



T.R.  
EGE UNIVERSITY  
Graduate School of Applied and Natural Science



# **ENHANCEMENT OF THE THERMAL ISOLATION PROPERTIES OF POLYURETHANE FOAMS USED IN HOUSEHOLD COOLING DEVICES**

**Msc Thesis**

**BERK ŞAHAN ŞAHİN**

Department of Materials Science and Engineering

İzmir  
2023

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IN HOUSEHOLD COOLING DEVICES**

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Programme with Thesis

İzmir  
2023

Berk Şahan ŞAHİN tarafından yüksek lisans tezi olarak sunulan “Enhancement of the thermal isolation properties of polyurethane foams used in household cooling devices” başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve ..... tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

**Jüri Üyeleri:**

**İmza**

**Jüri Başkanı** : ..... 

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## **EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ**

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İmzası

**BERK SAHAN ŞAHİN**



## ÖZET

### Ev Tipi Soğutma Cihazlarında Kullanılan Poliüretan Köpüklerin Çeşitli Katkı Maddeleriyle Yalıtım Özelliklerinin İyileştirilmesi

BERK ŞAHAN ŞAHİN

Yüksek Lisans Tezi, Malzeme Bilimi ve Mühendisliği Anabilim Dalı  
Tez Danışmanı: Dr. Öğr. Üyesi Nilay GİZLİ  
Ocak 2023, 63 Sayfa

Bu tez öncelikle buzdolabı ve dondurucu gibi soğutucu cihazların izolasyonun iyileştirilmesine odaklanmaktadır. Soğutma cihazları, dünyadaki en yaygın ev aletleridir. Enerji verimliliğini artırmak önemli bir kriterdir. Bu nedenle piyasa izolasyon sistemini iyileştirmeye önemlidir. Poliüretan, polimerler arasında kritik öneme sahip olan bir malzemedir. Poliüretanlar kapsamlı bir ticari çevrede farklı tiplerde kullanılmaktadır. Bu çalışmada rıjît poliüretan köpük üzerine çalışmalar yapılmıştır. Bu sert köpükler genellikle buzdolaplarında izolasyonu sağlamak için kullanılmaktadır. Poliüretanın izolasyon yeteneklerini artırmak için farklı katkı malzemeleri kullanılmıştır. İzolasyon yeteneklerini izolasyon kalınlığını artırarak malzemenin daha da verimli bir şekilde izolasyon yeteneği kazandırılması hedeflenmiştir. Bu çalışmada üçü doğal olmak üzere dört farklı dolgu malzemesinin poliüretan köpük ısı yalıtım özelliklerine etkisi üzerine çalışılmıştır. Doğal dolgu olarak fındık, ceviz ve yumurta kabukları üzerinde çalışılmıştır. Ana amaç doğal döngü içinde bulunan malzemelerin geri dönüşüm katı sağlanması ve polimer yapısına dahil edilmek istenmiştir. Dolgu malzemesinin tane yapısı poliüretanın termal iletkenlik, hücre yapısı ve hücre boyutunu değiştirebileceğini gözlemlmeye çalışıldı. Ek olarak aerogelin %10 ve %15 katkılı poliüretan üzerindeki etkileri de incelendi. Ağırlıkça %10, %15, %20 ceviz kabuğu ve ağırlıkça %10, %15 fındık kabuğunun yanı sıra ağırlıkça %10, %15, %20 değerinde yumurta kabuğu kullanıldı. Araştırma esnasında; yoğunluk, Thermogravimetrik, Fourier dönüşümlü kızılıötesi titreşimi, hücre morfolojisi, kapalı hücre sayısı, basınç testi, termal iletkenlik, mikroskop incelemesi ve taramalı elektron ile gözleme yapılmıştır.

Kullanılan dolgu malzemeleri, rıjît poliüretan üzerinde genel anlamda olumlu etkilere sebep olduğu gözlemlenmiştir. Hücre yapısındaki küçülme, hidrofobik davranışlar, kapalı hücre yapıları ve termal-mekanik davranışlar gözlemlendiğinde dolgu malzemelerinin etkilerini görmekteyiz.

**Anahtar Sözcükler: Sert Poliüretan Köpük, Polyol, İzosiyonat, Doğal Katkı Malzemeleri, Şişirici Ajanlar, Aerojel**



## ABSTRACT

### **Enhancement of the Thermal Isolation Properties of Polyurethane Foams Used in Household Cooling Devices**

BERK ŞAHAN ŞAHİN

MSc in Materials Science and Engineering

Supervisor: Nilay GİZLİ, Dr.

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This thesis primarily focuses on improving insulation from refrigerators and freezers. Cooling devices are the most common household appliances in the world. Increasing energy efficiency is an important criterion. For this reason, the market tends to improve the insulation system. Among the polymers, polyurethane is a material with critical importance. Different types of polyurethanes are used in an extensive commercial environment. In this study, studies were carried out on rigid polyurethane foam. These rigid foams are generally used to provide insulation in refrigerators. Different additives have been used to increase the isolation capabilities of polyurethane. It is desired that the material, whose insulation capabilities are not increased by increasing the insulation thickness, should gain the ability to insulate more effectively. Studies were carried out on 4 different filling materials. Three of them are natural filling materials. It has been studied on hazelnuts, walnuts and egg shells. The main purpose is to contribute to the recycling of materials in the natural cycle and to be included in the polymer structure. In addition, it was desired to observe the effects of the aerogel material, which has a strong thermal conductivity, on the polyurethane. The process to be observed in the beginning was as follows; We have tried to observe that the grain structure of the filling material can change the thermal conductivity, cell structure and gas flow structure of the polyurethane. In addition, the effects of aerogel 10%, 15% wt on polyurethane were also investigated. In addition to 10%, 15%, 20% by weight walnut shell and 10%, 15% by weight hazelnut shell, 10%, 15% and 20% by weight egg shells were used. Primarily, 5% and 20% of the filling material in hazelnut and walnut shells was turned into powder and used in powdered pieces. During the research; Thermogravimetric, Fourier transform infrared spectrophotometer, compression strength test and scanning electron microscopy were executed on all filling samples. In addition, cell angle, cell wall and cell structure were investigated.

It has been observed that the filling materials used cause positive effects on rigid polyurethane in general. When the shrinkage in the cell structure, hydrophobic behavior, closed cell structures and thermal – mechanic behaviors are observed, we see the effects of the filling materials.

**Keywords: Rigid Polyurethane Foam, Polyol, Isocyanate, Natural Additives, Blowing Agents, Aerogel**



## PREFACE

It is a pleasure to find the chance to present this study on the advantages of natural fillers on rigid polyurethane foam. As it is known, rising ecological awareness leads the raw materials producers to seek for new ways. I shall be more than happy if my study provides some contribution in due course of rising awareness.

In fact, these good performance outcomes could not have been achieved without the back up of a strong support group. I am very grateful for the encouragement and helpfulness of whoever supported me for this study.



İZMİR  
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BERK ŞAHAN ŞAHİN

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## ACRONYMS

<u>Symbol</u>	<u>Definition</u>
Annual growth rate	CAGR
Carbodiimides	CDIs
Carbon dioxide	CO2
Derivative of change	DTG
Differential scanning calorimetry	DSC
Eggshell %10 wt	EG10
Eggshell %15 wt	EG15
Eggshell %20 wt	EG20
Expanded polystyrene.	EPS
European	EU
Glass fiber	GF
Glass wool	GW
Global warning potential	GWP
Hazelnut shell %10 wt	HN10
Hazelnut shell %15 wt	HN15
Hazelnut shell %20 wt	HN20
Infrared spectroscopy	FTIR
Methylene diphenyl diisocyanate	MDI
Mass change	TG
Normal polyurethane	N

Ozone depletion potential	ODP
Pistachio shell	PN
Polymeric MDI	pMDI
Peak of heat release rate	pHRR
pHENOL formaldehyde resin	PF
Rigid polyurethane foam	RPUF
Polyisocyanurate	PIR
Polyurethane	PU
Polyurethane	PUR
Scanning electrom microscopy	SEM
Stone Wall	SW
Thermogravimetric Analysis.	TGA
Toluene diisocyanate	TDI
Triethylenediamine	TEDA
Ultraviolet	UV
Vacuum insulation panels	VIP
Walnut shell %10 wt	WN10
Walnut shell %15 wt	WN15
Walnut shell %20 wt	WN20
X-ray fluorescence	X ray



## 1. INTRODUCTION

### 1.1 Research Target

Rising ecological awareness causes new ways for raw materials producers. In addition, policies restricting the use of petroleum derived materials owing to certain regulatory processes have become imperative. Sustainable progress aims to prevent the depletion of natural resources and provide cost stabilization. The use of conversion parts is quite important (Leszczyńska et al., 2020).

Household include %36.7 metals, %16.7 plastics, 11.9% electric goods, %10.10 electro mechanicals, %6.4 electronics and 5.5% chemicals. The household production is important for Turkey. The Turkish household sector ranks second position in production worldwide, first manufacturing among European (EU) countries and also 5th in household exports worldwide. Polyurethane has for 5 % of the worldwide consumption of plastic polymers. Polyurethane (PU) is a cheap and efficient product (Fortune Business Insight, 2020).

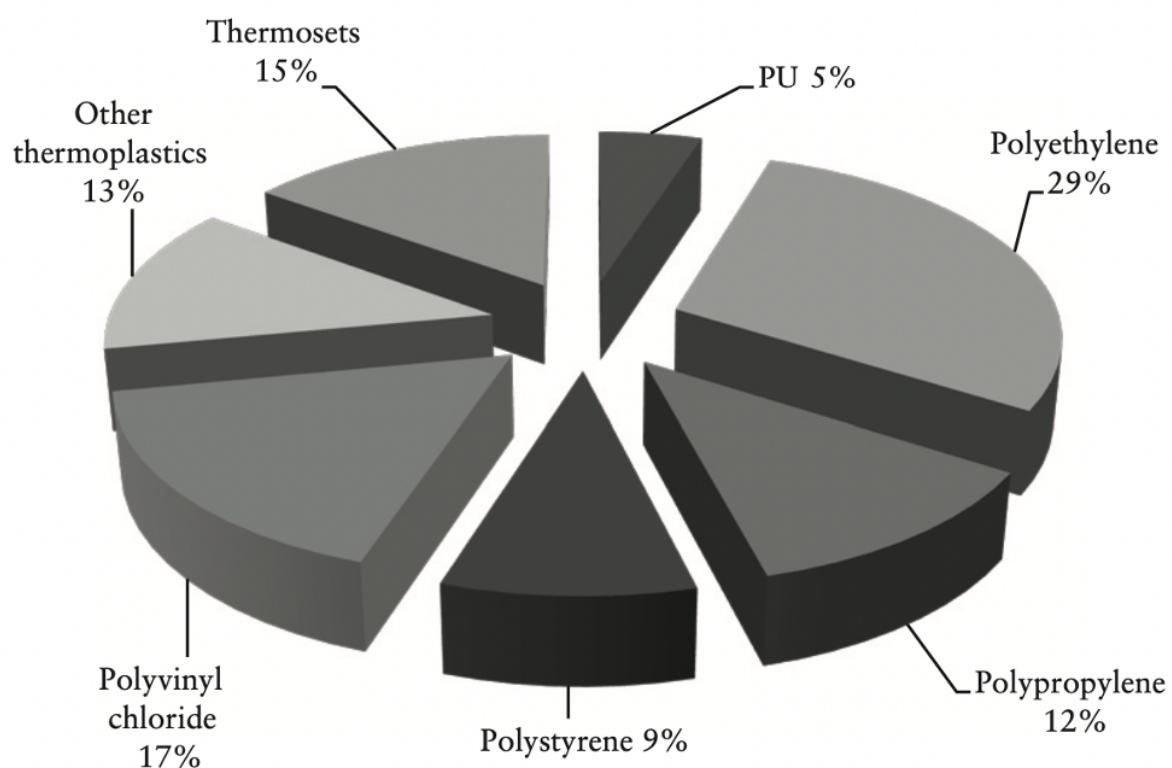


Figure 1.1. Consumption polymer material by household appliances

Figure 1.1 shows a comparison of the demand for polyurethane, and we can see that PU usage in all defined area has improved potential. The usage rate is expected to increase with the addition of recycled materials to polyurethane.

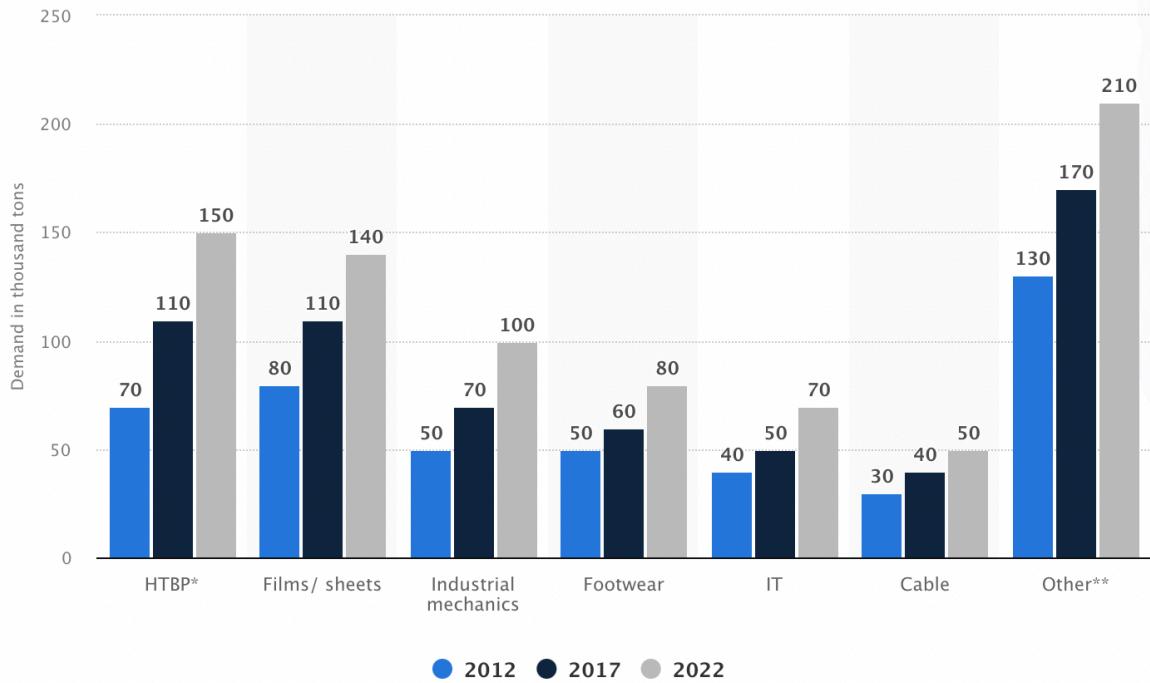


Figure 1.2. Comprasion of demand for polyurethane worldwide from 2012 to 2022

Increasing energy efficiency due to the energy labeling performance program and minimum energy performance criteria is a very important criterion for both environment and the future of cooling components. Different options may enhance the energy performance of the cooling compounds. The most effective products are advanced insulation rigid polyurethane foam (RPUF), improved gaskets, low global warning potential (GWP), advanced defrost systems such as back wall heaters, frame heater, enhanced fan motors, well-equipped evaporators, vacuum insulation panels (VIPs), condenser, capillary-tubes and effective compressors. As shown in Figure 1.2, polyurethane (PU) has been used in different parts of household devices such as films, industrial mechanics, footwear, cable and other.

The use of potentially green products in refrigerators can be considered to diminish both the high emissions and energy consumption which are directly effective for cooling devices. To enhance the cooling specialities, it is important to extent the thickness of the insulating materials that come to mind and prevent air leaks that affect the thermal cycle. Generally, in improvement ideas enhancing the insulation thickness to decrease the cabinet heat gain is the desire of appliance footprints appliance footprints desire to provide footprint reduction.

In our study, it will be developed not only by thickening the insulation properties, but also by products that can be recycled green. It is used in VIP (vacuum isolation panel) products as well as polyurethane as an insulation reinforcer. However, advanced VIP materials cannot be used at corners or sharp points (Bansal et al., 2011). VIPs, which are expensive contain chemical and flammable materials. On the other hand, natural fillers are accessible, inexpensive and provide fewer health risks. As a result, it was observed that natural fillers have a significant effect compared to other isolation products, considering their applicability, cost, environmental impact, accessibility, flammability, chemical-physical properties and accessibility. There is a case where the developed polyurethane is used at every point in the structural areas of the cabinet.

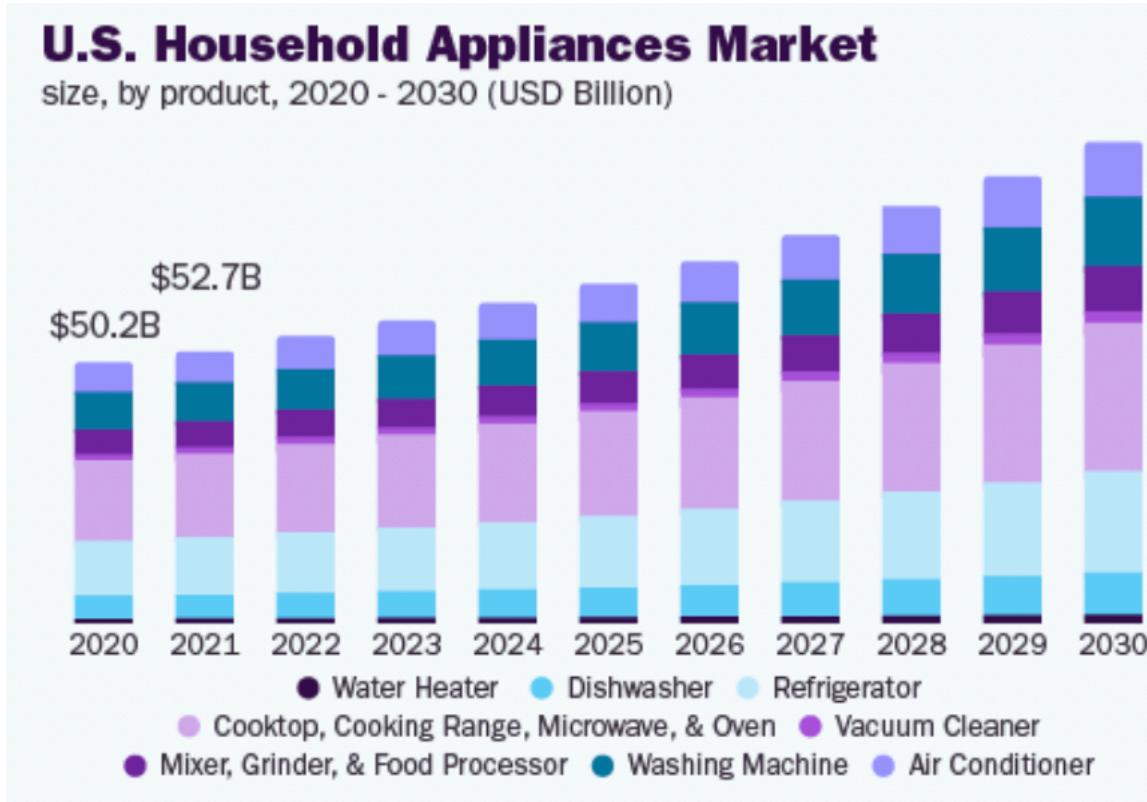


Figure 1.3. US household appliances market

The household appliances market is desired to grow from \$308.11 billion in 2020 to \$331.57 billion in 2021 at a compound annual growth rate (CAGR) of 7.6%, and we can clearly see that in Figure 1.3 the production growth value was stable but it will be gradually improve in future production value (The Business Research Company, 2022).

## 1.2 Historical Enhancement of Polyurethane

### The timeline of rigid polyurethane foams;

Polyurethane has a significant background in this field. The hierarchical structure of polyurethane developed since 1937 is as follows:

- 1937 ; Polyurethane was obtained from Dr. Otto Bayer.
- 1940 ; Rigid polyurethane foam began to be used in the aircraft sector.
- 1948 ; Polyurethane was used as insulation structure in beer barrel.
- 1953 ; Polyurethane was first used in shoes the sector as a leather.
- 1954 ; Flexible PU foam was used in the cushions.
- 1959 ; Chlorofluorocarbons has been used as blowing agents for the first time.
- 1960 ; Building construction panels have begun to be used.
- 1967 ; First all the produced plastic car had polyurethane foam.
- 1970 ; Polyurethane began to be used in medical products.
- 1972 ; Polyurethane was used as the track surfacing in the Munich Olympic Stadium.
- 1973 ; For the first time , thermoplastic polyurethane was used .
- 1979 ; Construction sector has gotten spray polyurethane.
- 1980 ; Polyurethane sandwich panels were used.
- 1981 ; Surfboards were first made of polyurethane.

1985 ; Polyurethane was used as the energy absorbing component.  
 1989 ; Polyurethane was used as an energy absorbing foam in cars.  
 1990 ; Polyurethane was used as an insulation material in the cooling parts.  
 1991 ; Memory foam was first produced in the USA.  
 1995 ; Bicycle tires are produced using polyurethane foam to improve performance.  
 2001 ; Car tires were produced using polyurethane foam to improve performance.  
 2003 ; Through EU regulations only HCFC-free polyurethane has been used.  
 2008 ; First high speed swimsuits were improved with polyurethane foam.  
 2011 ; Apple used in Ipad2 cover material made of polyurethane.  
 2011 ; Formula teams integrated polyurethane as safety blocks to replace tires.  
 2011 ; In Germany , the first plant was using carbon dioxide as an ingredient in foam.  
 2011 ; Airbus produced isolation foam in their 10000 orders.

As seen in the timeline, polyurethane has been used in very different areas; such as transportation, construction, furniture, home appliances, packaging, textiles and footwear. Polyurethane foam (RPUF) is crucial in the cooling sector owing to its thermal insulation properties. Rigid polyurethane foam (RPUF) also has many benefits in cooling devices (Ashida, 2006);

- Production cost is price performance product.
- It is quite light and affects the complete transportation skills of the refrigerant.
- Polyurethane is a runny part shaped in a mould.
- Polyurethane has a low thermal conductivity and great insulators.
- RPUF's thickness provide more optimum structure.
- Polyurethane is affordable products and it makes cooling appliances being more price competitor.

### 1.3 Rigid Polyurethane Foam (RPUF)

RPUF is an important component of household appliances, especially refrigerators. In line with the current energy shortage and the measures taken against global warming, the main purpose is to obtain enhanced polyurethane with natural fillers obtained from recycling. Industry and academics have studies many articles on similar studies. In our study, it was primarily aimed to improve the insulation properties by adding walnuts, hazelnuts, egg shells and aerogel to the foam material. Structural characterizations of related additives were characterized and evaluated.

RPUF has been using from 1940s until now, because the product has lots of great talents. RPUF that is lightweighted, have powerful performance and low thermal conductivity characteristic. Because of its specialities, nowadays RPUFs are the most desirable products among the polymer substances. Polyurethane materials are generally stands out with isolation skills.

Polyurethanes are parts used in different areas of industry. It emerges with the formulation of basic components such as polyols and isocyanates. Many processes and items are included under the properties of the polymer. These are cell distribution, agglomerate formation, cell size, cell structure and density which are all important indicators (Verdolotti et al., 2017).

Isocyanate group and hydroxyl group of polyol react with each other. It is the most used method. Urethane reaction is shown in Figure 1.4. (Ionescu, 2016)

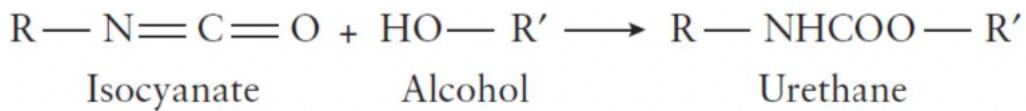


Figure 1.4. Urethane reaction from isocyanate and hydroxyl group.

Preparation of rigid polyurethane foams formed by the reaction of polyisocyanate, polyol, blowing agents, catalyst and surface active materials without heating process (Landrock, 1995).

By modulating the formulation of polyurethane consist of isocyanate and polyols. Flexible foams have been acquired with open cell and also rigid polyurethane foams have been acquired with close cell (Verdolotti et al., 2017).

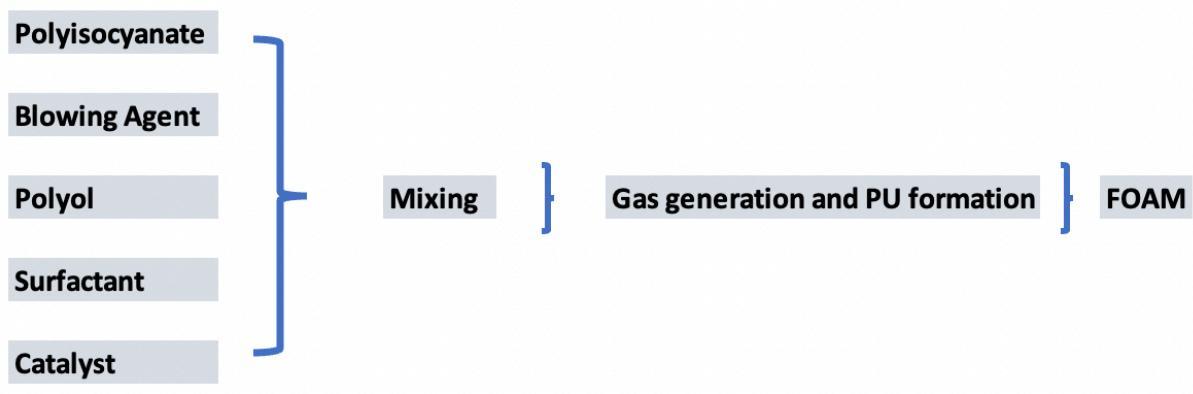


Figure 1.5. Process of RPUF production

As it is seen in Figure 1.5, polyurethane foaming process include different materials. The first step is the mixing of the reactants and then the polymerization reaction occurs between these reactants with the OH groups of the polyol as an alcohol group and these reactants with the isocyanate functional group. With the initiation of the polymerization reaction, blowing agents provide foam-forming expansion.

### 1.3.1 Rigid Polyurethane Foam Polyols

Polyols are reactive materials which are typically liquid bases. Polyols contain at least two hydroxyl groups. The isocyanate and hydroxyl groups of polyol react with each other to produce polyurethane synthesis. Commonly used polyols are classified into two categories hydroxyl-terminated and amino-terminated polyols. Polyols have a significant effect on the properties of completed polyurethane foams. While associating polymer specialty with urethane linkage, the polyol structure of the polyol is directly related to both the polyurethane polymer specialty and processing. Many linkages in polyurethanes are produced from polyol bonds. The most important properties of polyols are their chain units flexibility, rigidity, functionality and equivalent of weight. The polyol determines the type of polyurethane that we want. Polyol has a direct effect on the physical properties. The final product of being rigid, flexible or being fragile also has an effect on gas and moisture permeability. Rigid parts were formed with a low molecular weight structure and branched resins. Figure 1.6 shows that the type of hydroxyl groups of polyols that are used for processing polyurethane products can be acquired with polyether-based and polyesters-based that have mainly hydroxyl groups. Polyethers include

glycerin, sorbitol, trimethylpropane, methyl glucoside, sucrose and aromatic derivatives. Generally polyesters have the advantage of providing self-extinguishing characteristics. The hydroxyl numbers of polyethers are generally in the range of 350-600 in order to get rigid polyurethane foam and also the range of 40-75 of polyether is used for flexible polyurethane foams (Szycher, 2013).

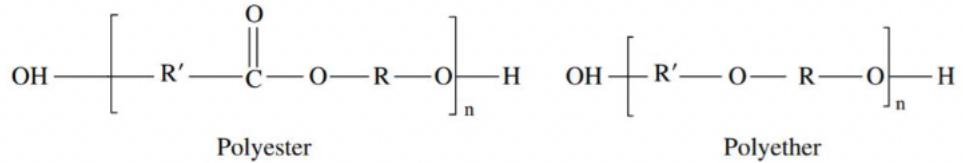


Figure 1.6. Chemical structure of polyester and polyether

Figure 1.7 shows the Polyether is the most preferred part in worldwide to obtain polyurethane foams. The manufacturers generally prefer polyether instead of polyesters.

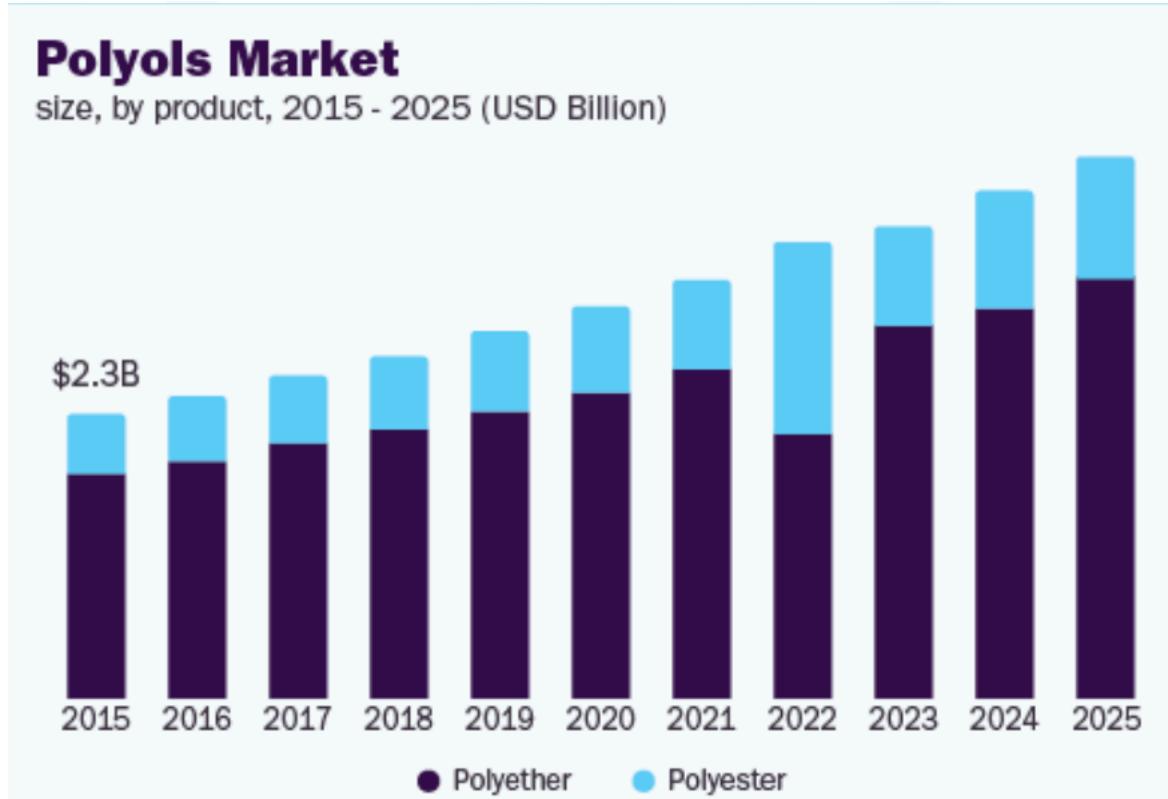


Figure 1.7. Production of polyether and polyester for PU Worldwide between 2015-2025

### 1.3.2 Rigid Polyurethane Foam Isocyanates

One of the basic components of polyurethane reaction is isocyanate.

- It reacts with water to form carbon dioxide. This creates a suitable gas for the foam structure, as shown in Figure 1.4. and Figure 1.6.
- It is made by linking polyol molecules through the reaction between isocyanate and hydroxyl groups to serve as a di or polyfunctional reactant. Thus, a highly cross-linked polymer was formed. It provides heat for good rigidity of the foam for the evaporation of inert blowing agents.
- Isocyanate produced polyurea urea. The polyurea linkages provide rigidity and thermal resistance to polyurethane foam.

Generally, Methylene diphenyl diisocyanate (MDI) based polyisocyanates are selected to obtain rigid polyurethane foams because the polyfunctional part has a lower vapor pressure which decreases the toxicity of isocyanates.

Isocyanates and water generate gaseous carbon dioxide (CO<sub>2</sub>) and urea groups. The cellular structure of PU foams is generated by a convenient gas source.

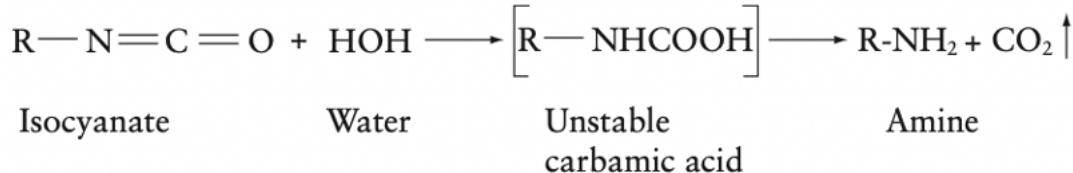


Figure 1.8. Reaction of isocyanate and water

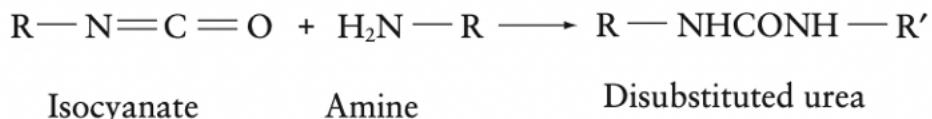


Figure 1.9. The amine reacts with isocyanate molecules and create a disubstituted urea.

The reaction between isocyanate and water is more exothermic than that between the alcohols. Water acts as a chemical blowing agent because gas generation result from chemical reactions (Ionescu, 2016).

Toluene diisocyanate (TDI) is manufactured via the phosgenation of diaminotoluene, which is obtained by the reduction of nitrotoluene. Modified TDI and undistilled TDI are mostly used for rigid urethane foams and in part for semi-rigid foams. Thus, TDI is not suitable for preparing polyisocyanurate foams.

MDI was obtained by the phosgenation of the condensation product of aniline with formaldehyde. Polymeric and oligomeric MDI are in the liquid form. MDI (or monomeric MDI) is obtained by the distillation of a crude reaction product and is used for elastomers and coatings. Polymeric MDI is used for rigid and semi-rigid urethane foams, as well as polyisocyanurate

foams. Recently, a polymeric MDI-based flexible foam technology has been developed. (Lee et. al., 2004)

Isocyanates can be subdivided into aromatic, aliphatic, and cyclo-aliphatic types. Owing to their higher reactivity and favorable economics, aromatic isocyanates account for more than 95% of the isocyanate consumption of rigid polyurethane foams. Early developments were primarily based on toluene diisocyanate (TDI), but this changed during the 1960s when diphenylmethane diisocyanates (MDI) and their polymeric byproducts (pMDI) became commercially available. Since then, MDI and pMDI production has seen significant capacity growth. In 1984, the global use of MDI/ pMDI surpassed that of TDI and has outperformed the latter ever since (Lee et al., 2004).

The production of MDI/pMDI was based on aniline and formaldehyde as the main raw materials. Aniline is produced from benzene. The preferred commercial production method with the lowest cost is via nitration of benzene to nitrobenzene, using a mixed acid process whereby aniline is produced from nitrobenzene through a reduction step.

Following the reaction of the polymeric amine mixture with phosgene, excess phosgene and acid were removed and the solvent was distilled off. Undesired secondary reactions are initiated when amines react with isocyanates to form ureas, which can be dehydrated by phosgene to form carbodiimides (CDIs)

In production of what, pure MDI is separated from the MDI/pMDI product mixture by means of distillation. The bottom product of this distillation is known as polymeric MDI (pMDI), which is the isocyanate of choice for the production of rigid polyurethane foam. Depending on the market demand and plant capacity, pMDI is sometimes produced as a straight-run product by changing the plant operating conditions. Their chemical structures are shown in Figure 1.10 and 1.11 (Ashida, 2006).

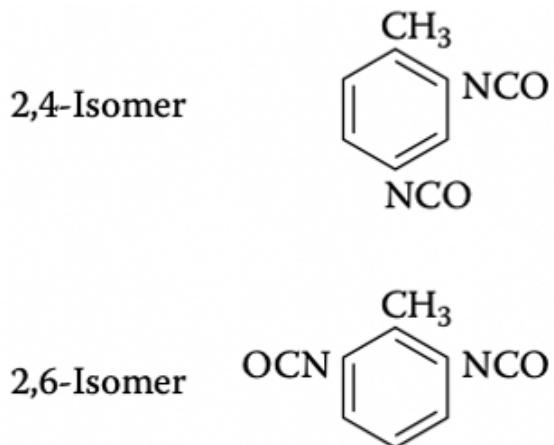


Figure 1.10. Chemical structure of TDI

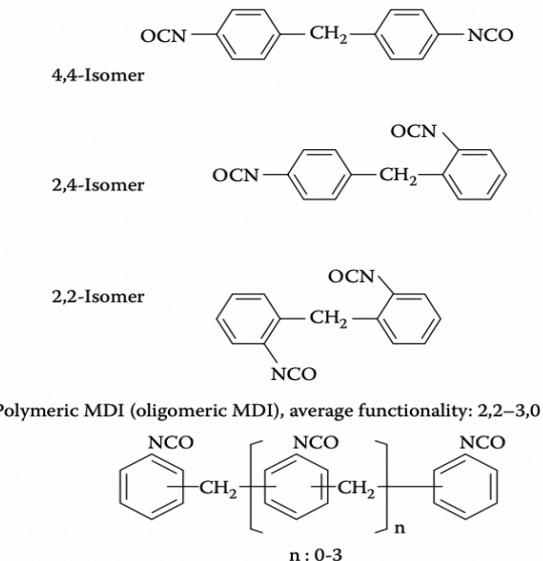


Figure 1.11. Chemical structures of MDI

### 1.3.3 Formation of Cells in Rigid Polyurethane Foams

Close cells are required for rigid foams. The cell membranes must be elastic to permit stretching and breaking. The cell walls shouldn't break during at the maximum gas evolution. From gas formation to induration, the cell shape needs to be improved to avoid complete damage.

A small amount of isocyanate was sufficient the against heat distortions. Increasing the amount of isocyanate has a negative effect on brittleness, while increasing heat decomposition healing. The excess portion increases the density by acting as a plasticizer. In this case, longer curing is required at higher temperatures (Szycher, 2013).

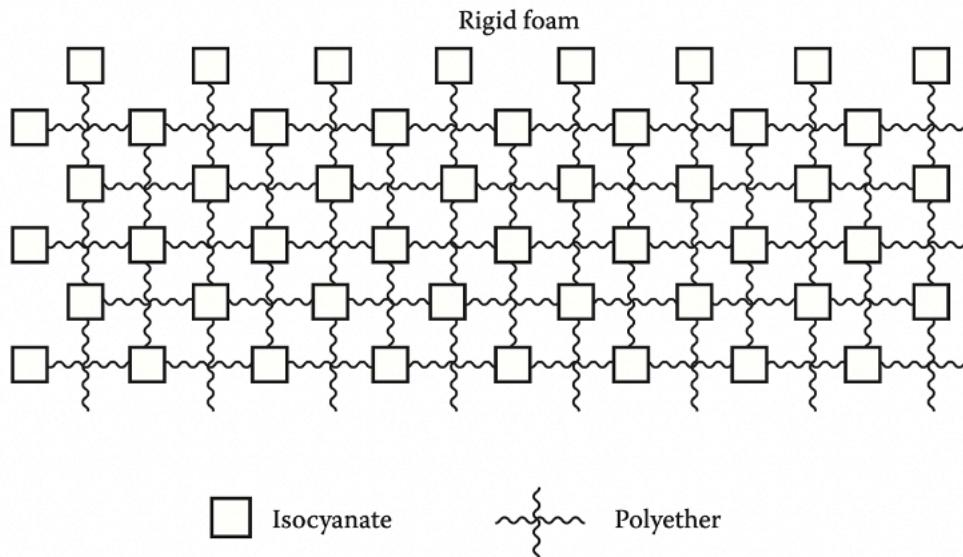


Figure 1.12. Cross-linked structure of isocyanate and polyether

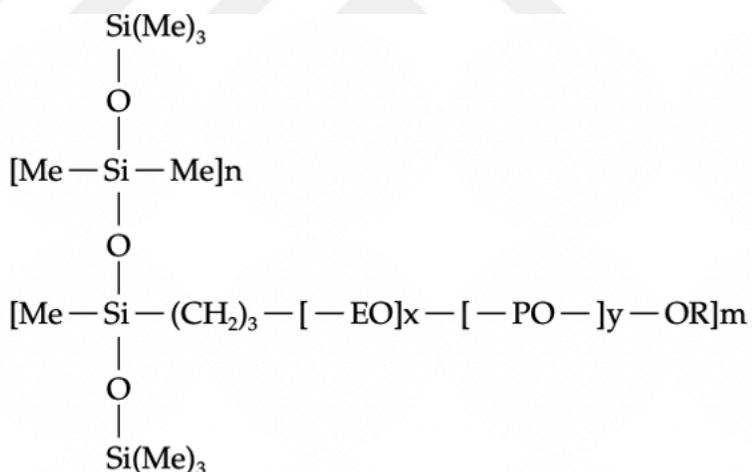
### 1.3.4 Rigid Polyurethane Foam Surfactants

To obtain a normal cell structure and a stable foam; rigid polyurethane requires surfactants. Surfactants are also known as stabilizer (Szycher, 2013).

Surfactants have two specific effects on the rigid polyurethane structures;

1. Surfactants stabilize the rigid foam after mixing polyol and isocyanate by decreasing the surface tension of the emerging gas-liquid interface and probably by emulsifying the polyol-isocyanate interface.
2. Stabilize by polymerizing the liquid-gas interface during a roughly 50-fold volume increase of the rising foam. Here, the mechanism is dynamic, the expanding foam continuously creates new surface area of high tension that needs to be stabilized by fast migration of surfactant towards the interface (The Marangoni effect).

Anionic surfactants should not be added to foaming components. The most commonly used surfactants are dimethyl polysiloxane and polysiloxane-based copolymers. Some of these silicones have been prepared using ethylene and propylene oxides. Some silicones containing Si—O—C bonds are hydrolytically unstable. High viscosity silicone polymers have fine cell structure and are more efficient. It can affect cell structure even with low usage (Lee and Ramesh, 2004). The silicone surfactant reaction is illustrated in Figure 1.13.



Note:

Me:  $\text{CH}_3$

EO:  $—\text{O}—\text{CH}_2—\text{CH}_2—$

PO:  $—\text{O}—\text{CH}_2—\text{CH}—$   
 $\text{CH}_3$

Figure 1.13. Silicone surfactants

### 1.3.5 Rigid Polyurethane Foam Blowing Agents

The blowing agent has two primary duties. First, the reactions between isocyanate and polyol produce polyurethane conjugation with the emission of the heat of reaction. Second, the blowing agent evaporates because of the heat of the reaction and the gas is trapped in the closed cells of the foam resulting in the extremely low thermal conductivity of the RPUFs (physical blowing agents). In the presence of water, isocyanate also reacts with water to form urea bonds and generates a carbon dioxide “chemical blowing agent” (Kim, et al., 2008).

A chemical reaction occurs between the blowing agent and isocyanate. With this reaction, carbon dioxide gas is formed. A chemical reaction occurs between the blowing agent and the isocyanate. The use of halocarbons as blowing agents directly affects the production of rigid polyurethane (Ashida, 2006).

Table 1.1. Common blowing agents

Compound	Molecular Formula	Molecular Weight (g/mol)	$\lambda_{\text{gas}}$ @25°C mW/mK	Boiling Point (°C)	Vapor Pressure 20°C (bars)	Flammability Limits (% vol. in air)	Indicative Price \$/lb	GWP			Atmosph. lifetime (yrs)	Phase-out target
								ODP	100 yr ITH	HGWP		
CFC-11	C-Cl <sub>3</sub> F	137.5	7.8	24	0.88	none	n.a.	1.0	4000	1.0	<0.1	50-60
HCFC-141b	CH <sub>3</sub> C-Cl <sub>2</sub> F	116.9	9.8	32	0.69	5.6-17.6	~0.9-1.0	0.11	630	0.12	10	8-10
HCFC-22	CHClF <sub>2</sub>	86.5	11.2	-41	8.92	none	~1.0	0.05	1700	0.35	6	13-15
HCFC-142b	CH <sub>3</sub> C-ClF <sub>2</sub>	100.5	9.8	-10	2.50	6.7-14.9	~1.0	0.06	2000	0.36	5	19-20
HCFC-124	CHClFCF <sub>3</sub>	136.5	12.3	-11	3.27	none	~2.0	0.02	480	0.10	12	5-6
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	120	14.0	-48	12.41	none	~2.5-3.0	0	2800	0.58	1	32-35
HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	102	14.1	-23	4.53	none	~1.8-2.0	0	1000	0.20	8	10-12
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	102	14.3	-26	5.62	none	~1.5-1.8	0	1300	0.26	6	14-16
HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	66	13.8	-25	5.06	3.9-16.9	~2.0-2.5	0	140	0.03	14	1.5-2
HFC-245 fa	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	134	12.2	15	1.24	8.9-11.2	~3.0-4.0	0	820	0.18	11	7-10
HFC-365 mfc	CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	148	10.6	40	0.47	3.5-9.0	~3.0-4.0	0	840	0.18	7	9-12
n-Pentane	C <sub>5</sub> H <sub>12</sub>	72	14.6	36	0.65	1.4-8.3	~0.25	0	11	0.002	500	0.03
Iso-Pentane	C <sub>5</sub> H <sub>12</sub>	72	13.8	28	0.80	1.4-7.6	~0.25	0	11	0.002	500	0.03
Cyclo-Pentane	C <sub>5</sub> H <sub>10</sub>	70	12.6	50	0.34	1.4-7.8	~0.75	0	11	0.002	400	0.05
Iso-Butane	C <sub>4</sub> H <sub>10</sub>	58	15.9	-12	2.99	1.8-8.4	~0.3	0	5	0.001	650	0.02
n-Butane	C <sub>4</sub> H <sub>10</sub>	58	15.3	-1	2.08	1.6-8.4	~0.3	0	5	0.001	650	0.02
Carbon dioxide	CO <sub>2</sub>	44	16.3	-78	56.55	none	n.a.	0	1.0	1.10-4	0	120-200
Air	N <sub>2</sub> /O <sub>2</sub>	28.8	26.5	-193	624.03	none	n.a.	0	0	0	0	none

ODP = Ozone Depletion Potential

GWP = Global Warming Potential

ITH = Infinite Time Horizon

HGWP = Halocarbon Global Warming Potential (R-11 = 1.0)

POCP = Photochemical Ozone Creation Potential (methane = 1)

SFP = Smog Formation Potential (methane = 1)

The boiling point, molecular weight, reactivity, heat of vaporization, solubility, coefficient of thermal conductivity and other materials used to prepare the foam are all features that require attention, such as cyclopentane. Thus, the blowing agents have a significant effect on RPUF formation. A list of the blowing agents in Table 1.1.

Chlorofluorocarbon CFC-11 has been used as a blowing agent in the rigid polyurethane foam industry for almost 30 years, because of its high molecular weight, low toxicity, boiling temperature (23.8 °C), and very low gas K-factor of 7.8 mW/mK. In summary, CFC-11 can be considered the best blowing agent ever used for thermal insulation foam applications, and rigid polyurethane foams containing high amounts of CFC-11 can reach K-factors as low as 15-17 mW/mK (Szycher, 2013).

The new technology requires enhanced compounds with low thermal conductivity due to new restriction regulations. New type should be cheap and have to show many other characteristics in order to fit within rigid polyurethane foam applications. Characteristics vary widely and include qualities such as being non-toxic, environmentally friendly, zero ozone depletion potential (ODP), low global warming potential (GWP), chemical inertness, good solubility in polyol and isocyanate components, a usable boiling point (ideally in the range of -10 to 50°C), low diffusion coefficient in the PU foam matrix, and of course being readily available in commercial quantities (Lee and Ramesh, 2004).

### 1.3.6 Rigid Polyurethane Foam Catalysts

A material that does not permanently affect the reaction and causes a chemical reaction when a small amount is added to the reactants is known as a catalyst. If the reaction is not sufficient to create gas trapping, the catalyst must add a reaction. Polyurethane foaming, network kinetics and phase separation are highly comprehensive and sensitive phenomena. The effects of the catalyst combinations are described below.

- The blowing reaction of pMDI with H<sub>2</sub>O to form CO<sub>2</sub> and polyurea
- The gelling reaction of pMDI with polyol to form polyurethane
- The trimerization of pMDI (as well as related reactions, such as carbodiimide and dimer formation)

Catalysts can be used in rigid polyurethane foams such as tertiary amines, aromatic amines, quaternary and ammonium salts (Lee and Ramesh, 2004).

## 1.4 Types of Polyurethanes

There are two types of polyurethanes, rigid foamed polyurethane and flexible foamed polyurethane. Flexible foams can be further divided into semi-flexible and flexible foams. The physical property differences resulting from these are mainly due to the molecular weight per crosslink and the performances of the polyols and isocyanate. In general, it can be observed which type of foam formation will occur with the average values in Table 1.2 (Landrock, 1995).

Table 1.2. Common blowing agents list

Classification of Urethane Foams					
	Polyol		Functionality	Elastic Modulus at 23 °C	
Foams Type	OH No (mgKOH/g)	OH Equivalent		MPA	lb/in <sup>2</sup>
Rigid Foam	350-560	160-100	3.0-8.0	>700	>100,000
Semi - Rigid Foam	100-200	560-280	3.0-3.5	700-70	100,000-10,000
Flexible Foam	50-150	10,000-800	2.0-3.0	<70	<10,000

Sofa groups are manufactured with flexible upholstered polyurethane, gradually accounting for 30% of the total production capacity worldwide. Automotive industries have also used flexible and semi-flexible polyurethane for soundproofing, bumpers and seat cushioning. Rigid polyurethane is used as a heat insulator in the cooling of household appliances, refrigerated transportation and building construction insulation. Elastomers and

polyurethane are used in the footwear industry. Industrial tires. Adhesive polyurethanes, sealants, binders, coatings and fibers were used. In Figure 1.14, the utilization rates of foam types are indicated (Szycher, 2013).

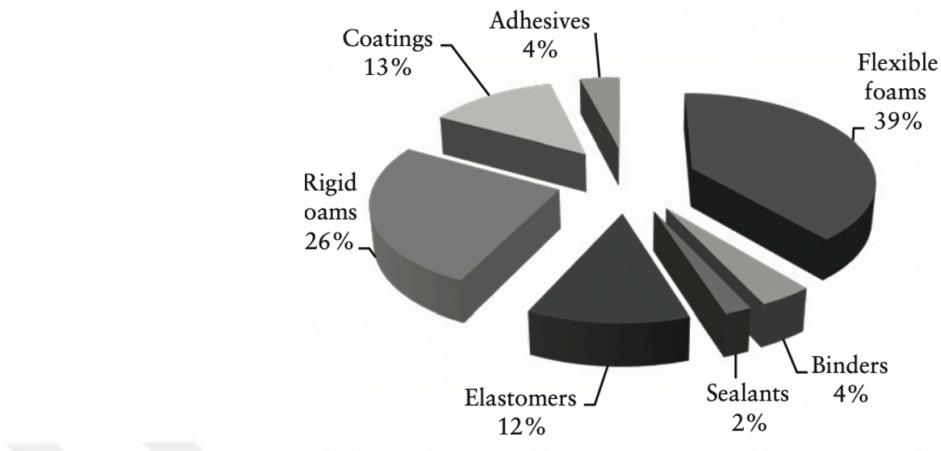


Figure 1.14. Usage rate of PU types

## 1.5 Cell Structure

Cellular structure affects the thermal, mechanical and physical properties of porous materials. The correlation between the filler concentration, viscosity of the PU system and distribution of filler particles in the PU matrix is a crucial factor in obtaining PU materials with a well-developed morphology (Czlonka et al., 2020).

This depends on the chemical and physical parameters used to obtain the correct morphology. Temperature of the environment during the reaction, bubble nucleation stage, cell growth structure, organic-inorganic particles, hydroxyl number, NCO index, polyol, isocyanate and catalysts have a great effect.

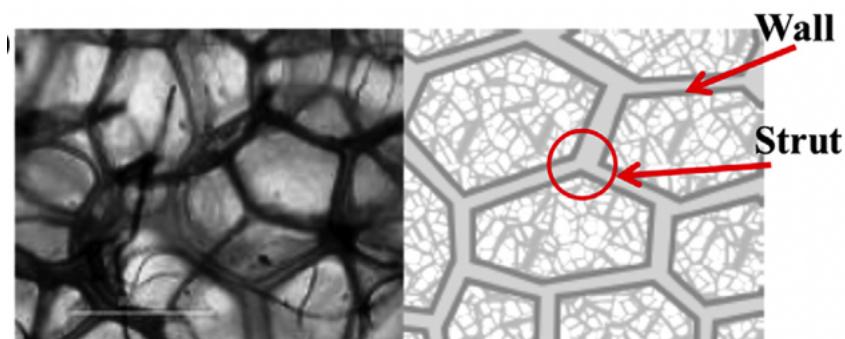


Figure 1.15. SEM images of wall, strut and the closed cells of rigid foam

The foam structure can be clearly observed including the heat transfer area in the gas and solid phases, wall area and strut surface as shown in Figure 1.15. Whereas a micrograph of the same can be observed in Figure 1.16.

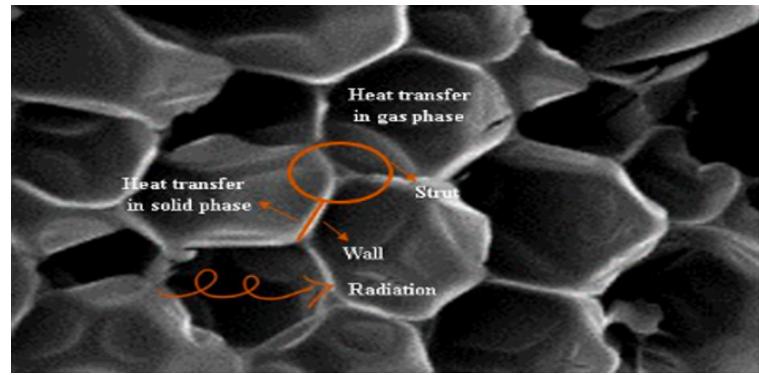


Figure 1.16. SEM micrograph showing the closed cells of rigid foam

The increase in gas pressure inside the growing bubbles causes higher internal pressure and surface energy. It has a significant effect on bubble growth and stabilization depending on shear rate, temperature, viscosity. Bubble growth stops when the viscosity becomes too high due to the increased molecular weight. It is important to control the viscosity of the polymerization reaction and the growing cell structure in order to stabilize the cells in the reacting medium during solidification and to obtain the desired porous structure. If the viscosity is too low during growth, the cells become unstable. This allows us to have an inhomogeneous collapsed structure (Verdolotti et al., 2017).

## 1.6 Foam Preparation Process

As urethane foams, there exists different preparation methods that can be produced by one shot process, semi-prepolymer (quasi-prepolymer) process or prepolymer process. The most common process is the one-shot method ((Landrock, 1995).

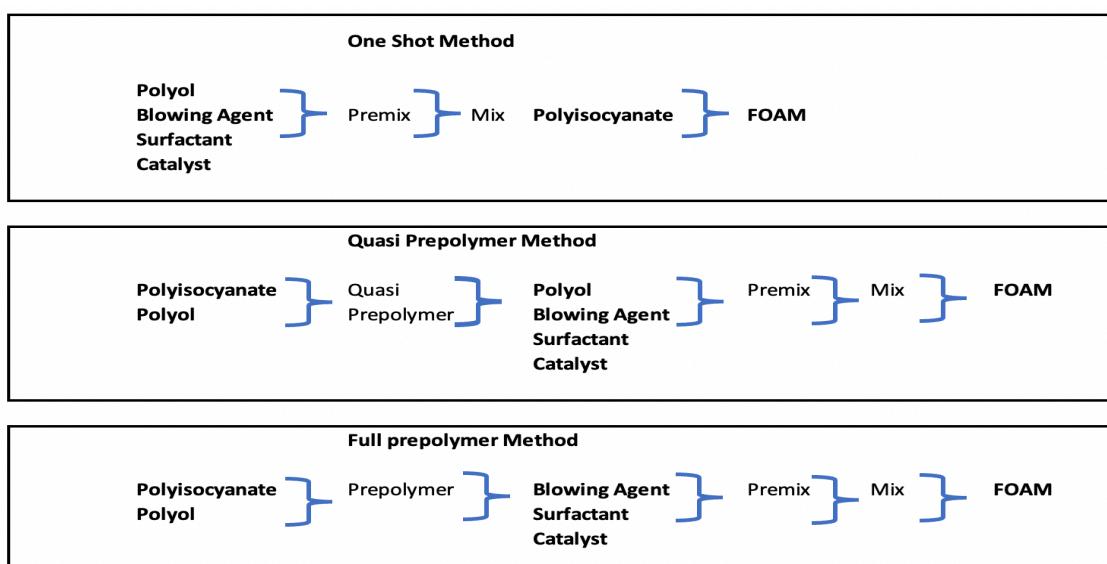


Figure 1.17. Preparation types

In the one shot method, all the components, namely polyol, isocyanate, surfactant, water or volatile solvent and catalysts are combined at once at the same time to produce a foam, and the resulting reaction completes in one shot as shown in Figure 1.17. The reaction producing the foam is exceptionally rapid and the viscosities and other physical relationships between the mentioned five materials are not always very easy to handle; therefore, producing the number of ingredients being mixed at one time is desirable. For the development of the quasiprepolymer method, this is the reason.

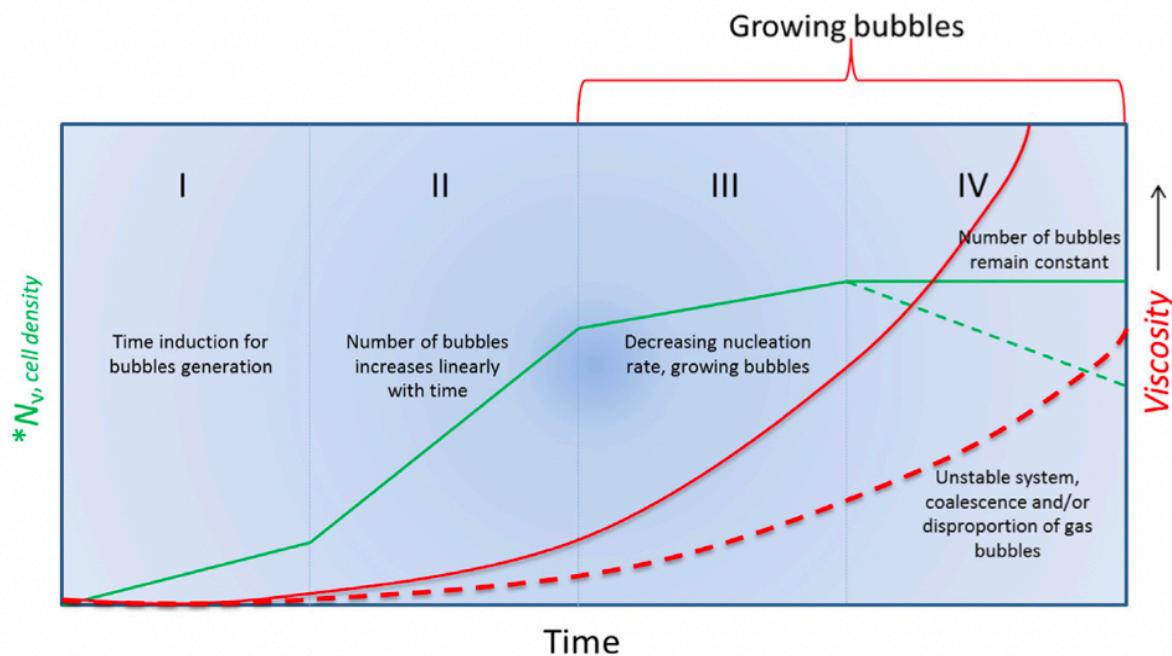
The probability of direct contact with the toxic and irritating diisocyanate is quite strong with this system. Furthermore, the one shot foam reactions produce a very high exothermic temperature and this is why in many cases, the center of the part formed is charred. This is especially observed in larger foam parts (Szycers, 2013).

### 1.6.1 Growing bubbles structure and Gel Situation

Sequence of bubble growing are given below

- Time induction for bubbles generation
- Number of bubbles, increases linearly with time
- Decreasing nucleation rate growing bubbles
- Number of bubbles remain constant

Evaluation of foam cell is also given in Figure 1.18.



\* $N_v$  = number of cells per unit of volume of the solid material

Figure 1.18. Evolution of foam cell

## 2. LITERATURE REVIEW

Insulation effectiveness is the most important issue for cooling sector, because of that reason the number of studies that focus on increasing energy efficiency.

Nazeran and Moghaddas studied on the cell structure and thermal conductivity coordination by using silica aerogel in RPUF. This study presents the synthesis of silica aerogels on rigid polyurethane foam with thermal insulation properties. This thesis included a different trial. The adding silica aerogel was added to the MDI matrix, and silica aerogel was added to the polyol matrix using various weight percentages of silica aerogel (1–5 wt. %). The prepared composites were characterized using scanning electron microscopy (SEM), Thermal Conductivity, Fourier transform infrared spectroscopy (FTIR) and Contact Angle measurements. According to this study, the results submitted that the mechanical properties and cell structure of nanocomposites were affected by the silica aerogel content. The amount of silica aerogel to RPUF foam can directly enhance foam quality, mechanical, hydrophobic and insulating properties of RPUF. When the two different methods were observed, it was been emphasized that the addition of silica aerogel to the MDI matrix improved the distribution and properties of the aerogel. However, this method was not repeated, as correct results could not be obtained from the filling material that we wanted to react with the first MDI during our experimental study. In the case where we proceeded by reacting the filling material with the polyol, a rather smaller cell structure was obtained compared to the 15% wt value, in the case of adding 10% wt aerogel. As observed in the article by Nazeran and Moghaddas, an increase in cell size and a decrease in mechanical properties were observed with increasing wt% ratio (Nazeran and Moghaddas, 2017).

Leszczyńska et. al., shows effectiveness of natural fillers. Natural fillers such as peanut, hazelnut, walnut and pistachio shells were used in RPUF. Polyol, MDI, surfactants, blowing agents and catalyst were used and one shot method was followed by using Polyol, MDI, surfactants, blowing agents and catalyst. Each of the added materials had a different particle size. Between 45-180 micrometer. SEM, Sieve analysis, viscosity, FTIR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), water absorption was used in this article. Natural filler particles affected the RPUF structure. For instance, it had a substantial effect on size shape, surface area, characteristic structure, foam morphology and foaming process properties of the developed rigid polyurethane foam. The changes in the viscosity of the polyol premix were related to the particle size, shape and surface area of the natural fillers. In our study, the effects on polyurethane were investigated by using large-sized fillers and we attempted to observe its negative effects by leaving 250-150 micrometers in hazelnut natural filling. We observed its negative effect on the foam. In addition, we also observed in our study that the stable structure and small particle size of the eggshell have a direct positive effect on its thermal and chemical properties. As a result, the accuracy of the relevant article has been proven by us (Leszczyńska et. al., 2020).

Kumar et. al., submitted about reinforced of rigid polyurethane foam (RPUF) by the addition of glass fibers. The mechanical properties of the reinforced foam were investigated including, mechanical properties such as flexural strength, hardness, tensile, compressive strength and morphology. For example, castor oil, 4,4'-diphenylmethanediisocyanate, triethylenediamine (TEDA) (99%), coupling agent (A-189 gamma-mercaptopropyltrimethoxysilane) silicon oil (C-63148-62-9), chopped glass fiber (GF) (25  $\mu$ m in diameter) and n-pentane (C-109-66-0) glycerol were pre-treated with silane as a coupling agent to attain uniform dispersion of the glass fiber inside the foam. The mechanical properties,

tensile strength, compressive strength, water absorption, flexural strength and average hardness of the foams were also investigated. Consequently, the mechanical structure of the foam was affected by the addition of GF. The density increases with the addition of the material. The cell sizes were decreased by the glass fiber material (Kumar et. al., 2017).

Czlonka et. al., investigated the emphasis on nutmeg filler. RPUF foams were reinforced with different concentrations (1 wt%, 2 wt% and 5 wt%) of nutmeg filler. In their study, in addition to the thermal and mechanical properties, the anti-aging and antimicrobial properties were also examined. In addition, SEM, compression test, impact test, three-point bending test, impact strength, TGA, flammability, ultraviolet (UV)-aging, apparent density, dimensional stability, surface hydrophobicity, water absorption and color characteristic tests were performed to observe the added RPUF structure. The foam included polyester polyol (functionality of 2, hydroxyl number of 230–250 mgKOH/g), flame retardant, catalyst and chain extender and diphenylmethane 4, 4'-diisocyanate. The synthesized PU composite foams were first stabilized at 5000 rpm for 60s and poured into an open mold. Subsequently, the one-shot method was applied. As a result of the study, it has been observed that the filling material had positive effects. The foaming kinetics, foam morphology, mechanical and thermal properties of PU with the addition of coconut filler were similar to those obtained for eggshells. In addition, the effect of coconut on nonflammability was observed in a previous study (Czlonka et. al., 2020).

Tiuc et. al., enhanced the acoustic properties of the RPUF of a closed-cell, by incorporating various quantities of textile waste into the matrix. In that study, as sound absorption was the primarily priority was not given to mechanical and thermal properties. By examining its positive effects on sound isolation processes, a successful study can be performed using this method (Tiuc et. al., 2015).

Jarfelt and Ramnes, attempted to obtain a good PU, the points of low foam density, small cell structure and low thermal conductivity are emphasized PU from isopentane with  $13.4\text{--}14.8\text{ mW}\cdot\text{m}^{-1}\text{ K}^{-1}$  ensured the best conductivity value. They stated that the best ratio was achieved with a mixture of carbon dioxide and cyclopentane at this ratio. The best result is achieved in terms of the mechanical and thermal properties when the specified low foam density, small cell structure and low thermal conductivity points are considered (Jarfelt and Ramnes, 2006).

Saha et al., investigated the effects of different types of nanoparticles on thermal and mechanical performance of rigid polyurethane (PUR) foam. Three different types of nanoparticles, namely spherical  $\text{TiO}_2$ , platelet nanoclay, and rod-shaped carbon nanofibers (CNFs) were considered. The foam materials were characterized by scanning electron microscopy (SEM), FT-IR and thermogravimetric analysis (TGA). Tensile, tension, compression, flexure tests were conducted to examine the mechanical features. Sanitation was used to diffuse the nanoparticles into the foam. In all the thermal and mechanical tests conducted, it was observed that polyurethane/carbon nanofibers showed the highest increase and Polyurethane/ $\text{TiO}_2$  showed the lowest increase. Adding only 1% by weight of carbon nanofibers to polyurethane foam increases its modulus by approximately 86% in tension, 40% in compression and 45% in bending, while strength increases by approximately 35% in tension, 57% and 40% in compression (Saha et al., 2008).

Estravis et al., were used water-blown rigid polyurethane (PU) formulation was used to produce cellular nanocomposites containing montmorillonite nanoclays at different concentrations. The formulation was based on methylene diphenyl diisocyanate (MDI) and a mixture of polyether polyol, catalysts, additives and a blowing agent (water). Cloisite 30B

nanoclay is a natural montmorillonite modified with a quaternary ammonium salt. When clays were added, a strong reduction in cell size and changes in cell size distribution, anisotropy ratio and material fraction in the struts were detected. In addition, a decrease in thermal conductivity was observed. This indicates some kind of chemical interaction between the nanoclays and evolving foam. This interaction plays an important role in foam formation, leading to a slight imbalance in the gelling and blowing reactions compared to uniform foam formation. In addition, this interaction promoted the insertion of clay particles during foaming. (Estravis et al., 2016).

Czlonka et al., studied on Shine Powder, a proteinaceous solid tent waste which has been used as a reinforcing filler in rigid polyurethane foams (RPUFs). RPUFs were modified with shine powder in the range of 0.1-5% by weight based on the total mass of the polyol. It was found that the addition of BD leads to noticeable changes in several properties, notably foam morphology, apparent density, thermal conductivity, and mechanical strength. The results obtained in this study confirm that the addition of Shine Powder above a certain optimal level has a negative effect on cell morphology, leading to the deterioration of the physico-mechanical properties of the modified foams. Chemical structure (FTIR), thermal properties (TGA), dynamic mechanical properties (DMA), physico-mechanical properties (compressive strength, three-point bending test, apparent density), foam parameters and morphology of PU composites were investigated. RPUFs modified with powder exhibited favorable properties (Czlonka et al., 2018).

Czlonka et al., were chosen potato protein as a reinforcing filler in polyurethane foams. Rigid polyurethane foams (RPUFs) were obtained from a two-component system and modified with PP in the range of 0.1-5% by weight of the total polymer mass. The effect of potato protein on the RPUF morphology and the physical and mechanical properties of the obtained porous materials were investigated. The PU foams were characterized using morphological, mechanical and thermal analyses. The results showed that the addition of 0.1% by weight of PP improved the compressive strength (final strength up to 230 kPa) due to the reinforcing effect of the filler, low thermal conductivity (0.029 W/m.K) and low water absorption (14.3%). As observed in other articles, in this article as well, it has been observed that if the wt % ratio is kept too high, it has a negative effect on the foam (Czlonka et al., 2018b).

Rising ecological awareness and policies based on restricting the use of petroleum derived materials have led us to use recycled food materials such as eggshell, walnutshell and hazelnutshell as an filler to enhance the thermal isolation properties of conventional polyurethane foams. Natural fillers have numerous advantages, including easy availability, low cost, low density, recyclability, renewability, biodegradability and low health risks. In our study, the effects of natural fillers (walnut, hazelnut and egg) material on polyurethane were observed. Mesaporous silica based particles, namely silica aerogels were also used as an filler for PU foams due to the light-weight and highly porous structure of the aerogel materials they are considered as promising filler for polymer matrix in thermal insulation applications. Specific tests were conducted to reveal the chemical, morphological and thermal properties of polyurethane. The density, cell size, closed cell number, SEM, FT- IR, thermal conductivity, microscopic and contact angle tests were performed. It has been observed that some specialties such as additive material size, density, cell size, structure of the fillers have a significant effect on polyurethane. Similar results were observed in majority of articles.

### 3. EXPERIMENTAL

#### 3.1 Foaming Process

The one shot method by hand chosen as was chosen to prepare the RPUF. The polyol to pentane ratio in the mixture was 100:13. The polyol and fillers were mixed for one minute before the addition of isocyanate. The polyol pentane mixture was being mixed with a mechanical stirrer, 150 grams of MDI (methylenediphenyldiisocyanate) was added into the polyol pentane mixture. Polyol which included pentane and isocyanate was mixed for 10 seconds with a high-speed mechanical stirrer at 2000 rpm. Subsequently, the mixture was poured into a mold. The mold was heated before pouring the mixture. The average mold temperature was  $34\pm2^{\circ}\text{C}$ . The curing time for RPUF was 5 minutes. A laboratory scale mold was used to produce rigid polyurethane foam. Finally, foam can grow quickly. Foaming time depends on amount of filler materials. A schematic of the diagram experimental procedure is shown in Figure 3.1.

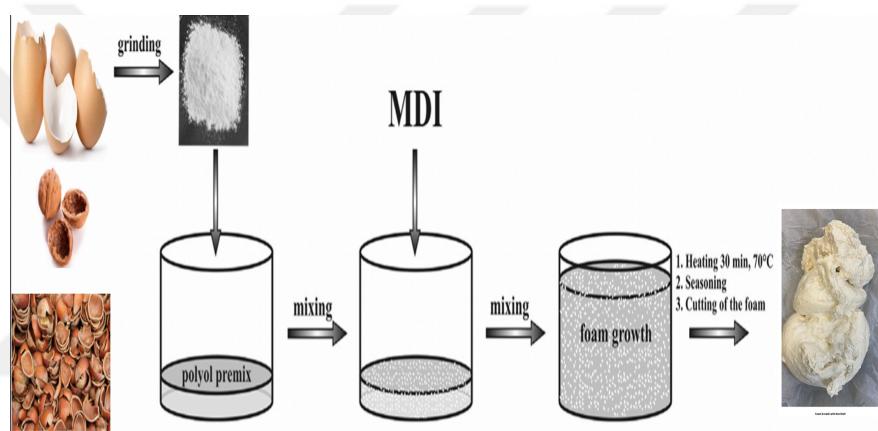


Figure 3.1. Production of polyurethane foam for the foam experimental method

#### 3.2 Preparation of Filler Material

Natural fillers were previously exposed to the sun for three days then they were ground with a Bosch brand multitalent 800 W blender machine. Hazelnut shell, walnut shell, egg shell were chosen as natural additive material. In addition, a study was conducted with the addition of aerogel. In egg shells successful reinforcement was achieved with different concentrations (10 wt%, 15 wt%, 20 wt%) of egg shells  $<45$  micrometers in hazelnut shells (10 wt%, 15 wt%) 250-150 micrometers in walnut shells 10 wt%, 15 wt% 75-45 micrometer, in aerogel at 20 wt% values on the other hand additions of 10 wt% and 15 wt% with  $<45$  micrometer.

Natural fillers have many advantages over synthetic fillers are frankly much more, such as easy availability, low cost, low density, recyclability, renewability, biodegradability and low health risks. This thesis reports the use of natural fillers such as eggshell, walnut shell and hazelnut shell in order to improve the properties of polyurethane foam (Leszczyńska et al., 2020).

### 3.3 Test Methods

#### 3.3.1 Characterization of Materials

In this thesis, the materials were characterized by TGA, FT-IR, contact angle measurement, gas pycnometry, tensile-compressive strength, SEM and XRF analysis. Device images are not used in the thesis due to confidentiality agreements and copyrights.

TGA analyses were carried out by the model of device was HITACHI STA7200 Thermogravimetric Analysis (TGA) is a technique that shows total weight changes with the increasing temperature (averagely 200 C°) of the sample. In the TG analysis, the dehydration and degradation processes of the material could be clearly observed depending on the time and temperature. Weight change at the beginning and end of the test occurs because of physical and chemical bond breaks (Ebnesajjad, 2011).

The infrared spectroscopy (FTIR) was used to analyze the chemical composition and degree of phase separation of the RPUFs. Each sample was scanned in 4000e400 m-1 range of wave-numbers using a Nicolet 6700 (Thermo Electron Corporation) FTIR spectrophotometer. Omnic Spectra 2.0 software by Thermo was used for data processing and analysis (Kuhn, 1992). Whether the two compounds are the same, the binding sites in the structure and the bonding status determine whether the structure is aromatic or aliphatic (ArelPOTKAM, 2022).

Contact angle measurement is an effective method for understanding surface interaction with three phase system (solid/liquid/air). The drop was placed on a flat horizontal surface. The observed angle allowed us to determine whether it was hydrophobic or hydrophilic. The angle formed by the intersection of the liquid vapor and liquid solid interface (geometrically integrated by drawing a tangent line from the contact point along with the liquid vapor interface of the droplet) is called the contact angle (Hebbar, 2017). The contact angle was measured using a Krüss instrument. Additives weaken their dispersion in polyurethane foam because of their tendency to form agglomerates and are hydrophilic. With this test, we can determine whether the additives are hydrophobic or hydrophilic.

X Ray Fluorescence spectrometry was used determine the plane distance of nutshell, walnutshell, eggshell and aerogel modified RPUFs. Analyses were conducted by the Zetium XRF spectrometer with a PANalytical device. The conditions were as follows: target anode Rh, 50 kV, 50mA, 2θ angles from 140.00 to 142.00 (Malvern Pan Analytical, 2022). XRF (X-ray fluorescence) is a non-destructive analytical technique which is used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays (a fingerprint) that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition (Termofisher, 2022).

The thermal properties of materials are very important for achieving optimum performance. Thermal conductivity is the most important thermophysical property used to describe the heat transport properties of materials. Thanks to the thermal conductivity analyzer, the thermal conductivity constant (k) of the materials was determined in W/mK. The result of the thermal conductivity measurements were used to determine the refrigerator performance. The thermal conductivity refers to the ability of a material to conduct heat. Thermal conductivity is the most important of the thermophysical properties used to describe the heat

transport properties of materials. The thermal conductivity of the rigid polyurethane foam was measured a Hesto ALC A206 device.

The cell size distributions and morphology of the RPUFs were investigated from the cellular structure images of the foam. Leica EM ACE 200 was used with an optical stereomicroscope at different magnifications. All modified RPUFs were scanned. The cell pore size was investigated and provided the study of the foam structure was studied in the presence of additives (Czlonka, 2018).

Closed cell values of the polyurethane foams were specified by (The AccuPyc II Series of Gas pycnometer). The thermal conductivities of foams were directly affected by the blowing agent. In the cell structure, blowing agents diffused out. Atmospheric gases with high thermal conductivity move inwards in the cell structure. Therefore, a decrease in the closed-cell content results in a higher thermal conductivity value of RPUF owing to the outward diffusion of gases inside the cells over time.

The cell size was measured with a Nikon shuttlepix p-mfsc microscope. A accelerating voltage of 10 kV and between 50x and 150x magnification values was used in our test.

SEM, the dehydration of the sample to be examined is very important to be suitable for the vacuum feature of the device and to obtain an efficient image from the sample surface. The samples were initially coated with gold for 100 s at 10 mA using a Leica EM ACE200. Then cell structure was investigated with Tescan Vega 3 for SEM analysis. The porous structure of the obtained materials was analyzed using the scanning electron microscopy (SEM).

The pressure applied to the inner surface of the foam piece is called the compressive strength test. In addition to, conversely in the tensile test, pressure was applied outward from both the ends. A tensile test was performed by Zwick Z010.

The apparent densities of the PUF samples were measured by Sartorius balance assay device. The density was calculated by taking a small amount of foam piece and then mixing it with water.

Mechanical properties are important for refrigerators. Damage to the thermal conductivity of polyurethane surfaces owing to its mechanical behavior can negatively affect its thermal properties.

The compressive strength of the rigid polyurethane foam samples was measured with Zwick Z2.5 device.

The pressure applied to the inner surface of the foam piece is called the compressive strength test. In addition to, conversely in the tensile test, pressure was applied outward from both the ends. A tensile test was performed by Zwick Z010.

#### 4. TEST RESULTS

Polyurethane (PU) composite foams were successfully reinforced with different concentrations (10 wt%, 15 wt%, 20 wt%) of eggshell, nutshell, walnutshell and aerogel filler. The effect of filler concentration on the mechanical and thermal properties of PU composite foams was investigated. PU foams were examined for rheological behavior, processing parameters, cellular structure (Scanning Electron Microscopy analysis), mechanical properties (compression test, impact strength), thermal properties (Thermogravimetric Analysis), as well as selected application properties (thermal conductivity, apparent density and surface hydrophobicity).

##### 4.1 Production of Foaming Material

The characteristics of the foam producing RPUF using the one-shot method are explained in Table 4.1. MDI undergoes a crystallization reaction as a result of air contact and more agglomerate formation. For this reason, we added aerogel and natural additives to the polyol. After the RPUF samples were produced, the cell size was measured with stereomicroscope, thermal conductivity measurement, pressure strength measurement, scanning electron microscope analysis and cell structure analysis with TGA and FTIR were performed. The corresponding raw material values are listed in Table 4.1.

Table 4.1. Properties and value of raw material for foaming

Characteristic	Unit	Isocyanate	Polyol
Hydroxyl Number	KOH/g	-	380
Water	%	-	2.48
NCO	%	32	-
Density (25 °C )	g/ml	1.24	1.08

##### 4.2 Assessment of the filler particle size

After our natural filling materials were dried by exposure to the sun for 3 days, the natural filling materials were first particulated with a Bosch brand multitalent 800 W blender machine. Then, since it is known that particle sizes affect the results, aerogel and egg shells were selected at the smallest scale and hazelnut shells were selected at the largest scale, and the test processes have been started. The particle sizes of the filler materials are presented in Table 4.2. The natural filler was ground mechanically using a Retsch ZM 200 centrifugal mill.

Table 4.2. Filler materials particle size

Material	Particle Size ( $\mu\text{m}$ )
Eggshell	<45
Hazelnutshell	150-250
Walnutshell	45-75
Aerogel	<45

Particle size plays an important role in the overview. The porous structure of the RPUFs directly affects their thermal and mechanical properties. The addition of small particles helps to prevent agglomerate formation and form a smaller cell structure. With the addition of larger particles, as with hazelnut, we directly affected the viscosity during RPUF production. For this reason, we made the gelling longer during production and caused the formation of agglomerates. With this, it was difficult to produce the desired improved RPUF.

### 4.3 Density Evaluation

Density is an important parameter in the properties and structure of the RPUF. With the addition of additives, the cell wall became smaller and the cell wall thickness decreased. Density was determined by two different measurement techniques. First, the density was calculated using a Sartorius precision balance with water. Another factor is the compressive strength. During the measurement, the Zwick Roell machine also provided density. The results were compatible with each other. This indicator is inversely proportional to the thermal conductivity. Viscosity is expected to increase when the filling materials are added to the polyol in the foam sample, resulting in a higher density.

Table 4.3. Apparent density change values found with manual examination and density calculation with Zwick Roell

Samples	Content	Sartorius Assay Balance kg/cm <sup>3</sup>	Density Calculation by Zwick Roell Machine kg/cm <sup>3</sup>
N	Neat	0.022	0.023
EG10	10 wt% eggshell	0.026	0.025
EG15	15 wt% eggshell	0.028	0.028
EG20	20 wt% eggshell	0.049	0.054
HN10	10 wt% hazelnutshell	0.023	0.023
HN15	15 wt% hazelnutshell	0.021	0.022
WN10	10 wt% walnutshell	0.025	0.024
WN15	15 wt% walnutshell	0.026	0.025
WN20	20 wt% walnutshell	0.028	0.028
AG10	10 wt% aerogel	0.031	0.031
AG15	15 wt% aerogel	0.032	0.032

Density is one of the main variables controlling the most of the mechanical properties and it has an effect more remarkable than that of other possible changes in the polymer and foam structure. RPUF with different densities were prepared by changing the amount of filler material used as the blowing agent. Changes in the fillers and density were observed with the Zwick Roell Machine and Sartorius Assay Ballance tests. An increase in the density with the addition of additives was observed for each sample. However, it was observed that the egg shell additive material had an extremely high value in the 20 wt% sample. When the relevant sample was observed, it has been seen that the resistance properties increased tremendously, and there have been significant improvements in the mechanical and thermal properties. The corresponding density results are shown in Table 4.3 and Figure 4.1. It was observed that the mechanical properties of the PUFs changed with the foam density. The results of water absorption of the PUFs indicated that water absorption increased with a decrease in density, due to the increase in cell size increase and decrease in cell-wall thickness. Thermal conductivity measurements showed that the thermal conductivity decreased with increasing density. This was due to the decrease in the cell size.

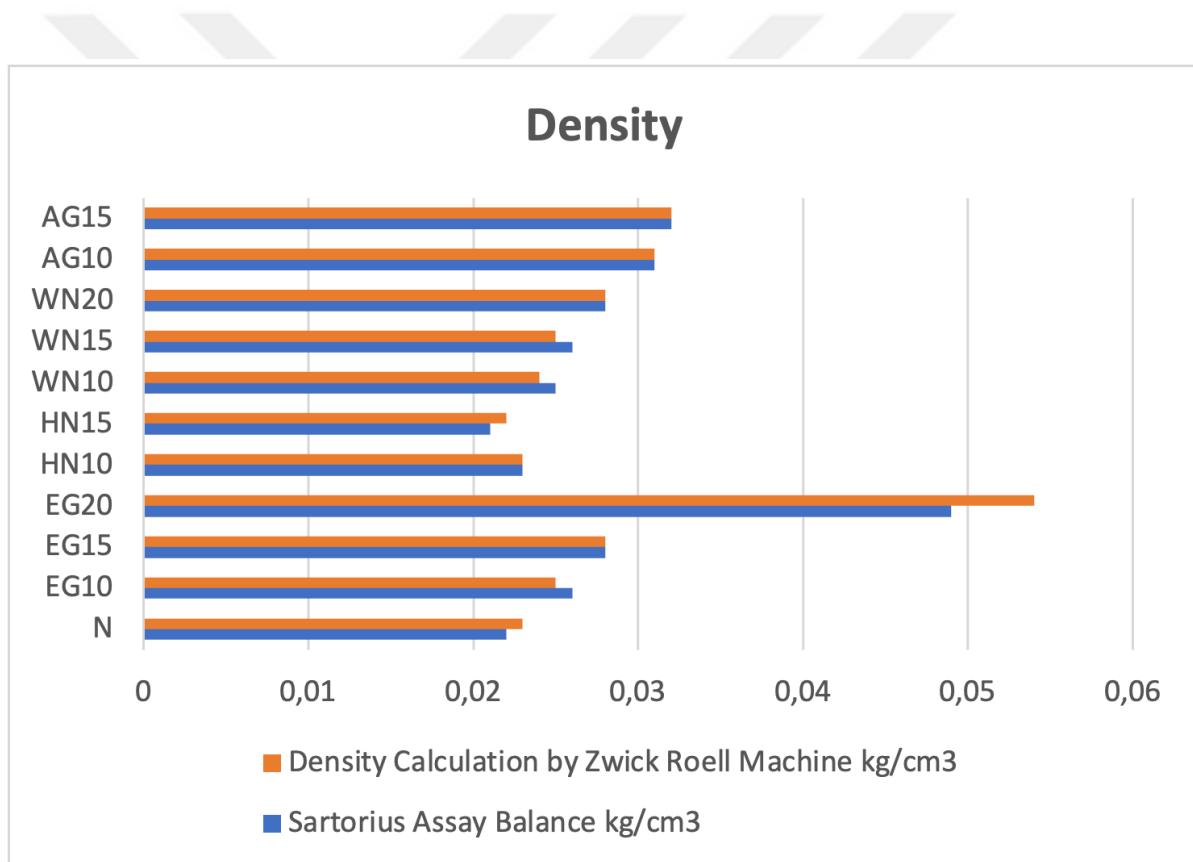


Figure 4.1. Apparent density change with added materials

#### 4.4 Cream Time Evaluation

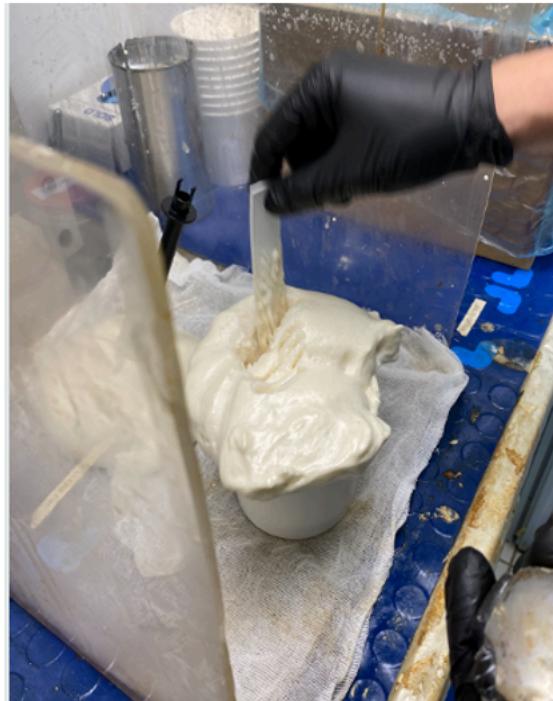
After mixing the isocyanate and polyol with the fillers, the cream structure started to swell and it was observed that polyurethane was formed at the end of the cream time.

During polyurethane foam formation, we pressed and pulled a piece of a stick onto the reacting foam. At this process, the time was maintained until the hardening was felt while pulling back the bar. At the end of this time the reaction was somewhat completed.

As expected, the more filler materials were added, the more cream time was observed. The gelation time is constantly increased in the filler samples. In our Hazelnut sample, leaving large pieces from the sieve had a direct negative effect on gelling. It is undesirable to observe such loss in time during mass production. The gelation times for the added materials are shown in Table 4.4.

Table 4.4. Gelation times change with added materials

<b>Samples</b>	<b>Fibrous Time (second)</b>
N	50
EG10	54
EG15	56
EG20	58
HN10	65
HN15	67
WN10	60
WN15	63
WN20	65
AG10	60
AG15	62



In addition Czlonka et al. total processing time increased with increasing filler material. This may be related to the role of solid filler particles during the foaming process. It has been observed that the solid particles affect the foaming time. A higher coconut filler concentration results in a higher viscosity of the PU system and a limited expansion of the bubble cells (Czlonka et al., 2020).

#### 4.5 Thermogravimetric Evaluation

The purpose of these tests is to measure the decrease in the mass of the sample piece placed in the test by increasing its contact with temperature. Egg- and aerogel-added samples of the developed composite materials were examined using thermogravimetric analysis. This allowed us to examine the thermal degradation processes of the substrates (fillers). Thermograms containing mass change (TG) and derivative of change (DTG). For the test, 6-7 mg samples were examined.

Four different TGA curves were obtained. The reason for these steps was to observe the removal of water formed in different ways in the samples.

Aerogel wt 10% and aerogel wt 15% also have relatively similar characteristics to EG15 and EG 20. In general, four decompositions are observed. The weathering observed after 600 degrees was ignored.

The first degree of degradation was in the average temperature range of 0-300 °C. The first decay stage was generally observed to be less severe. The second and third decay stages were much more severe and mass loss occurred in this region. The most severe part, the third decay stage, caused a loss of 2.7 mg of sample mass (58.46 %) and EG15 at a final temperatures of 2.8 mg (56.92 %), as shown in Figure 4.2.

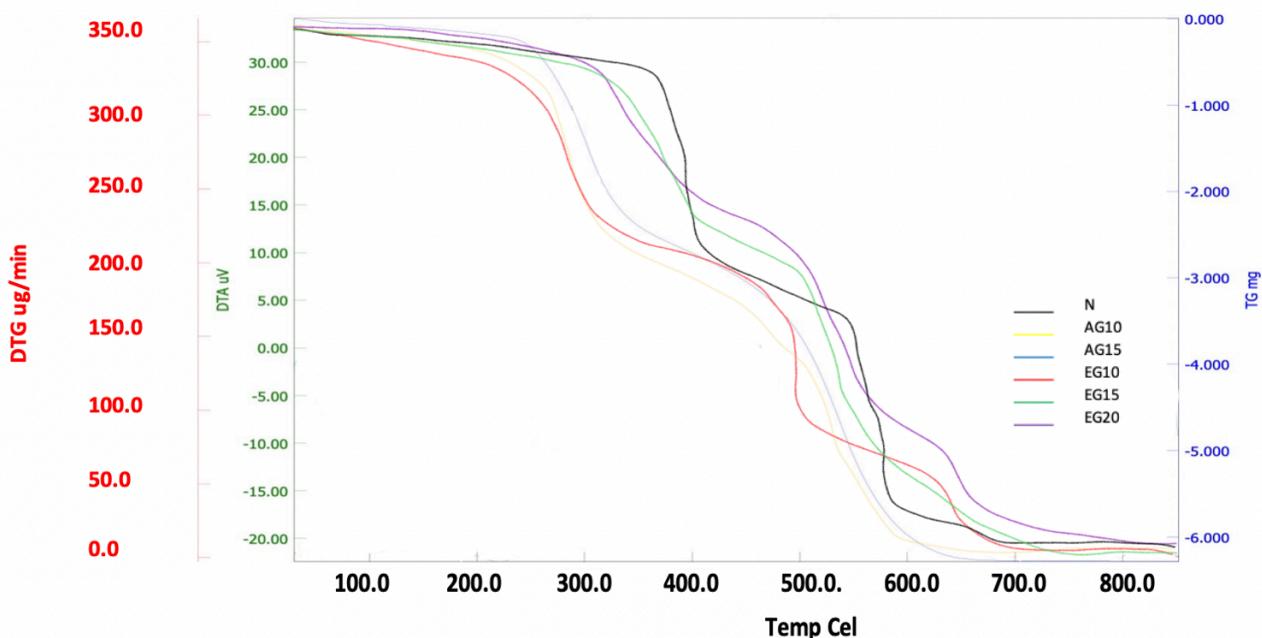


Figure 4.2. DTG curve of filled materials

Table 4.5. Weight degradation results

	Weight Degradation (mg) & T (°C)				Total Change
	T1	T2	T3	T4	
<b>N</b>	0.4 mg & 0-360 (°C)	2.4 mg & 370-400 (°C)	0.5 mg & 410-560 (°C)	2.3 mg & 580-680 (°C)	5.6 mg
<b>AG10</b>	0.6 mg & 0-220 (°C)	1.6 mg & 260-320 (°C)	1.5 mg & 270-500 (°C)	1.6 mg & 500-600 (°C)	5.4 mg
<b>AG15</b>	0.4 mg & 0-250 (°C)	2.5 mg & 250-370 (°C)	1 mg & 370-500 (°C)	1.6 mg & 500-625 (°C)	5.5 mg
<b>EG10</b>	0.8 mg & 0-240 (°C)	2.2 mg & 240-290 (°C)	1.0 mg & 290-320 (°C)	2.0 mg & 320-490 (°C)	6.0 mg
<b>EG15</b>	0.7 mg & 0-340 (°C)	2.1 mg & 340-390 (°C)	0.4 mg & 390-520 (°C)	2.8 mg & 650-700 (°C)	6.0 mg
<b>EG20</b>	0.6 mg & 0-330 (°C)	1.6 mg & 330-470 (°C)	2.7 mg & 470-575 (°C)	1.3 mg & 575-650 (°C)	6.2 mg

Weight degradation amounts depending on the four main temperature range are given in Table 4.5.

Compared with the neat and filler samples, the filler samples were less stable. While the degradation process starts at 360 degrees in the unfiller sample, the decomposition of the filler PU composite foam tends to decompose before the decomposition of the unfiller sample, depending on the concentration of aerogel and eggshell filler.

In addition, since the filler foams have a higher open void content in their structure, it accelerates the degradation process and causes the thermal properties of the analyzed materials to degrade somewhat faster. In addition, the TGA results show that the use of additives reduces the weight loss of the PU composites during the second stage of degradation. Due to the barrier effect of the incorporated filler particles, the oxygen and heat fluxes towards the polymer surface were limited and the weight loss was reduced.

Derivative of change (DTG) analysis provides information on the degradation rate of PU foams during the heating process. Figure 43 shows the TG and DTG curves of PU containing fillers and a single peak observed at a low temperature is related to the degradation of most of the filler parts as well as the solid and flexible parts. The second degradation rate observed in  $T_{max1}$ - $T_{max2}$  was related to the slow degradation of the products formed in the first step of degradation. The difference between the pure PU foam and PU composite foams was also confirmed by DTG analysis, and was defined as the first derivative of TGA. DTG analysis provided information on the degradation rate of PU foams during the heating process. All samples showed a similar 2-step degradation path with maximum degradation intensity in the range of 320–400 °C, which refers to the degradation of the hard parts of PU. In the case of the composite foams, an additional, slightly overlapping inflow occurred at approximately 325°C. This may be attributed to the faster breakdown of the urethane bond formed between the urethane groups and the hydroxyl groups of the filler. The addition of an organic filler, which may contain a small amount of residual water, leads to the formation of more urea bonds, increasing the activation energy of thermal decomposition compared with unmodified foams.

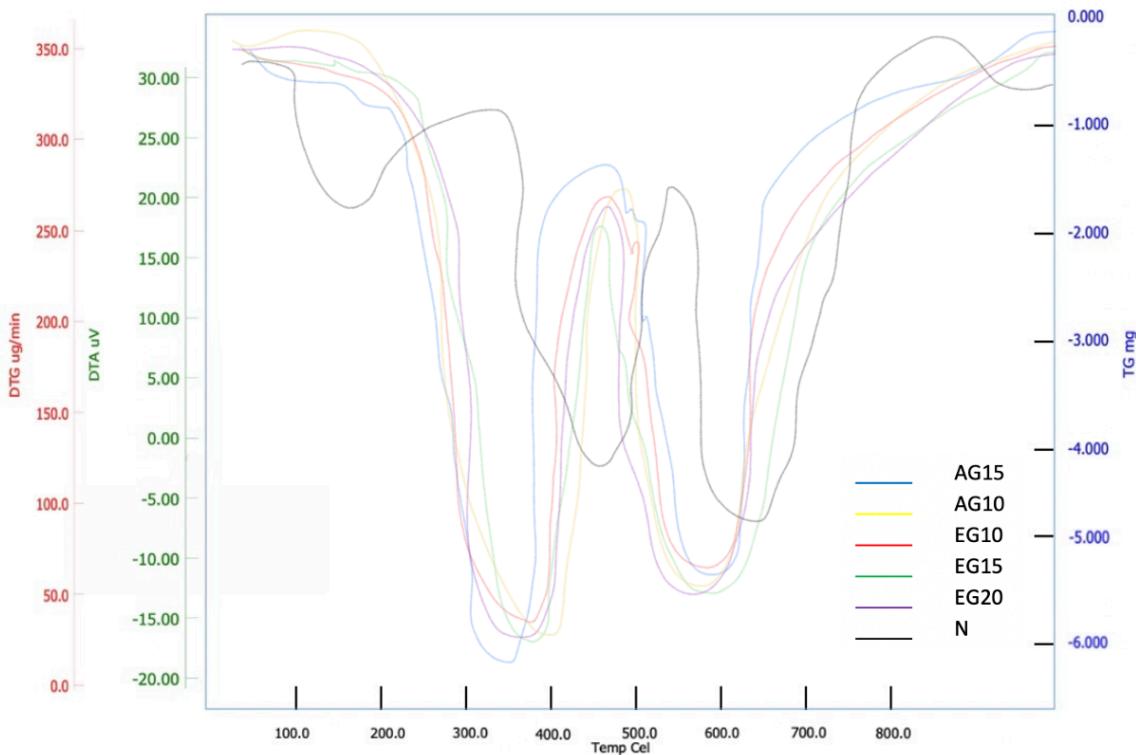


Figure 4.3. Mass Change (TG) curve of composite foam materials

When the foam without additives, foam with eggshell and aerogel foams are examined; it is considered that the presence of hydration water in the eggshell structure causes more water loss.

According to another study conducted by Leszczyńska et al; the greatest amount of water was released from natural fillers with the smallest particle size hazelnut shell and walnut shell, but they contain similar total water amounts as the filler pistachio shell, which is related to the easy access of the reaction mixture to the material. The filler particle surface and lower viscosity of the polyol premix enable greater expansion of the polyurethane foam. In foams containing natural fillers, the water absorption properties of the materials increased significantly, which may be a result of the defective foam structure as well as the chemical composition of the filler particles (Leszczyńska et al., 2020).

#### 4.6 XRF Evaluation

XRF analysis can be used to determine the chemical structure of filler samples by measuring the fluorescence or secondary X-rays emitted. Various filler investigations of polyurethane have been conducted. Thanks to XRF test results, measurement of the elements in the samples and the elemental information of the samples emerged. Calcium levels were observed in the egg structure. XRF results of neat and composite PU are given between Table 4.6-Table 4.10.

Table 4.6. XRF result of Neat Foam

	Compound Name	Conc. (%)	Absolute Error (%)
1	O	83.77	5.
2	Si	6.56	0.1
3	Cl	3.94	0.09
4	Fe	3.30	0.05
5	Zn	1.04	0.03
6	Cr	0.74	0.03
7	Ni	0.22	0.01
8	Na	0.15	0.03
9	S	0.14	0.01
10	Mg	0.08	0.01
11	Al	0.05	0.01
12	Mo	0.01	0.004

Table 4.7. XRF result of Eggshell foams of 10%, 15%, 20% respectively

Content: 10% Eggshell

15% Eggshell

20% Eggshell

	Compound Name	Conc. (%)	Absolute Error (%)
1	O	77.41	5.
2	Si	6.17	0.1
3	Fe	5.76	0.07
4	Cl	3.84	0.08
5	Zn	2.94	0.06
6	K	2.11	0.06
7	Cr	0.85	0.03
8	Na	0.45	0.05
9	Ni	0.23	0.01
10	S	0.12	0.01
11	Mn	0.06	0.007
12	Al	0.06	0.01

	Compound formula	Concentration
1	O	79.198
2	Na	0.437
3	Si	4.440
4	S	0.131
5	Cl	2.828
6	K	1.434
7	Ca	5.743
8	Cr	0.607
9	Fe	3.389
10	Ni	0.143
11	Zn	1.639
12	Sr	99.6

	Compound Name	Conc. (%)	Absolute Error (%)
1	O	77.57	5.
2	Ca	13.95	0.1
3	Si	3.38	0.07
4	Cl	2.17	0.04
5	Fe	1.24	0.03
6	Zn	0.46	0.02
7	Na	0.33	0.03
8	Cr	0.29	0.02
9	K	0.15	0.01
10	S	0.11	0.01
11	Ni	0.11	0.01
12	P	0.07	0.008
13	Mg	0.06	0.008
14	Al	0.05	0.009
15	Sr	0.02	0.004
16	Mo	0.01	0.003

The main chemical component of the egg shells of poultry species is  $\text{CaCO}_3$ , and the glow loss is due to the  $\text{CO}_2$  gas together with the  $\text{CaO}$  released by the thermal decomposition of this compound. It is seen that the ratio of Ca value increases as the amount of filler materials increase in Table 4.7.

Table 4.8. XRF result of Hazelnutshell foams of 10%, 15% respectively

Content: 10% Hazelnutshell

15% Hazelnutshell

	Compound Name	Conc. (%)	Absolute Error (%)
1	O	75.13	5.
2	Fe	7.22	0.08
3	Si	5.98	0.1
4	Zn	3.77	0.07
5	Cl	3.46	0.07
6	K	2.18	0.06
7	Cr	0.79	0.03
8	Na	0.50	0.05
9	Ca	0.36	0.02
10	S	0.21	0.01
11	Ni	0.17	0.01
12	Mg	0.10	0.01
13	Mn	0.07	0.008
14	Al	0.06	0.01

	Compound Name	Conc. (%)	Absolute Error (%)
1	O	76.56	5.
2	Fe	6.13	0.07
3	Si	5.36	0.1
4	Cl	3.41	0.07
5	Zn	3.24	0.06
6	K	2.28	0.06
7	Na	1.06	0.08
8	Cr	0.87	0.03
9	Ca	0.38	0.02
10	S	0.31	0.02
11	Ni	0.19	0.01
12	Mg	0.13	0.02
13	Mn	0.09	0.009

Table 4.9. XRF result of Walnutshell foams of 10%, 15%, 20% respectively

**Content: 10% Walnutshell**      **15% Walnutshell**      **20% Walnutshell**

	<b>Compound Name</b>	<b>Conc. (%)</b>	<b>Absolute Error (%)</b>		<b>Compound Name</b>	<b>Conc. (%)</b>	<b>Absolute Error (%)</b>		<b>Compound Name</b>	<b>Conc. (%)</b>	<b>Absolute Error (%)</b>		
1	O	84.33	5.		1	O	79.21	5.		1	O	79.05	5.
2	Si	5.77	0.1		2	Si	6.38	0.1		2	Ca	9.94	0.1
3	Cl	3.73	0.07		3	Fe	4.54	0.06		3	Si	3.96	0.08
4	Fe	2.26	0.04		4	Cl	3.49	0.08		4	Fe	2.51	0.05
5	K	2.03	0.06		5	K	2.09	0.06		5	Cl	2.33	0.05
6	Cr	0.85	0.03		6	Zn	1.70	0.04		6	Zn	0.72	0.03
7	Na	0.39	0.05		7	Cr	1.10	0.03		7	Cr	0.68	0.02
8	Ni	0.22	0.01		8	Ca	0.61	0.03		8	Na	0.22	0.03
9	S	0.16	0.01		9	Na	0.34	0.04		9	S	0.22	0.01
10	Mg	0.08	0.01		10	Ni	0.25	0.01		10	Ni	0.17	0.01
11	Mn	0.07	0.008		11	S	0.16	0.01		11	K	0.09	0.009
12	Al	0.06	0.01		12	Mn	0.09	0.009		12	Mn	0.06	0.008
13	Zn	0.05	0.007		13	Al	0.04	0.009		13	Al	0.03	0.006
					14	Mo	0.02	0.004		14	Sr	0.01	0.003

It was observed that the oxygen rate decreased in all parts, except for the 10% walnut. The assumption is that walnut fillers size is directly effect the foam structure for that reason oxygen rate acted unstabled.

Table 4.10. XRF result of Aerogel foams of 10%, 15% respectively

**Content: 10% Aerogel**      **15% Aerogel**

	<b>Compound Name</b>	<b>Conc. (%)</b>	<b>Absolute Error (%)</b>		<b>Compound Name</b>	<b>Conc. (%)</b>	<b>Absolute Error (%)</b>	
1	O	64.3	5.		1	O	64.6	4.
2	Si	30.9	0.2		2	Si	30.6	0.2
3	Cl	2.8	0.07		3	Cl	2.1	0.06
4	Fe	1.2	0.03		4	Fe	1.6	0.04
5	Cr	0.4	0.02		5	Zn	0.6	0.02
6	S	0.1	0.01		6	Cr	0.3	0.02
7	Ni	0.1	0.01		7	Ni	0.1	0.009
8	Zn	0.1	0.02		8	Mo	0.0	0.003
9	Mn	0.0	0.007					
10	Al	0.0	0.007					
11	Mo	0.0	0.002					
12	Mg	! 0.0						

XRF analysis of the sample surfaces revealed the occurrence of different combinations of O, Si, Fe, S, Zn among the foams. O, Si, Fe, S and Zn were, however, more commonly encountered and at variable concentrations. A trace proportions of sodium, chlorine and potassium may have arisen due to contact with the hands.

#### 4.7 FT-IR Evaluation

Fourier Transform Infrared Spectrophotometer (FTIR) is an important method for evaluating polyurethane structures. FTIR analysis is one of the general techniques used in classical structural analysis. In the FTIR technique, the process of interaction between matter and light is used. When radiation of a certain wavelength belonging to the infrared region of electromagnetic radiation is incident on molecules with additives, certain structural changes occur in the molecule. Transitions occur at the vibrational, electronic and rotational levels of the molecule. Infrared spectroscopy examines these transitions, especially at the vibrational and rotational levels. This is a positive feature in the application of the test with a low number of solid samples. The possible functional group and their corresponding wavelengths are listed on Table 4.11.

Table 4.11. Functional group of eggshell and aerogel of polyurethane

Wavenumber (cm <sup>-1</sup> )	Functional Groups
3650-3850	N-H
2920	C-H in CH <sub>2</sub>
2350	O-C-O
2250	N-C-O
2050-2110	N-C-N in isocyanate
1700-1750	CO
1600	C-C in aromatic ring
1550	CH <sub>2</sub>
1220	C-N & N-H
1150	Si-O-Si
1100	C-O-C in urethane

The results of general peak behaviours are shared in support of literature. In all spectrums peak at 2220 cm<sup>-1</sup> that peak can be attributed to diisocyanates, which are the main monomers used in the synthesis of polyurethane. When considering the other peaks appearing in the eggshell sample, there is a wide range of hydroxyl stretching vibrations at 3300-38000 cm<sup>-1</sup>. The presence of a broadband peak indicates the presence of hydroxyl groups on the polymer surface. Another finding proving the formation of a polyurethane structure is that carbonyl stretching vibrations in the urethane bond are observed at 1750 cm<sup>-1</sup>. The N-H stretching vibration in the urethane bond was evident at 1550 cm<sup>-1</sup>. These groups show the presence of urethane bonds in the structure (Kantarcioğlu, 2017). The FTIR spectrum of the aerogels filler foam, eggshell foams, hazelnut shell foams and walnut shell foams are respectively listed on between Figure 4.4 and Figure 4.11.

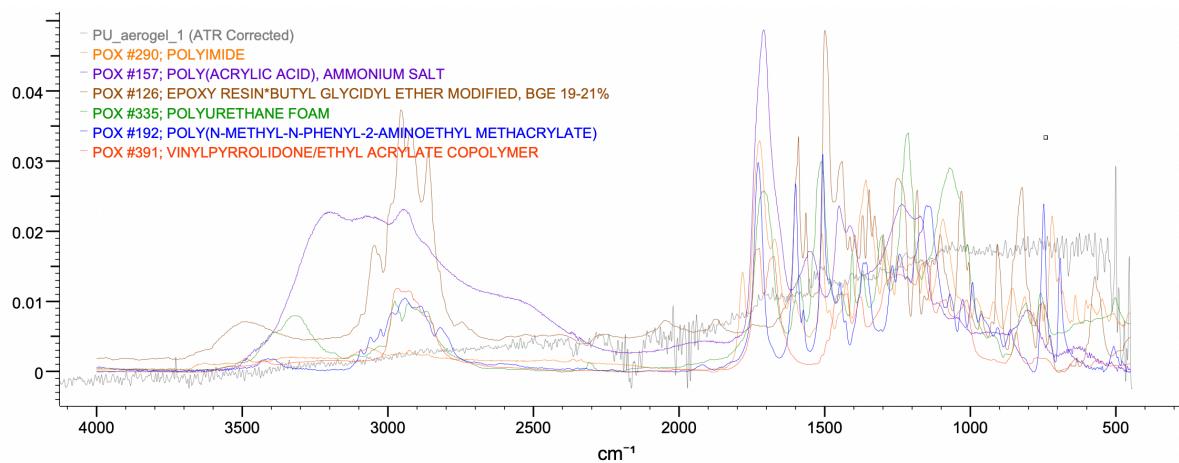


Figure 4.4. Aerogel 10% wt FTIR spectrum

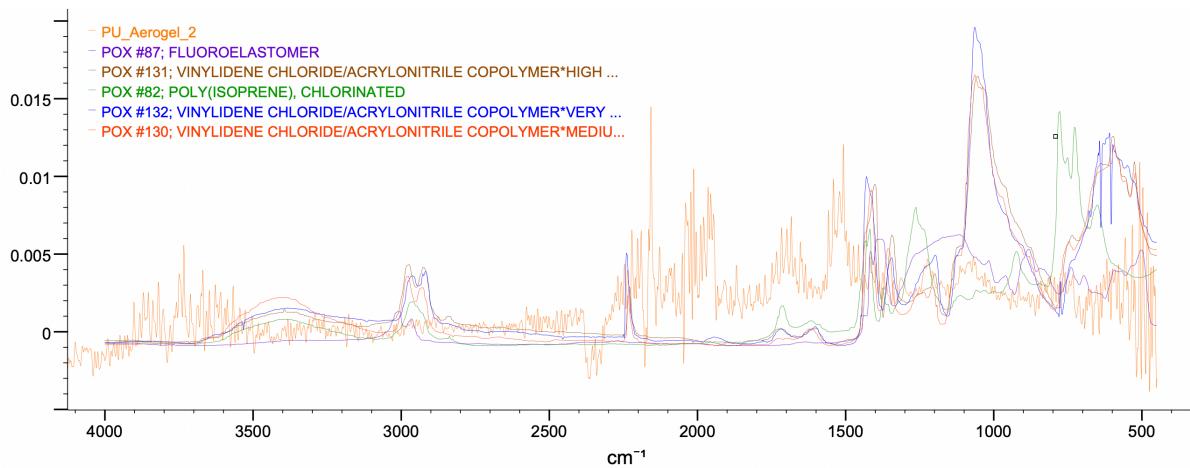


Figure 4.5. Aerogel 15% wt FTIR spectrum

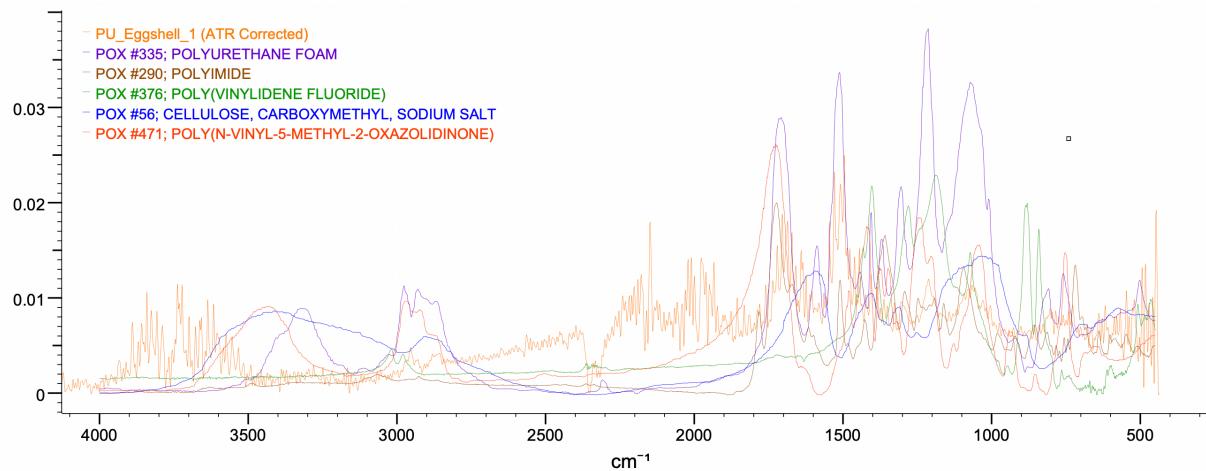


Figure 4.6. Eggshell 10% wt FTIR spectrum

Lignin exhibits hydrophobic properties preventing the natural fibers from swelling and microbial activity while the presence of cellulose enhances the mechanical strength of natural additives and increases hydrophilicity similarly to the hemicellulose.

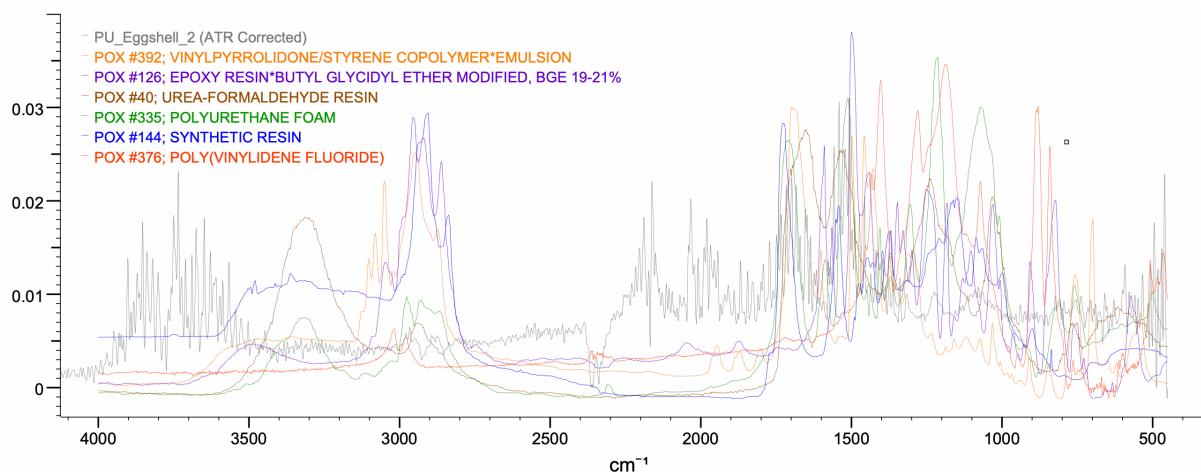


Figure 4.7. Eggshell 15% wt FTIR spectrum

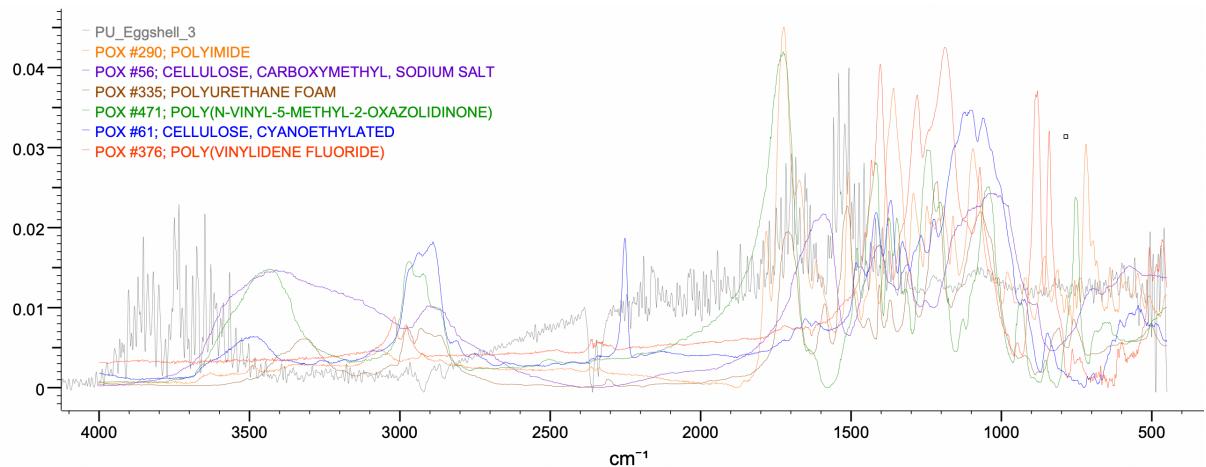


Figure 4.8. Eggshell 20% wt FTIR spectrum

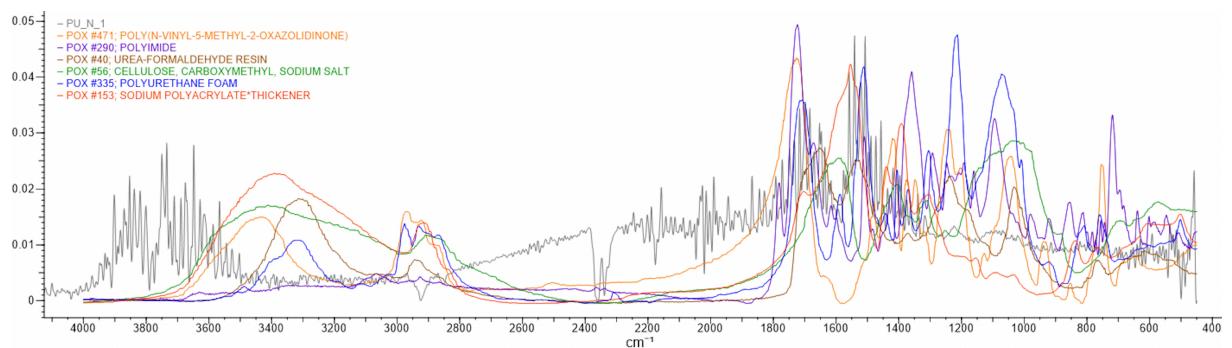


Figure 4.9. Hazelnutshell 10% wt FTIR spectrum

The chemical composition analysis indicates that the hazelnut and walnut shells exhibit higher content of the hydrophilic hemicellulose and cellulose as well as lower proportion of hydrophobic lignin.

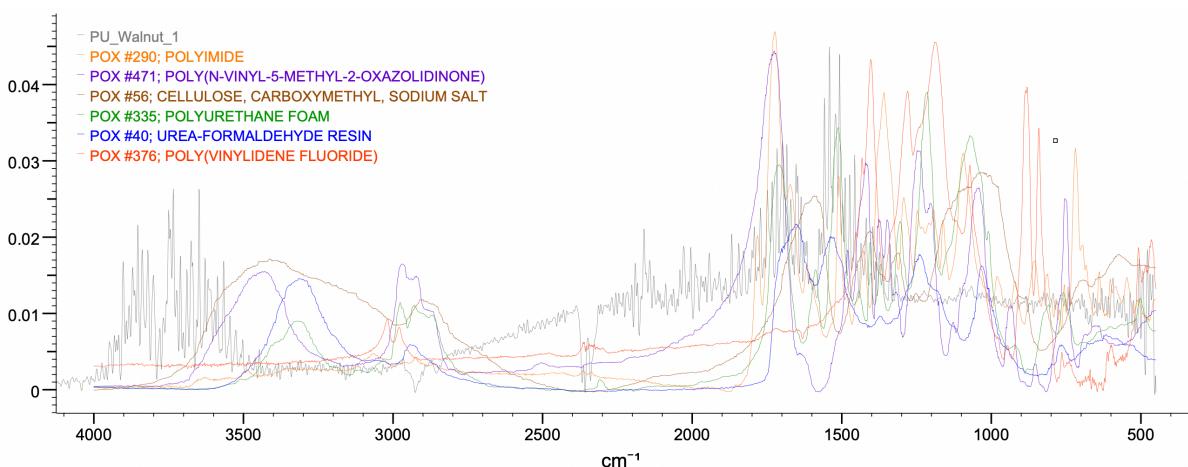


Figure 4.10. Walnutshell 10% wt FTIR spectrum

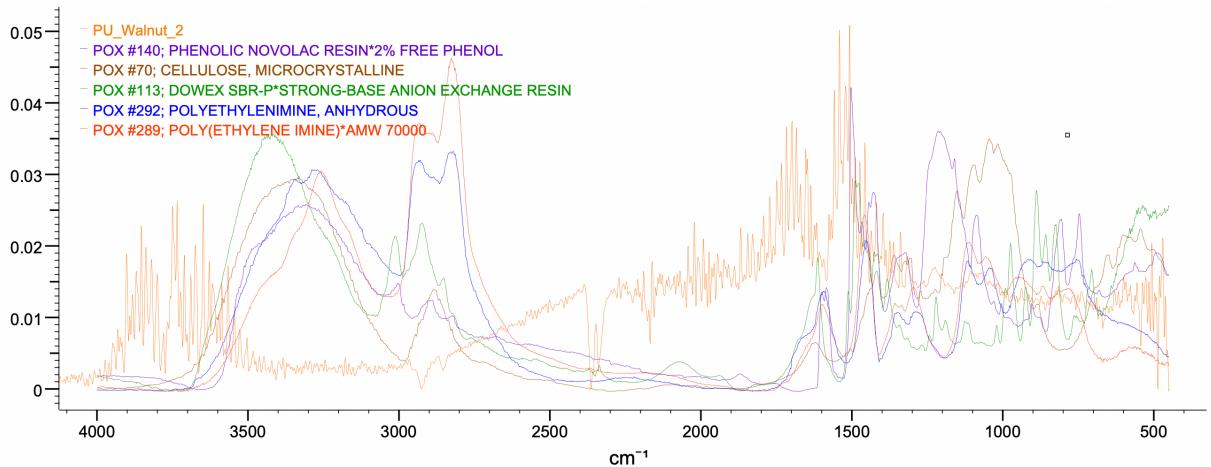


Figure 4.11. Walnutshell 15% wt FTIR spectrum

#### 4.8 Contact Angle Measurement Evaluation

The contact angle value between the water and the surface is very important property for defining the hydrophilic and hydrophobic characteristic of the material is nature. Water droplets tend to be  $<90^\circ$  hydrophilic and  $>90$  represents hydrophobic.

The contact angles result of the neat, aerogels filler foam, eggshell filler foams, hazelnut filler shell foams and walnut filler shell foams are respectively given in between Figure 4.12 and Figure 4.22.

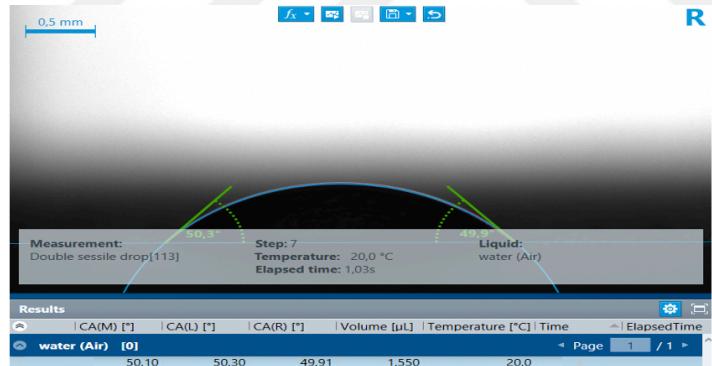


Figure 4.12. Contact angle result of neat foam

Contact angle of neat foam has averagely  $50^\circ$  in Figure 4.12. Neat foam has the greatest degree against filler polyurethane results. Because neat foam has the one of the less agglomerate formation.

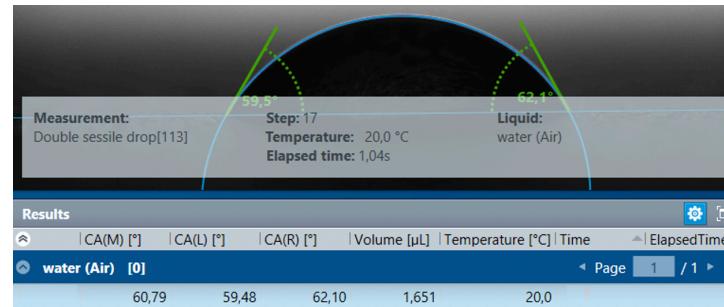


Figure 4.13. Contact angle result of %10 Aerogel filled foam

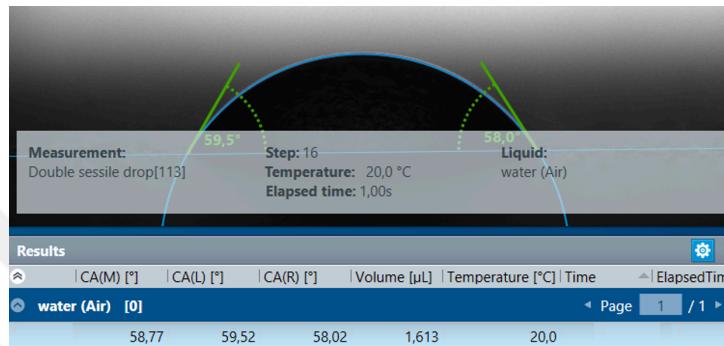


Figure 4.14. Contact angle result of %15 Aerogel filled foam

Contact angle of %10 and %15 aerogel foams result averagely  $60^\circ$  in Figure 4.13 and Figure 4.14. The results move forward hydrophilic structure compared to hazelnut and walnut polyurethanes. Aglomarete structure of aerogel additives are less than hazelnut and walnut. For this reason the aerogel polyurethanes have better hydrophilic structure against to walnut and hazelnut polyurethanes.

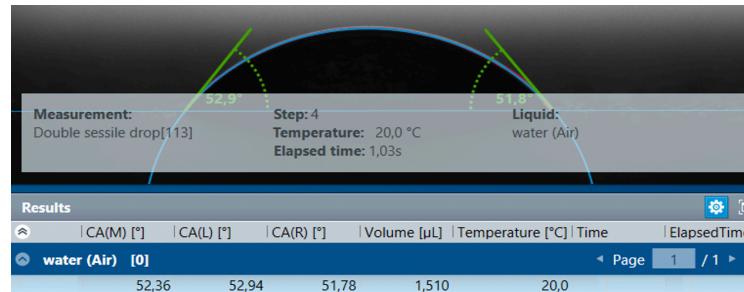


Figure 4.15. Contact angle result of %10 Eggshell filled foam

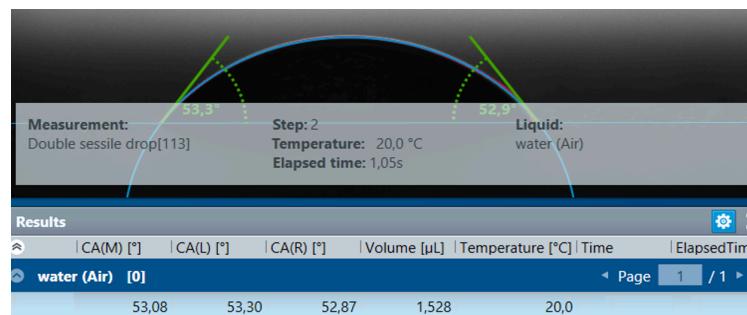


Figure 4.16. Contact angle result of %15 Eggshell filled foam

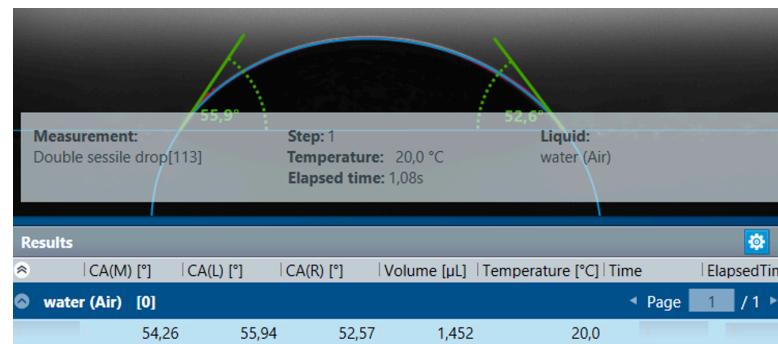


Figure 4.17. Contact angle result of %20 Eggshell filled foam

Contact angle of %10, %15 and %20 eggshell foams result averagely  $53^\circ$  in Figure 4.15, Figure 4.16 and Figure 4.17. Eggshell foams similarly behaviour like aerogel in contact angle test.

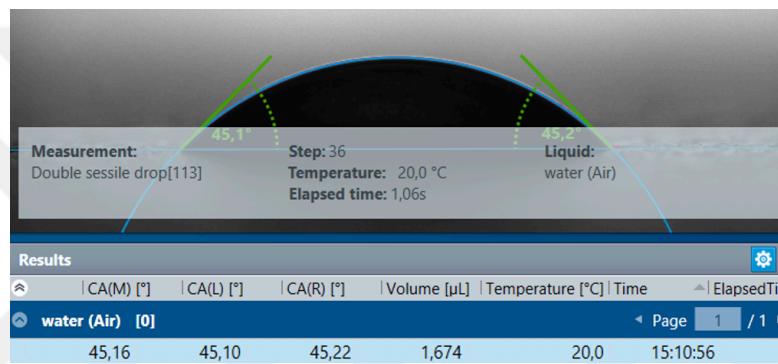


Figure 4.18. Contact angle result of %10 Hazelnutshell filled foam

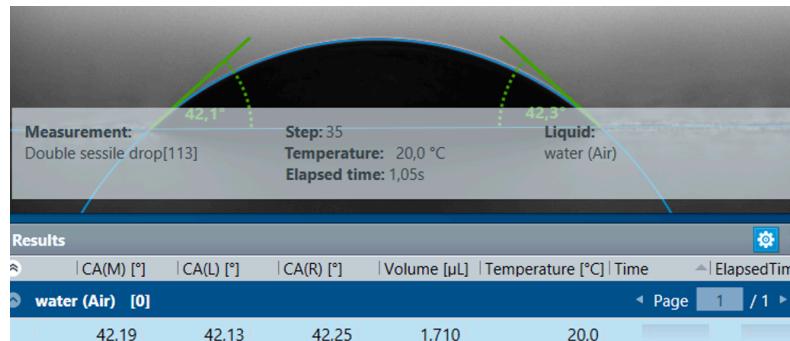


Figure 4.19. Contact angle result of %15 Hazelnutshell filled foam

Particle size of fillers create agglomerate formation. Hence, big particle size negatively affect contact angle. It can be observed that, particle size of walnut and hazelnut is bigger than aerogel and eggshell particles. Water drop tend to be hydrophilic by big particle size. As shown between Figure 4.18 and Figure 4.22.

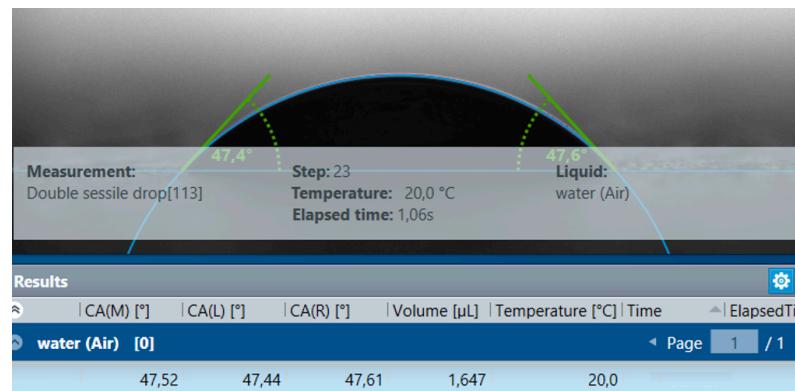


Figure 4.20. Contact angle result of %10 Walnutshell filled foam

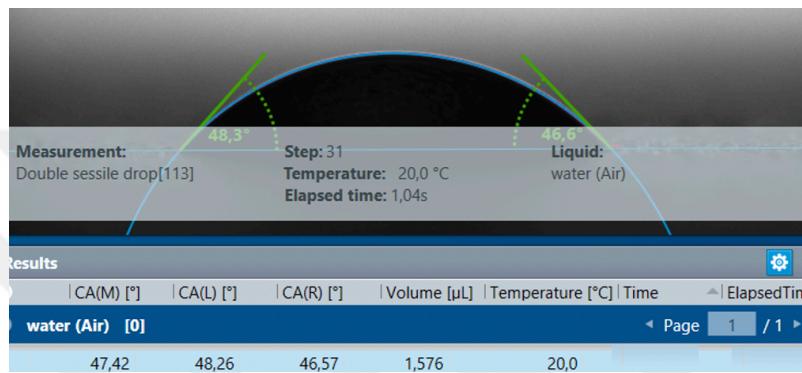


Figure 4.21. Contact angle result of %15 Walnutshell filled foam

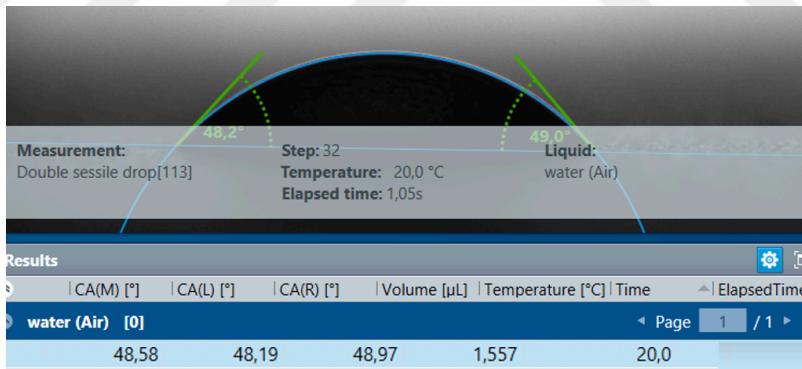


Figure 4.22. Contact angle result of %20 Walnutshell filled foam

The contact angle values of PU filler with various amount of fillers are also listed in Table 4.12.

Table 4.12. Contact angle values of PU composites

Sample Code	Contact Angle
N	50.3°
EG10	52.9°
EG15	53.3°
EG20	55.9°
HN10	45.1°
HN15	42.1°
WN10	47.4°
WN15	48.3°
WN20	48.2°
AG10	59.5°
AG15	59.5°

According to Nazeran and Moghaddas, it can be observed from the obtained results that, silica aerogel and pure polyurethane foam are super hydrophobic and hydrophilic, respectively. It is assumed that by increasing the silica aerogel content, the water-contact angle of the nanocomposite foams is enhanced. When silica aerogel content is added, aerogel filler RPUFs become increasingly hydrophobic (Nazeran and Moghaddas, 2017).

Leszczyńska et al. observed that the use of plant-based fillers resulted in a reduction in the final apparent density of the foams, although it was relatively high. It also exhibits hemicellulose and cellulose content as well as a lower percentage of hydrophobic lignin (Leszczyńska et al, 2020).

While aerogel and natural additives have slightly hydrophobic characteristic, the foam exhibits hydrophilic properties. In our study, the test was conducted on foam with filler materials. It can be observed that it tries to convert the hydrophilic foam to its hydrophobic structure with the aerogel added foam, and a change in angle of almost 20 percent was observed. Eggshell fillers have also effected the PU to steer hydrophobic area due to small particle size. It can be observed in Table 4.12 that natural additives have lower hydrophobic properties than aerogel. Especially, walnut and hazelnut fillers make the polyurethane more hydrophilic. Fillers should have the smallest particle size to avoid agglomerate formation. Hence, it seems filler size effects contact angle result and big size of filler cannot provide positive result for improving.

#### 4.9 Evaluation of cell structure with microscope

The cell size was measured with a Nikon shuttlepix p-mfsc microscope. Cell images were taken at 100 x magnification and 50 micro meter focusing. Images were taken with the help of a computer program and cell size measurements performed using another program. The visuals of aerogels filler foam, walnut filler foams, hazelnut shell foams and eggshell filler shell foams thanks to microscope are respectively shown in Figure 4.23, Figure 4.24, Figure 4.25, Figure 4.26, Figure 4.27, Figure 4.28, Figure 4.29, Figure 4.30, Figure 4.31 and Figure 4.32.

A good relationship between the RPUF viscosity and the dispersion of the filler particles is essential to achieve good and improved morphology. The foam structures were generally uniform and had a high closed cell content. The addition of filling material enabled, us to obtain a more open cell structure and a less homogeneous structure. For the purpose of the operation, homogeneity has been at least affected by the number of open cells and an appropriate feature was tried to be obtained by making it possible to increase the number of open cells.

The structure of the normal pure foam is almost uniform and contains a high percentage of closed cells. In all the fillers, the homogeneity of the cell structure was affected and the formation of agglomerates was observed. The closed cell structure was better protected than the other fillers.

In general, it was observed in most articles that solid adducts affect rheology around growing air bubbles and nucleation reduces nucleation by turning the homogeneous structure into heterogeneous, and we observed similar situations in our study.

As a result of the addition of filling materials, it was observed that the cell size generally decreased in Figure 4.31.

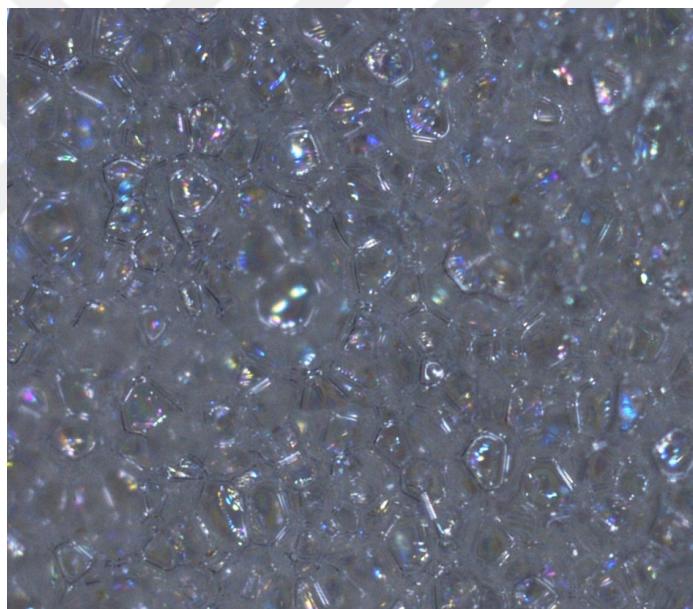


Figure 4.23. Microscope image of %10 Aerogel filled foam

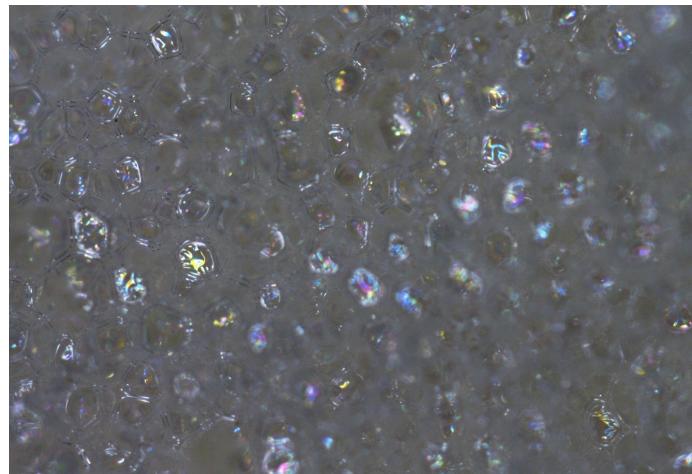


Figure 4.24. Microscope image of %15 Aerogel filled foam (5x)

If aerogel fillers are spread correctly and appropriately, these aerogels can act as nucleating agent and increase the number of nuclei and increase the number of new bubbles. When comparing the 10% and 15% aerogels, a smaller cell size distribution of the 10% aerogel was observed in Figure 4.23 and Figure 4.24.

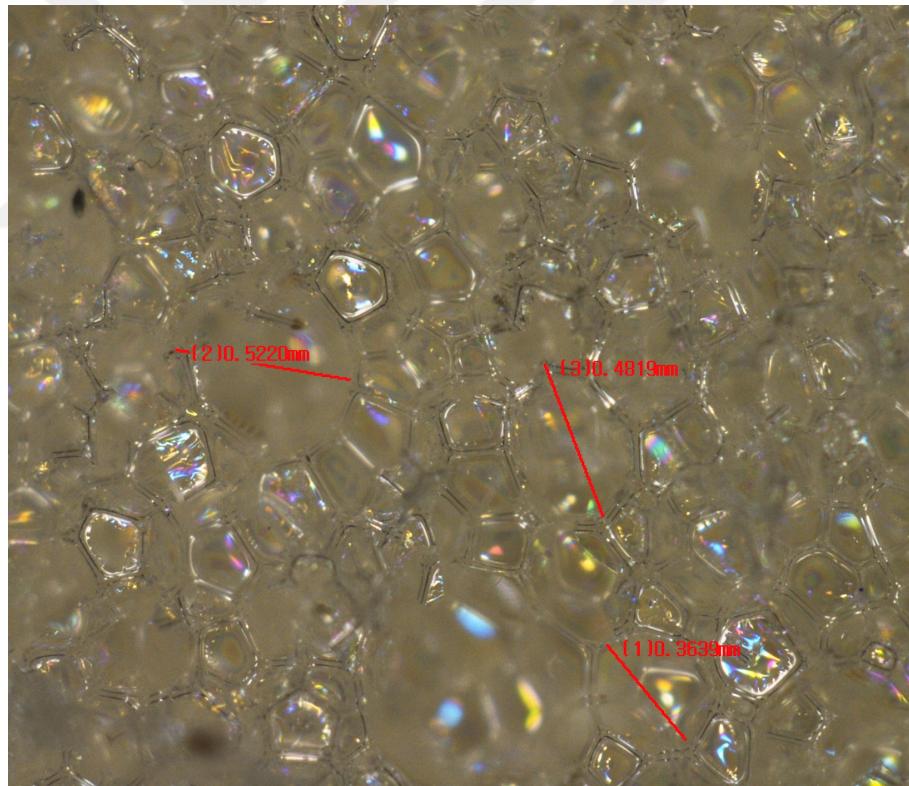


Figure 4.25. Microscope image of %10 Walnut shell filled foam (5x-5x)

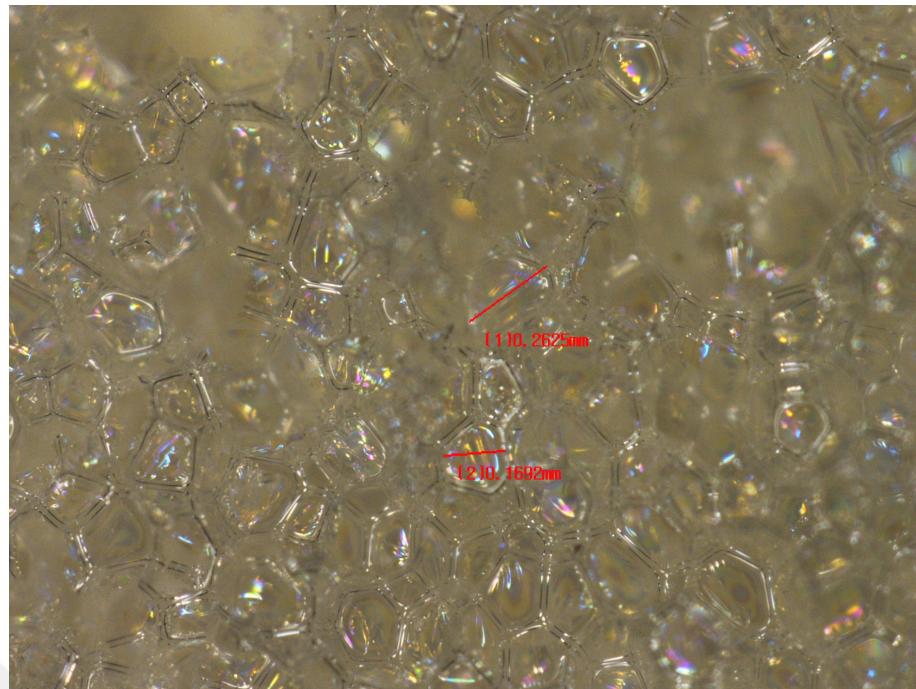


Figure 4.26. Microscope image of %15 Walnut shell filled foam (4x-6x)

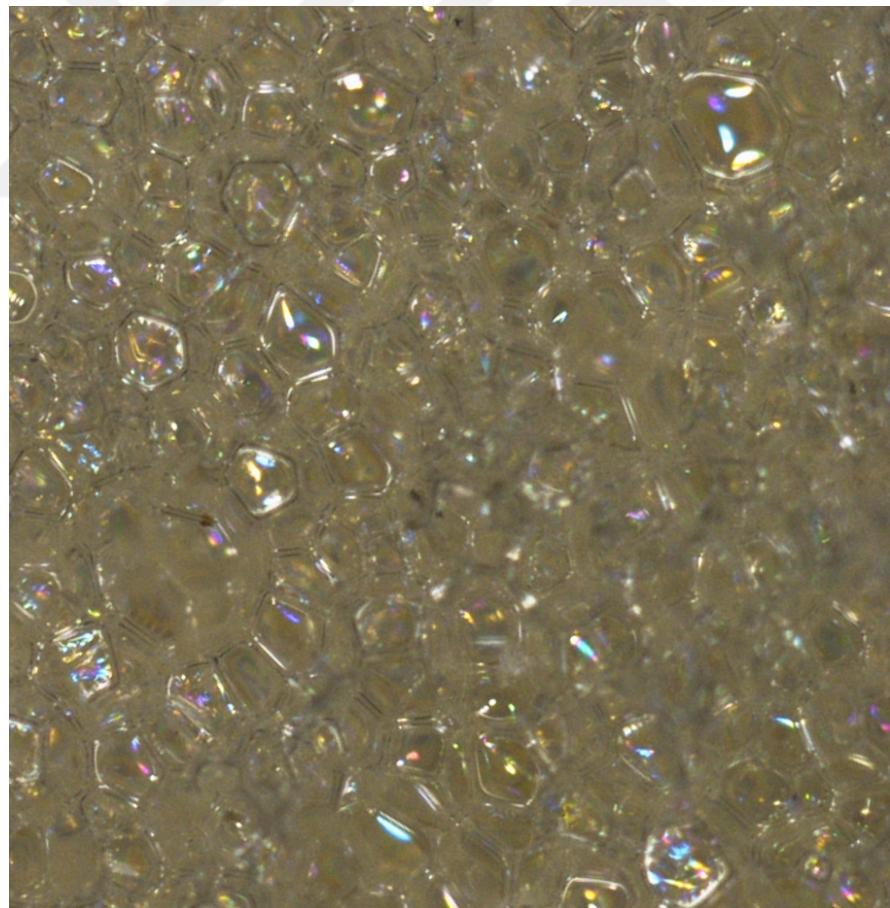


Figure 4.27. Microscope image of %20 Walnut shell filled foam (5x-3x)

Even though walnut fillers are spread correctly and appropriately, big walnut size directly affect in a negative way for cell structure. Close cell and cell structures are not stable. When comparing walnut samples, 20% walnut samples has more particle than other walnut samples in Figure 4.27. Particle size and excess particle create bigger structure. But thesis aim is to create small structure due to diffusion barrier. These kind of results steer to watch out for particle size and particle values.

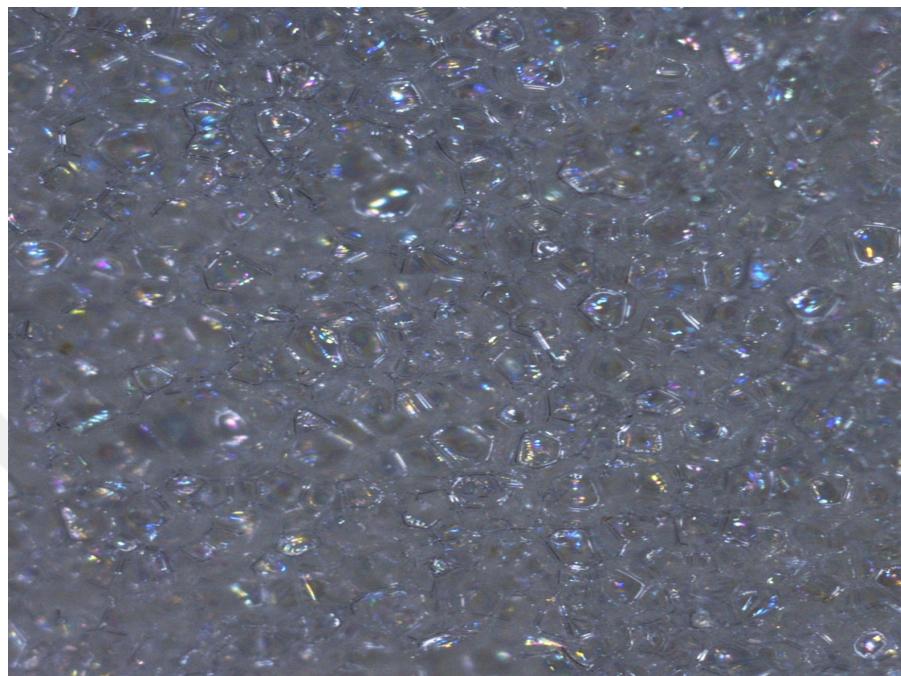


Figure 4.28. Microscope image of %10 Hazelnut shell filled foam (2.5x)

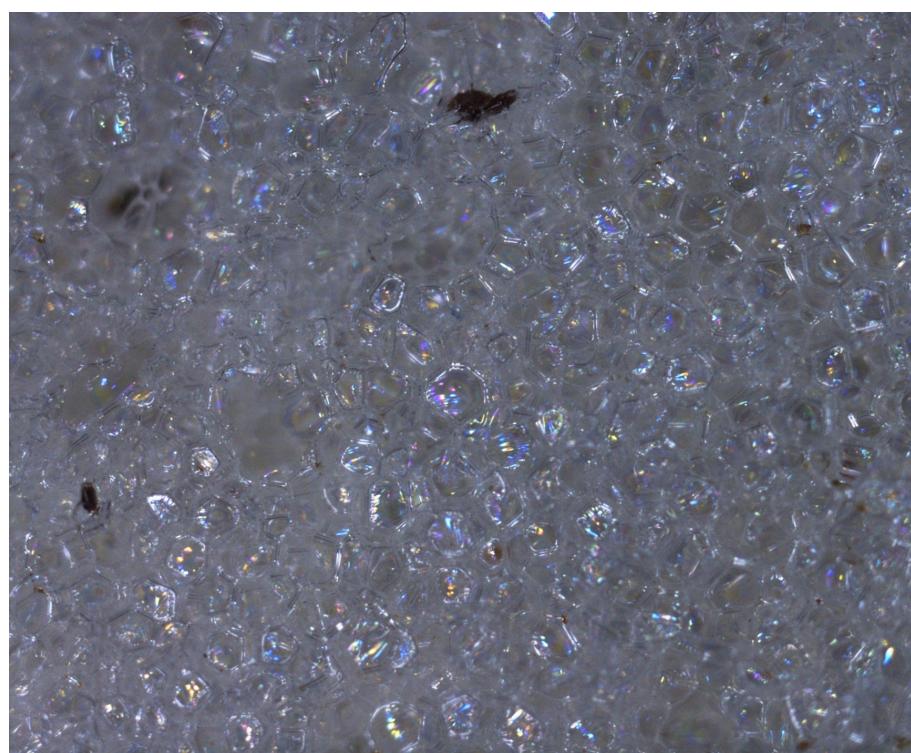


Figure 4.29. Microscope image of %15 Hazelnut shell filled foam (2.5x)

When additives were added, it was observed that the increased filler material resulted in a reduction in the cell size. It was observed that the cell wall shrinks depending on the average cell size. However, agglomerate formation is also observed. It can be seen that black particles inside polyurethane in Figure 4.29. Especially, big particles size help to generate agglomerate. This kind of particles directly collapse cell structure.

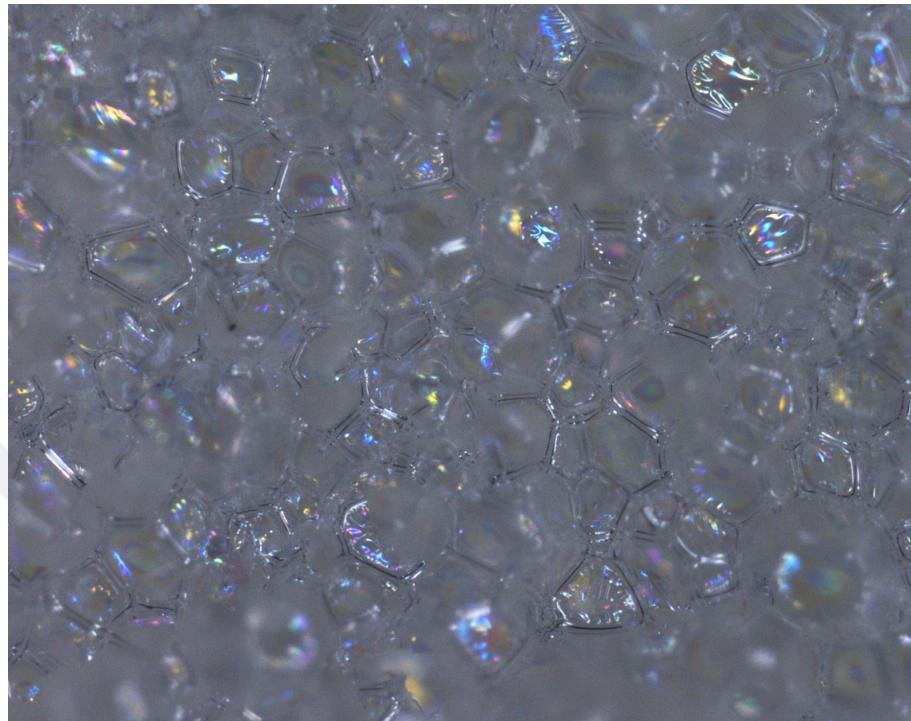


Figure 4.30. Microscope image of %10 Eggshell filled foam (5x)

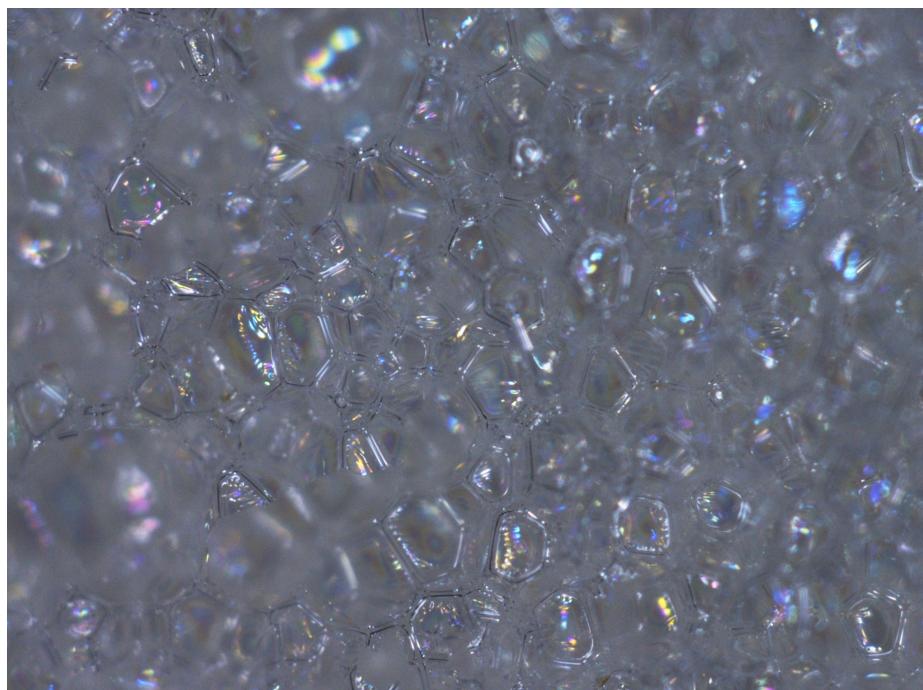


Figure 4.31. Microscope image of %15 Eggshell filled foam (6x)

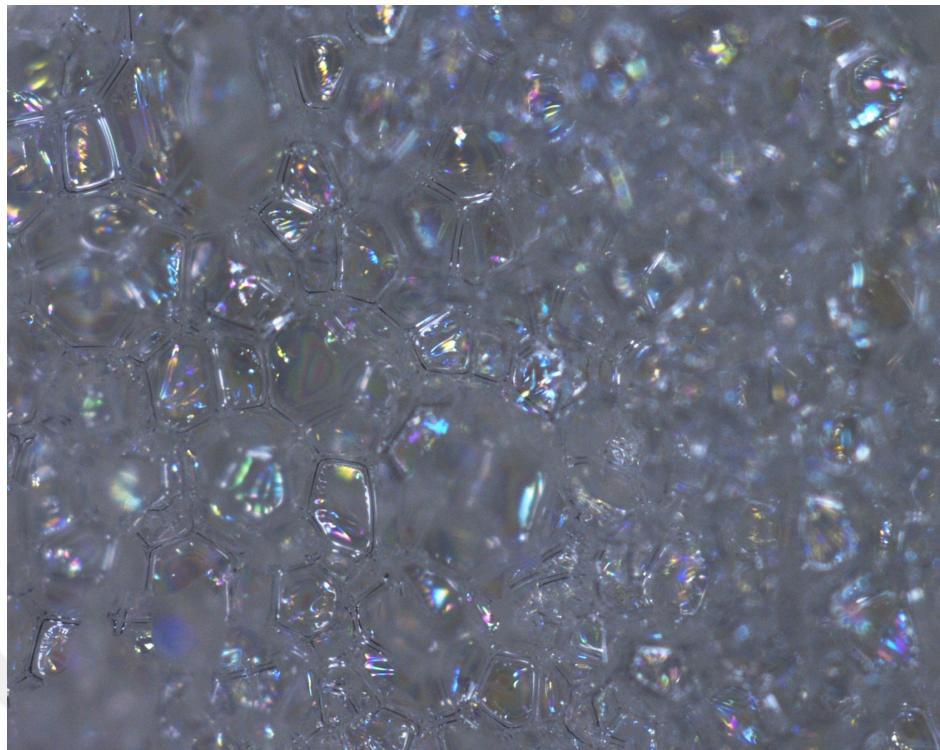


Figure 4.32. Microscope image of %20 Eggshell filled foam (5x)

The size, shape and surface area of the natural filler particles, which had a significantly affected on the characteristic times of the foaming process, foam surface morphology and physico-mechanical properties of the developed porous polyurethane composites (Leszczyńska et al, 2020). The cell size measurement result of samples prepared in this study are given in Table 4.13.

Table 4.13. Cell size measurement results

Sample Code	Cell Size (mm)
N	0.3250
EG10	0.2136
EG15	0.1961
EG20	0.1562
HN10	0.2833
HN15	0.3607
WN10	0.2510
WN15	0.2412
WN20	0.2990
AG10	0.2158
AG15	0.2225

#### 4.10 Evaluation of close cell content

The literature is reviewed regarding close cell content was reviewed. The thermal conductivity of the foams is mainly affected by the conductivity of the PU matrix, as well as by the gas trapped in the closed cell structure (in this case a mixture of cyclopentane and CO<sub>2</sub>) and by radiation heat transport between the cells (Barczewski et al., 2019). Hence, it is very important to encourage the close cell formation for good thermal isolation properties.

Open cell size ratio measurements were performed with a gas pycnometry device.

The water uptake of the PU composite foams slightly increases with increasing the amount of the natural fillers. This leads to formation of the inhomogeneous open cell structure in the modified foams. The addition of the additive causes the foam cells to open. PU foams with broken cell structures can absorb more water than those with closed cell structures. The result are presented in Table 4.14 and Figure 4.33.

Table 4.14. Close cell measurement results

Sample Code	Close Cell Content (%)
N	84,5
EG10	82,1
EG15	81,8
EG20	80,5
HN10	72,5
HN15	70,8
WN10	79,4
WN15	78,9
WN20	77,2
AG10	79
AG15	78,5

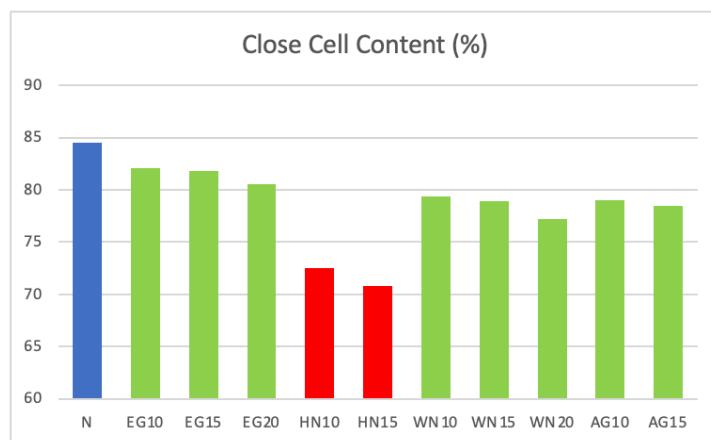


Figure 4.33. Close cell measurement results diagram

Closed cell amount of neat polyurethane is higher than composite polyurethanes. Because fillers tend to damage the cell structure. There is a 15% - 17% reduction of closed cell quantity. Hazelnut fillers has the worst amount of closed cell in our study. The least affected material is

EG10 which has the smallest filler particles and include the fewest eggshell. Thus, we observed the size of the filler material and the quantity of filler effect the closed cell measurement.

#### 4.11 Evaluation of SEM

Particle dispersion of fillers in PU is important for obtaining well-developed parts. The SEM images of neat foam, eggshell filler foams, aerogel filler foams, hazelnut filler foams and walnut filler shell foams are presented in between Figure 4.34 and Figure 4.44.

The structure of the neat foam is uniform and it has closed cell sufficiently however the cell sizes were bigger than composite foams compared. It was observed that the fillers affected negatively cell structure that disrupted the uniformity were formed. Filler materials that affect the foaming process result in the formation of defective parts. Larger aggregates with high visibility indicated poor interfacial adhesion between the additive and polyurethane, resulting in cell collapse and open pores.

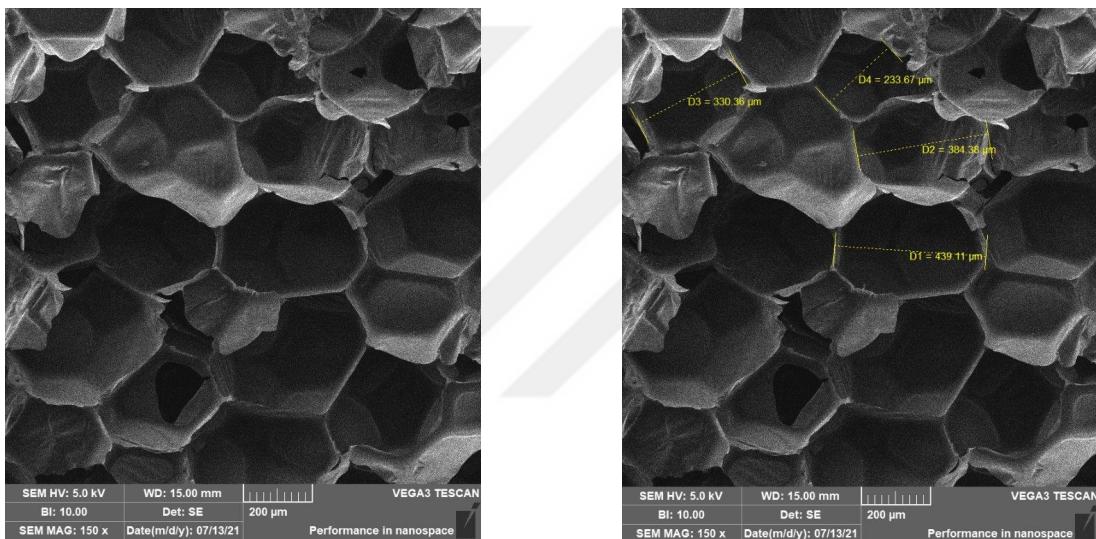


Figure 4.34. SEM image of neat foam

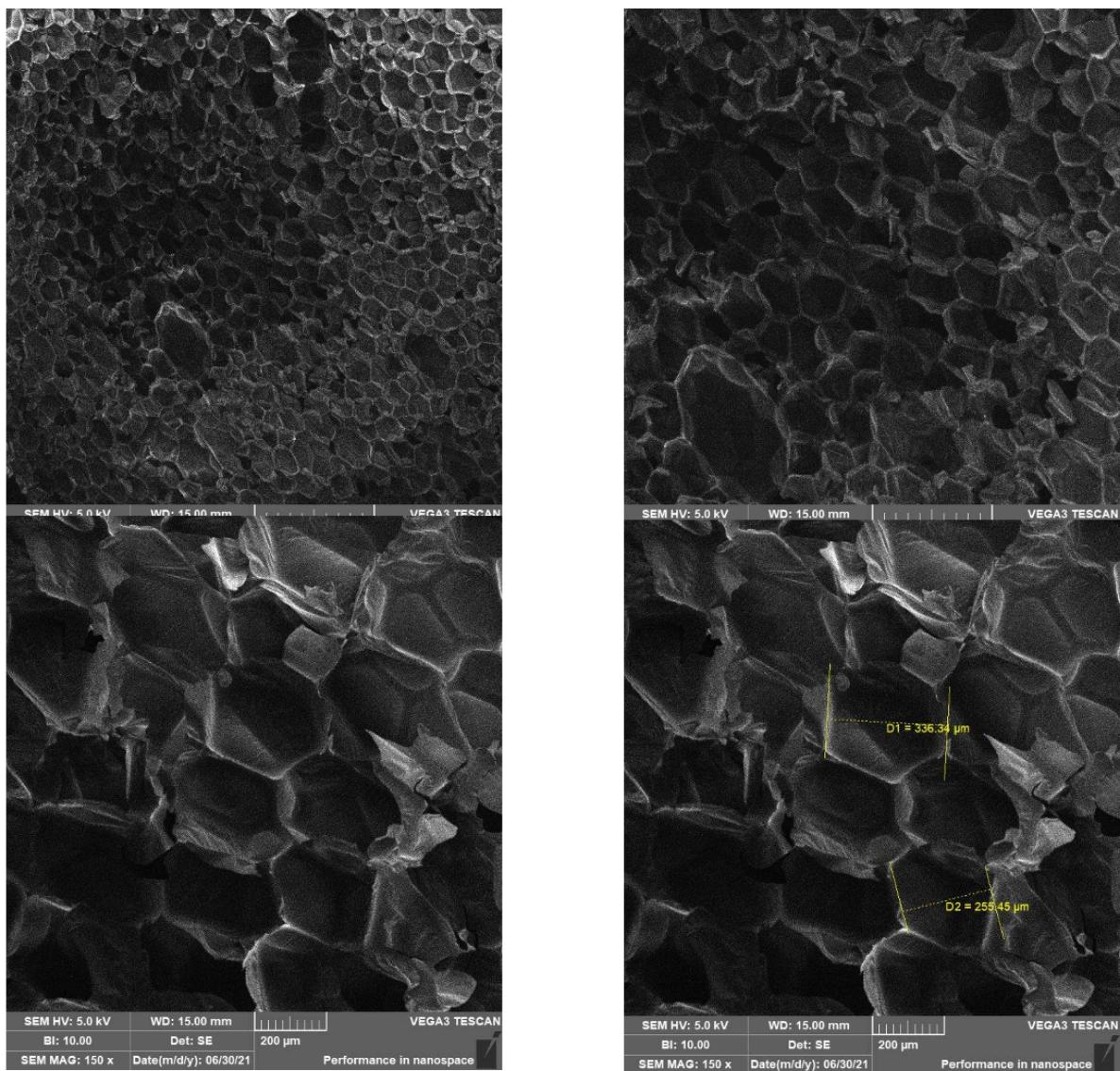


Figure 4.35. SEM image of 10% wt eggshell foam

The structure of the 10% eggshell foam is like ellipse uniform and the cell sizes were smaller than neat foams compared. Particles affected negatively cell structure but eggshell particles are smaller than walnut and hazelnut, small particles help to create small structure.

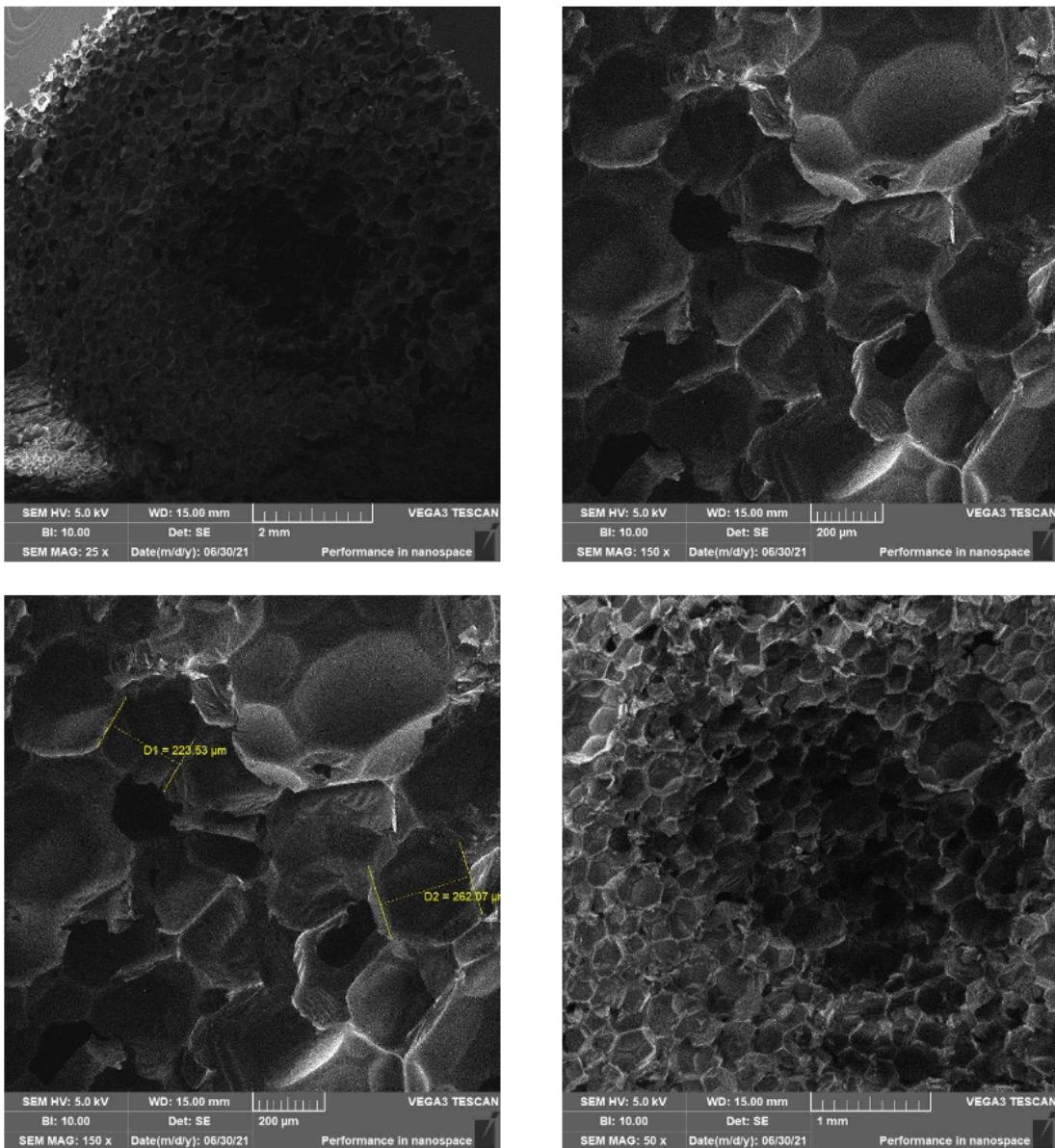


Figure 4.36. SEM image of 15% wt eggshell foam

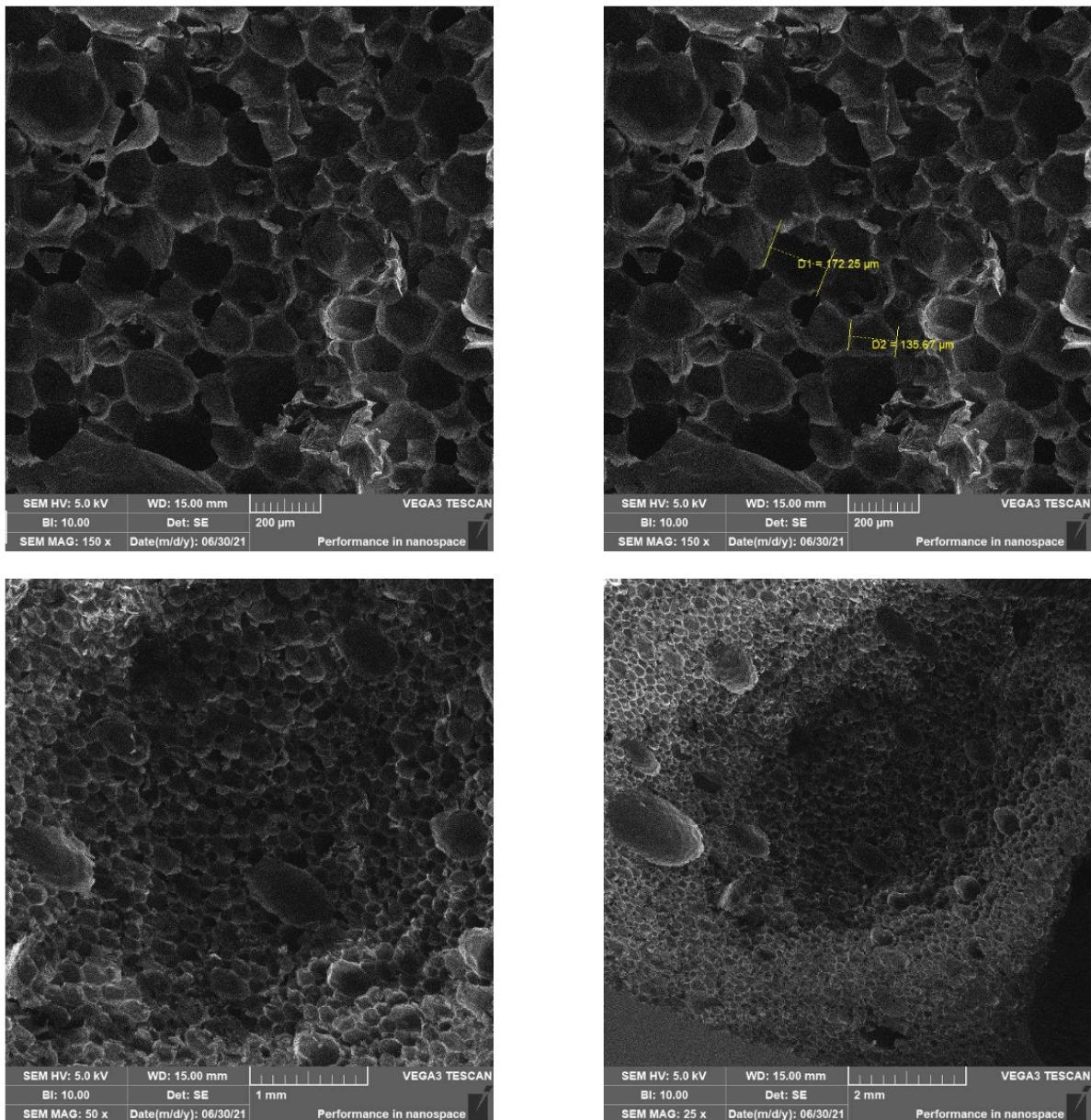


Figure 4.37. SEM image of 20% wt eggshell foam

It can see that the cell diameter is diminished. However, the additives cause structural defects in some area in Figure 4.37. As a result, it is thought that some large-size additives pass through the sieve.

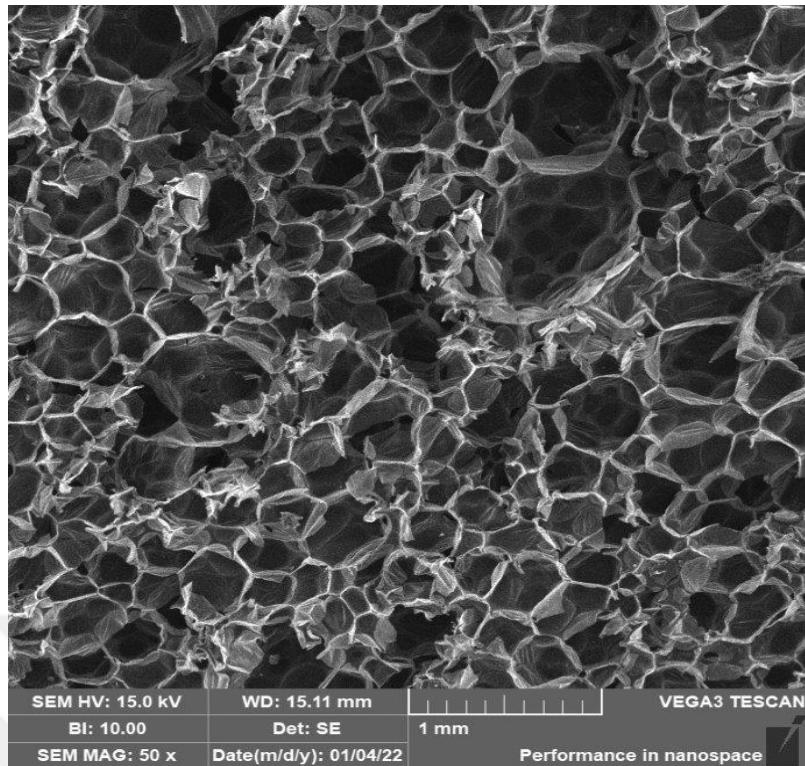


Figure 4.38. SEM image of 10% wt aerogel foam

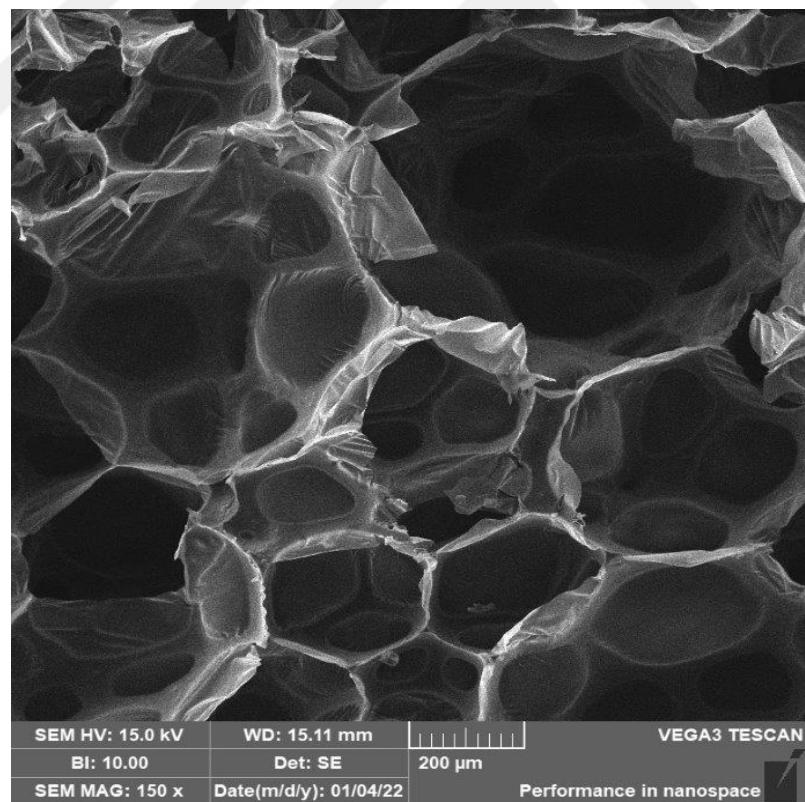


Figure 4.39. SEM image of 15% wt aerogel foam

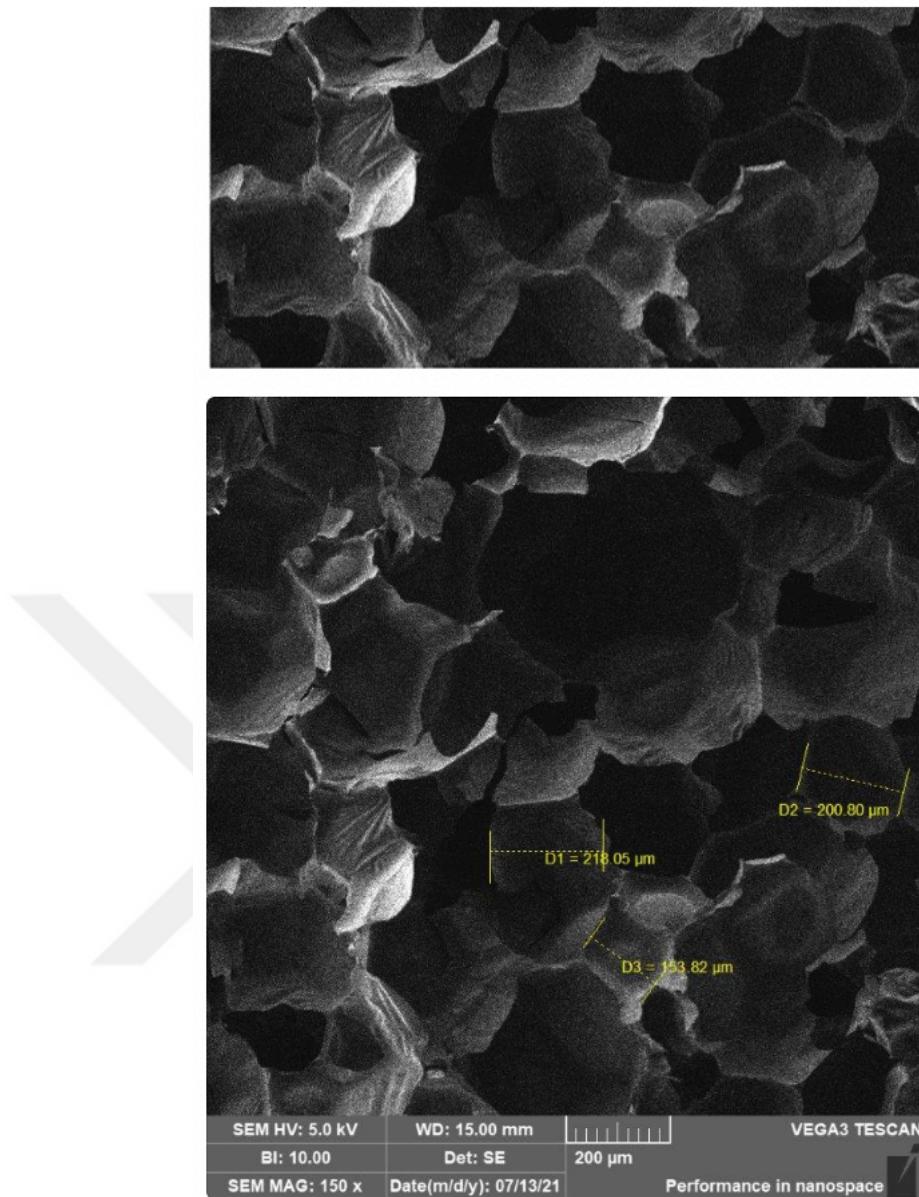


Figure 4.40. SEM image of 10% wt hazelnut shell foam

It can be observed that big size particles disrupt the cell structure and hazelnut samples destroy wall structure due to the large size of the additive material in Figure 4.40.

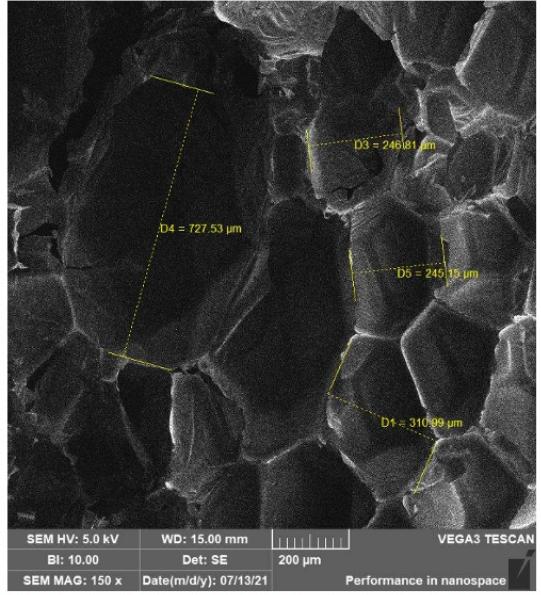
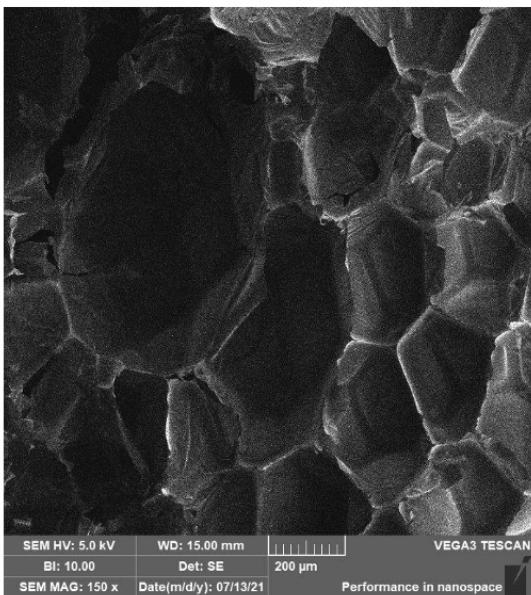
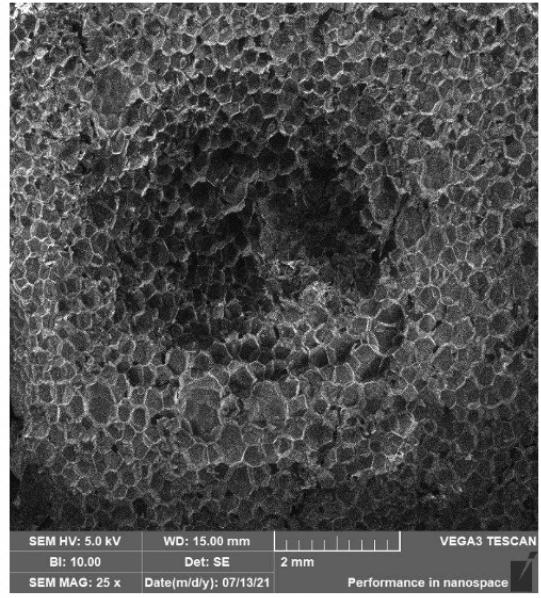
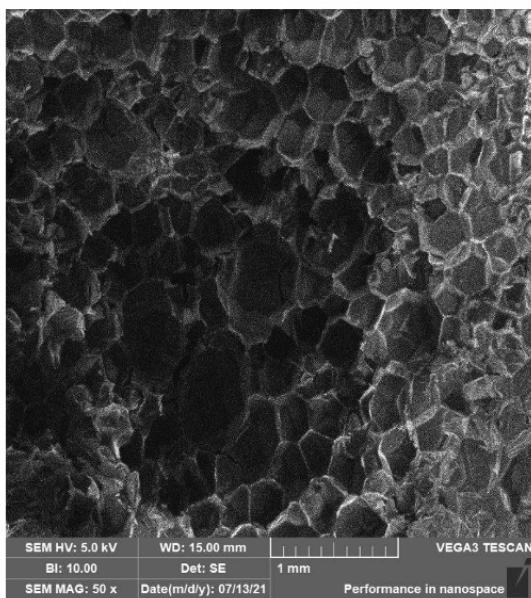


Figure 4.41. SEM image of 15% wt hazelnut shell foam

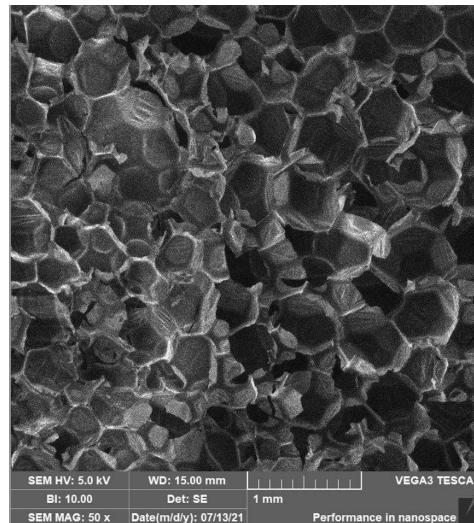


Figure 4.42. SEM image of 10% wt walnut shell foam

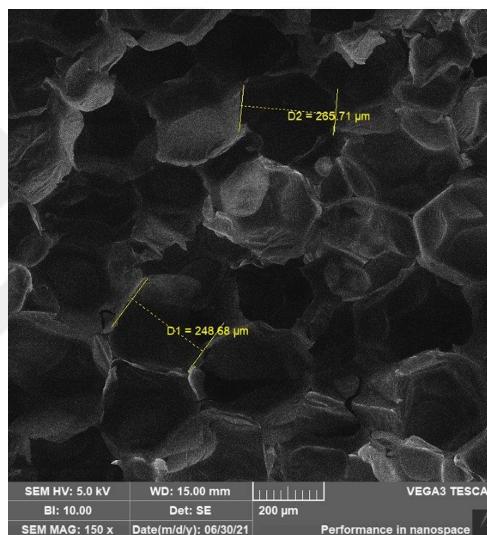


Figure 4.43. SEM image of 15% wt walnut shell foam

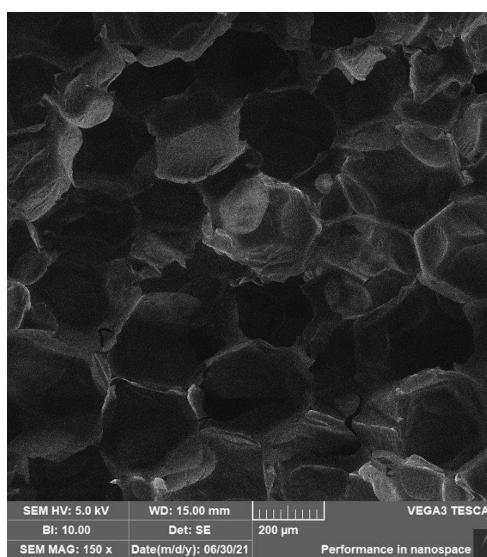


Figure 4.44. SEM image of 20% wt walnut shell foam

Upon the addition of the additive material, regular deformations of the neat foam structure were observed. In particular, since the particles of the nutshell and walnut shell additives are larger than those of the aerogel and eggshell, more structural property degradation was encountered in these parts. Cellular shrinkage was observed with the use of additives. The number of closed cells was also lower than that in the neat foam. The negative effects of the additives on the structure should not be ignored. This is one reason why many studies cannot be applied to the industry. According to the SEM results, the smaller the particle structure of the additive material, the healthier the results can be obtained. A good thermal energy value can be obtained with cell structure stability, cell geometry, cell size and closed cell structures.

#### 4.12 Evaluation of thermal conductivity

The thermal conductivity of an insulating foam depends on the conductivity of the cell gas mixture conductivity of the solid polymer and radiation between cells. The radiation of heat has been reduced by making the cells smaller and conduction of heat in the solid polymer has been reduced by decreasing the foam density. However, conduction in the cell gas mixture stands for the main part of the thermal conductivity of the foam.

Samples were prepared square format with the dimensions of 250x250 mm for thermal conductivity measurements. The thermal conductivity coefficient determines the energy efficiency of RPUFs. Thermal conductivity properties are related to morphological structure. Small cell and close cell structures provide thermal barrier for refrigerators.

It has been observed that most of the additive materials used in our study have a positive effect on thermal conductivity and also observed that the wt ratio and large-scale additives used in 15% HS and 15% WS materials adversely affect the thermal conductivity. The best result of thermal conductivity is 20% EG which has small particle size. Although 20% EG has more quantity of filler than 10% EG, we observed that the optimum ratio %20 for eggshell fillers. Although close cell quantity of 10% AG and 15% AG are less than neat PU, the cell size of 10% AG and 15% AG are smaller than neat PU as a result performance of thermal conductivity is more related with the cell size than the close cell. The measurement results are listed in Table 4.15.

Table 4.15. Thermal Conductivity measurement results

Specimen No	Thermal Conductivity W/m K
Neat	0,026
10 % EG	0,022
15 % EG	0,021
20 % EG	0,019
10 % HN	0,024
15 % HN	0,029
5 % WN	0,025
10 % WN	0,022
15 % WN	0,024
10 % AG	0,020
15 % AG	0,021

The leading thermal conductor materials are illustrated in Figure 4.45. In this study, by forming a composition with eggshell and aerogel on polyurethane, the effect of aerogel and eggshell fillers on strong thermal conductivity value.

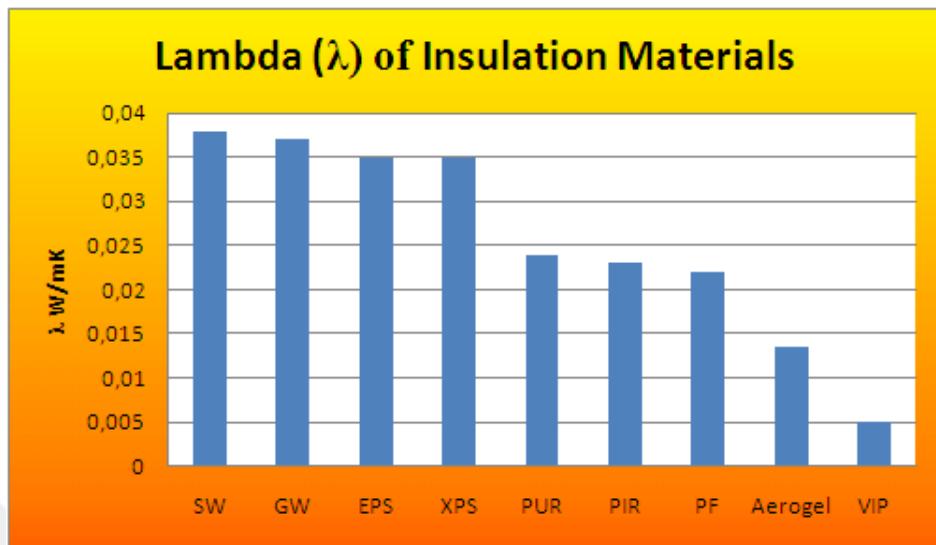


Figure 4.45. Comparison of commercial insulation materials (Danışman B.C, 2019, Smart insulation presentation, 5p (unpublished))

#### 4.13 Evaluation of compressive strength

In addition to the insulation properties of RPUF, the rigidity of household appliances is a cornerstone for non-flexing. The decrease in the compressive strength of RPUF foam is undesirable in terms of rigidity.

Table 4.16. Compressive strength measurement results

Sample	h0 mm	S0 mm <sup>2</sup>	F(10%) Fapply N/cm <sup>2</sup>
N	24,8	2787	5,97
EG10	24,5	2787	12,92
EG15	24,5	2787	15,28
EG20	24,3	2787	29,45
HN10	24,9	2787	5,41
HN15	25	2787	4,82
WN10	24,6	2787	6,41
WN15	24,6	2787	6,62
WN20	24,6	2787	10,39
AG10	24,5	2787	15,22
AG15	24,5	2787	16,42

The density increases as it has an effect on the viscosity during the comparison of filling materials with polyol. The density and mechanical properties are directly proportional. For this reason, an increase in the compressive strength is expected. As observed in the related test, the compressive strength increased as a result of the addition of additive material. It was observed that the hazelnut piece, which has a large additive material structure, causes structural deterioration and also damages the mechanical properties. All samples have prepared cylindrical format before implementation of compressive test. Samples of height is averagely 24.8 mm and surface area is 2787 mm<sup>2</sup>. The results are shown in Table 4.16 and Figure 4.46.

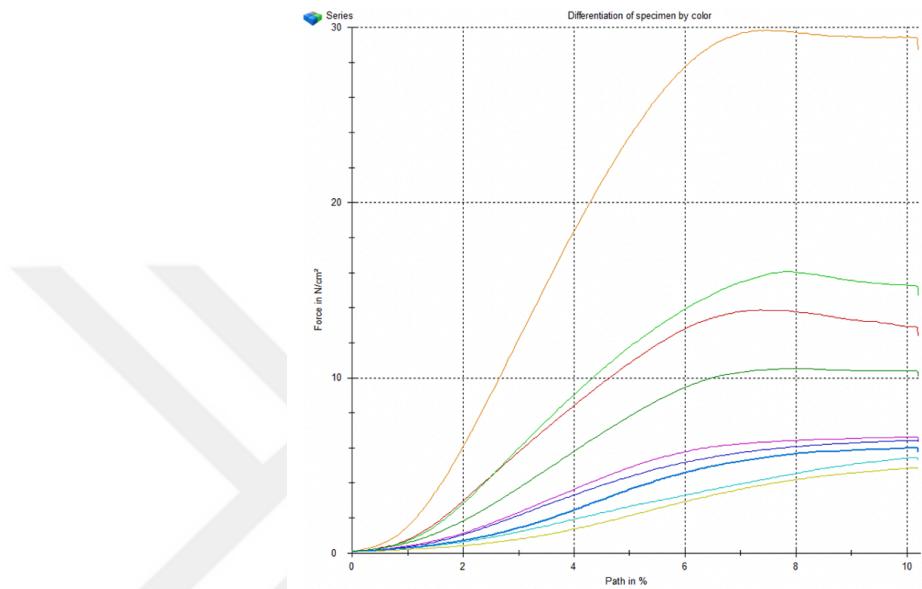


Figure 4.46. Compressive strength of neat and composites PU foam diagram

The overall brittleness of the foams increased with the addition of eggshell fillers because of their lower apparent density and higher structural anisotropy.

## 5. CONCLUSION

In our study, the effects of natural additives (walnut, hazelnut and egg) and aerogel material in polyurethane composites on the thermal properties were investigated. Chemical, morphological and thermal characterization of prepared materials were done by conducting density, cell size and close cell measurements, SEM, FTIR, TGA analysis and thermal conductivity measurement.

The advantages of natural fillers over synthetic fillers are numerous, including easy availability, low cost, low density, recyclability, renew- ability, biodegradability and less health risks

- The EG 20 highest density value was obtained in the range of 0.049-0.054 kg/cm<sup>3</sup>
- The additives had a direct negative effect on the creaming time. Neat was observed to be closest to EG10. It was observed that the EG 15 and EG 20 values required a shorter time than the other additives.
- Aerogel wt% 10 and aerogel wt% 15 also had relatively similar thermal degradation characteristics to those of EG15 and EG 20. In general, four decompositions were observed. The first degree of degradation occurred in the average temperature range of 0-300 degrees. The first decay stage was generally observed to be less severe. The second and third decay stages were much more severe and mass loss occurred in this region. The most severe part, the third decay stage, caused a loss of 2.7 mg of the sample mass and EG15 at a final temperatures of 2.8 mg.
- Elemental values were observed in the XRF tests. The largest decrease in the oxygen ratio was observed for the aerogel additives.
- In foams containing natural fillers, the water absorption properties of the foam are generally significantly enhanced, which may be a result of the chemical composition of the filler particles. It was observed that negative results were obtained due to the fact that the hazelnut shells were in a larger structure than the other additives in the pieces that were sieved before the additives were added. The smaller the particle size of the additive, the more positive are the results obtained.
- When comparing 10% and 15% of aerogel PU, with 10% EG a smaller cell size distribution was observed with aerogel containing PU. In addition, 15% EG and 20%EG has the smallest cell size. It has been observed that increasing the filler material when additives were added resulted in a reduction in the cell size. It has been observed that the cell wall shrinks depending on the average cell size. However, we also observed agglomerate formations.
- There must be a significant number of closed cell structures to form a rigid polyurethane foam. The best results were obtained for the EG10 wt value. Its value is less than that of the neat foam owing to the additive material.
- Thermal conductivity is the most critical value in the insulation parts. With a  $\lambda$  value of 0.019 W/m K, the most effective value was achieved at 20% wt.

- No additional work has been performed to improve the compressive values. the results showed that significantly increased with the EG20 value.
- As observed in the SEM image of composites polyurethane, between the walls became thinner and smaller cell structures were formed. The relevant results were observed through microscopic examinations.

Based on the results, it can be concluded that the addition of 20 wt% of eggshell filler leads to PU composite foams with improved density (e.g. improvement by ~50%), higher compressive strength (e.g. increase of ~500%), and comparable thermal conductivity (0.019 W m<sup>-1</sup> K<sup>-1</sup>). Moreover, the incorporation of eggshell filler has a positive effect on the close cell and cell structure of PU materials. On the other hand, it was observed that the gelation time was 65 seconds in the 20 wt% eggshell additive, reducing the reaction state. During weight degradation, the sample was completely evaporated at 800 °C. Similarly, because of the large particles of hazelnut shell additives, a delay was observed during the reaction.

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## **8. RESUME**

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