# PREPARATION AND CHARACTERIZATION OF COMBUSTION MODIFIED POLYURETHANE

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Approval of the thesis:

# PREPARATION AND CHARACTERIZATION OF COMBUSTION MODIFIED POLYURETHANE

submitted by **PELİN BAYSAL** in partial fulfillment of the requirements for the degree of **Master of Science in Polymer Science and Technology Department**, **Middle East Technical University** by,

Prof. Dr. Halil Kalıpçılar
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Necati Özkan
Head of Department, **Polymer Science and Technology**

Prof. Dr. Jale Hacaloğlu
Supervisor, **Chemistry Dept., METU**

Prof. Dr. Ayşen Yılmaz
Co-supervisor, **Chemistry Dept., METU**

**Examining Committee Members:**

Prof. Dr. Necati Özkan
Polymer Science and Technology, METU

Prof. Dr. Jale Hacaloğlu
Chemistry Dept., METU

Prof. Dr. Ahmet M. Önal
Chemistry Dept., METU

Prof. Dr. Cevdet Kaynak
Metallurgical and Materials Engineering, METU

Prof. Dr. Nursel Dilsiz
Chemical Engineering Dept., Gazi University

**Date:** September 9, 2019

**I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.**

Name, Last name: Pelin Baysal
Signature:

# ABSTRACT

## PREPARATION AND CHARACTERIZATION OF COMBUSTION MODIFIED POLYURETHANE

Baysal, Pelin
M.S., Polymer Science and Technology Department
Supervisor: Prof. Dr. Jale Hacaloğlu
Co-Supervisor: Prof. Dr. Ayşen Yılmaz

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Polyurethane (PU) flexible foam is a cushioning material which is very versatile and high quality. Among them, high resilience (HR) foam provides better support factor which means it is highly comfortable. Polyurethane foam is combustible due to its chemical nature. Ignition of upholstered furniture caused increasing in residential fires and also people died. In this work modified high resilience polyurethanes with Polyisocyanate Polyaddition (PIPA) Polyol will be prepared to improve combustion characteristics and thermal stability. Besides, British Standard 5852 which the United Kingdom bedding and furniture legislation is based was used to classify combustion properties of modified HR foam. Important variables are the filler and the liquid flame retardant (halogenated phosphorus type). PIPA

Polyol which is one of the combustion modified polyether polyol is used for polyurethane production as an additive. The most important characteristic of this polyol usage is its contribution to combustibility of polyurethane foam. For this aim, 20% solid content PIPA and Tris(2-chloroisopropyl) Phosphate (TCPP) are used as an additive in PU foam. After conducting several trials, formulation of polyurethane includes PIPA Polyol was rearranged and obtained working polyurethane.

The foam samples were analyzed structurally by density, hardness, resilience and compression set tests. By the additives, these properties showed slight changes. Density, support factor (SAG) and resilience properties were developed. Furthermore, mechanical properties of foams which are tensile strength and elongation at breaks were also studied. After making combustion modified foam, tensile strength and elongation at break decreased. Decrease of both tensile strength and elongation at break is associated with the shortening of soft segment length.

Thermogravimetric Analysis (TGA) and Direct Pyrolysis Mass Spectrometry (DP-MS) has been used to support thermal characterization. Addition of PIPA and flame retardant increased the thermal stability of foam. Modification of flexible HR PU foam showed the effective way of the flammability and the thermal stability. BS 5852 test result indicated that overall combustion behavior depends on filled polyol.

**Keywords:** Combustion Modified High Resilience (CMHR) Polyurethane (PU), PIPA Polyol, Flammability, Thermogravimetric Analysis (TGA), Direct Pyrolysis Mass Spectrometry.

# ÖZ

# YANMAYA KARŞI MODİFİYELİ POLİÜRETANIN HAZIRLANMASI VE KARAKTERİZASYONU

Baysal, Pelin
Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü
Tez Yöneticisi: Prof. Dr. Jale Hacaloğlu
Ortak Tez Yöneticisi: Prof. Dr. Ayşen Yılmaz

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Poliüretan (PU) esnek sünger çok yönlü ve kaliteli bir yastıklama malzemesidir. Aralarında yüksek elastikiyetli (HR) sünger daha iyi destek faktörü sağlar, bu da oldukça rahat olduğu anlamına gelir. Poliüretan sünger kimyasal yapısı nedeniyle yanıcıdır. Döşemeli mobilyaların ateşlenmesi konut yangınlarında artışa neden olmuş ve insanlar ölmüştür. Bu çalışmada, yanma özelliklerini ve ısıl kararlılığını geliştirmek için Polyisocyanate Polyaddition (PIPA) Polyol ile modifiyeli yüksek esnekliğe sahip poliüretanlar hazırlanacaktır. Ayrıca, modifiye edilmiş HR süngerin yanma özelliklerini sınıflandırmak için Birleşik Krallık yatak ve mobilya mevzuatının dayandığı İngiliz Standardı BS 5852 kullanılmıştır. Dolgu maddesi ve sıvı alev geciktirici (halojenli fosfor tipi) önemli değişkenlerdir.

Yanmaya karşı modifiyeli polieter poliollerden biri olan PIPA Polyol, katkı maddesi olarak poliüretan üretimi için kullanılır. Bu polyol kullanımının en önemli nedeni poliüretan süngerin yanmazlığına katkı sağlamaktır. Bu amaçla, % 20 katı içerikli

PIPA ve Tris (2-kloroizopropil) Fosfat (TCPP) katkı maddesi olarak, PU sünger içinde kullanılır. Birçok deneme yapıldıktan sonra, PIPA Poliol içeren poliüretan formülasyonu yeniden düzenlenmiş ve amaca uygun bir poliüretan elde edilmiştir.

Sünger örnekleri yapısal olarak yoğunluk, sertlik, esneklik ve deformasyon testleri ile analiz edildi. Katkı maddeleri kullanımı ile bu özellikler düşük miktarda değişiklikler göstermiştir. Yoğunluk, destek faktörü (SAG) ve esneklik özellikleri geliştirilmiştir. Kopma direnci ve kopma uzama ile de süngerlerin mekanik özellikleri çalışılmıştır. Yanmaya karşı modifiye edilmiş sünger yapıldıktan sonra, kopma direnci ve kopma uzaması azalmıştır.

Thermogravimetrik Analiz (TGA), ve Direk Piroliz Kütle Spektrometresi (DP-MS) termal analizi desteklemek için kullanılmıştır. PIPA ve alev geciktiricinin eklenmesi süngerin termal kararlılığını arttırmıştır. Esnek HR PU süngerin modifikasyonu; yanıcılığın ve ısıl stabilitenin etkili bir yolunu gösterdi. BS 5852 test sonucu, toplam yanma davranışının dolgulu poliole bağlı olduğunu göstermiştir.

**Anahtar kelimeler:** Yanmazlık Katkılı Yüksek Elastikiyetli (CMHR) Poliüretan (PU), PIPA Polyol, Yanmazlık, Thermogravimetrik Analiz (TGA), Direk piroliz kütle spektrometresi.

***to the memory of my father...***

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ABBREVIATIONS

| | |
|---|---|
| **PU** | Polyurethane |
| **CMHR** | Combustion Modified High Resilience |
| **PPHP** | Parts (by weight) per hundred parts of polyol. |
| **DP-MS** | Direct Pyrolysis Mass Spectrometer |
| **TCPP** | Tris (2-chloroisopropyl) Phosphate |
| **PIPA** | PolyIsocyanate Polyaddition |
| **TDI** | Toluene Diisocyanate |
| **BS** | British Standard |
| **ASTM** | American Society for Testing and Materials |
| **TWL** | Total Wight Loss |
| **Dns** | Density |
| **DEOA** | Diethanolamine |
| **SO** | Stannous octoate |
| **SAG** | Support factor |
| **IFD** | Indentation force deflection |
| **TIC** | Total ion current |
| **TGA** | Thermal Gravimetric Analysis |

# CHAPTER 1

# INTRODUCTION

## 1.1. Historical Development of Polyurethane Materials

Polyurethane is a significant member of polymer family being a versatile product. Basically it is produced by the reaction of the isocyanate and polyol. Prof. Dr. Otto Bayer and co-workers explored polyurethane via polymer addition reaction of the diisocyanate and alcohols in the German laboratory I.G. Farben Industrie in 1937 [1].

Polyurethane was produced as an alternative for rubber by Otto Bayer during the first years of World War II. Afterwards, many implementations were applied. It found a wide usage area in the automotive sector through the development of cheap polyols in polyurethane foam industry in the 1950s. Since then, consumption of the polyurethane rises 5% per year in the world. In the developing countries such as; Turkey this amount is nearly 7-8% [2].

First commercial polyether, (poly (tetramethylene ether) glycol (polyol) was discovered by DuPont in 1956 by polymerizing tetrahydrofuran. Lower cost polyalkylene glycols were developed in 1957 by BASF and Dow companies. Polyether polyols offered technical and commercial advantages such as low cost, easy usage and better hydrolytic stability. Thus polyether polyols have replaced rapidly polyester polyols in the production of polyurethane materials. Union Carbide and Mobay were also other polyurethane pioneers as an American Monsato / Bayer joint venture. In 1960, more than 45000 $m^3$ of flexible polyurethane foam was produced. After a decade of progress, the use and development of chlorofluoroalkene blowing agents, cheap polyether polyols and methylene diphenyl diisocyanates (MDI) have emerged as polyurethane rigid foams as high-performance insulating materials [3].

Polymeric MDI (PMDI) based rigid polyurethane foams showed better thermal stability and combustion resistance than TDI based rigid polyurethane foams. In

1960s, semi-rigid foams with thermoplastic surfaces were started to be used as parts in automotive interior security elements and in door panels as filling material. In 1967, urethane-modified polyisocyanurate rigid foams were appeared. These materials offered better thermal stability and combustion resistance compared to low density insulating materials [3].

In 1969, Bayer made a car composed of plastic material Düsseldorf in Germany. These parts of the car were produced by a new process called (Reaction Injection Molding (RIM). This technology uses the collision of high- pressure fluids and the rapid flow of the reaction mixture into the mold cavity. Large parts such as; automotive bodies and body panels can be molded in this way. Polyurethane RIM technique has been applied in production of several different products. Poly (urethane), poly (isocyanurate) and polyurea RIM material were produced by the use of diamine chain extenders and trimerization technology. Reinforced (R-RIM) was produced by addition of filling materials such as; ground glass, mica and mineral fibers, which enables improvement of the resilience modulus and thermal stability. Via this technology, Pontiac Fierro's first plastic car coachwork has been provided in America. Further development of the resilience modulus was determined by the insertion of the glass matrix in the RIM mold cavity. This production method is known as structural RIM (S-RIM) [3].

In the early 1980s, water-blown micro-cellular flexible foams were used in the automotive industry as panels and radial air filters. Since then, the market shares of water-blowing micro-cellular flexible foams increased considerably, because of the increase in energy prices and the limitations of use of PVC plastisol. In some applications, these substantially low mass materials replace the expensive raw materials, which are metal plugs and filter housings. Highly filled polyurethane elastomers and unfilled polyurethane foams are currently used in high temperature oil filter applications [3].

## 1.2. Types of Polyurethane Materials

Depending on the used reagents; polyol, isocyanate, catalysts, additives different kind of polyurethanes can be produce as foams which are rigid and flexible, elastomers, rubbers, adhesives and coatings.

Polyurethane materials are classified according to their physical properties, production methods and usage areas. These are divided into five types: rigid polyurethane (PUR) foam materials, flexible polyurethane (PUF) foam materials, integral (semi-rigid) polyurethane (PUI) materials, RIM polyurethane materials and thermoplastic polyurethane (TPU) materials.

### 1.2.1. Rigid Polyurethane Foam Materials

Rigid foam systems are mainly produced for insulation purposes. The polyol system and the polymeric isocyanate (PMDI) mixture expand with the help of a blowing agent to form rigid foam. Polyether polyol based rigid polyurethane foams have strong hydrolysis resistance and are compatible with additives to be added to their formulation. However, their combustion and mechanical properties are low. Polyester polyol based rigid polyurethane foams provide much better flame retardancy and thermal stability characteristics. They have low dust ratio and do not have a fragile structure. Since 90-92% of the foam cells are closed, rigid structure and are called rigid foams. These materials are good heat sink which means heat absorber. Figure 1.1 shows the thicknesses of different construction materials providing the same insulation.

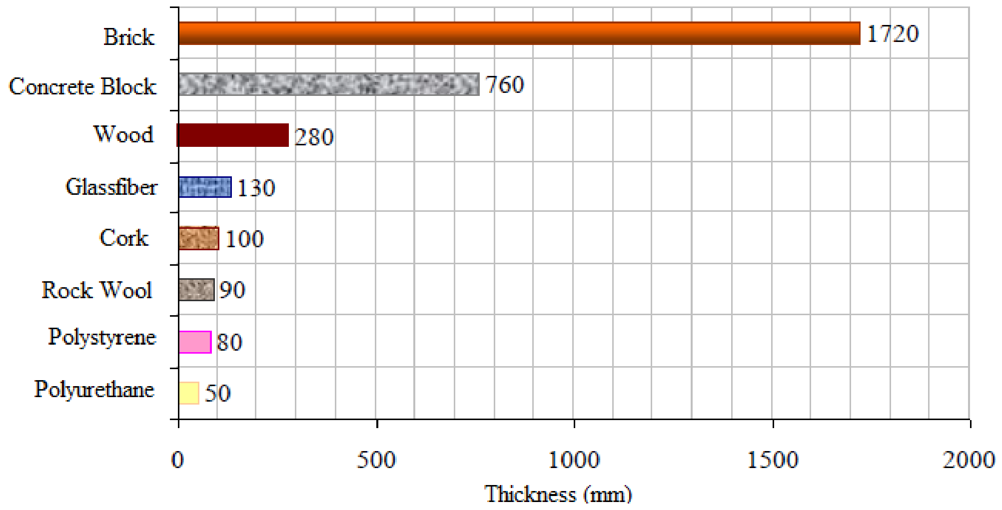
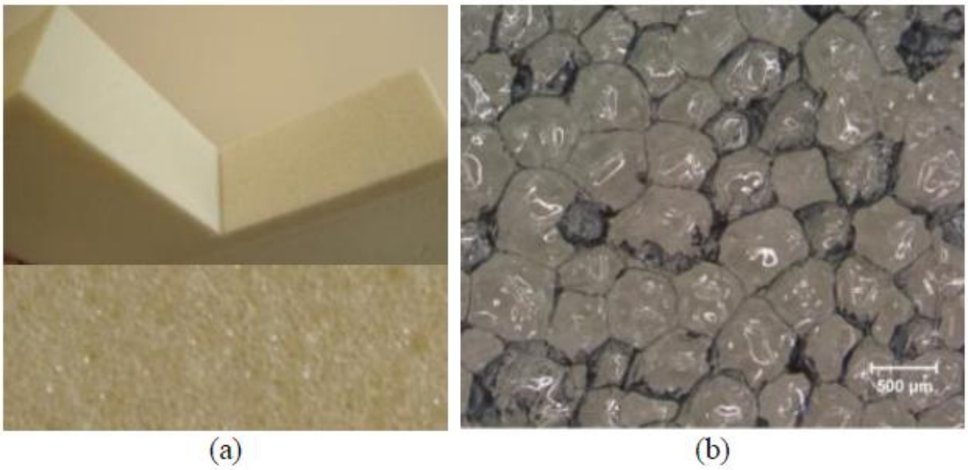


**Figure 1.1.** Thickness of different building materials for the same insulation property [3].

It can be seen that rigid polyurethane foam is the most suitable material for thermal insulation purposes.

Only a small part of rigid polyurethane materials consists of solid material. The density of rigid polyurethane material used in building applications is generally 40 kg/m$^3$ and has volume only 4.5% of the total volume of solid plastic-based materials. Such materials are rigid in mechanical loading and resistant to buckling. Macro and micro scale structure of rigid foam polyurethane material is shown in Figure 1.2. Rigid polyurethane foam materials are used in refrigerators, coolers, pipe and tank insulations, automotive sound and heat insulation, roof wall panels, cold room panels, prefabricated buildings and guard cabins.



(a) (b)

**Figure 1.2.** a) Macro-scale structure of the PUR material and b) micro-cell structure [1].

### 1.2.2. Semi-Rigid Polyurethane Foam Materials

The foam materials with flexible and open-celled inner structure with hard and partially stretchable shell part are called semi-rigid polyurethane foams. Integral polyurethane materials are sometimes referred as semi-rigid polyurethane foams. The most important features of semi-rigid foams are shock absorption, quenching and absorption. Therefore, they are mainly used for anti-vibration, noise insulation and sound insulation. An example of vibration damping is the car steering wheel.

Integral polyurethane materials are widely used in the automotive industry, (in steering wheels, gear knobs), door armrests and dashboards, filters and various sports equipment, vacuum cleaners, coolers, fans and air conditioning. Figure 1.3 shows some examples of the applications of various integral polyurethane materials.

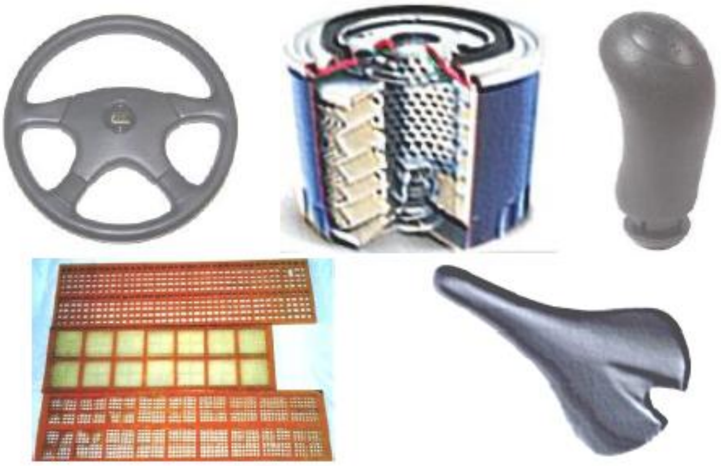


**Figure 1.3.** Some applications of semi-rigid (integral) polyurethane materials [3].

### 1.2.3. Flexible Polyurethane Foam Materials

Flexible polyurethane foam (cold cure) is opened cell polyurethane materials with limited resiliency and recovery. It is known as foam in daily life. At the same time, semi-flexible, very flexible and memory (viscoelastic structure) foams enter into this group. Nowadays, it is possible to produce foam with the desired elasticity, hardness and density by the developing technology and needs. Flexible polyurethane foam has a wide usage area in automotive, furniture, mattresses, and textile products and in medical beds and pillows. Figure 1.4 shows some examples of applications of flexible polyurethane foam materials.

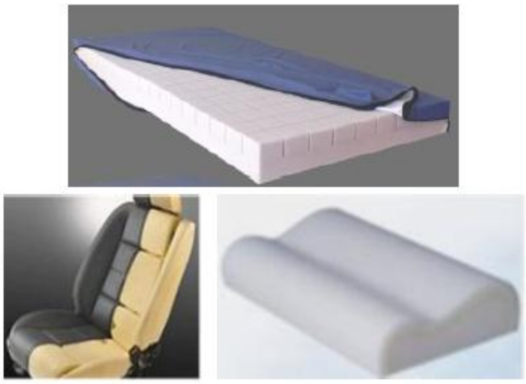


**Figure 1.4.** Flexible polyurethane foam (cold cure) applications [3].

### 1.2.4. RIM Polyurethane Materials

Reaction Injection Molding (RIM) polyurethane materials are known as molded foams. Molded foams are hard, impact-resistant, resistive and have high density.

Especially the outer parts of automobiles are produced by this production method. In RIM method a mixture of two or more components are used. The mixture is poured into a mold by injection. Molding process creates the desired shapes of the polyurethane materials after curing. It is widely used in automotive industry in production of torpedo, front hood, door panels, bonnet, sun visor and other parts. Many truck parts are made with the RIM system. For example, bumpers, grids, fenders and windbreakers are produced by this system. The applications of RIM polyurethane materials are shown in Figure 1.5.

**Figure 1.5.** RIM polyurethane material applications [4].

### 1.2.5. Thermoplastic Elastomer Polyurethane Materials

They are rigid; high density polyurethanes can be stretched to a limited extent when exposed to an impact and can be re-formed when they are over pressure. There are also elastomers which are resistant to abrasion have high elongation and heat resistant. Figure 1.6 shows the mold spring, wheel, roller covering and star coupling applications.

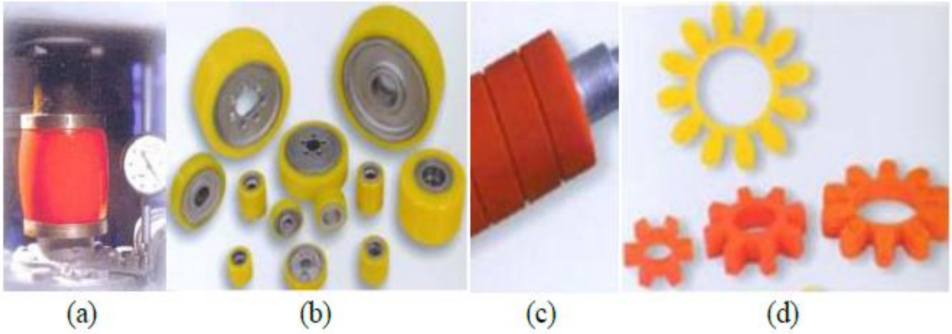


**Figure 1.6.** Elastomer polyurethane material applications (a) mold spring, (b) wheel, (c) roller coating and (d) star coupling [5].

High levels of versatility of elastomers provide a wide range of applications in automotive, floor slat and footwear industries. Foaming and non-foaming elastomers are used in different areas. Densities vary between 400-1100 kg/m$^3$. Polyether and polyester based polyol systems are used in shoe production. Their hardness ranges from 60 to 80 Shore D.

## 1.3. Polyurethane

Polyurethane is formed by urethane (carbamate) reactions. The reaction of the polyurethane is a condensation reaction. The difference from condensation polymerization is that the molecule is not lost. It is composed of the reaction of diisocyanate and oligo-polyols; that’s sis oligo-diols, the synthesis name as the polyaddition reaction.

Molecular weight of the polyurethane depends on the amount of the reactive side of the isocyanate (included –NCO part) and polyol (included –OH part).

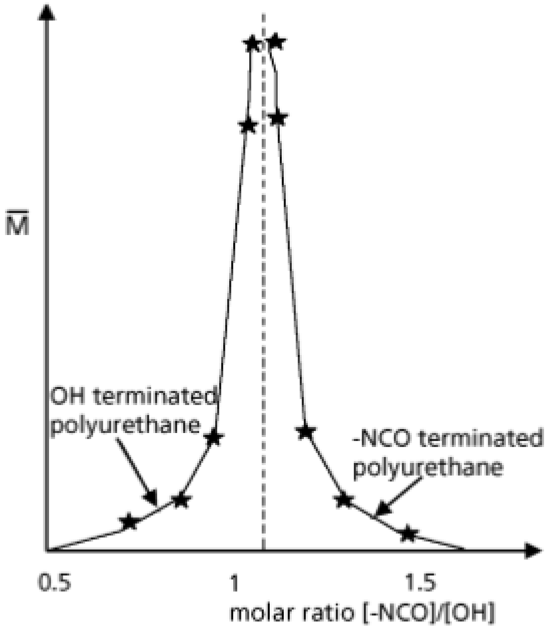


**Figure 1.7.** The effect of the molar ratio [-NCO]/ [OH] on MW of the Polyurethanes [8].

Polyurethane is known as a solid-gas composite polymer. Polyurethane polymer is the continuous solid phase whereas the gas phase is the discontinuous. Types of polyurethanes are varied according to crosslink density and stiffness from very hard to soft. Variation of the polyurethane through density and stiffness changes are given in Figure 1.8 as follows:

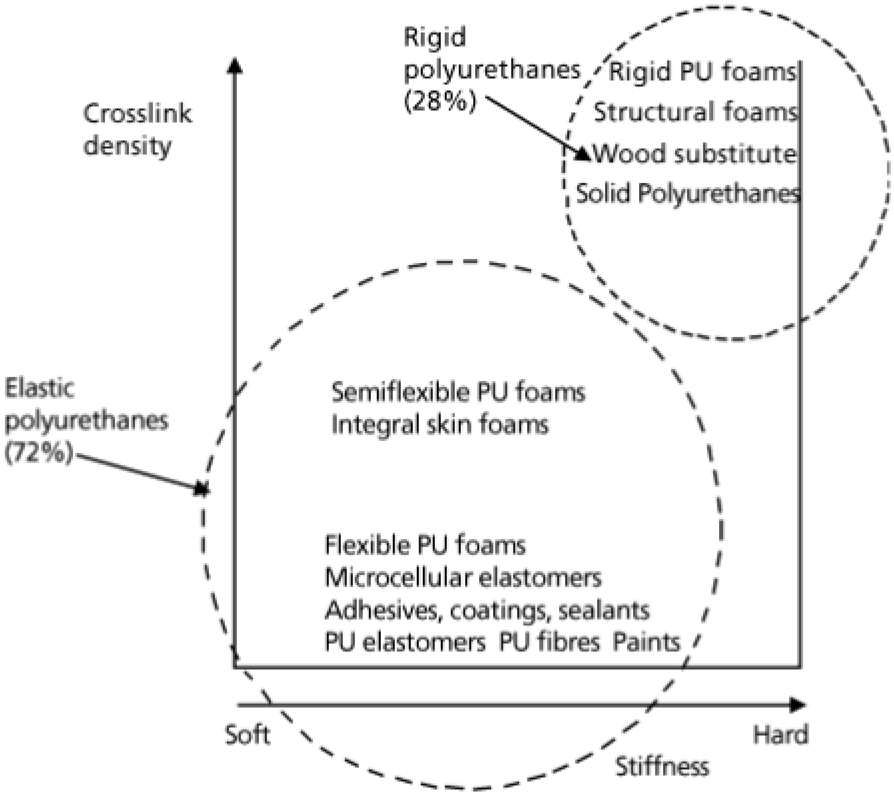


**Figure 1.8.** Classification of polyurethanes as function of crosslink density and stiffness [10].

When the hardness of polymer increases rigidity of the polyurethane also increases.

### 1.3.1. Flexible Polyurethane Foam

Foam is produced by polymerization reaction of petrochemical raw materials. Due to its polyurethane structure it is known as polyurethane foam. Foam, which constitutes an important input of many industries such as; automobile, textile, furniture and bedding, is produced according to the field of application with different methods. Two different methods, known as mold

foam and block (slab stock) foam methods, are used to provide two different structures having properties, generally hard or flexible.

The main usage area of the polyurethane is the furniture/mattresses, automotive, construction, technical insulation, shoes industries and about %30 of the polyurethane production is the slab-stock flexible polyurethane foam used in furniture mattresses. Usage areas are demonstrated in Figure 1.9.

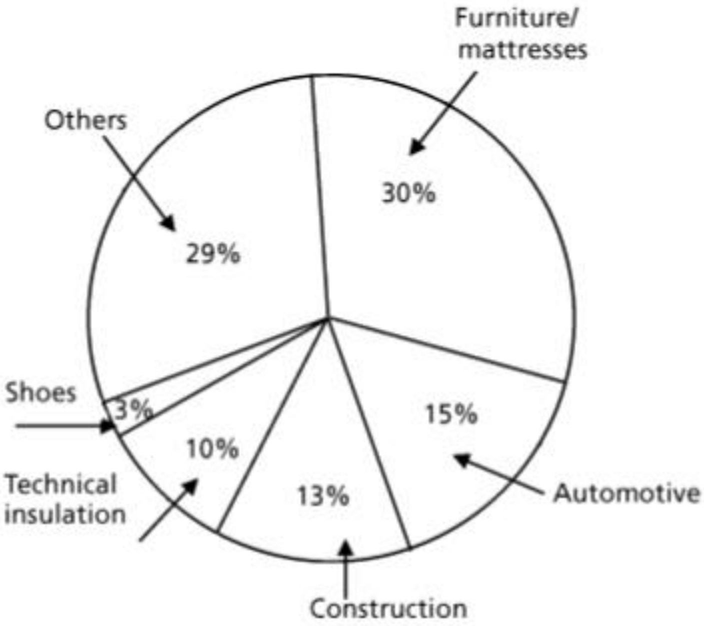
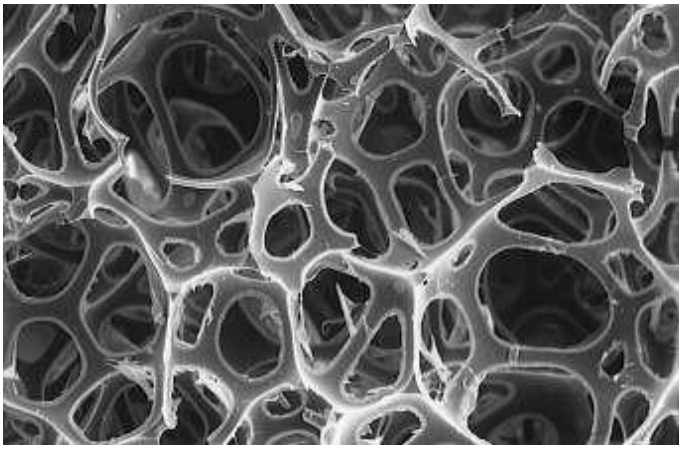


**Figure 1.9.** Usages of the polyurethanes [24].

Polyurethane foams, flexible foams and rigid foams are very essential thermoset polymers and are produced in tremendous amounts. Polyurethane supplies approximately 5% of the worldwide plastic needs. The flexible polyurethane foam; used especially in furniture and mattress cushioning, includes 48% of the production, the rigid polyurethane foam used in the sectors of construction, carpet layer, refrigerator insulation, packaging and automotive, provides only 28% of the polyurethane production [6].

In the production technology of rigid and flexible foams, both mold and slab stock methods, which make some differences in the raw materials usage and process, can be used [7].



**Scheme 1.1.** Open cell structure polyurethane foam, 50 times enlarged [7].

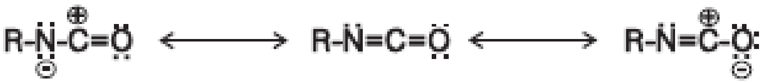
The polyurethane chemistry is based on the reaction of active hydrogen containing compounds and isocyanates. Isocyanates are compounds containing one or more high reactivity isocyanate groups (-N = C = O).

These groups react directly with hydrogen atoms by attacking more electro negative atoms than carbon. Many compounds that comply with this definition are given in Table 1.1.

**Table 1.1.** Active hydrogen compounds with reduced reactivity with isocyanate.

| **Active Hydrogen Compounds** | **Structure** | **Uncatalyzed Relative Reaction Rate (25 °C )** |
|---|---|---|
| Primary Aliph. Amine | $R\text{-}NH_2$ | 100000 |
| Secondary Aliph Amine | $R_2\text{-}NH$ | 20000-50000 |
| Primary Aromatic Amine | $Ar\text{-}NH_2$ | 200-300 |
| Primary Hydroxyl | $R\text{-}CH_2\text{-}OH$ | 100 |
| Water | $H_2O$ | 100 |
| Carboxylic Acid | R-COOH | 40 |
| Secondary Hydroxyl | $RR_2 – CH\ \text{-}OH$ | 30 |
| Urea | R-NH-CO-NH-R | 15 |
| Tertiary Hydroxyl | $RR_2R_3\text{-}C\text{-}OH$ | 0.5 |
| Urethane | R-NH-CO-O-R | 0.3 |
| Amide | $R\text{-}CO\text{-}NH_2$ | 0.1 |

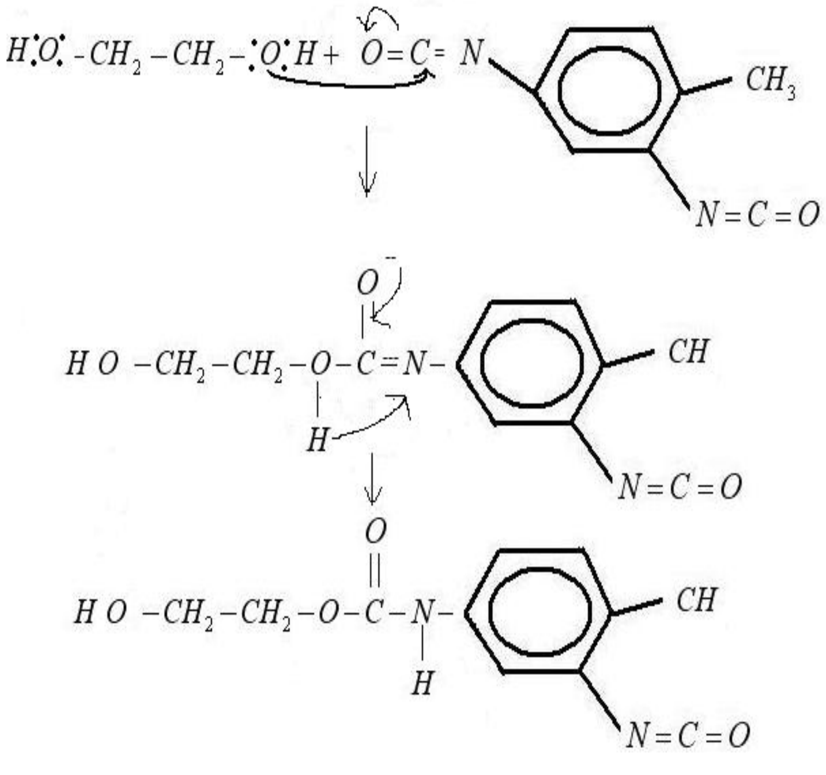
The reactivity of the isocyanate group can be explained by the resonance probability of isocyanate shown in Scheme 1.2.



**Scheme 1.2.** Resonance structures of isocyanate group [9].

Electron density is expected to be highest on oxygen atom and least on the carbon atom. This creates highest total negative charge on the oxygen atom, total positive charge on carbon and intermediate total negative charge on nitrogen. Normal reactions generally occur in carbon - nitrogen double bonds. The nucleophilic center of the active hydrogen-containing compound has an effect on the electrophilic carbon. The active hydrogen atom is then added to the nitrogen atom. Electron-withdrawing groups act on the isocyanate molecule, which increases reactivity of NCO group towards the nucleophilic groups. This reduces reactivity of electron donor group. In many reactions, aromatic isocyanates are much more reactive than aliphatic isocyanate. Steric hindrance in both isocyanate and active hydrogen compound affects the reaction.

The reaction mechanism of the polyurethane is given below in Scheme 1.3. As mentioned above, the free electrons on the oxygen atom in OH group of the polyol (PEG) attacks the C=N double bond in the TDI. The double bond is broken and hydrogen bond between N and H is captured.



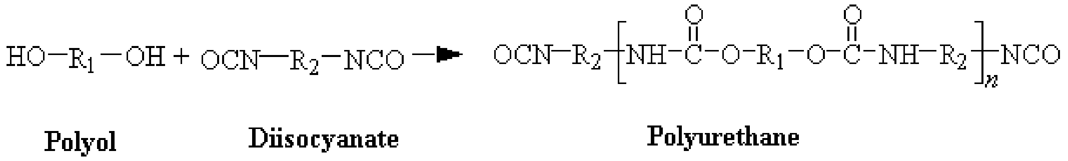
**Scheme 1.3.** The reaction mechanism of the polyurethane synthesis.

### 1.3.2. Flexible Polyurethane Foam Reactions

The production of flexible polyurethane foams is a complex process involving many components and at least two competing reactions. There are two main reactions for the polyurethane synthesis, which are gelling (polymerization) and blowing reaction.

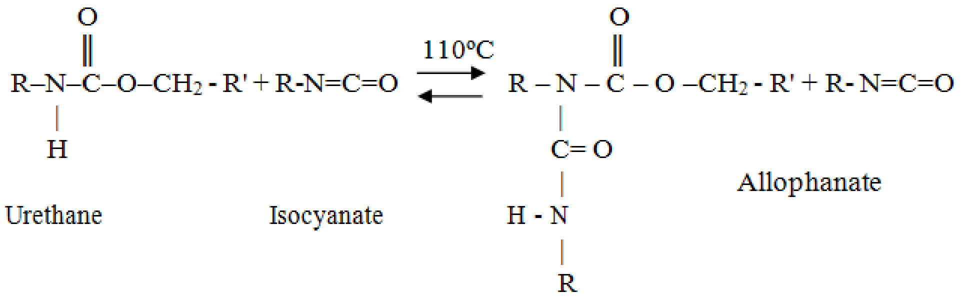
#### 1.3.2.1. Polymerization Reaction

The main polyurethane reaction that’s gelling or polymerization is represented in Scheme 1.4. It occurs between diisocyanate and polyol and so polyurethane is obtained. This exothermic reaction’s heat (Δ) has been declared nearly 5, 73 kJ/mol [9]. Depending on the starting materials; the $R_1$ and $R_2$ groups may optionally contain isocyanate and isocyanate reactive groups.



**Scheme 1.4.** Generalized polyurethane reaction [10].

If hydrogen at the nitrogen atom in the urethane group reacts with the appropriate isocyanate, it may form allophones (Scheme 1.5.).

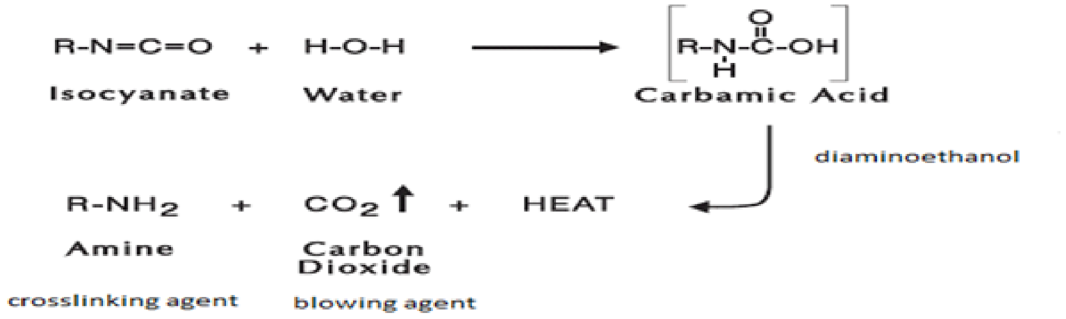


**Scheme 1.5.** Formation of urethane-isocyanate allophanate [9].

Reversible allophanate formation reaction occurs at high temperatures. In fact, if flexible foam is produced normally, the allophanate bonds will be cross-linked to other parts of the polymer. Catalysts used in the foam formulation do not allow this reaction and temperatures more than 110 ° C are required for the formation of a substantial amount of allophanate.

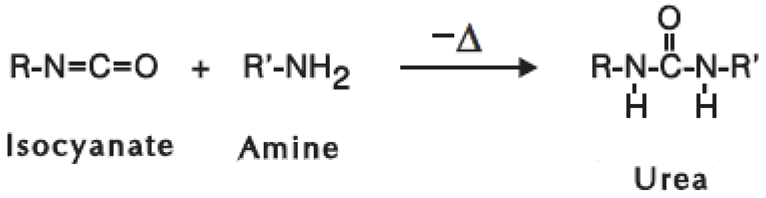
### 1.3.2.2. Blowing Reaction

Polyurethane's most important property is tendency for foaming. After the polymerization (gelling) reaction, foaming, the expansion of the polyurethane is occurred by the gas formation. Since the reaction of the polyurethane is exothermic blowing agent vaporizes and fills the cells. This reaction is called blowing reaction and obtained via the gas formation. The blowing or injection of the gas causes expansion of the cells of the polyurethane polymer. In this reaction gas source is the carbon dioxide. When isocyanate (TDI) reacts with water carbamic acid is produced. Since carbamic acid is an unstable component it turns to amine and carbon dioxide. The blowing reaction is given in Scheme 1.6. In the literature, generally chlorofluorocarbon, methylene chloride and trichloroethane are used as blowing agents to activate the blowing reaction.



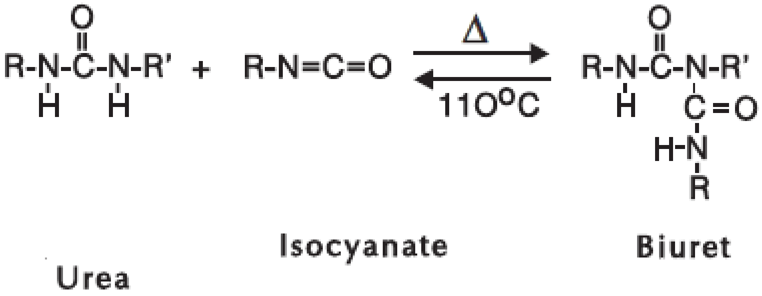
**Scheme 1.6.** $CO_2$ formation [10].

Subsequent reaction of the amine with the corresponding isocyanates produces urea (Scheme 1.7.).



**Scheme 1.7.** Reaction of amine and isocyanate [9].

Approximately 197 kJ of heat is released per mole of water. Isocyanate and amine molecules are polyfunctional. The crosslinked polymer will be formed. Another accepted method for crosslinking the polymer is the generation of biuret bonds by the reaction of hydrogens in the urea with free isocyanate groups as shown in Scheme 1.8. [9].



**Scheme 1.8.** Urea and isocyanate reaction [11].

Since this reaction is reversible, it is controversial whether the final polyurethane foam actually contains biuret and allophanates [10]. Blowing is achieved by the physical addition of low boiling non-reactive liquid to the foam formulation. The evaporation of these liquids by heat from exothermic reactions forms gas molecules that diffuse into nucleated bubbles and allow the foam to expand.

## 1.4. Flexible Polyurethane Foam Main Components

Polyurethanes are formed by the reaction between isocyanate, -N=C=O and hydroxyl (alcohol) groups, -OH. The reaction also involves catalysts and additives. Flexible polyurethane foam recipes can be varied to obtain the desired foam [11]. The most common components used in the production of flexible polyurethane foam and the general use ranges are given in Table 1.2.

**Table 1.2.** Flexible polyurethane foam general formulation.

| Components | Parts (php) |
|---|---|
| Polyol | 100 |
| Inorganic Filler | 0–150 |
| Water | 1,5–7,5 |
| Surfactant | 0,5–2,5 |
| Amine | 0,1–1,0 |
| Tin | 0–0,5 |
| Cell Opener | 0–10 |
| Cross-linker | 0–5,0 |
| Additive | Variable |
| Blowing Agent | 0–35 |
| Isocyanate | 25–85 |

The polyol is known as the hydroxyl source or isocyanate reactive group. With the selection of polyol structure and type, foam properties and properties of formation process can be varied quite effective. 90% of all flexible foams are obtained from polyether-based polyols. These polyols can be grouped into the following categories:

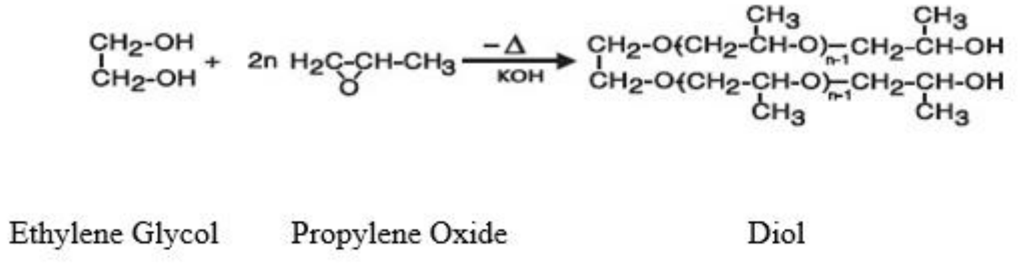
- Polyoxypropylene diols,
- Polyoxypropylene triols,
- Polyoxypropylene tetriols and higher equivalents,
- Ethylene oxide capped diols, triols and higher analogs,

- Random and block polymer polyols made using both ethylene oxide and porpylene oxide,
- Grafted or copolymer polyols containing stable distribution of solid particles in the liquid polyol phase,
- Cross linkers to which short chain polyfunctional molecules are added to increase initial foam stabilization and foam load bearing capacity.

### 1.4.1. Polyol

The second important raw material for the polyurethane reaction is the polyols. Polyols are named according to the number of the hydroxyl groups. If it contains two hydroxyl group names as diol or three-hydroxyl group it is triol, etc. They are classified through the hydroxyl number (hydroxyl, –OH, value in mg KOH/g), their ethylene oxide (EO) content and their functionality [12].

The reaction of the initiator containing two or more active hydrogen atoms and organic oxide yields polyether polyols. Under base catalysis, the active hydrogen compound initiates chain opening and oxidation at the same time. This continues until the desired molecular weight is achieved. If the initiator has two active hydrogens, diols are formed (Scheme1.9.).



**Scheme 1.9.** Diol formation reaction [12].

When a trifunctional initiator such as; glycerin is used, triols are formed by chain growth in three directions. These reactions are exothermic; for example, 92 kJ/mol heat is generated when propylene oxide is used. Initiators used in the production of flexible foam are shown in Table 1.3 below.

**Table 1.3.** Flexible polyurethane foam frequent initiators.

| **Desired Functionality** | **Specimen Initiator** | **Initiator Structure** |
|---|---|---|
| 2 | Water | $H_2$ O |
| 2 | Ethylene glycol | $C_2$ -$H_6$ -$O_2$ |
| 2 | 1,2 Propylene glycol | $C_3$ -$H_8$ -$O_2$ |
| 3 | Glycerin | $C_3$ -$H_8$ -$O_3$ |
| 3 | Trimethylolpropane | $C_6$ -$H_{1\ 4}$ -$O_3$ |

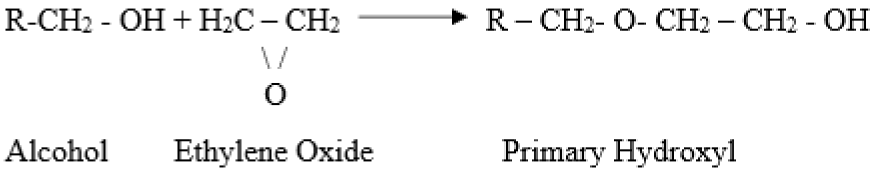
In real applications, two side reactions inhibit the production of the polyol from the selected initiator compound. The first side reaction involves the formation of diol when the oxide is added to water. A small amount of water is usually present in the initiator compound, in catalysis and in the newly developing oxide nutrient. It is possible to include polyol with a small proportion of two mole percent diol. For some applications, polyols can contain up to 25% diol. The polyol functionality decreases when propylene oxide isomerizes in the reactor conditions to form allyl alcohol [13, 14].

This polyol serves as the initiator for the production of monohydroxy molecules. Equation 1 is used to determine the polyol net functionality from the monol and diol information.

$$\text{Functionality} = \frac{\text{OH\%} \div 1.7}{UNSAT. + \frac{\text{OH\%} \div 1.7 - \text{UNSAT.}}{\text{NOMINAL FUNC.} - \text{DIOL MOL\%}}} \qquad (Eqn. 1)$$

Unsaturation is mili equivalent concentration of mono in 1 g sample of the final polyol (meq / g) [15].

The nominal functionality is estimated from the initiators. The diol composition comes from process modeling and analysis. The properties of the final polyol broadly depend on the oxide or oxide mixtures. Ethylene oxide and propylene oxide are most commonly used. When polymerization is carried out using propylene oxide, it results in secondary terminal hydroxyls. If polymerization is carried out with ethylene oxide or propylene plus ethylene oxide, primary hydroxyl groups are formed (Scheme 1.10.).



$$R\text{-}CH_2 - OH + \underset{O}{\underset{\backslash\,/}{H_2C - CH_2}} \longrightarrow R - CH_2\text{-}\, O\text{-}\, CH_2 - CH_2 - OH$$

**Scheme 1.10.** Primary hydroxyl group formation reaction [15].

The reaction temperature for ethylene oxide is 113 kJ /mol. If ethylene oxide has side reactions at certain conditions, a cloudy polyol is formed [16, 17].

The primary hydroxyl groups are three times more reactive than the secondary ones in their reaction with isocyanate. If the oxide mixture is used, the hetero polyol is obtained with improved water and isocyanate compatibility. This is very useful in the production of slabstock foams. Although ethylene oxide has a much higher polymerization rate than propylene oxide, the primary hydroxyls are more reactive than the secondary. Essentially, polymerization is random and there is a wide variation in the hetero polyol composition. Polyols can be classified as follows.

Propylene Oxide - Ethylene Oxide Polyether Polyols

Rigid Foam Polyether Polyols

Polyether Polyols for Flexible Foam Applications

Modified Polyether Polyols (Graft Copolymer Polyols, Chain-Developed Copolymer Polyols, PHD Polyols, PIPA Polyols)

Other Copolymer Polyols (Epoxy Dispersion Polyols, Polyisocyanurate Dispersion Polyols, Melamine Dispersion Polyols)

Polyester Polyols

### 1.4.2. Polyol Characterization

#### 1.4.2.1. Functionality

Functionality is an average number of hydroxyl groups in a polyol molecule. It is also expressed as the average number of isocyanate-reactive side in the polyol. It depends on the selection of the initiator. Monol and diol levels should be taken into account when calculating the functionality as indicated in Equation 1.

#### 1.4.2.2. Hydroxyl Number

The hydroxyl number, which is known OH number, is expressed as the number of reactive hydroxyl groups required for the reaction. It is determined by analytical method (ASTM D 4274-99) and is determined as the equivalent number of mg KOH in 1 g of polyol [18, 19].

$$\text{OH number} = \frac{\text{Formula weight of KOH } \times 1000}{Equivalent\ Weight} \qquad (Eqn. 2)$$

#### 1.4.2.3. Equivalent Weight

Equivalent weight is the weight of the compounds in the reactive portion. It is obtained by dividing the molecular weight by functionality.

The calculation of equivalent weight and functionality is somewhat complex due to the presence of monols derived from isomerization of propylene oxides and diols derived from water. It can also be found in the hydroxyl number.

#### 1.4.2.4. Primary Hydroxyl Composition

The distribution of primary and secondary hydroxyl groups directly affects isocyanate and polyol reactivity. The reactivity increases if the primary hydroxyl group composition increases. Details are given in ASTM D 4273–88.

### 1.4.2.5. Degree of Unsaturation

It is a measure of the concentration of unsaturated finite groups (allyl and propenyl) in the polyol. It is mg-equivalent weight of unsaturated species in 1 g polyol. For example, the polyol produced with propylene oxide containing 50-100 ppm of water has an unsaturation value of 0.05 meq /g.

### 1.4.2.6. Reactivity

It is a measure of the speed of the reacted polyol to form a polyurethane polymer. The fact is that, all of the polyols are liquid at room temperature or at low temperatures. This advantage is that the high molecular weight polyurethane polymer can only be processed from low to medium viscosity liquid intermediates. Viscosity is an indication of the workability of the polyol [83].

Since the 1960s, model reaction with isocyanate has been carried out with viscosity test [20, 21]. In recent years, the improved Brookfield Viscometer test has proven to be useful for determining the reactivity of ethylene oxide terminated polyols [22]. Figure 1.10 shows how the polyol reactivity changes with increasing primary hydroxyl number.

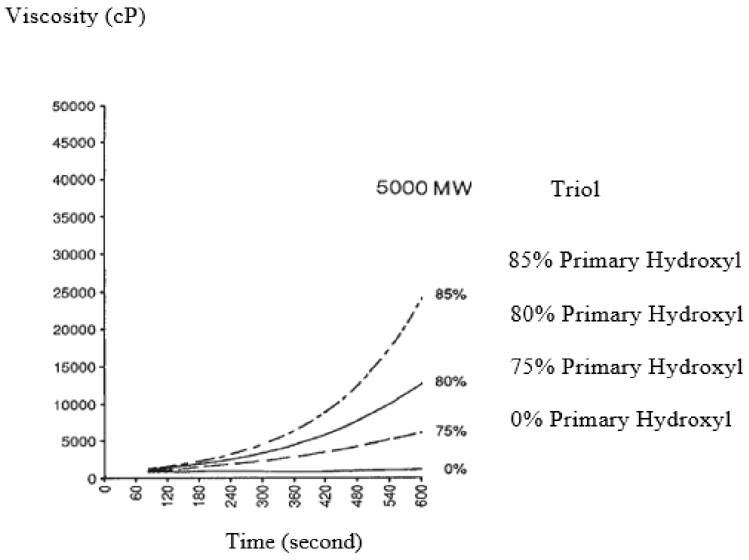


**Figure 1.10.** Effect of primary hydroxyl composition on reactivity [54].

### 1.4.3. Isocyanate

The main raw material of the polymerization reaction is surely isocyanate. Since isocyanate contains two functional isocyanate groups in its chemical structure, it is named as diisocyanate. The aromatic isocyanate groups are the most significant component of the polyurethane production, which are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), and their structures are shown in Figures 1.11 and 1.12, respectively.

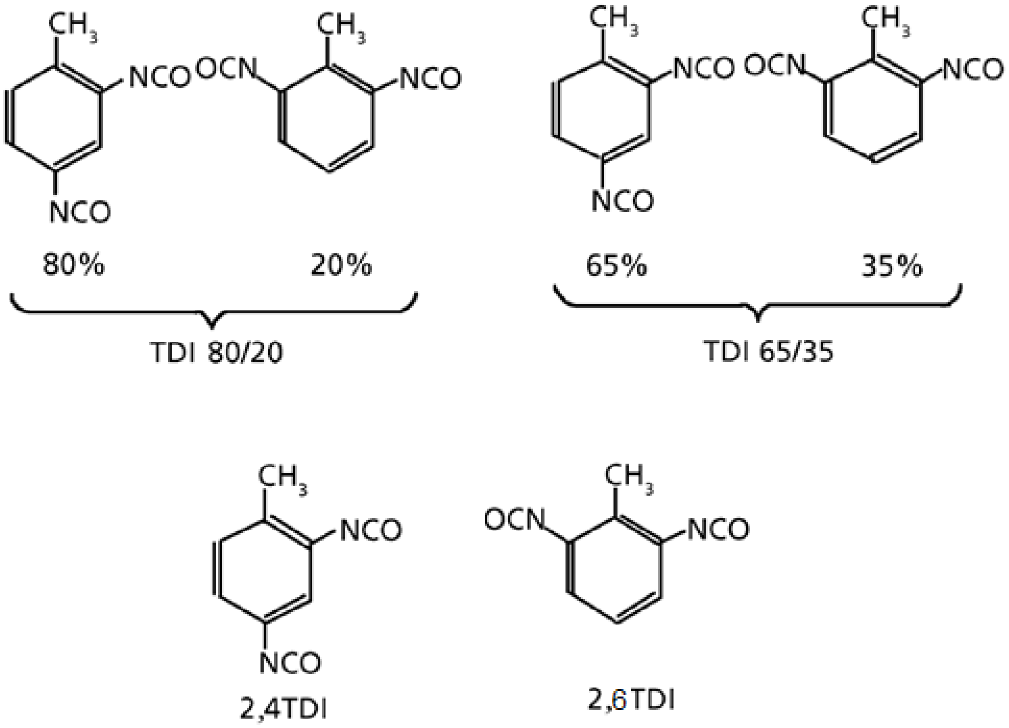


**Figure 1.11.** The chemical structures of commercial TDI [23].

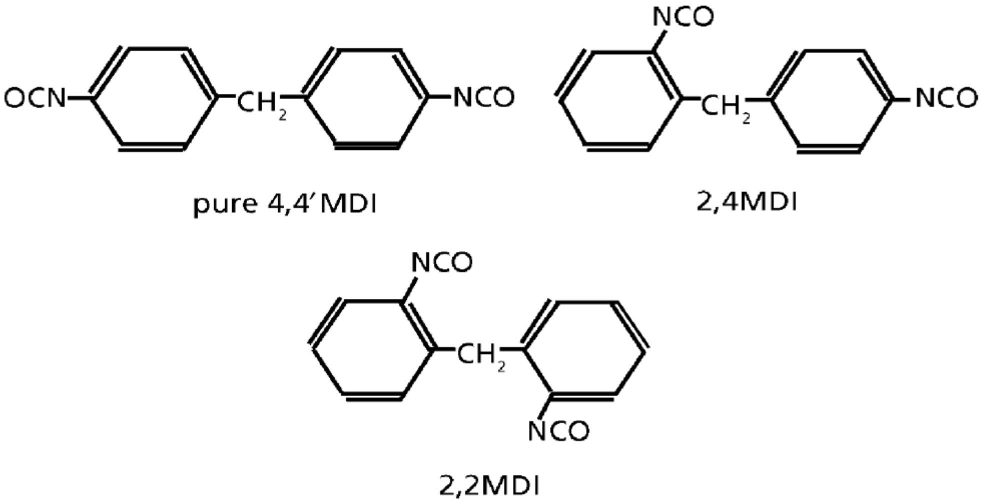


**Figure 1.12.** The chemical structures of pure MDI [23].

All isocyanates used in the polyurethane industry contain at least two isocyanate groups. The most widely used isocyanates in polyurethanes are toluene diisocyanate (TDI), diphenylmethane - 4 - 4’- diisocyanate (MDI) and the polymer form of MDI. TDI is generally used in the manufacture of flexible foam and polymeric MDI in the manufacture of rigid foam. The most commercially important basic isocyanates exist in two isomers. 2, 4-toluenediisocyanate (TDI) and 2,6-toluene diisocyanate (TDI) as shown in Figure 1.11. The mixture of 2,4-toluenediisocyanate (TDI) and 2,6-toluene diisocyanate isomers of toluene diisocyanate can also be used in the production of flexible polyurethane foam.

The ability of the isocyanate groups to react has substantial effect for the quality of the foam product [23, 24, and 25].

The ortho position reactivity in the isomer 2, 4 is approximately 12% of the reactivity of the para position which is dependent on the steric hindrance of the methyl group. However, when the reaction temperature approaches 100 ºC, the steric hindrance effects prevail and the two positions reach approximately the same reaction rate.

As indicated in Figure 1.13., polyurethane has rigid and flexible part due to the TDI and polyol. Rigidity depends on the amount of TDI used; that is polyurethane can be both rigid and flexible like flexible and rigid foam.

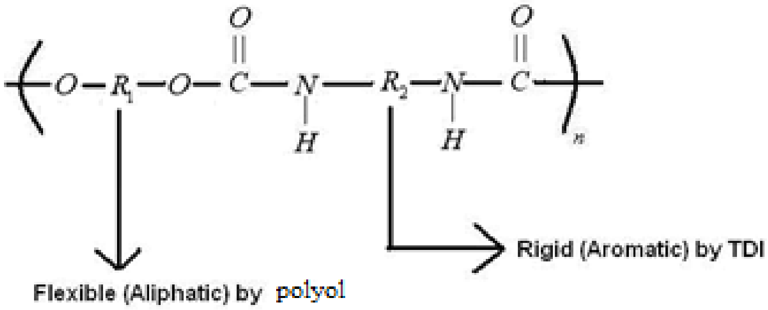


**Figure 1.13.** General structure of polyurethane [24].

### 1.4.4. Water

Water is the active hydrogen source. Only demineralized water should be used in the production of foams. Water reacts with isocyanate to give carbon dioxide gas and polyurea molecules. The resulting gas diffuses into bubbles that begin to nucleate and assist in the expansion of the foam. It gets inside polyurea molecules and contributes to the final polymer properties [26]. Water also affects density, which is one of the most important properties of foam. Therefore, caution should be exercised when making changes to the amount of water.

### 1.4.5. Surfactants (Silicones)

All polyurethane flexible foams can be made using nonionic silicone-based surfactants. Silicones can contribute to different functions of the foam. These are;

- Low surface tension,
- Emulsifying formulation components that do not reach each other,
- Supports and advances nucleation of bubbles during mixing,
- Reducing the concentration of tension on the cell walls to ensure that it remains stable,
- It eliminates the not foaming formation effect of any solid that is formed or added [27].

Among these functions, stabilization of cell walls is the most important. During the self-supporting formation of the polymerization, these cells prevent the fast-growing cells from merging until they obtain sufficient strength. Without this effect, continued cell integration will allow the entire foam to collapse. Silicones are also used to control the exact timing and degree of cell opening [28].

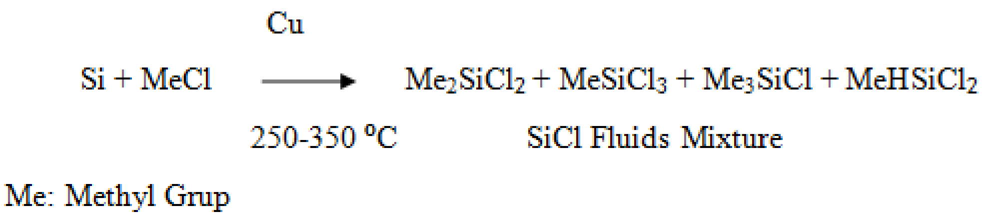
In the absence of silicone, the foam system will boil intensively. With the addition of a small amount of silicon unperfected foam can be produced. By increasing silicone part, the foam system will reach more stable level and cell size can be controlled. Stable and open cell foam can be obtained at optimum concentrations. At higher levels of silicon, excessive stabilization will occur at the cell windows and very tight foams with impaired physical properties will be obtained. Today, most of the flexible foams are made of silicones, which are described as polysiloxane-polyoxyalkylene copolymers.

Typical silicon synthesis begins with the reduction of sand to silicon methal. This occurs in an electric oven at high temperatures [29, 30].

$$SiO_2 + 2\ C \longrightarrow Si + 2CO$$

**Scheme 1.11.** First step of the silicone synthesis reaction [29].

The silicon metal is transformed into a very fine powder after cooling down. The methyl chloride is then reacted in the presence of copper catalyst to form a mixture of methyl chlorosilane (commonly referred to as SiCl liquids).

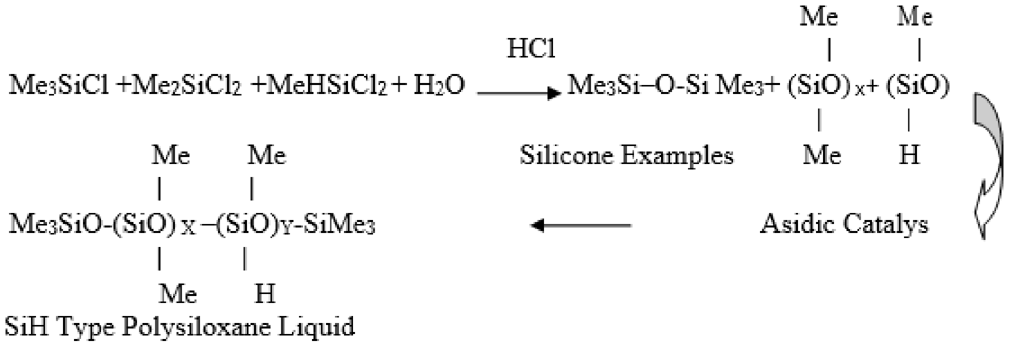


$$Si + MeCl \xrightarrow[250\text{-}350\ ^{o}C]{Cu} \underbrace{Me_2SiCl_2 + MeSiCl_3 + Me_3SiCl + MeHSiCl_2}_{\text{SiCl Fluids Mixture}}$$

Me: Methyl Grup

**Scheme 1.12.** Second step of the silicone synthesis reaction [29].

The mixture obtained from these methyl chlorosilanes is hydrolyzed to give the exemplification silicone products shown in Scheme 1.13.

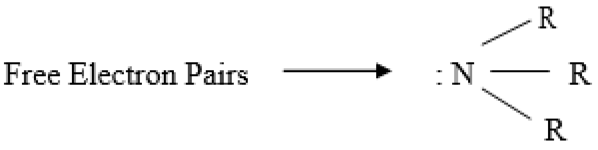


**Scheme 1.13.** Third step of the silicone synthesis reaction [29].

With the appropriate process and acidic catalyst input, SiH type polysiloxane liquid product is obtained [31]. For each type of slabstock foam, silicon should have an optimum balance between silicon and glycerol bonds [32]. Mixtures of conventional silicone surfactants and polyoxyethylene / polyoxy propylene block copolymers are used to improve foam porosity [33].

### 1.4.6. Amine

The most important catalyst used in the production of flexible polyurethane foam is the amine catalyst. The first function of the amine catalyst is blowing reaction and it also affects the gelling reaction by controlling the rate of the relief reaction. For production, it is important to determine the type and the amount of the amine catalyst. Especially in the production of flexible foams, properties of amine catalysts have to be determined because of the evaluation of A-1 standards. The choice of amine catalysts is related to appropriate process conditions, rise time, reaction times (such as cremation, rise, gelation times), and even foam surface structure. The amine catalysts used in the industrial field have different amine structures and different activities. Therefore, the structure of the amine catalyst used will affect the amount of amine required. Third degree amines are widely used in the production of flexible foam. The catalytic reactivities of amines depend on the presence of nonbonding electron pairs on the nitrogen atom as shown in Scheme 1.14 below.



**Scheme 1.14.** Free electron pairs in the nitrogen [54].

The steric hindrances around the nitrogen atom and the electronic effects of the instead atom groups are the main factors affecting the catalytic activity of various amines.

The type and concentration of the amine catalyst may vary according to the process requirements such as creaming time, gelling time and curing time of the outer surface skin. The choice of amine also affects the load bearing and air permeability properties due to its effect on primary and secondary foam reactions.

General requirements for good catalytic activity;

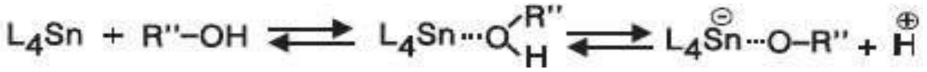
1. The catalyst must be strong nucleophile capable of attacking the carbon of the isocyanate group,

2. The catalyst should have the ability to form easily an active hydrogen-amine complex,

3. The catalyst is capable of forming stable hydrogen bonds with water and it should be water soluble.

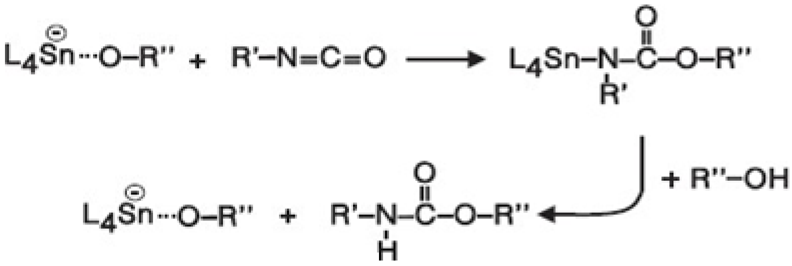
### 1.4.7. Organometallic Catalysts (Tin)

Gelling or polymer formation reaction between isocyanate and polyol is supported by organometallic catalysts. Many suitable metal tin compounds are widely used. These compounds act as Lewis acids and function by interacting with essential part in isocyanate and polyol compounds. Three complementary reactions are designed for the formation of activated complexes. First, the polyol is activated by tin catalyst.



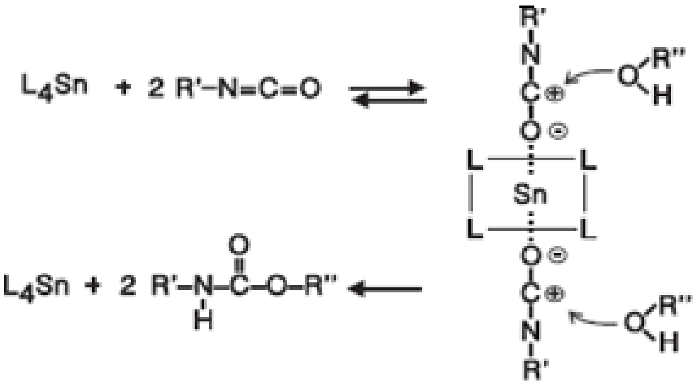
**Scheme 1.15.** Tin-Polyol complex formation reaction [54].

Tin alkoxide reacts with isocyanate to form carbamate. The resulting compound reacts with the polyol to initiate polymer production and the catalytic species is regenerated.



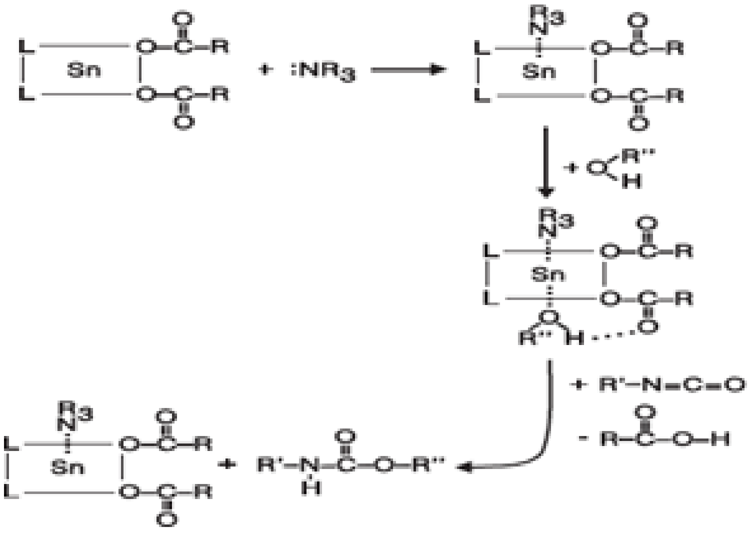
**Scheme 1.16.** First polymerization reaction with tin [54].

The secondary conceptual mechanism involves the activation of isocyanate molecules.



**Scheme 1.17.** Activation reaction of isocyanate molecules with tin [54].

When the polyol acts on the isocyanate carbon atom in this compound, the polymer begins to develop and the catalyst is regenerated. The final mechanism is formed by the combination of amine and tin catalyst. The amine and metal compound form a complex. When this complex accepts the polyol compound, an additional active complex is formed and tin alkoxide begins to form. The separated carboxylic acid salt protonates and creates a suitable piece for isocyanate binding. In the subsequent reaction, this complex forms the polymer with the polyol and regenerates the catalytic species [34, 35].



**Scheme 1.18.** Amine and tin mechanism [54].

### 1.4.8. Cross-Linking Agents

Crosslinking agents in flexible polyurethane foams are preferred for low molecular weight (hydroxyl or amine group) and for functionality 3 or greater than 3. Diethanol is the most commonly used amine and accelerates the viscosity development. It reduces foam hardness.

### 1.4.9. Additives

Additives such as colorants, UV stabilizers, flame retardants, anti-bacteria, plasticizers, cell openers, antistatic agents etc. are used in polyurethane foam applications.

## 1.5. Structure, Types and Properties of Foams

Polyurethane foams divided into two characteristic groups which are open-cell and closed-cell foams. The main difference between them is the cells of the polyurethane foams contact to each other in the open-cell whereas in the closed-cell foam does not touch. The cell structure of the foams is shown in Figure 1.14.

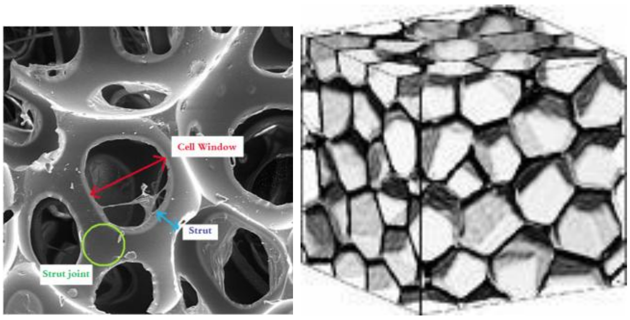


**Figure 1.14.** Open cell foam [41]. Closed cell foam [36].

Rigid polyurethane foams are closed cell. Polyols are branched and mostly aliphatic polyether polyols are used. Besides functionality of the polyols are higher than 8. Polymeric MDI is preferred with functionality equal to 2.5-3 [36]. They are used in insulation, buildings, refrigerators, decoration, etc.

Flexible polyurethane foams (PU) are produced in two general groups, which are the *Polyester Foams* and *Poyether Foams*. Type of the polyester foams appeared initially in 1952. The production process was complicated and expensive, the foam was unstable at different temperature and humidity conditions due to crumbled away [1, 6, 8, 12, 36-38]. Nowadays it covers only 3-5% of the flexible PU foams. Flexible PU foams were produced commercially in 1954 [1, 6, 8, 12, and 36]. Firstly, aromatic isocyanate reacted with the polyester polyol. Foam with the polyether polyol was developed to get better performance. Hence more durable, less affected by the hydrolysis and more durable foam was captured. Main difference of the two groups is higher tensile strength and longer elongation at break values for polyester foams. Polyether foams are much softer and more elastic that’s why it is the number one in the upholstery (furniture and bedding industry, mattresses, etc.). The continuous slabstock process is used to produce the most of the flexible PU foams. It has three sub groups that are conventional slabstock, high resilience (HR) slabstock and ester slabstock. Although flexible PU foams are not chemically different from the rigid PU foams; it has open cells. PU foams are used many application areas due to physical properties, excellent cushioning and ease of handling [37-40].

### 1.6. Flexible Polyurethane Foam Fire Behavior

PU is an organic material; natural flame will spread easily when it ignites. In 1998, 543 people died in the USA because of the fire accidents (11,600 fire events) results from the burning of upholstery furniture [41]. Consequently, PU foam fire behavior is important issue both economically and socially.

Flexible PU foam has porous structure that affects the fire behavior of the foam. Oxygen spreads into the cells and easily flame. This means morphology is the key parameter for better understanding the fire process. Figure 1.14 shows the SEM image of the cell window, strut and strut joins of the polyurethane foam without filler.

PU foam is a highly flammable material due to the used raw materials such as; isocyanate, polyol and catalyst systems. Besides density and hard segments content (urea) [42] and porosity are important and demanding property throughout the foaming process.

The foam density (water index) is most significant properties of the PU because it affects load bearing and cost values. If the foam has lightweight and is porous, flames spreads fast and foam has high thermal emission [43]. Therefore, combustion modified high resilience (CMHR) foams are the absolutely flame retardant since it contains polymer (presence of the solid particles) polyol [44, 45].

Various small-scale test methods are used to test fire behavior of the flexible PU. These test methods are British Standard (BS) 5852 part 2, Motor Vehicle Safety System 302, California 117A and 117D. Test methods are different from each other due to the foam sample size, source of heat, orientation and fabric (composite) presence used. In United Kingdom, there is legislation (1982) for the furniture and bedding industry to provide high safety. This legislation depends on the BS 5852 part 2, which is also known CRIB 5. Hence to provide this legislation, flammability additives are used in foam processing. The modified *PU foam is named Combustion Modified High Resilience (CMHR)* [45].

Polyurethane can fight flame down with different ways which are given below. According to the polyurethane structure and use of them, flame retardant can be used or polymer structure can be changed to resist fire.

Decrease in flame material

Decrease in air supplying

Increase in needed whole combustion process energy

Various flame retardants can be used according to one of the above categories. The flame retardants affect flame retardancy of polyurethanes depending on one of the following mechanisms [82].

The created free radical blocks reaction with flame and blocking flame spreading.

The oxygen diffusion is interrupted into the polymer.

Energy is moved from the system by lowering of the temperature of flame.

Char is formed between the polymer and area.

The free place and polymer expansion is formed between the fire and degraded polymer.

Halogenated phosphorus flame retardants act on flexible polyurethane combustion mechanism in gas phase. This is occurred by the emission of small radicals. The activity of fr materials is related to the dilution of flammable materials in the flame. It is also related to the isolation of OH and H radicals from the environment. Since these radicals react with flame exothermically.

$R_1X \rightarrow R_1 + X^\circ$ (Flame retardant decomposition)

$R_2H \rightarrow HX + R_2^\circ$ (Halogen radicals by reaction of fuel)

$HX + H° \rightarrow H_2 + X°$ (H radical trapping)

$HX + OH° \rightarrow H_2O + X$ (OH radical trapping)

The hydrogen halide obtained from the halogen phosphorus additive terminates the combustion reaction of polyurethane. The aim is to replace the less reactive halogen radical X by Hand OH radicals [74].

### 1.7. Polymer Polyol for Combustion Modified High Resilience Foams

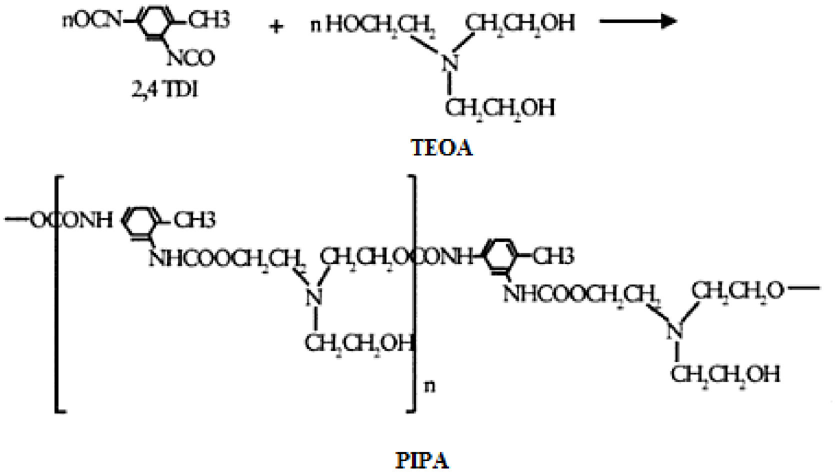
Polymer polyols are generally used for the molded and slabstock high resilience (HR) foams. They contribute to improvement of the cell opening of the high load bearing foams. HR foams have much more flammability performance compared to conventional foams. Hence they are succeeding in various flammability tests [47]. So-called combustion modified high resilience (CMHR) foams have been developed to pass severe BS 5852 Source 5 (CRIB 5) flammability test. This issue is provided via inclusion of solid filler, commonly used melamine, liquid flame retardant (FR) of the halogenated phosphorous-type or combination of both [48, 49]. As a consequence, dispersed particles of polymer polyols contribute to the flammability performance of the foam.

Three available (co)polymer polyol technologies are known as SAN (Styrene Acrylonitrile), PHD (PolyHarnstoff dispersion) and PIPA (PolyIsocyanate PolyAddition) each of them has their own advantages and limitations [15]. Throughout the years, solid levels in polymer polyol dispersion have been increased for higher hardness foam at various density range. Especially, SAN copolymer polyol (CPP) technology is the most apparent one. Providing these high hardness properties with combustion modified high resilience (CMHR) foam is challenging as the limitation of the raw material for the flammability performance will be rise by increasing of the SAN CPP amount [50]. Foam industry demands new flame retardants to reduce foam emission and extractable compounds and if it is possible eliminate the use of the halogenated flame retardant [51]. Not only flammability properties but also loads bearing capacity of the foam are important.

### 1.7.1. PIPA Polyol

There are three modified polyols. These are Polyvinyl-Modified Polyethers, PolyHarnstoff dispersion (PHD) and PolyIsopropylene adipate (PIPA) polyols, poly isocyanate addition. PolyIsocyanate PolyAddition (PIPA) is one of the polymer polyol which is the filled polyol. Synthesis of PIPA and PHD polymer polyols are very similar to each other. The only difference is instead of polyurea dispersion in PHD polymer polyol, polyurethane is gathered in liquid polyether polyol [52-54]. Formation reaction of PU involves an isocyanate and an alkanolamine reaction [55-62]. Mostly used alkanolamines are triethanol (TEOA) and diethanolamine (DEOA) [52-54] and diisocyanates used are toluendiisocyanate (TDI) and low functional methylenediisocyanate (MDI).

Generally, the reaction given below is much more ideal for the reaction of PIPA polyols synthesis.



**Scheme 1.19.** PIPA polyol reaction [68].

The hydroxyl group reactivity of the TEOA is lower than TDI. For the activation of PIPA production catalysts are used such as; stannous octoate and dibutyl tin diluarate (DBTDL) [59-67].

In general, the amine is poured into conventional polyol then diisocyanate (TDI or MDI) is added to polyol mixture with the addition of the above mentioned catalysts (0.05-0.1%) and for digestion, the mixture is stirred rapidly (one or two hours) until all the –NCO groups are consumed. Reaction temperature can be between 40 and 70 °C depending on the TDI amount. If the TDI amount is high, the increase in the temperature will be high [68, 69].

To prevent undesired crosslinking, high viscosity and big molecule formation TEOA and TDI ratio can be adjusted as [70]:

TDI: TEOA $\leq 1$

TDI: TEOA $\approx 0.6:1$ (for the high solid content)

If the solid content is 50% there is no need for the use of the tin catalyst for the TEOA activation [58, 59, and 71]. However tin catalyst should be used for the activation when the solid content is around 10-20% [68]. When PIPA polyol is used; the hardness, tensile strength and tear strength properties of the flexible PU foam increases. The flexible PU foam with the PIPA polyol is better than the PU by the unfilled polyol. Also flammability and recyclability of the PU foam increases.

PIPA polyol can also be synthesized by the glycols:

TDI + Glycols → PIPA

$\text{nOCN-R-OCN+nHO-}C_2H_4OC_2H_4\text{-OH} \rightarrow \text{-[OCNH-R-NH-}CO_2\text{- }C_2H_4OC_2H_4\text{-O]-}$

Unfortunately, this reaction causes high viscosity for PIPA polyol. For this reason, reaction with TEOA or DEOA is used at industry [70].

PIPA Polyol is typically produced and used by the foam manufacturer having patent licenses. Process up to 80% solid content is represented [72]. Production of the PIPA takes place in the static mixer and continuously stirred reactor. Scheme for PIPA polyol synthesis process is shown in Figure 1.15.

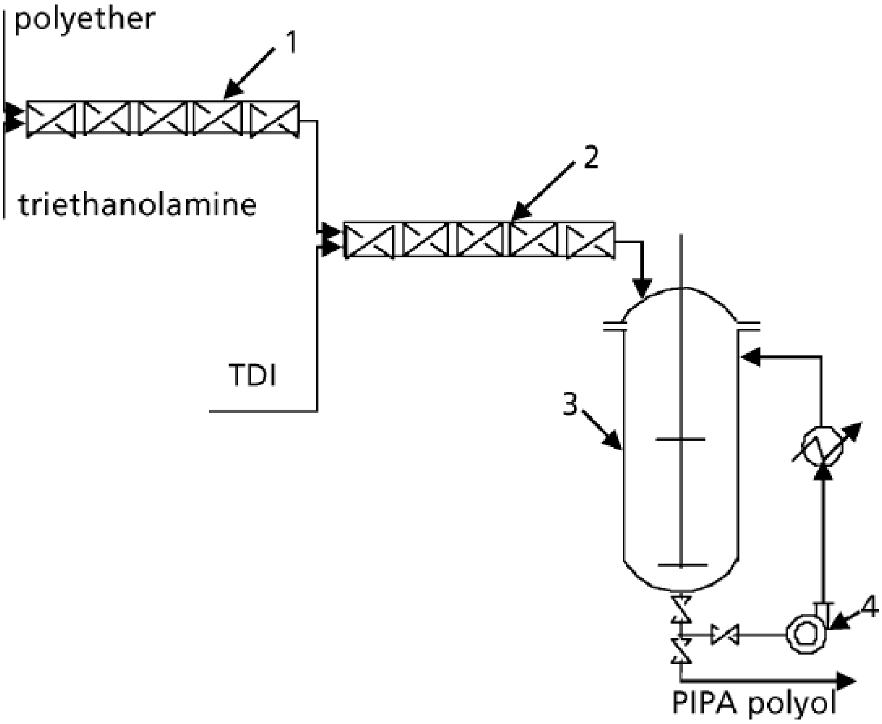


**Figure 1.15.** Technological scheme for PIPA polyols synthesis (variant). 1) Static mixer for polyether with triethanolamine (TEOA); 2) Static mixer for the reaction of TEOAwith TDI; 3) Loop reactor with total recirculation; 4) Recirculation centrifugal pump [57].

PIPA Polyols have some draw backs such as shrinkage of the foam and scorching. Nevertheless, it is successful for the production of the flexible PU foams and high resilience (HR) foam.

## 1.8. Literature Survey

The flammability of the flexible polyurethane foams with a combination of halogenated phosphate type flame retardant and with solid filler melamine or without melamine was studied by Lefebvre and Le Bras [46]. Lefebvre and Le Bras have suggested that an FR material which decomposes and evaporates early should be preferred if melamine does not used. This provides not only flame dilution but also scavenging of H° and OH° radicals. It restricts combustion of the flexible polyurethane foam. They used 10% weight hard segment Polyisocyanate Polyaddition (PIPA) Polyol. Also, they preferred two types of halogenated phosphorus flame retardants that are Tris (1, 3-dicholoroisopropyl) phosphate (TDCP) and Tris (2-chloropropyl) phosphate (TMCP). TDCP with melamine showed better results than TMCP. In the without melamine modified polyurethane, TDCP and TMCP showed almost the same characteristics, whereas TDCP had a lower total weight loss (TWL) and burn time.

The TDCP is used mostly in flexible polyurethane foams in the literature. Batt and Appleyard have developed combustion modified polyurethane foam using PHD, PIPA and SAN Polyol. They stated that PHD and PIPA Polyol requires less halogenated phosphorous flame retardant than SAN Polyol. In their study, melamine amount was decreased by the usage of halogenated phosphorus FR [85].

Cookson et al. have studied combustion modified high resilience foam with PIPA Polyol and melamine. When the PIPA polyol was reduced, the tear resistance was weakened and the compression set value at 75% improved positively. Not only that, but also the non-combustible foam was trialed using only melamine. However, this product failed at the flammability test. In addition, the foam did not attend using only PIPA polyol in their experiment. When both melamine and halogenated flame retardant were used, the physical properties were affected negatively. Since the PIPA polyol were higher than 65% parts per hundred parts of polyol (pphp) [84].

### 1.9. Aim of the Work

The most important aim of this study is to prepare *Combustion Modified High Resilience foam (CMHR).* In this study, it is aimed to better understand the burning behavior of PU foam by studying flammability of melamine free modified foam. CMHR with high resilience will be prepared. In addition to this, the number of studies using PIPA polyol in the literature is inadequate. Furthermore, this new generation PIPA polyol will be used in this study for the first time. Usually, melamine and flame retardant materials use together in fireproof foams to obtain desired properties. The aim of this study is to obtain the same properties without the support of melamine. Moreover, 60 pphp PIPA polyol with 20% weight hard-segment will be used in this study whereas in the literature 100 pphp PIPA polyol with 10% hard segment is used.

For this purpose, firstly, PIPA polyol solid content to produce modified PU is optimized. PIPA polyol not only improve physical properties of PU foam but also contributes fire retarding. For the first aim, PIPA polyol hard-segment is chosen as 20% by weight.

Secondly, different PIPA polyol and flame retardant ratios are conducted to produce the PU foam for lab (box) and tunnel trials. PU foam formulation is optimized to obtain work foam. For the formulation of PIPA, flame retardant ratios are the most significant factors affecting flexible PU foam characteristics.

Thirdly, physical properties such as density, hardness, tensile strength, elongation at break and deformation, of PU are investigated. Finally, BS 5852 Part 2 (CRIB 5) test is conducted to determine flammability characteristics of PU foam the mass loss has to be ≤ 60g at the end of CRIB 5 test.

The fourth and last aim of the study is to investigate, its thermal characteristics via thermogravimetry analyses (TGA). After characterization by TGA, ‘’direct pyrolysis mass spectrometry’’ (DPMS) techniques is used to complete thermal analyses.

# CHAPTER 2

# EXPERIMENTAL

The second chapter includes the materials and test machinery used in this study. Theory of analyses for the prepared specimens is also included.

## 2.1. Materials Used in the Study

In this study, raw materials, catalysts, stabilizers, additives and flame retardants are used to synthesize PU flexible foam.

### 2.1.1. Toluene Diisocyanate (TDI)

Toluene Diisocyanate (TDI) is produced by The Dow Chemicals Company. Commercial name is VORANATE* T-80 Type I TDI. Toluene diisocyanate (TDI-80) is 80:20 mixtures of 2,4 and 2,6 isomers (2,4-isomer/2,6-isomer = 80/20) of TDI. TDI is a highly toxic chemical.

### 2.1.2. Tris(2-chloroisopropyl) Phosphate

Tris (2-chloroisopropyl) phosphate (TCPP) is one of the most commonly used halogenated liquid flame retardant and produced by ICL Industrial Products. Commercial name is FYROL PCF LO. At ambient temperature, it is clear, colorless and not volatile. TCPP is used for producing rigid and flexible polyurethane foam.

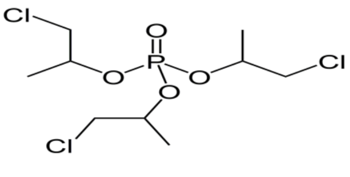


**Figure 2.1.** TCPP, Tris(1-chlor-2-propyl) phosphate.

### 2.1.3. High Resilience (HR) Foam Polyol

VORALUX* HF 505 Polyol is the high resilience (HR) foam polyol and provides HR specialities to PU foam. The hydroxide number (OH number) is equal to 29.5 mg KOH/g and water content is 0.05%. The producer of the raw material is The Dow Chemicals Company. The dynamic viscosity of the polyol is 1600 mPa.s at 25 °C.

### 2.1.4. Cell Opener Polyol

VORANOL* CP 1421 Polyol DA is used for soft and hyper soft flexible slabstock polyether foam polyol. Supplier of the polyol is The Dow Chemicals Company. It is initiated by glycerine and is a polyether polyol. The polyol is a polyether triol. The hydroxide number (OH number) is equal to 33mg KOH/g and water content is 0.05%.

### 2.1.5. Amine and Blowing Catalyst

DABCO ® BL-11 Catalyst is manufactured by the Air Products and Chemicals, Inc. The composition of the catalyst is 70% Bis (2-dimethylaminoethyl) and 30% ether Dipropylene glycol. It is a tertiary amine and a blowing catalyst. The hydroxide number (OH number) is equal to 251mg KOH/g.

### 2.1.6. Amine Catalyst

DABCO 33 LV ® Catalyst is a soluble tertiary amine and supplied by the Air Products and Chemicals, Inc. It is composed of 33% triethylene diamine (TEDA) and 67% dipropylene glycol. The hydroxide number (OH number) is equal to 558 mg KOH/g.

### 2.1.7. Amine

DIETHANOLAMINE (DEOA) LOW FREEZING provides stability, acts as a catalyst and generates cross linking. It contains 85% N, N-diethanolamine and 15%

water. It is produced by The Dow Chemicals Company. The OH number is 1362 mg KOH/g.

### 2.1.8. Cross Linker

ORTEGOL® 204 is a cross linking agent. It helps to cool the flow during the flexible PU HR production. Ortegol 204 is supplied by the Evonik. The hydroxide number (OH number) is equal to 860mg KOH/g and water content is 25%.

### 2.1.9. Water

Demineralized water is used throughout this study.

### 2.1.10. Polyisocyanate Polyaddition (PIPA) Polyol

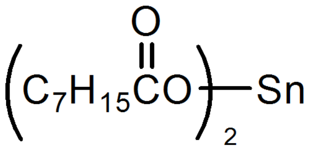
Commercial name of Polyisocyanate - Polyaddition (PIPA) Polyol is XZ 1101. It has 20% solid content. Manufacturer is The Dow Chemicals Company. It is designed for the HR and CMHR foams that have broad density and hardness ranges. The polyol design criteria are summarized in Table 2.1.

**Table 2.1.** Polyol design criteria.

| Property | Units | Target |
|---|---|---|
| Catalyst | | Organo-tin free |
| Solids content | % | min. 20 |
| Viscosity @ 25 °C | mPa.s | <4000 |
| Particle size | µm | <5 |

### 2.1.11. Tin Catalyst

Stannous octate is Tin(II) 2-ethylhexanoate. It is a polyaddition catalyst produced by SIGMA-ALDRICH.



$$(C_7H_{15}C(=O)O)_2Sn$$

**Figure 2.2.** Structure of Stannous Octoate.

### 2.1.12. Zinc Catalyst

Commercial name of zinc catalyst is KOSMOS® 54 and helps to cool the flow of the flexible PU foam supplied by the Evonik and also uniforms the density distribution.

### 2.1.13. Silicone

TEGOSTAB® B 8783 is a HR silicone and cell stabilizer supplied by the Evonik. it is used in combination of co-polymer polyols such as; PIPA, PHD polyols. B 8783 is prepared from organo-modified polysiloxanes.

## 2.2. Preparation of Combustion Modified High Resilience Foam (CMHR)

In this part, PU foam preparation is represented. The basic principles of the production were applied by the lab-scale cup-foaming and then developed by the slab stock production method.

### 2.2.1. Lab-Scale Cup-Foaming

Lab-Scale Cup-Foaming is a crucial part of polyurethane foam research and development. Foam samples were prepared in SAFAS SAF PLASTIK A.Ş. Research and Development Laboratory (Ankara). All stages of the foaming process were carried out in a conditioned lab (23±2°C and 50±5% relative humidity) and in a laboratory fume hood because of the toxicity of the isocyanates. Before using all the chemicals were allowed to equilibrate at room temperature.

The processing of the foam was done by blending of TDI and XZ 101 according to the following steps in Figure 2.3.

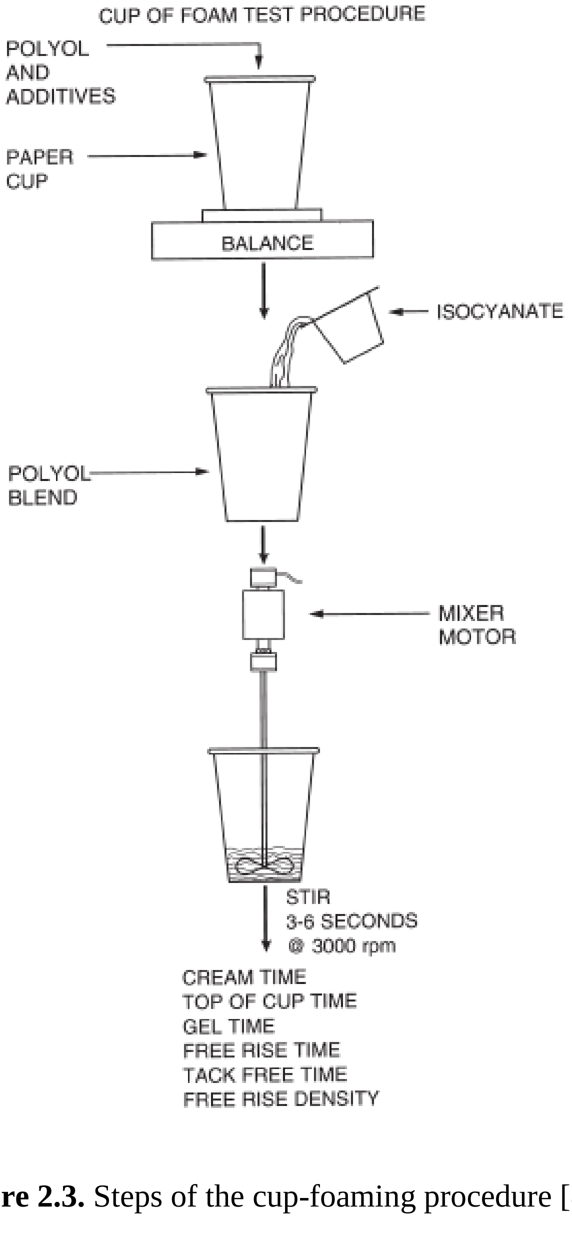


**Figure 2.3.** Steps of the cup-foaming procedure [8].

The lab-scale cup-foaming experiments were conducted several times until the best results were captured. Firstly, DEOA, ORTEGOL 204, liquid FR, KOSMOS 54, tertiary amine, TEGOSTAB B 8783 and adequate water were added using syringes into HF 505, CP 1421, PIPA XZ 101 Polyol mixture and then they were blended smoothly in paper cup for 45 seconds in a 3000 rpm mixer. Secondly, tin commercially named as SO was added into the polyol blend. After premixing, TDI was added to the paper cup and blended for an additional 3-6 seconds up to a cream time that means material volume started to rise and the final blend was poured into a box where the foam expanded. Then foam was cured in an oven at 80°C for 10 minutes and it was removed from the cardboard box. Several samples were prepared to get the best results. The foam was placed for 48 hours in a conditioned room at 23±2°C and 50±5% relative humidity to ensure the curing of the foam.

### 2.2.2. Slab Stock Production

Slab stock foams are the largest volume of flexible PU foam production which present for 70% of the foam volume [43]. Trial productions were carried out in SAFAS SAF PLASTIK A.Ş. production line by the LAADER BERG MAX FOAM Machine 2020 shown in Figure 2.4.

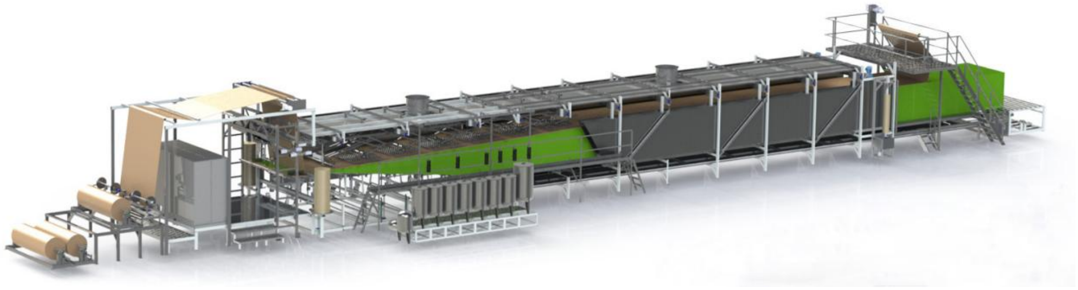


**Figure 2.4.** Laader berg max foam machine 2020 [80].

Max Foam Machine includes an inclined five fall plate (FP) and a moving conveyor with sidewalls. Paper feed were maintained to bottom line and sidewalls of the conveyor by brown paper. To exhaust the gases produced during the PU foam production, the conveyor and mixing head placed in a ventilated tunnel. Block cutter of the slab stock into foam buns is placed at the end of the tunnel and then it is moved to curing area by lift trucks. In Table 2.2 formulations of the trial productions are stated.

**Table 2.2.** CMHR formulations for slab stock production.

| | **7** | **8** | **9** |
|---|---|---|---|
| **Components** | **pphp*** | **pphp** | **pphp** |
| VORALUX HF 505 | 40 | 40 | 40 |
| XZ 1101 | 60 | 60 | 60 |
| VORANOL CP 1421 | - | - | 2 |
| Fyrol PCF-LO | 10 | 10 | 10 |
| NIAX A-1 | 0,06 | 0,06 | 0,06 |
| DABCO 33LV | 0,12 | 0,12 | 0,12 |
| DEOA (85%) | 0,8 | 0,7 | 0,7 |
| Ortegol 204 | 1,5 | 1,5 | 1,5 |
| Tegostab B8783 LF2 | 0,3 | 0,3 | 0,3 |
| Kosmos 54 | 0,3 | 0,3 | 0,3 |
| SO | 0,08 | 0,08 | 0,08 |
| Water added | 1,83 | 1,83 | 1,83 |
| Total water | 2,38 | 2,36 | 2,36 |
| TDI | 35,5 | 35,1 | 35,1 |

*pphp: Parts (by weight) per hundred parts of polyol.

The CMHR PU raw materials as illustrated in Table 2.2; TDI, poly- ols, water, catalysts, surfactants and flame retardant were stored in tanks and then their streams were metered to the mixing head, that is usually a spinning cylindrical drum with mixing pins or blades, which fully mixes all the incoming streams. All mixed streams were poured to the moving conveyor belt with 3.5 m/sec conveyor speed by low pressure production machine by mixer speed at 4000 rpm and with air injection at 1.1 bars. Then mixer pressure was adjusted to 2 bars. When passing through a wellventilated conveyor belt, they were produced as continuous slabs (or “loaves” or “buns”) which polymerized and cured (Figure 2.5.).

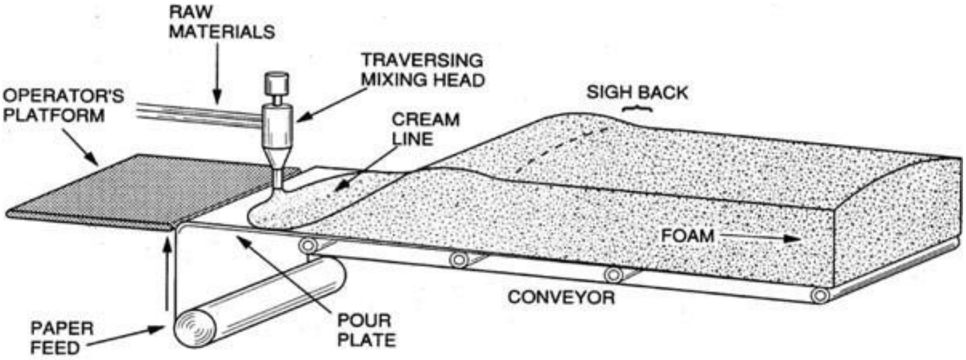


**Figure 2.5.** Slab foam production. Images courtesy of Dow Chemical Company.

### 2.3. Characterization Techniques

### 2.3.1. Structural Properties of Foams

All foams are described by foam type, density (kg/m$^3$) and hardness (N or kPa). For the density and hardness of a chosen material, the respective requirements for support factor, resilience, compression set, thickness and hardness loss by fatigue, tensile strength, elongation at break and recovery time (only viscoelastic foam) should be met. Any change in the recipe is re-tested.

### 2.3.1.1. Density

The density **(ρ)** which is apparent overall density or core density defines kilogram per cubic meters of the test specimens, is measured by the below formula. The PU foam density (kg/m$^3$) is the most significant physical property and also the primary factor affecting the quality and performance of foam.

$$\rho = \frac{m}{V} X 10^6 \qquad (Eqn. 1)$$

m is the mass of test specimen, in gram

v is the volume of test specimen, in cubic millimeter

The density of the foam material is determined according to *ISO 845 (ASTM D3574-A DIN 53420, JIS K6400-5*). After conditioning standardized ambient conditions (23 ºC, %50 RH, PU foam shall be kept 72 hours before the cutting specimens. If the density loss is less than 10%, this period may be reduced to 16h or 42h dimensions. At least three separate measurement of the specimen, in millimeters, are recorded and the mean value of each dimension is recorded to calculate the volume. Weight of the test specimen is measured in grams and the density is expressed as kg/m$^3$.

Note: The density according to EN ISO 845 refers to net density, and not gross density which is also used for suppliers. Gross density includes surface part of the foam.

### 2.3.1.2. Resilience

The resilience of the foams was measured in a ball rebound test according to *ISO 8307 (ASTM D3574-D, DIN 4651, JIS K6400-9B).* The ball resilience test apparatus as illustrated in Figure 2.6 consists of a 30 mm to 60 mm inside diameter transparent tube and 16±0.5mm diameter and 16.8 ±1.5 g

steel ball. The steal ball was dropped 556 mm above surface of the test piece on 100*100*50 mm foam test specimen visually measuring the height of rebound. The same procedure was performed at least three rebounds. For each test, mean of the three rebound height values was determined and result was obtained in percentage unit. The results of this test describe one factor of cushion comfort.

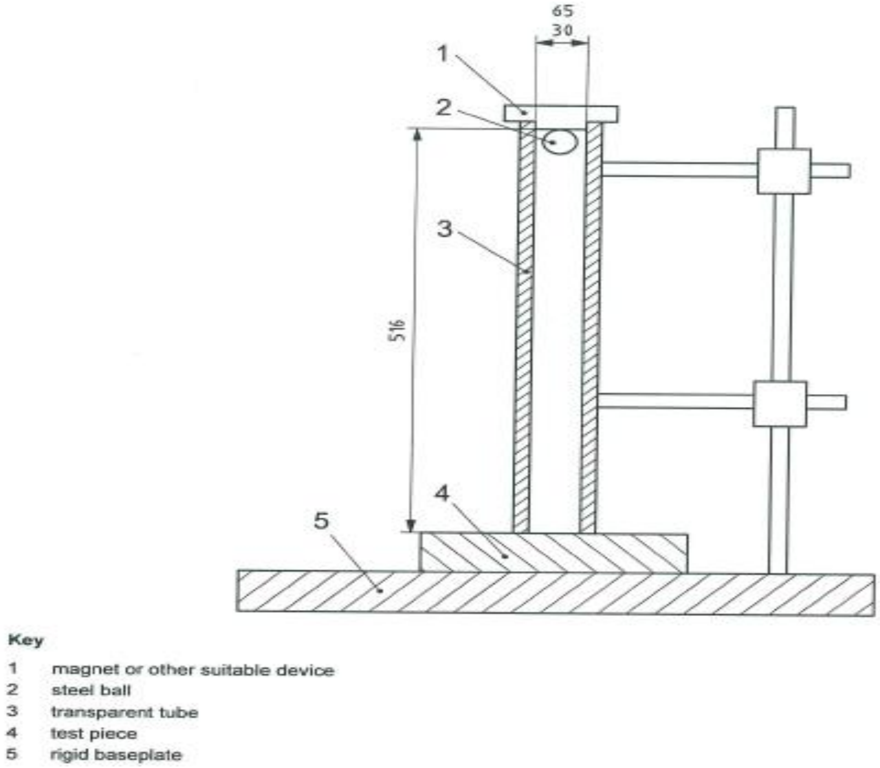


**Figure 2.6.** Test apparatus [81].

### 2.3.1.3. Compression Test

The compression test describes the change in thickness of a statically compressed foam sample after being stored and is defined as compression set. The test is done according to *ISO 1856, Method A (ASTM D3574-D, JIS K6400-7).* The sample should be compressed by 75% and preferably to 90% of its original thickness. It is already stated in the standard. After conditioning (at least 16h) five test specimens, 50±1mm square sized and 25±mm thickness was prepared. The thickness of the specimen ($d_0$) was measured as stated in ISO 1923 before stored. Test specimens, not in contact with each other, were placed and compressed to 75% and 90% of the original values on a compression device. The compression device consists of two parallel plates by the help of bolts or clamps. The compression device with specimens was stored in an oven at 70±2 $^0$C for a period off 22h. After 22 hours, compression device was removed and the final thickness of the test specimens were measured and given in Eqn. 2.

$$Compression\ Set = \frac{d_0 - d_r}{d_0} \times 100 \qquad (Eqn. 2)$$

where

$d_0$: the original thickness of the test specimen, in millimeters;

$d_r$: the thickness of the test specimen after compression, in millimeters.

**Figure 2.7.** Schematic representation of compression test.

Note: For a compression level of 90 %, maximum compression set is 90 %.

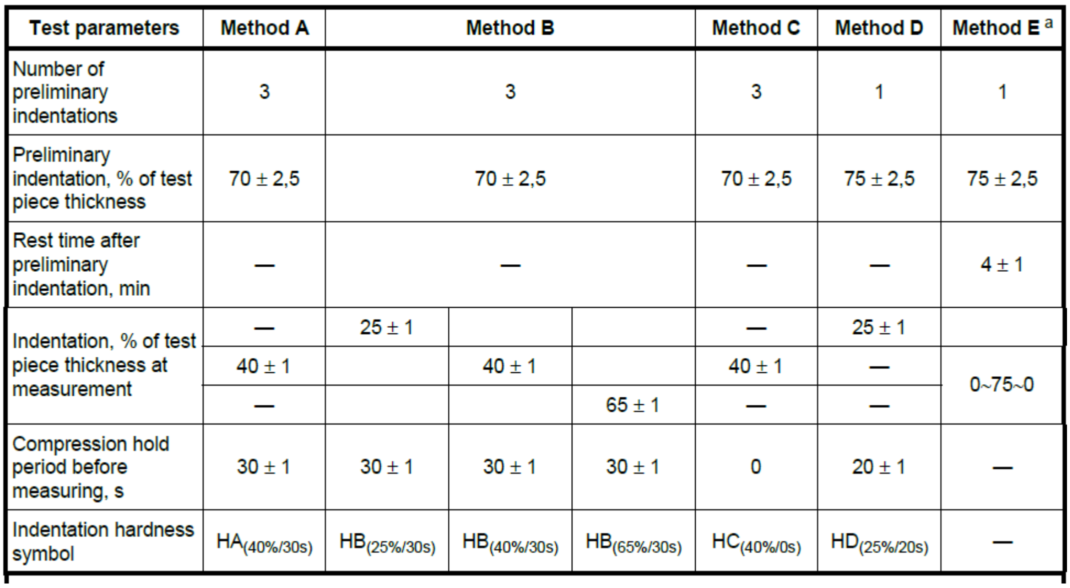
### 2.3.2. Mechanical Analysis

The mechanical analysis includes hardness and tensile strength of the flexible polyurethane samples at given standards and environmental conditions**.**

#### 2.3.2.1. Hardness

The *indentation hardness*, which is total force needed to produce specific indentation for test piece, test measures the ability of flexible porous materials to withstand loads. *ISO 2439* international method indicates four methods A to D to find indentation hardness and another one is method E, compressive deflection coefficient and hysteresis loss parameters are tabulated in Table 2.3.

**Table 2.3.** Parameters of test methods



| Test parameters | Method A | Method B | | | Method C | Method D | Method E [a] |
|---|---|---|---|---|---|---|---|
| Number of preliminary indentations | 3 | 3 | | | 3 | 1 | 1 |
| Preliminary indentation, % of test piece thickness | 70 ± 2,5 | 70 ± 2,5 | | | 70 ± 2,5 | 75 ± 2,5 | 75 ± 2,5 |
| Rest time after preliminary indentation, min | — | — | | | — | — | 4 ± 1 |
| Indentation, % of test piece thickness at measurement | — | 25 ± 1 | | | — | 25 ± 1 | |
| | 40 ± 1 | | 40 ± 1 | | 40 ± 1 | — | 0~75~0 |
| | — | | | 65 ± 1 | — | — | |
| Compression hold period before measuring, s | 30 ± 1 | 30 ± 1 | 30 ± 1 | 30 ± 1 | 0 | 20 ± 1 | — |
| Indentation hardness symbol | HA$_{(40\%/30s)}$ | HB$_{(25\%/30s)}$ | HB$_{(40\%/30s)}$ | HB$_{(65\%/30s)}$ | HC$_{(40\%/0s)}$ | HD$_{(25\%/20s)}$ | — |

The foam hardness is measured according to *ISO 2439, Method B (40 % IFD), ISO 3386-1. (ASTM D3574-B, DIN 53576, JIS K6400-K).* Energy difference between the loading and unloading of a test piece under cyclic deformation is defined hysteresis loss rate. After conditioning, as given in ISO 23529, the hardness test was applied to each specimen $380^{+20}_{-0}$ square sized and 50±20 mm thickness at a crosshead speed of 100±20 mm/min, with a 5 kN load cell by Devotrans Instruments shown in Figure 2.8.

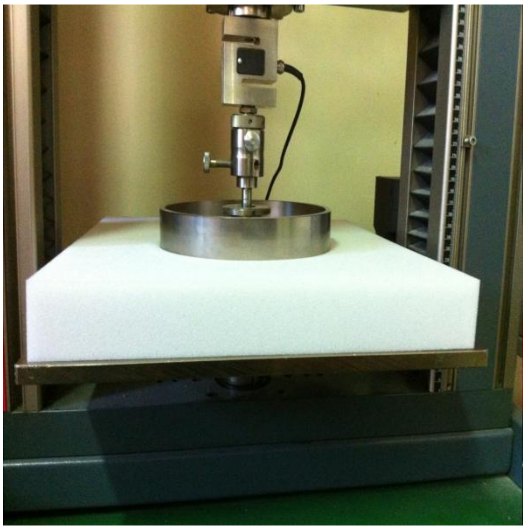


**Figure 2.8.** Schematic representation of indentation hardness machine.

Firstly, force was applied to produce an indentation of 70 ± 2.5% thickness. Then, the force was removed at the same rate. This method was repeated twice more. Secondly, 25 ± 1% of the thickness of the test piece was indented and maintained this indentation for a period of 30 ± 1s. Force required was measured. Same procedure was applied to 40 ± 1 % and 65 ± 1 % of the test specimens' thickness and force needed was recorded. Indentation force at 40 ± 1% is the hardness of the test specimen. Graphical representation for detecting indentation force for Method B is given in Figure 2. 9.

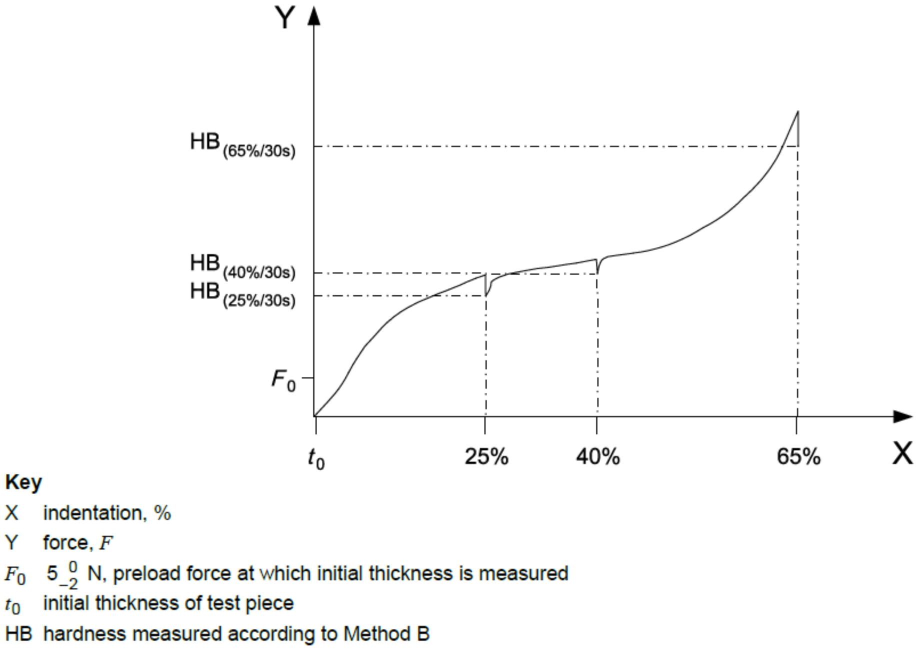


**Figure 2.9.** Sample force-indentation graph using Method B.

#### 2.3.2.1.1. Support Factor (SAG)

The support factor (SAG) is a compressive deflection coefficient ratio of the 65 % indentation force deflection to the 25 % indentation force deflection *(ISO 2439 or ISO 3386-1: 65%IFD to 25%IFD)* at indentation hardness test (Eqn. 2). This number indicates cushioning quality. Higher support factor (>2.4) means better cushioning comfort. Especially, for CMHR it is very important to make a decision for cushioning comfort.

$$SAG\ factor\ (Sf) = \frac{65\%IFD}{25\%IFD} \qquad (Egn. 2)$$

### 2.3.2.2. Tensile Strength and Elongation at Break

This test measures the strength of the foam at break according *to ISO 1798 (ASTM D3574-E, DIN 53571, JIS K6400-10).* After conditioning in accordance with *ISO 23529*, the preparation of the Type 1 (ISO 1798) specimen in hydraulic press; dog-bone shaped five samples were cut carefully from these specimens as shown in Figure 2.10 and were exposed to tensile loading test by Devotrans Instruments at a crosshead speed of 500±50 mm/min, with a 2 kN load cell.

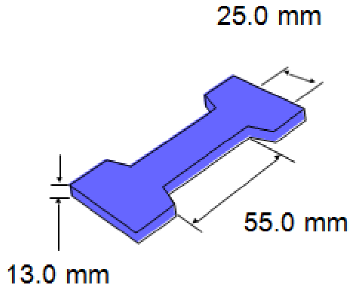


**Figure 2.10.** Schematic representation of dog-bone specimen.

The tensile strength (TS) of each specimen was expressed in kPa, is given by the Egn. 3.

$$TS = \frac{F}{A} x10^3 \qquad (Eqn. 3)$$

where

*F* is the maximum force, in newtons;

*A* is the average initial cross-sectional area, in square millimeters.

The prepared specimens of elongation at break were centered between the apparatuses (jaws) of the Devotrans Instruments and the distance between the two jaws were set to 95 mm. The elongation at break, $E_{b,}$ expressed as a percentage of the gauge length, is given by the Eqn. 4.

$$E_b = \frac{L - L_0}{L_0} \times 100 \qquad (Eqn. 4)$$

where

$L$ is the gauge length at break, in millimeters;

$L_0$ is the initial gauge length, in millimeters.

### 2.3.3. Thermal Analysis

Thermal analysis is a group of methods in which the physical properties of a material are measured as a function of temperature when applied to a controlled temperature program.

#### 2.3.3.1. Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) were carried out by the Perkin Elmer Instrument STA6000, heating of the 5 mg sample from room temperature to 600ºC at a 10 ºC/min rate. This was occurred under inert medium by continuous nitrogen flow which was 20 mL/min rate. Thermal stability of the prepared foam was tested by the TGA.

#### 2.3.3.2. Direct Pyrolysis Mass Spectrometry (DPMS)

Direct pyrolysis mass spectrometry (DPMS) analyses were performed 5973 HP quadruple mass spectrometry system, which with a mass interval of 10-800 Da, coupled to a JHP SIS direct insertion probe. At the pyrolysis, all samples heated to 450ºC at a 10 ºC/min rate and maintained at 450ºC additionally 5 minutes. In the pyrolysis, 70 eV EI mass spectra was with a rate 2 scan/s, was occurred when it recorded. All the samples are tested at least twice to make sure reproducibility of results.

### 2.3.4. Flammability Analysis

Flammability of flexible PU samples was tested by BS 5852: Part 2 - Source 5 which is English standard for CMHR particularly.

#### 2.3.4.1. CRIB 5 BS 5852: Part 2:

Flammability analysis was performed according to *BS 5852: Part 2 1982* which is the first version of standard and revised two times in 1990 and 2006 years. The experimental set up depends on the provided ignition energy source. For PU foam Ignition Source 5 which is also known CRIB 5 is used. CRIB 5 consists of a frame of 20 dry soft sticks of Pinus silvestris (Scots pine) and soft lint at bottom side. Foams were passed with 75% organic fiber fabric over the product and measured the weight of the prepared assembly in grams. The CMHR samples were placed seat assembly on a grid-like metal rig which were hinged together at right angles to each other. The Crib 5 apparatus was centered at intersection of base and back of prepared seat assembly. Seat Assembly of BS 5852 Part 2 and Crib 5 Apparatus is given in Figure 2.11. 1.4 mL of isopropyl alcohol was injected into the Crib 5 apparatus [42, 43]. The whole seat assembly was put on the weighted balance to measure the dynamic weight loss. Then crib was ignited.

Crib 5 is flamed. After the flame completely extinguished, weight of assemble was measured. The validity of the test was determined by evaluating the difference in weights before and after combustion. The weight loss should not exceed 60g [42].

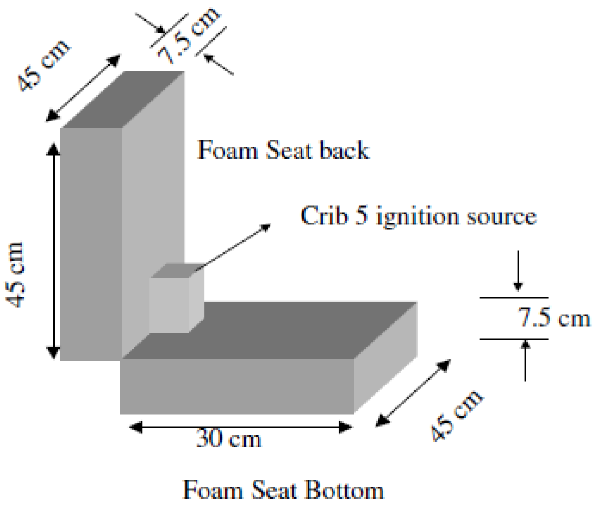


**Figure 2.11.** Seat Assembly of BS 5852 Part 2 and Crib 5 apparatus [74].

# CHAPTER 3

# RESULTS AND DISCUSSION

The third chapter of this dissertation submits the structural properties, mechanical, thermal properties and flame retardancy of the modified high resilience polyurethane.

## 3.1. Structural Property Testing Results

To determine structural properties of polyurethane density, resilience and compression set tests are performed and results are tabulated. Customers first test the density of the polyurethane foam. Therefore, mattress and furniture manufacturers must also check the density. Density was measured as shown in Figure 3.1. The density increases top to bottom due to gravitational force.

Density value is the key parameter of the performance of foam in terms of comfort, support and durability. High density foam supports the weight better because it is manufactured with more materials. Its capacity to carry weight is excessive. For the mattress application density is much more important. For example, when a person lies in the bed, the bed has to be carried. This means that the bearing force of the higher density will be better.

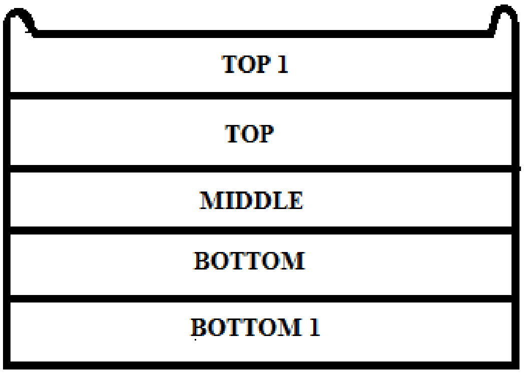


**Figure 3.1.** Density measurement in polyurethane block.

**Table 3.1.** Density & Resilience of samples.

| CMHR | PU-000 | PU-007 | PU-008 | PU-009 |
|---|---|---|---|---|
| **Top dns (kg/m³)** | 33,33± 1,5 | 37,39± 1,5 | 38,08 ± 1,5 | 38,49 ± 1,5 |
| **Top-1 dns (kg/m³)** | 33,68± 1,5 | 37,98± 1,5 | 38,18 ± 1,5 | 38,29 ± 1,5 |
| **Middle dns (kg/m³)** | 33,99± 1,5 | 38,62± 1,5 | 38,71 ± 1,5 | 38,68 ± 1,5 |
| **Bottom dns (kg/m³)** | 34,56± 1,5 | 39,05± 1,5 | 39,25 ± 1,5 | 39,28 ± 1,5 |
| **Bottom-1 dns (kg/m³)** | 34,62± 1,5 | 39,12± 1,5 | 40,18 ± 1,5 | 41,46 ± 1,5 |
| **Mean** | 34,04 | 38,43 | 38,88 | 39,24 |
| **Ball Resilience (%)** | 60 | 64 | 64 | 66 |

Density tolerance values are -7%/+15% kg/m³. For the reference polyurethane density 35 kg/m³ modified test values should be between 32,55 and 40,25 kg/m³. Also, density distribution is very important to prevent densification of the polyurethane foam. For example, top density of PU-007 is 33,68 kg/m³, middle density is 33,99 kg/m³ and bottom is 34,56 kg/m³. This distribution was acceptable. After analyzing top to bottom density results, density of the modified polyurethanes foams was increased nearly 14% which is 38,8 kg/ m³.

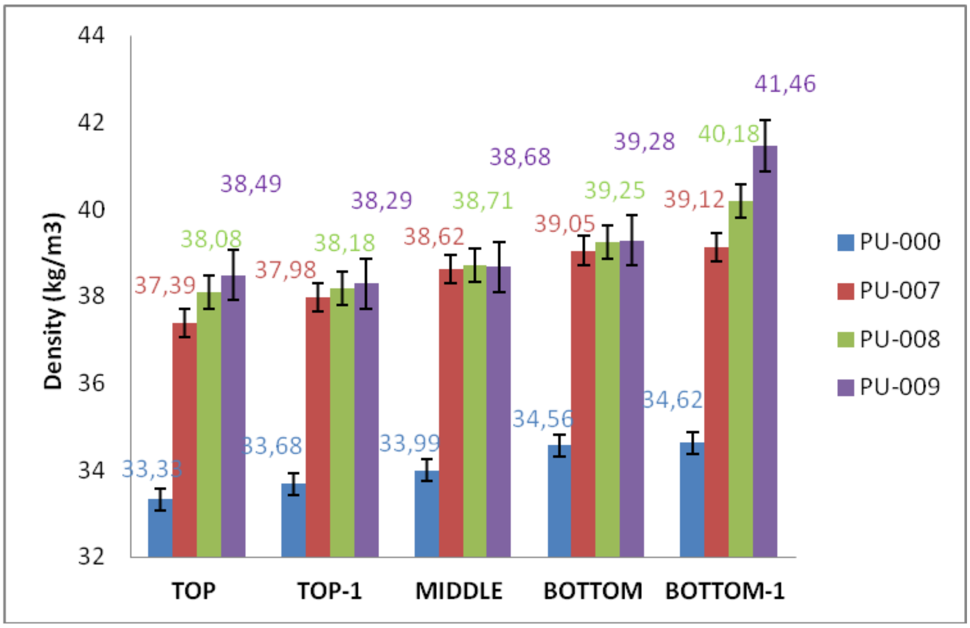


**Figure 3.2.** Density of PU-000, PU-007, PU-008 and PU-009.

Resilience is a measurement of surface elasticity and springiness. The elasticity of foam is measurement of comfort. Softness and elasticity is crucial for upholstered furniture.

Density, resilience and compression values were increased. Since the resilience is the important property for HR foam, this increase in resilience was ideal. Also, compression test results were given in table 3.2. Compression values increased nearly 15%.

**Table 3.2.** Compression Test results.

| **CMHR** | **PU-000** | **PU-007** | **PU-008** | **PU-009** |
|---|---|---|---|---|
| Compression Set 75% (%) | 9.65 | 10.73 | 11.29 | 11.32 |
| Compression Set 90% (%) | 13.5 | 15.57 | 19.99 | 19.8 |

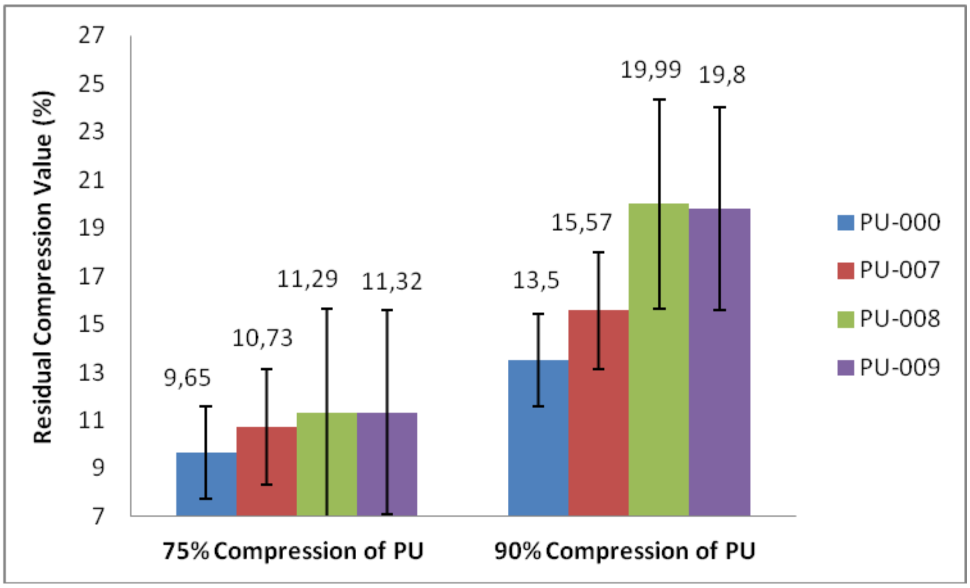


**Figure 3.3.** Residual Compression Value of PU-000, PU-007, PU-008 and PU-009 at 75% and 90% compression of PU.

### 3.2. Mechanical Test Results

This section covers the results of the mechanical tests. The Hardness, tensile strengths and percentage elongation at break values of the samples are tabulated and discussed. Stress-strain and hardness graphs were given in Appendix A.

#### 3.2.1. Hardness

Hardness directly affects comfort of furniture foam whereas it is not important for the upholstery. Since the thickness of the upholstered furniture is thinner. So, low or high hardness level will not affect the surface contact or sense of the foam. If support factor is high, foam is more comfortable. In load carrying applications like cushions, 2 or higher support factors are appropriate. As given in Table 3.3 hardness of the CMHRs decreased. IFD 40% is used to compare the hardness values. As, DEOA which has 1362 OH number (mg KOH/g) was used in modified PU foams, this caused hardness loss of foam samples. For the combustion modified polyurethane foams hardness is not critical. Because, for them flammability is more important. Obtained test results were acceptable.

**Table 3.3.** Hardness of samples.

| CMHR | PU-000 | PU-007 | PU-008 | PU-009 |
|---|---|---|---|---|
| IFD 25% (N) | 164,1 ± 2 | 118,4 ± 2 | 129,7 ± 2 | 123,7 ± 2 |
| IFD 40% (N) | 210,7 ± 2 | 161,6 ± 2 | 167,8 ± 2 | 167,5 ± 2 |
| IFD 65% (N) | 467,3 ± 2 | 397,7 ± 2 | 348,6 ± 2 | 388,4 ± 2 |
| IFD SAG | 2,85 | 3,36 ± 2 | 2,69 ± 2 | 3,14 ± 2 |
| IFD Hysteresis (%) | 41,88 | 32,31 ± 2 | 32,09 ± 2 | 32,46 ± 2 |

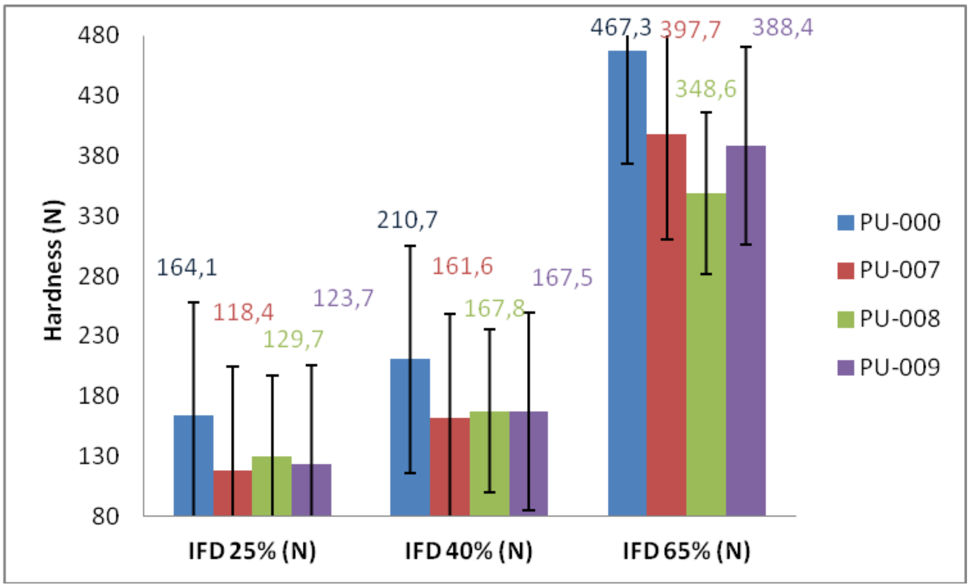


**Figure 3.4.** Hardness of PU-000, PU-007, PU-008 and PU-009 at IFD 25%, IFD 40% and IFD 65%.

### 3.2.2. Tensile Strengths

Tensile strength value plays an important role especially in field require endurance of foam like furniture sector. The effect of combustion modified additives on mechanical properties of PU HR foam was performed by the measurement of the universal tensile testing method according to ISO 1798 standards. Tensile measurements of each sample were carried out at least three times and the average values are given in the table. When the tensile results of the samples are examined, it is observed that the tensile strength value of PU-007 is almost similar to that of PU. Generally, all the modified foam samples showed statistically the same tensile strength properties.

**Table 3.4.** Tensile Strength & Elongation at Break values of the PU-000, PU-007, PU-008 and PU-009 samples.

| **Tensile Strength (MPa)** | **PU-000** | **PU-007** | **PU-008** | **PU-009** |
|---|---|---|---|---|
| Sample 1 | 0,092 ± 0,026 | 0,092 ± 0,03 | 0,083 ± 0,03 | 0,083 ± 0,03 |
| Sample 2 | 0,112 ± 0,026 | 0,098 ± 0,03 | 0,083 ± 0,03 | 0,086 ± 0,03 |
| Sample 3 | 0,098 ± 0,026 | 0,092 ± 0,03 | 0,089 ± 0,03 | 0,08 ± 0,03 |
| Mean | 0,101 | 0,094 | 0,085 | 0,083 |
| **Percentage Elongation at Break (%)** | **PU-000** | **PU-007** | **PU-008** | **PU-009** |
| Sample 1 | 105,27 ± 1,3 | 97,15 ± 3,1 | 87,28 ± 5,8 | 94,52 ± 5,87 |
| Sample 2 | 131,25 ± 1,3 | 102,7 ± 3,1 | 88,15 ± 5,8 | 102,42± 5,87 |
| Sample 3 | 111 ± 1,3 | 97,5 ± 3,1 | 97,7 ± 5,8 | 90,95 ± 5,87 |
| Mean | 115,84 | 99,12 | 91,04 | 95,96 |

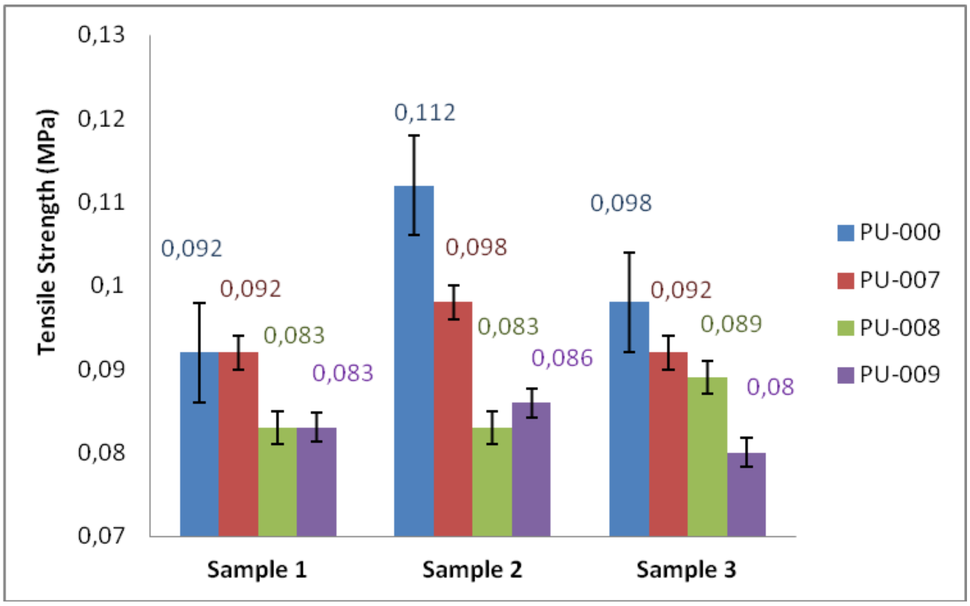


**Figure 3.5.** Variation of Tensile Strengths.

In Table 3.4, the percentage elongations at break values of the samples are tabulated. The PU-008 was found to perform extremely poor in terms of elongation ability, according to the results obtained from mechanical tests.

Addition of TCPP and PIPA into PU decreased the percentage elongation gradually. It means that the percent strain at break is decreased and corresponding ultimate strengths for these samples are lowered as seen in the Figure 3.6 below. Decrease of elongation at break is associated with the shortening of soft segment length.

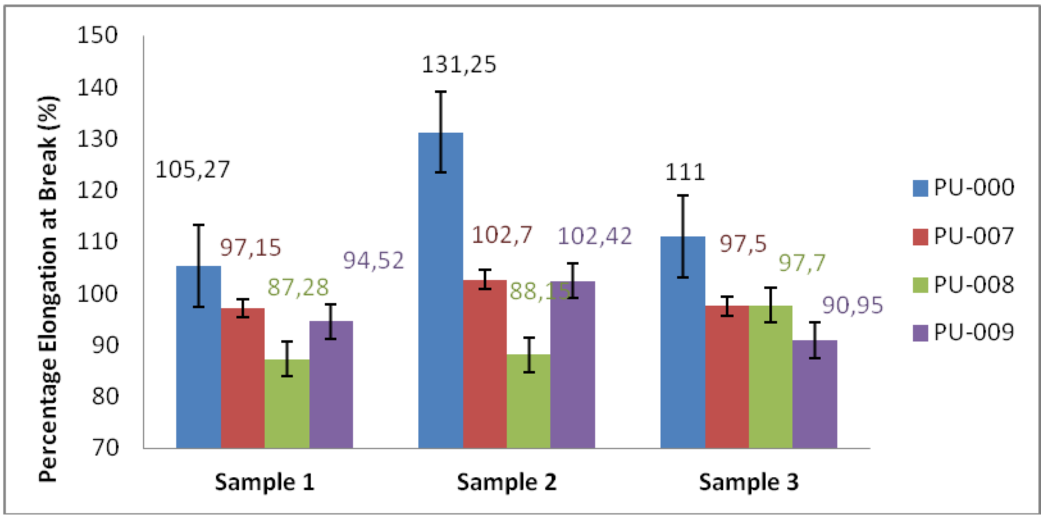


**Figure 3.6.** Percentage Elongation of the samples.

## 3.3. Thermal Analyses

To observe thermal characteristics of the modified PU, TGA and DPMS techniques were performed.

### 3.3.1. Thermogravimetric Analyses (TGA)

TGA was performed to show the effect of the addition of phosphorous and modified filler polyol on the thermal stability of the flexible polyurethane foam. Figure 3.7 and 3.8 show thermograms of the foams.

TGA results of the CMHR with different PU contents are given in Table 3.5. Among three samples, PU 008 weight loss was shifted to slightly high temperatures. Since PU 009 involved cell opener, degradation was shifted nearly 10°C to low temperature.

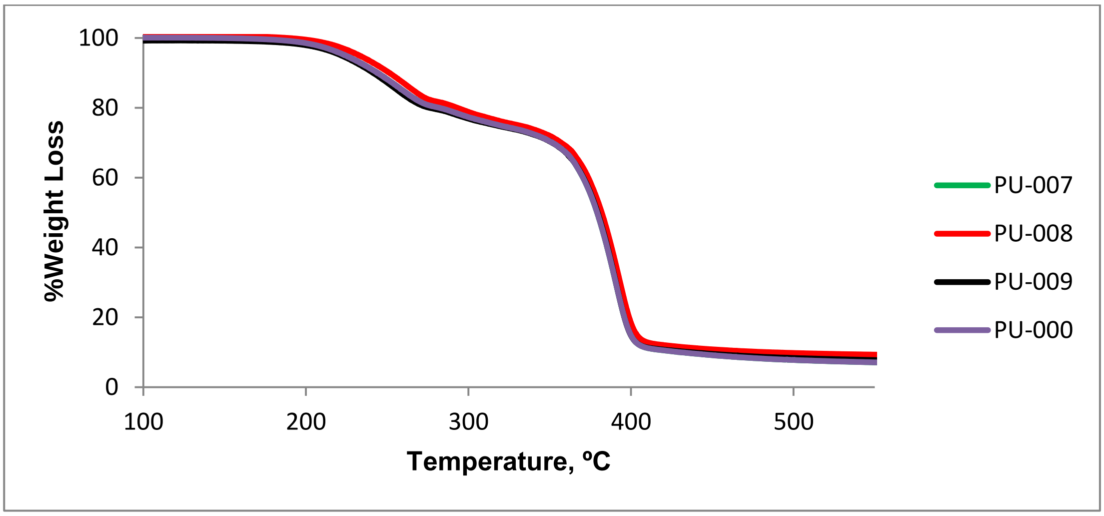


**Figure 3.7.** TGA curves of CMHR; PU-007, PU-008 and PU-009.

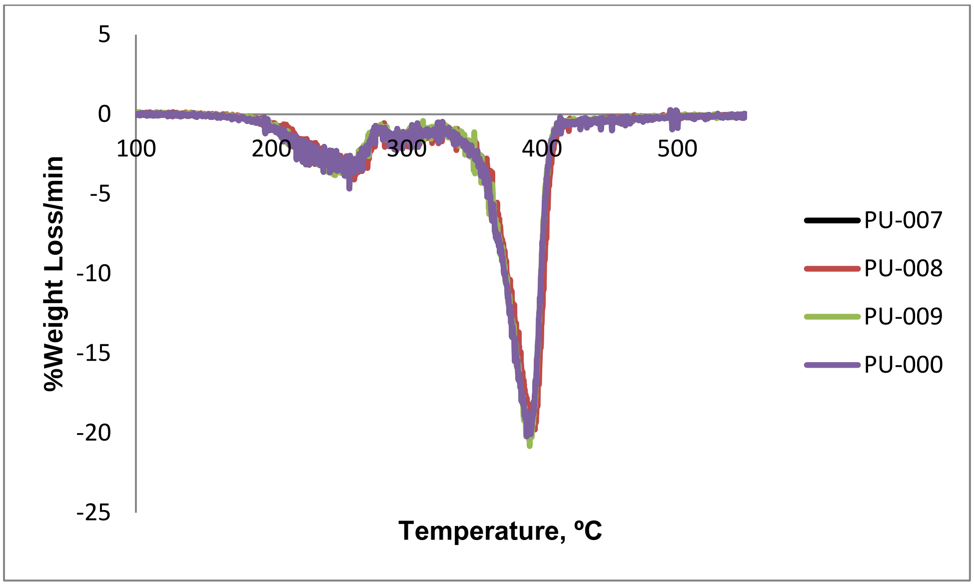


**Figure 3.8.** First derivative curves of TGA for CMHR; PU-007, PU-008 and PU-009.

The polyurethanes decomposition consists of two well-known stages [18, 19]. The initial temperature of the sample's decomposition process is assumed to the temperature corresponding to 5 % mass loss [20]. The temperature value for 5 % mass loss increased in the foam with the addition of TCPP and filled PIPA polyol in comparison to the value for pure PU. The temperature range of the decomposition of soft segments corresponds to the temperature of 75 % mass loss. The temperature of 50 % mass loss values of the PU 008 and 009 was bigger than PU 007. The value of this temperature was increased with the presence of fillers. The foam involving highest amount of DEOA had the largest increase. The value of tmax2 increased by the addition of fillers. According to the results of TGA, the thermal stability of the modified foams with the addition of filler polyol was higher than that of the foams without modification. The value of Tmax1 corresponds to the maximum rate of decomposition of rigid segments in polyurethane. The highest value of the residue occurred in the PU 008 foam with TCPP and PIPA.

**Table 3.5.** TGA data for pure HR PU and CMHR PU compounds with PIPA polyol.

| Material | T5%, °C | T75%, °C | Tmax1, °C | Tmax2, °C | % Residue at 600°C |
|---|---|---|---|---|---|
| **PU** | 220.8 | 363.3 | 233.52 | 387.7 | 5.9 |
| **PU + PIPA 07** | 224.36 | 379.16 | 249.06 | 388.73 | 6.64 |
| **PU + PIPA 08** | 232.99 | 381.89 | 239.81 | 389.42 | 8.99 |
| **PU + PIPA 09** | 221.99 | 379.45 | 236.63 | 388.33 | 7.3 |

### 3.3.2. Direct Pyrolysis Mass Spectrometry (DP-MS) Analyses

Pyrolysis mass spectrometer analysis was used to investigate the effect of PIPA polyol compound on thermal decomposition of PU CMHR foams. DP-MS analysis of each composite containing different amount of PIPA and fire proof compounds were studied and compared to investigate the effects of modifications.

#### 3.3.2.1. PU HR

The total ion current, TIC curve, which is the variation of total ion yield as a function of temperature, the pyrolysis mass spectrum at the maximum of the TIC curve, at 374°C during the pyrolysis of PU are given in Figure 3.8. The base peak is at m/z=117 Da is attributed to $CO_2C_2H_4OCOH$. The spectrum is dominated by the known homologous series related with CO2(C2H4O)xCOH for x=1 to 6 fragments. Peaks due to low mass fragments, for instance, NHCO2 (59 Da), C6H5 (77 Da) and C7H7 (91 Da) are mainly generated by random chain cleavages.

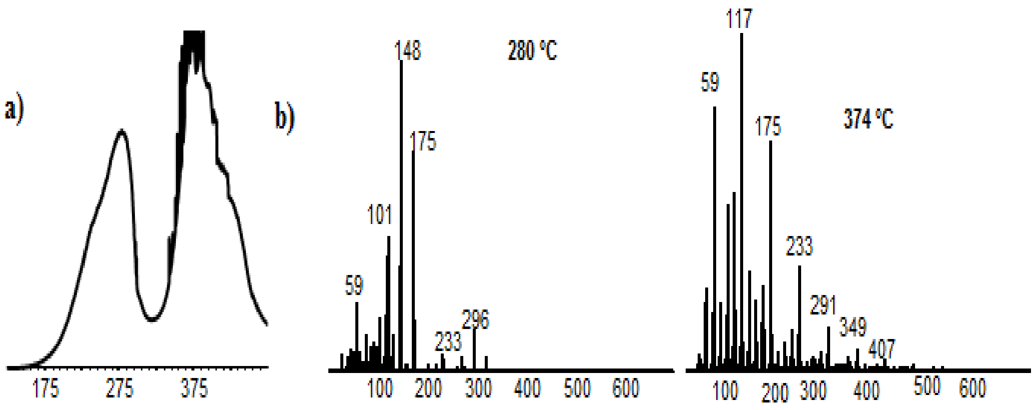
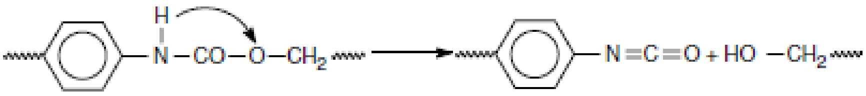


**Figure 3.9.** The TIC curves and the pyrolysis mass spectra of PU000 HR.

The thermal degradation reaction for the polyurethane is shown in Scheme 3.1.



**Scheme 3.1.** The decomposition pathway of linear polyurethanes.

Single ion evolution profiles of some of the representative fragments of PU HR, such as; $NHCO_2$ (59 Da), $CO_2C_2H_4OCOH$ (117 Da), $NHCO_2(C_2H_4O)_2$, and/or $NH(C_2H_4CO_2)C_2H_4CO_2NH_2$ (175 Da), NHCO2(C2H4O)3 (233 Da), [CH3C6H3(NHCO)2](OC2H4O)2 (296 Da) and NHCO2(C2H4O)6 (407 Da) are shown in Figure 3.9. Thermally less stable C6H6 (77 Da), CH2C6H4NH2, and/or $NCH_3C_6H_3$ (106 Da), $C_3H_4(NCO)_2$ (148 Da), $CH_3C_6H_3(NCO)_2$**,** and/or $NH(C_2H_4CO_2)_2$ (174 Da) decomposed firstly. Lastly, more stable ones $C_7H_7$ (91 Da), $CH_2C_6H_4N$ (104 Da) and $CO_2(C_2H_4O)C_2H_4$ (144 Da) fragments were formed.

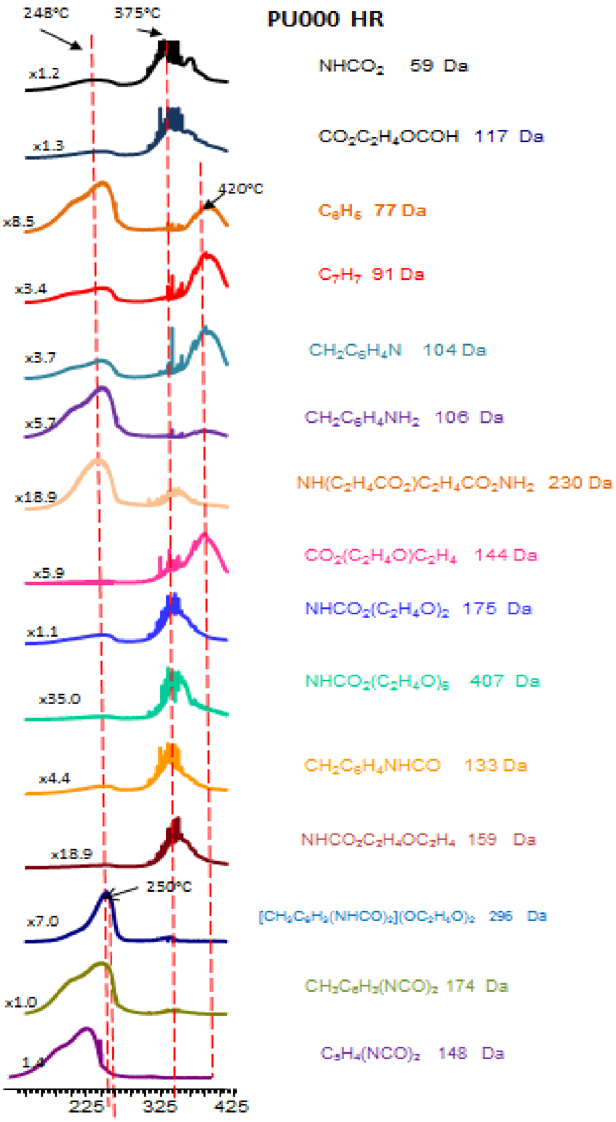


**Figure 3.10.** The single ion evolution profiles of selected fragment recorded during the pyrolysis of PU000 HR.

### 3.3.2.2. PU CMHR

The TIC curve and the pyrolysis mass spectra set at maximum peak of combustion modified high resilience polyurethane foams PU008 and PU009 are shown in Figure 3.10. The base peaks 148 Da and 117 Da may be related with both $C_5H_4(NCO)_2$ and $CO_2C_2H_4OCOH$ fragments, in the mass spectrum recorded at around 265°C and 395°C. Unlike PU008, PU009 had a cell opener, which did not affect its thermal decomposition. Therefore, TIC curves and pyrolysis mass spectra were nearly same each other. Other intense peaks were attributed with may be attributed from urethane and urea fragmentation reactions.

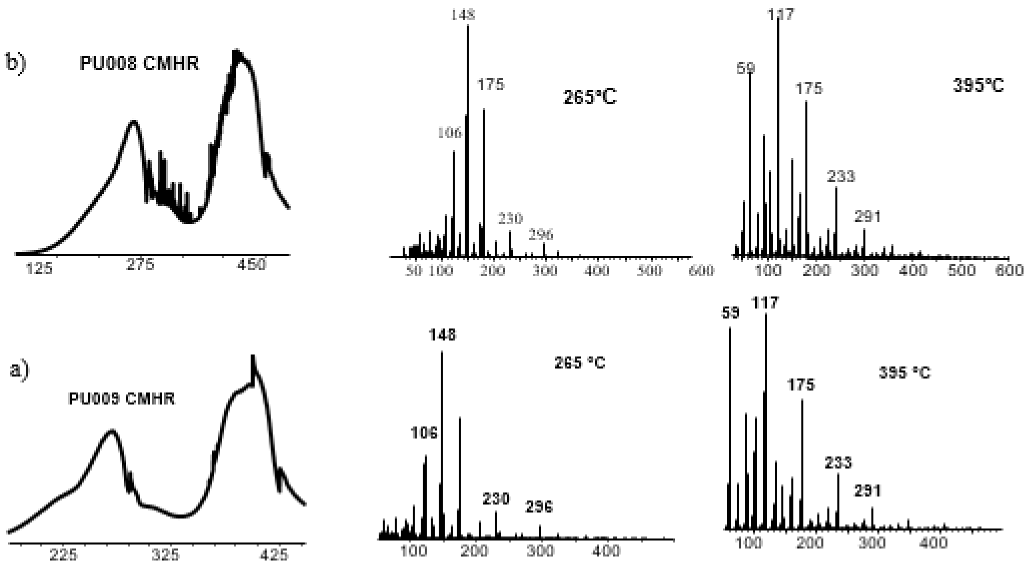


**Figure 3.11.** The TIC curves and the pyrolysis mass spectra of PU008 & PU009 CMHR and PU composites involving PIPA polyol.

Other intense peaks that appeared in polyurethane foam and did not appeared in combustion modified polyurethane foam with PIPA polyol and flame retardant material were as follows C5H4(NCO)2 (148 Da), NHCO2C2H4OC2H4 (159 Da), CH3C6H3(NCO)2 (174 Da) and [CH3C6H3(NHCO)2] (OC2H4O)2 (296 Da). In Figure 3.11 $NHCO_2C_2H_4$ (87 Da) and $NHCO_2C_2H_4$ (101 Da) fragments of PU 008 and PU009 CMHR decomposed unlike PU HR.

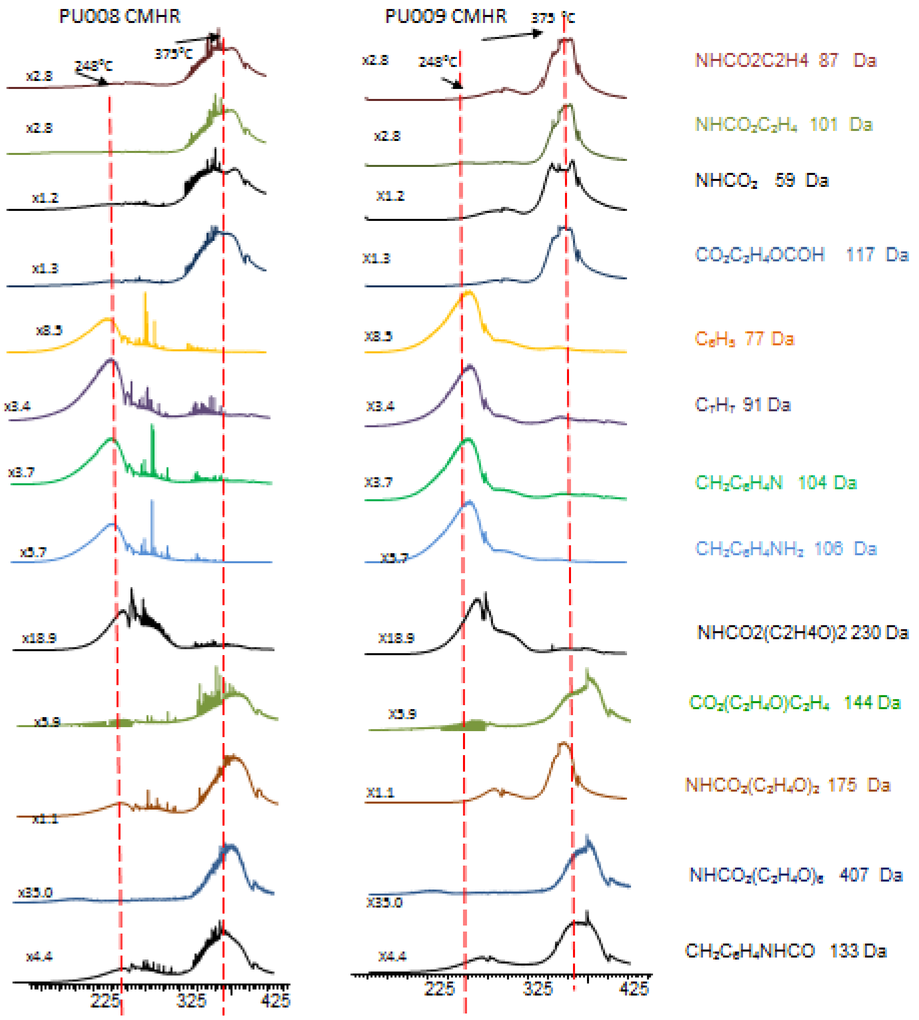


**Figure 3.12.** The single ion evolution profiles of selected fragment recorded during the pyrolysis of PU CMHR composites involving PIPA.

In Figure 3.12. evolution profiles of selected fragment were recorded during the pyrolysis of both PU HR and PU CMHR composites involving PIPA.

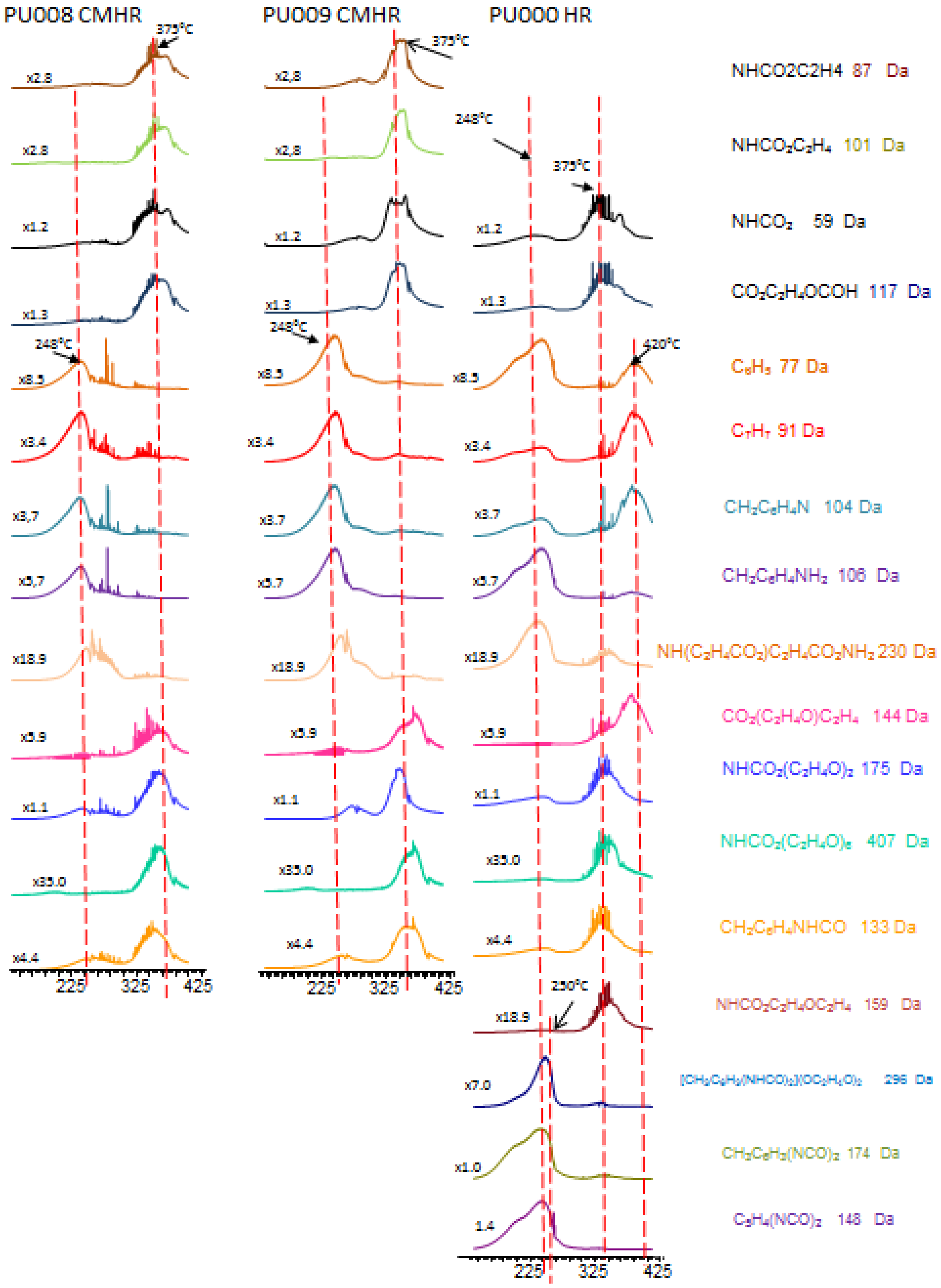


**Figure 3.13.** The single ion evolution profiles of selected fragment recorded during the pyrolysis of PU HR and PU CMHR composites involving PIPA.

## 3.4. Flammability Properties

### 3.4.1. CRIB 5 BS 5852: Part 2:

Two samples of CMHR PIPA foam were sent to Mobilite, IFS Laboratories for Crib 5 test and further analysis. Crib 5 test was made to investigate the flame retardancy behavior of PU foams. The CRIB 5 test results and observations made for prepared PU foams were summarized in Table 3.6. Among these results weight loss and time to extinguish are the most important.

**Table 3.6.** CRIB 5 test results and observations for the samples prepared.

| **Experiment** | **PU-08** | **PU-09** |
|---|---|---|
| **Crib Weight /g** | 17.3 | 17.4 |
| **Start /g** | 9700 | 9705 |
| **Finish /g** | 9658 | 9667 |
| **Weight Loss /g (TWL)** | 42 | 38 |
| **Drips /g** | 19 | 35 |
| **Self-Extinguish** | **YES** | **YES** |
| **Time to Extinguish /s** | 287 | 260 |
| **Burn through base** | **YES** | **YES** |
| **Burn through back** | NO | NO |
| **Damage base /cm** | 17 | 22 |
| **Damage back /cm** | 14 | 22 |
| **PASS / FAIL** | **PASS** | **PASS** |
| **Results** | No Char. Quite Active Gas Phase. Huge melting. Back extinguished in a timely fashion, seat continued to burn through ejected all molten material into the drip try and fire was left isolated from the foam in the middle of the seat piece-self extinguish. | No Char. Very Active Gas Phase. Huge melting. Large material and therefore heat and flame loss at burn through. Followed by some extended burning before self-extinguished. |

Modified PU foams were prepared by mixing PIPA polyol and TCPP. Flaming time should not exceed 10 minutes after crib ignition. All flames self-extinguished at 4 minutes and 47 seconds in the PU 008 and 4 minutes and 20 seconds in the PU 009 as seen in Figures 3.14 & 3.15. Mass loss limitation is sixty grams. As tabulated in Table 3.6. final mass loss was 42 grams for PU 008 and 38 grams for PU 009. Last criteria were the thickness of the seat base burned during tests PU 008 and PU 009. Therefore, flaming should not exceed 10 minutes from crib ignition and resultant mass loss should not exceed60 grams for combustion modified PU samples. Especially, there should not be char and huge active gas phase. Seat base should only burn during the test and then should be test self-extinguished.

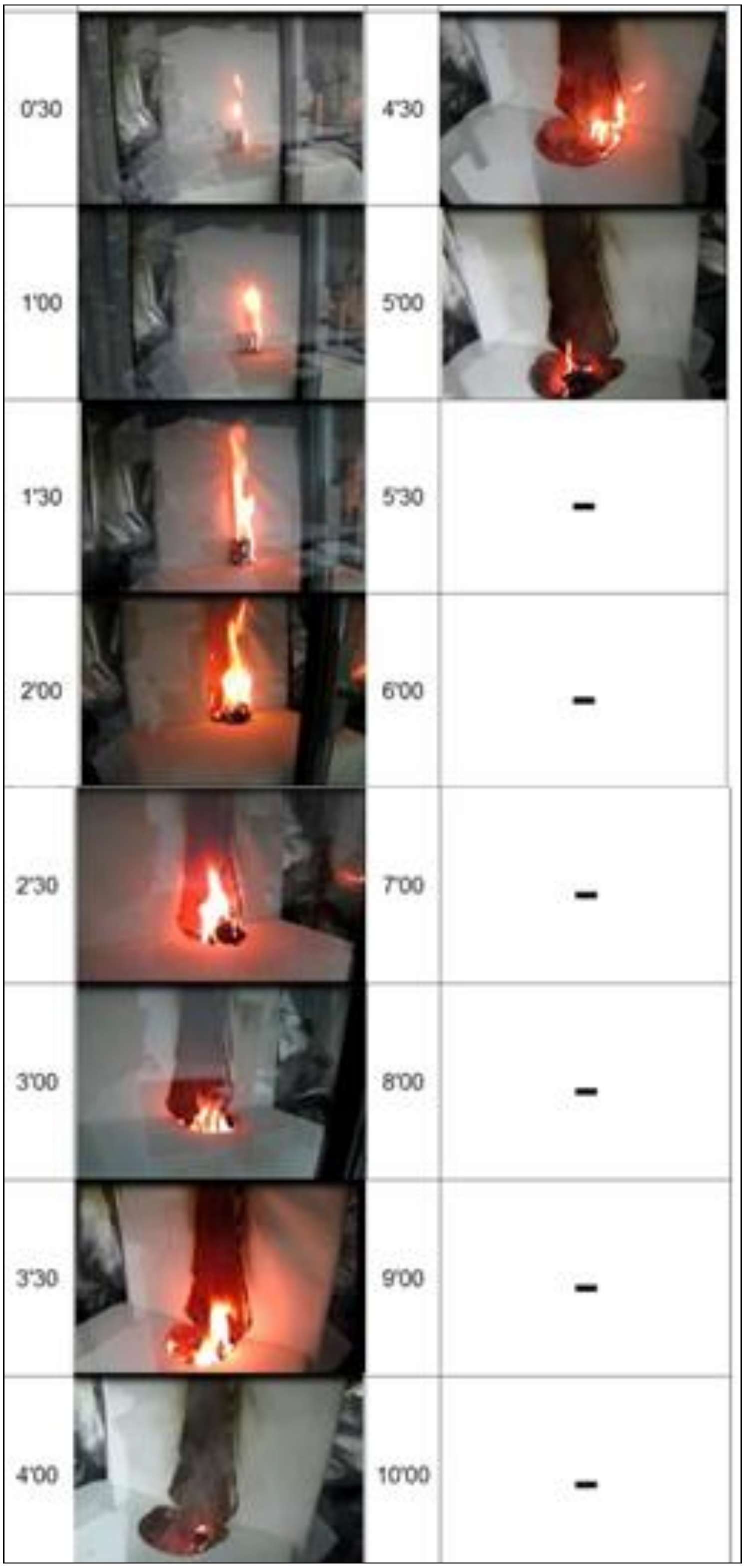
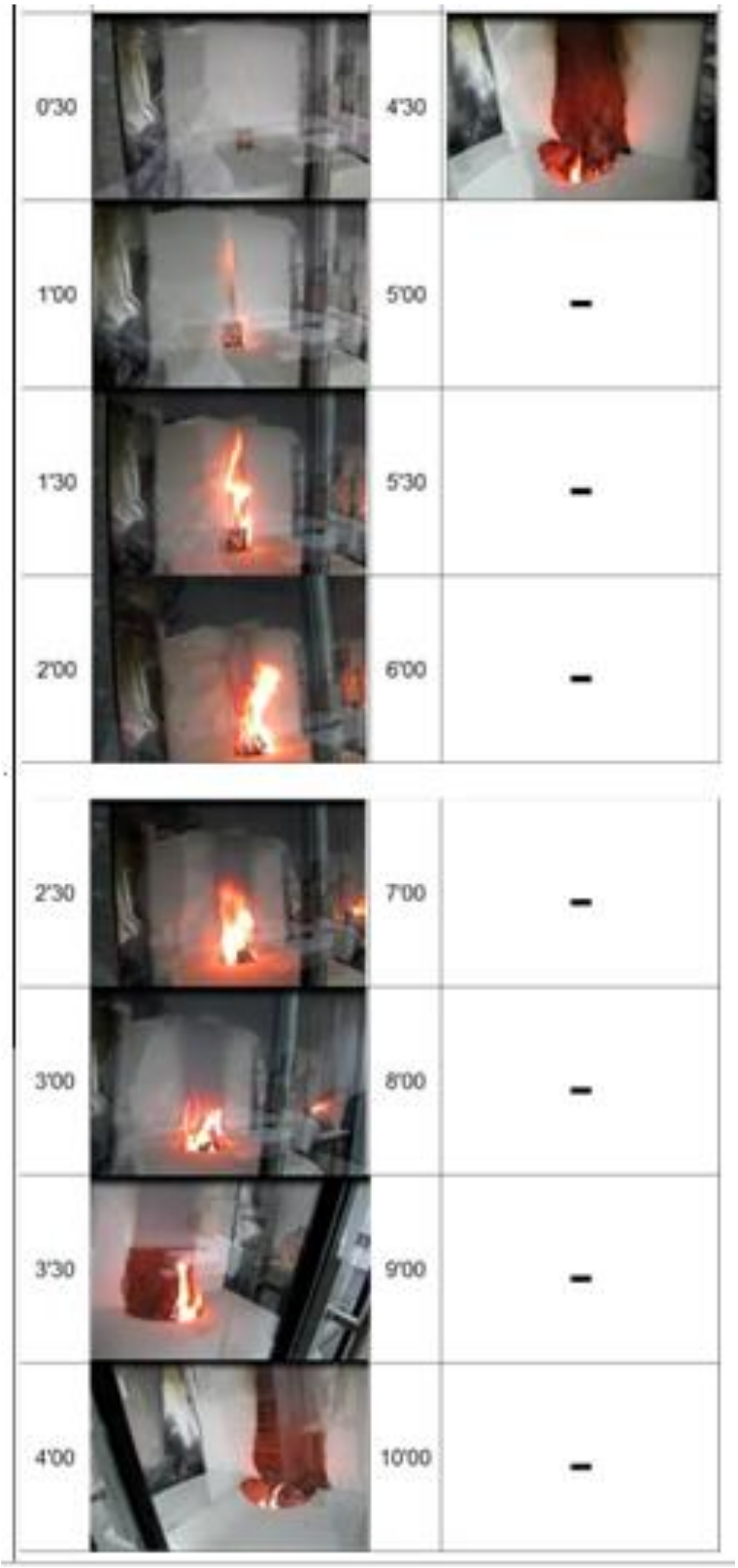


**Figure 3.14.** Crib 5 fire resistance test of PU 008 during the test.

**Figure 3.15.** Crib 5 fire resistance test of PU 009 during the test.



# CHAPTER 4

# CONCLUSIONS

Modification of polyurethane caused small changes in the structure and mechanical properties. The results obtained were acceptable. Addition of filled polyol and TCPP increased density, resilience and compression. Moreover, for the mechanical properties; hardness, tensile strength and elongation at break were decreased.

As a result of the thermal gravimetry analysis by TGA and flammability measurements, it was found that the addition of TCPP and PIPA allows better thermal stability and fire retardancy properties to be obtained.

Thermal decomposition of polyurethanes started at biuret and allophanate bonds because these are the thermally weakest links in the PU network. The urethanes are the next weakest in thermal stability. Ureas are almost similar in thermal stability and most stable ones are undoubtedly isocyanurate group. Their respective precursors are regenerated by decomposition of these groups. TCPP which is the phosphorus-containing flame- retardant material decreased thermal stability of the PU, by the way it promoted cross-linking and charring. Whereas thermal degradation of polyurethane occurred nearly at around 420 ºC, combustion of modified polyurethanes completed at around 375ºC. Since the cell opener did not affect thermal degradation temperature of PU008 CMHR and PU009 CMHR was very similar.

Whereas highly porous lightweight PU foams are very combustible and have fast flame-spread and high heat-release rates, PU HR foam has lower flame tendency. Moreover, PIPA modified polyether polyol was adapted to PU HR foam. For this purpose, many lab scale and production line trials were conducted. The effect of addition of flame-retardant (PIPA) to these foams provided the major contributions to combustion performance test results.

PU008 and PU009 samples passed from BS 5852 CRIB 5 test indicating high success.

As indicated in the literature the amount of flame retardant material needed for PIPA polyol is lower however in our case only a small difference in the amount of flame retardant was detected. 10 part Fyrol PCF-LO was used in this study. This amount is standard for PU foams for combustion modification.

The results were in accordance with BS 5852: 1982 Part 2 ignition source 5, Schedule 1, Part 1 fire test for foam in slab form as stated in The Furniture & Furnishing (Fire) (Safety) Regulations 1988 No. 132 & FFFSR 2010 and the specified requirements of BS 5852 Part:2 1982. Consequently, both PU 008 and PU 009 CMHR foams were succeed in all test criteria and passed from English standard BS 5852 test.

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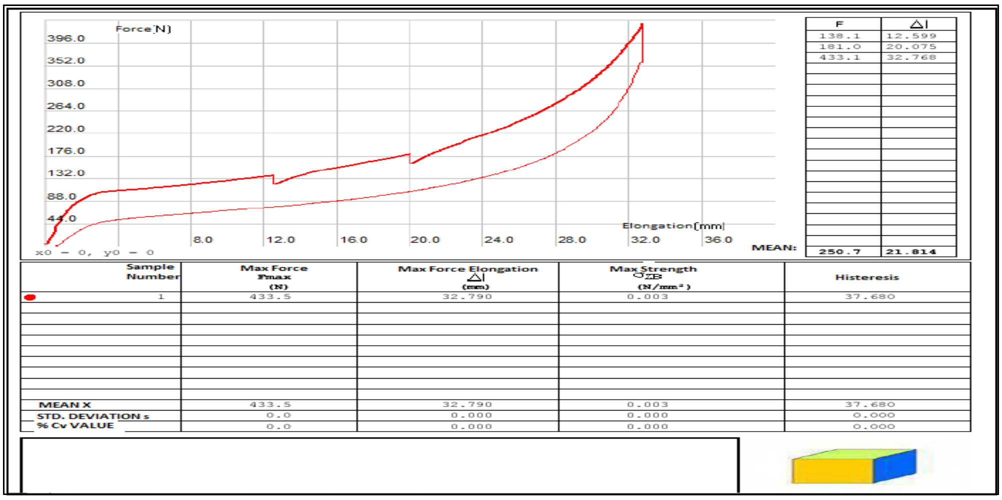
# APPENDICES

## A. MECHANICAL TESTING DATA



| F | $\Delta l$ |
|---|---|
| 138.1 | 12.599 |
| 181.0 | 20.075 |
| 433.1 | 32.768 |
| MEAN: 250.7 | 21.814 |

| Sample Number | Max Force Fmax (N) | Max Force Elongation $\Delta l$ (mm) | Max Strength $\sigma_{ZB}$ (N/mm²) | Histeresis |
|---|---|---|---|---|
| ● 1 | 433.5 | 32.790 | 0.003 | 37.680 |
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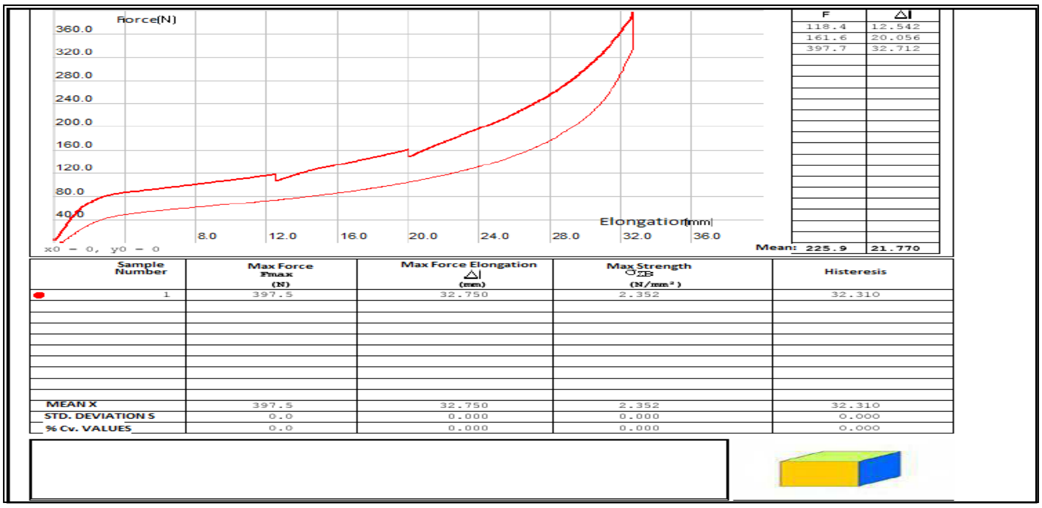
| | | | | |
| | | | | |
| MEAN X | 433.5 | 32.790 | 0.003 | 37.680 |
| STD. DEVIATION s | 0.0 | 0.000 | 0.000 | 0.000 |
| % Cv VALUE | 0.0 | 0.000 | 0.000 | 0.000 |

**Figure A.1.** Hardness graph of HR (PU 000).



| F | $\Delta l$ |
|---|---|
| 118.4 | 12.542 |
| 161.6 | 20.056 |
| 397.7 | 32.712 |
| Mean: 225.9 | 21.770 |

| Sample Number | Max Force Fmax (N) | Max Force Elongation $\Delta l$ (mm) | Max Strength $\sigma_{ZB}$ (N/mm²) | Histeresis |
|---|---|---|---|---|
| ● 1 | 397.5 | 32.750 | 2.352 | 32.310 |
| | | | | |
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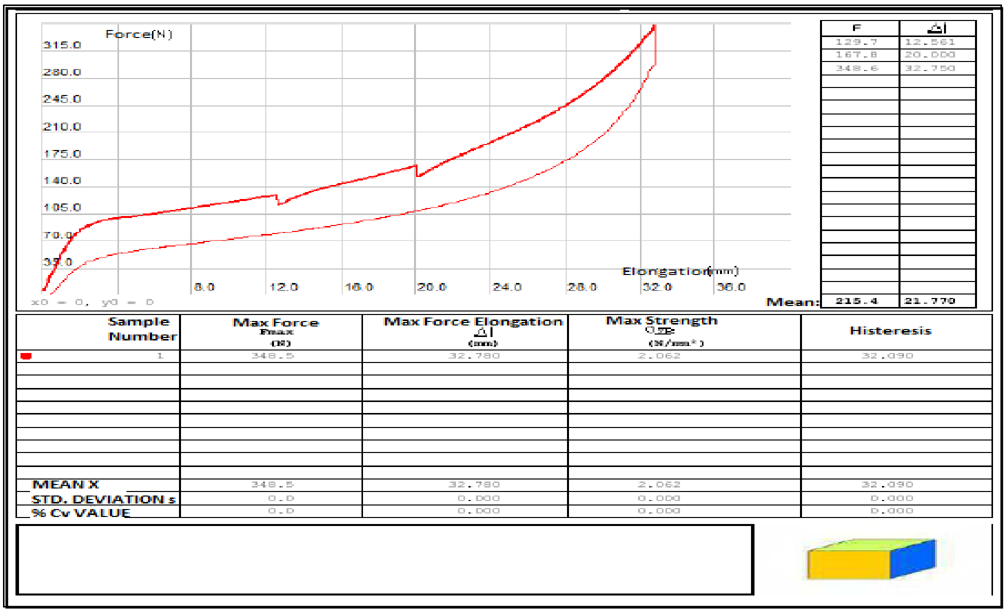
| | | | | |
| MEAN X | 397.5 | 32.750 | 2.352 | 32.310 |
| STD. DEVIATION S | 0.0 | 0.000 | 0.000 | 0.000 |
| % Cv. VALUES | 0.0 | 0.000 | 0.000 | 0.000 |

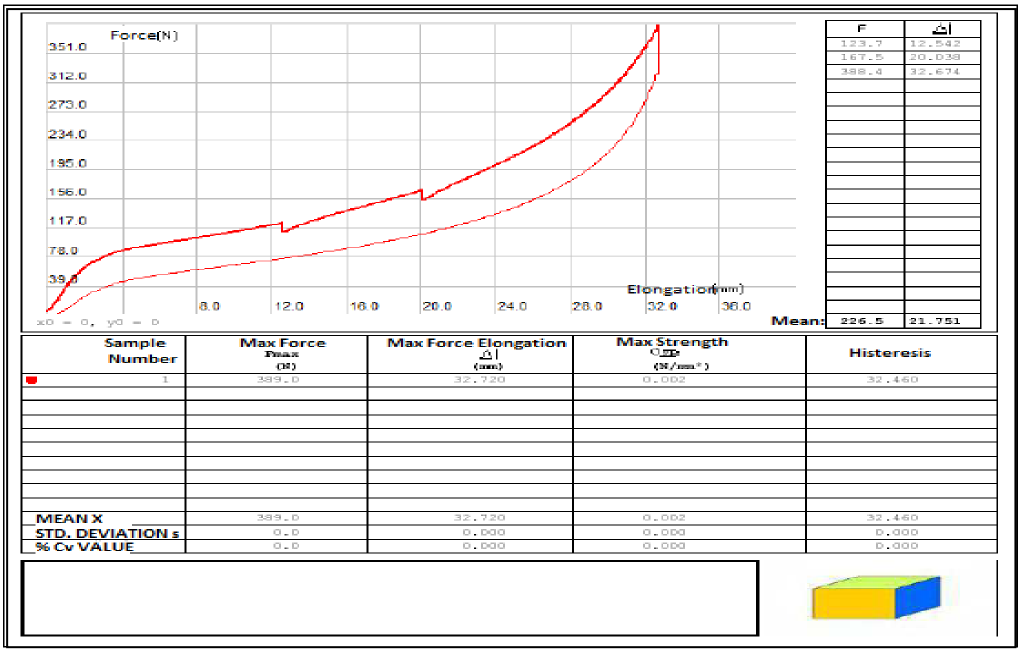
**Figure A.2.** Hardness graph of CMHR 7 (PU 007).



| F | Δl |
|---|---|
| 129.7 | 12.561 |
| 167.8 | 20.000 |
| 348.6 | 32.750 |
| **Mean:** 215.4 | 21.770 |

| Sample Number | Max Force Fmax (N) | Max Force Elongation Δl (mm) | Max Strength $\sigma_B$ (N/mm²) | Histeresis |
|---|---|---|---|---|
| 1 | 348.5 | 32.780 | 2.062 | 32.090 |
| MEAN X | 348.5 | 32.780 | 2.062 | 32.090 |
| STD. DEVIATION s | 0.0 | 0.000 | 0.000 | 0.000 |
| % Cv VALUE | 0.0 | 0.000 | 0.000 | 0.000 |

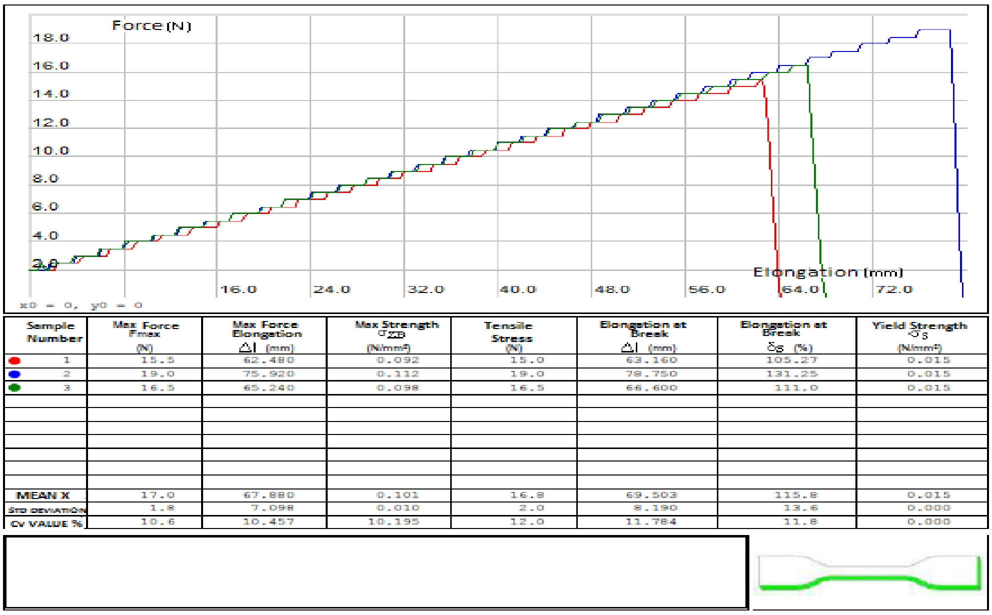
**Figure A.3.** Hardness graph of CMHR 8 (PU 008).



| F | Δl |
|---|---|
| 123.7 | 12.542 |
| 167.5 | 20.039 |
| 388.4 | 32.674 |
| **Mean:** 226.5 | 21.751 |

| Sample Number | Max Force Fmax (N) | Max Force Elongation Δl (mm) | Max Strength $\sigma_B$ (N/mm²) | Histeresis |
|---|---|---|---|---|
| 1 | 389.0 | 32.720 | 0.002 | 32.460 |
| MEAN X | 389.0 | 32.720 | 0.002 | 32.460 |
| STD. DEVIATION s | 0.0 | 0.000 | 0.000 | 0.000 |
| % Cv VALUE | 0.0 | 0.000 | 0.000 | 0.000 |

**Figure A.4.** Hardness graph of CMHR 9 (PU 009).



| Sample Number | Max Force Fmax (N) | Max Force Elongation $\Delta l$ (mm) | Max Strength $\sigma_{ZB}$ (N/mm²) | Tensile Stress (N) | Elongation at Break $\Delta l$ (mm) | Elongation at Break $\delta_S$ (%) | Yield Strength $\sigma_S$ (N/mm²) |
|---|---|---|---|---|---|---|---|
| ● 1 | 15.5 | 62.480 | 0.092 | 15.0 | 63.160 | 105.27 | 0.015 |
| ● 2 | 19.0 | 75.920 | 0.112 | 19.0 | 78.750 | 131.25 | 0.015 |
| ● 3 | 16.5 | 65.240 | 0.098 | 16.5 | 66.600 | 111.0 | 0.015 |
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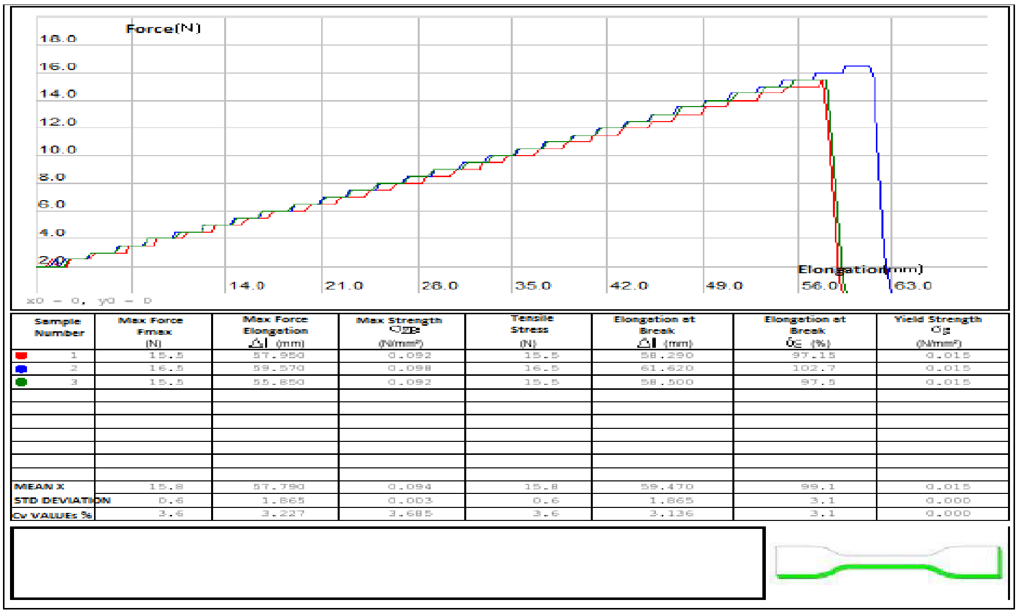
| MEAN X | 17.0 | 67.880 | 0.101 | 16.8 | 69.503 | 115.8 | 0.015 |
| STD DEVIATION | 1.8 | 7.098 | 0.010 | 2.0 | 8.190 | 13.6 | 0.000 |
| CV VALUE % | 10.6 | 10.457 | 10.195 | 12.0 | 11.784 | 11.8 | 0.000 |

**Figure A.5.** Tensile test graph of graph of CMHR 0 (PU 000).



| Sample Number | Max Force Fmax (N) | Max Force Elongation $\Delta l$ (mm) | Max Strength $\sigma_{ZB}$ (N/mm²) | Tensile Stress (N) | Elongation at Break $\Delta l$ (mm) | Elongation at Break $\delta_{\varepsilon}$ (%) | Yield Strength $\sigma_S$ (N/mm²) |
|---|---|---|---|---|---|---|---|
| ■ 1 | 15.5 | 57.950 | 0.092 | 15.5 | 58.290 | 97.15 | 0.015 |
| ■ 2 | 16.5 | 59.570 | 0.098 | 16.5 | 61.620 | 102.7 | 0.015 |
| ● 3 | 15.5 | 55.850 | 0.092 | 15.5 | 58.500 | 97.5 | 0.015 |
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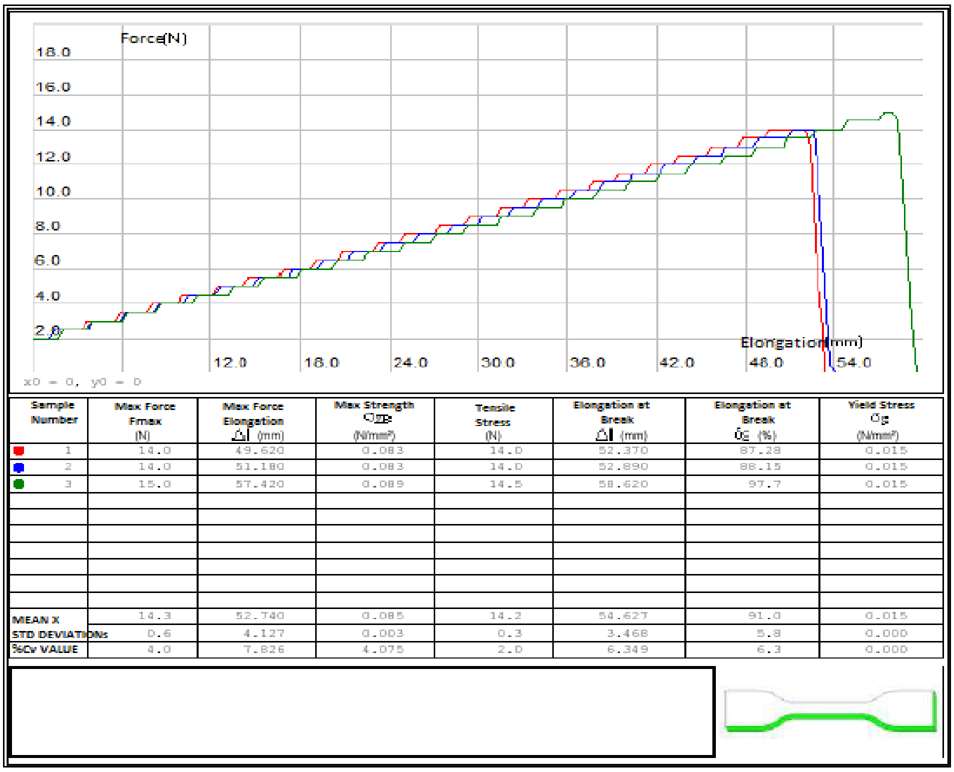
| | | | | | | | |
| MEAN X | 15.8 | 57.790 | 0.094 | 15.8 | 59.470 | 99.1 | 0.015 |
| STD DEVIATION | 0.6 | 1.865 | 0.003 | 0.6 | 1.865 | 3.1 | 0.000 |
| CV VALUES % | 3.6 | 3.227 | 3.685 | 3.6 | 3.136 | 3.1 | 0.000 |

**Figure A.6.** Tensile test graph of CMHR 7 (PU 007).



| Sample Number | Max Force Fmax (N) | Max Force Elongation Δl (mm) | Max Strength σB (N/mm²) | Tensile Stress (N) | Elongation at Break Δl (mm) | Elongation at Break δε (%) | Yield Stress σs (N/mm²) |
|---|---|---|---|---|---|---|---|
| 🟥 1 | 14.0 | 49.620 | 0.083 | 14.0 | 52.370 | 87.28 | 0.015 |
| 🟦 2 | 14.0 | 51.180 | 0.083 | 14.0 | 52.890 | 88.15 | 0.015 |
| 🟩 3 | 15.0 | 57.420 | 0.089 | 14.5 | 58.620 | 97.7 | 0.015 |
| | | | | | | | |
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| | | | | | | | |
| MEAN X | 14.3 | 52.740 | 0.085 | 14.2 | 54.627 | 91.0 | 0.015 |
| STD DEVIATIONs | 0.6 | 4.127 | 0.003 | 0.3 | 3.468 | 5.8 | 0.000 |
| %Cv VALUE | 4.0 | 7.826 | 4.075 | 2.0 | 6.349 | 6.3 | 0.000 |

**Figure A.7.** Tensile test graph of CMHR 8 (PU 008).