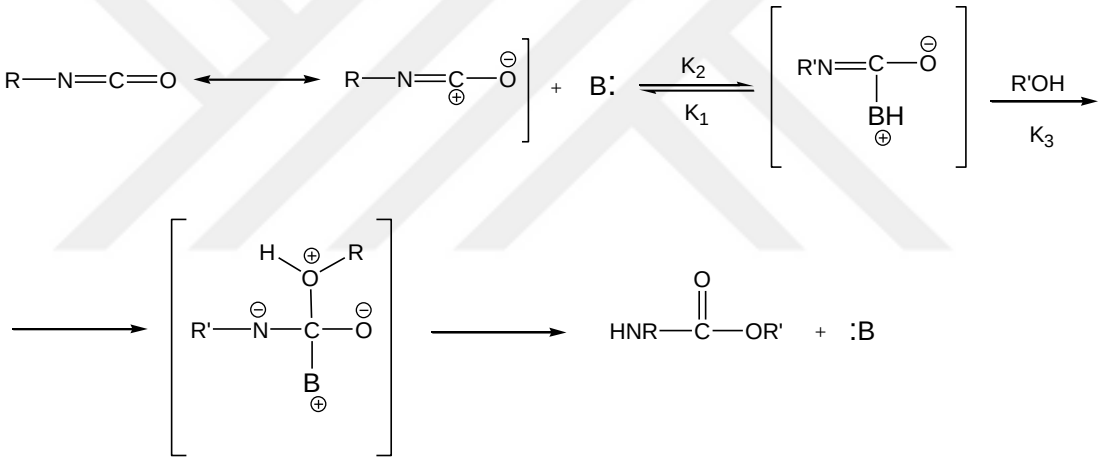


Figure 2.15 : Basic catalysis mechanism.

2.2 Ketonic Resins

Ketonic resins are generally used as additives in many applications including surface coating industry. Their preparations goes back to 1890s (Hurst et al., 1951; Novotny, 1940; Hauben, 1890). They are prepared by the reaction of ketones with aldehyde especially formaldehyde in the presence of basic catalyst. The first step of the condenzation is a cross-aldol addition reaction to form methylol ketones. Further reaction at higher temperatures gives the ketonic resin. First step of methyl ethyl ketone-Formaldehyde resin formation is an acidic α-hydrogen on methylene carbon

rather than methyl carbon is removed by the base and the formed carbanion attacks the carbonyl group of formaldehyde to form methylol ketone (Figure 2.16). Sometimes dimethylol ketone might also be formed depending on the ratio of formaldehyde to ketone. Through the condensation of methylols, the resin is formed by the effect of base and temperature.

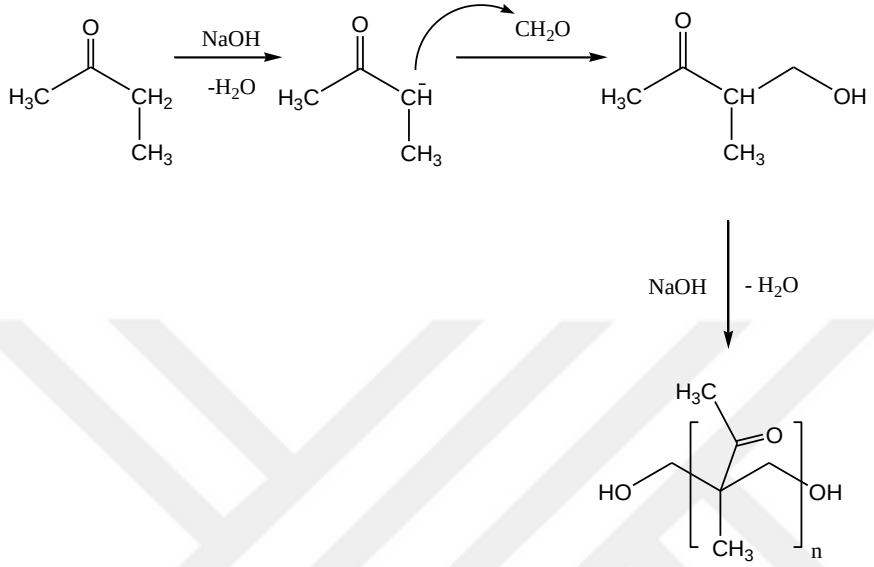


Figure 2.16 : Methyl ethyl ketone-formaldehyde resin formation.

Formation of acetophenone formaldehyde resin is similar as seen below (Figure 2.17). First step is removal of acidic α-hydrogen on methyl carbon by the base and the formed carbanion attacks the carbonyl group of formaldehyde to form methylol ketone

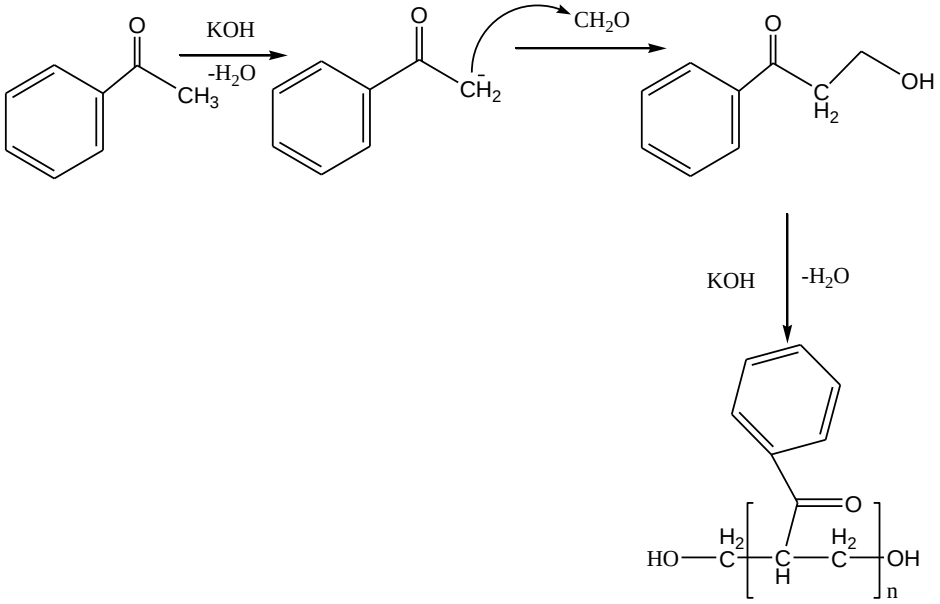


Figure 2.17 : Formation of acetophenone-formaldehyde resin.

Cyclohexanone-formaldehyde resin can also be prepared from cyclohexanone and formaldehyde and its structure as follows. Sometimes dimethylol ketone is also formed depending on the ratio of formaldehyde to ketone (Figure 2.18).

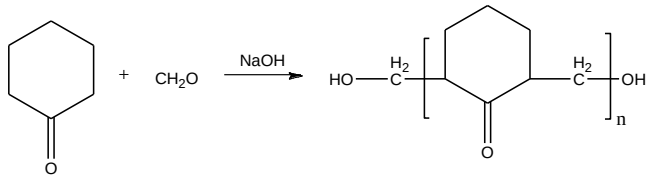


Figure 2.18 : Cyclohexanone formaldehyde resin.

Better preparation methods of ketonic resin have been recently achieved by using solvent and phase transfer catalysts such as benzyl trimethyl ammonium chloride. Resin formation time is reduced considerably (Doerfell et al., 1988 and Gloeckner et al., 2009).

2.2.1 Modification of ketonic resin

By modifying ketonic resins, their desired physical properties such as melting point and solubilities in solvents can be improved, and the number of application of the ketonic resin can be increased. The modification is classified as modification of ketonic resin during the preparation and modification of ketonic resin after the preparation.

2.2.1.1 Modification of ketonic resin during the preparation (in situ modifications)

Modification of ketonic resin can be achieved in situ by adding reactive compounds to the polymerization flask during resin preparation (Kızılcan, 1999; Kızılcan, 2005). The modifier may be added to the polymerization system either at the beginning or later stage of polymerization depending on its reactivity. Phenolic compounds such as phenol, cresols, bisphenol-A, acetaldehyde, glyoxal, amines such as melamine, silicone tegomer with amine chain ends were used as in situ modifier compounds. Recently, in situ alendronic acid modified ketonic resin was prepared (Figure 2.20). Nano clay composites of modified ketonic resin and used for polyurethane preparation (Önen, 2015). Structure and formation of alendronic acid modified ketonic resins could be represented as Figure 2.19.

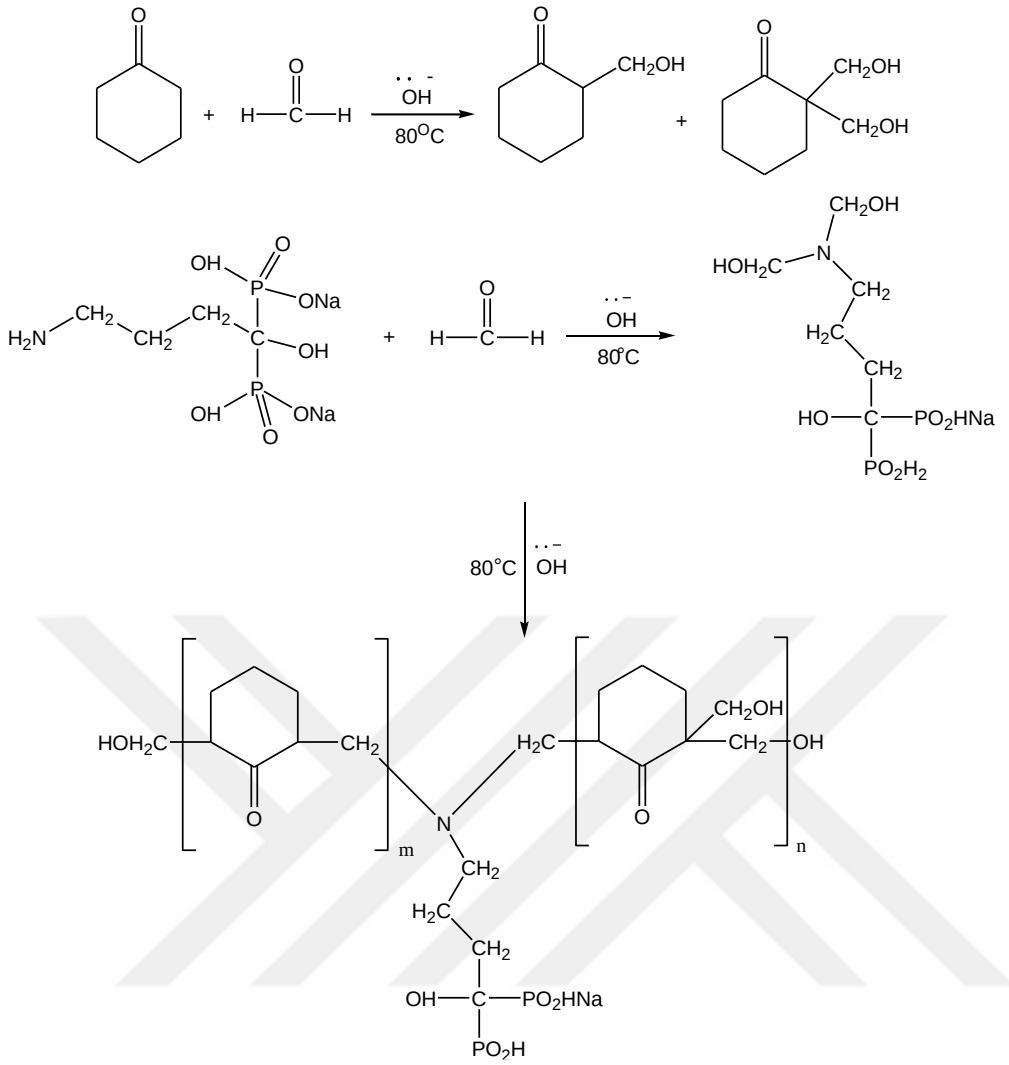


Figure 2.19 : Formation of alendronic acid modified ketonic resin.

Other examples of in situ modified ketonic resin with bisphenol-C and rezorsine are shown in the Figüre 2.20 below.

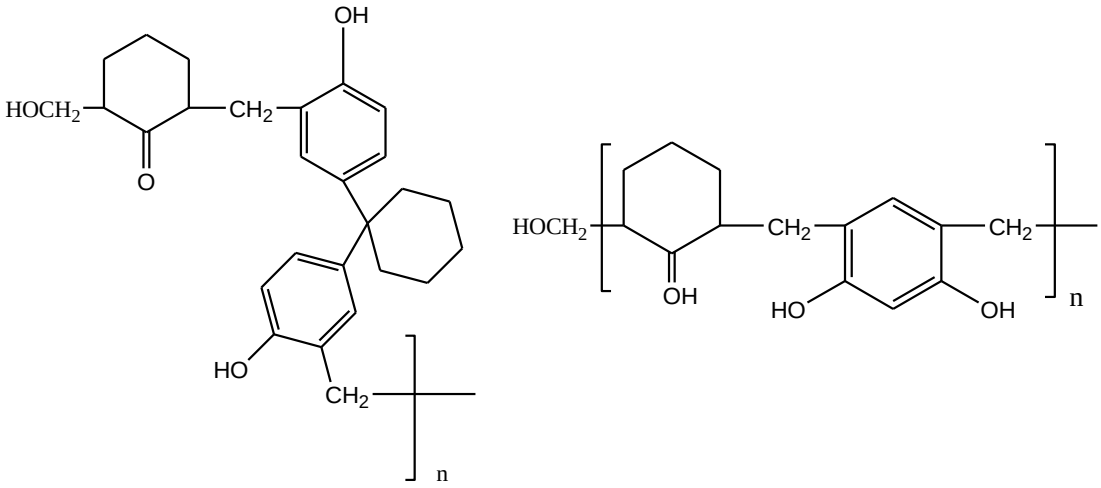


Figure 2.20 : In situ bisphenol and rezorsine modified CF-Resin.

Modified ketonic resins show changes in their melting temperature, solubility and molecular weight.

2.2.1.2 Modification of ketonic resin after preparation via their functional groups

Ketonic resins are also modified by the reaction of their functional groups with appropriate reagents (Akar et.al., 1988 and Kızılcan et.al., 1993). Properties such as solubility, melting point of modified resin are affected by the degree of modification. Modifier compound such as acid chloride, acid anhydride, reacts with hydroxyl groups of the resin. Hydroxyl amine, hydrazines, bisulfite may condense with carbonyl groups. Besides, ketonic resin and modified ketonic resin have been used for production of copolymer (Kızılcan et.al. 2012; Akar et.al., 1989) and as polyol in polyurethane preparation (Baslas 1981; Eugene, 2004).

In the following Figure 2.21 after modification of acetophenone-formaldehyde resin via its hydroxyl and carbonyl functional groups is shown.

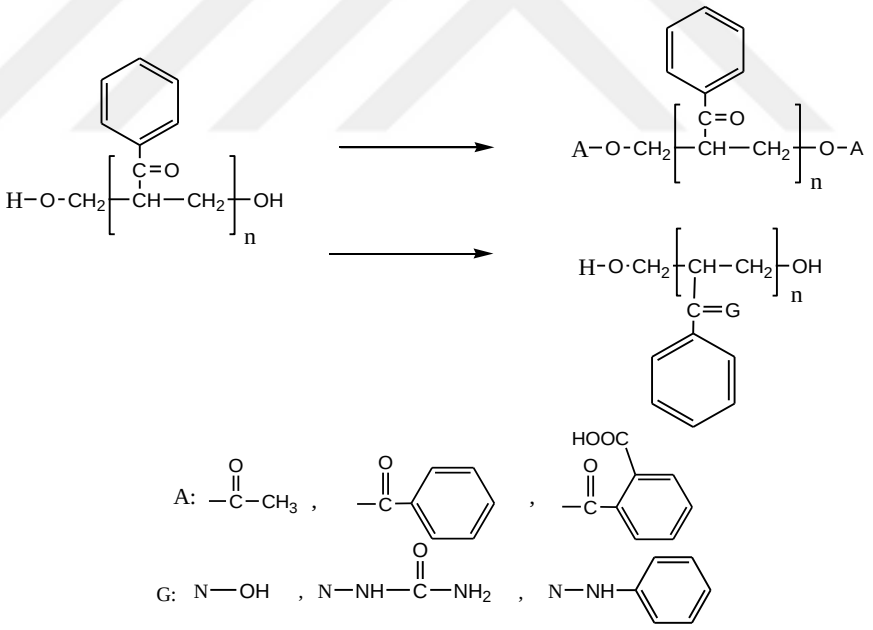


Figure 2.21 : After modification of acetophenone-formaldehyde resin via its hydroxyl and carbonyl functional groups (Kızılcan, 1993).

2.2.1.3 Kabachnik-Fields reaction

Kabachnik-Fields reaction is a three component reaction. Carbonyl component, amine component and dialkyl phosphite or trialkyl phosphite. General scheme is shown in the Figure 2.22 below (Zefirov, 2008 and Keglevich, 2012).

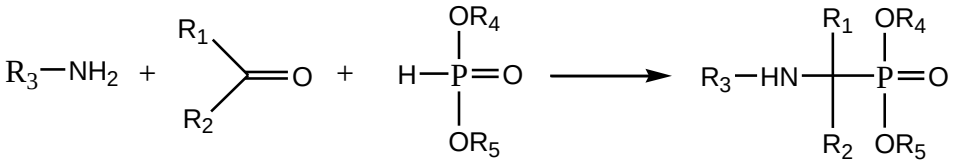


Figure 2.22 : Three component reaction.

There are a number of proposed mechanisms (Matveeva et.al., 2008). Several ketones such as aliphatic ketones, aromatic ketones and cyclic ketones are used for this reaction.

Phosphite may be alkyl and aryl phophites. Different aliphatic and aromatic amines can also be used for this reaction. Water formed during the reaction and it is removed azeotropically or by a proper water absorber such as Na_2SO_4. The conversion is generally 80-95%. However, sometimes higher temperature and longer reaction time might be necessary. It is reported that some catalysts increase the yield of conversion as shown in the Figure 2.23 (Zefirov, 2008).

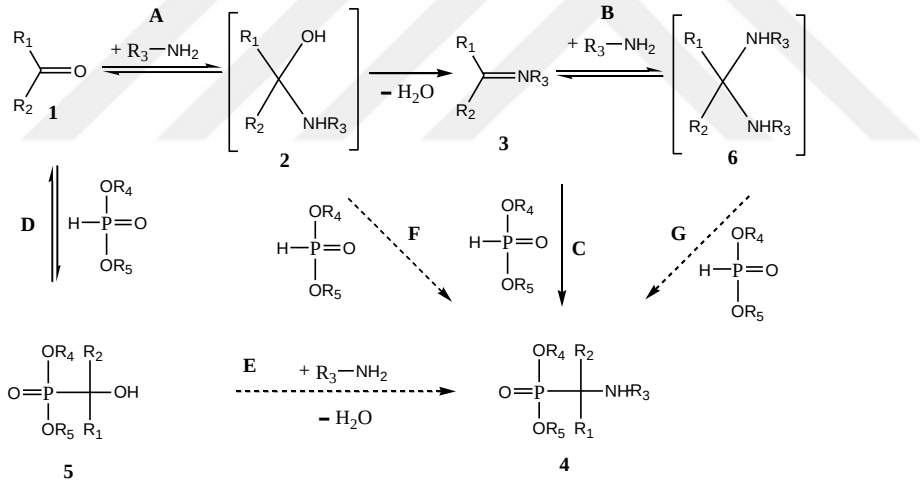


Figure 2.23 : Kabachnik-Fields reaction mechanism (Matveeva et.al., 2008).

Cyclohexanone and acetone react with an ethanol amine and diethyl phosphite reagents (Kabachnik-Fields reaction) to produce diethyl 1-(2-hydroxyethyl) amino cyclohexyl phosphonate and 1-(2-hydroxyethyl) amino acetone phosphonate respectively (Figure 2.24) (Hindersin, 1968 and Smith 1974) and they are now commercially available. Acetophenone gives the same Mannich reaction with ethanolamine and diethyl phosphite at higher temperature and in longer reaction time to get similar high yield.

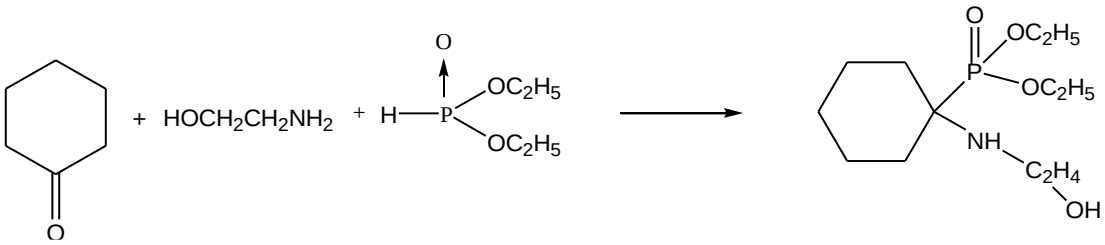


Figure 2.24 : The structure of the product produced from cyclohexanone, ethanol amine and diethyl phosphite.

2.3 Flame Retardants

A Flame Retardant (FR) is a molecule/polymer (inorganic or organic) useful for inhibiting flame growth by one of the three mechanisms. FR is used to put out a fire in three main ways: (i) passively (guard against fire), (ii) actively (extinguishing agent) and (iii) some FR additives have multiple chemical applications (Ionescu, 2005; Wilkie, 2009)

2.3.1 General approaches of flame retardant for polymers

Fire retardants can be broadly classified into 3 different additives: (i) gas phase, (ii) endothermic, (iii) char forming / condensed phase.

They can also be classified in 7 different fire retardants in terms of their structures: (1) Halogenated (gas phase): Decabromo diphenyl ether, hexabromo cyclododecanone. (2) Phosphorus (gas and condensed phase): Encapsulated red phosphorous, ammonium polyphosphate, aluminum phosphinate, tri phenyl phosphate, tricrecyl phosphate, DOPO, phosphate polyols. (3) Mineral fillers (Endothermic): $Al(OH)_3$, $Mg(OH)_2$ and Carbonates $CaCO_3$, huntite, boehemite (AlOOH), talc, kaolinite. (4) Intumescent (char forming / condensed phase): Polyol + ammonium polyphosphate + melamine (melamine borate, melamine phosphate). (5)

Inorganic (mostly condensed phase): Zinc borate ($2ZnO•3B_2O_3•3.5H_2O$). (6) Nitrogen based (gas and condensed phase): Melamine, melamine phosphate, melamine cyanurate, HALS. (7)

Polymer nanocomposites (condensed phase): Organically treated layered silicates (clays), carbon nanotubes/nanofibers, or other submicron particles at low loadings (<10%).

2.3.1.1 Gas phase flame retardants (Examples: Halogen, Phosphorus)

They reduce heat in gas phase from combustion by scavenging reactive free radicals, resulting in incomplete combustion. Halogen (F, Cl, Br, I) or Phosphorus (P-O or P) are the most commonly used vapor phase radical scavenger/inhibitors. They can be very effective at low loadings. However, they cause increase in carbon monixide and smoke.

Gas phase flame retardants interact chemically with the free-radical process in polymer combustion. The effectiveness of a gas phase flame retardant is determined by its effective "Release Temperature" and the polymer degradation pathway of the material being flame retarded.

2.3.1.2 Endothermic flame retardants (Examples: Metal Hydroxides, Carbonates)

The decomposition of these flame retardants is endotermic. Its function is in the gas phase and condensed phase by releasing non-flammable gases (H_2O, CO_2) which dilutes the fuel and cools the polymer. They are generally very cheap in cost. However, high loading is necessary and this degrades mechanical properties of polymer.

Endothermic decomposition cools the condensed phase, slowing down degradation, or taking away heat that would lead to fuel release. The well known fire retardands are $Al(OH)_3$, $Mg(OH)_2$ and some mineral carbonates such as hydromagnesite.

The effectiveness of a endothermic flame retardant is also determined by its effective "release temperature" and the polymer degradation pathway of the material being flame retarded.

2.3.1.3 Char forming flame retardants (Examples: Intumescents, Nanocomposites)

They operates in condensed phase by preventing fuel release and providing thermal insulation for underlying polymer. They provide a very robust method at providing fire safety. However, they are not universally acceptable for all polymer systems and it can be expensive.

With the use of high char-forming, crosslinking, and pre-ceramic materials, one can potentially: (i) prevent fuel molecules from reaching the flame front and (ii) prevent

further depolymerization of the plastic. However, the char formation must activate before peak decomposition temperature so it has time to set up and provide protection (Figure 2.25).

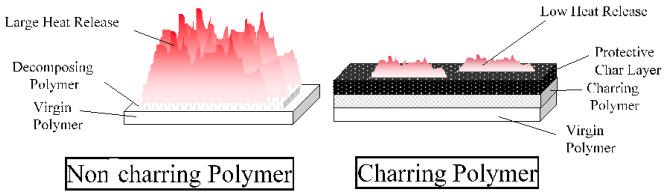


Figure 2.25 : Char forming flame retardants.

2.3.2 Phosphorus flame retardants

Phosphorus is a functional element for flame retardants since the element exists in several oxidation states. It can be inorganic such as ammonium polyphosphate, red phosphorus or organic such as phosphates, phosphonates, phosphinates.

Its main flame retardant action is formation of char layer on substrate surface and some of them sometimes may operate simultaneously in both phases.

Phosphorus FR additives cover a wide range of chemical structures and can be both gas and condensed phase FR additives. They can be very effective at lowering heat release rate at low loadings of additive.

Phosphorus FR additives do not typically need synergists, but they are sometimes more effective when combined with other types of flame retardants or elements, such as halogenated FR (Phosphorus-halogen vapor phase synergy) and nitrogen compounds (Phosphorus-nitrogen condensed phase synergy).

2.3.2.1 Mechanism of the effect of phosphorus-based fire retardants

Gas phase effect:

To act in the gas phase through the formation of PO• , PO_2•, HOPO•, and $HOPO_2$• radicals which terminate the highly active flame-propagation radicals (HO• and H•). These radicals are formed after the decomposition of the parent compound in the flame. Therefore, flame inhibition does not depend on the form of the parent compound. Gas phase effect on free radicals can be seen in Figure 2.26 in example of phosphorus compounds.

$$P \longrightarrow PO\bullet + P\bullet + P_2$$

$$PO\bullet + H\bullet \longrightarrow HPO$$

$$HO\bullet + PO\bullet \longrightarrow HPO + \bullet O\bullet$$

$$P_2 + PO\bullet \longrightarrow PO\bullet + P\bullet \text{ and so on}$$

Figure 2.26 : Gas phase effect via free radicals.

Condensation phase effect:

In the condensed phase mechanism, the phosphorus flame retardant is thermally broke down to give phosphoric acid which is further dehydrated to polyphosphoric acid in the Figure 2.27.

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$n\ H_3PO_4 \longrightarrow \text{polyphosphoric acid} + (n\text{-}1)\ H_2O$$

Figure 2.27 : Condensed phase mechanism.

Polyphosphoric acid esterifies and dehydrates the polymer giving rise to unsaturated carbonous species that make up a residue that protects the polymer surface from further degradation.

Nitrogen based flame retardants are typically melamine and melamine derivatives (e. g., melamine cyanurate, melamine polyphosphate, melem, melon). They are often used in combination with phosphorus based flame retardants (Figure 2.28).

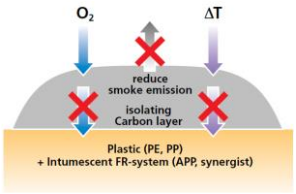


Figure 2.28 : Char forming flame retardant.

2.3.3 Fire resistance polyurethanes

Polyurethanes are high combustible material and burn completely in case of fire. High number of research have been carried out to increase the fire resistance of polyurethanes. Fire retardants used in polyurethane formulation are halogenated fire retardants, Organic phosphorus compounds and inorganic fire retardands.

2.3.3.1 Halogenated fire retardants

In the flame, halogenated organic fire retardants act by blocking the chain reactions characteristic for the flame (W. Lyons, 1970). So any organic compound containing chlorine or bromine decomposes by the effect of flame into the corresponding acids (HCl or HBr) and these acids react with the most reactive radical existing in the flame, the hydroxyl radical, HO* (Figure 2.29).

$$HO^* + HCl \longrightarrow H_2O + Cl^*$$

Figure 2.29 : Hydroxyl radical reaction mechanism.

The chlorine radical reacts with the organic substrate in Figure 2.30.

$$Cl^* + RH \longrightarrow HCl + R^*$$

Figure 2.30 : Chlorine radical reaction mechanism.

Thus the chain reactions in the flame are terminated. This phenomenon is called self-extinguishing.

2.3.3.2 Organic phosphorus compounds

Organic phosphorus compounds, irrespective of their structure, decompose to polyphosphoric and methaphosphoric acids, which retain the acidity at higher temperatures and catalyse the rapid decomposition of the polyurethane to carbon. During fire extinguishing process, carbonaceous layer containing phosphorus is formed, which is very difficult to burn. It provides a true protective layer for the rest of polyurethane material and the process of burning is stopped (Hilado, 1969).

2.3.3.3 Organic phosphorus and halogen compounds as fire retardants

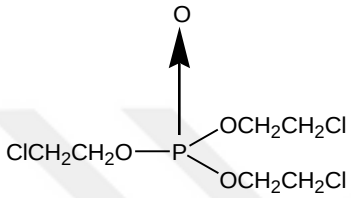
Generally, halogens act in the flame and phosphorus compounds in the polymeric substrate. Having both groups of elements (halogens and phosphorus), in the same structure leads to a synergism. The significance of synergism is that a phosphorus – halogen combination has the same flame retardance effect at the lower concentration of each element.

The presence of nitrogen in the structure of a flame retardant is very beneficial because nitrogen is an element which is difficult to burn (Papa, 1970, Papa, 1972 and Ionescu, et.al, 1998).

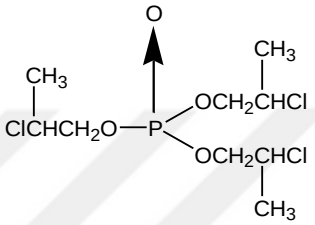
There are two types of organic flame retardants for polyurethanes: (i) Additive flame retardants and (ii) reactive flame retardants (Backus, 1971).

2.3.3.4 Additive type flame retardants

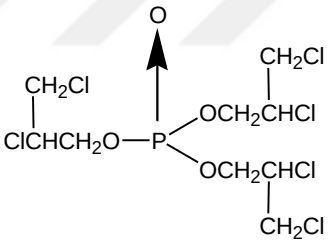
The additive type of flame retardants are compounds containing chlorine, bromine or phosphorus, boron and silicone without reactive groups to get involved in polyurethane chemistry (without -OH, $-NH_2$ or -NCO groups) as seen in the Figure 2.31. These compounds are physically added to polyurethane and are not part of the polyurethane structure.



Tris-(2-chloroethyl) phosphate (TCEP)



Tris-(2-chloroisopropyl) phosphate (TCPP)



Tris-(2,3 dichloropropyl) phosphate

Figure 2.31 : Examples of well known additive flame retardants for polyurethane.

Dimethyl methyl phosphonate (DMPP) is another important flame retardant additive. DMPP has a very high phosphorus content (P= 25%) (Papa, 1970):

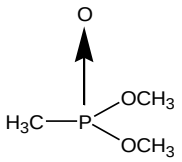


Figure 2.32 : Dimethyl methyl phosphonate (DMPP).

Unfortunately, DMPP is not hydrolysis resistant and the acidity increases with significant decrease in reactivity of the polyurethane formulation. Besides, the flame retardant additives of his types of organic compounds such as tris (2-chloroethyl) phosphate have a tendency to migrate, which later causes loss of flame retardancy.

For example, a rigid polyurethane foam containing tris (2-chloroethyl) phosphate (TCPP) as a flame retardant, completely loses its flame retardancy after a year.

2.3.3.5 Reactive flame retardant

The chemically reactive flame retardants are generally polyols containing halogens, phosphorus, boron, silicone and nitrogen (Backus, 1971).

These flame retardant polyols, have hydroxyl groups (generally terminal), react with isocyanates in the process of polyurethane synthesis and they are chemically bound to the polyurethane structure.

Chemically linked reactive flame retardants assure a permanent flame retarding effect and stable physical properties in long term (Hilado, 1969).

Halogen containing polyols; Bromine containing polyols are very effective, reactive flame retardants in polyurethane. One of the most representative bromine polyols used in rigid and flexible flame retardant PU foams is 2,3 dibromobutene diol (Frisch, 1972) is shown in the Figure 2.33.

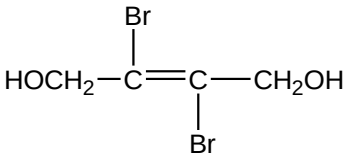


Figure 2.33 : 2,3 dibromobutene diol.

Dibromo neopentylglycol is another low molecular weight reactive flame retardant, (Termine and et.al., 1985 and Boulet, and et.al., 1974) with labile aliphatic -C-Br bonds as shown in Figure 2.34.

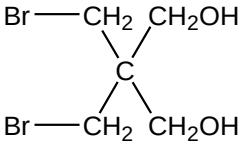


Figure 2.34 : Dibromo neopentylglycol.

The bromine linked to a double bond or linked to an aromatic nucleus are much more stable structures. Bromine containing diol is based on tetrabromophthalic anhydride as shown in Figure 2.35, and it is industrially produced (Papa, 1970; Jensen and et.al, 1982).

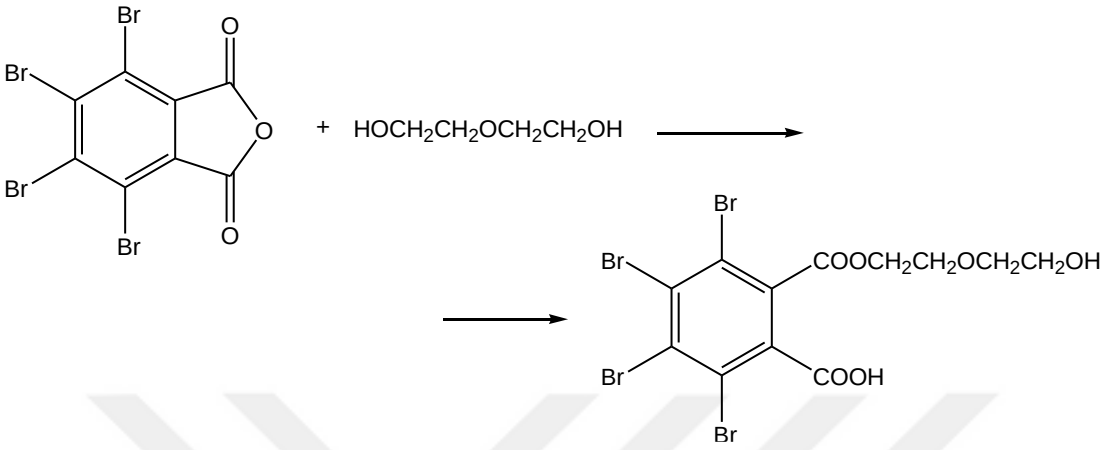


Figure 2.35 : Formation bromine containing diol fromtetrabromophtalic anhydride.

A bromine aromatic polyol is obtained by the Mannich type reaction between 2,4 dibromophenol (or 2,6 dibromophenol) with diethanolamine and formaldehyde (Paulik, 1998) or with oxazolidine (Modesti and et.al.,1994), followed by the propoxylation of the resulting Mannich base with 2-3 mols of PO (Paulik, 1998; Modesti and et.al.,1994) (Figure 2.36).

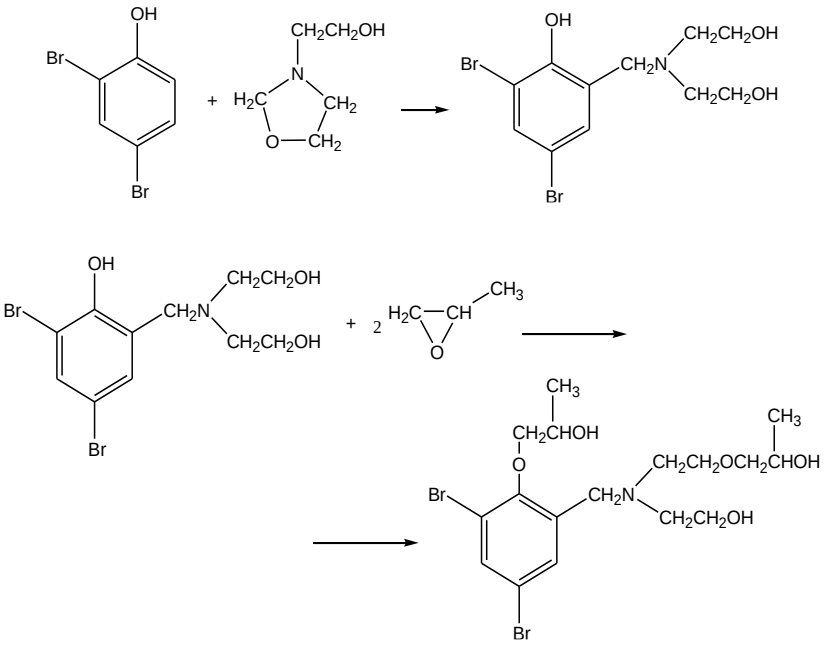


Figure 2.36 : Mannich type reaction between 2,4 dibromophenol (or 2,6 dibromophenol) with diethanolamine and formaldehyde.

The resulting bromine polyol has a bromine content of about 33-38% with hynumber of 360-390 mg KOH/g and a viscosity in the range 16,000-25,000 mPa-25 °C.

Tetrabromobisphenol A is bromine containing raw material produced industrially. By the ethoxylation of tetrabromobisphenol aromatic bromine diol is obtained with 8-9 moles of ethylene oxide (EO), (Figure 2.37).

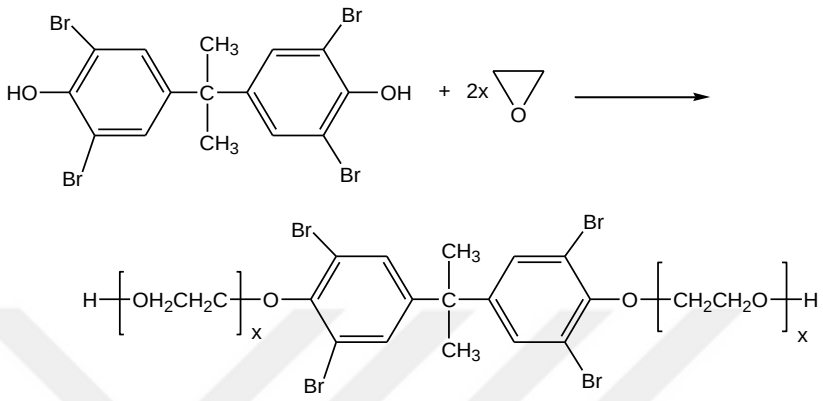


Figure 2.37 : Ethoxylation of tetrabromobishenol A.

Recent trends of flame retardants in polyurethane;

In recent years, there has been an effort to eliminate halogens from all flame retardant compounds, and utilize only halogen free flame retardants. Therefore, there is a tendency to avoid and in turn finally ban the use of TCEP and TCPP, which are two of the most widely used additive flame retardants for fabrication of fire resistant PUs.

This ban is due to the toxic and corrosive gases formed during combustion and envorinmental concerns. Environmental and health concerns are now gaining importance since toxic TCPP migrates and evaporates during the use of flame retardant PU material and contaminate the atmosphere. The relative order concerning the fireproofing efficiency of halogens is: Cl < Br < P. A flame retarded rigid PU foam needs about 20-25 % chlorine or 5-6 % bromine or 1.5-2 % phosphorus (Lyons, 1970; Hilado, 1969; Papa, 1970; and Backus, 1971).

Many reactive flame retardants for PU were developed, unfortunately only a few are used effectively in practice. Phosphorus polyols are the most important reactive flame retardants in PU. They can be examined in the following groups: Esters of ortho-phosphoric acid, esters of phosphorus acid; phosphonate polyols, phosphine oxide polyols,phosphoramidic polyols.

Esters of Ortho-Phosphoric Acid; These phosphorus polyols are produced by using the following two methods; by the reaction of propylene oxide with polyphosphoric acids (Papa, 1970 and Ferrigno, 1967) (Figure 2.38).

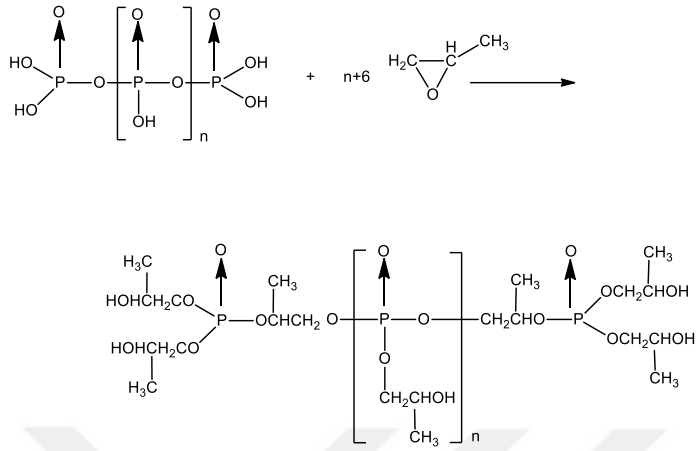


Figure 2.38 : Propoxylation of polyphosphoric acid.

The resulting phosphorus polyol (18.8) has a hydroxyl number of 300-310 mg KOH/g, a phosphorus content of 9.5-10% and a viscosity of 1,600-3,000 mPa-s at 5 °C.

They can also be produced by the condensates of phosphorus pentoxide with n-butanol (Papa, 1972) and the resulting product reacted with propylene oxide (Figure 2.39).

The resulting phosphorus diol has a hydroxyl number of 210-215 mg KOH/g and a phosphorus content of 11.2% (Papa, 1972).

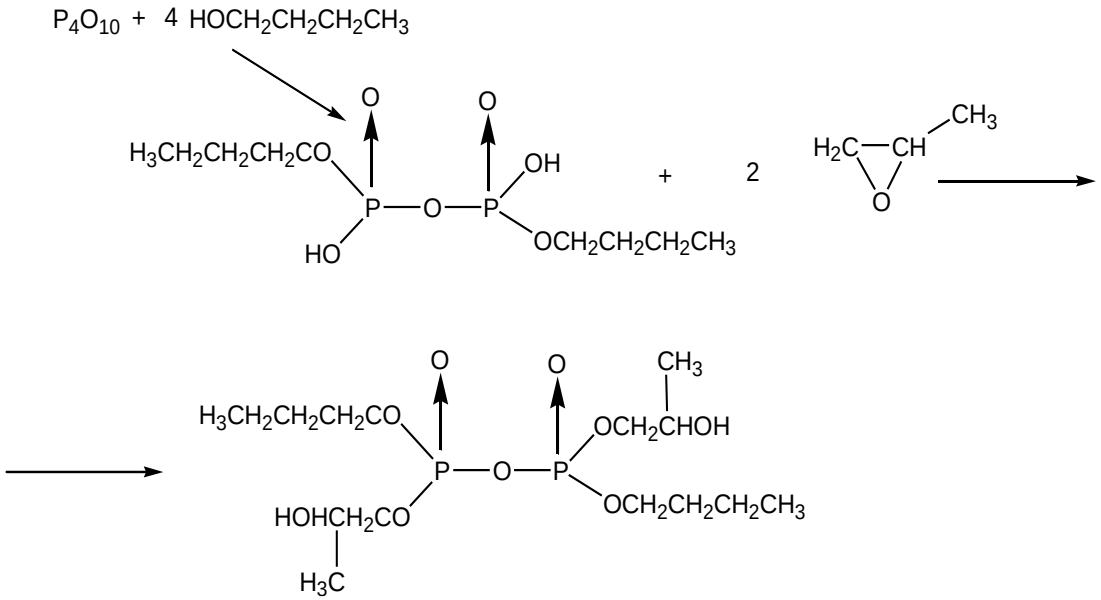


Figure 2.39 : Propoxylation of phosphorus pentoxide with n-butanol condensate.

These phosphorus polyols with ortho-phosphoric ester structure are not preferred in PU formulation because they are not resistant to hydrolysis (Figure 2.40).

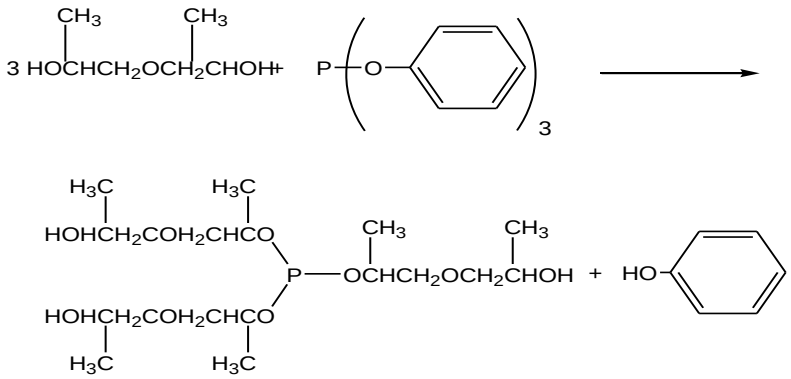


Figure 2.40 : Formation of tris (dipropylene glycol) phosphite.

Unfortunately, trialkyl phosphites are also extremely susceptible to hydrolysis and they hydrolyze morerapidly than the ortho-phosphoric esters. Therefore, they are not currently used in industry.

Phosphonate Polyols;

a) By Mannich reaction with dialkyl phosphite

The phosphonate polyols contain -P-C- bonds which are very resistant to hydrolysis. The phosphonate (Figure 2.41) polyols are one of the most important groups of reactive flame retardants. They are used in many formulations of polyurethane foams (Beck and et.al. 1963, Ferrigno, 1967).

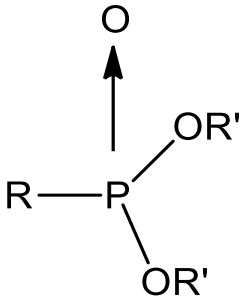


Figure 2.41 : Phosphonate.

One of the phosphorus polyol of significant commercial importance is diethyl-N,N bis (2-hydroxyethyl) aminomethyl phosphonate. It is obtained by a Mannich reaction between diethylphosphite, formaldehyde and diethanolamine (Figure 2.42) (Papa, 1972; Beck and et.al., 1963; Raymond and Hindersin, 1968):

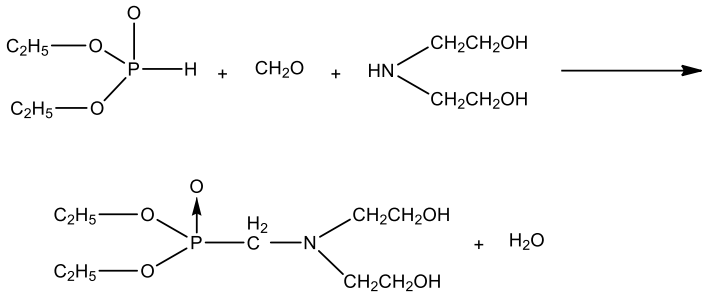


Figure 2.42 : Formation of Diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate.

The same product is easily obtained by reacting diethylphosphite with an oxazolidine (Figure 2.43) (Ionescu, 1998; Ionescu, et.al. 2003).

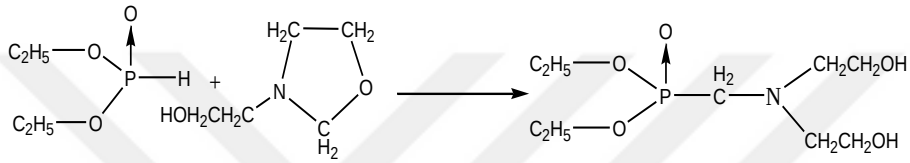


Figure 2.43 : Diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate from oxazolidine.

This phosphonate polyol is very resistant to hydrolysis and has in its structure both phosphorus and nitrogen.

b) Mannich reaction with bishydroxyalkyl phosphite: Phosphorus acid is alkoxylated with propylene oxide to produce a bis (hydroxypropyl) phosphite which is then reacted with oxazolidine. As final product, a tetrafunctional phosphonate polyol is obtained (Ionescu, 1998) (Figure 2.44).

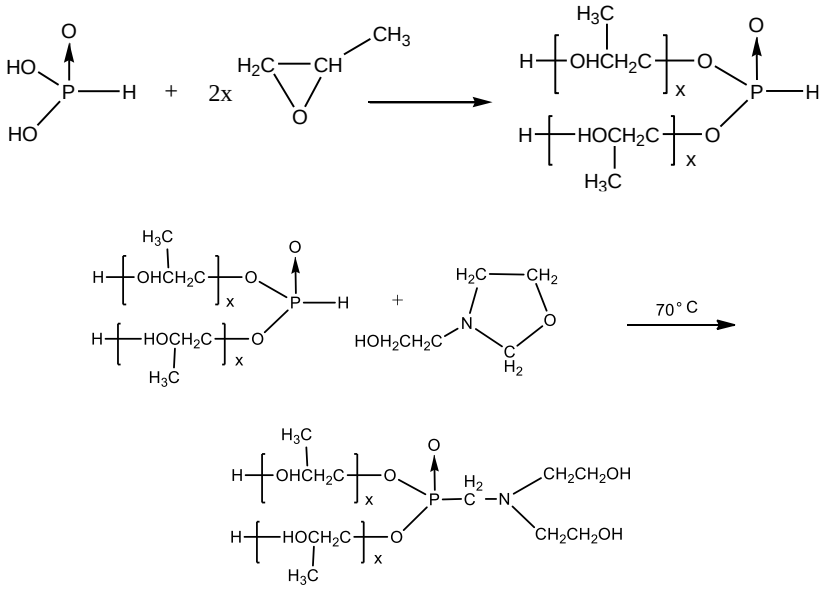


Figure 2.44 : Formation of tetrafunctional phosphonate polyol.

This phosphonate polyol has a phosphorus content of 7-7.5 %. By reacting of dimethylphosphite with acetone and monoethanolamine higher phosphorus content (15%) phosphonate polyol is formed (Figure 2.45) (Kabachnik-Fields).

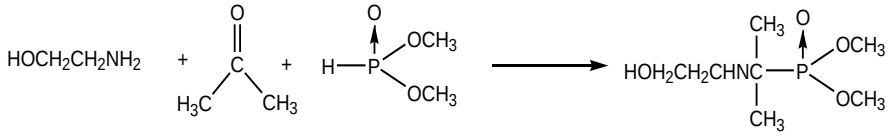


Figure 2.45 : Reaction of dimethylphosphite with acetone and monoethanolamine.

Using reactive cyclic phosphites as raw materials gives a different polyol. (Figure 2.46) (Salkowski, 1974):

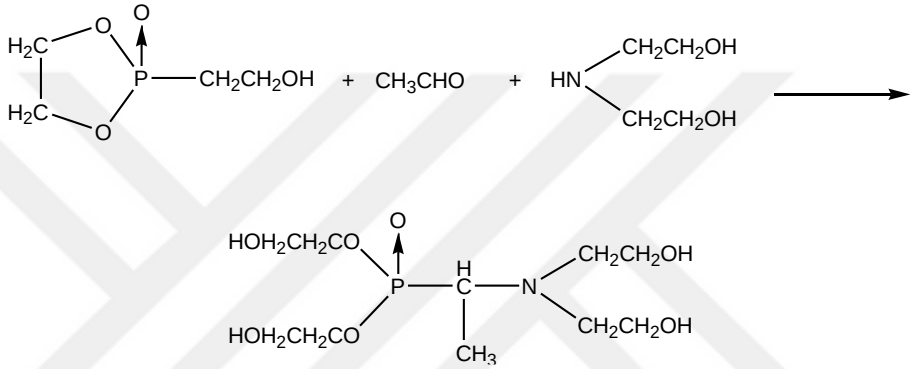


Figure 2.46 : Reaction of cyclic phosphite with formaldehyde and diethanolamine.

Phosphonate polyols may be obtained by the direct alkoxylation of phosphonic acids with propylene oxide (Figure 2.47), at moderate temperatures (70-90 °C) (Papa, 1972; Ionescu, et.al, 1998).

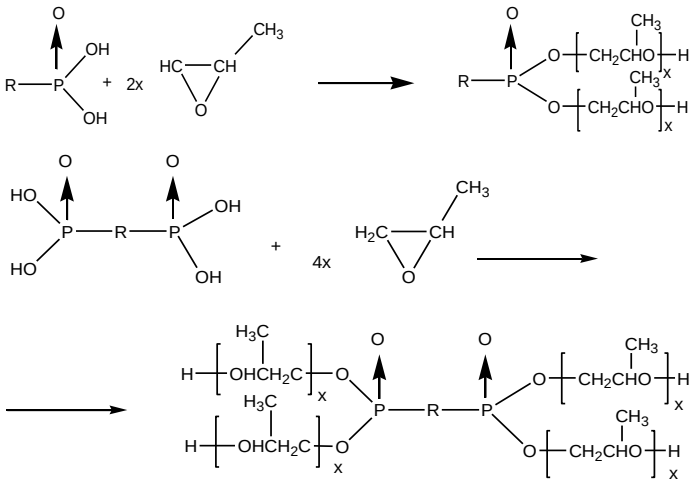


Figure 2.47 : Phosphonate polyols obtained by the direct propoxylation of phosphonic acids.

A phosphonate polyol is obtained by the propoxylation of phenylphosphonic acid in Figure 2.48 (M. Ionescu et.al, 1998):

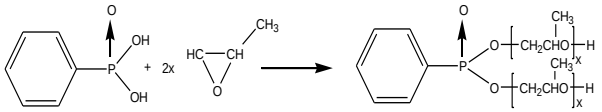


Figure 2.48 : A phosphonate polyol is obtained by the propoxylation of phenylphosphonic acid.

Phosphonate polyols are very efficient flame retardants in practice. These phosphorus polyols is stable over time of formulated polyols containing phosphonate and water as reactive blowing agent, with no significant loss of reactivity.

Cyclic and aromatic compounds and polyısocyanurate;

Improving method of the flame retardancy of rigid PU is to introduce highly thermostable structures such as aromatic structures, thermostable isocyanuric, oxazolidone or imidic rings. This effect is due to the high char yield resulting from the burning process of the aromatic structures with very low ratio of H:C and to the presence of the rigid cyclic aromatic nuclei (Figure 2.49) (Ionescu, et.al, 1998).

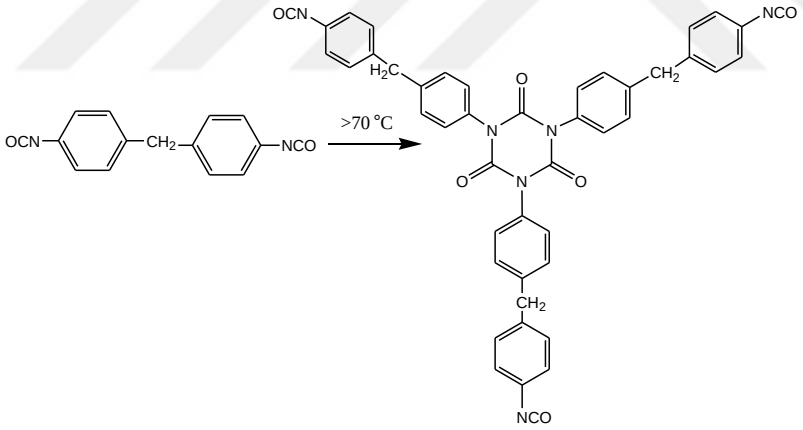


Figure 2.49 : Isocyanurate Reaction.

A very high efficiency of flame retardancy is obtained by generation in the foaming process of very thermostable isocyanuric rings, by the trimerisation of an excess of -NCO groups. The resulting PU / polyisocyanuric foams (PIR) foams, having both urethane groups and isocyanuric rings, in combination with phosphorus compounds, and additive or reactive flame retardants, give a very high fireproofing efficiency.

3. EXPERIMENTAL

3.1 Materials

The list of chemicals used in the experiment are listed with their companies. Dimethyl sulfoxide (Merck), toluene (Merck), isopropyl alcohol (Merck), styrene (Merck), trimethiol propane (Merck), benzyl peroxide (Merck), formaldehyde (Merck), isocyanuric acid (Merck), methyl ethyl ketone (Merck), 2,4 dichloro acetophenone (Merck), diethanol amine (Merck), acetone (Merck), deuterated chloroform (Merck), hydrochloric acid (Merck).

Tris (1-Chloro-2 propyl) phosphate (TCPP-Lanxess), tetra-isopropyl titanate (Dorf Ketal), polymeric methylene diphenyl diisocyanate (PMDI-Bayer), polyether polyol (Voranol RN 411-Dow Company), n- pentane (Shell), silicone stabilizer (Tegostab B 8443-Evonik), catalyst (Dabco TMR-Air Products) 4,4'-methylene diphenyl diisocyanate (Bayer) 1,4 butanediol (Lyondell), natural oil based polyol (Priplast 3192, f:2, Croda), adipic acid (Invista), diethylene glycol (Sabic), acetone (J. T. Baker), tetrahydrofurane (VWR Prolab), vinylphosphonic acid dimethyl ester (VPADME-Basf), dimerdiol (Pripol 2033-Croda), sodium hydroxide (Carlo Erba Reagents), potassium hydroxide (Carlo Erba Reagents), dichloromethane (J. T. Baker), cyanuric acid.

Diethyl phosphite (Aldrich), diphenyl phosphite DPP (Aldrich), ethanol amine (Aldrich), cyclohexanone (Aldrich), methanol (Aldrich), benzyl trimethyl ammonium chloride (Aldrich), diethhyl phosphite DEP (Aldrich), diphenyl phosphate (Aldrich), tris (hydroxyethyl) isocyanurate (THEIC-Aldrich), melamine (Aldrich), acetophenone (Aldrich).

Analyzes are performed with the equipments that given on Table 3.1. Also that table interiors company of equipments and their explanation.

Also Figure 3.1 shows pictures of LOI, horizontal test chamber and UL94 cabinet's pictures.

3.2 Measurments

Table 3.1 : Equipments.

Method	Company	Explanation
FT-IR Spectroscopy	Thermo Nicolette 5700 with ATR	Used for the monitoring of the reaction steps
Stress Strain Test Machine	Zwick	Used for measurement of % modulus and elongation at break.
Martindale	Atlas	Used for measuring abrasion resistance of synthetic leather.
GPC	Waters	Used for the monitoring of the molecular weight distribution.
Shoe Sole Lab Trial Machine	Gusperti	Used for defining cream time, demoulding time, flowability of polyurethane in the mould
Shoe Sole Flex Machine	Çiftçi Makina	Used for defining flexibility of certain shoe sole.
Horizontal Flame Chamber	Atlas	Used for measurement of flame retardant properties of synthetic leather
GC-MS	Agilent	1-chloropropan-2-ol was recorded using Agilent 5975C MSD with triple-axis detector and Agilent 7890A GC system.
Thermogravimetric Analysis	Seiko Exstar TG/DTA 7200	Measurements were performed, under a nitrogen atmosphere with a heating rate of 10 ˚C min-1, 30 ˚C to 500 ˚C and a sample weight from 1 to 2 mg.
Limiting Oxygen Index **(LOI)**	Marestek Company	The test was performed per ASTM D 2863. The specimens were 120/12/12mm3(Length/Width/Thickness), five specimens per sample were measured, and their average values are reported.

Table 3.1. (continued) : Equipments.

UL-94V	Marestek Company	Test was performed according to the testing procedure of ASTM D3801.
OH Value	Metrohm Autotitrator	Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols ASTM D4274-05 was applied as procedure.
Acid Value	Metrohm Autotitrator	Determination of Acid and Alkalinity Numbers of Polyols ASTM D4662-03 was applied as procedure .
Viscosity	Brookfield RVDV-II+ Model viscosimeter.	Determination of Viscosity of Polyols ASTM D4878-03 was applied as procedure and viscosity measurement.
H-NMR & P-NMR	Agilent VNMRS (Varian 500 MHz) spectrometer	$CDCl_3$ solution on a chemical shifts (d in ppm) were reported down field from tetramethylsilane.
Foam Qualification System	Foamat	Simultaneous measurement of foam rise height, reaction temperature, rise pressure, curing, weight loss and viscosity. Determination pf cream time, gel time and tack free time of foam.

Figure 3.1 : Picture of LOI, horizontal test chamber, UL 94 cabinet and foamat.

3.2.1 Evaluation of flame retardancy

The following describes the different techniques used to assess the flame retardancy of polyurethane systems including composite materials.

3.2.1.1 Thermal gravimetry analysis (TGA)

TGA determines the thermal stability of the cured formulation by monitoring the loss of mass of a heated sample with increasing temperature. When discussing the flame retardancy of a polymer, one commonly quotes the decomposition temperature (Td), which represents the temperature at which 10 % of the initial weight is lost. The charring ability of the formulation can also be extrapolated from the residual weight once all solid is thermally stable (T> 600 °C).

3.2.1.2 UL 94 test

UL 94 test is a common test for flame retardancy. It measures the flammability of a material by a defined ignition source. During the test, a small sample (13 mm width x 4 mm thick x 50 -125 mm high) is exposed for 10 s, either vertical or horizontally, to a small calibrated Bunsen burner flame (25 mm of height). To test a specific formulation, five samples are ignited twice and the time to extinguishment after each

ignition is recorded. The flammability is rated as a function of the time the specimen keeps on burning after the removal of the flame and the total time to extinguishment. A material is considered non-flammable once it is classified as V0 (ISO 1210).

3.2.1.3 Oxygen index test

LOI measures the minimum concentration of oxygen in the atmosphere required to maintain a candle like burning of a material. Materials with a higher LOI value are less flammable. Materials with LOI under 21 %, which is the concentration of oxygen in air,are considered as flammable (ISO 4589-2). On the other hand, materials with LOI over 26 % are considered self-extinguishing.

3.3 Synthesis Of Styrene Graft Polyester Polyol

3.3.1 Synthesis of saturated polyester polyol

Condensation of adipic acid with ethylene glycol and 1:2 molar ratio was carried out at 225–230 °C. Volatiles were distilled-off under ambient pressure for 5 h. Then additioned Tyzor TPT catalyst increased the rate of esterification and shortened the distillation time to about 2 hour. At this point the acid number ranged between 15 and 20 mg KOH/g. Further lowering of the acid number was accomplished by distilling-off water from the reaction mixture under reduced pressure (1 atm). This brought the reaction to almost completion and the acid number to about 0,5 mg KOH/g. The atmospheric Pressure distillate contained mostly water (70–90 %), and the distillate obtained under reduced pressure contained mostly ethylene glycol (90%). Reaction media is cooled rapidly (Figure 3.2).

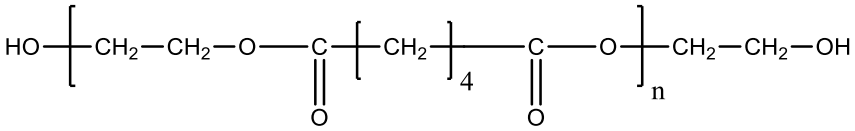


Figure 3.2 : Polyester polyol.

3.3.2 Styrene grafting saturated polyester polyol

Four necked flask was charged with 50 g polyester polyol and temperature increased 50 ^{o}C. Styrene monomer (6, 9, 12, 15%) and BPO [(1,2,4) g / 1000g Styrene] added at 2 hour while nitrogen feeding and stirring. Temperature increased 120 ^{o}C and reaction carried out 6 hour at this temperature. At the end of the reaction hold 1 hour under vacuum and cool.

3.3.3 Synthesis of unsaturated polyester polyol

Maleic anhydride and eyhlene glycol and catalyst (Tyzor TPT; 0.0013 g /Total Mixture g) kept in a pilot reactor (25 ml) bottomed, mechanical stirrer, nitrogen inlet, fraction column and set temperature at 100 ^{o}C. Adipic acid add in the reactor and adjust mixer to 50 rpm. When raw material completely melt, reaction mixture was slowly heated up to 150 ^{o}C with continuous nitrogen flow. Side product water formed result of reacting acid and glycol, collected into collection container. When water in flow is very slowly, vacuum was opened and temperature set 230 ^{o}C The reaction (Figure 3.3) was monitored periodically by checking the acid value and was stopped when the acid value reached 0.5 mg KOH via titration.

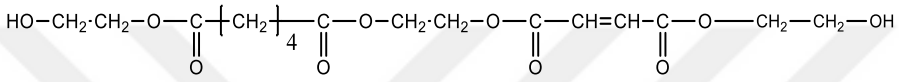


Figure 3.3 : Unsaturated polyester polyol.

3.3.4 Styrene grafting unsaturated poliester polyol

Four necked flask was charged with 50 g polyester polyol and temperature increased 50 ^{o}C. Styrene monomer (6, 9, 12, 15%) and BPO [(1,2,4) g / 1000g Styrene] added at 2 hour while nitrogen feeding and stirring. Temperature increased 120 ^{o}C and reaction carried out 6 hour at this temperature. At the end of the reaction hold 1 hour under vacuum and cool. Equation is shown in Figure 3.4.

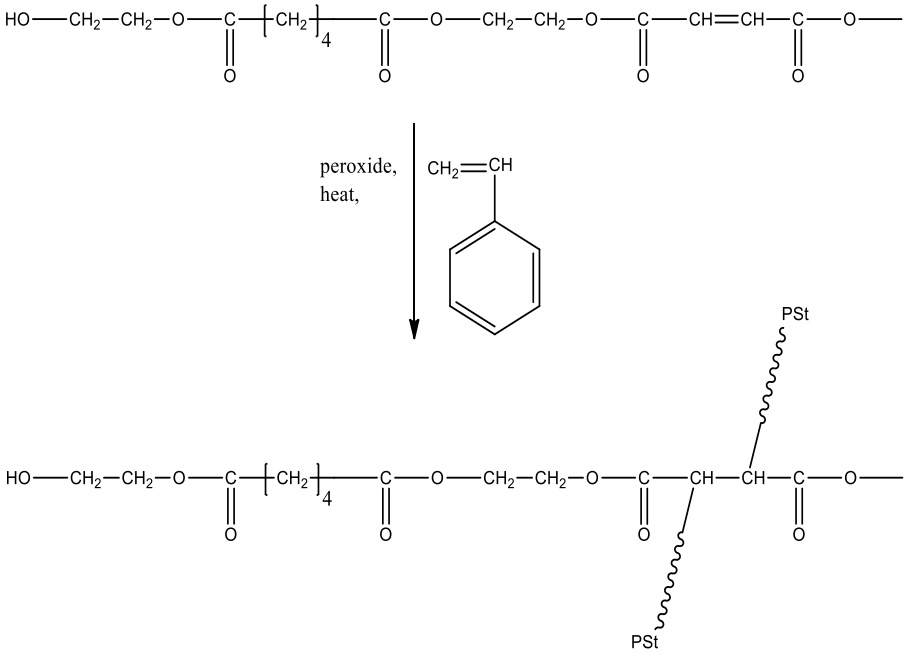


Figure 3.4 : Styrene grafted unsaturated polyester polyol.

3.4 Synthesis Of Ketonic Resins

3.4.1 Mek-formaldehyde resin

Four necked flask was charged with 72 g methy ethyl ketone and 162 ml formaline (%37 formaldehyde solution) and heated to 70 ^{o}C while stirring. Then 6,7 ml %35 NaOH solution was added with dropping funnel (mechanical srirrer speed: 50 rpm) When the temperature of the mixture rose to 80 ^{o}C, 3.3 ml %35 NaOH solution was added. Stirring operation was going on 2.5 hours. When reaction (Figure 3.5) was completed PH was arranged to 7 with diluted HCl and te upper phase was decanted. The resin was washed several times with hot water and dried at 120 ^{o}C under vacuum.

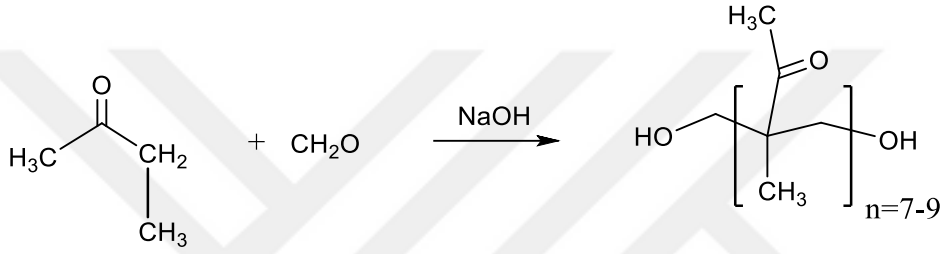


Figure 3.5 : Mek-formaldehyde resin formation.

3.4.2 Cyanuric acid-formaldehyde reaction

Four necked flask was charged with 5.16 g cyanuric acid and 10 g formaline (%37 formaldehyde solution) and heated to 70 ^{o}C while stirring. Cyanuric acid was solved in formaline and 30 min later colour of the solution became yellow and viscosity increased dramatically. The resin was washed several times with hot water and dried at 120 ^{o}C under vacuum (Figure 3.6).

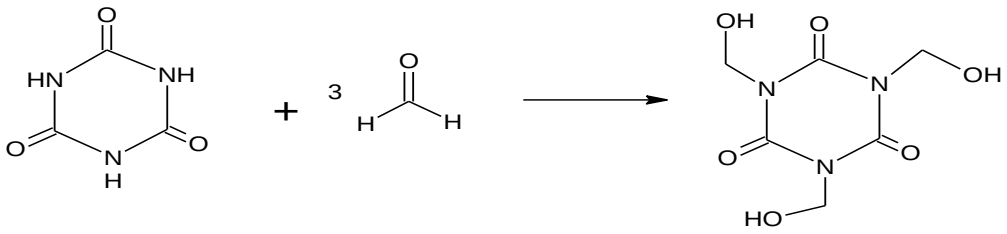


Figure 3.6 : Reaction of cyanuric acid and formaldehyde.

3.4.3 Acetophenone-formaldehyde resin

Method 1;

Four necked flask was charged with 67 g acetophenone and 30 g formaldehyde (100mL of %37 formaldehyde solution) and heated to 90^{o}C while stirring. Then 10 g

%40 NaOH solution was added with dropping funnel. After 8 hour, 6.5 g %40 NaOH solution was added. 7 hour later, the upper phase was decanted. The resin was washed several times with hot water and dried at 150^{o}C under vacuum. Solubility of resin was measured at DMF, toluene and acetone.

Method 2 (after patent 4731434, Dörffel, 1988, and us 2009/0012245 A1, Glockner, 2009);

60 g acetophenone, 17 mL methanol, 18 mL formalin (30%) solution and 0.15 gbenzyl trimethylammonium chloride are introduced into a reaction flask and mechanically stirred while heating to 50^{o}C. This is followed by dropwise addition of aqueous 50% by weight KOH solution with further stirring in 20-30 minutes. In the meantime the temperature is brought to 84^{o}C. This is followed by dropwise addition of further 30 mL formalin (30%) solution over a course of 1.5 hours and the mixture is maintained under reflux for a further 2 hours. After cooling, supernatant aqueous phase above the resin separated. The residue crude resin is washed with hot water several times and acidified with acetic acid and finally dried under vacuum at 130^{o}C (Figure 3.7).

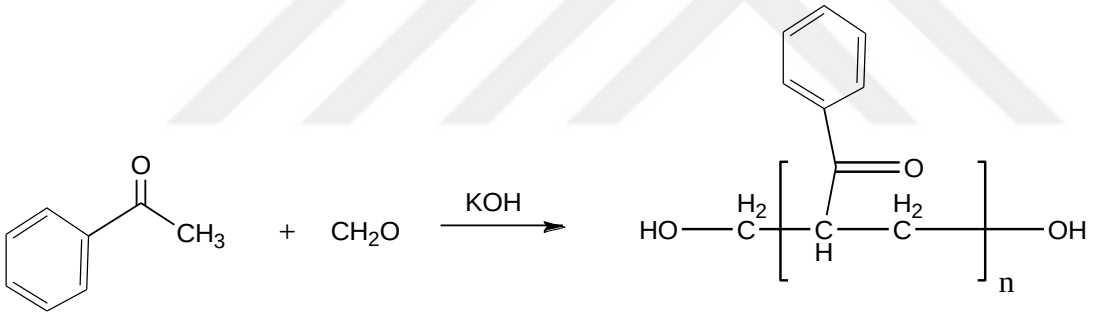


Figure 3.7 : Reaction of acetophenone and formaldehyde.

3.4.4 Acetophenone-formaldehyde-dichloroacetophenone resin

Four necked flask was charged with 67 g acetophenone 30 g formaldehyde (100 mL of % 37 formaldehyde solution) and 10 g 2,4-dichloracetophenone and heated to 90^{o}C while stirring. Then 10 g 40% NaOH solution was added with dropping funnel. After 8 hour, 6.5 g 40% NaOH solution was added. 7 hour later, the upper phase was decanted.

The resin was washed several times with hot water and dried at 150 ^{o}C under vacuum. Solubility of resin was measured at DMF, toluene and acetone. Reaction is shown in Figure 3.8.

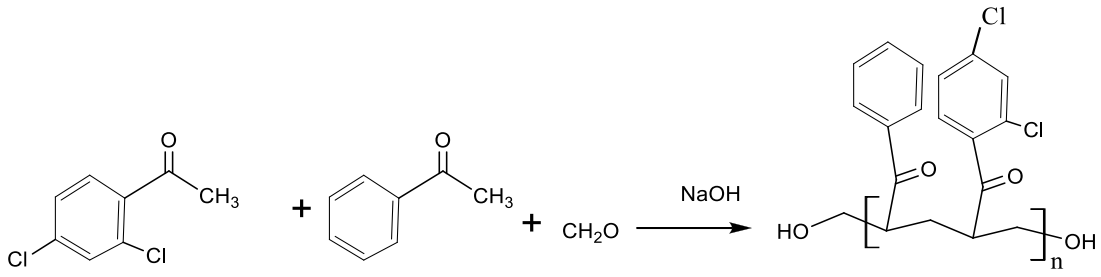


Figure 3.8 : Reaction of acetophenone, formaldehyde and dichloroacetophenone.

3.4.5 Acetophenone-formaldehyde-dichloroacetophenone-cyanuric acid

Four necked flask was charged with 70 g Acetophenone-Formaldehyde-Dichloroacetophenone resin (3.3.4.) and 4 g cyanuric acid and heated to 70 ºC while stirring. After 45 minutes 7 g formaldehyde added because of the solubility of cyanuric acid. One hour later dried at 150 ºC under vacuum.

3.4.6 MEK-formaldehyde-melamine reactions (a)

Four necked flask was charged with 7.2 g (0.1 mol)methy ethyl ketone and 41.1 g (0.5 mol) formaline (37% formaldehyde solution) and to increased pH to 11, 0.67 g triethylamine added and heated to 80ºC while stirring. At this temperature 6 hours reaction carried out. At the end of the reaction transparent liquid resin obtained and dried 120ºC under vacuum. Four necked flask was charged with 9 g resin, 0.5 g melamine, 0.5 ml water and to decreased pH to 3.5, 1 N HCl added while stirring. Viscous liquid resin obtained. Reaction is shown in Figure 3.9.

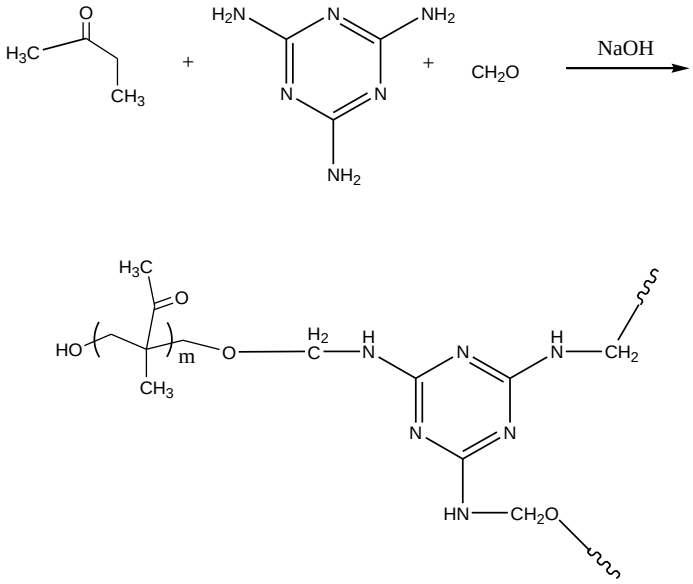


Figure 3.9 : Reaction of methyl ethyl ketone, formaldehyde and melamine.

3.4.7 MEK- formaldehyde –melamine reactions (b)

Four necked flask was charged with 72 g methy ethyl ketone and 162 ml formaline (37% formaldehyde solution) and heated to 70^{o}C while stirring. Then 6.7 ml 35% NaOH solution was added. When the temperature of the mixture rose to 80^{o}C, 3.3 ml 35% NaOH solution , melamine (7.2 g) was added that 22 g formaline (37% formaldehyde) were mixed and added continously at a gradually increasing rate sufficient to maintain vigorous reflux. After 3 hours, the reaction was completed and the upper phase was decanted. The resin was washed several times with hot water and dried at 120^{o}C under vacuum.

3.4.8 MEK-formaldehyde-cyanuric Acid

Four necked flask was charged with 72 g methy ethyl ketone and 162 ml formaline (37% formaldehyde solution) and heated to 70^{o}C while stirring. Then 6.7 ml 35% NaOH solution was added. When the temperature of the mixture rose to 80^{o}C, 3.3 ml 35% NaOH solution , cyanuric acid (7.2 g) was added that 22 g formaline (37% formaldehyde) were mixed and added continously at a gradually increasing rate sufficient to maintain vigorous reflux. After 3 hours, the reaction was completed and the upper phase was decanted. The resin was washed several times with hot water and dried at 120^{o}C under vacuum.

3.4.9 Synthesis of cyclohexanone-formaldehyde resin (CF-R)

The resin product which generated by reaction between cyclohexanone and formaldehyde is shown in the Figure 3.10.

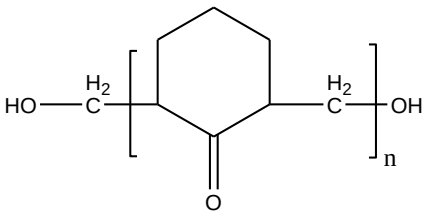


Figure 3.10 : Cyclohexanone formaldeyhde resin.

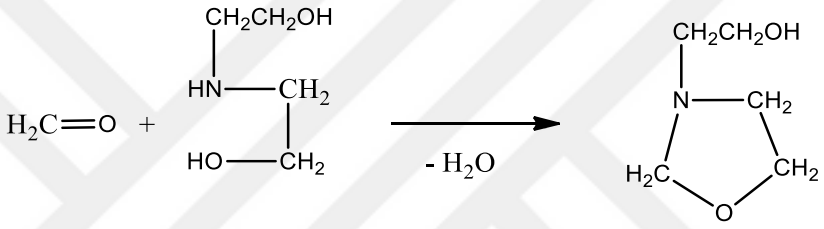
Into a three-necked flask, 98 g of cyclohexanone and 30 g of formalin 20 g cyclohexane were added and heated to 60^{o}C while stirring then added was 0.5 mL of 20% NaOH solution in equal portions. When the temperature of mixture rose to 75-80^{o}C, refluxing began and a mixture of 3.7 mL of 20% NaOH solution and 100 mL formalin was added in equal potions in 30 minutes. Speed of Stirring was increased

while keeping pH about 10-11. Reaction is completed after 3 hours then water phase was decanted. Residue was washed with hot water 5-6 times.

3.4.10 Cyanuric Acid - formaldehyde - diethanol amine

a) Synthesis of N-hydroxy-ethyl-1,3-oxazolidine:

Synthesis of N-hydroxy-ethyl-1,3-oxazolidine and of the Mannich base was performed in a one litre four-neck round-bottom flask filter with stirrer, thermometer, dropping funnel and condenser.N-hydroxy-ethyl-1,3-oxazolidine was obtained by the reaction of 1 mol of diethanolamine (98%) with 1 mole of formaldehyde (as paraformaldehyde 97-98 %) at 55-65^{o}C during 1-2 hours. The 1,3-oxazolidine was anhydrized by vacuum distillation, during 2 hours at 15-20 mm Hg and temperature of 80-95^{o}C (Figure 3.11).

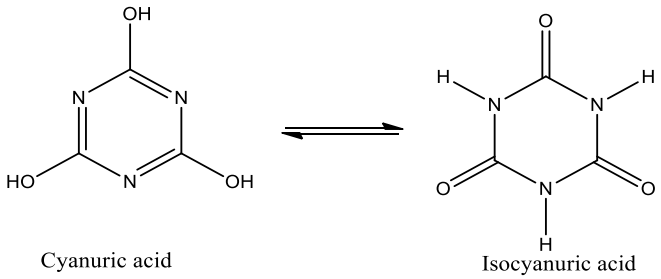


Formaldehyde Diethanolamin

Figure 3.11 : Formation of 1,3 Oxazolidine from diethanol amine.

b) Mannich Base synthesis

351 g (3 moles) N-hydroxy-ethyl-1,3-oxazolidine with 1,5 % water content 129 g (1 mol) anhydrous cyanuric acid was added in portions at temperature between 45-50^{o}C. The reaction is slighty exotherm. After the entire amount of cyanuric acid was added, temperature was increase to 110 – 120^{o}C and maintained for 1 h under stirring. The reaction is practically quantitative (99.2% yield) after 2 hours. Cyanuric acid – isocyanuric acid keto – enol equation is shown in Figure 3.12.



Cyanuric acid Isocyanuric acid

Figure 3.12 : Keto – enol equation of cyanuric acid.

Figure 3.13 shows the reaction between cyanuric acid, formaldehyde and diethanol amine.

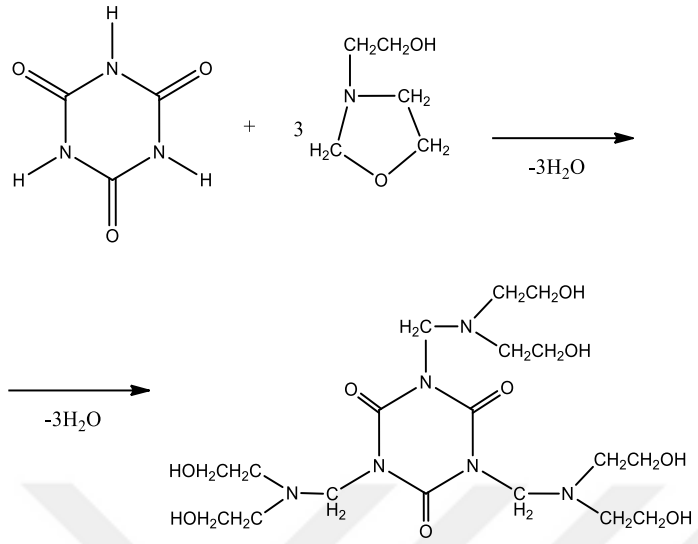


Figure 3.13 : Mannich base produced from cyanuic acid - formaldehyde – diethanol amine.

3.4.11 Modification of ketonic resins with ethanol amine/DEP and DPP

Modification of ketonic resin with ethanol amine and DEP is shown in Figure 3.14.

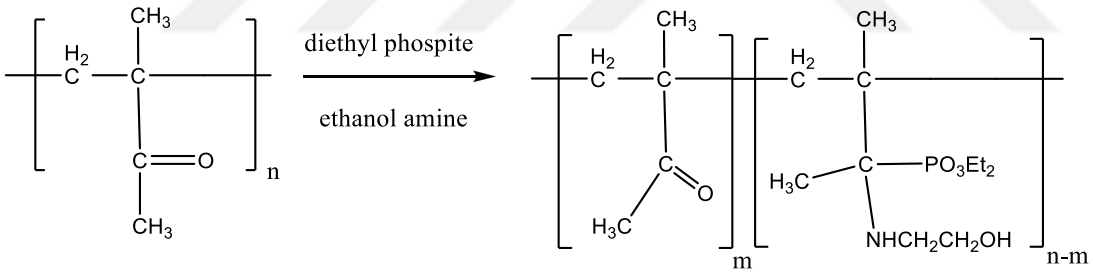


Figure 3.14 : Modification of MEK-F resin by reaction with ethanol amine and DEP.

Reaction of ketonic resins with Diethyl phosphite (DEP) and diphenyl phosphite (DPP) with the methods based on modified US Patent 3905922 (Smith et .al., 1975) and US patent 3385914 (R.R. Hindersinn et.al.1968).

Method I:

Two steps process; Into a three-necked flask 10 g CF-Resin and 6.1 g (0.1 mole) of ethanolamine were added in 100 ml toluene. The resulting mixture was heated under reflux and the water was collected continuously by Dean-Stark trap for 2 hours. Then, 25 mL toluene solution of 0.1 mole diethyl phosphite was added over a period of 20 minutes. During the addition, the temperature was kept below 55^{o}C by cooling. The

resulting mixture was stirred for further 2 hours. At the end of this period, toluene was removed under reduced pressure at 50 ^{o}C and the formed product was dried in vacuum. The modified resin was dissolved in a small amount of CH_2Cl_2 and poured into excess hexane to precipitate the resin. Solvent was decanted and the resin was washed with hexane twice and dried under vacuum.

Method II:

Using Na_2SO_4 as water absorber; 20 g acetophenone –formaldehyde resin was dissolved in hot toluene and cooled to room temperature. 9.2 g ethanol amine and 35 g diphenyl phosphite was added and stirred and then 30 g dry Na_2SO_4 added. The temperature of the mixture was increased to 80^{o}C and kept for 4 hours. After cooling to room temperature, the mixture was filtered and the filtrate evaporated with a rotary evaporator to dryness at the temperature below 80^{o}C.

Method III:

Modification of AF-R with ethanolamine and DEP using $Mg(ClO_4)_2$ catalyst; 20 g acetophenone-formaldehyde resin 9.2 g ethanol amine and 26.1 diethyl phosphite were dissolved in 50 ml dichloroethylene. 2 g of $Mg(ClO_4)_2$ was added as drying agent and catalyst. The temperature of the mixture was increased to 80^{o}C for 4 hours. After cooling to room temperature, the mixture was filtered and the filtrate evaporated with a rotary evaporator to dryness at the temperature below 80^{o}C.

3.5 Synthesis THEIC-Tris (2-chloroethyl) Phosphite

Reaction of tris isocyanurate with tris phosphite and the final product is shown in the Figure 3.15.

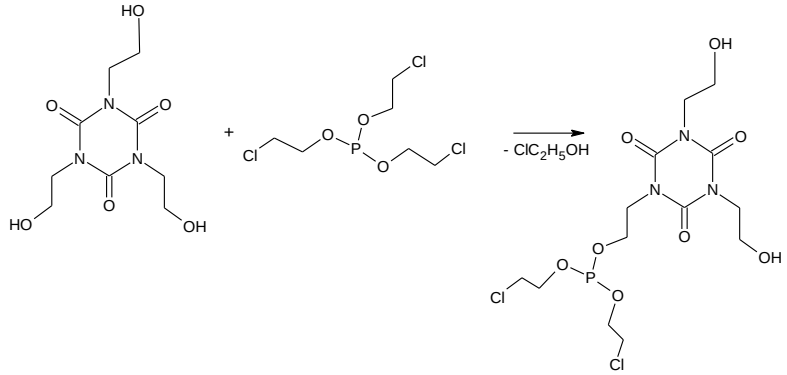


Figure 3.15 : Reaction of tris (hydroxyethyl) isocyanurate (THEIC) with tris (1 Chloro-2 propyl) phosphite.

After putting THEIC (0.05 mol; 13.05 g) to 50 mililitre tri-neck round-bottom flask, reaction temperature was increased to 100 ˚C. When melting of THEIC was complete, mixture of tris (2-chloroethyl) phosphite (0.05 mol; 85%; 15.847 g) were dropped with dropping funnel during 3 hours. The reaction was continued at 100˚C during 3 hours. Distilled by vacuum distillation, during one hour at 47-51 mmHg . FR is a slightly viscose liquid, with the following characteristics: viscosity at 25°C 2560 cP; OH content 314 mg of KOH/g.

3.6 Synthesis THEIC-TCPP

Reaction of tris isocyanurate with tris phosphate and final product is shown in the Figure 3.16.

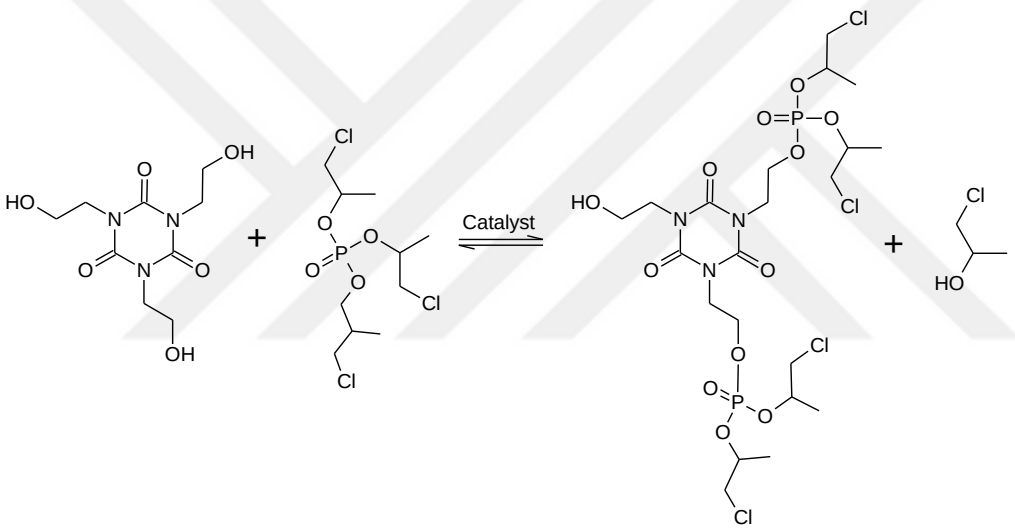


Figure 3.16 : Reaction of tris (hydroxyethyl) isocyanurate (THEIC) with tris (1 Chloro-2 propyl) phosphate (TCPP).

After adding THEIC (0.65 mol; 130.5 g) to 500 mL three-necked round-bottom flask, reaction temperature was increased to 165˚C. When melting of THEIC was complete, mixture of TCPP (0.65 mol; 212.94 g) and dibutyltin diluarate (0,07 %) were dropped with dropping funnel during 2 hours.

The reaction was continued at 180˚C during 5 hours. The 1-chloropropan-2-ol was distilled by vacuum distillation, during 8 hours 65 mm Hg and temperature of 140˚C. THEIC-TCPP product is a slightly viscose light yellow liquid. Picture of reaction system is shown in the Figure 3.17.

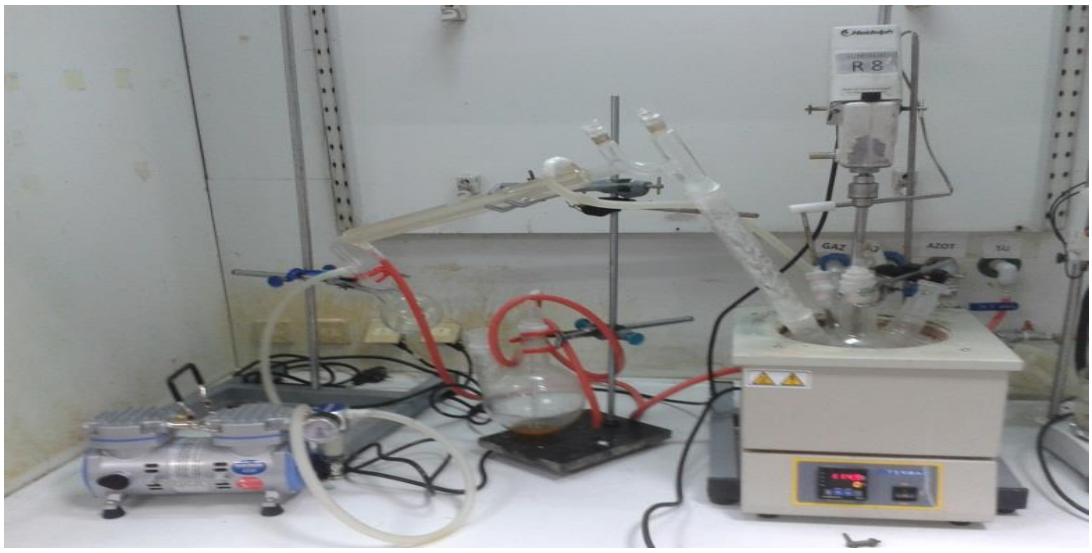


Figure 3.17 : Picture of reaction system of tris (hydroxyethyl) isocyanurate (THEIC) with tris (1-Chloro-2 propyl) phosphate (TCPP).

3.6.1 Preparation of the polyurethane rigid foam

PUR rigid foams were prepared by a one-shot and free-rise method. The chemical compositions are shown in Table I. All of the raw materials (including FR) were mixed well in a paper cup with the a high-speed mechanical stirrer (3000 rpm). After waiting for removing the foam at the surface of mixture, PMDI which was calculated from mixture OH equivalent weight was used excess (NCO/OH=1.3). Calculated PMDI amount was poured to mixture, and then, were mixed with high speed mechanical stirrer (3000 rpm). After mixing 10 s mixture was poured to mold. After preparation, the foam samples were kept in an desiccator at room temperature for 24 h before testing. Composition of rigid polyurethane foam is shown in Table 3.2.

Table 3.2 : Chemical composition of rigid polyurethane foam.

Material	**Phpa**
Polyether polyol	100
Pentane	0.7
Tegostab B 8443	2.0
Distilled water	0.3
Flame retardant (FR)	5-10-15
Dabco TMR	1,5
PMDI	130

a Parts per hundred of polyol by weight.

3.7 Vinyl Phosphonic Acid Dimethyl Ester Grafting Onto Unsaturated Polyester Polyol

Polyol which obtained from AA + DEG , kept in a four necked round bottomed flask, which is placed over an laboratory heater mantle and equipped with thermometer, mechanical stirrer, nitrogen inlet, fraction column and set temperature at 150 ^{o}C. Mixture that is vinylphosphonic acid dimethyl ester or vinylphosphonic acid (VPADME or VPA) and benzoyl peroxide, dropped into the flask. The reaction (Figure 3.18) was monitored periodically by checking the acid value and was stopped when the acid value reached below one. Water that is occurring result of reaction, was removed by vacuum (700 bar).

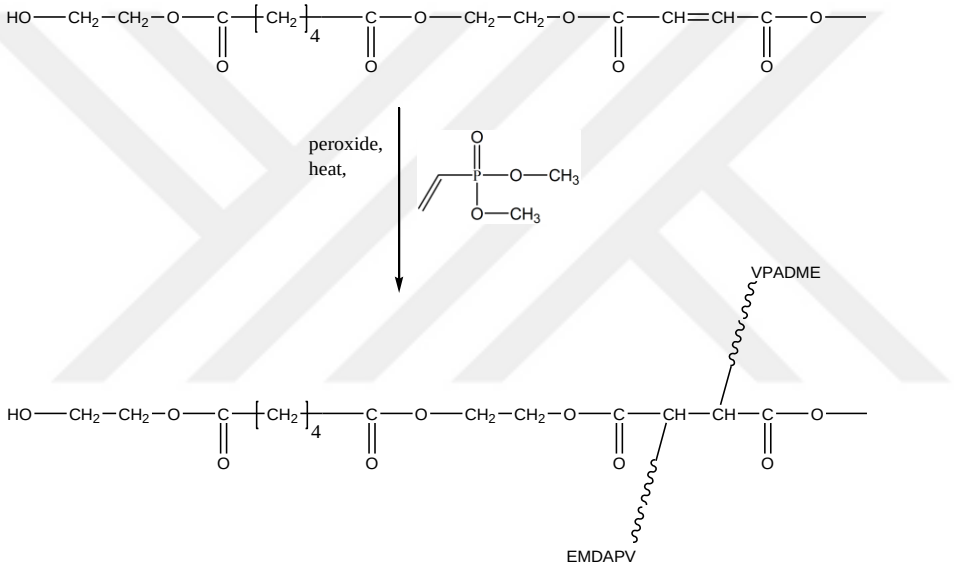


Figure 3.18 : VPADME grafting on unsaturated polyester polyol.

3.8 Other Mixture Polyols

3.8.1 Dopo - maleic anhydride reaction

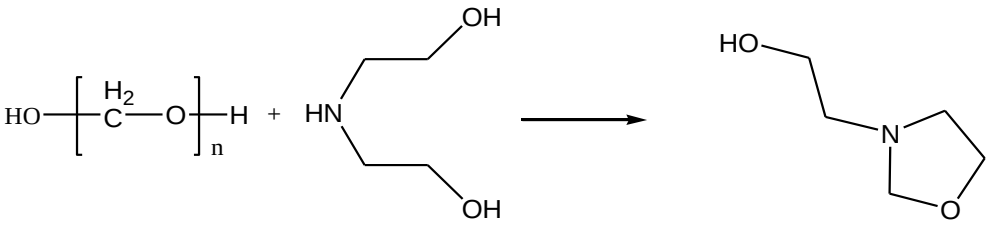
50 mL 3-necked flask DOPO (0.2 mol; 43.2 g) is loaded . On 60 g of toluene was added. Temperature of 80^{o}C is brought, and N_2 is fed to the system. In 45-60 min dissolution is complete. Maleic anhydride dissolved in THF by addition funnel over 60 g (0.2 mole; 19.6 g) was added over 1 hour . With added color starts to turn yellow. Additional finishes the reaction was terminated after 24 hours. After cooling to room temperature the solvent is removed in rotary evaporator. Consistency of the obtained resin is obtained slightly greenish substance. The resin obtained was washed with

water and oven and water is removed. Viscous liquids are solidified cooled to room temperature.

The solids were pulverized and formed into a white powder.

3.8.2 Oxazolidine-diethyl phosphite reaction

Reaction of paraformaldehyde and diethanolamine is shown in Figure 3.19.

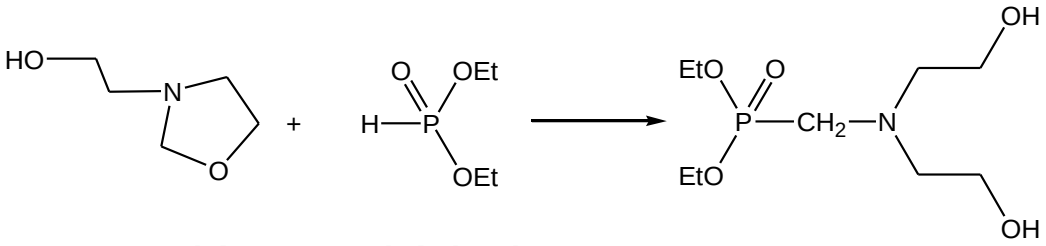


Paraformaldehyde Diethanolamine Oxazolidine

Figure 3.19 : Formation of oxazolidine.

Paraformaldehyde (3 mole, 105.3 g) and diethanolamine (3 mole, 315 g) are fed 3-necked flask and start mixing at N_2 atmosphere and room temperature. Set temperature 55 ^oC. The reaction is continued for 2 hours at this temperature. Then the temperature is raised to 85 ^oC (This step is very important.

The temperature is 105-115 ^oC product degradation is occured) . Reaction carried out under vacuum (3,5-4 hour) than vacuum is terminated when humidity reaches 0.5-1.0 ppm. Reaction of oxazolidine with DEP is shown in Figure 3.20.



Oxazolidine Diethyl Phosphite

Figure 3.20 : Reaction between oxazolidine and diethyl phosphite.

3-necked flask was fed oxazolidine. Diethyl phosphite is added at 35 ^oC in 0.5 - 1 hour. After the addition was finished the temperature is raised to 50°C .

After waiting for half an hour at 50 °C temperature is increased to 115 ^oC. Color change will be observed over time (first bright yellow , then brown shiny). 1.5 – 2 hours OH, acid, moisture, refractive index and GC-MS analysis is performed and the reaction is terminated.

3.9 Synthesize Biobased Synthetic Leather

Four necked flask was charged with 14.5 g, pripol 2033, 25.1 g monomeric mdi , 8.4 g 1,4-butanediol , 83.10 g toluene and 83.10 g DMSO heated to 60 ^{o}C while stirring. 1 hour later 6 g MDI added then viscosity of the mixture start to increase. When viscosity of the reaction reached 20,000 cps at 60 ^{o}C. Isopropyl alcohol added and temperature of the resin decreased at 25 ^{o}C. (Polyol / Chain extender / MDI - 1 / 3 / 4)

Pripol 2033; (Dimerized linoleic acid based polyol): OH Value: 196 mgKOH/g, Acidiy: 0,2 mgKOH/g, Mw: 570 Dalton, Viscosity: 2200 cps, Renewable % Carbon: 100. And the reaction is shown in Figure 3.21. Also molar ratio of poliol, diol and isocyanate given in Table 3.3.

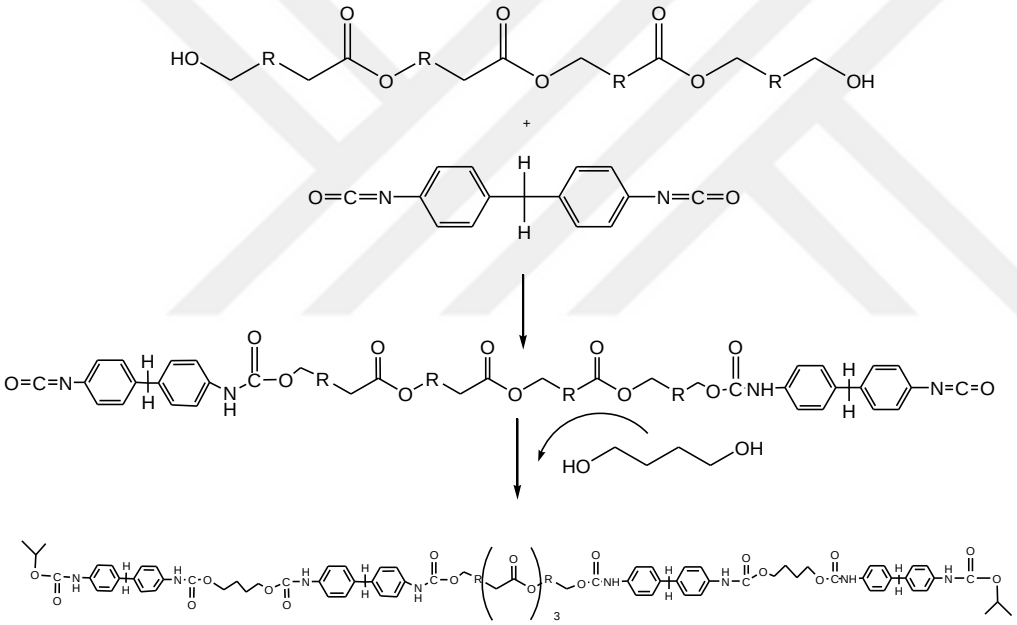


Figure 3.21 : Synthesize polyurethane.

Table 3.3 : Molar ratio of natural oil based polyol (Diol) / 1,4 butane diol / monomeric MDI.

Product Name	Natural Oil Based Polyol	1,4 Butane Diol	Isocyanate
Nat Pu 1	1	3	4
Nat Pu 2	1	5	6
Nat Pu 3	1	7	8
Nat Pu 4	1	9	10
Nat Pu 5	1	11	12
Nat Pu 6	1	13	14

4. RESULTS AND DISCUSSION

4.1 Polyurethane From Styrene Grafted Polyols

Grafting of styrene on polyester polyols were carried out with a number of different conditions to find the best product. Increasing styrene content results increasing product yield but the grafting efficiency is not effected. Amount of open cell increase related to amount of styrene increased.

4.1.1 Synthesis of polyester polyol

The product of polyester polyol is given in Figure 4.1.

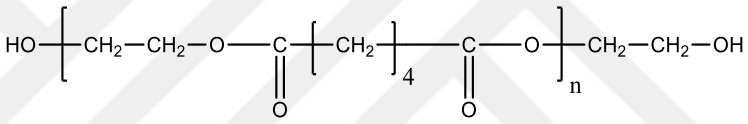


Figure 4.1 : Polyester polyol.

Polyester polyol properties; OH number: 63 mg KOH/g, acidity: 0.5 mg KOH/g, viscosity: 750 cPs. FTIR of polyester polyol is shown in Figure 4.2.

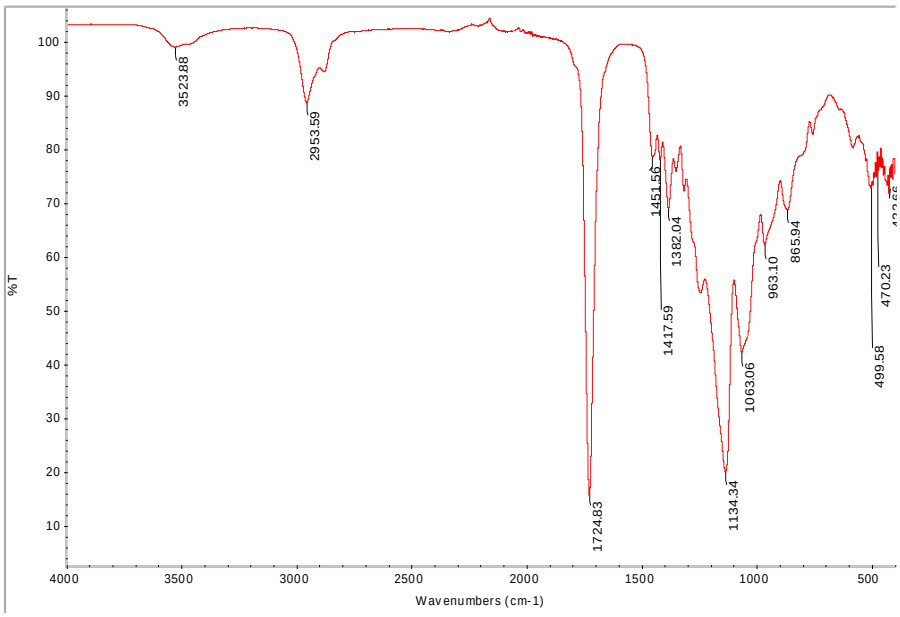


Figure 4.2 : FTIR of saturated polyester polyol.

4.1.2 Grafting styrene on saturated polyester polyol

Composition percentage and parameters of grafting styrene on polyester polyol is shown in Table 4.1

Table 4.1 : Grafting styrene on polyester polyol.

Number of Experiment	[M]/[I]	Polyester Polyol OH Number (mg KOH/g)	Polyester Polyol Viscosity (cP)	% Styrene Monomer	Viscosity (cP)	Theotrical OH Number (mg KOH/g)	Graft Polyol OH Number (mg KOH/g)
1	1000/1	63	360	6	1255	59	60
2	1000/1	63	360	9	1637	57	57
3	1000/1	63	360	12	1825	55	55
4	1000/1	63	360	15	2320	53	49
5	1000/2	63	360	6	1100	59	59
6	1000/2	63	360	9	1470	57	58
7	1000/2	63	360	12	1580	55	55
8	1000/2	63	360	15	2210	53	51
9	1000/4	63	360	6	1050	59	59
10	1000/4	63	360	9	1380	57	57
11	1000/4	63	360	12	1600	55	54
12	1000/4	63	360	15	2185	53	52

FTIR spectrum of product is shown in Figure 4.3.

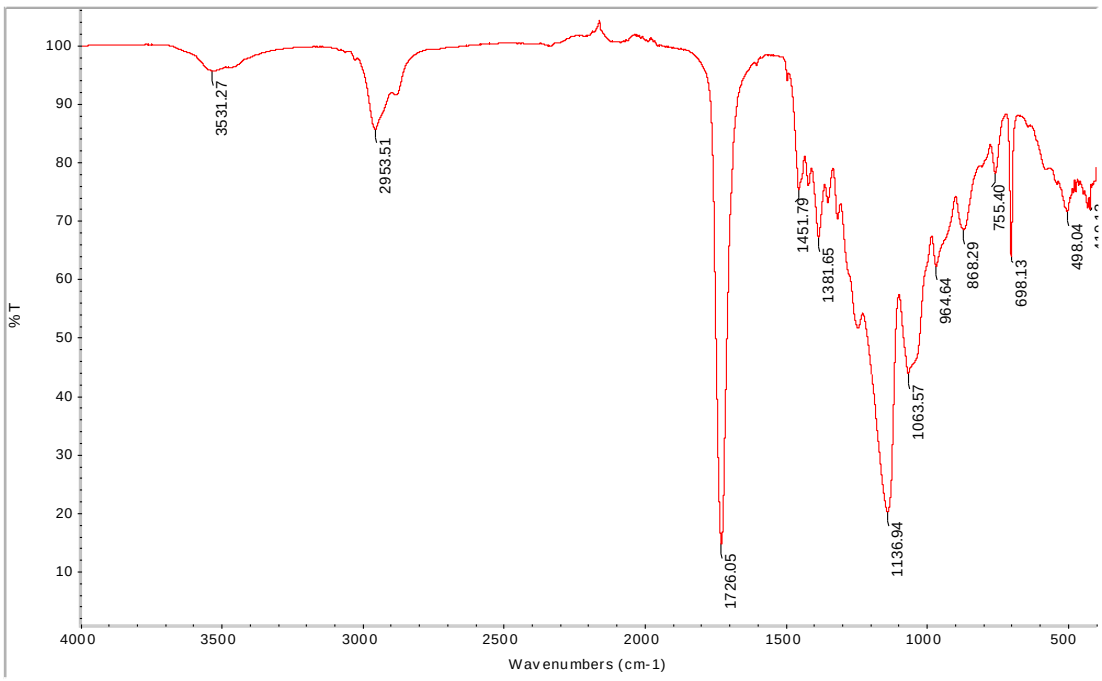


Figure 4.3 : FTIR of styrene grafted (%12) saturated polyester polyol.

4.1.3 Synthesize of unsaturated polyester polyol

Unsaturated polyester polyol is shown in Figure 4.4 and also properties of unsaturated polyester polyol is listed in Table 4.2. FTIR spectrum of this polyol is given in Figure 4.5.

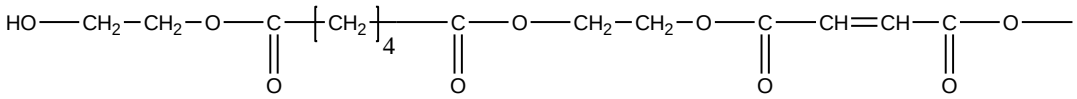


Figure 4.4 : Unsaturated polyester polyol.

Table 4.2 : Unsaturated polyester polyol properties.

Product Code	Amount (kg)	Acidity (mg KOH/g)	OH (mg KOH/g)	Viscosity (cP) (75 °C)	Vacuum Duration (Hour)	Side Product (g)
MD-1	16	0,67	64	520	05:30	1700
MD-2	15	0,51	85	440	06:00	1630
MD-3	17	0,41	75	480	06:00	1800
MD-4	17	0,37	57	570	06:00	1800

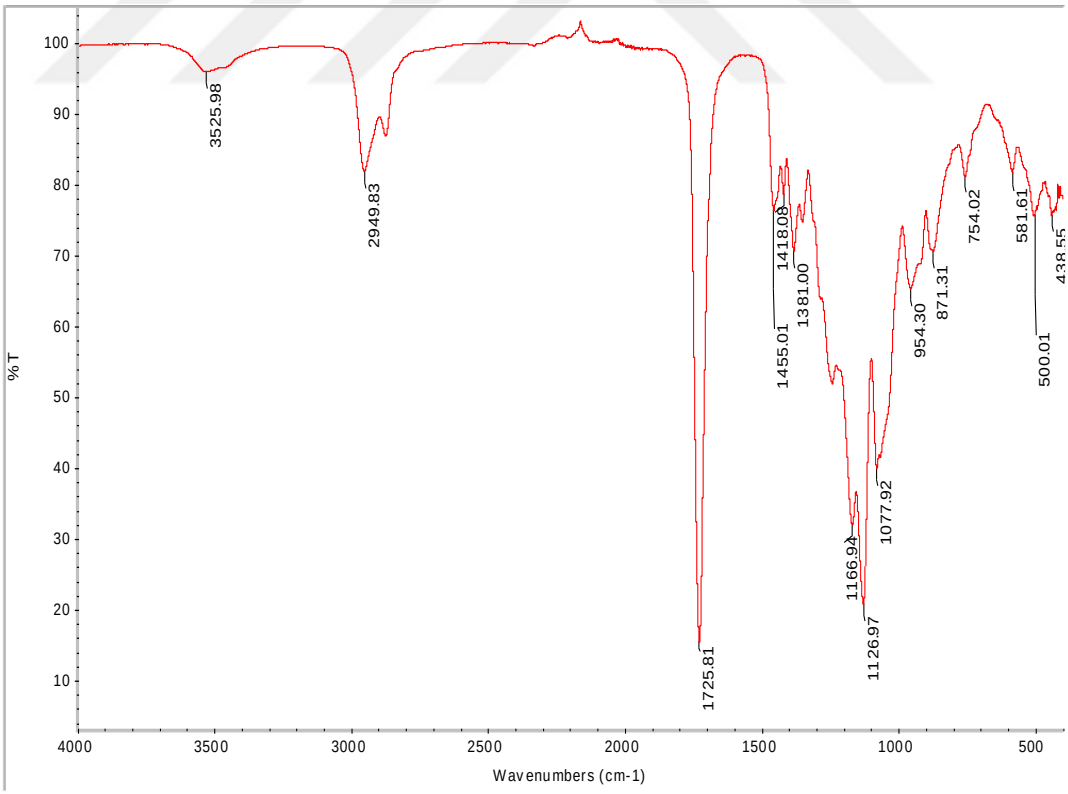


Figure 4.5 : FTIR of unsaturated polyester polyol.

4.1.4 Styrene grafting on unsaturated polyester polyol

The formation of styrene grafted polyester polyol from styrene and polyester poliol in presence of peroxide catalyst is shown in the Figure 4.6.

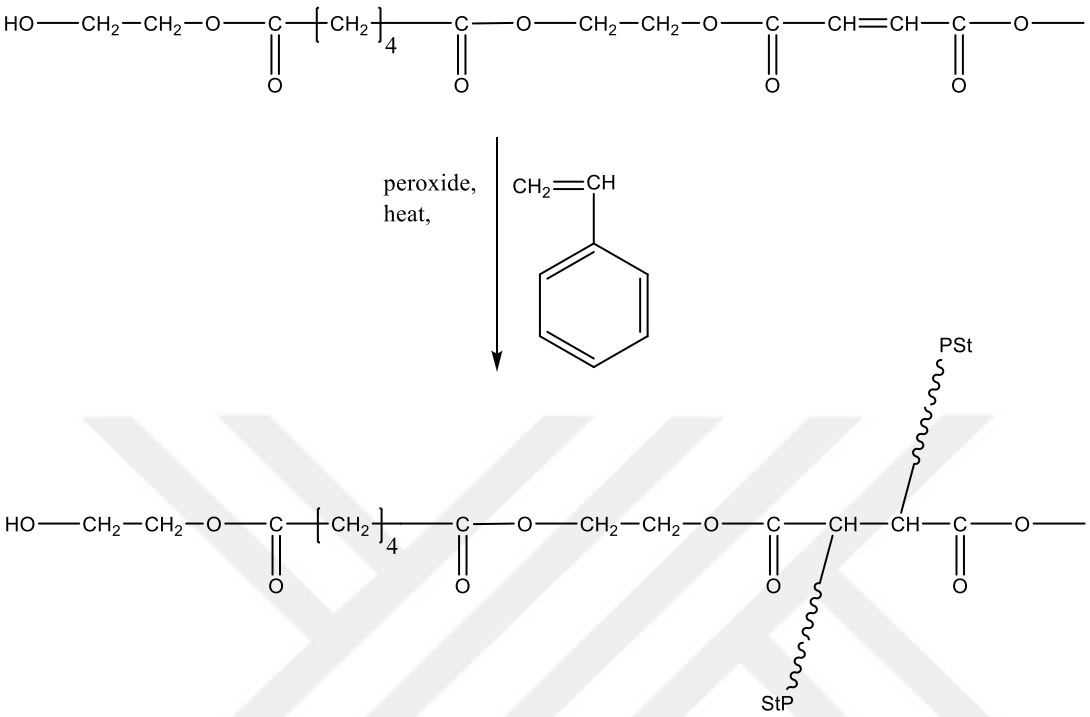


Figure 4.6 : Styrene grafted polyester polyol.

Properties of styrene grafted unsaturated polyester polyols are shown in Table 4.3.

Table 4.3 : Styrene grafted unsaturated polyester polyol properties.

Number of Experiment	[M]/[I]	OH Number (mg KOH/g)	Viscosity (cP) (75 °C)	% Styrene Monomer	Viscosity (cP) (75 °C)	Theotrical OH Number (mg KOH/g)	Graft Polyol OH Number (mg KOH/g)
1	1000/1	70	640	6	590	66	69
2	1000/1	70	640	9	957	64	65
3	1000/1	70	640	12	1020	61	58
4	1000/1	70	640	15	1480	59	55
5	1000/2	70	640	6	495	66	66
6	1000/2	70	640	9	750	64	60
7	1000/2	70	640	12	840	61	58
8	1000/2	70	640	15	1220	59	53
9	1000/4	70	640	6	440	66	67
10	1000/4	70	640	9	690	64	63
11	1000/4	70	640	12	730	61	60
12	1000/4	70	640	15	970	59	57

The final product styrene (%12) grafted polyester polyol's FTIR spectrum is shown in Figure 4.7.

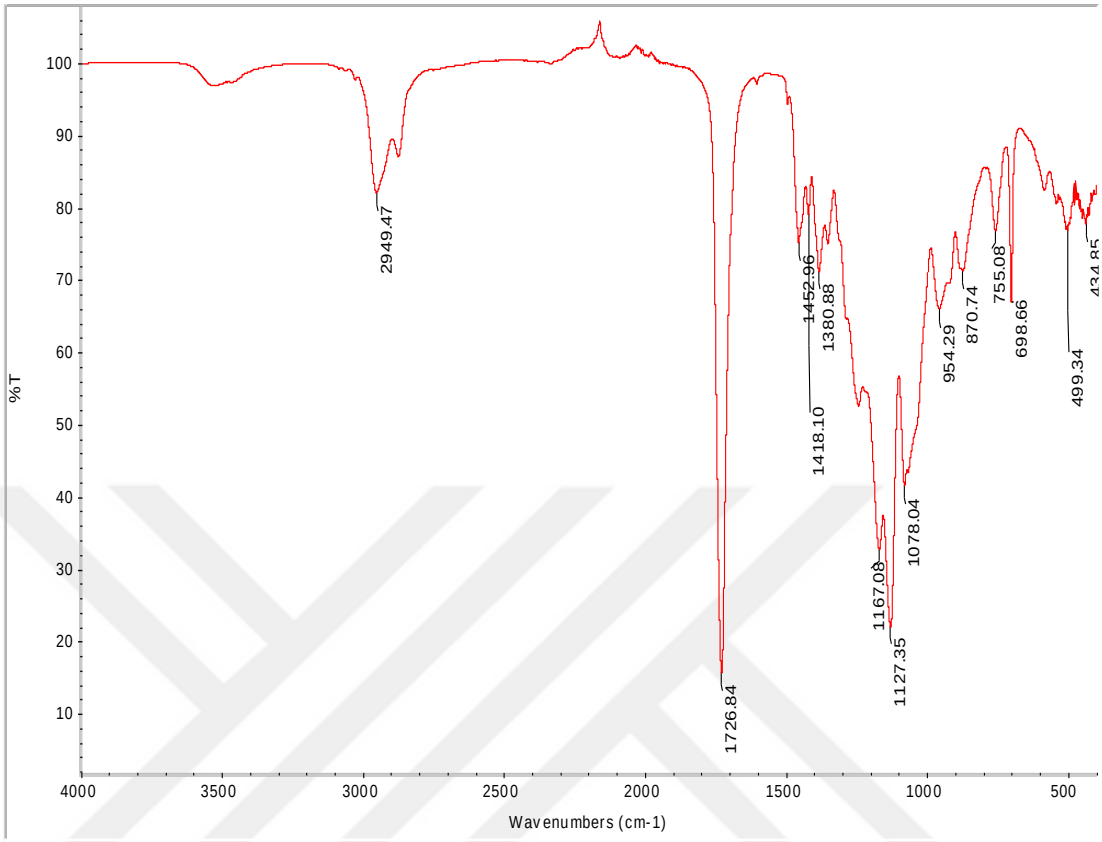


Figure 4.7 : FTIR of styrene (%12) grafted unsaturated polyester polyol.

FTIR spectrums of unsaturated polyester polyol, styrene grafted unsaturated polyester polyol, styrene grafted polyester polyol are shown together in Figure 4.8.

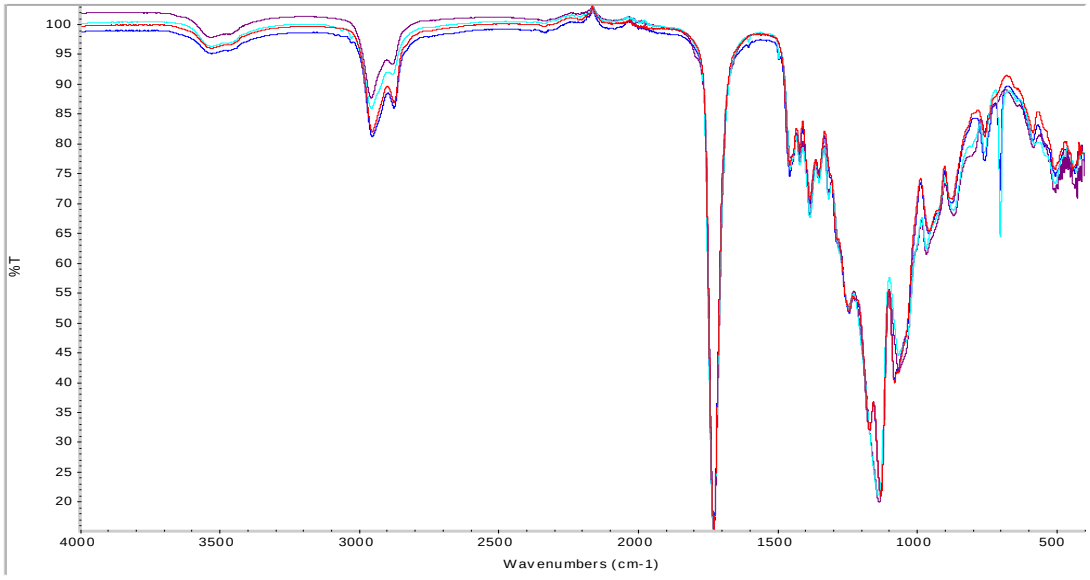


Figure 4.8 : FTIR Comparision of unsaturated polyester polyol, styrene grafted unsaturated polyester polyol, styrene grafted polyester polyol.

The amount of styrene used for grafting is limited since some agglomeration starts during the polymerization. The final product is probably a mixture of polyester polyol, grafted polyester polyol and polystyrene homopolymer and the mixture is in the form of micoemulsion due to surfactant effect of initial polyol.

The foam samples produced from styrene grafted poylester polyols are compared with the foam produced from polyester polyols under the same conditions. As seen in the pictures in appendices section, foam produced from styrene grafted poylester polyols is much more stable and has much lower shrinkage value.

4.2 Synthesis of Fire Retardant Modified Ketonic Resins

4.2.1 Kabachnik-Fields reaction of cyclohexanone- formaldehyde resin (CF-Resin) with diethyl phosphite (DEP) and ethanolamine

Blank experiments of the reaction (Figure 4.9) of cyclohexanone with a mixture of DEP and ethanolamine was carried out as described earlier (34,35). This method was modified for the Kabachnik-Fields reaction between CF-R and the mixture of DEP and ethanolamine. The product has low carbonyl peak intensity at about 1700 cm-1 compared to the peak of CF-Resin as seen ATR-FTIR spectra in the Figure 4.10 and Figure 4.11. As expected that the conversion of the carbonyl group of CF-Resin is not completed. The conversion was also calculated from phosphorous contents measured by microanalysis. Since the material is not burning well, microanalysis results of carbon, nitrogen were lower than theoretical values. ^{1}H NMR, C-13 NMR, P-31 NMR spectrum of modified resins are shown in the Figure 4.12, Figure 4.13, Figure 4.14.

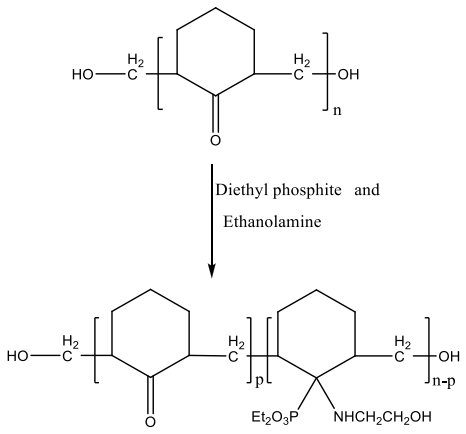


Figure 4.9 : Diethyl phosphite and ethanolamine reaction.

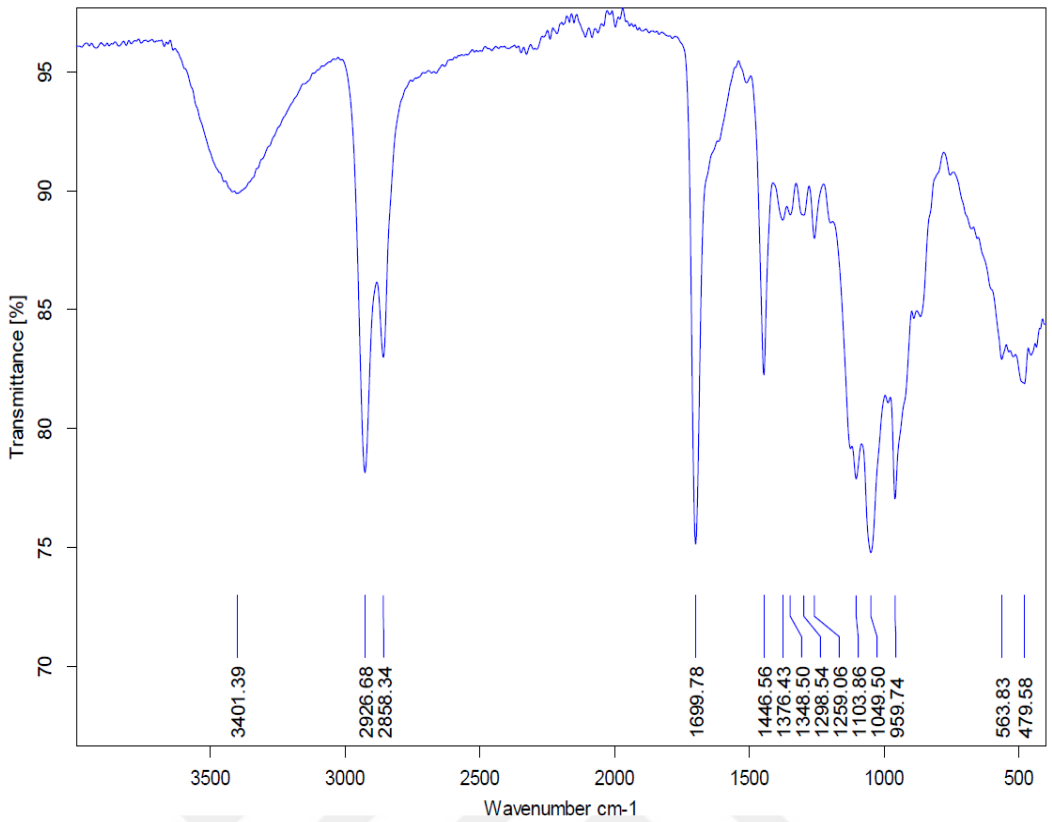


Figure 4.10 : FTIR spectrum of CF-Resin.

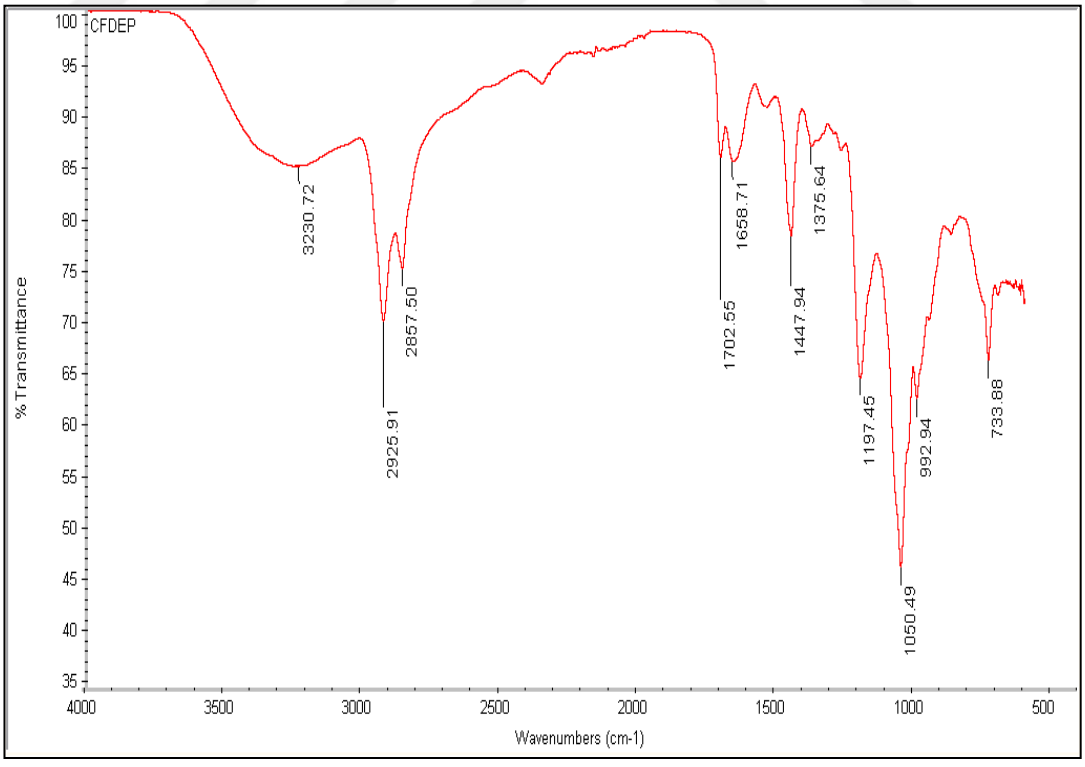


Figure 4.11 : FTIR of CFR+EA+DEP.

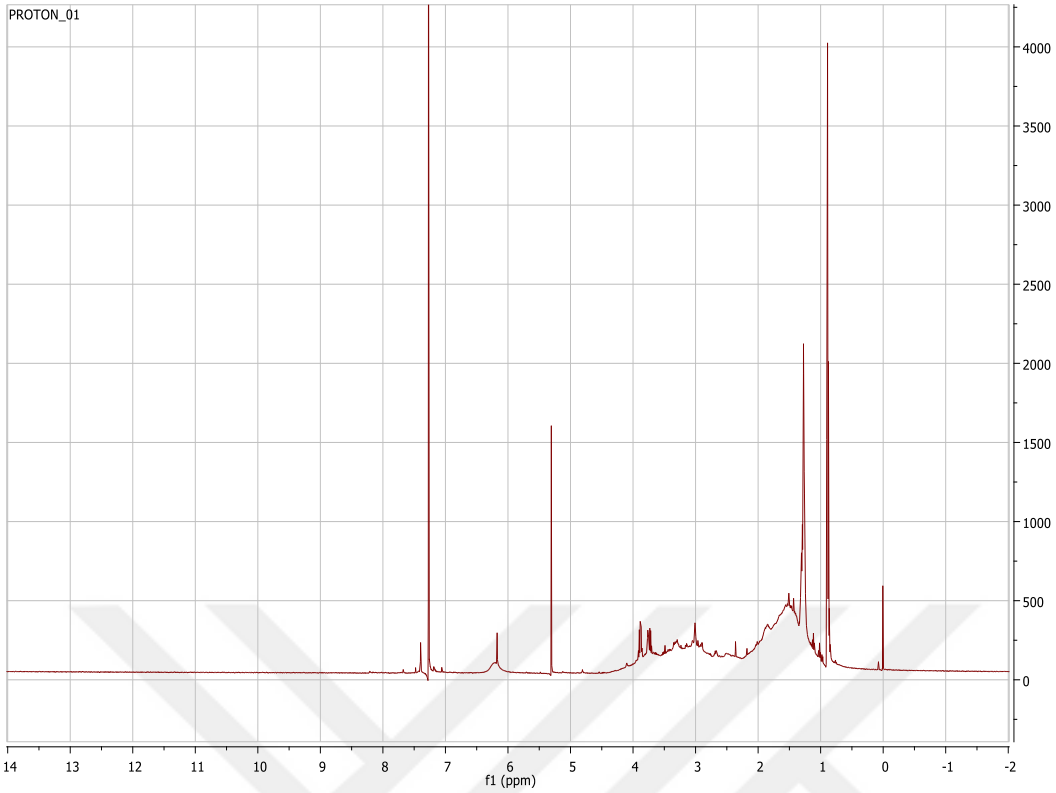


Figure 4.12 : ^{1}H NMR of CFR+EA+DEP.

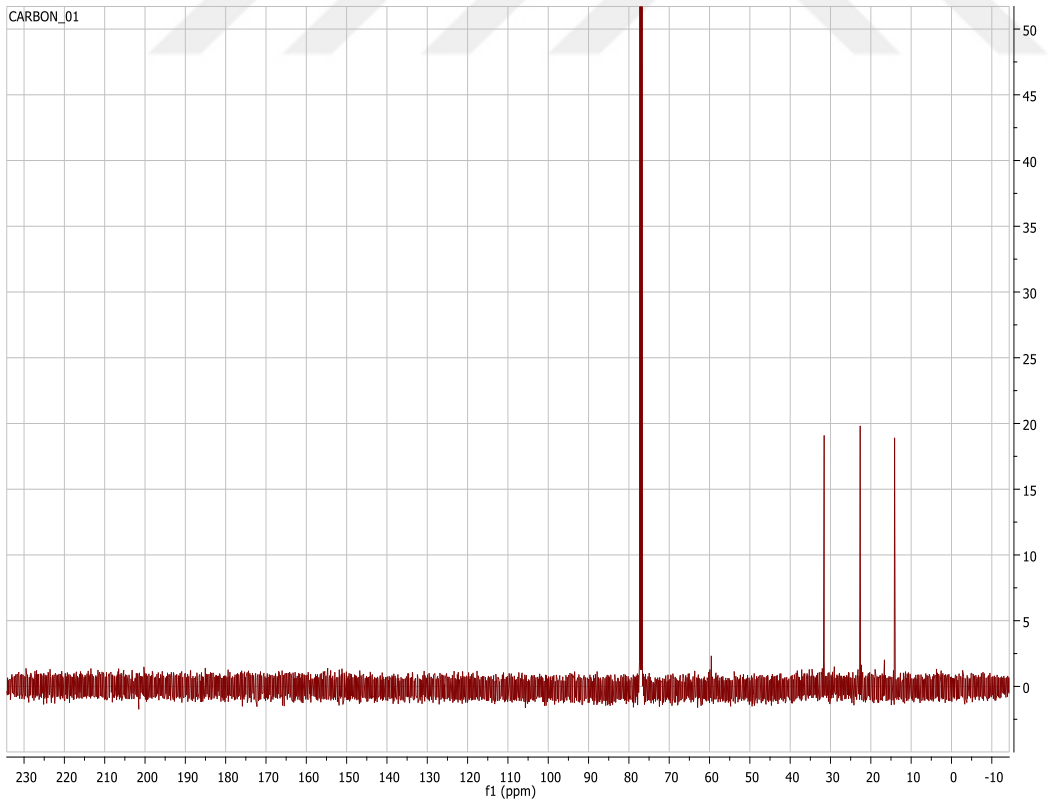


Figure 4.13 : C-13 NMR of CFR+EA+DEP.

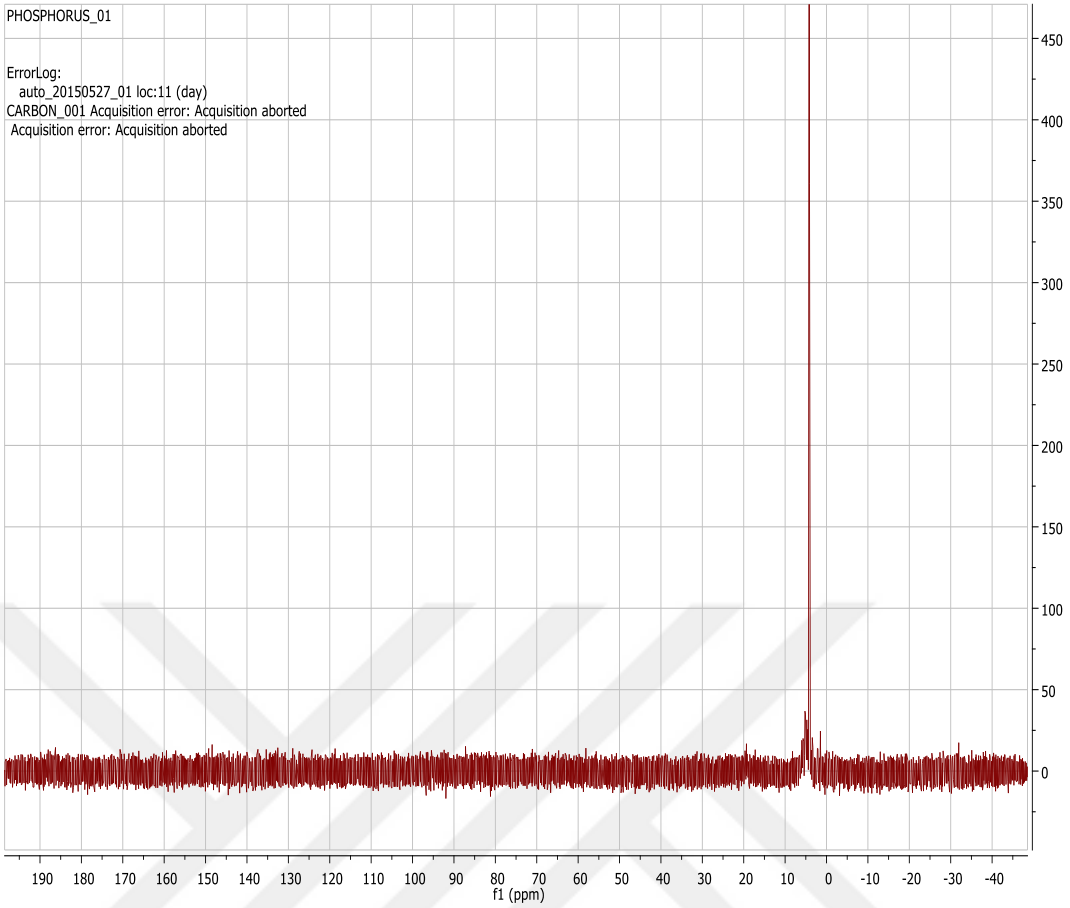


Figure 4.14 : P-31 NMR of CFR+EA+DEP.

4.2.2 Kabachnik-Fields reaction of methyl ethyl ketone-formaldehyde resin (MEKF-Resin) with DEP and ethanolamine

The kabachnik fields reaction between MEK resin, DEP and etanolamin is shown in Figure 4.15.

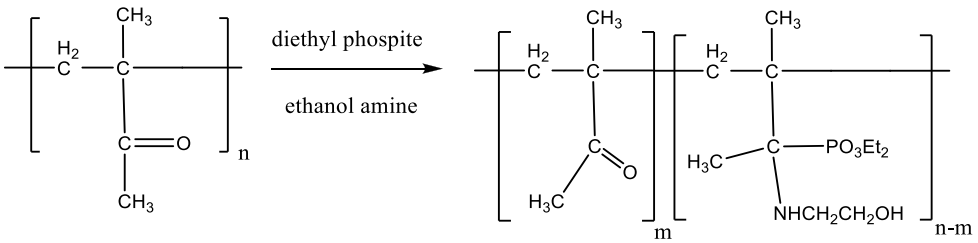


Figure 4.15 : Methyl ethyl ketone-formaldehyde resin (MEKF-Resin) with diethyl phosphite and ethanolamine.

Kabachnik-fields reaction product between MEKF-R and ethanolamine and phosphite compound was also characterized by FTIR (Figure 4.16), microanalysis and NMR techniques. The conversion of carbonyl groups was much lower than model

compounds. ^{1}H NMR, C-13 NMR, P-31 NMR spectrum are shown in the Figure 4.17, the Figure 4.18 and the Figure 4.19.

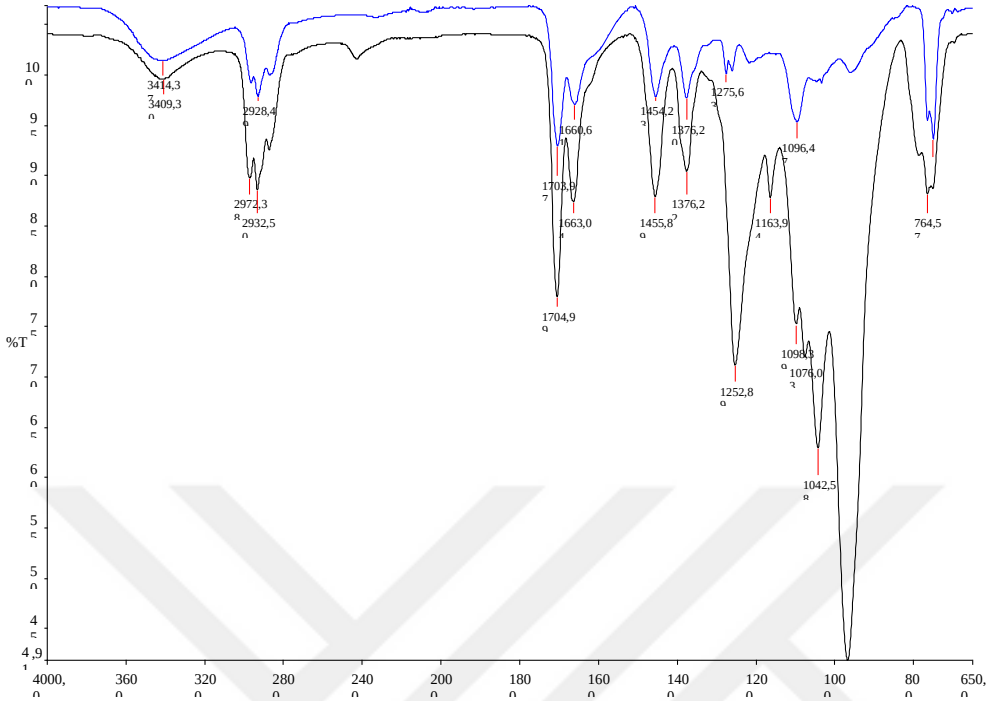


Figure 4.16 : FTIR comparison of MEK-F resin and modified MEK-F resin.

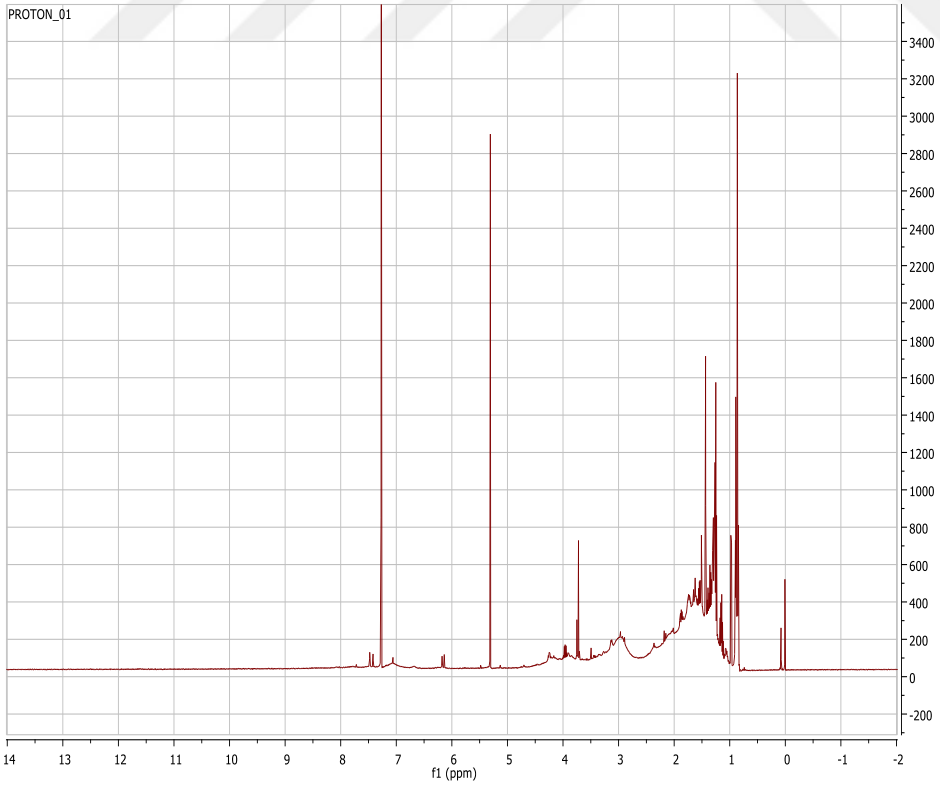


Figure 4.17 : ^{1}H NMR of MEK-FR+EA+DEP.

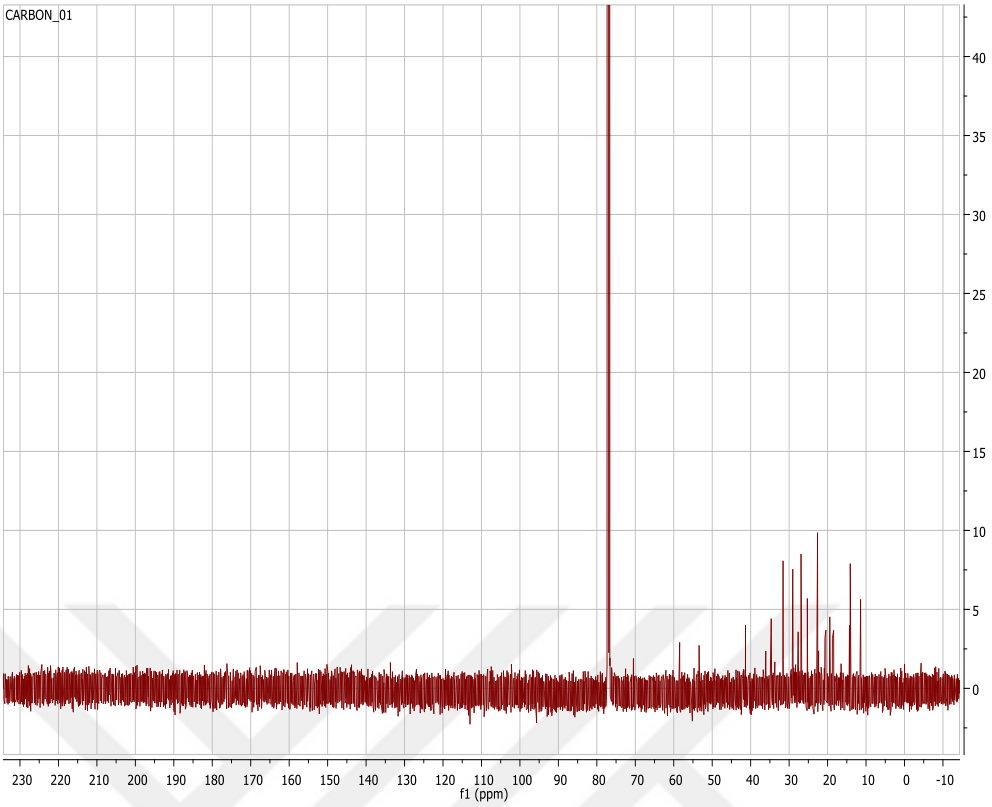


Figure 4.18 : C-13 NMR of MEK-FR+EA+DEP.

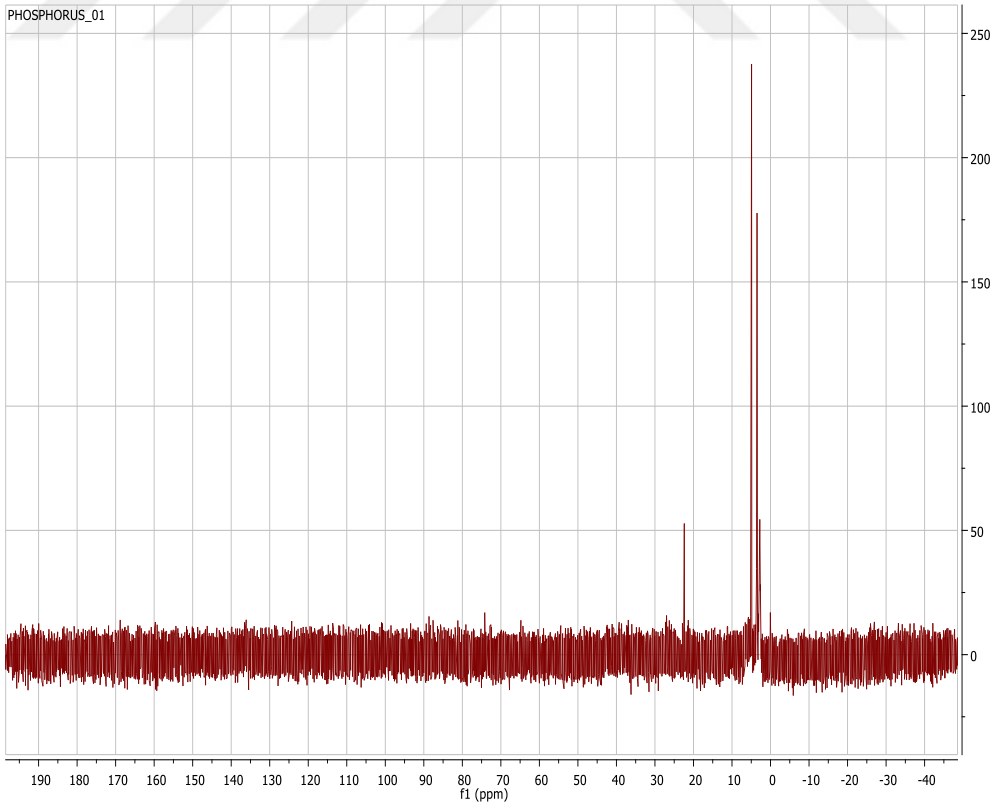


Figure 4.19 : P-31 NMR of MEK-FR+EA+DEP.

Carbon, hydrogen, nitrogen and phosphorus content of modified resins is given in Table 4.4.

Table 4.4 : Microanalysis result of modified ketonic resins.

No	Sample	C (%)	H (%)	N (%)	P (%)
CFR-DEP 1	Cyclohexanone –formaldehyde resin modified with ethanolamine + diethyl phosphite(CFR-DEP)	51.45 (53.6)*	8.71 (8.9)	6.02 (4.8)	5.38 (10.6)
CFR-DEP 2	Cyclohexanone –formaldehyde resin modified with ethanolamine + diethyl phosphite(CFR-DEP)	52.1 (53.6)	8.36 (8.9)	5.47 (4.8)	4.74 (10.6)
MEKR-DEP	Methyl ethyl ketone-formaldehyde resin modified with ethanolamine + diethyl phosphite (MEKR-DEP)	50.9 (49.8)	8.74 (9.05)	2.85 (5.28)	4.28 (11.7)
MEKR-DPP	Methyl ethyl ketone-formaldehyde resin modified with ethanolamine + diphenyl phosphite (MEKR-DPP)	63.5 (56.5)	7.34 (6.6)	2.72 (3.8)	3.32 (8.5)

*Values in the paranthesis are theoretical values calculated from 100% conversion product.

4.2.3 Kabachnik-Fields reaction of acetophenone-formaldehyde resin (AF-Resin) with DEP and ethanolamine

Reaction of acetophenone resin with DEP and ethanolamine is shown in Figure 4.20.

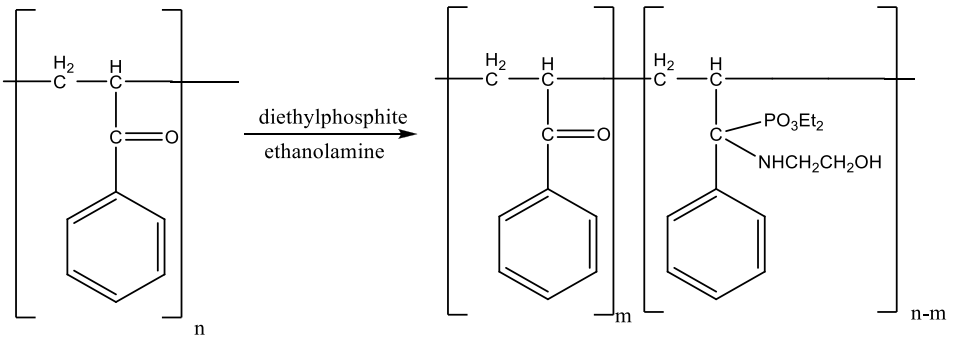


Figure 4.20 : Modification reaction of AF-Resin with ethanol amine and diethylphosphite.

The product has low carbonyl peak intensity at about 1700 cm^{-1} compared to the peak of AF-Resin as seen ATR-FTIR spectra in the Figure 4.21. The conversion of the

carbonyl group of AF-Resin is not completed. Kabachnik-Fields reaction of acetophenone needs higher temperature and longer time. Decreasing of carbonyl peak can be observe in Figure 4.22, Figure 4.23, Figure 4.24. Mg $(ClO_4)_2$ may increase the reaction rate. The reaction of AFR with ethanolamine and diethyl phosphite was carried out at comparably higher temperature in the presence of $Mg(ClO_4)_2$ and Na_2SO_4 at different reaction times. However, after 6h reaction time, the yield was not changed significantly. ^1H NMR, C-13 NMR, P-31 NMR and FTIR spectrum of modified resins are shown in the Figure 4.25, Figure 4.26, Figure 4.27, Figure 4.28.

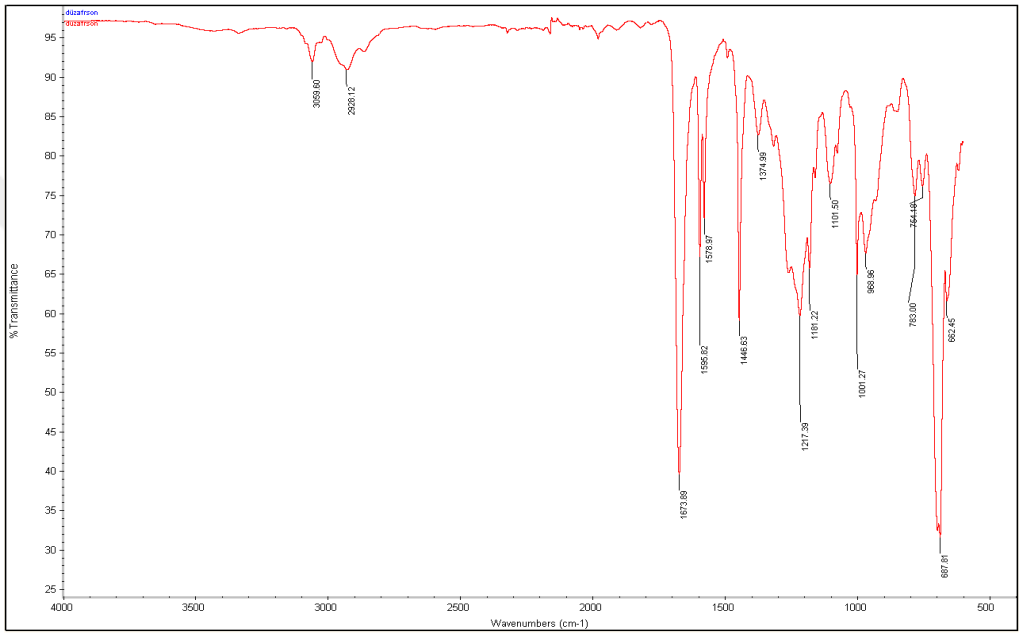


Figure 4.21 : FTIR of AF resin.

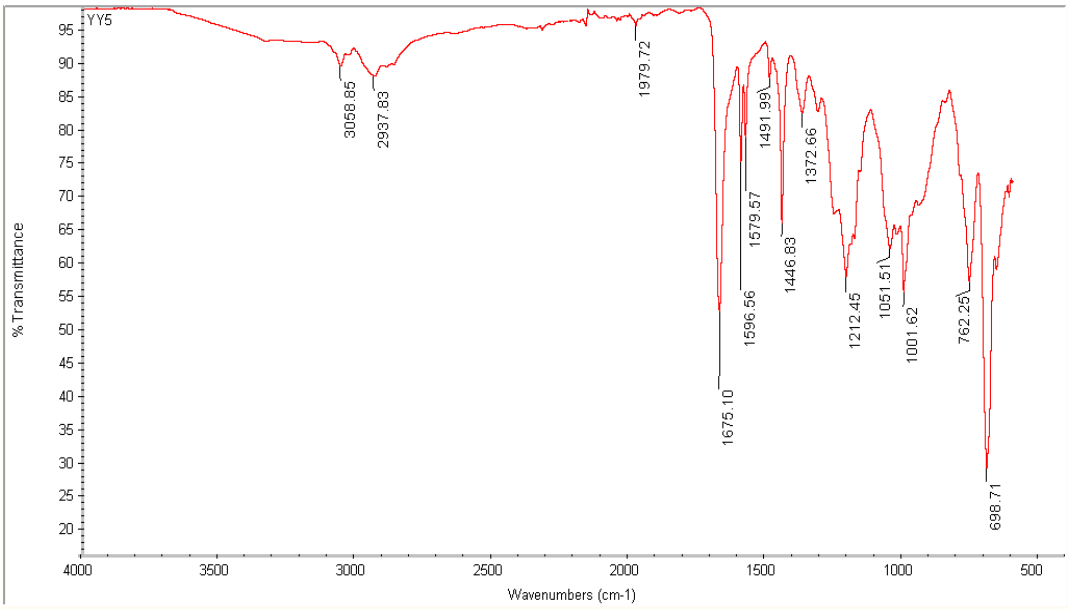


Figure 4.22 : FTIR of AFR+EA+DEP purified and dried (1).

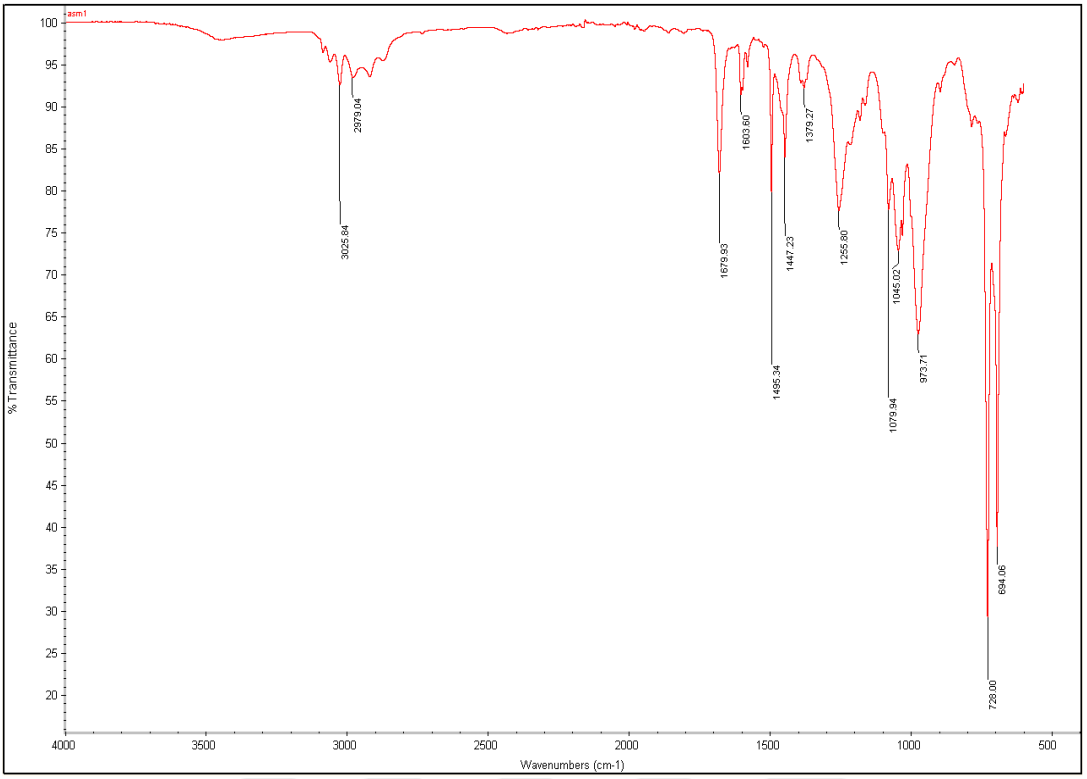


Figure 4.23 : FTIR of AFR+EA+DEP (2).

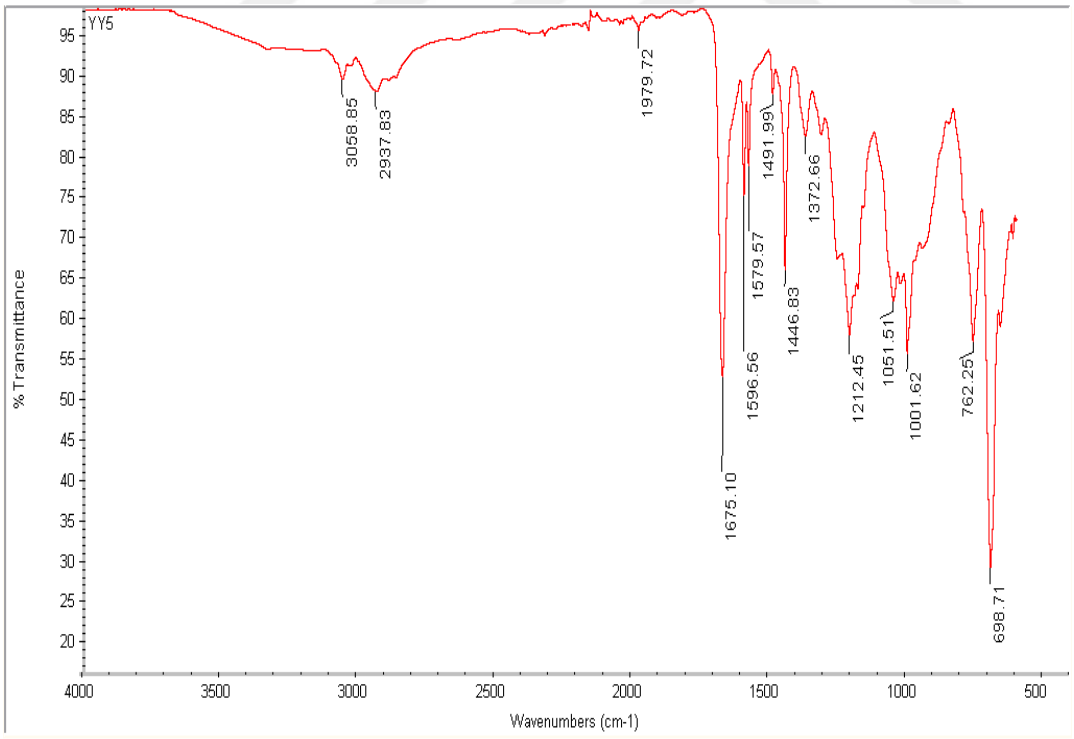


Figure 4.24 : FTIR of AFR+EA+DEP purified and dried (3).

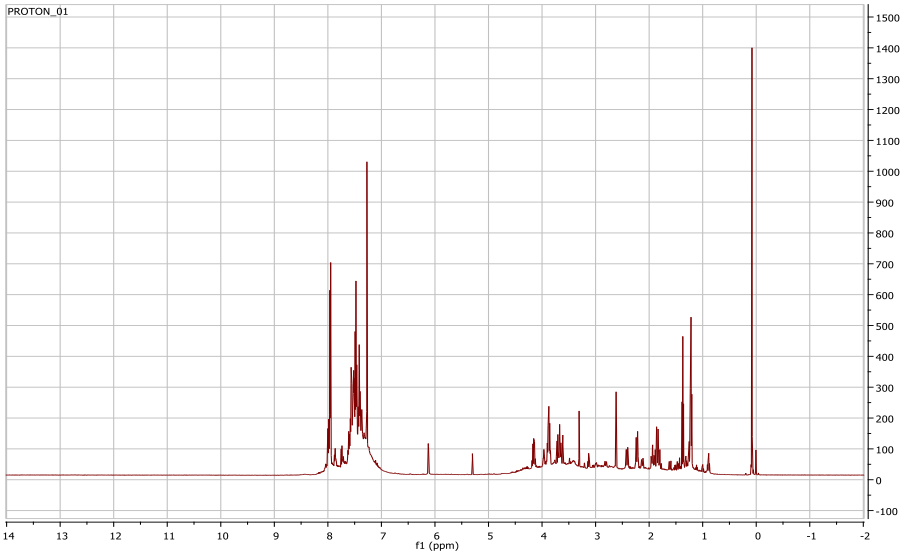


Figure 4.25 : ^{1}H NMR of AFR+EA+DEP purified and dried.

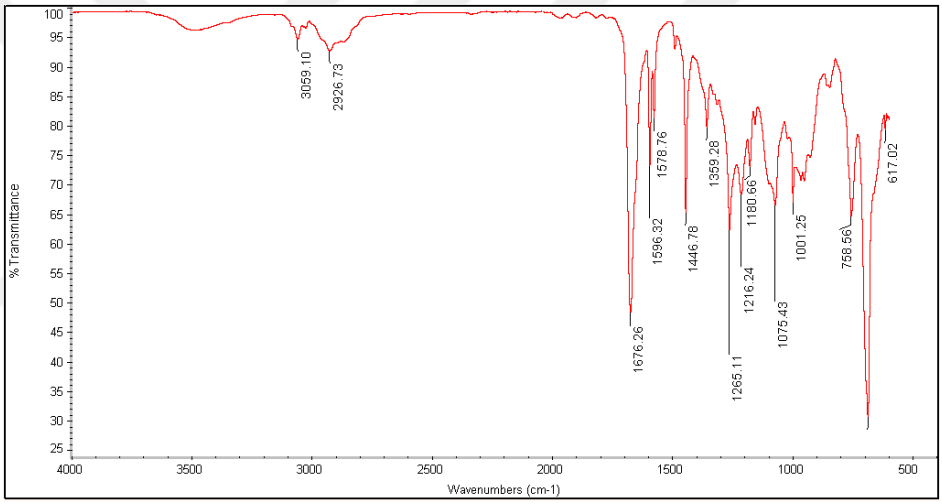


Figure 4.26 : FTIR of DiCAF-Resin.

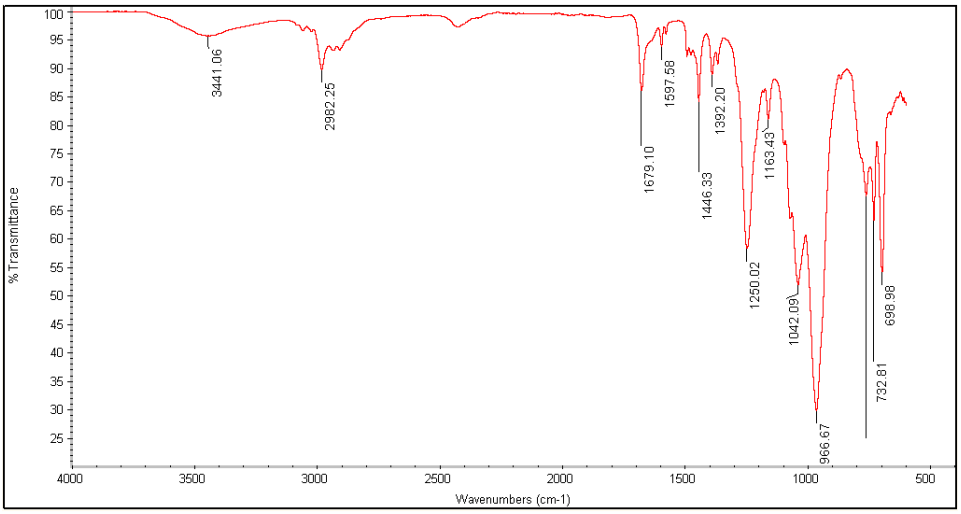


Figure 4.27 : FTIR of DiCAFR+EA+DEP.

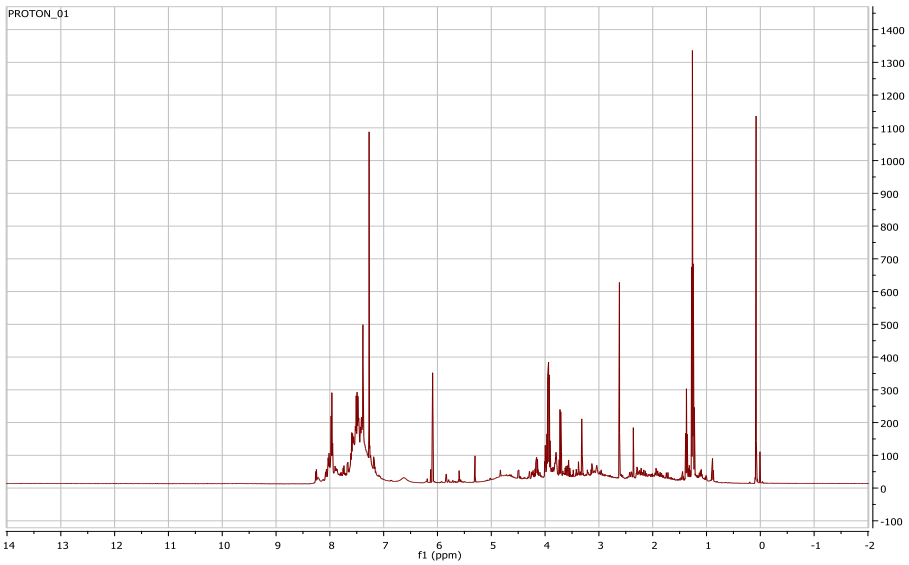


Figure 4.28 : ^{1}H NMR of DİCAFR+EA+DEP.

Solubilities of the modified resins at room temperature are shown in Table 4.5.

Table 4.5 : Solubility of the modified resins at room temperature.

Resin	CH_2Cl_2	toluene	asetone	metanol	THF
Acetophenone-formaldehyde resin (AF-R)	+	+	+	-	+
Acetophenone-2,4-dicholoroacetophenone-formaldehyde resin (DiCAF-R)	+	+	+	+	+
Acetophenone-formaldehyde resin modified with ethanol amine +diethylphosphite (AFR.EA.DEP)	+	slightly	+	slightly	+
Acetophenone-formaldehyde resin modified with ethanol amine +diphenylphosphite (AFR.EA.DPP) (catalyst:$Mg(ClO_4)_2$)	+	-	+	-	+
Acetophenone and 2,4-dicholoroacetophenone formaldehyde resin (DiCAF-R) modified with ethanol amine+diethylphosphite (DiCAFR.EA.DEP)	+	slightly	slightly	+	+
Acetophenone-formaldehyde resin modified with ethanol amine +diphenylphosphite (AFR.EA.DPP) (catalyst:Na_2SO_4)	+	-	-	+	+

+: soluble, -: insoluble at room temperature

TGA analysis of modified acetophenone-formaldehyde and 2,4-dichloro acetophenone-formaldehyde resins are shown in the Figure 4.29, Figure 4.30, Figure 4.31, Figure 4.32, Figure 4.33, Figure 4.34. Resin are listed as follows:

Modified AF-F Resins (AD);

- AD1: AF-F Resin (reference)
- AD2: AF-Dichloroacetophenone-formaldehyde resin
- AD3: AF-F Resin + Ethanolamine+DEP
- AD4: AF-F Resin + EA+ DEF + 4 times perchlorate + DCE 24 hour
- AD5: AF- Dichloroacetophenone- formaldehyde Resin + Ethanolamine+DEP
- AD6: AF-F Resin +EA+Diphenylphosphite (DPP)

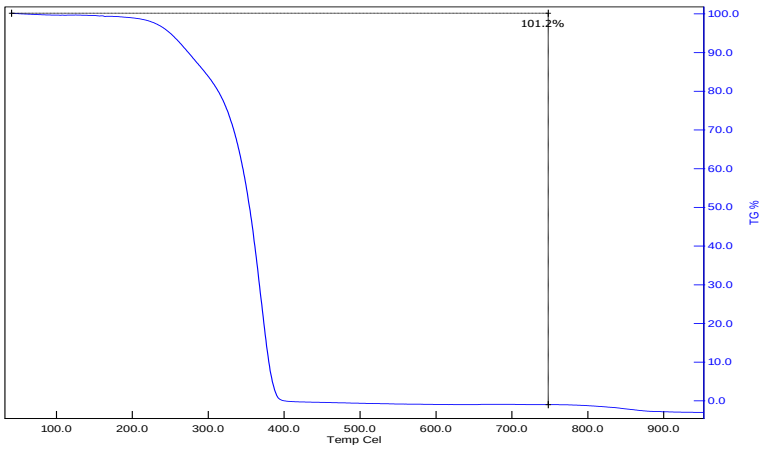


Figure 4.29 : TGA analysis of AF Resin (AD1).

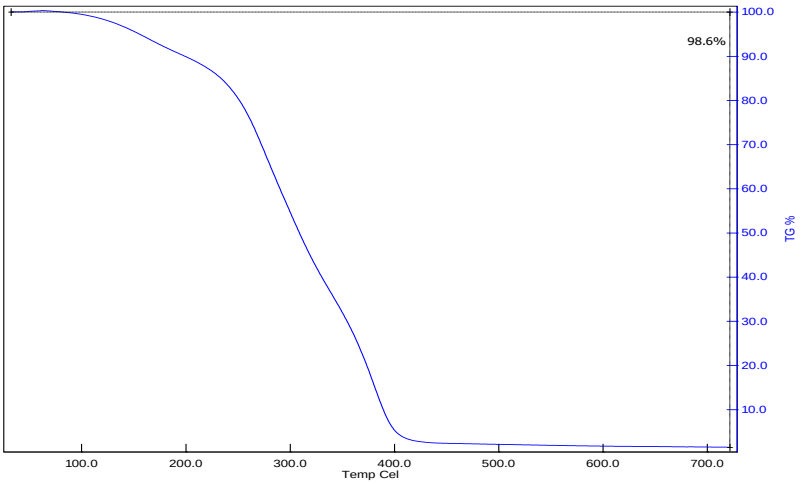


Figure 4.30 : TGA analysis of DİCAF Resin (AD2).

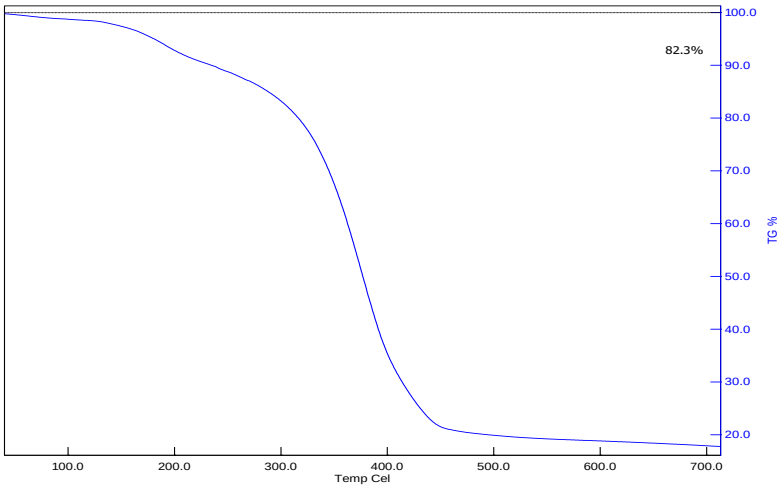


Figure 4.31 : TGA analysis of AFR+EA+DEP (AD3).

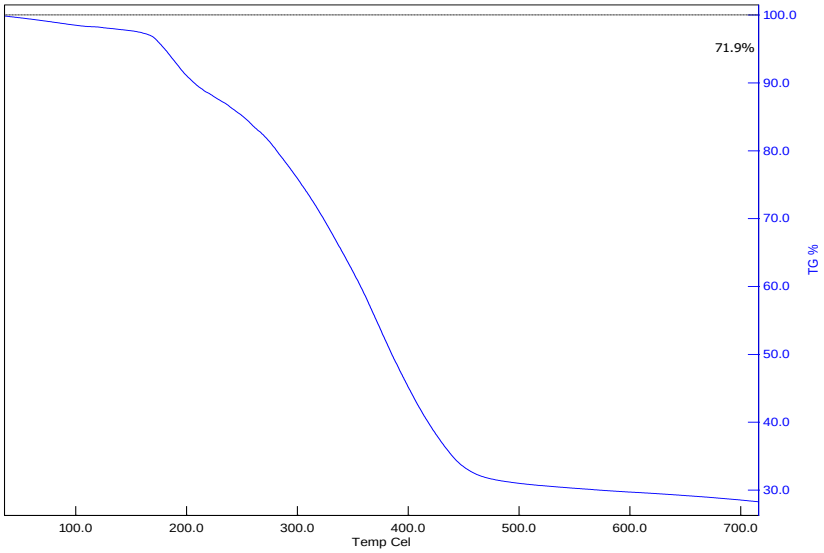


Figure 4.32 : TGA analysis of AFR+EA+DEP (AD4).

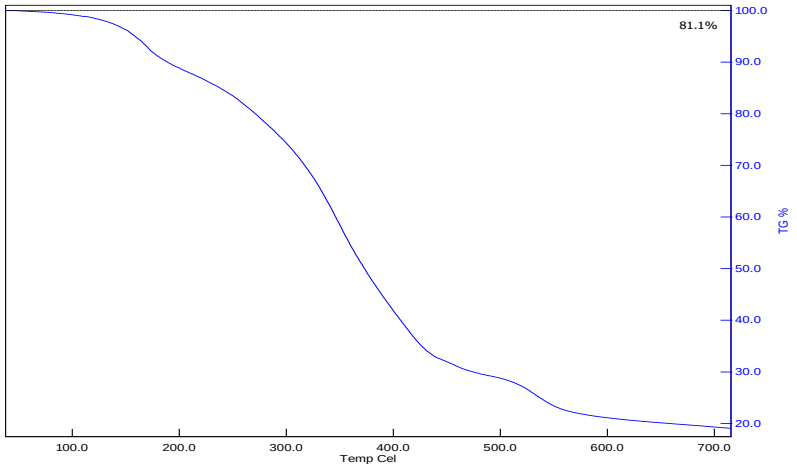


Figure 4.33 : TGA analysis of DİCAFR+EA+DEP (AD5).

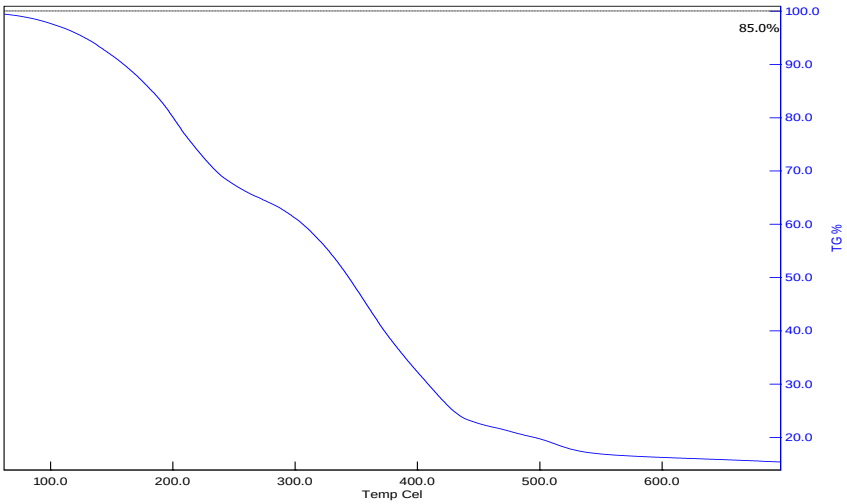


Figure 4.34 : TGA analysis of AFR+EA+DEP (AD6).

4.2.4 Fire retardant polyurethane production using fire retardand modified ketonic resins containing halogen, phosphorous and nitrogen

4.2.4.1 Polyuretane produced using fire retardant modified CF-resin and MEK-F resin

Modified CF-R and MEKF-R were mixed with polyol used for rigid PU formulations. The amount of modified resin was in the range of 10-25 % of polyol. TGA shows an increase in the residue at the temperature of 550^{0}C in Figure 4.35, Figure 4.36, Figure 4.37, Figure 4.38, Figure 4.39. Foam production formulation:

12.5 g Modified resin (AD) + 12.5 g DCM + 25 g Polymix + 72 g NCO

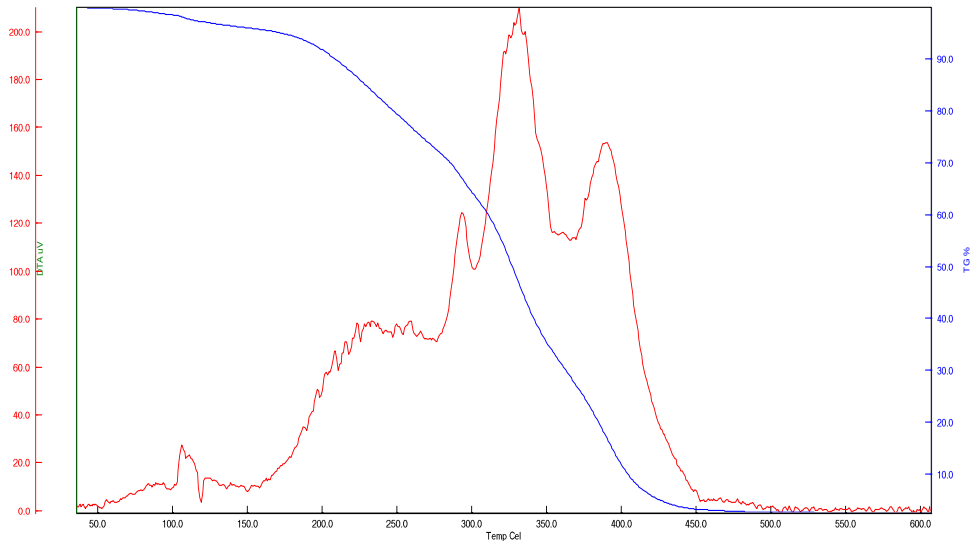


Figure 4.35 : TGA analysis of CFR in polyurethane foam.

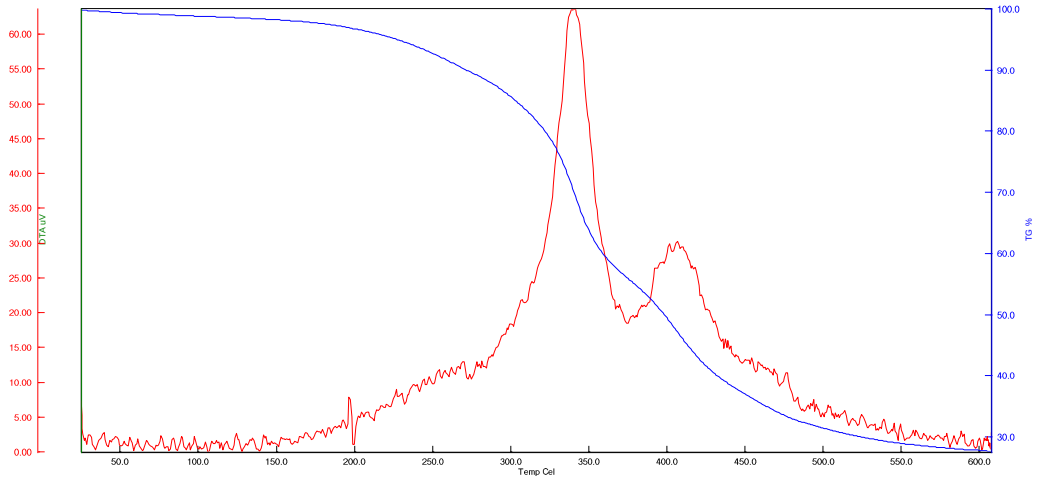


Figure 4.36 : TGA analysis of 10% CFR-EA-DEP at polyurethane foam.

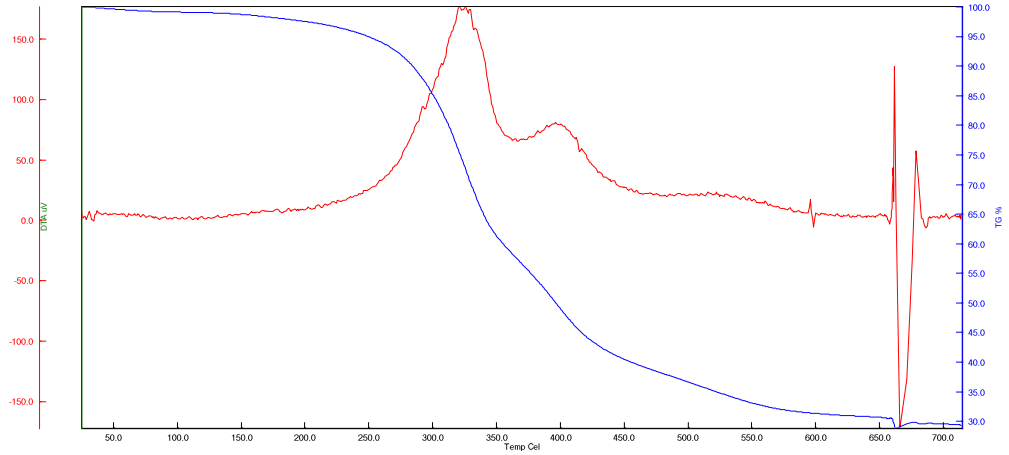


Figure 4.37 : TGA analysis of 15% CFR-EA-DEP at polyurethane foam.

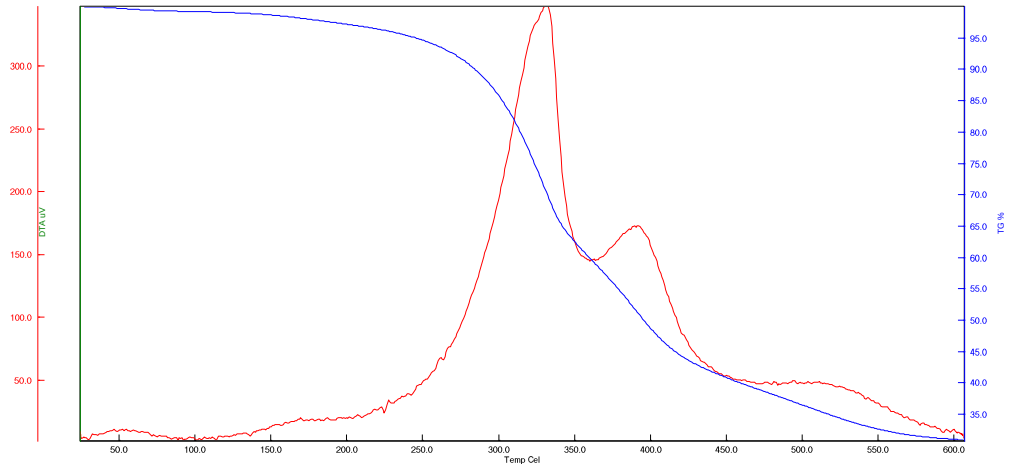


Figure 4.38 : TGA analysis of 20% CFR-EA-DEP at polyurethane foam.

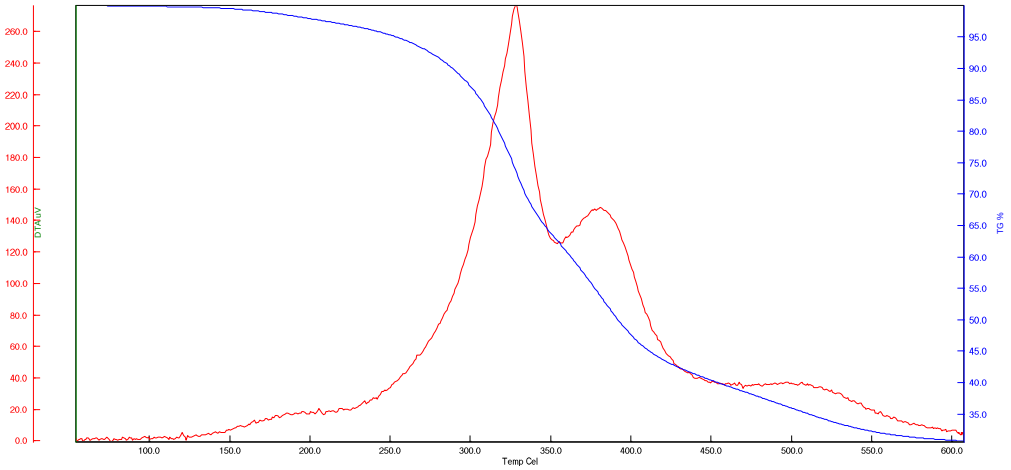


Figure 4.39 : TGA analysis of 25% CFR-EA-DEP at polyurethane foam.

4.2.5 Polyurethane produced using modified AF-resin and DiCLAF- resin

TGA analysis of polyurethane which produced by using modified resins is shown in Figure 4.40, Figure 4.41, Figure 4.42, Figure 4.43, Figure 4.44, Figure 4.45.

Foam using modified AF-F resins (AD);

- AD1 at foam: AF-F Resin (reference)
- AD2 at foam: AF-Dichloroacetophenone-formaldehyde resin
- AD3 at foam: AF-F Resin + Ethanolamine+DEP
- AD4 at foam: AF-F Resin + EA+ DEP + 4 times perchlorate + DCE 24 hour
- AD5 at foam: AF- Dichloroacetophenone- formaldehyde Resin + Ethanolamine+DEP

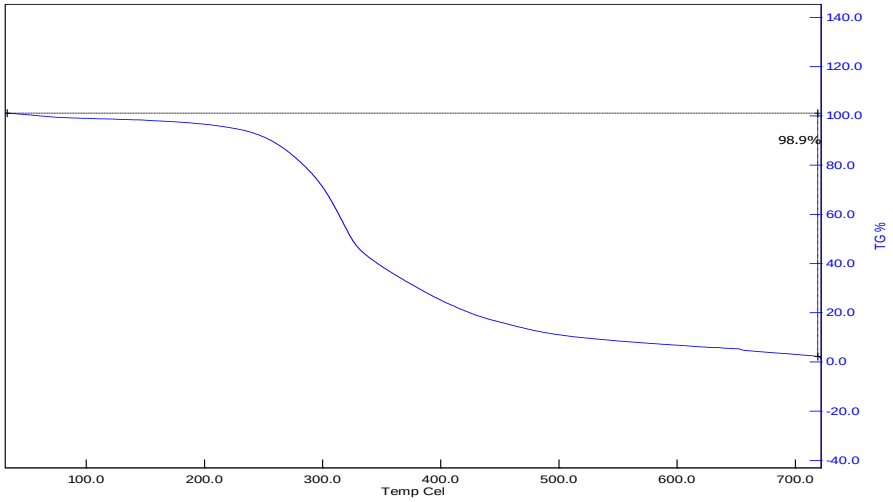


Figure 4.40 : TGA analysis of AD1 at polyurethane foam.

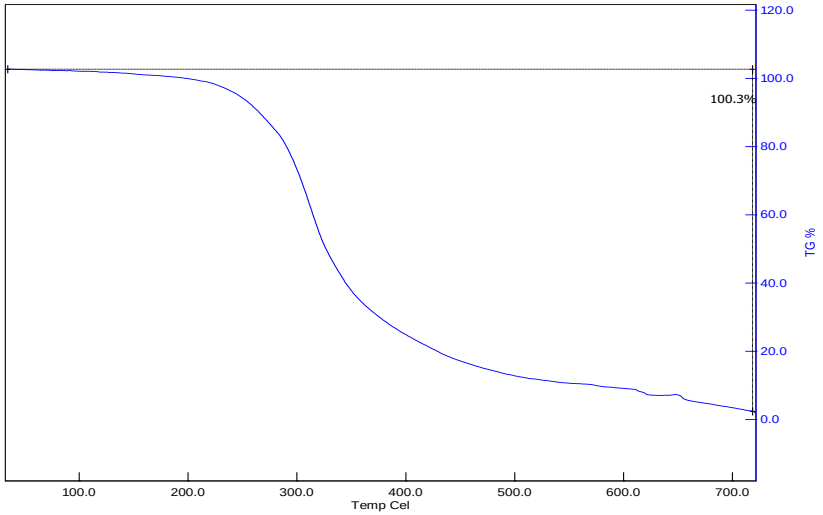


Figure 4.41 : TGA analysis of AD2 at polyurethane foam.

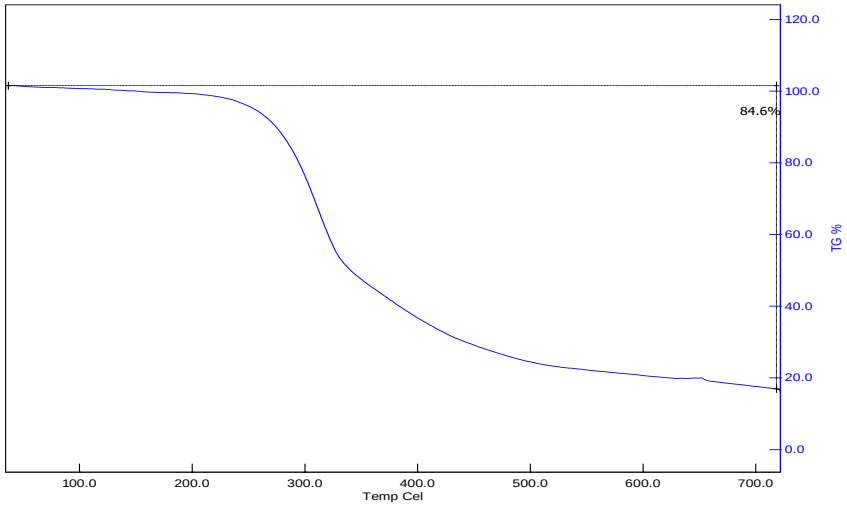


Figure 4.42 : TGA analysis of AD3 at polyurethane foam.

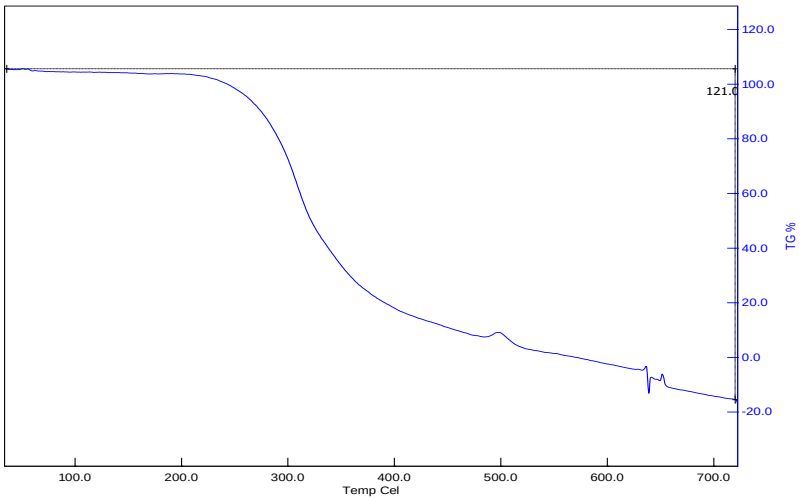


Figure 4.43 : TGA analysis of AD4 at polyurethane foam.

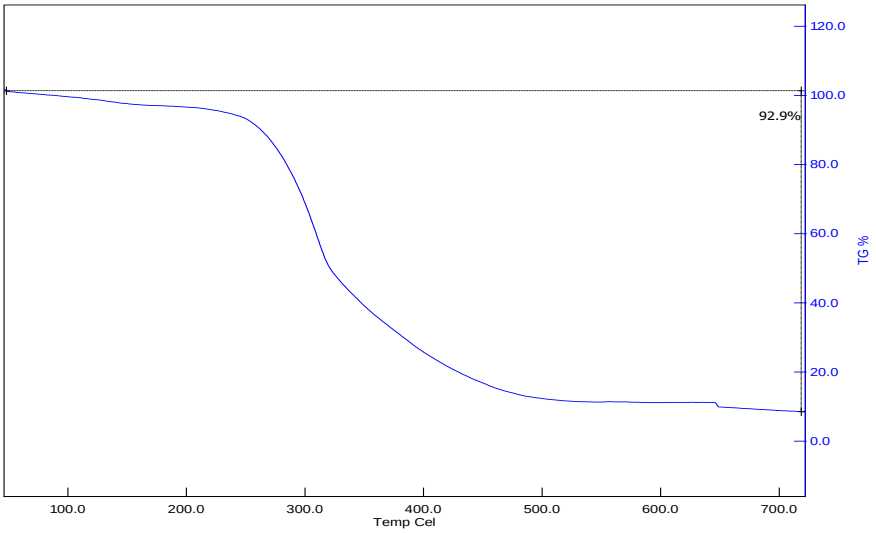


Figure 4.44 : TGA analysis of AD5 at polyurethane foam.

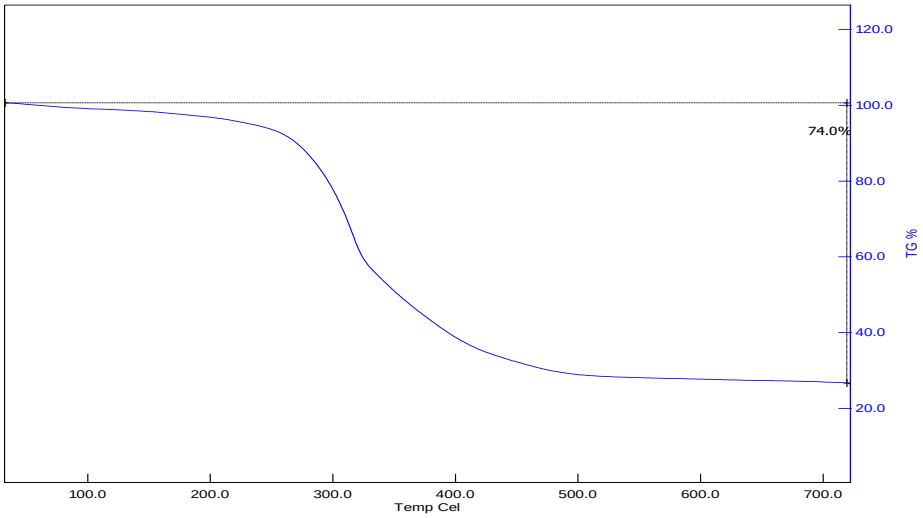


Figure 4.45 : TGA analysis of AD6 at polyurethane foam.

LOI results of AD products in foam listed in Table 4.6.

Table 4.6 : LOI results at AD products in foam.

Products at Foam	Limiting Oxygen Index
AD1	20
AD2	22
AD3	22
AD4	23
AD5	22
AD6	21

Two foam samples that left side has not any flame retardant, right side include AD5 at %20. At polymix ignite at same time. Right side foam is self- extinguished within 2 seconds. The left foam continues to fast burning. Picture of the this test shown at Figure 4.46.

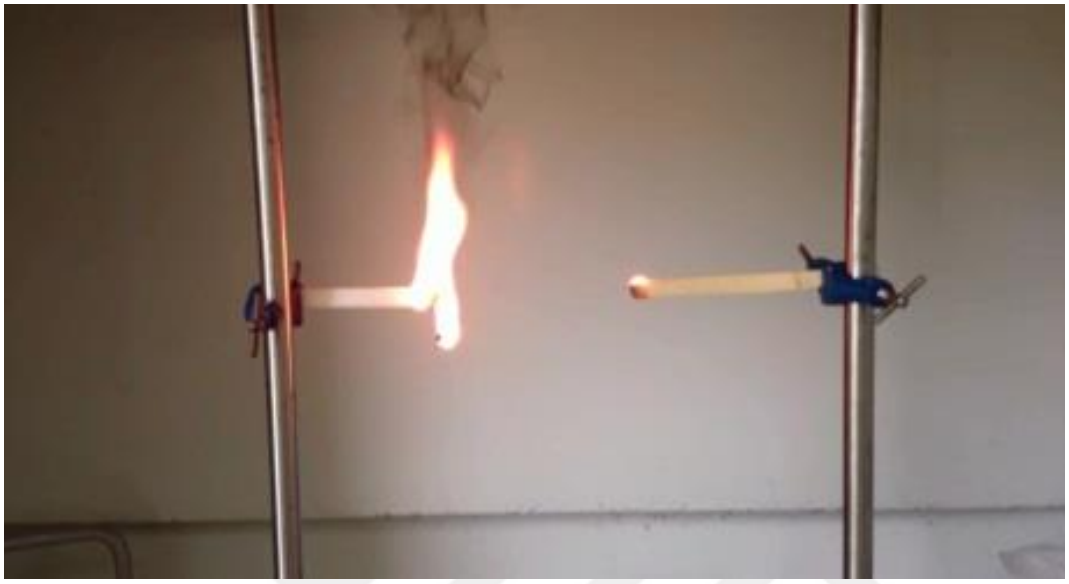


Figure 4.46 : Foam flammability test (Left: without resin, Right: %20 AD 5 resin).

4.3 Fire Resistant Polyurethane Using THEIC-Tris (2-chloroethyl) Phosphite Products

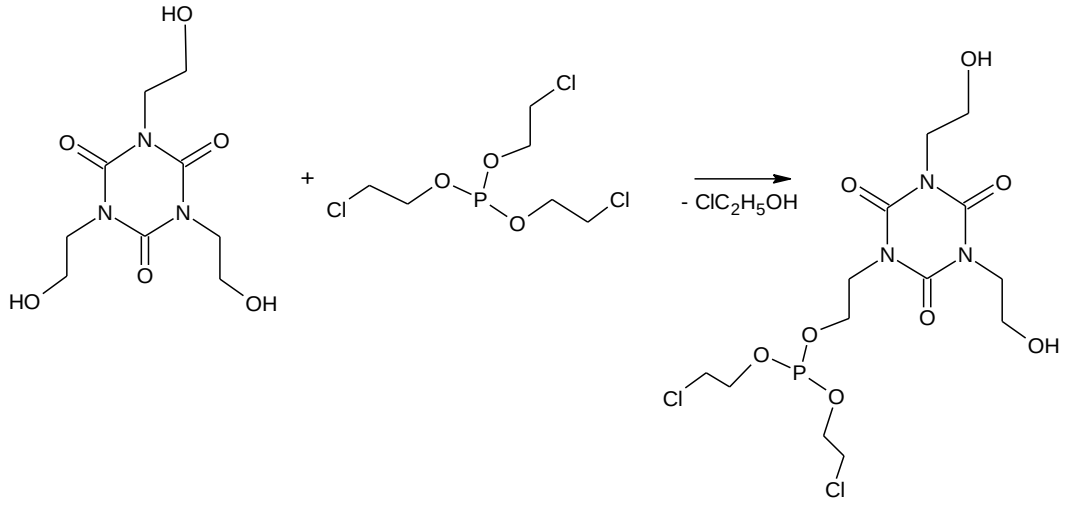


Figure 4.47 : Reaction mechanism THEIC and tris(2-chloroethyl) phosphite.

The reaction product of the THEIC- Phosphite is slightly viscose liquid has the following properties; viscosity: 2560 cP at 25°C; OH value: 314 mg of KOH/g. FTIR

spectrum of theic-tris(2-chloroethyl) phosphite product is shown in Figure 4.48. Also FTIR of theic shown in Figure 4.49.

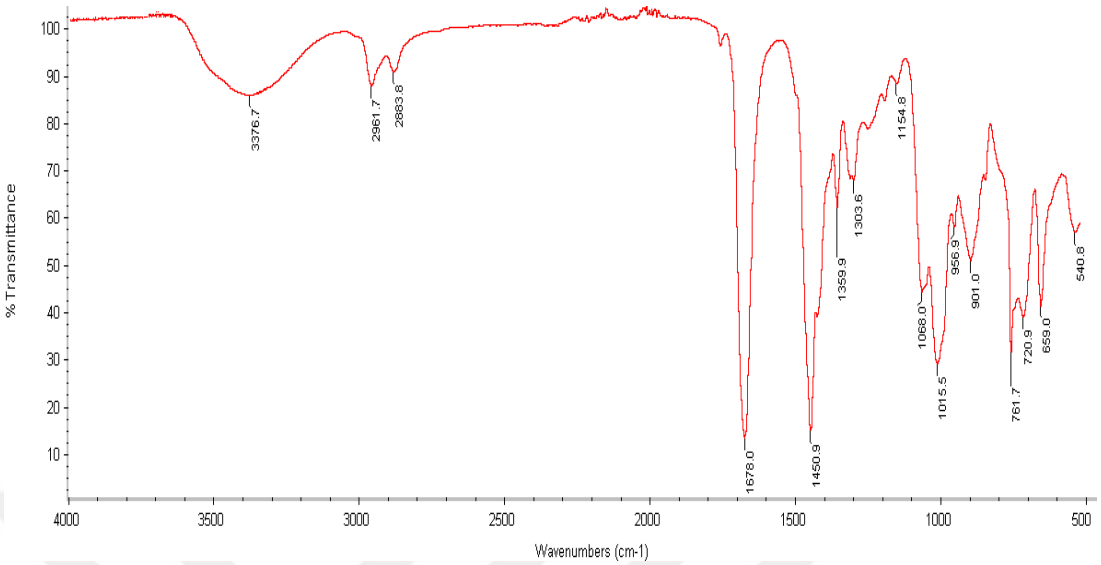


Figure 4.48 : FTIR of theic-tris(2-chloroethyl) phosphite product.

3000-3600 cm^{-1} : O-H stretching

2980-2900 cm^{-1} : Aliphatic C-H stretching

1678 cm^{-1} : C=O stretching of cyanuric acid ring

1015 and 901 cm^{-1} : P-O stretching

800-600 cm^{-1} : C-Cl stretching (especially 659 cm^{-1})

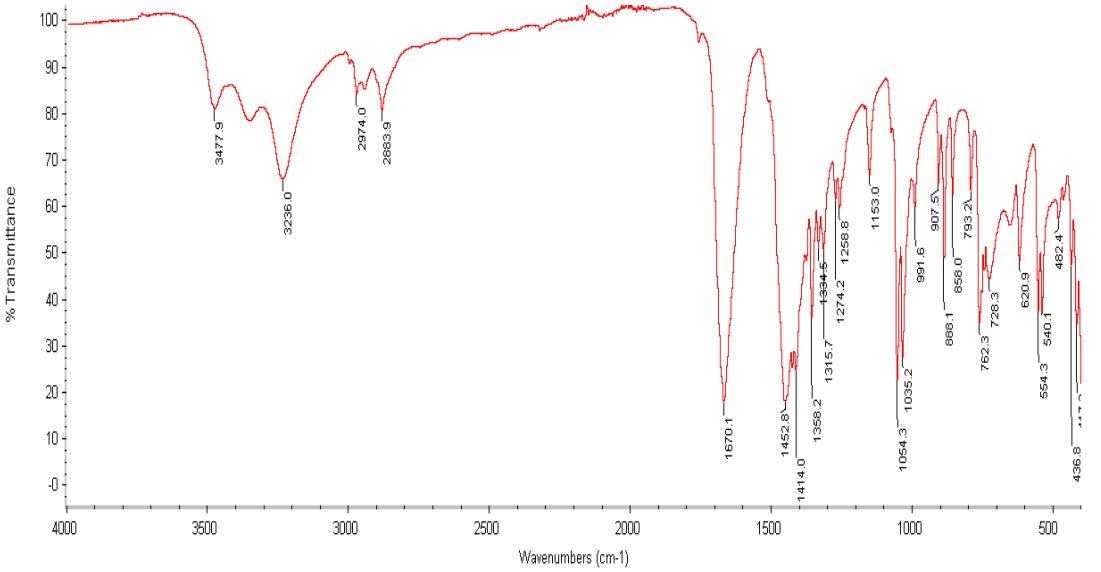


Figure 4.49 : FTIR of THEIC.

TGA of TCPP and theic-tris(2-chloroethyl) phosphite product is shown in the Figure 4.50 and the Figure 4.51.

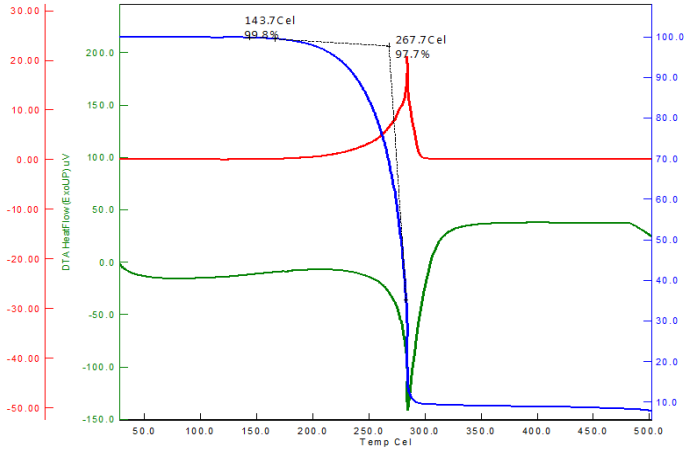


Figure 4.50 : TGA of TCPP.

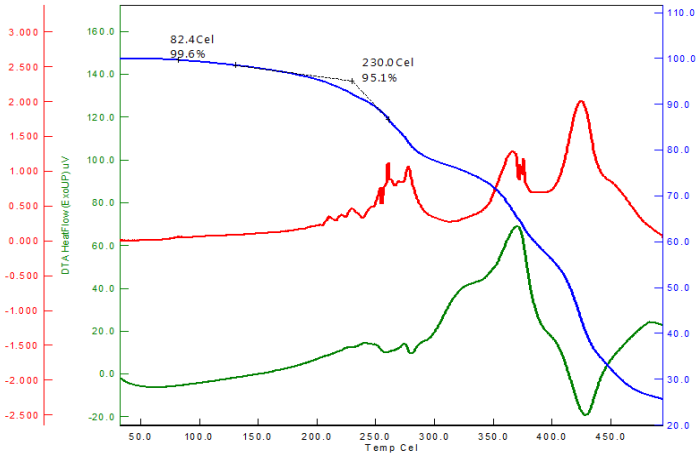


Figure 4.51 : TGA result of theic-tris(2-chloroethyl) phosphite product.

Polymix formulation is listed in Table 4.7.

Table 4.7 : Polymix formulation.

Polymix Formulation	Mass Concentration (%)
Polyether polyol	91,1
Silicone	2
Pentane	0,7
Water	3
Catalyst	3,2

Table 4.8 and Table 4.9 polymix containing different amount of flame retardants and foam properties.

Table 4.8 : Polymix with different amount of flame retardants and foam properties.

	D 1	D 2	D 3	D 4	D 5	D 6	D 7	D 8	D 9	D 10	D 11
Polymix (g)	85	80	75	70	80	75	70	65	75	70	65
THEIC-Phosphite (g)	10	10	10	10	15	15	15	15	20	20	20
TCPP (g)	5	10	15	20	5	10	15	20	5	10	15
Mixing Time (s)	6	6	6	6	6	6	6	6	6	6	6
Cream Type (s)	11	11	9	9	10	11	9	9,5	10	10	10
Gel Time (s)	30	30	28	27	28	28	27	27	27	27	28
Tack Free Time (s)	38	38	36	36	35	36	35	34	35	34	35

Table 4.9 : Polymix with different amount of flame retardants and foam properties.

	D 12	D 13	D 14	D 15	D 16	D 17	D 18
Polymix (g)	60	90	85	80	90	85	80
THEIC- Phosphite (g)	20	10	15	20	0	0	0
TCPP (g)	20	0	0	0	10	15	20
Mixing Time (s)	6	6	6	6	6	6	6
Cream Type (s)	10	10	11	11	10	10	9
Gel Time	26	31	34	36	32	32	28
Tack Free Time (s)	34	40	44	49	43	42	37

Results of horizontal test chamber are shown in Figure 4.52.

Figure 4.52 : Picture of horizontal test chamber results.

When examined Table 4.8 and Figure 4.52 it is clearly seen that THEIC-Phosphite fire retardant compound can be used in place of TCPP in polyurethane rigid foam. The experiment of D15 and D18 shown that foam forming properties didn't change (cream

time, gel time and tack free time). TGA results of theic-tris(2-chloroethyl) phosphite product and TCPP are shown in the Figure 4.53 and the Figure 4.54.

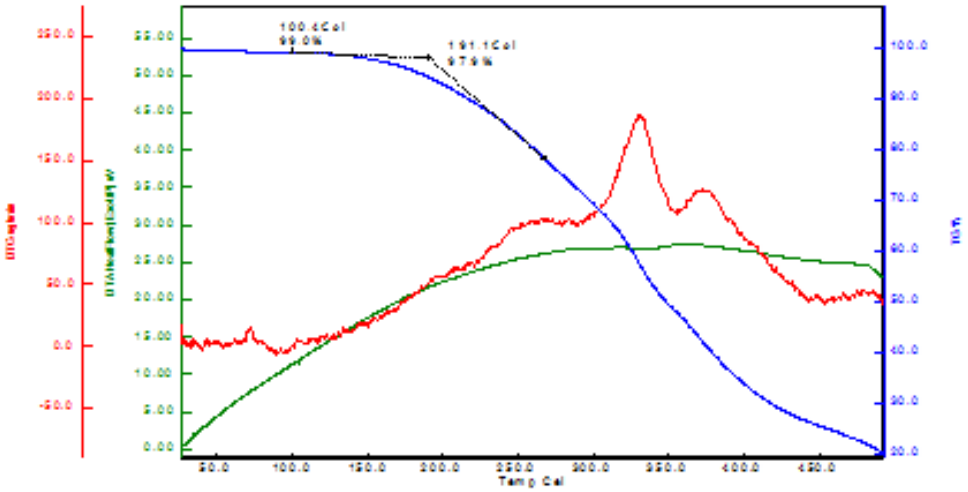


Figure 4.53 : TGA result of theic-tris(2-chloroethyl) phosphite (18 % at polymix) at foam.

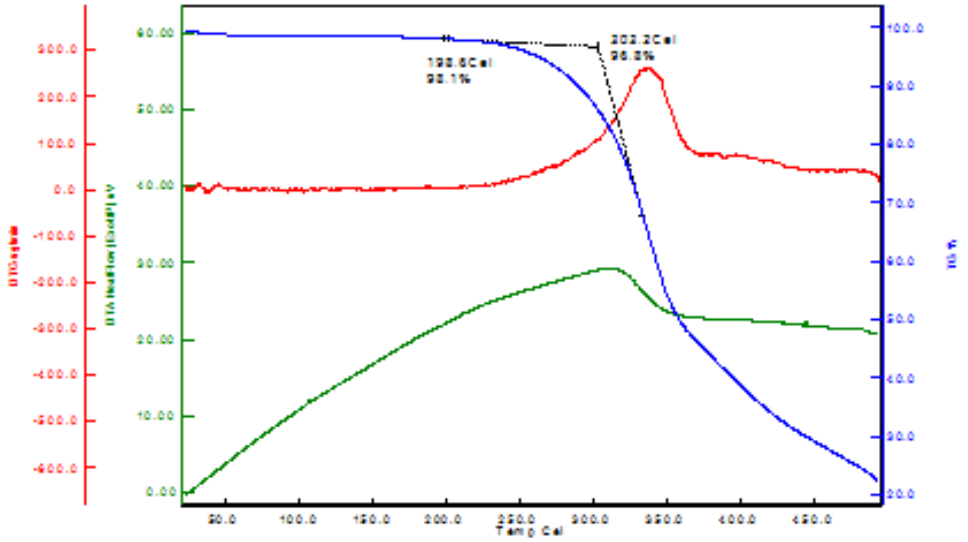


Figure 4.54 : TGA result of TCPP (18 % at polymix) at foam.

4.4 Fire Resistant Polyurethane From THEIC-TCPP Products

4.4.1 Formation of THEIC-TCPP products

In the classical transesterification reaction, THEIC reacts with TCPP by the help of transesterification catalyst such as dibutyltin diluarate followed by elimination of 1-chloropropan-2-ol which is removed by vacuum distillation. Possible mechanism of the formation of the product (FR-1) from 1 mol of THEIC and 2 moles of TCPP is shown in the Figure 4.55

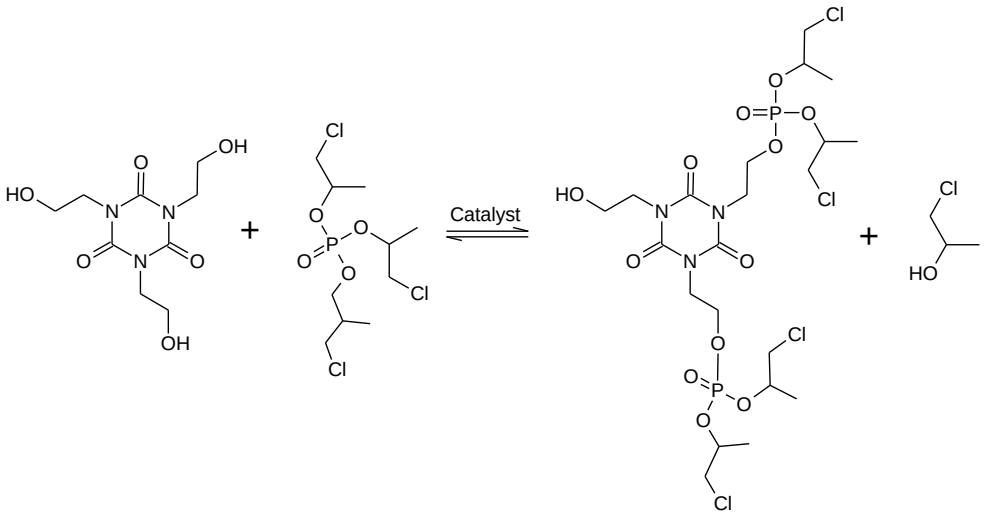


Figure 4.55 : Formation of FR-1.

Theic and tcpp reactions were performed in 1:1, 1:2, 1:3 and 1:5 molar ratios. The reaction conditions and yields are summarized in Table 4.10. Distilled products were analyzed by GC-MS and found that they are a mixture of 1-chloropropan-2-ol and excess tcpp. As seen from the Table 4.10, increasing initial tcpp content results increasing distilled product.

Table 4.10 : Theic-tcpp reaction condition.

	T:T(1:1) (g)	**T:T(1:2) (g)**	**T:T(1:3) (g)**	**T:T(1:5) (g)**
THEIC	169,65	104,4	104.4	104,4
TCPP	212.94	262,08	393.12	655,2
Distilled Products (%)	3	15	29	56
Time (h)	18	16	14	14

Hydroxyl, acid and viscosity values of obtained products are shown in Table 4.10.

Polycondensation reaction also occurs as a side reaction between theic and tcpp when the molar ratio of tcpp decreases Figure 4.56. As a result, viscosity increases excessively. Generally low viscosity is desirable for polyurethane applications especially in rigid foam application. Viscosity and OH value decrease when 1:5 molar ratios are used. In this case, the possibility of bounding FR molecules to the polyurethane structure is low because of its low hydroxyl value.

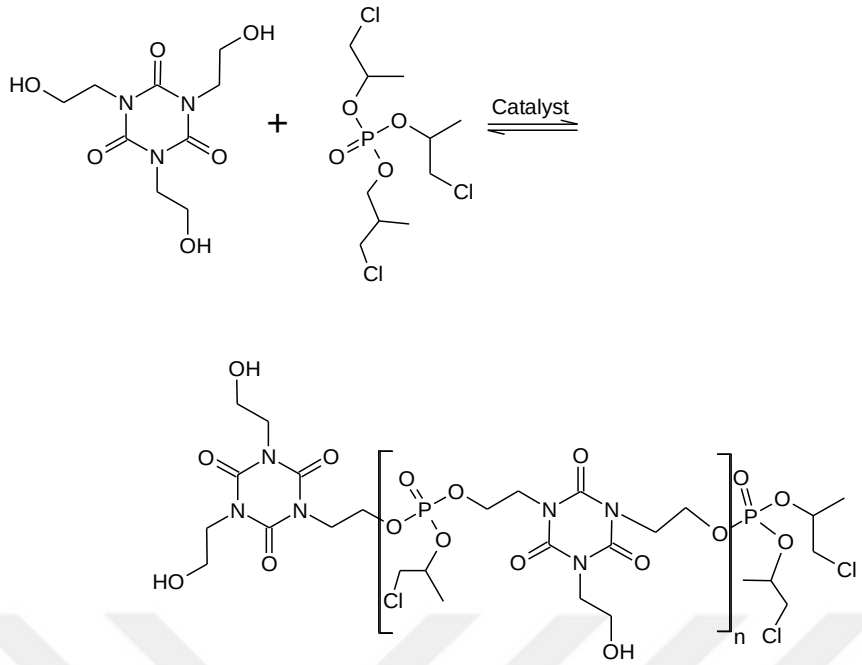


Figure 4.56 : Polycondensation of THEIC and TCPP.

Trials have been performed on rigid polyurethane foam systems where both FR-1 and FR-2 used as fire resistant. Fort the application, including FR at different ratios and not including FR foams are prepared. Only FR and the ratio have been changed during the formulation. Quality control test results are given in the Table 4.11.

Table 4.11 : THEIC-TCPP quality control test results.

Product code	THEIC:TCPP molar ratio	OH content (mg KOH/g)	Acid content (mg KOH/g)	Viscosity (25 °C) (cP)	Distiled Product (g)
FR	1:1	74	11	950	3
FR-1	1:2	146	12	1250	15
FR-2	1:3	90	25	250	29
FR-3	1:5	55	26	55	56

4.4.2 Characterization of FR obtained from THEIC and TCPP

FTIR of fire retardants (FR) are shown in the Figure 4.57, Figure 4.58, Figure 4.59, Figure 4.60, Figure 4.61, Figure 4.62, Figure 4.63, Figure 4.64, Figure 4.65, Figure 4.66, Figure 4.67. The absorptions of $–CH_3$ and $–CH_2–$ were observed at 2975–2920 cm^{-1}, and the absorption of –C-N-C was at 1453 cm^{-1}. A broad absorption band at 3600-3400 cm^{-1} due to O–H stretching. The peaks at 1261 and 990 cm^{-1} are due to the

P=O and P–O–C in the phosphate, respectively. The strong band at 1685 cm^{-1} clearly indicates the C=O stretching frequency of theic. Furthermore, the C-Cl stretching was at about 760 cm^{-1}.

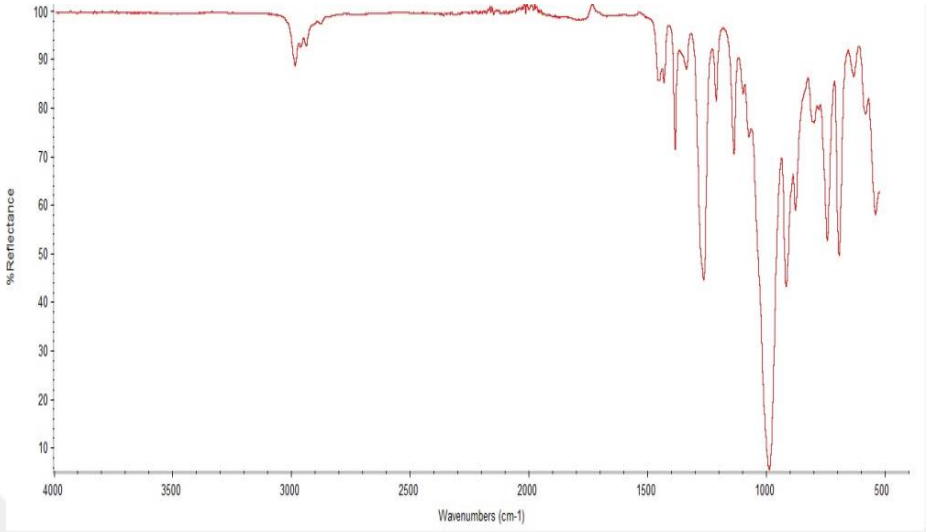


Figure 4.57 : FTIR spectrum of TCPP.

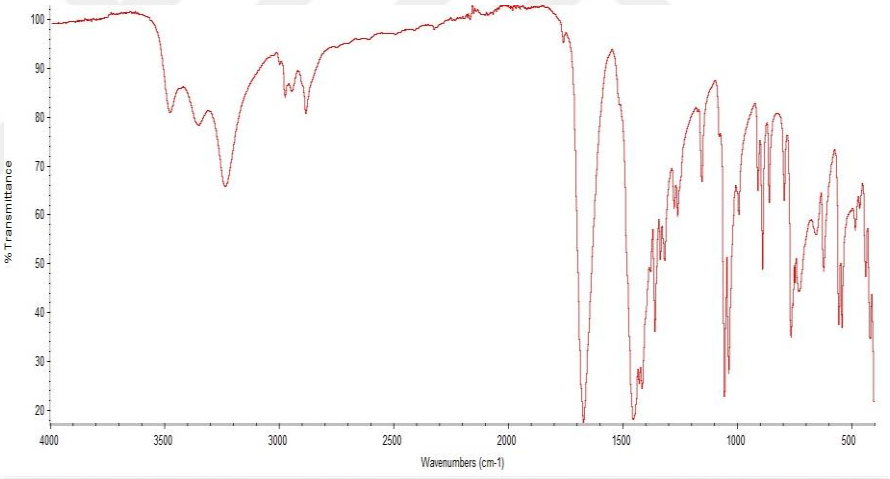


Figure 4.58 : FTIR spectrum of THEIC.

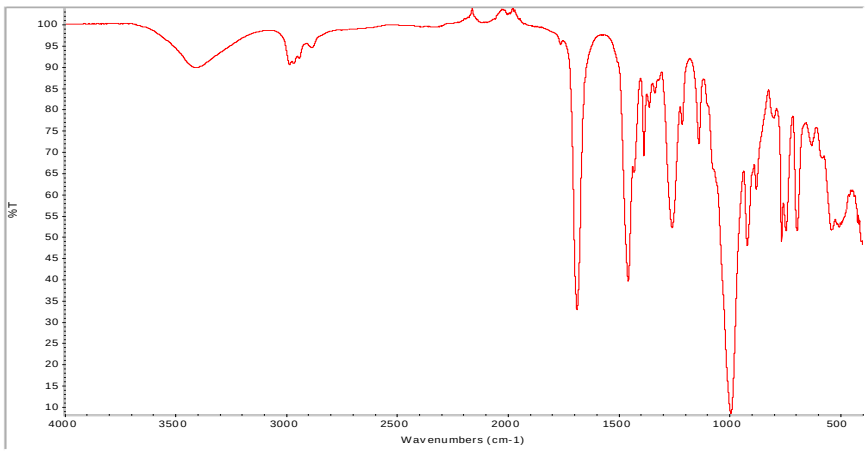


Figure 4.59 : FTIR spectrum of THEIC + TCPP (1:1) (FR).

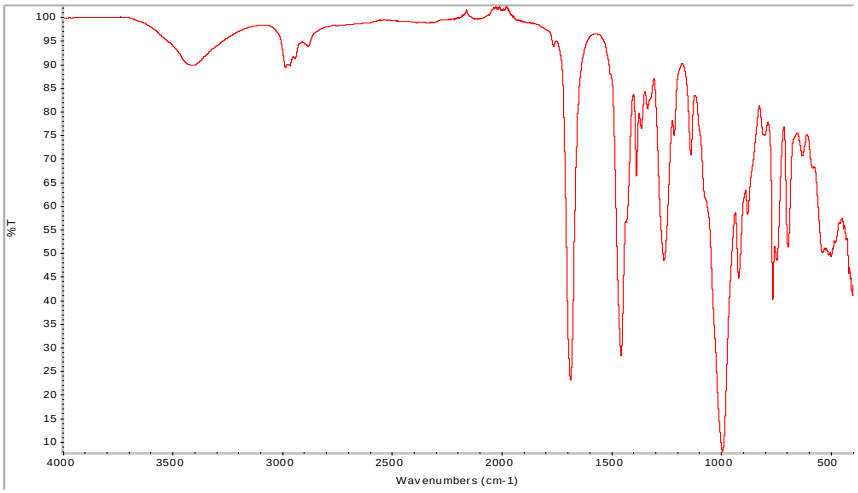


Figure 4.60 : FTIR spectrum of THEIC + TCPP (1:2) (FR-1).

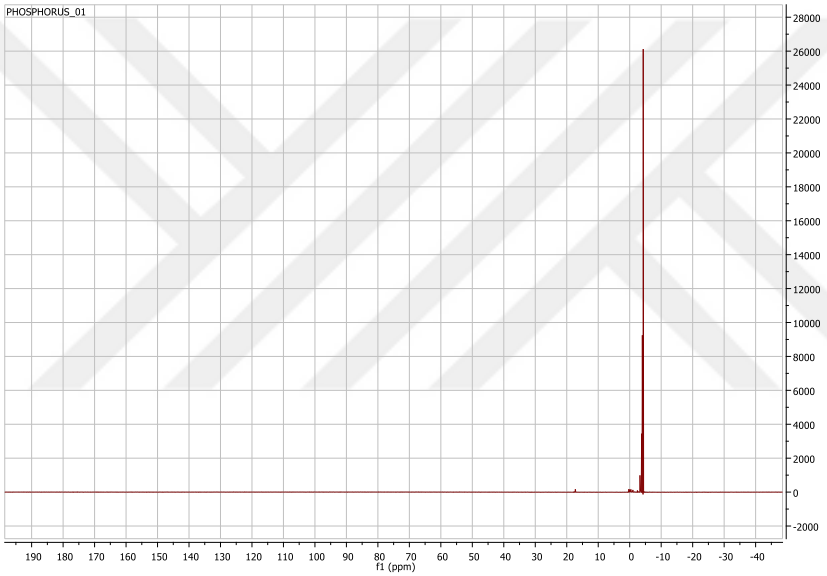


Figure 4.61 : Phosphorus NMR spectrum of FR-1.

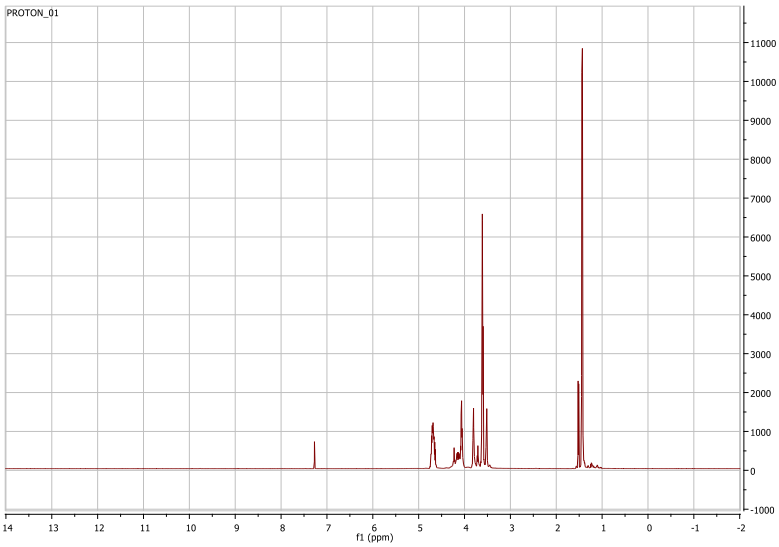


Figure 4.62 : ^{1}H NMR spectrum of FR-1.

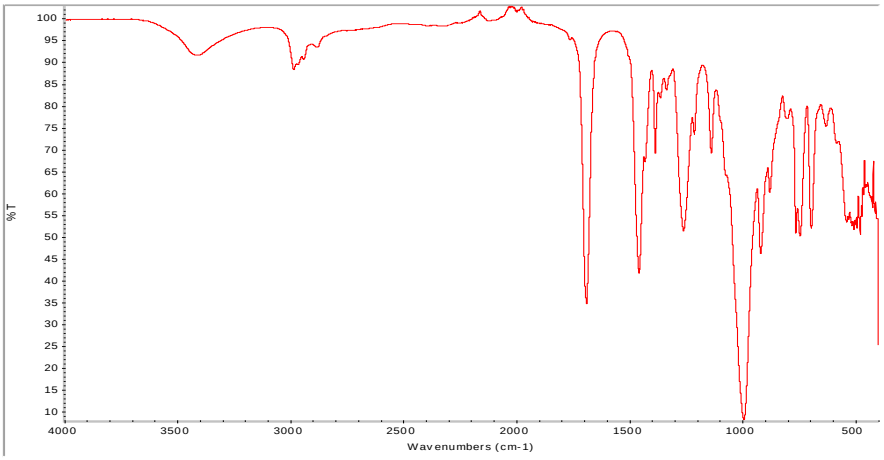


Figure 4.63 : FTIR spectrum of THEIC + TCPP (1:3) (FR-2).

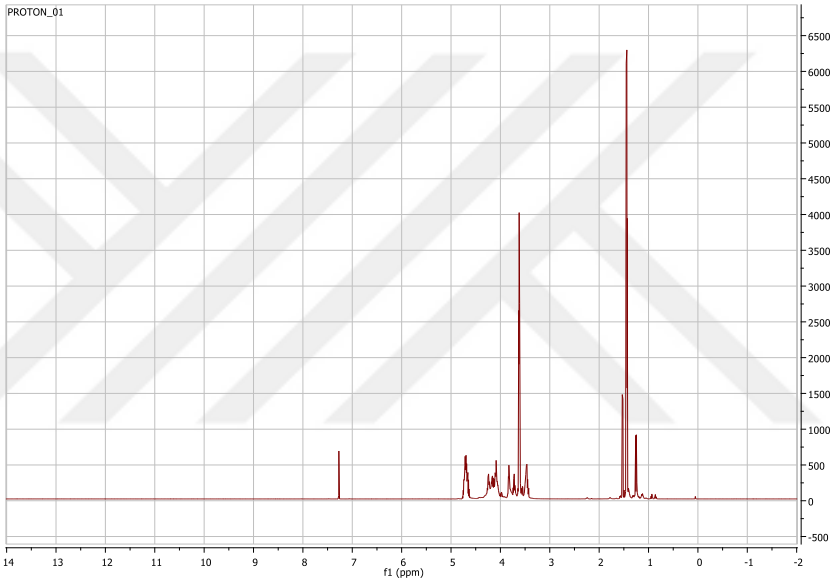


Figure 4.64 : ^{1}H NMR spectrum of (FR-2).

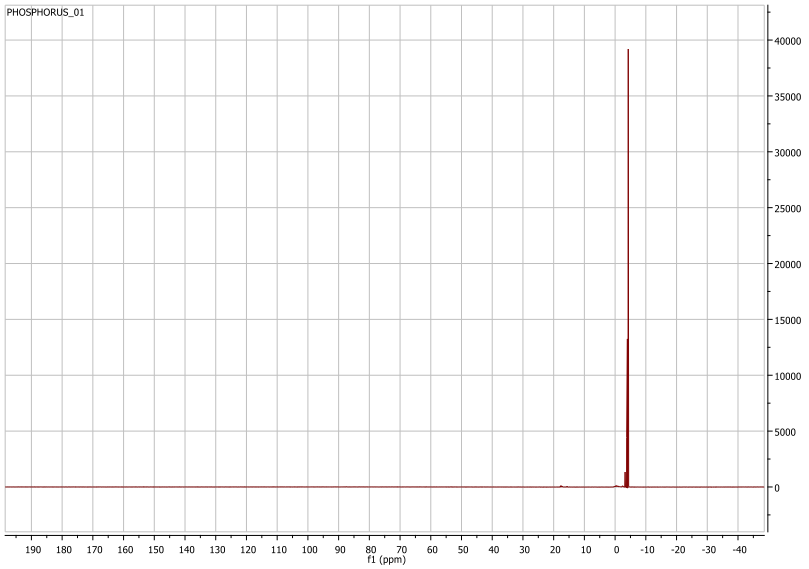


Figure 4.65 : P-31 NMR spectrum of (FR-2).

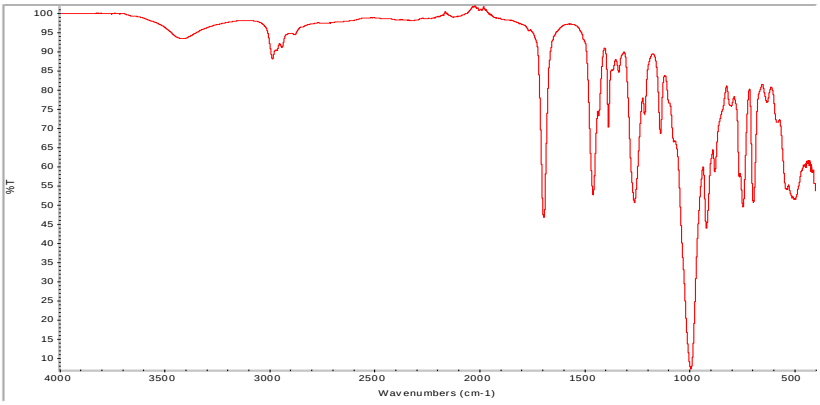


Figure 4.66 : FTIR spectrum of THEIC+TCPP (1:5) (FR-3).

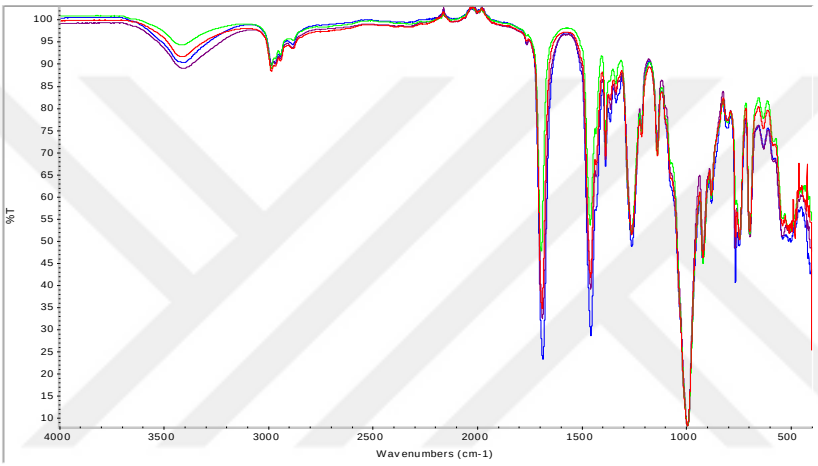


Figure 4.67 : FTIR spectrum of all FR products.

[Purple (1:1); Blue (1:2); Red (1:3); Green (1:5)]

4.4.3 The flame retardant effect of FR products

4.4.3.1 Structure of the polyurethane containing flame retardant (FR)

FTIR spectrum of PUR-3 is shown in Figure 4.68.

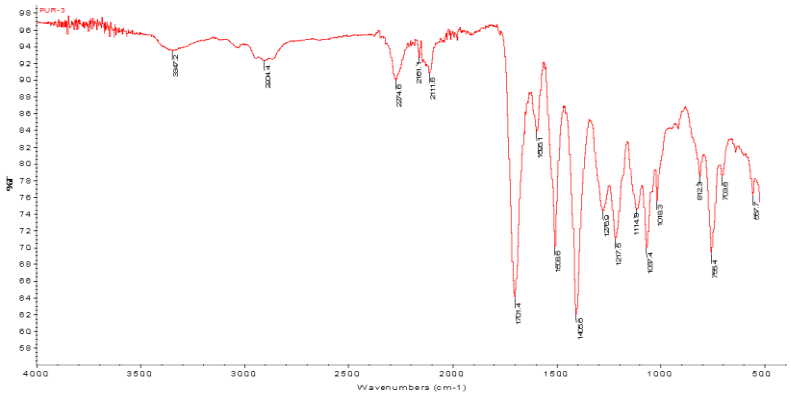


Figure 4.68 : FTIR spectrum of PUR-3.

IR spectra of PU foam (PUR-3) shows broad bands around 3450-3310 cm^{-1} due to N-H bond. The stretching absorption of –C-N 1405 cm^{-1} and the band 1701 cm^{-1} confirm the presence of R-O-CO-N groups. The absorption bands around 2274 cm^{-1} show the presences of terminal NCO groups in PU. The bands around 1217 cm^{-1} and 1067 cm^{-1} are due to P=O and P-O-C stretching frequencies respectively. Furthermore, the C-Cl stretching was seen at about 755 cm^{-1}.

4.4.3.2 The flame retardant effect of FR type and amount

Initial trials have been performed on rigid polyurethane foam systems where both FR-1 and FR-2 used as fire retardant reactive additive. For the application, including polyurethane foam containing FR at different ratios and foam without FR were prepared. Only FR and the ratio have been changed during the formulation. The formulations are shown in the Table 4.12.

Table 4.12 : Polyurethane foam formulations.

Material	**PUR-1**	**PUR-2**	**PUR-3**	**PUR-4**	**PUR-5**	**PUR-6**	**PUR-7**
Polyether polyol	100	100	100	100	100	100	100
Pentane	0,7	0,7	0,7	0,7	0,7	0,7	0,7
Tegostab B 8443	2	2	2	2	2	2	2
Distilled water	0,3	0,3	0,3	0,3	0,3	0,3	0,3
FR-1	-	5	10	15	-	-	-
FR-2	-	-	-	-	5	10	15
Dabco TMR	1,5	1,5	1,5	1,5	1,5	1,5	1,5
PMDI	130	130	130	130	130	130	130

The larger value of LOI is, the harder it is for the material to catch fire and to burn. Generally speaking, fort he case of oxygen index below 21, the material is considered flammable; for oxygen index = 22-25, the material is self-extinguishable; and for the case of oxygen index > 26, the material is hard to burn [8] To investigate the flame retardancy of polyurethane foam, we tested the limiting oxygen index (LOI) of flame retardant PUR systems with a 5 wt% - 10 wt% -15 wt% FR loading. As can be seen from Table 4.12 with increases in FR content, the LOI values increase.

The highest LOI value is obtained with 15 wt% FR loading. As seen in the pictures (appendices section) FR-2 is better fire retardancy property than TCPP alone at the same concentration (20 %). LOI test results of polyurethane foam are shown in Table 4.13.

Table 4.13 : LOI test results of polyurethane foam.

FOAM	% FR	LOI
PUR-1	0	15,5
PUR-2	5	22
PUR-3	10	24
PUR-4	15	25,5
PUR-5	5	21
PUR-6	10	23
PUR-7	15	23

4.4.3.3 Further studies on fire resistance polyurethane foam production

Further studies were carried out using formulation given in the table 4.13 to produce fire resistance polyurethane foam. Physical properties including LOI values of these produced fire resistance polyurethane foams were measured. Some new additives such as DOPO, zinc borate were also included to improve fire resistance and smoke suppressant properties of polyurethane. The results are summarized in the table 4.13. In UL94 test method for the sample to get a V-0 rating it must self-extinguish within 10 s and there should not be any sign of dripping of burning polymer. If the sample continuously burns or if it drips polymer, a V-1 or V-2 rating is given. For PU foams UL94 results are shown in Table 4.14.

Table 4.14 : Flammability properties comparison dopo and zinc borate with FR products in foam.

Foam	**Density (kg/m3)**	**Thermal Conductivity (W/m K)**	**Compressive Strenght at % 10 (kPa)**	**LOI**	**UL 94**
TCPP (%23)	31	0,02652	185	24	V0
THEİC-TCPP (1:1) (%23)	34	0,02788	325	24	V0
THEIC-TCPP (1:2) (%23)	36	0,02835	276	25	V0
THEIC-TCPP (1:3) (%23)	33	0,02647	250	25	V0
THEİC-TCPP (1:5) (%23)	33	0,02754	195	25	V0
DOPO (% 23)	30	0,04834	105	19	V2
THEIC-TCPP(1:5)-10+DOPO-5 (%23)	32	0,03395	130	22	V1
THEIC-TCPP(1:5)-5+DOPO-10 (%23)	30	0,04256	100	21	V1
Zn(BrO3)2	33	0,02787	85	18	V2
THEIC-TCPP(1:5)-5+ Zn(BrO3)2-10 (%23)	31	0,02821	150	22	V1
THEIC-TCPP(1:5)-10+ Zn(BrO3)2-5 (%23)	35	0,02767	125	19	V1

4.4.3.4 TGA results of THEIC-TCPP products

The TGA is one of the commonly used techniques for rapid evaluation of thermal stability of different materials, and can also indicate the decomposition behavior of polymers at various temperatures.

The TGA measurements were performed under a nitrogen atmosphere with a heating rate of 10 ˚C min-1, 30 ˚C to 500 ˚C and 800 ˚C. TGA analysis was performed on liquid FR, FR-1, FR-2, FR-3 samples and foams containing reactive fire retardants of FR, FR-1, FR-2, and FR-3. And results are given in Figure 4.69 and Figure 4.70.

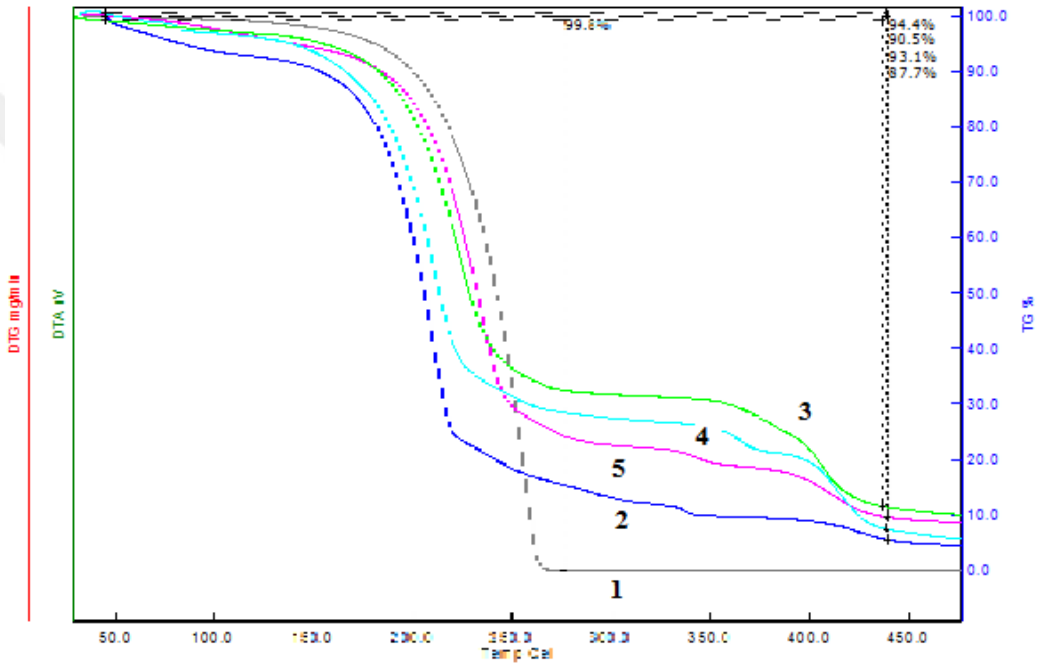


Figure 4.69 : TGA result of flame retardant products.

1 : Black : TCPP

2 : Blue : THEİC+TCPP 1/1

3 : Green : THEİC+TCPP ½

4 : Turqoise : THEİC+TCPP 1/3

5 : Pink : THEİC+TCPP 1/5

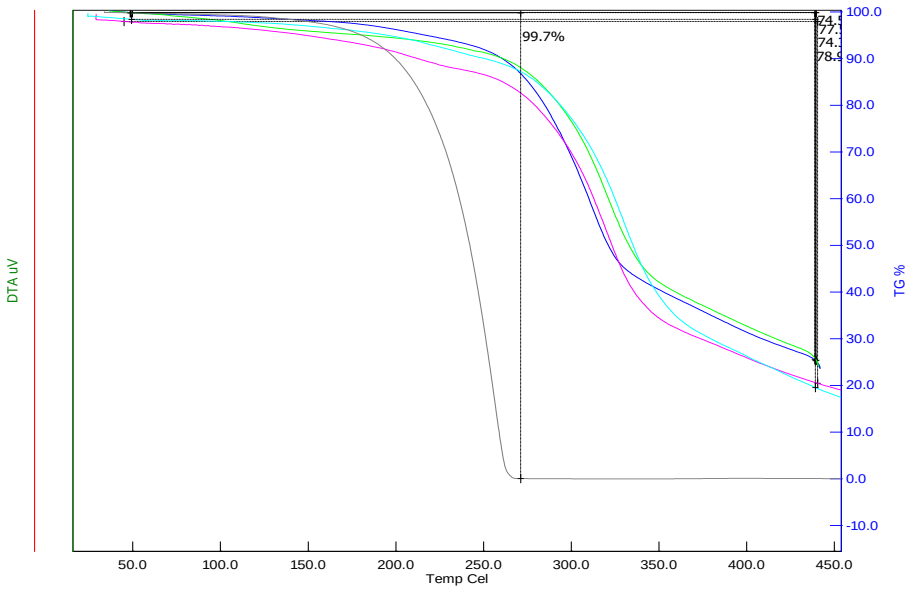


Figure 4.70 : TGA result of flame retardant products at polyurethane foam.

Black: TCPP

Turqoise:THEİC+TCPP 1/1

Blue:THEİC+TCPP 1/2

Green: THEİC+TCPP 1/3

Pink:THEİC+TCPP 1/5

4.5 Fire Resistant Polyurethanes From Mixture of Polyols

a) Cyanuric acid-formaldehyde condenzation product:

Reaction of cyanuric acid and 3 mol formaldehyde is shown in Figure 4.71.

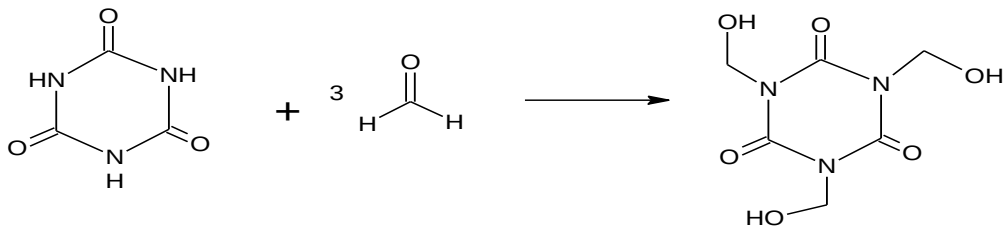


Figure 4.71 : Cyanuric acid and formaldehyde reaction mechanism.

This trimethylol cyanuric acid was added into polyol component with 5% and 20% weight ratios and the produced rigid PU foam was tested with UL94. 20% addition of trimethylol isocyanurate showed considerable fire retardant effect and the product has

V-0 value in UL-94. However, Foam production was not appropriate if its addition value is 20%. So this product, alone, is not suitable as fire retardant for rigid PU foam**.**

b) Cyanuric acid-formaldehyde-diethanol amine condenzation product:
Mannich base produced from isocyanuric is shown in Figure 4.72.

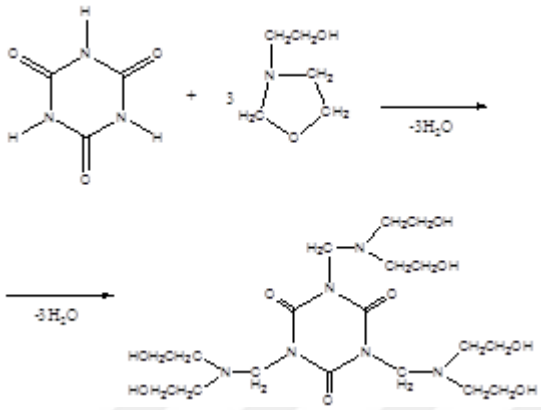


Figure 4.72 : Mannich base with isocyanuric reaction.

This product was tested in textiles and showed some fire retardancy effect. However, its fire retardancy is not very satisfactory. This compound should be mixed some strong fire retardant compounds containing phosphorus and boron.

a) Formation of methyl ethyl keton-melamine formaldehyde resin is shown in Figure 4.73.

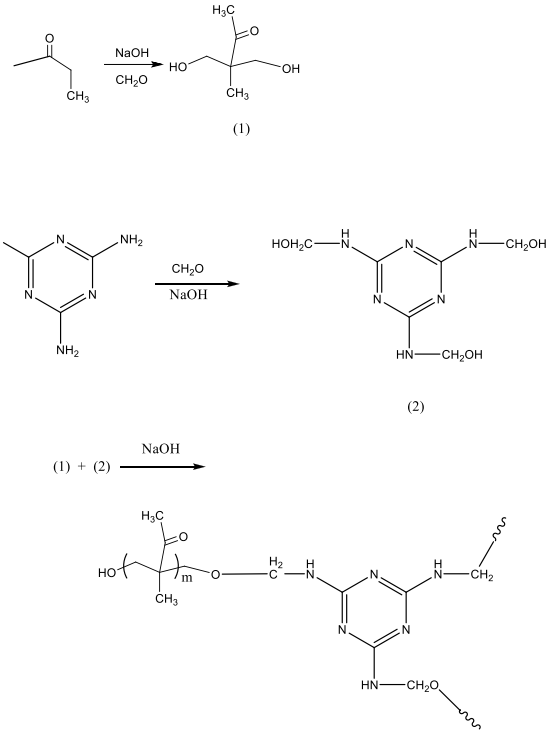


Figure 4.73 : Methyl ethyl keton-melamine formaldehyde reaction.

Melamine content of this resin should be below 15% otherwise some precipitation forms during resin production. The resin containing 15% melamine is not very efficient fire retardant.

4.6 Fire Resistant Polyurethanes From Vinyl Phosphonate Grafted Polyols

Vinyl phosphonic acid dimethylester was grafted onto unsaturated polyester synthesized in section 3.3.3 (see also section 4.1.3) using different radical initiators (Table 4.15). Besides, both vinyl phosphonic acid dimethylester and hydroxyl butyl acrylate were grafted together.

The properties of grafted polyester polyols are shown in the Table 4.15 and Table 4.16. These grafted polyol were used for rigid polyurethane foam production as explained in the section 3.5.1. FTIR spectrum of vinyl phosphonic acid dimethyl ester grafted polyol is shown in Figure 4.74.

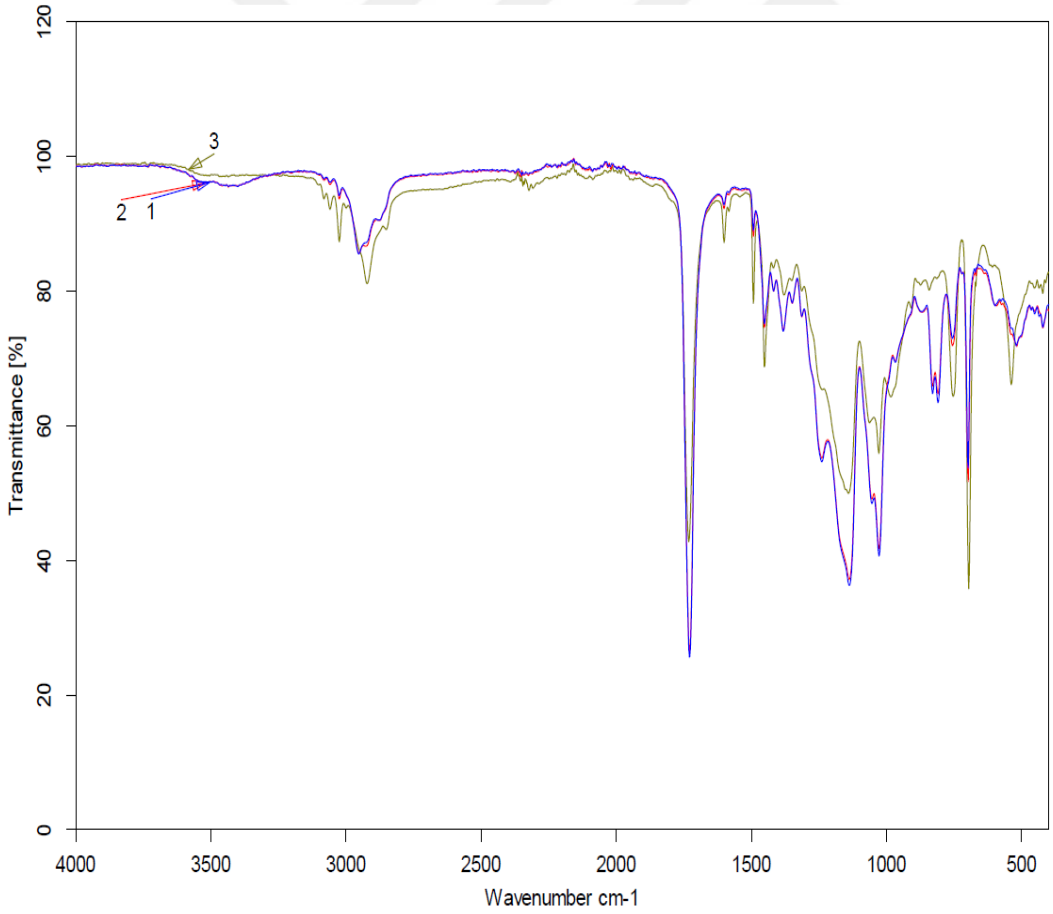


Figure 4.74 : FTIR of vinyl phosphonic acid dimethyl ester grafted polyol (1: inıtial mixture, 2: one hour polymerization time, 3 : final grafted product).

Table 4.15 : VPADME grafting on unsaturated polyester.

	Unsaturated polyester polyol	(Polyol-22) (PVPADME+ PES+AIBN)	(Polyol 33) PES+VPADME+ HBA+ TBHP
		Grafting conditions	
Polyol (g)	-	90	1921
VPADME(g)	-	20,4	136g +144 g HBA
Temperature (C)	-	150	120
Properties of polyols			
OH (mg KOH/g)	70	67,13	83
Viscosity cps)	640	1730 (50)	872
Acidiy	0,5	1,61	0.79
Hummidty (%)	0,04	0,079	0,055

The produced polyurethane foam products were tested with TGA and UL 94. The results were shown below. These results suggest that the polyurethane foams produced from both VPADME and VPADME+HBA grafted PES polyols show fire retardancy properties.

Table 4.16 : Properties of polyurethane produced VPADME and HBA grafted polyester polyol.

	PES+VPADME	PES+VPADME+HBA
UL 94 (reference: 9.5 cm max)	9.5	9

TGA of PU foam from polyester grafting with VPADME and different intiators is shown in Figure 4.75 and Figure 4.76.

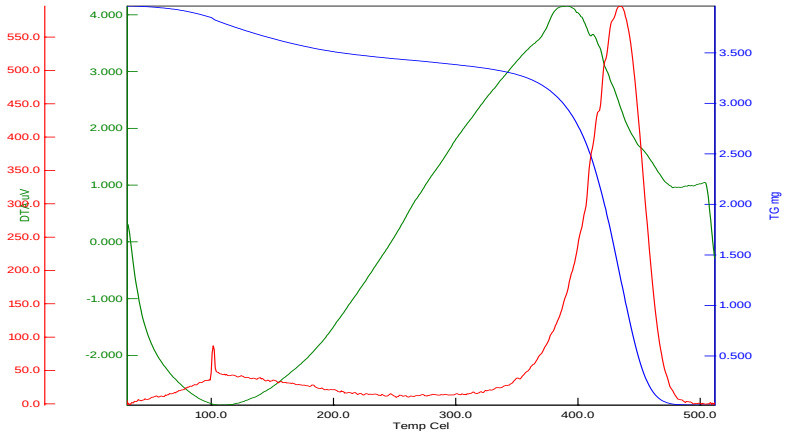


Figure 4.75 : TGA of Pu foam from polyester grafting with VPADME and BP for initiator.

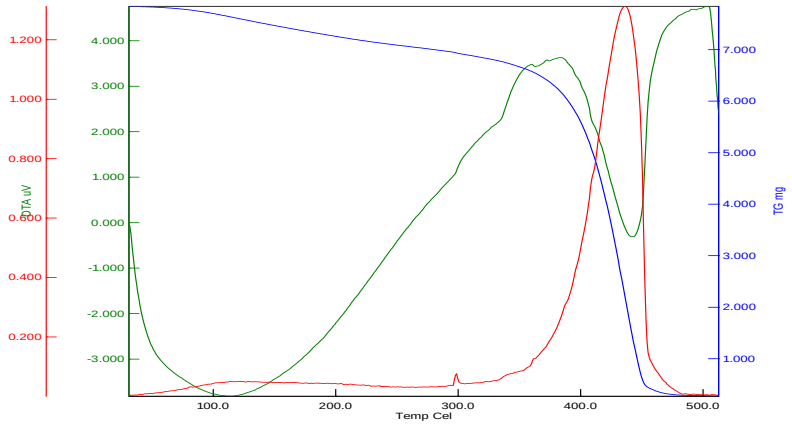


Figure 4.76 : TGA of Pu foam from polyester grafting with VPADME and AIBN for initiator.

4.7 Synthesis of Synthetic Leather Polyurethane From Biobased Polyol

In Figure 4.77, polyurethane synthesis for synthetic leather is shown. The product which is synthesized by using the polyol, diol and MDI in different ratios analyzes by using FTIR spectroscopy. Results are shown in Figure 4.78, Figure 4.79, Figure 4.80, Figure 4.81, Figure 4.82, Figure 4.83 and Figure 4.84. FTIR bond streching values are shown in Table 4.17.

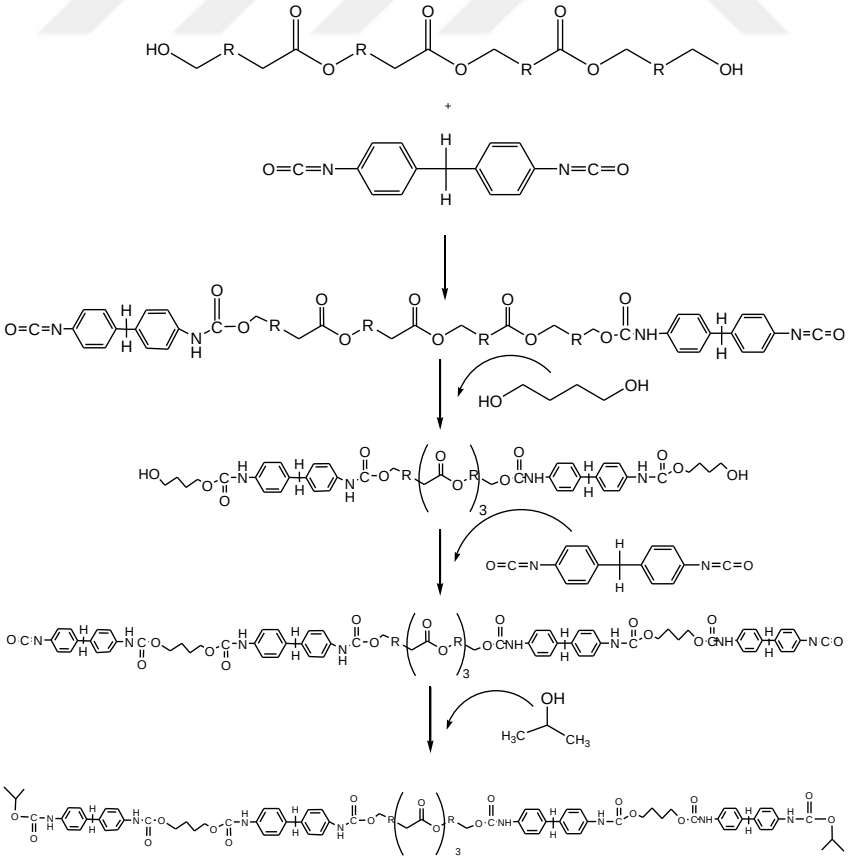


Figure 4.77 : Biobased solvent based polyurethane synthesis for synthetic leather.

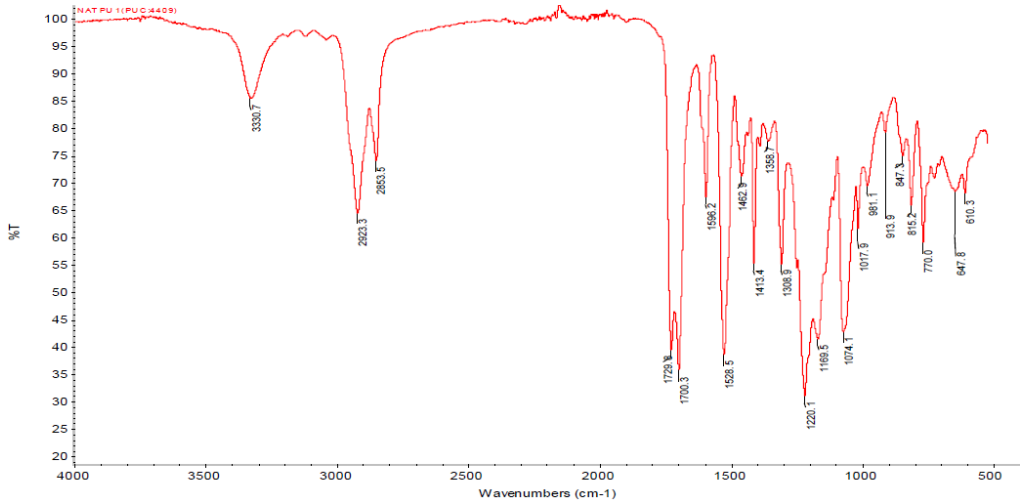


Figure 4.78 : Nat Pu 1 – biobased polyol / 1,4 butanediol / MDI (1 / 3 / 4).

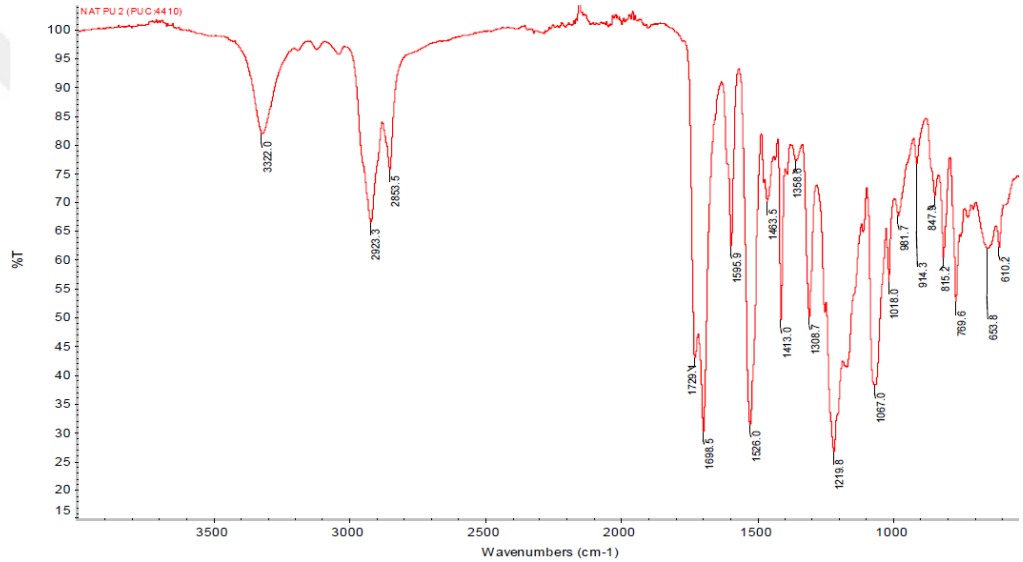


Figure 4.79 : Nat Pu 2 – biobased polyol / 1,4 butanediol / MDI (1 / 5 / 6).

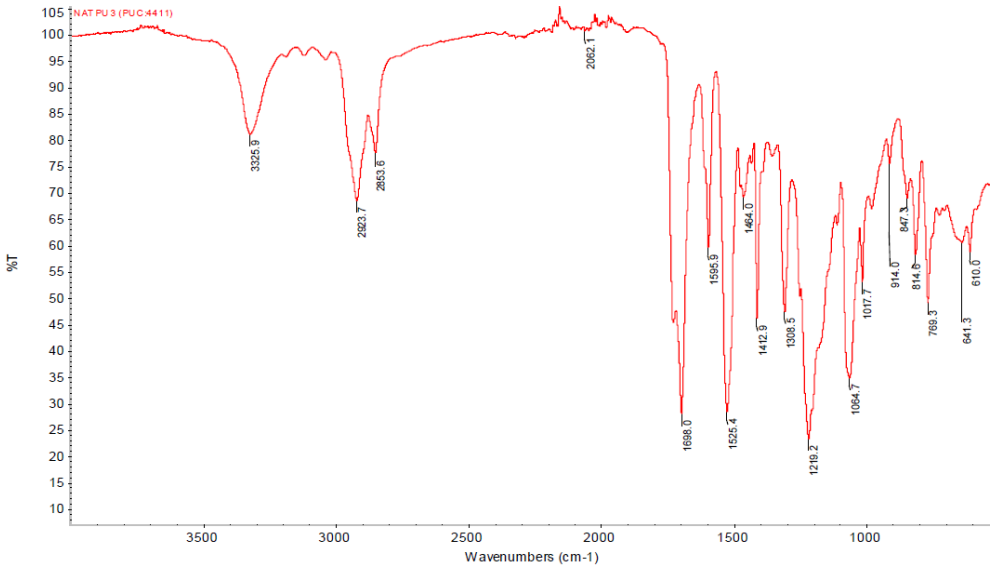


Figure 4.80 : Nat Pu 3 – biobased polyol / 1,4 butanediol / MDI (1 / 7 / 8).

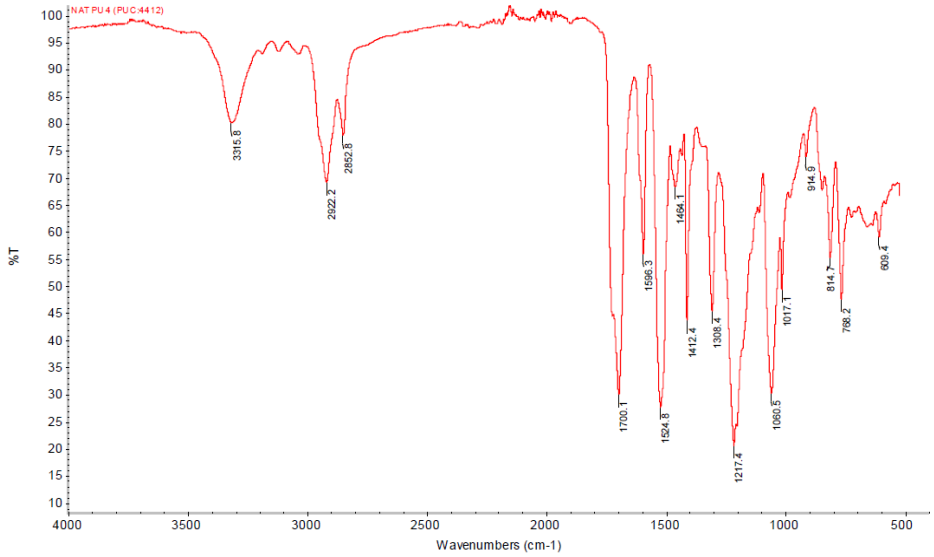


Figure 4.81 : Nat Pu 4 – biobased polyol / 1,4 butanediol / MDI (1 / 9 / 10).

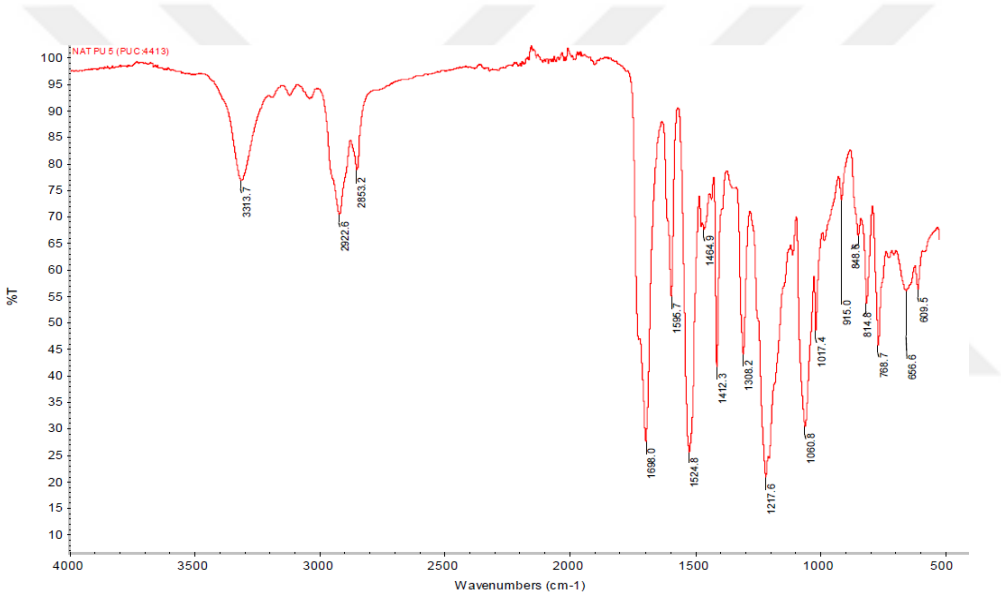


Figure 4.82 : Nat Pu 5 – biobased polyol / 1,4 butanediol / MDI (1 / 11 / 12).

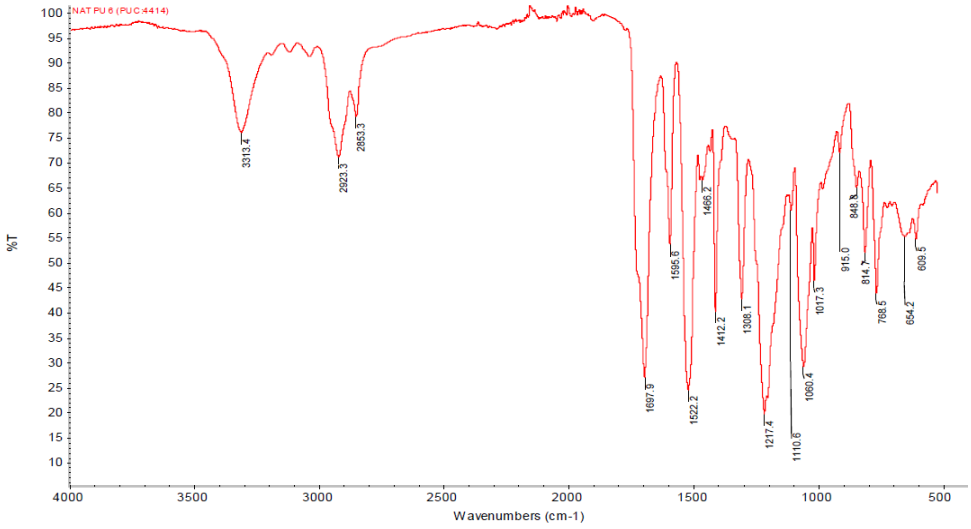


Figure 4.83 : Nat Pu 6 – biobased polyol / 1,4 butanediol / MDI (1 / 13 / 14).

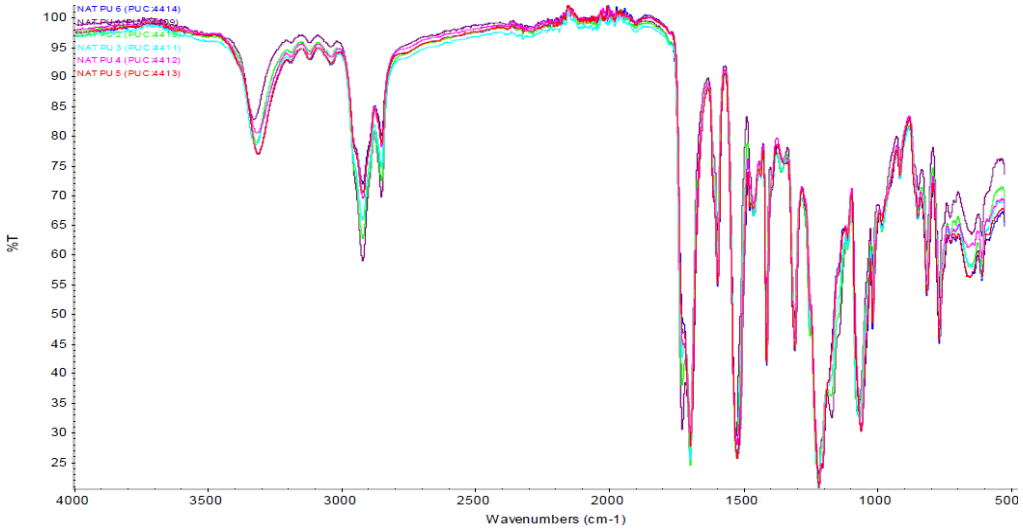


Figure 4.84 : FTIR comparision of all polyurethanes.

Table 4.17 : FTIR bond strechings.

Wavenumber	Assignment
3446	st N-H (free)
3330	st N-H (bonded)
3000-2840	st C-H
2270	st N=C=O
1729	st C=O (free ester and urethane)
1707	st C=O (bonded ester and urethane)
1700-1690	st C=O (free urea)
1640	st C=O (bonded ordered urea)
1520	st C-N + δ N-H
1475-1450	δ CH2
1450-1400	st sym (COO-)
1078	st sym N-CO-O + st (C-O-C)
954	st C-O-C

Stress strain tests are shown in Figure 4.85, Figure 4.86, Figure 4.87, Figure 4.88, Figure 4.89, Figure 4.90.

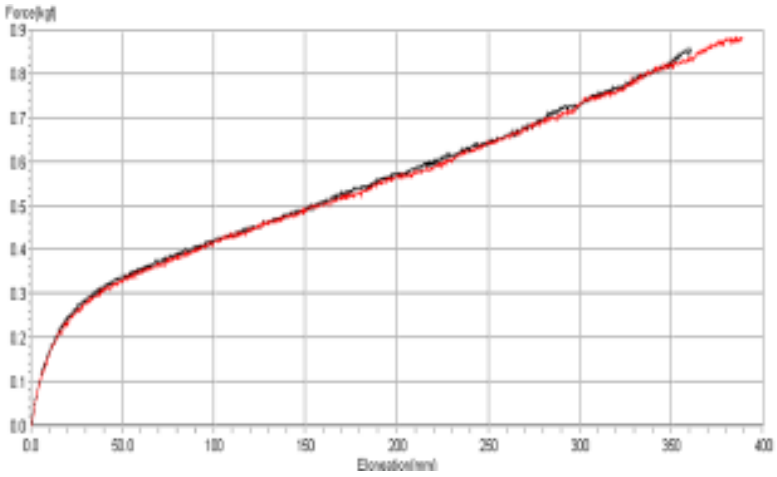


Figure 4.85 : Stress strain test result of Nat Pu1.

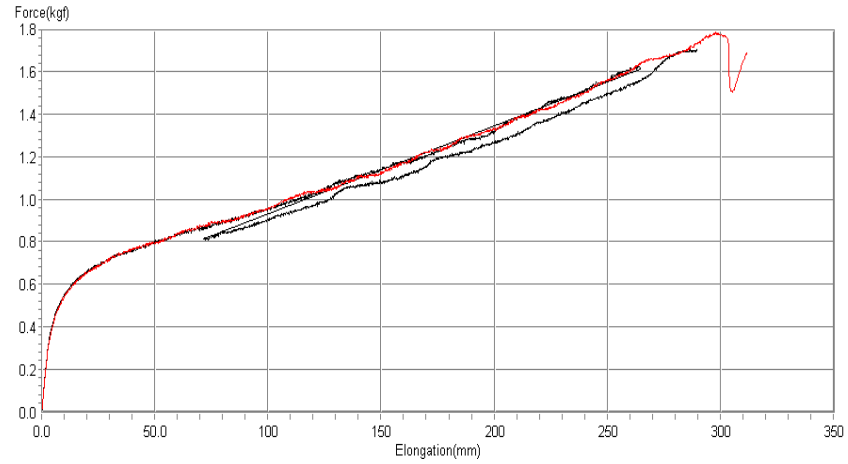


Figure 4.86 : Stress strain test result of Nat Pu2.

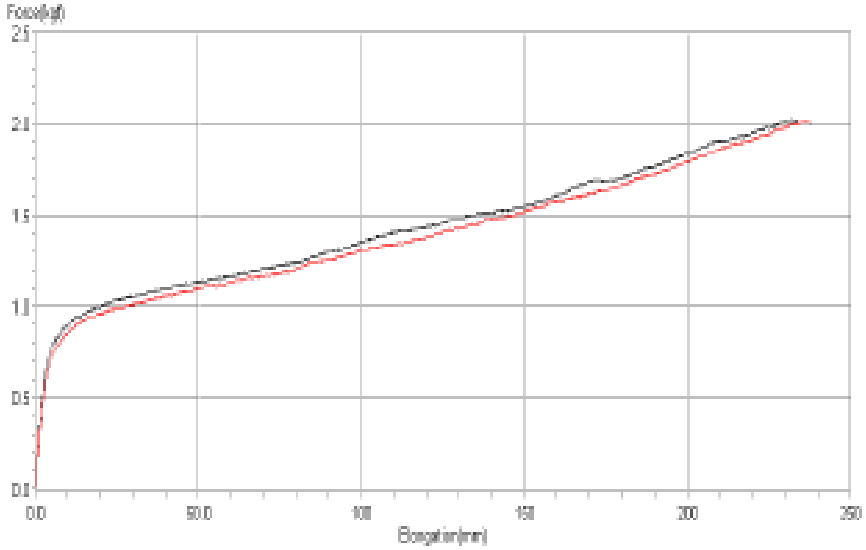


Figure 4.87 : Stress strain test result of Nat Pu3.

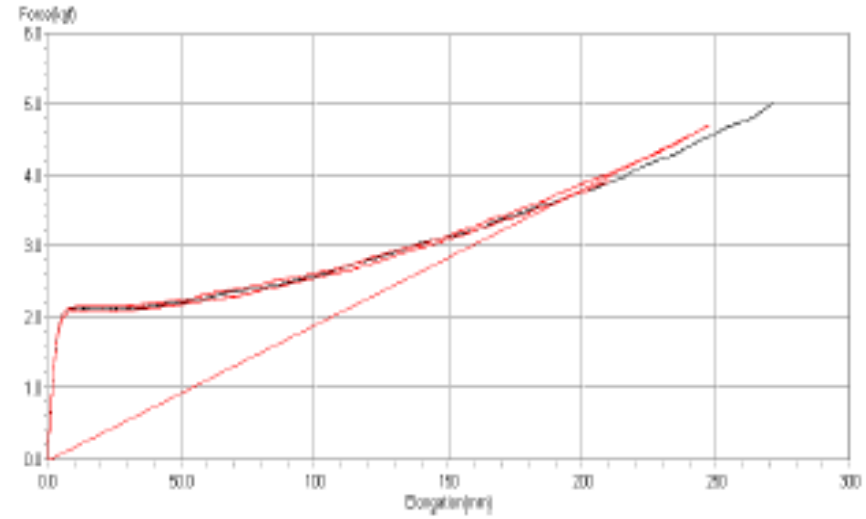


Figure 4.88 : Stress strain test result of Nat Pu4.

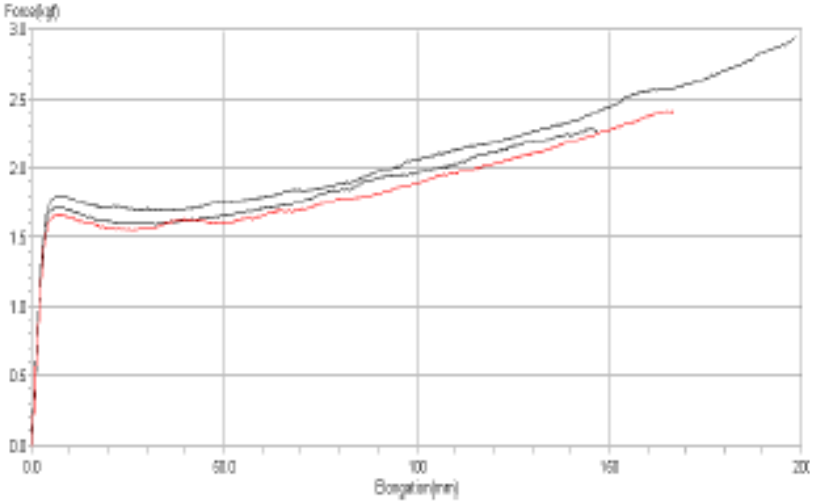


Figure 4.89 : Stress strain test result of Nat Pu5.

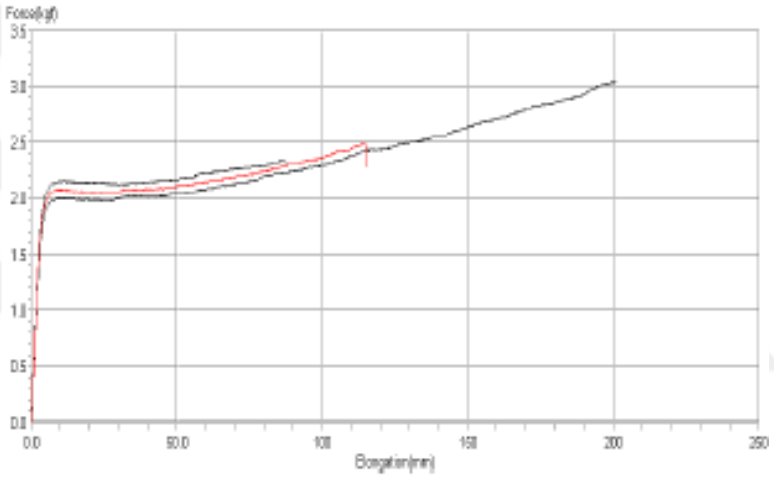


Figure 4.90 : Stress strain test result of Nat Pu6.

Mechanical properties of polyurethane products are given in the Table 4.18.

Table 4.18 : Summary of polyurethane mechanical properties.

	Product Name					
	NatPu1	NatPu2	NatPu3	NatPu4	NatPu5	NatPu6
%100 Modulus (kgf)	44,1	96,1	133,3	187,4	198,1	233,85
%200 Modulus (kgf)	57	132,9	181,3	275,21	0	303,6
%300 Modulus (kgf)	73,4	178,2	0	0	0	0
Elongation at Break (mm)	388,8	311,5	271	238	201	190
Load at Break (kgf)	336	300	280	254	203	164

Abrassion test applied on Nat PU 1, Nat PU 2, Nat PU 3, Nat PU 4, Nat PU 5, and Nat PU 6 leather and results are shown in Figure 4.91.

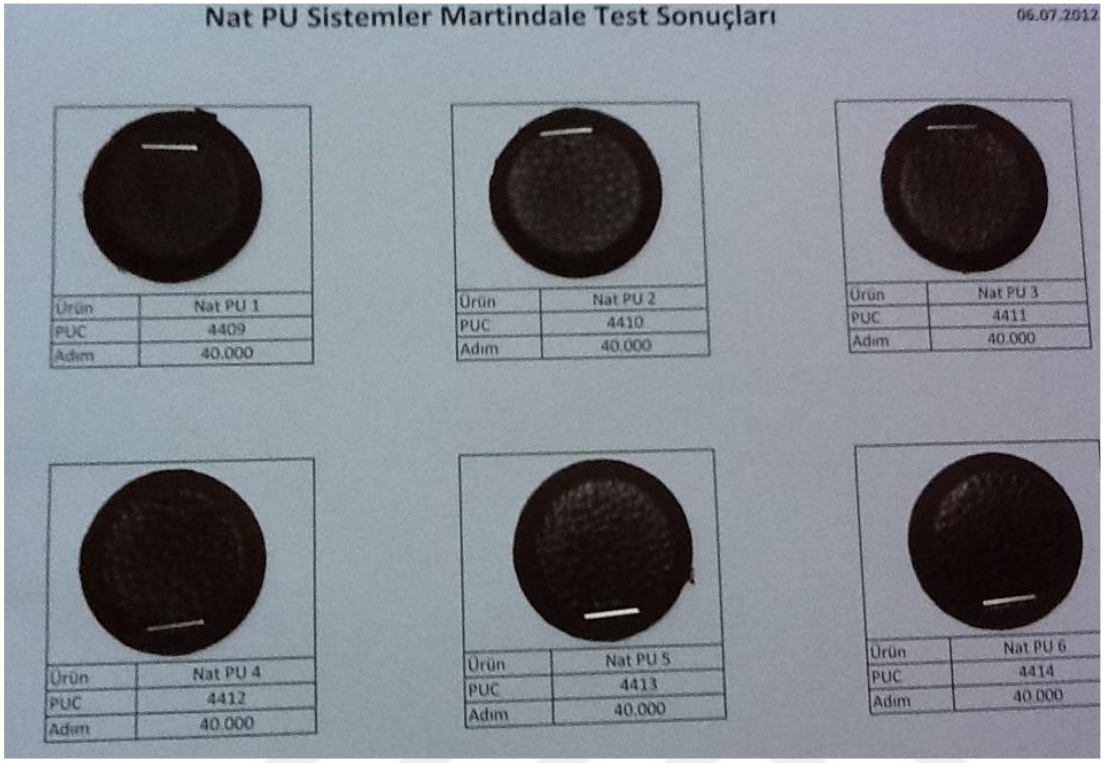


Figure 4.91 : Abrasion Test Results (Martindale at Leather).

5. CONCLUSIONS

Polyols and styrene grafting; Polyester polyols were synthesized and used for rigid PU production and microcellular elastomer for shoe sole application. These saturated polyester polyols and unsaturated polyols were post modified by grafting styrene and the modified poyester polyols were used to prepare PU with a more open cell structure.

Modifiying fire retardant additive of TCPP; TCPP, one of the most used fire retardand for rigid PU, is a toxic organic compound and evaporates slowly from PU to enviroment. TCPP was reacted with THEIC to produced new reactive liquid fire retardands with better fire retardancy and much lower vapor pressure.

Synthesis of a new fire retardant from trichloro propyl phosphite and THEIC:

Trans esterification reaction between trichloro propyl phosphite and THEIC resulted compounds containing both the ring of isocyanuric acid and dichloro propyl phosphite moeity as well as reactive hydroxyl groups. These products showed rather good fire retardand effect to rigid PU. However, the raw material, trichloro propyl phosphite is difficult to find in the market.

Synthesis of new reactive fire retardands from keton-formaldehyde resin:

Carbonyl groups Ketonic resins such as MEK-formaldehyde, Cyclohexanone-formaldehyde and acetophenone-formaldehyde resin were reacted with ethanolamine-diethyl phosphite and ethanolamine-diphenyl phosphite to produce ketonic resins containing both hydroxyl groups and phosphorous (Tri component Kabachnik-Fields reaction). Adding these reactive resins into polyol component with 20-30% resulted raher good fire retardand rigid PU foam with better physical properties. Grafting of vinyl phosphonic acid dimethyl ester to unsaturated polyester polyols: Dimethyl vinyl phosphonic acid were grafted by radical initiators such as AIBN and BP to polyester polyols containing some unsaturation. 20-30 w % phosphonic monomers grafted polyester polyols resulted good fire retardant rigid PU foam.

Mixture polyols; Polyols containing high percent of nitrogen and ring structure were synthesized and used to produce rigid PU foam. However, their fire retardancy effect were limited.

Biobased polyurethane was synthesized with different strenght for synthetic leather application. DMSO-Toluene mixture is used instead of DMF because of DMF's solubility and toxic property.

Future works:

1) Organic and inorganic fire retardand compouds containing only phosphorous atom will be tested.
2) Grafting of cheap monomers containing phosphorous to unsaturated polyester with double bond in the side chain will be studied.

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APPENDICES

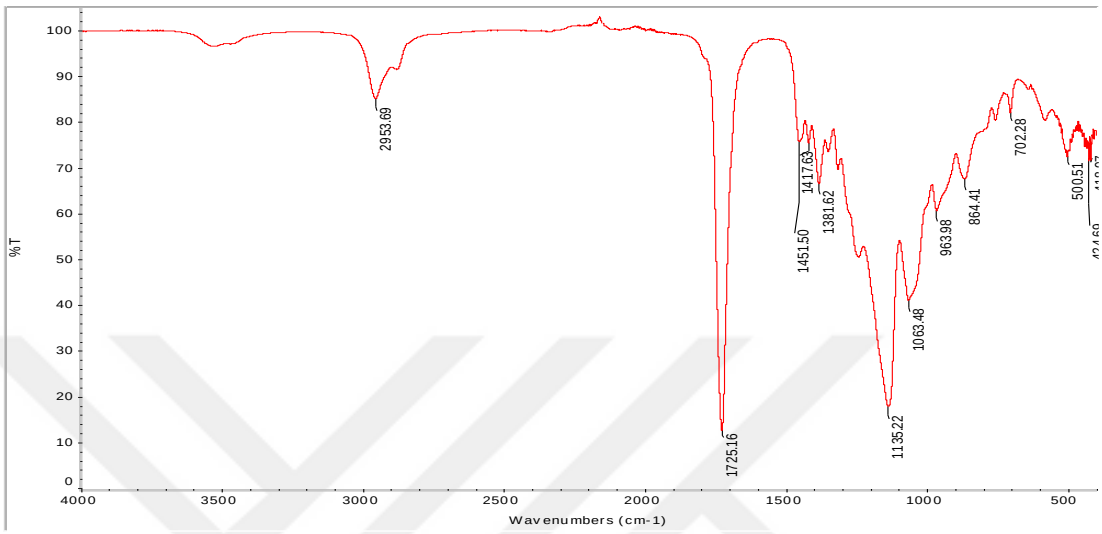


Figure A.1 : FTIR spectrum of 6 % styrene grafted onto saturated polyester polyol

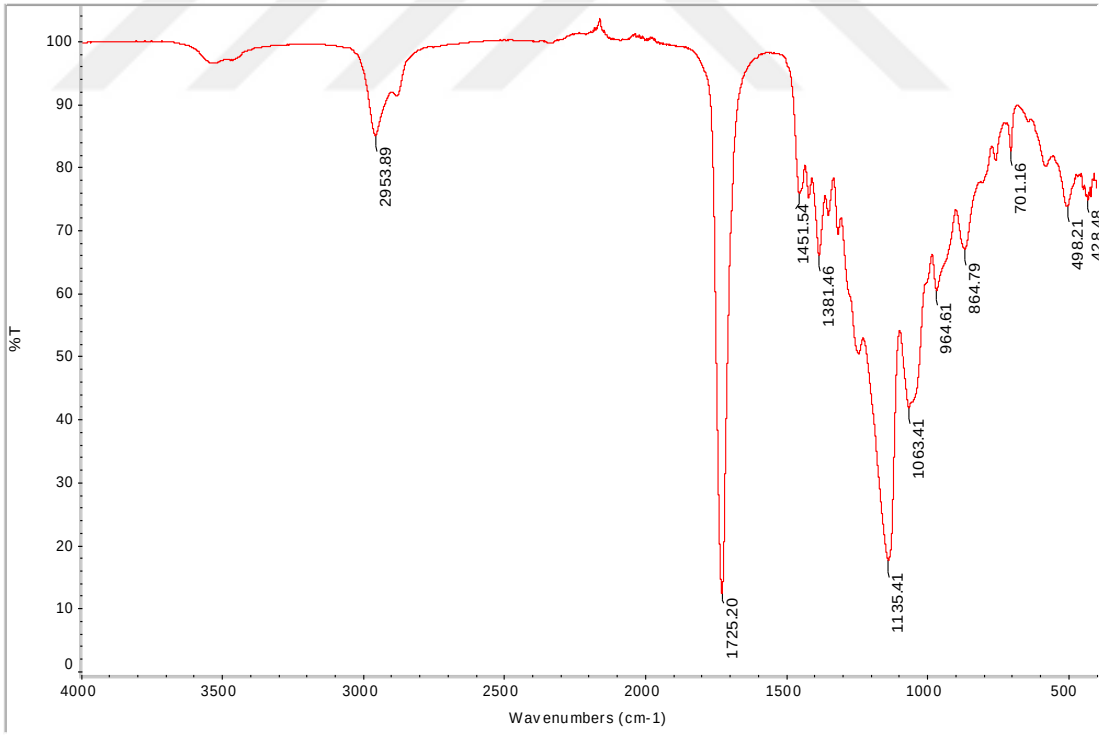


Figure A.2 : FTIR spectrum of 9 % styrene grafted onto saturated polyester polyol

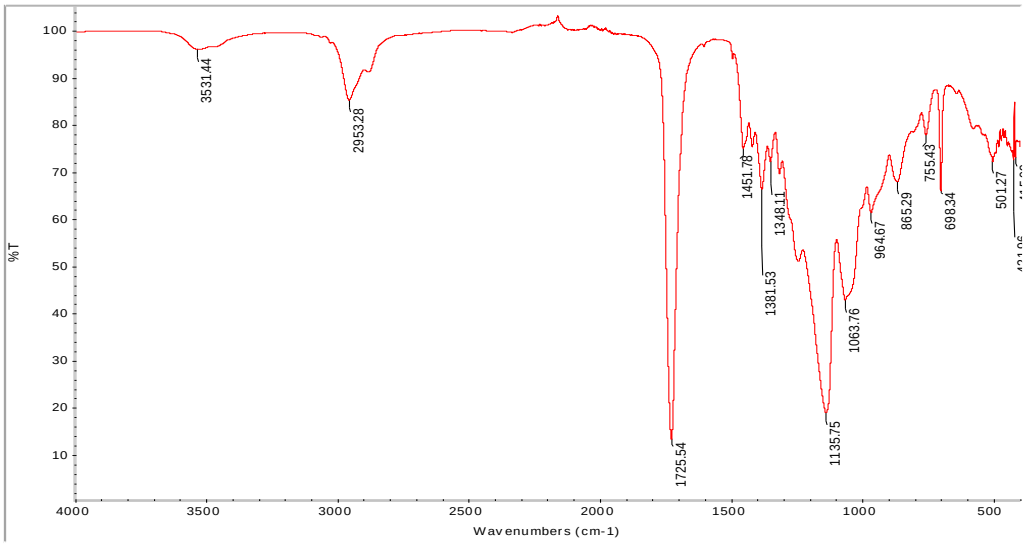


Figure A.3 : FTIR spectrum of 12 % styrene grafted onto saturated polyester polyol

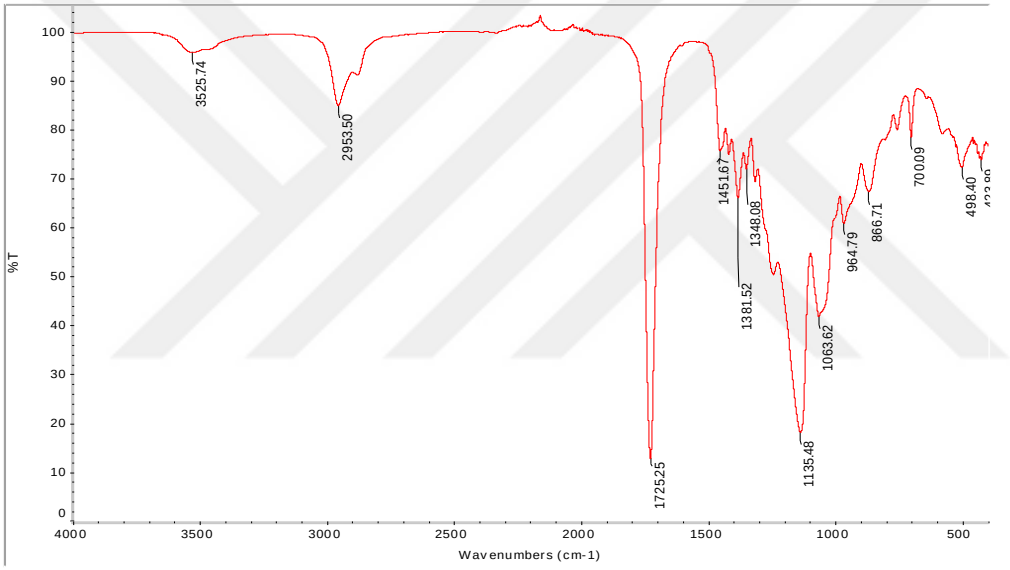
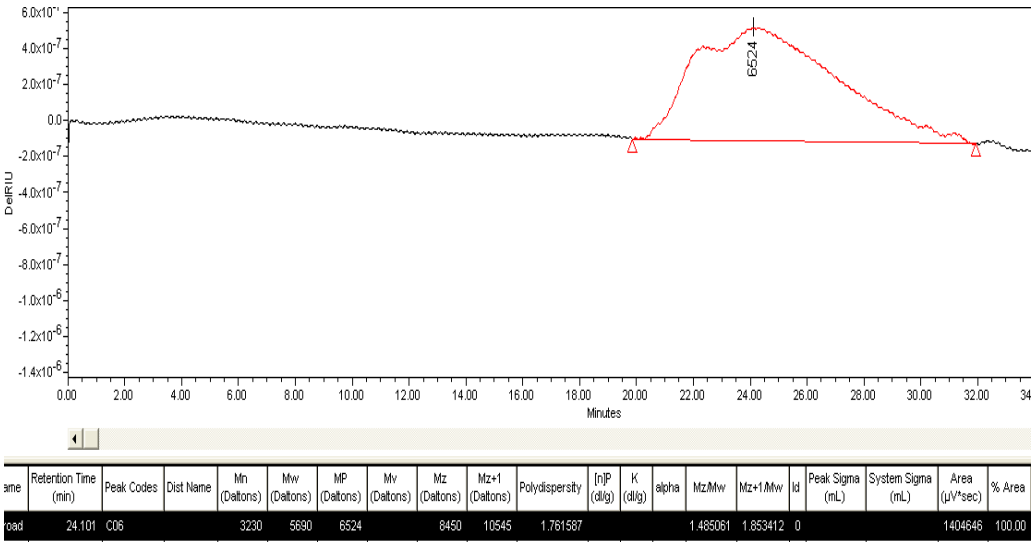
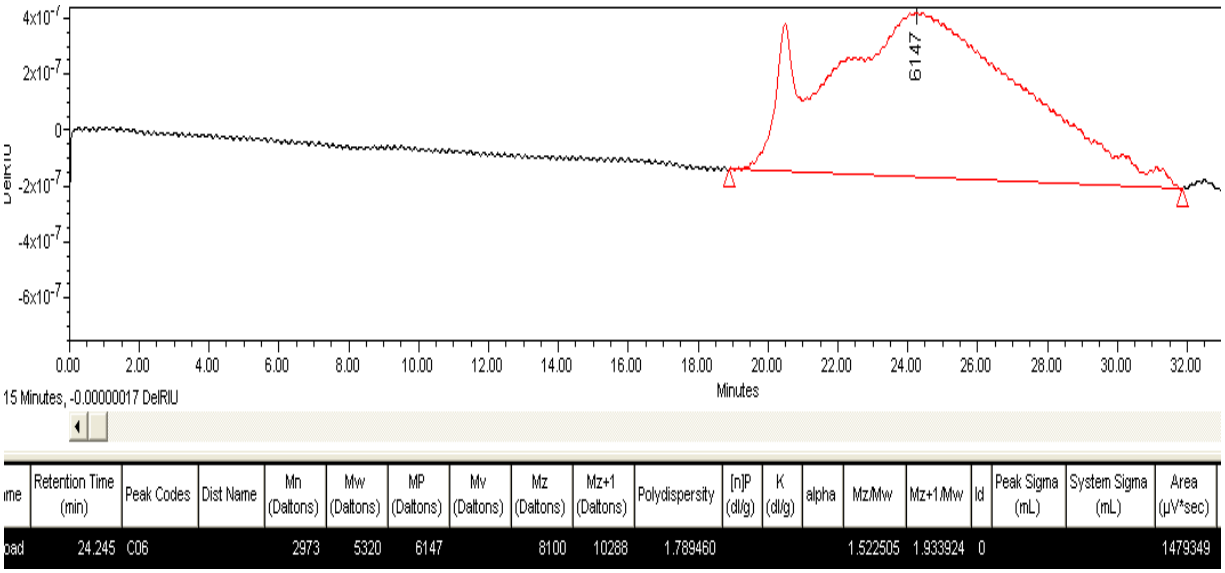


Figure A.4 : FTIR spectrum of 15 % styrene grafted onto saturated polyester polyol



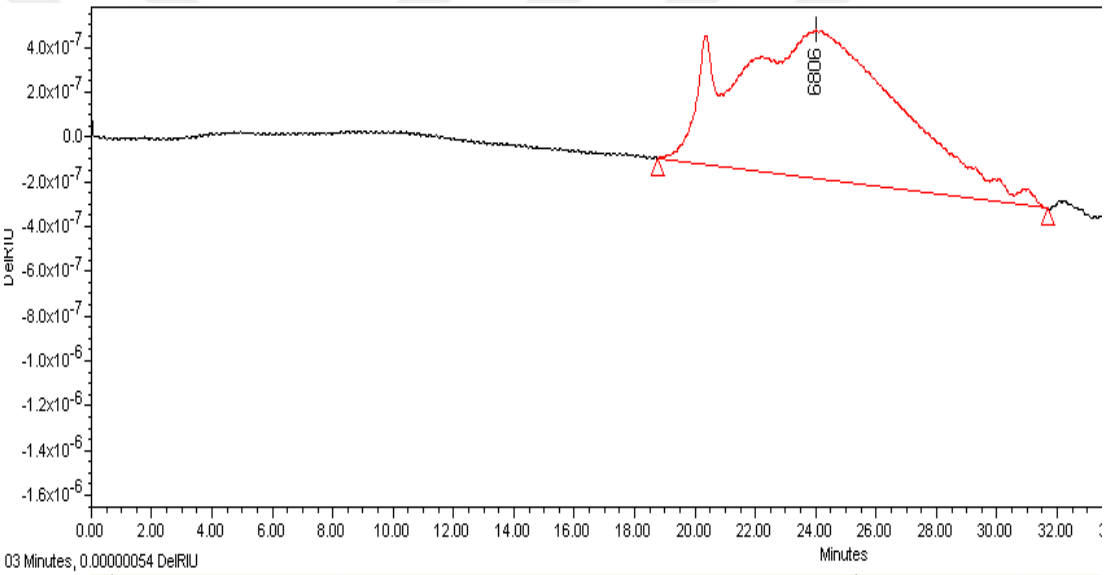
ame	Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	[n]P (dl/g)	K (dl/g)	alpha	Mz/Mw	Mz+1/Mw	Id	Peak Sigma (mL)	System Sigma (mL)	Area (µV*sec)	% Area
oad	24.101	C06		3230	5690	6524		8450	10545	1.761587				1.485061	1.853412	0			1404646	100.00

Figure A.5 : GPC graph of 6 % styrene grafted onto saturated polyester polyol



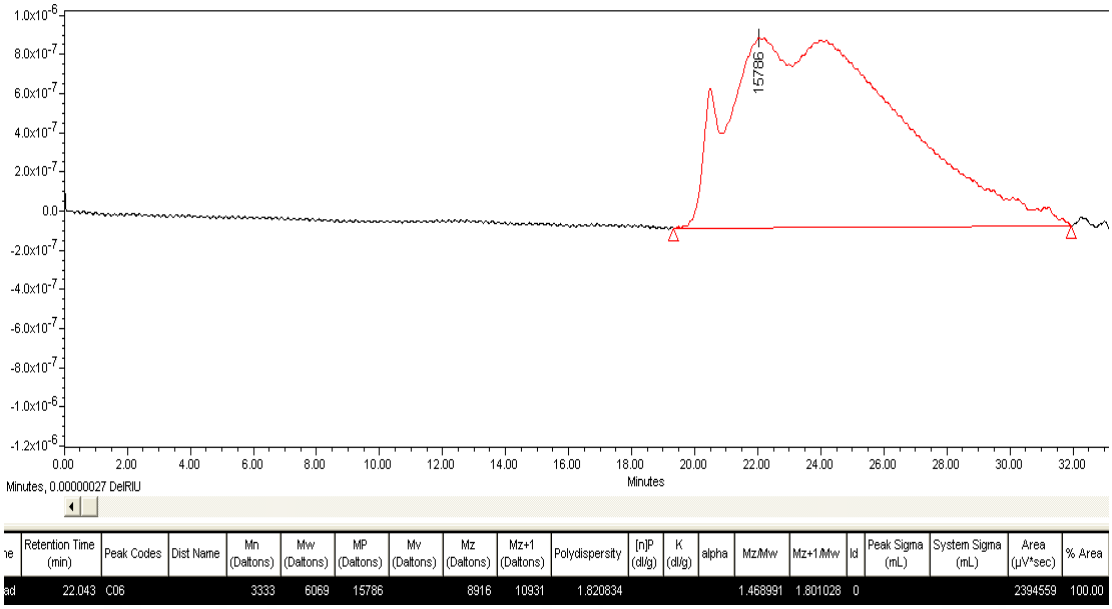
ıme	Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	[n]P (dl/g)	K (dl/g)	alpha	Mz/Mw	Mz+1/Mw	Id	Peak Sigma (mL)	System Sigma (mL)	Area (µV*sec)
oad	24.245	C06		2973	5320	6147		8100	10288	1.789460				1.522505	1.933924	0			1479349

Figure A.6 : GPC graph of 9 % styrene grafted onto saturated polyester polyol



ıme	Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	[n]P (dl/g)	K (dl/g)	alpha	Mz/Mw	Mz+1/Mw
oad	23.999	C06		3333	5785	6806		8463	10509	1.735676				1.462875	1.816572

Figure A.7 : GPC graph of 12 % styrene grafted onto saturated polyester polyol



Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	[n]P (dl/g)	K (dl/g)	alpha	Mz/Mw	Mz+1/Mw	Id	Peak Sigma (mL)	System Sigma (mL)	Area (µV*sec)	% Area
22.043	C06		3333	6069	15786		8916	10931	1.820834				1.468991	1.801028	0			2394559	100.00

Figure A.8 : GPC graph of 15 % styrene grafted onto saturated polyester polyol

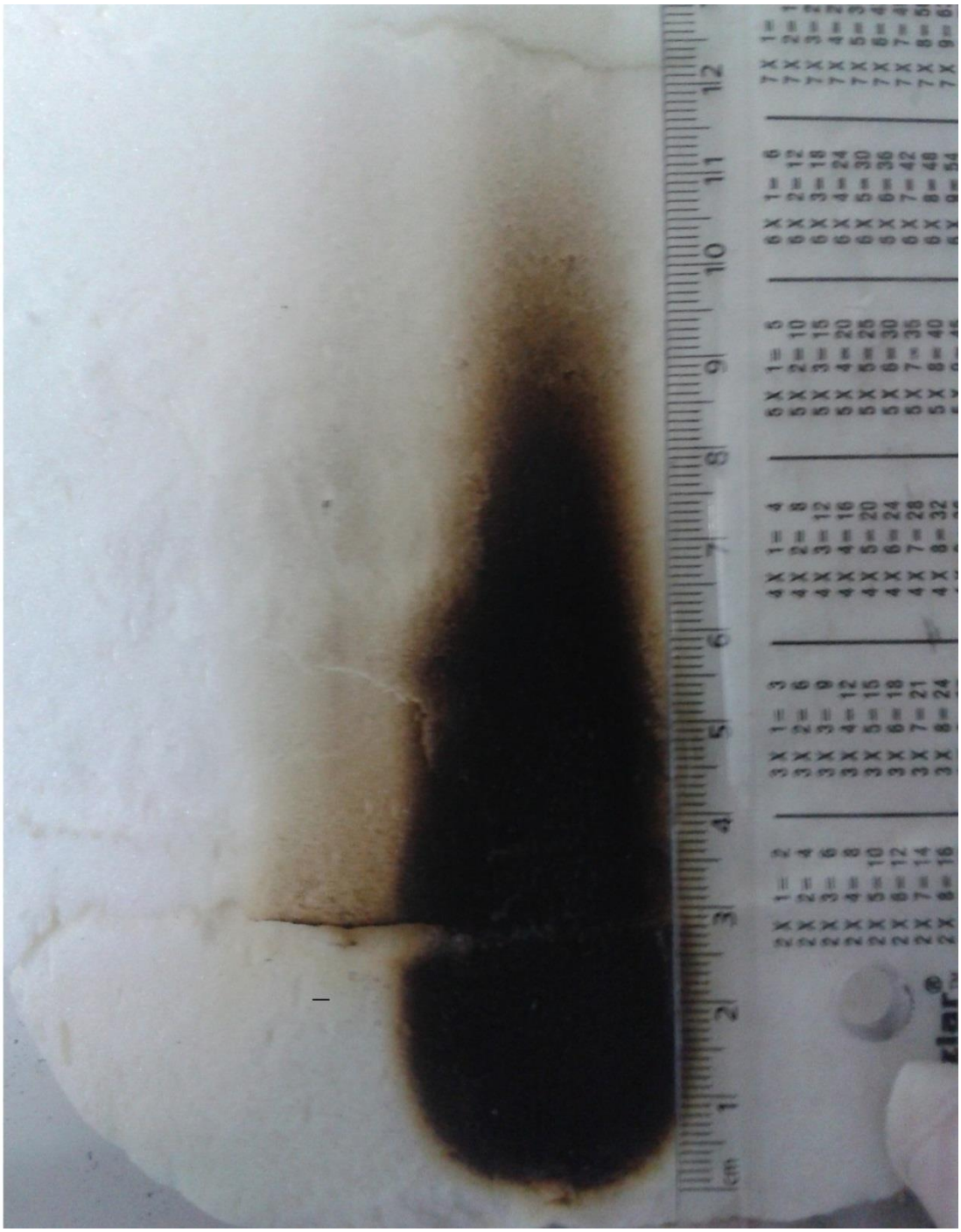


Figure A.9 : TCPP (20 % in polymix) at polyurethane rigid foam (9 cm)

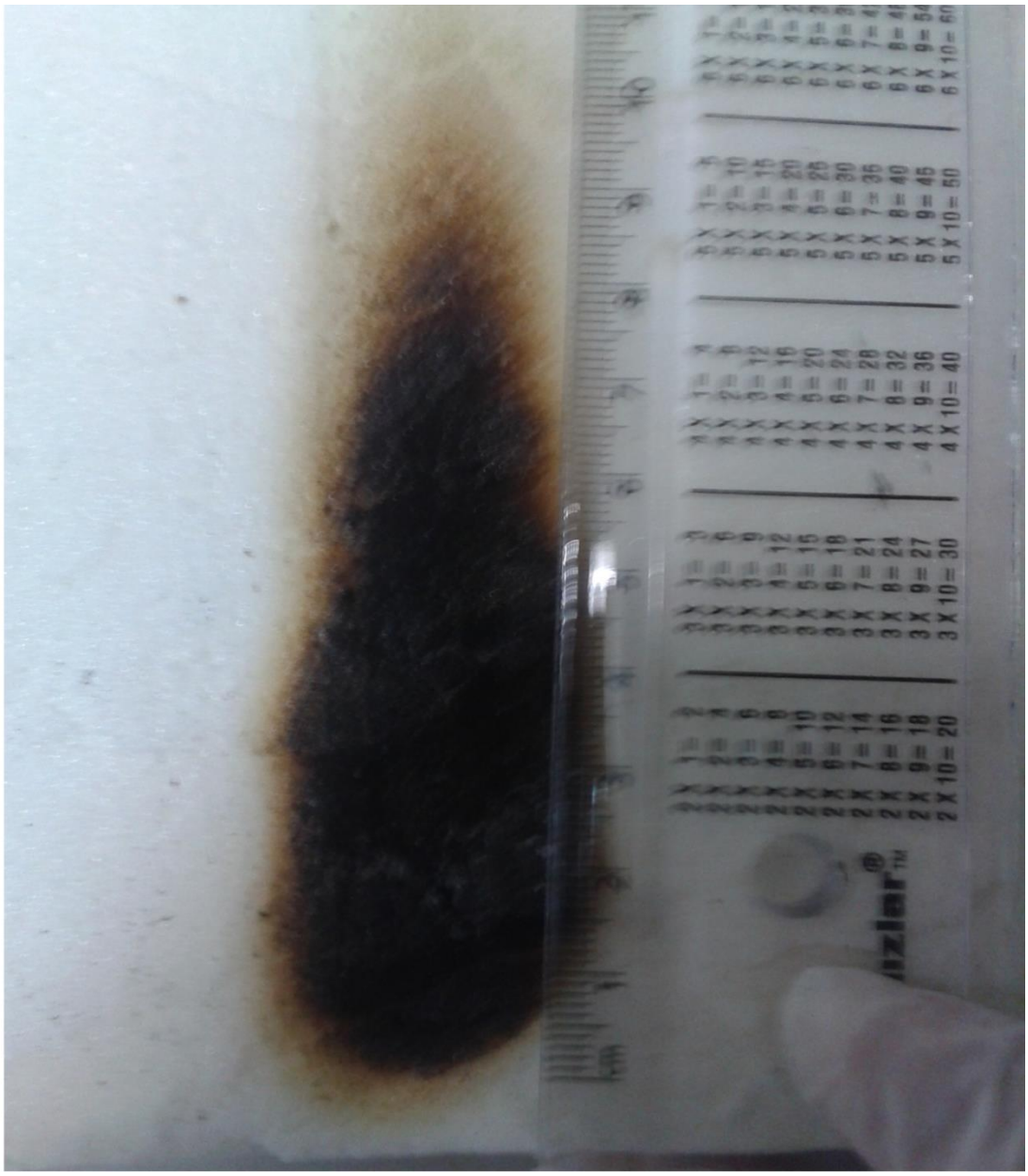


Figure A.10 : THEIC-TCPP (FR-2 20 % in polymix) at polyurethane rigid foam (8 cm)

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- **Yıldız B.**, Seydibeyoğlu M., Ö., Güner S., (2009). Polyurethane–zinc borate composites with high oxidative stability and flame retardancy, *Polymer Degradation and Stability*, *94*(7), 1072-1075.
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