DEVELOPMENT OF POLYURETHANE NANOCOMPOSITES WITH LOW THERMAL CONDUCTIVITY BY ADDITION OF MODIFIED VERMICULITE

Ceren IRMAK KARAMEŞE

M.Sc. Thesis

Eskişehir, 2019

Sensitivity: Public

DEVELOPMENT OF POLYURETHANE NANOCOMPOSITES WITH LOW THERMAL CONDUCTIVITY BY ADDITION OF MODIFIED VERMICULITE

Ceren IRMAK KARAMEŞE

M.Sc. Thesis
Department of Materials Science and Engineering
Supervisor: Prof. Dr. Ender SUVACI

Eskişehir
Eskisehir Technical University
Institute of Gradute Programs
September, 2019

FINAL APPROVAL FOR THESIS

This thesis titled “Development of Polyurethane Nanocomposites with Low Thermal Conductivity by Addition of Modified Vermiculite” has been prepared and submitted by Ceren Irmak Karamese in partial fullfillment of the requirements in “Eskişehir Technical University Directive on Graduate Education and Examination” for the Degree of Master of Science in Materials Science and Engineering Department has been examined and approved on …../…../……..

Committee Members	**Title, Name Surname**	**Signature**
Member (Supervisor)	: Prof. Dr. Ender SUVACI	....
Member	: Prof. Dr. Murat ERDEM	....
Member	: Prof. Dr. Necmettin CANER	....

....

Prof. Dr. Murat TANIŞLI

Director of Institute of Graduate Programs

ÖZET

MODİFİYE VERMİKÜLİT İLAVESİ İLE DÜŞÜK ISIL İLETKENLİĞE SAHİP VERMİKÜLİT KATKILI NANOKOMPOZİT POLİÜRETAN KÖPÜKLERİN GELİŞTİRİLMESİ

Ceren IRMAK KARAMEŞE
Malzeme Bilimi ve Mühendisliği Anabilim Dalı
Eskişehir Teknik Üniversitesi, Lisansüstü Eğitim Enstitüsü, Eylül 2019

Danışman: Prof. Dr. Ender SUVACI

Poliüretan malzemeler, bugünün dünyasında çok çeşitli kullanım alanına sahip malzemelerdir. Mükemmel ısı yalıtımı, kimyasal direnç ve tokluğa sahip ilginç bir polimer ailesi olan sert poliüretan köpükler, buzdolabı endüstrisinde yaygın olarak ısı yalıtımı amaçlı olarak kullanılırlar. Sert poliüretan köpükler, buzdolaplarını soğuk tutmak için gereken enerjiyi azaltarak sürdürülebilirliğe ve eko-tasarıma büyük katkı sağlarlar. Gereken enerjiyi azaltmak için, sert poliüretan köpüğün termal iletkenliği azaltılmalı ve termal iletkenliği azaltmak için hücre boyutu daha küçük olmalıdır. Sert poliüretan köpüğün hücre boyutunu azaltmak için çeşitli katkı maddeleri kullanılır. Kil, bu malzemelerden biridir. Kilin, polimer matrise uyumluluğunun sağlanabilmesi için, modifikasyonu gereklidir. Bu çalışmada, sert poliüretan köpüğün ısıl iletkenliğini düşürmek için, kil olarak nanopartikül büyüklüğüne sahip vermikülit kullanılmıştır. Vermikülitin modifikasyonu için 1 CEC, 2 CEC ve 3 CEC oranlarında, kuaterner amonyum tuzu olarak CTAB kullanılmıştır. Modifiye edilmiş vermikülitin, ağırlıkça %1, %3, %5, %7 ve %10 katkılanmasıyla, sert poliüretan köpüğün ısıl ve mekanik özellikleri üzerine etkisi incelenmiştir. Modifiye edilen vermikülitin, tabakalar arası mesafesi ölçülerek, temas açısı belirlenmiştir. Temas açısının en yüksek elde edildiği CTAB oranı 2 CEC olarak belirlenmiştir. 2 CEC oranında CTAB ile modifiye edilen, ağırlıkça %5 vermikülit katkılı katı poliüretan köpükte, optimal sonuç elde edilerek hücre boyutunda standart poliüretan köpüğe göre %59 küçülme sağlanmıştır. Hücre boyutundaki küçülme ile termal iletkenlik katsayısında %8 azalma sağlanmıştır.

Anahtar Kelimeler: Sert Poliüretan Köpük, Isıl İletkenlik, Enerji Verimliliği, Nanokompozit

ABSTRACT

DEVELOPMENT OF POLYURETHANE NANOCOMPOSITES WITH LOW THERMAL CONDUCTIVITY BY ADDITION OF MODIFIED VERMICULITE

Ceren IRMAK KARAMEŞE

Department of Materials Science and Engineering

Eskisehir Technical University, Institute of Graduate Programs, September 2019

Supervisor: Prof. Dr. Ender SUVACI

Polyurethane is one of the most miscellaneous material that has many usage area in the world, today. Rigid polyurethane foams that are an interesting family of polymers, with excellent thermal insulation, chemical resistance and toughness. They are extensively used as thermal insulation in refrigerator industry. Rigid polyurethane foam makes a major contribution to sustainability and eco-design by reducing the energy required to keep refrigerators cold. To reduce the energy required, the thermal conductivity of rigid polyurethane foam must be decreased and to decrease thermal conductivity, the cell size must be smaller. Various kinds of additives are used to decrease cell size of rigid polyurethane foam such as clay. It is important that the compatibility of clay particles and polymer matrix is crucial to achieve nanodispersion of clay. In this study, nanosize vermiculite was used as the clay to decrease thermal conductivity of rigid polyurethane foam. To provide compatibility, 1 CEC, 2 CEC and 3 CEC ratios of quaternary ammonium salt CTAB was used to achieve modification of vermiculite and effect of modified nanosize vermiculite which added 1%, 3%, 5%, 7% and 10% by weight on thermal and mechanical properties of rigid polyurethane foam was investigated. To determine whether vermiculite was modified or not, interlayer distance was measured and hydrophobicity with different modifier agent ratios was examined. The amount of modifier agent that gave highest contact angle was 2 CEC. The smallest cell size was obtained with addition of 2 CEC modified, 5% by weight vermiculite. Decreasing in mean cell size was 59% and thanks to that, decreasing in thermal conductivity was 8%.

Keywords: Rigid Polyurethane Foam, Thermal Conductivity, Energy Efficiency, Nanocomposite

ACKNOWLEDGEMENTS

I have been working for the completion of this master's thesis at Eskisehir Technical University, Department of Material's Science and Engineering. I am greatly thankful to a number of very important people for supporting and helping me for this project.

First, I would like to show my appreciation to my supervisor, Prof. Dr. Ender SUVACI, for his mentorship, support, technical guadiance. I am sincerely thankful Prof. Dr. Murat ERDEM, Research Assistant Emre AKDOĞAN and Dr. Oktay UYSAL for their support, advice and helpful suggestions.

Also, I would like to thank Arcelik Inc., Eskisehir for providing me with the necessary materials and equipment for my experiments. In particular, I would like to thank Dr. Metin KAYA, Gökşin SAYER, Halit EKMEKÇİ and PU Mixing Laboratory in Arcelik Inc. for supporting to complete my thesis. Besides, I am greatful Production Engineering and Research and Development Department for their support in conducting my thesis and for encouraging me.

I would also like to thank my friends Kübra ORTAÇ SARPER, Aysun GENÇTÜRK, Pınar ŞENGÜN and İsmail ŞAHİN for supporting me no matter what.

Finally, I want to express my gratitude to my husband Aytuğ KARAMEŞE, my mother Naide IRMAK, my father Mustafa IRMAK and my sisters İlke IRMAK and Gizem IRMAK DİRİ for all of the sacrifices that they made on behalf for the succesful completion of the thesis.

Ceren IRMAK KARAMEŞE

September, 2019

..../..../20....

STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and that this study has been scanned for plagiarism with "scientific plagiarism detection program" used by Eskişehir Technical University, and that "it does not have any plagiarism" whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved.

Ceren IRMAK KARAMEŞE

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

ABBREVIATIONS

r_{cr} : Critical Radius

ΔG : Gibb's Free Energy of the System

r : Cell Radius

γ : Surface tension

ΔP : Supersaturation level

λ_f : Total thermal conductivity of rigid polyurethane foam

λ_m : Thermal conductivity of the matrix

λ_g : Thermal conductivity of the gas within the foam cells

λ_r : Thermal conductivity with radiation

f_s : Strut Fraction

Π : Porosity

p_s : Polymer Density

ρ_f : Foam Density

σ : The Stefan-Boltzmann Coefficient

K^* : The Extinction Coefficient of the Foam

T : Temperature

RPUF : Rigid Polyurethane Foam

CEC : Cation Exchange Capacity

ODP : Relative Ozone Depletion Potential

GWP : Relative Global Warming Potential

CFC : Chlorofluorocarbon

HFC : Hydroflorocarbon

HC : Hydrocarbons

1. INTRODUCTION

1.1. Research Objective

Nowadays, nearly 80% of people are able to use electrical energy. According to the New Policies Scenario, 1.7 billion people to be added to urban areas, especially in developing countries, are expected to increase global energy demand by 25% in 2040. If there are no ongoing improvements in energy efficiency and sustainability projects, increase in energy demand is expected to double. (http-1).

Home appliances are most commonly used goods that consumes electrical energy in houses thanks to meet basic needs that are food preparation, cleaning chlotes, food preservation, dish washing, household cleaning etc. It is reported that household appliances constitues 15% of global energy demand and growth of use in electricity by consumer goods is approximately 3% since 2010. Total energy use of household appliances have reached 3.000 TWh. Figure 1.1. shows electrical consumption of household appliances by region between 2000-2018 and exprected values for 2025 and 2030 (http-2)

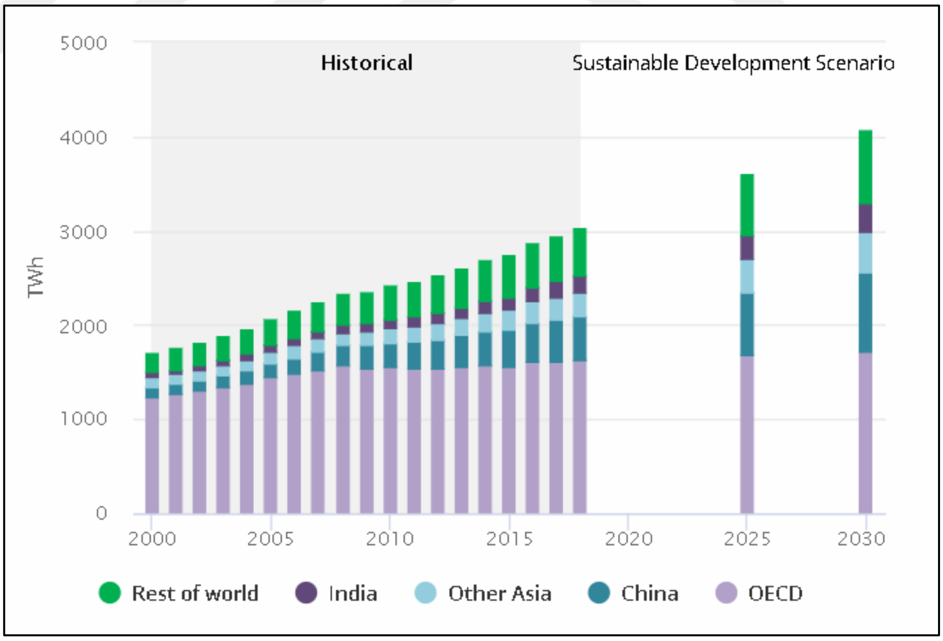


Figure 1.1. *Consumption by household appliances and plug loads by region (http-2)*

Refrigerators are one of the most energy consuming items in all electrical appliances. In household,between 20-30% consumption of total electrical energy belong to refrigerators.

According to International Energy Agency, electrical energy consumption of refrigerators and freezers was approximately 500 TWh and is expected to increase 35% by 2050. (http-2) Figure 1.2. explains energy consumption of household appliances per household type.

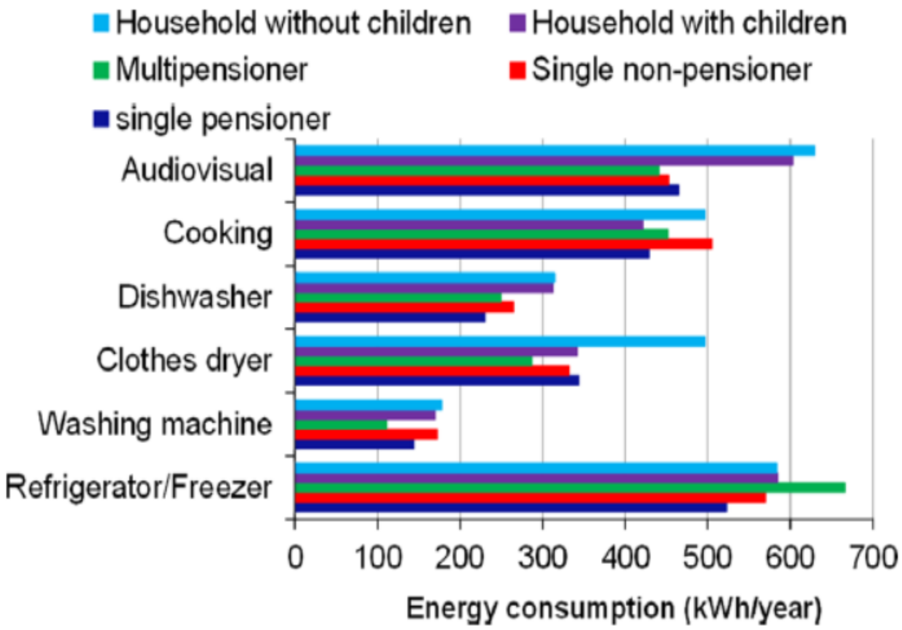


Figure 1.2. *Energy consumption (kWh/year)of differentappliances per householdtype*

(Zimmerman et al, 2012, p.242)

Energy consumption is restricted by regulations for cooling business. Furthermore, there are many projects to improve energy consumption of refrigerators. Using of more efficient compressor, improvement of vacuum insulation panels, more efficient gaskets or optimization of rigid polyurethane foam are some of the projects to aim decreasing in electrical energy consumption.

Rigid polyurethane foam (RPUF) is the main and most commonly used insulation material for refrigerators. RPUF prevents transportation of air in the room into the refrigerator and reduces the electrical energy consumption to keep the food cold.

The thermal conductivity of polyurethane foam is relatively low by comparison with other insulation materials. Figure 1.3. shows comparison of the thermal conductivity of insulation materials.

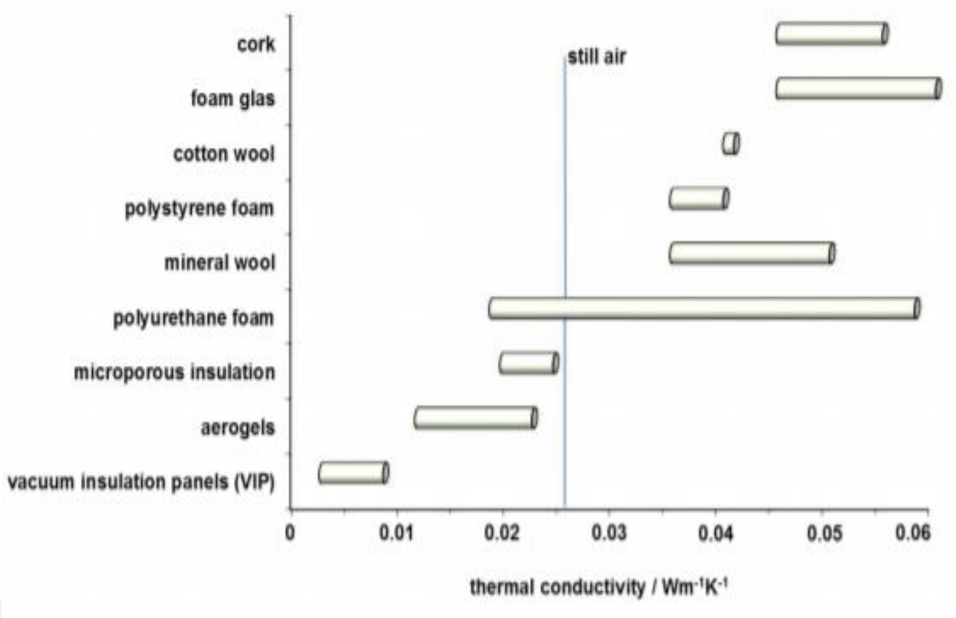


Figure 1.3. *Typical thermal conductivity values of thermal insulation materials (Ebert, 2015, p.2)*

On the other hand, there are many studies to decrease thermal conductivity of rigid polyurethane foams to provide lower thermal conductivity and improve insulation property of the foam. For this purpose, some researchers focuse on improving thermal conductivity by adding some fillers such as nanoparticles, clay into RPUF. Thermal conductivity coefficient of RPUF can be reduced with modified nanoclay particles with modifying agents and making them compatible with solid matrix. It requires a good dispersion and compatibility between nanoclay particlues and polymeric matrix to provide improvement in thermal conductivtiy of RPUF. (Estravis et al, 2016, p. 2)

The main research objective of this project was to investigate effects of nanoclay particules on thermal conductivity of RPUF. A polymer-nanoclay composite material was obtianed with the using of modified nanoclay while rigid polyurethane foam processing. For this purpose, different ratios of quaternary ammonium surfactant were used to determine optimal cation exchange capacity (CEC) of nanclay to provide optimal dispersion. In addition, the structure-property relationship between nanoclay and RPUF was established.Besides effects of nanoclay on thermal conductivity coefficient of RPUF, effects on cell size and compressive strength was investigated with this project.

1.2. Historical Development of Polyurethane

Polyurethane was developed by Dr. Otto Bayer and his team who worked to find an alternative material to nylon in the early years of World War II. Isocyanate polyaddition process which provides to manufacture various types of polyurethane materials was discovered by Dr. Otto Bayer and his team.Polyurethane technology is based on isocyanate chemistry and studies which were related with isocyanate chemistry has been started approximately 150 years ago. Aliphatic isocyanates were first syntesized by A. Wurtz. (Bora, 1998, p.11). Initially, studies to produce PU products have been based on aliphatic diisocyanate reactions. Then, diisocyanate addition polymerization reaction was discovered by Dr. Otto Bayer and his collaborates. Toluene diisocyanate was discovered and commercial scale of polyurethane products was started after World War II. (Zafar et al, 2012, p. 3)

The historical time line of polyurethane:

- 1937: Dr. Otto Bayer and his collaborates was discovered the basis of polyurethane
- 1940: RPUFs were started to use for aircraft technology
- 1941: Polyurethane was used as an adhesive
- 1948: Polyurethane has been first used as an insulation material into beer barrel
- 1949: Rollable polyurethane rubber was produced
- 1953: Polyurethane was started to use in shoes
- 1954: Flexible polyurethane foam was started to use in cushions
- 1959: NASA was improved space suits by using polyurethane material for their Mercury mission
- 1960: For construction, polyurethane was started to use in steel sandvich panels
- 1967: K67 cars which were all produced with plastics had polyurethane interior were exhibited.
- 1970: Polyurethane was started to use for medical applications
- 1973: Thermoplastic polyurethane was developed
- 1979: Spray polyurethane technology was developed for buildings
- 1985: Polyurethane foams was started to use for energy absorbing material in cars
- Mid 1980s: RPUFs were started to use for insulation in refrigerators
- 1991: First polyurethane memory foam was produced in US

• 1992: NASA used polyurethane as a protector for external tanks of Endeavour space shuttle

• 2010: Polyurethane was used in the light frame of solar powered plane (http-3)

As it is used in many different areas, polyurethane is the major insulation material of coolers, refrigerators and freezers. In addition being the major insulation material, RPUF is suitable material for ensuring the rigidity of the refrigerators. There are many advantages to use rigid polyurethane foams for refrigerators:

• RPUF is one of the low thermal conductivtyinsulation material. • RPUF adheres to plastic inner body and metal panel and provides rigidity

• Manufacturing cost of RPUF is affordable

• Thickness of RPUF related to energy efficiency level of refrigerator can be optimized and provides more storage area for food in refrigerator.

• Production process is moldable and provides to produce different size and shape

• RPUF is a light material and helps to improve transportation cost (http-3)

Demand for polyurethane products in the market is growing fast because of product variety. According to estimates, worldwide polyurethane consumption was 60.5 billion USD in 2017 and it was expected to reach up to 79 billon USD in 2021. (Gama N.V. et al, 2018, p. 2) In 2016, growth rate of polyurethane market was about 4.0% and total market size was reach to 22.3 million tonnes. Figure 1.5 shows the projection of worldwide PU production related to region between 2014-2020. (Austin et al, 2017, p. 3)

Nowadays, polyurethane and polyurethane technology are being used in many different application areas; construction, transportation, furniture&bedding, household appliances, packaging, textile,electronics, footwear etc. Figure 1.4. shows polyurethane demand by end-segment in 2016. Figure 1.5. shows The projection of worldwide PU production related to region between 2014-2020 (in kt)

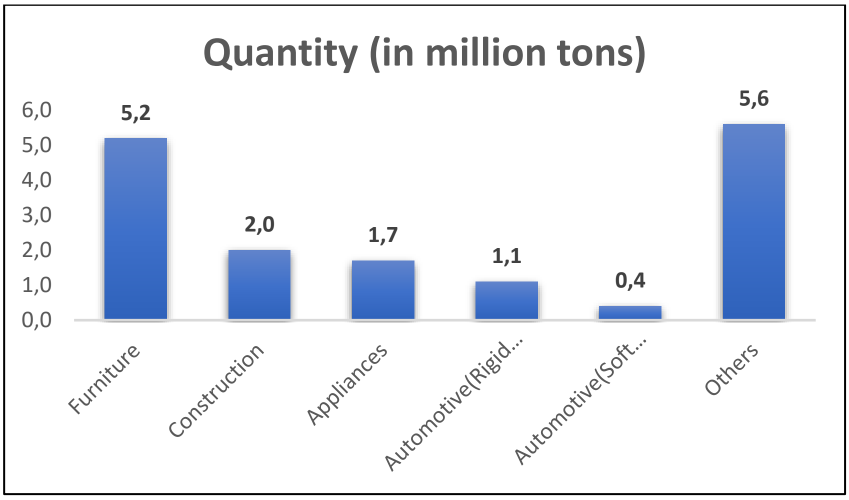


Figure 1.4. *Polyurethane demand by end-segment-2016 (http-4)*

Region	2015	AAGR '15/16	2016	AAGR '16/17	2017	CAGR '16/20	2020
NAFTA	3,616	6.1 %	3,835	5.6 %	4,048	4.1 %	4,750
South America	890	–3.9 %	855	1.9 %	871	2.9 %	975
China	8,165	3.2 %	8,425	3.7 %	8,740	7.3 %	11,600
EMEA	5,950	4.4 %	6,210	4.1 %	6,462	2.9 %	7,250
Asia Pacific	2,845	5.8 %	3,009	7.5 %	3,235	5.8 %	4,050
Total	**21,466**	**4.0 %**	**22,334**	**4.6 %**	**23,356**	**5.2 %**	**28,625**

Figure 1.5. *The projection of worldwide PU production related to region between 2014-2020 (in kt)*

(Austin et al, 2017, p. 4)

1.3. Rigid Polyurethane Foam

Rigid polyurethane foams were first used in Germany for aircrafts and tanks because of their weight and strength advantage. Nowadays, RPUFs are one of the most widely used materials in all polymer groups. The main usage area of rigid polyurethane foams is insulation.

Polyurethanes are urethane linkage groups that occurs from reactions between alcohols with two or more reactive hydroxyl groups (OH) such as diols, triols or polyols and isocyanate functional group (NCO). (Ashida, 2007, p.1) General emprical formula structure of polyurethane is shown in Figure 1.6. (Ionescu, 2016, p. 1)

$$\left[\text{OCONH} - \text{R} - \text{NHCOO} - \text{R}' \right]_n$$

Figure 1.6. *Emprical formula structure of polyurethane (Ionescu, 2016, p. 1)*

There are many methods to form urethane groups.All of these methods, reaction between hydroxyl group of polyol (alcohol group) and isocyanate functional group is the most used and important method. Urethane reaction between isocyanate group and hydroxyl group is shown in Figure 1.7. (Ionescu, 2016, p. 1)

$$\underset{\text{Isocyanate}}{\text{R}-\text{N}{=}\text{C}{=}\text{O}} + \underset{\text{Alcohol}}{\text{HO}-\text{R}'} \longrightarrow \underset{\text{Urethane}}{\text{R}-\text{NHCOO}-\text{R}'}$$

Figure 1.7. *Urethane reaction between isocyanate group and hydroxyl group (Ionescu, 2016, p. 1)*

The combination of different processes forms RPUFs and its expandable structure. Besides main reactants, defined catalyst, surfanct and blowing agents are used to manufacture RPUF that has desired propreties The first process is mixing of reactants and then polymerization reaction occurs between these reactans which are OH groups of polyol as an alcohol group and isocyanate functional group. With the onset of the polymerization reaction, blowing agents provides expansion that results foam.

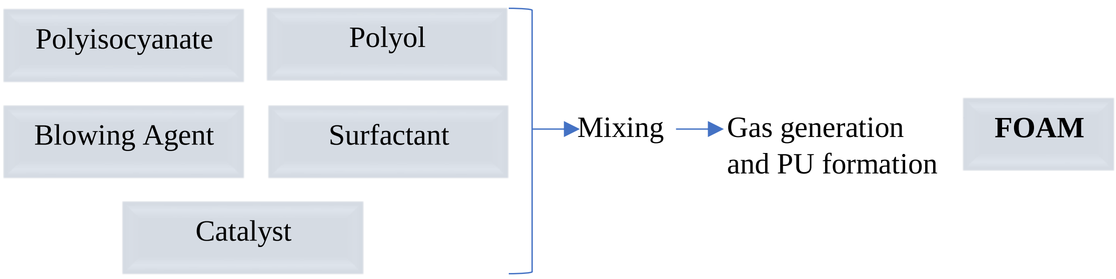


Figure 1.8. *Process of polyurethane foam manufacturing (Landrock, 1995, p. 41)*

As it is shown in Figure 1.8., polyurethane foaming process occurs variety of materials and depending on the type of all of these materials, different desired of foams could be obtained.

1.3.1. Polyols

Polyol compounds are alcohol compounds that have two or more hydroxyl groups. The reaction between hydroxyl groups of polyol and isocynate groups is the main reaction that involved polyurethane synthesis reaction. Generally, molecular weight of polyols that are used for polyurethane production is between 400-5000 Da. Chain length of alcohol groups changes molecular weight of the polyol and depending on the molecular weight of the polyol, properties of polyurethane product could be changed. Hard plastic materials could be obtained with polyols that have low molecular weight and flexible materials could be obtained with polyols that have high molecular weight.

Hydroxyl groups of polyols that are used for processes commercial polyurethane products can be obtained with polyethers, polyesters, and oils that have naturally hydroxyl groups. Polyethers are the most used to process rigid polyurethane foams. Figure 1.9.shows difference between structure of polyester and polyether. Figure 1.10. shows Worldwide production of polyether and polyester polyols that used to manufacture polyurethane between 2004 and 2014.

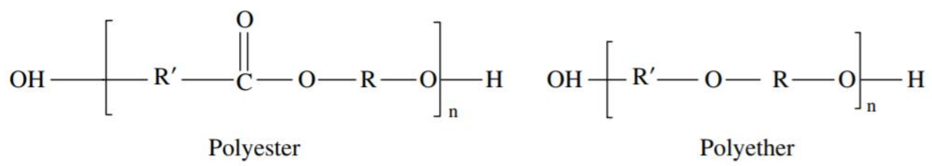


Figure 1.9. *Chemical sturctures of polyester and polyether (Sonnenschein, 2014, p.4)*

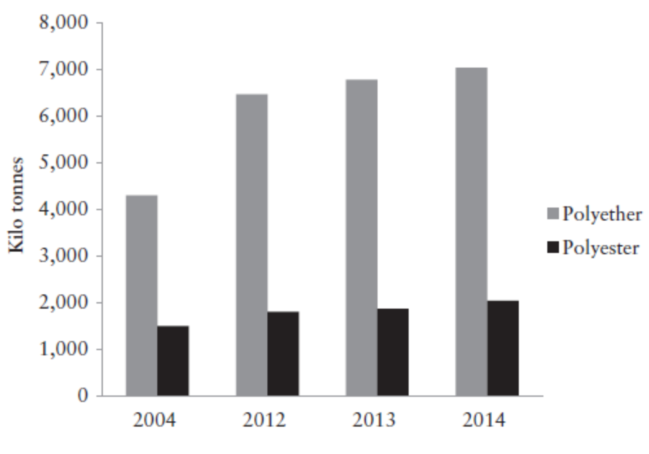


Figure 1.10. *Worldwide production of polyether and polyester polyols for PU in 2004-2014*

(Ionescu, 2016, p. 4)

The physical properties of end product which is RPUF are mainly effected by properties of polyol. Rigidity-flexibility properties, stifness and gas-moisture permeability of the rigid foam are examples of these properties that are depending on the properties of polyol. RPUFs are manufactured with lower molecular weight and highly branched resins. More flexible and softer foams that resist to hydrolysis can be obtained with polyols that based on polyethers. Foams that have better tensile strength and better oil and oxidation resistance can be obtained with polyols that based on polyesters.(Szycher, 2013, p. 267-269)

Low molecular weight polyols (150-1000 Da) with high functional hydroxyl group (3-9 OH groups/mol) are used to produce rigid polyurethane structure. Reaction between these high functionality polyol and diisocyanates or polyisocyantes (2-3 NCO groups/mol) provides rigid polyurethane. High crosslinked structure occurs thanks to these reaction and high crosslink density provides rigidity. Figure 1.1. shows Crosslinked structure of RPUFs (Ionescu, 2016, p. 4).

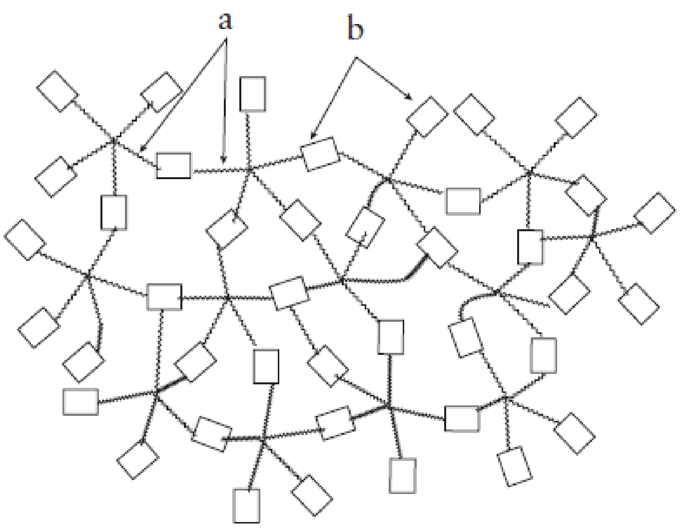


Figure 1.11. *Crosslinked structure of RPUFs. (a) Polymer chain that occurs from one hdyroxyl group (b) urethane occurs from isocyanate (Ionescu, 2016, p. 9)*

1.3.2. Isocyanates

Isocyanates are the one of the most important reactants in polyurethane chemistry. Isocyanate chemistry dates back to 1848 with the studies of Wurtz on aliphatic isocyanates. According to studies of Wurtz, reaction of the functional group of isocyanate with a primary alcohol and a secondary amine provides formation of urethanes (Szycher, 2013, p.93). Reaction of aliphatic isocyanates with OH groups in alcohol structure is slow Because of requirement of high reactivity for foaming reaction, aliphatic isocyanates could not be used for foaming reactions. In 1950, aromatic isocyanates are synthesised by Hoffmann with the pyrolysis of diphenyloxamide. That provides preparation of isocyanate based foams (Ashaida, 2006, p. 14).

Polymerization and structure of polyurethane are directly related with isocyanate and its reactions. Reactions with active hydrogens are the most regard with isocyanate reactions such as reaction with alcohol, amine groups or water molecules. Polyurethane gains a wide range of application area thanks to high reactivity and versatility of isocyanates and its types. Figure 1.12. shows the basic chemical structure of isocyanate.

Figure 1.12. *The basic chemical structure of isocyanate (Sonnenschein, 2014, p.62)*

Monomers that are involved in addition polymerization reaction must sustain polymer chain with multiple reactions. Because of that reason, there should be two or more isocyanate functional group in the structure of isocyanate. Polymerizable isocyanate monomers with low production cost provides improvement in polyurethane technology. The most commonly used isocyanates are toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) and polymethylene polyphenyl diisocyanate (pMDI) in polyurethane industry. Figure 1.13. shows chemical structures of TDI and Figure 1.14. shows chemical structures of MDI and pMDI. (Sonnenchein, 2014, p.62)

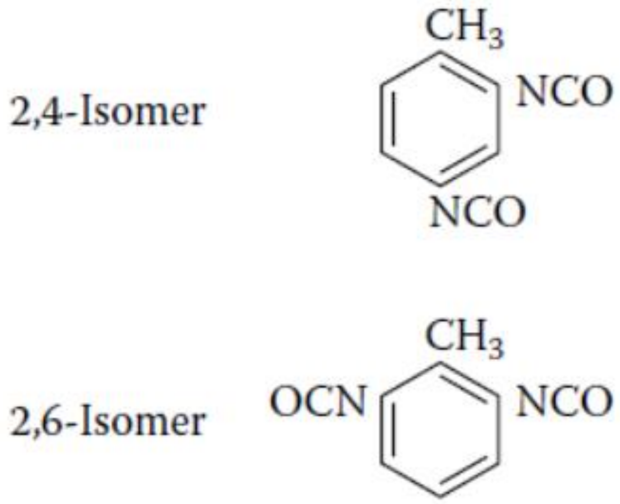


Figure 1.13. *Chemical structures of TDI (Ashaida, 2006, p. 14)*

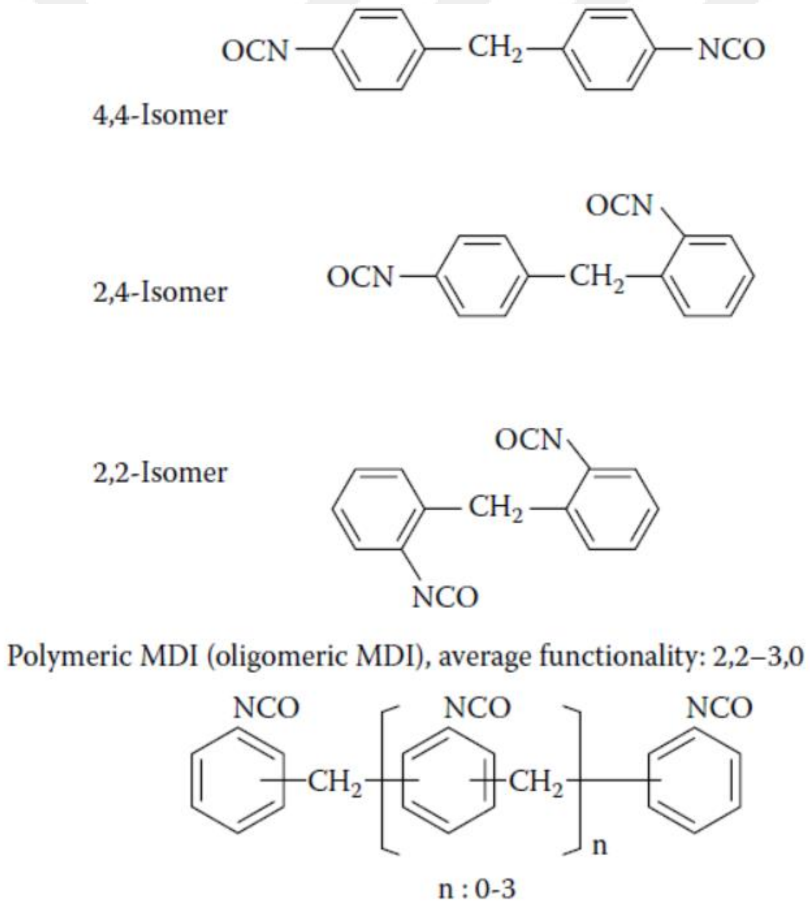


Figure 1.14. *Chemical structures of MDI(Ashaida, 2006, p. 15)*

1.3.3. Blowing agents

The mandatory process for polyurethane foam preparation is gas generation. There are two methods for blowing:chemical gas generation and physical gas generation. (Ashaida, 2006, p. 24). Also, combanation of these two methods can be used for gas generation process.

When chemical blowing agents are used as blowing materials; a chemical reaction occurs between blowing agent and isocyanate groups and carbon dioxide gas is the result of that reaction. Before usage of halocarbons as the blowing agents in 1958, the foaming process was carried out with carbon dioxide that resulted gas reaction between water and isocyanate groups. The use of halocarbons as blowing agents contributed greatly to the development of rigid polyurethane foams (Szycher, 2013, p. 282). Reaction between isocyanate group and water is shown in Figure 1.15.

$$2\,R{-}NCO + H_2O \longrightarrow CO_2\uparrow + R{-}NH{-}CO{-}NH{-}R$$

Figure 1.15. *Reaction between isocyanate and water. (Ashaida, 2006, p. 24)*

Blowing agent which used to form a foam strongly effects on properties of RPUFs. Because of that reason, selection of blowing agent should be made taking into consideration some of the properties that effects on last product. These properties are boiling point, molecular weight, reactivitiy, heat of vaporization, solubility, thermal conductivity coefficient and compatibility with the other materials that are used to prepare the foam (Singh, 2001, p. 7).

There are some other aspects of this selection from manufacturer's side. First of all, some of the blowing agents have affects on global environment and ozone depleting. Because of that reason, the use of blowing agents is regulated by strict regulations. The firms that use blowing agents and blowing agent manufacturers must meet these regulations. Table 1.1. shows RPUF blowing agents and properties, some of them are banned due to regulations. Second, the production cost of the blowing agent is one of the important issue for manufacturers. Also, because of directly effect on the properties of the last product, quality criteria are important factors in the selection of blowing agents.

Table 1.1. *Blowing agents which used to prepare RPUF (Sonnenschein, 2014, p. 282)*

Blowing agent	Chemical Formula	Molecular weight g/mol	Boiling point (°C)	*K*-factor (mW/mK)	ODP	GWP
CFC-11	Cl_3CF	137.5	23.8	7.9	1.0	3400
HCFC-123	$C_2HCl_2F_3$	152.9	27.9	9.5	0.02	93
HCFC-141b	CH_3-CCl_2F	116.9	32	8.7	0.11	610
HCFC-142b	CH_3-CF_2Cl	100.5	–9.8	11.6	0.065	1600
HCFC-134a	$C_2H_2F_4$	102	–26.5	14.5	0	1320
HFC-245fa	$CHF_2CH_2CF_3$	134	15	12.4	0	1020
HFC-365mfc	$C4H_5F_5$ (1,1,1,3,3 pentafluorobutane)	148	40	10.5	0	782
FEA-1100	1,1,1,3,3,3 hexafluoro 2-3 butene	164	33	10.7	0	9
Carbon dioxide	CO_2	44	–78	16.5	0	1.0
Air	N_2/O_2	28.8	–192	29	0	0
n-pentane	C_5H_{12}	72	36	14.8	0	20
Iso-pentane	C_5H_{12}	72	28	14	0	11
Cyclopentane	C_5H_{10}	70	50	12.9	0	10

ODP means relative ozone depletion potential, and GWP means relative global warming potential.

1.3.4. Catalysts

Catalysts are the materials which increase rate of chemical reaction and not react with any substances during reaction. In RPUF systems, catalysts play an important role. Catalysts provide balance the reaction kinetics between the chain extension and foaming If the reaction rate is not enough, there will be no gas trapping and because of that reason polyurethane foam will not occur. On the other side, polymer will occur before gas formation and density of the polyurethane foam will be high in the case of the reaction rate is too fast.

Depending on the type of polyurethane product, the catalyst used in the process varies. Generally, two main classes are chosen as catalysts: tertiary amines and metal salts, in general tin. The tertiary nitrogen give electrons to the carbonyl of the isocyanate group, and thanks to amine catalysts, the rates of both blowing and gelling reaction increase. Activity of metal salt catalysts are higher than amine catalysts and they reacts with hydroxyl group of the isocyanate and increase the rate of gelling reaction.

To provide balance of blowing and gelation, generally tertiary amine and metal salt catalysts are combined (Zhang, 1998, p. 31) (Aneja A., 2002, p.40). For example, the desired reaction rate is relatively highet in spray applications. Because of that reason, generally tin salts or tin salts and tertiary amines combination are used to foam rapid (Szycher, 2013, p. 278)

1.3.5. Surfactants

Surfactants are one of the important materials for polyurethane foam process. They can be called foam stabilizers. Surfactants provide thermodynamically stable state under increasing surface forces while polyurethane foam is hardening. There are two mechanism for stabilization. One of them is that surfactants decrease the surface tension and the other one is emulsification.

Activity of the surfactants' surface and surfactant-polymer compatibility are the factors that determine the performans of the surfactant. A monolayer is occurred by surfactant at the interface. Because of higher viscosity of that layer, foam bubbles are stabilized thanks to increasing surface elasticity. If the surface activity of foam stabilizer is higher, monolayer expands more. Thus, surface tension decreases.

Chemical properties of the surfactant directly effect the properties of polyurethane foam especially cell structure.The factors considered in the selection of surfactants are high surface activity and good emulsifier compatible with raw materials. Commonly, silicone based surfactants are used for polyurethane foam process. Figure 1.16 shows chemical structure of the polysiloxane. Polysiloxane provides surface activity because of its chain length. Higher chain lengths provides higher surface activity. However, polysiloxane part of the surfactant is not compatible with the bulk of polymer raw material. Because of these incompatibility problem, emulsification is provided with polyether segments of the surfactant. The moiety of polysiloxane and polyether segments should be optimized to obtain the best surface activity and emulsification (Szycher, 2013, p. 309).

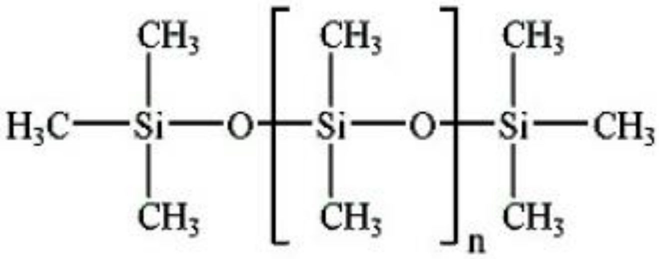


Figure 1.16. *Chemical structure of the polysiloxane*

1.4. Process of Rigid Polyurethane Preparation

The formation of isocyanate-based foams occurs by a combination of two steps: polymer formation and gas generation. Isocyanate and a mixing that includes polyol, catayst, surfactant are mixed to prepare the foam at room temperature. There are three classification of foaming systems: one-shot system, the quasi-prepolymer system, and the full prepolymer system. Today, one-shot system and the quasi-prepolymer system are used to manufacture polyurethane foam. Major process to manufacture flexible and rigid polyurethane foam is one-shot system. The full prepolymer system is rarely used in today's technology. Figure 1.17 shows foaming systems.

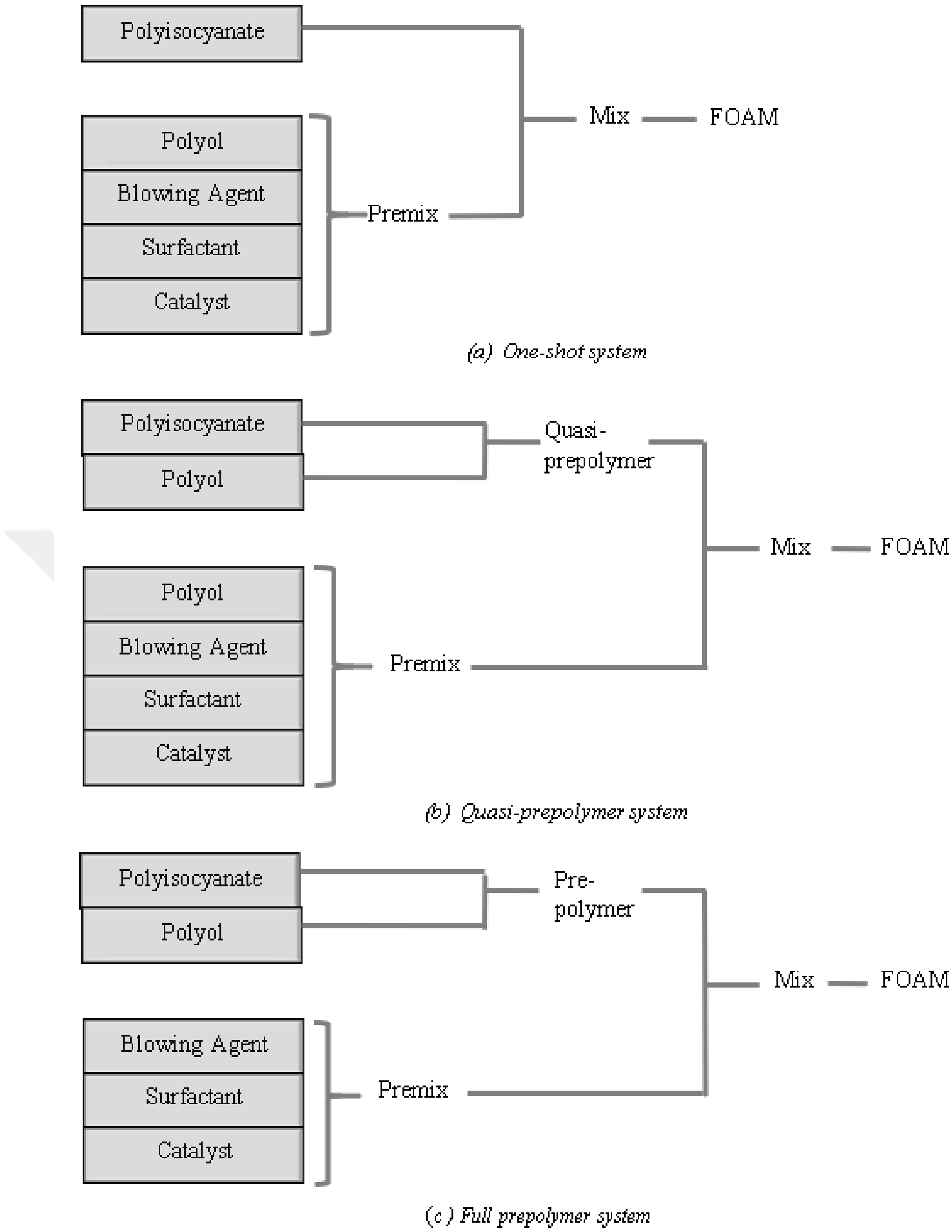
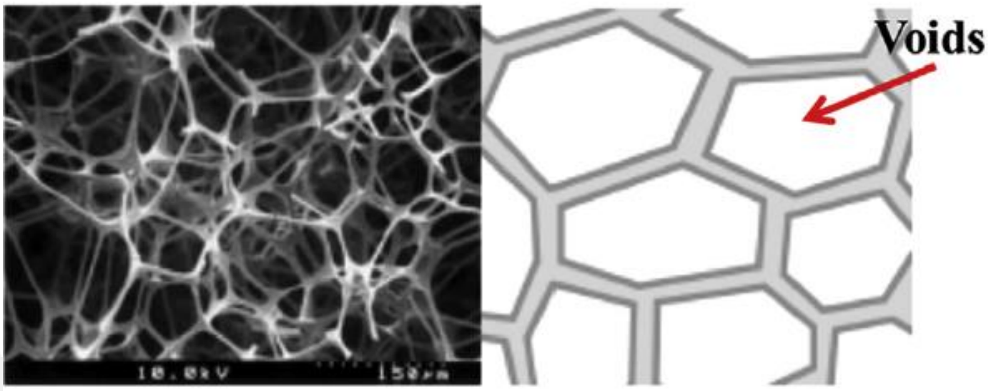


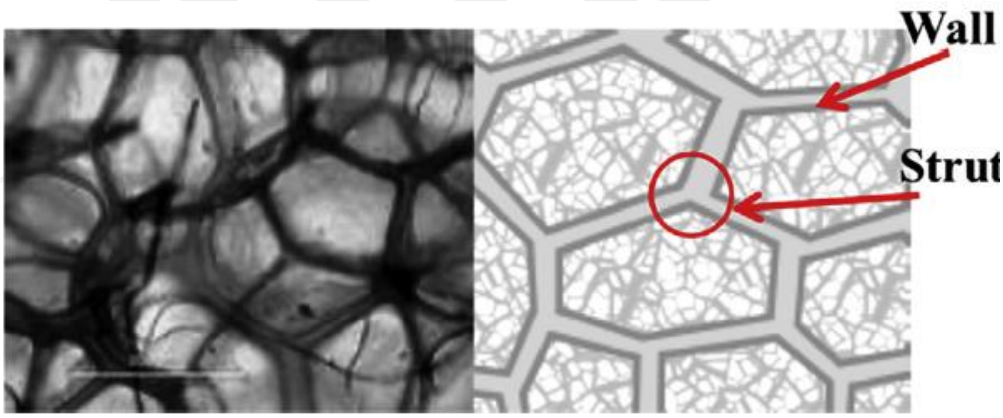
Figure 1.17. *Polyurethane foaming systems (Landrock, 1995, p. 44)*

The structure of polyurethane foams occurs cells. These cells includes flat faces and straight edges, and they basically called struts and walls. Morphology of the foam can be open cell morphology or closed cell morphology. Cells connects each other with continuous spaces in open cell morphology. In contrast, cells are isolated from each other in closed cell morphology.

The morphology of the foam is effected by many factors: materials that take place in foaming reaction (polyol, isocyanate, catalyst, surfactant), chemical structure of reactants (hydroxyl number of polyol, NCO index of isocyanate), reaction temperature, viscosity, additives etc. Figure 1.18 shows open and close cell structures.



(a)



(b)

Figure 1.18. *SEM images of the open and closed cells and their schematic representations. (a) SEM image of a open cell structure flexible foam (left) (http-5) and schematic representation (Verdolotti et al, 2017, p.280) (b) SEM image of a closed cell structure rigid foam (right) (http-6) and schematic representation (Verdolotti et al, 2017, p.280)*

In addition to all these effects, the foaming process must be controlled very well. The steps of the foaming process:

- Polymerization reaction
- Nucleation of the bubbles and formation of cells
- Cell growth

1.4.1. Polymerization reaction

There are two classification of polymers according to polymerization reaction: Addition type and condensation type polymers. Also, if polymers are classified according to kinetics of polymerization, there are two classifications: Chain-addition polymers and step-addition polymers. During chain polymerization, high polymer occurs very early, and polymerization continues on those chains which are the active propagating center. On the contrary, reaction occurs all species present in the step addition polymerization. High polymer occurs late steps of the polymerization reaction. Ionic polymerization proceeds near linearly. Generally, polyurethane polymerization reactions are step addition reactions. Figure 1.19. shows avarage molecular weight fraction graphic chain addition reaction and step addition reaction.

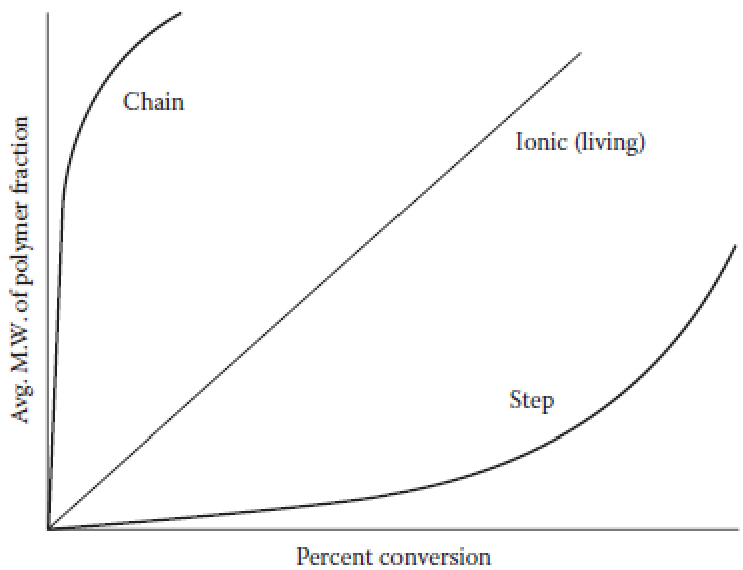


Figure 1.19. *Chain addition versus step addition polymerization (Szycher, 2013, p. 16)*

Properties of polyurethane polymerization can be summarized as:

- Polymer formation propagates with a single reaction.
- Monomers can contains few functional groups and all functional groups can react with other groups randomly.
- Early step of the polymerization reaction, monomers disappear.
- In contrast chain polymerization, avarage molecular weight does not increase fast. Late step of the polymerization, high polymer is obtained.
- Stoichiometric ratios should be precise.

• Monomers should be high purity. (Szycher, 2013, p. 17)

Urethane groups forms the three dimensional molecular network during polymerization reaction. This reaction starts from polyol with isocyanate in presence of catalysts and surfactants. (Verdolotti et al, 2017, p.277)The reaction between polyol and isocyanate is shown in Figure 1.20. Also, Figure 1.21. shows the three dimensional molecular network of the polyurethane polymers.

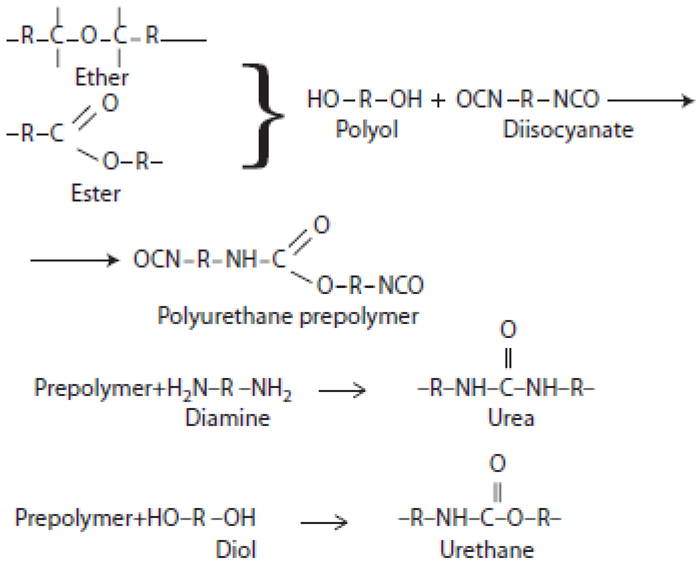


Figure 1.20. *Polyurethane forming reaction (Szycher, 2013, p. 19)*

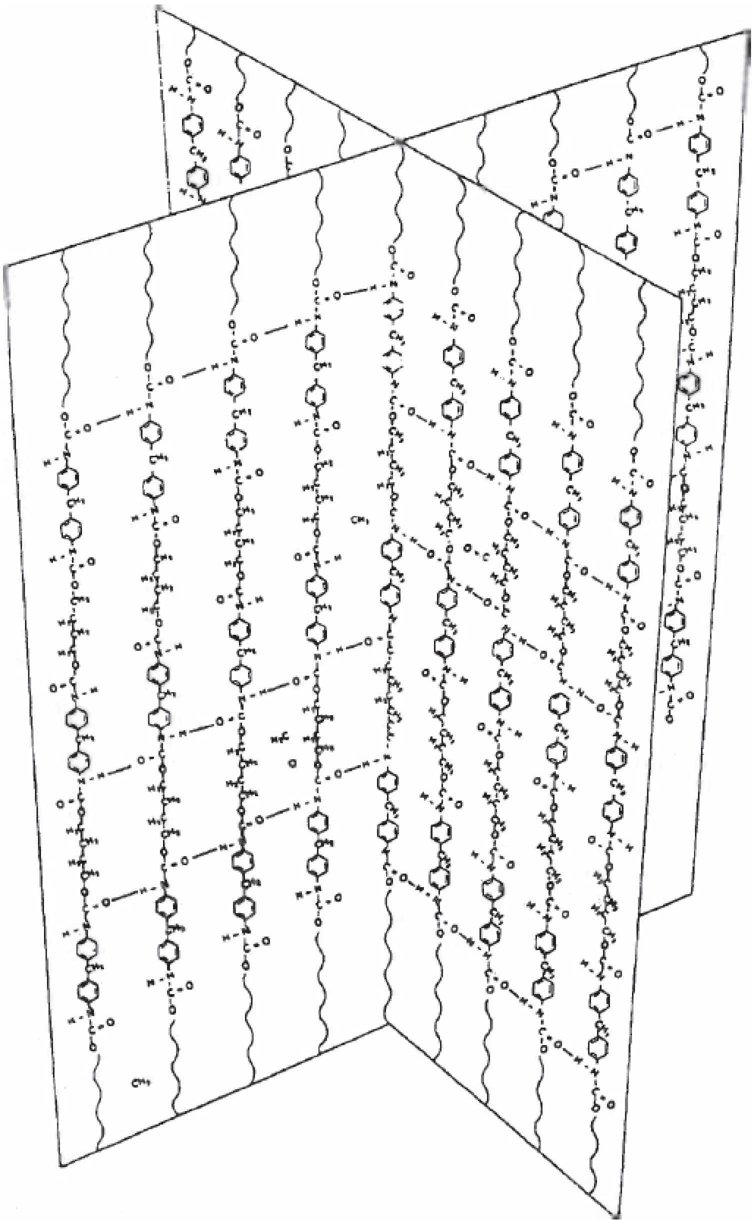


Figure 1.21. *Three dimensional network structure of the polyurethane polymers. (Szycher, 2013, p. 39)*

1.4.2. Nucleation of the bubbles & cell growth

The expansion process beside polymerization reaction provides porous structure of the polyurethane foam. This process can be achieved by chemically or physically with blowing agents. In the case of physical expansion, a blowing agent that has low boiling point is dissolved into polyol. Polymerization of the polyurethane foam is an exothermic reaction and temperature increases as a result of that reaction. With the rising temperature, the blowing agent passes to gaseous phase and bubbles are formed. At the end of the blowing, porous sturcture of the polyurethane foam is obtained. In the case of chemical expansion, water is used as a chemical blowing agent. Water molecules react with isocyanate. Carbamic acid occurs as a result of the reaction between water and isocyanate. This carbamic acid is thermodynamically unstable. Then, it decomposes amine and carbondioxide. Figure 1.22. shows decomposition of isocyanate to carbamic acide and amine. (Verdolotti et al, 2017, p.279)

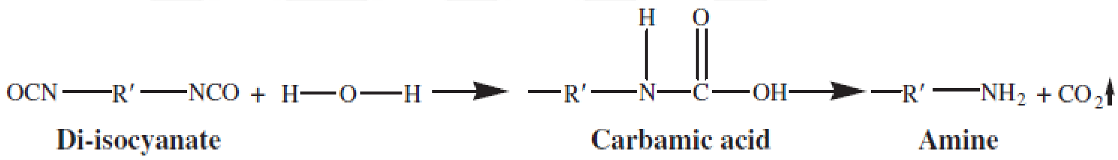


Figure 1.22. *Decomposition of isocyanate to carbamic acid and then amine*

The expansion process takes place in four steps:

- Gas formation
- Nucleation of cells and bubble formation
- Bubble growth
- Bubble stabilization

Gas bubbles occurs from phase transition of low boiling point blowing agent or carbon dioxide that occurs from carbamic acide as a result of the reaction between isocyanate and water. Nucleated gas bubbles grow with the effect of two factors: First, blowing gas expends. Second, additional gas molecules diffusesf from neighboring polymeric phases into the cells. That diffusion propagates expansion. Then, with the expansion of gas bubbles, spherical cells starts to growth. After a while, they are densely packed during polymerization process and conctact each other.

At the end of the process, cell formation is completed and porous structure occurs. These steps are shown in Figure 1.23.

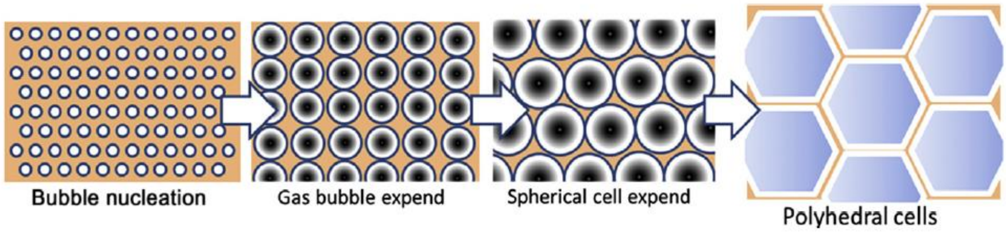


Figure 1.23. *Nucleation, growth and stabilization steps*

There are two nucleation type of bubble formation: Homogeneous nucleation and heterogeneous nucleation. In the case of homogeneous nucleation, the driving force is thermodynamically unstable system.Polymerization reaction is a exothermic reaction. During reaction, the temperature of system increases. A supersaturated solution occurs when the partial pressure of carbon dioxide or blowing agent in gaseous phase is greater than total pressure. That situation results simultaneously nucleation. After nucleation starts, foaming continues for the stable nuclei. Generally, homogeneous nucleation results broad cell size distribution because of simultaneous cell growth. In the case of heteregenous nucleation, particles in polymer matrix occurs surfaces for cell growth. These nucleation that begins from a surface provides narrow cell size distribution.

The two parameters of the nucleation are the critical radius r_{cr} and Gibb's Free Energy of the system ΔG. According to nucleation theory, simultaneously growth only achieved if nuclei radius is greater than $r_{cr.}$ If nuclei radius cannot exceed $r_{cr,}$ nuclei disseppears in the polymer matrix. The tendency is always to achieve minimal Gibbs Free Energy. The formulation of Gibb's Free Energy is below:

$$\Delta G = \frac{-4\pi r^3 \Delta P}{3} + 4\pi r^2 \gamma \quad (1.1)$$

In Gibb's Free Energy equation, r is cell radius, γ is surface tension, ΔP is supersaturation level. If radius of nuclei is equal to critical radius $r_{cr,}$ Gibb's Free Energy is maximumum. The tendency of all systems are minimize the free energy. Because of that reason, if there is any cells that have radius less than critical radius, they dissappear. Besides, cells that have radius greater than critical radius growth.

Critical radius is calculated by equation below when the derivative of the free energy.

$$r_{cr}=\frac{2\gamma}{\Delta P} \tag{1.2}$$

In nucleation occurs homogeneously, nuclei grows when the nuclei radius exceeds critical radius with energy barrier formulation below: (Verdolotti et al, 2017, p.283-284)

$$\Delta G_{hom} = \frac{16\pi\gamma^3}{\Delta P^2} \tag{1.3}$$

Figure 1.24. shows free energy barriers that must be exceed for homogeneous and heterogeneous nucleation and process differences by time between these two type nucleation shows schematically in Figure 1.21.

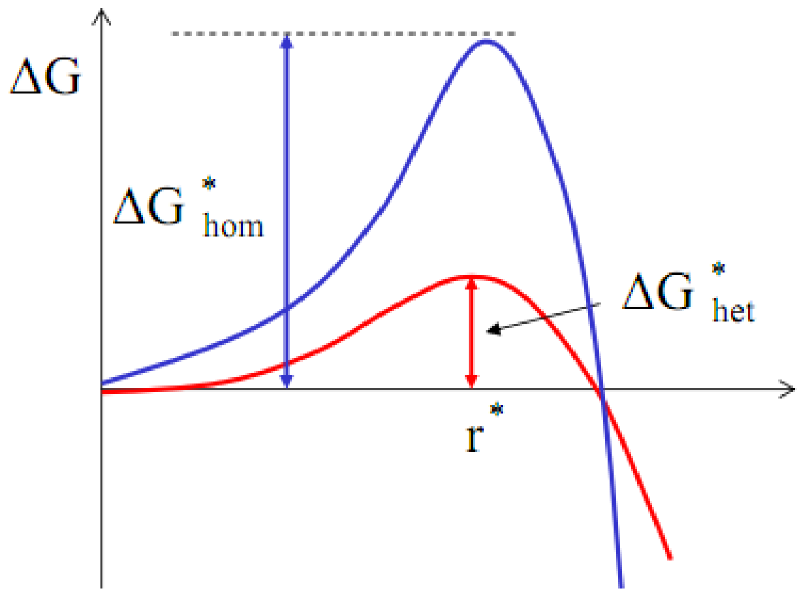


Figure 1.24. *Free energy barriers for homogeneous and heterogeneous nucleation. (http-5)*

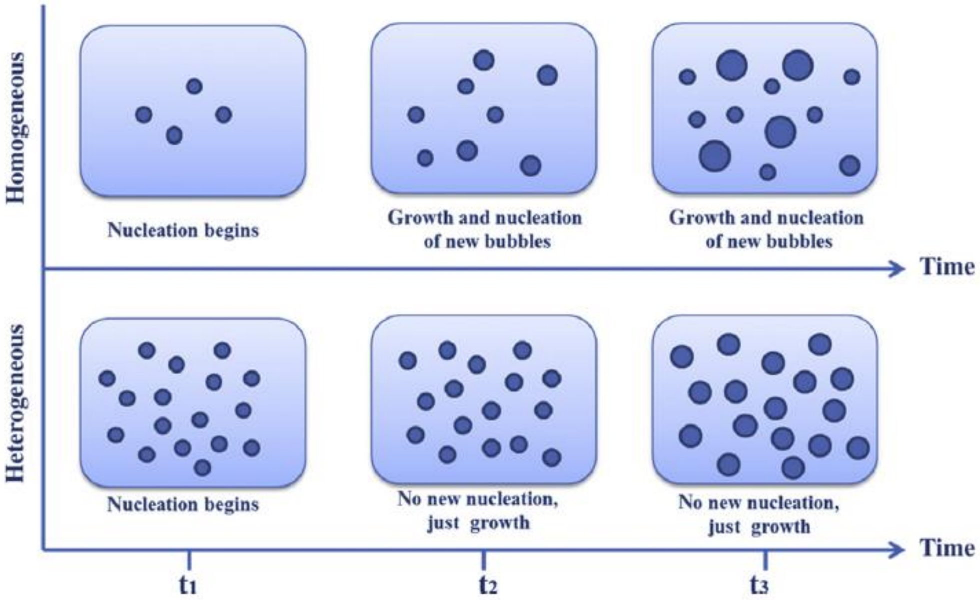


Figure 1.25. *Process of homogeneous and heterogeneous nucleation by time.*

(Verdolotti et al, 2017, p.284)

1.5. Thermal Conductivity of Rigid Polyurethane Foams

Energy efficiency one of the most important issues in today’s world. Because of that reason, researches on materials that are more thermally efficient become more important. Domestic appliances are the major electric energy consumers in houses, and decreasing energy consumption of these devices not only a financial issue but also environmental issue. To provide thermal insulation, rigid polyurethane foams are used for refrigerators. The reason for that is lower thermal conducticity coefficient. of RPUFs. Figure 1.26. shows comparison of reqiured thickness of some insulation materials to provide same thermal insulation. Rigid polyurethane foam provides same thermal insulation properties with lowest thickness than other insulation materials.

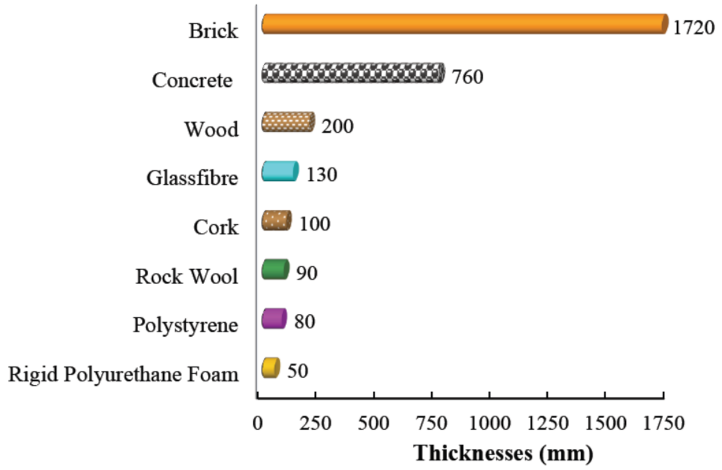


Figure 1.26. *Comparison of required thickness of some insulation materials to provide same thermal insulation properties. (Lee and Ramesh, 2004, p. 262)*

The concept of energy is used to determine the position of a system in thermodynamics. As it is known, energy cannot be created from nothing or cannot be destroyed when it exists, but it can change from one form to another. While the science of thermodynamics deals with the forms of heat and energy, the science of heat transfer deals with inter-system or system / ambient heat transitions. The energy transfer by the heat flow is not directly measured but makes sense when it is associated with a measurable magnitude of temperature. Since there is a heat flow when a temperature difference occurs in the system, it is important to know the temperature distribution of the system. When the temperature distribution is known, the heat flux per unit area per unit time can be calculated.

Thermal conductivity is provided with 3 mechanism in porous media of rigid polyurethane foam.

(a) Conduction
(b) Convection
(c) Radiation

Heat conduction is the heat transfer from a hot zone in a solid material or inert fluid to a cooler zone. If there are temperature differences in a solid object, the heat is transferred from the high temperature zone to the low temperature zone

Heat transfer with conduction is determined by Fourier law based on experimental observations. According to Fourier's law, the amount of heat passing in any direction (for example x direction) is proportional to the temperature gradient in the x direction (amount of temperature change) dT / dx and area A perpendicular to the heat transfer direction. The mathematical expression of Fourier's Law;

$$Q_x = -\lambda \frac{dT}{dX} \tag{1.4}$$

Qx is the amount of heat passing through the area A in the x direction and perpendicular to this x direction. The proportionality constant λ is called the thermal conductivity and is a property of the material. The unit of λ is J/msK or W/mK. The sign (-) in equation (1) determines the direction of heat transfer. (Sözbir, 2014, p. 1)

Heat transfer within RPUF dominates three heat transfer mechanism:

(a) Heat transfer in solid phase: Struts and cell walls
(b) Heat transfer in gas phase within the cells: Blowing agent
(c) Radiation

$$\lambda_f = \lambda_m + \lambda_g + \lambda_r \tag{1.5}$$

λ_f: Total thermal conductivity of rigid polyurethane foam

λ_m:Thermal conductivity of the matrix

λ_g:Thermal conductivity of the gas within the foam cells

λ_r:Thermal conductivity with radiation

Heat transfer mechanism in RPUF structure is shown in Figure 1.27.

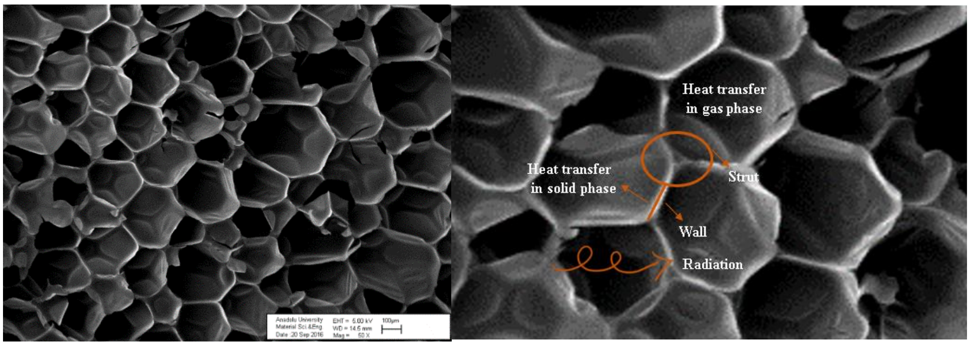


Figure 1.27. *Heat transfer mechanisms in rigid polyurethane foam structure*

1.5.1. Heat transfer in solid phase

Heat transfer in solid phase depends on thermal conductivity of the nonporous solid phase and the strut fraction f_s. The formulation for the thermal conductivity of the matrix:

$$\lambda_m = \lambda_s \frac{(1-\Pi)}{3} [f_s(\frac{a}{b})^{1/2} + 2(1 - f_s)(\frac{a}{b})^{1/4}] \tag{1.6}$$

a and b are the cell diameters that are perpendicular and parallel to the direction of the heat transfer, Π is the porosity, λ_s=205×10-3 W/(mK) (Kabakci, 2015, p.18)

The strut fraction is calculated by Glicksmann formula:

$$f_s = 1 - (\frac{3.46t\rho_s}{d\rho_f}) \tag{1.7}$$

t is the thickness of the cell wall, d is the cell diameter, $p_s = 1200\ kgm^{-3}$ which is polymer density andρ_f is the density of the foam.

1.5.2. Heat transfer in gas phase

Physical and chemical blowing agents are used to preapre rigid polyurethane foams. The thermal conductivity of the blowing agents effect on the thermal conductivity of the RPUF. Because of that reason, it is important to select of low thermal conductive blowing agent.CFCs and HCFCs have lower thermal conductivity coefficient than other physical blowing agents, but they are hazardous to ozone layer and have an huge affect on global warming. Now, hydroflorocarbons (HFCs) and hydrocarbons (HCs) such as pentane, isobutane etc. are used as blowing agents. Table 1.2. shows blowing agents and their properties.

Table 1.2. *Blowing agents and their properties (Lee et al., 2004, p. 275)*

Compound	Molecular Formula	Molecular Weight (g/mol)	λgas @25°C mW/mK	Boiling Point (°C)	Vapor Pressure 20°C (bars)	Flammability Limits (% vol. in air)	Indicative Price $/lb	ODP	GWP 100 yr ITH	HGWP	POCP or SFP	Atmosph. lifetime (yrs)	Phase-out target
CFC-11	$C\text{-}Cl_3F$	137.5	7.8	24	0.88	none	n.a.	1.0	4000	1.0	<0.1	50–60	1995
HCFC-141b	$CH_3C\text{-}Cl_2F$	116.9	9.8	32	0.69	5.6–17.6	~0.9–1.0	0.11	630	0.12	10	8–10	2003
HCFC-22	CHClF2	86.5	11.2	–41	8.92	none	~1.0	0.05	1700	0.35	6	13–15	2010
HCFC-142b	$CH_3C\text{-}ClF_2$	100.5	9.8	–10	2.50	6.7–14.9	~1.0	0.06	2000	0.36	5	19–20	2010
HCFC-124	$CHClFCF_3$	136.5	12.3	–11	3.27	none	~2.0	0.02	480	0.10	12	5-6	2020
HFC-125	CHF_2CF_3	120	14.0	–48	12.41	none	~2.5–3.0	0	2800	0.58	1	32–35	none
HFC-134	CHF_2CHF_2	102	14.1	–23	4.53	none	~1.8–2.0	0	1000	0.20	8	10–12	none
HFC-134a	CH_2FCF_3	102	14.3	–26	5.62	none	~1.5–1.8	0	1300	0.26	6	14-16	none
HFC-152a	CH_3CHF_2	66	13.8	–25	5.06	3.9–16.9	~2.0–2.5	0	140	0.03	14	1.5–2	none
HFC-245 fa	$CHF_2CH_2CF_3$	134	12.2	15	1.24	8.9–11.2	~3.0–4.0	0	820	0.18	11	7–10	none
HFC-365 mfc	$CH_3CF_2CH_2CF_3$	148	10.6	40	0.47	3.5–9.0	~3.0–4.0	0	840	0.18	7	9–12	none
n-Pentane	C_5H_{12}	72	14.6	36	0.65	1.4–8.3	~0.25	0	11	0.002	500	0.03	none
Iso-Pentane	C_5H_{12}	72	13.8	28	0.80	1.4–7.6	~0.25	0	11	0.002	500	0.03	none
Cyclo-Pentane	C_5H_{10}	70	12.6	50	0.34	1.4–7.8	~0.75	0	11	0.002	400	0.05	none
Iso-Butane	C_4H_{10}	58	15.9	–12	2.99	1.8–8.4	~0.3	0	5	0.001	650	0.02	none
n-Butane	C_4H_{10}	58	15.3	–1	2.08	1.6–8.4	~0.3	0	5	0.001	650	0.02	none
Carbon dioxide	CO_2	44	16.3	–78	56.55	none	n.a.	0	1.0	1.10-4	0	120–200	none
Air	N_2/O_2	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)

To understand the heat transfer in a foam, it is necessary to relate the foam morphology to the physical properties, polymer thermal conductivity, and gas conductivity. The walls are generally thinner than the columns and the cell diameter is greater than the column thickness. Complex foam geometry should be considered in the light of the interaction of solid and gas transmission with each other. Previous literature studies have created very simple models for foam geometry to achieve an approximate or complete solution in transfer.

The amount of blowing gas remaining in the cells affects the insulation property of the polyurethane foam. The blowing gas is replaced by air after a while and the air has higher thermal conductivity than most blowing gases. For polyurethane foam with a thickness of 5 cm, this process can take place within a few years. For longer periods, the blowing gas will diffuse out of the foam, the air concentration in the cells will increase and consequently the thermal conductivity will increase. Decreasing in insulation property of the RPUF is called as aging.

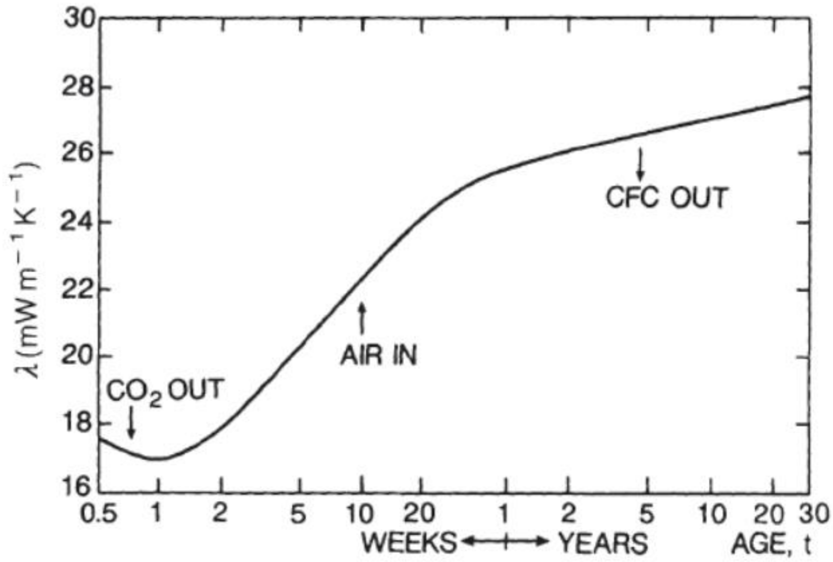


Figure 1.28. *Typical aging curve and gas change in polyurethane foam*

(Hoogendoorn C.J., 1994, p. 154)

1.5.3. Heat transfer with radiation

20-30% of total heat transfer in polyurethane foams occurs by radiation. According to Ball et.al study, heat transfer with radiation is proved with linear variation of cell size and heat transfer with conduction and convection in solid and gas phase should not be depend on cell size of the polyurethane foam. To calculate the percantage of heat transfer with the radiation, a modelling was worked about radition in cells. In that modelling, planes that are not transparent and same size with each other were used. According to Rosseland equation, consider these planes at T and $T + \Delta T$. These planes are shown in Figure 1.25. Because of the sheets are not transparent for light, the heat transfer with radiation can be expressed as;

$$q_r = \sigma T^4 - [\sigma T^4 + \Delta(\sigma T^4)] = -\Delta(\sigma T^4) \quad (1.8)$$

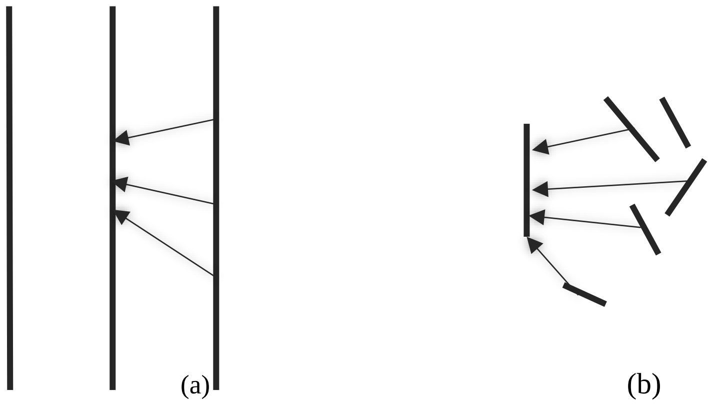


Figure 1.29. *Schematically expression of planes that considered as foam cells (a) idealized alignment (b) random alignment (Hoogendoorn, 1994, p.123)*

Figure 1.29. (a) is a schematically representation of idealized cell alignment. In real world, it is commonly looks like in Figure 1.29. (b) during heat transfer with radiation. There are solid particles that absorbing, emmiting and scattering the radiant energy.

Foam permeability measurements show the average distance between radiation emission and absorption of a foam as 1 mm or less. Since the average distance is much less than the thickness of a foam sheet, radiation heat transfer can be considered as a diffusion process. (Glicksman, p.153)

$$q_r = -\Delta(\sigma T^4) = -\frac{d(\sigma T^4)}{dx} l \tag{1.9.}$$

Every point in the rigid polyurethane foam absorbs, emits and scatters the radiant energy from different distances. The avarage distances is called as mean free path which is shown with "l" in the Equation 1.9.

$$q_r = -\frac{d((\sigma T^4)}{dx} = -\frac{d((\sigma T^4)}{Kdx} \tag{1.10}$$

In case of any radiation in the foam, the equation becomes:

$$q_r = -\frac{4d(\sigma T^4)}{3Kdx} = -\frac{16}{3K}\sigma T^3 \frac{dT}{dx} \tag{1.11}$$

And the expression for radiation heat transfer in total heat transfer mechanism:

$$\lambda_r = -\frac{16}{3K^*}\sigma T^3 \tag{1.12}$$

Where;

σ : The Stefan-Boltzmann Coefficient (5,667x10-8 W/m^{2}K^4)

K*: The Extinction Coefficient of the Foam (m^{-1})

T : Temperature in Kelvin

In other words, heat transfer is directly proportional to the fourth force of the absolute temperature gradient and inversely proportional to the absorbing property of the foam, ie the extinction coefficient. Recent results have shown that the extinction coefficient for conventional rigid foams can be estimated by simple modeling.

To estimate the extinction coefficient, Glicksman and Topey were studied on an equation.The Glicksman Extinction Coefficient (K_G) is as a function of cell diameter, foam density and solid polymer density for an isotropic foam with pentagonal dodecahedral cells:

$$K_G = 4.10\frac{\sqrt{f_s\frac{\rho_f}{\rho_s}}}{\emptyset} \quad (1.13)$$

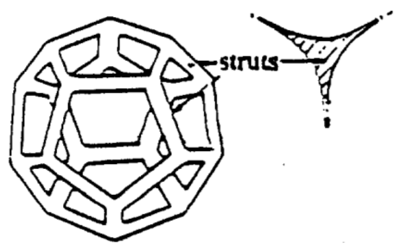
Where;

f_s : Fraction of Polymer in Struts

ρ_f: Foam Density (kg/m^3)

ρ_s: Solid Density(kg/m^3)

Pentagonal dodecahedral cell of RPUFs is schematically shown in Figure 1.30.



(a) (b)

Figure 1.30. *Schematically expression of pentagonal dodecahedral model of rigid polyurethane foam cel (a)Perspective View (b)Cross-section through Struts (Doermann et al.,1996, p. 2)*

Depending on cell geometry and fs, the value of 4.10 is fixed. Glicksman et al. expressed an equation including the contribution of cell walls ($K_H K_w$, Kw: extinction coefficient of solid polymer). If the struts and this additive are combined, the total radiation property is written as follows:

$$K_G = K_{struts} + K_H K_W \tag{1.14}$$

$$K_G = 4.10 \frac{\sqrt{f_s \frac{\rho_f}{\rho_s}}}{\emptyset} + (1 - f_s) \frac{\rho_f}{\rho_s} K_W \tag{1.15}$$

where;

$\emptyset$=Diameter of the cell

ρ_f=Foam Density (kg/m^3)

ρ_s=Solid Density(kg/m^3)

Kw = 60000 m^{-1} is calculated by Glicksman. (Doermann et al.,1996, p. 2)

When the cell diameter decreases at constant foam density, the number of struts which prevents radiation increases. Similarly, as the foam density increases, the thickness and surface area of the struts increases. Therefore, heat transfer by radiation is reduced (Glicksman, p.153).

1.6. Mechanical Properties of Rigid Polyurethane Foams

Rigid polyurethane foam is the main structure that provides rigidity of the refrigerators. Besides thermal conductivity of RPUF, mechanical properties are the important factor for that reason. While improving thermal properties, it should be taken into considered that mechanical properties of RPUF should not be worsed.

It can be classified of mechanical modelling in cellular solids in two categories: the phenomenological model and the micro-mechanical model. In phenomenological model, it is aimed to be the most compatible with experimental mechanical behavior without establishing a direct relationship with the physics of the event. Micro-mechanical models are based on analyzing the deformation mechanism of micro-cells under load applications. The most known and widely used micro-mechanical model is the Gibson model (Avalle M. et al., 2007, p.4.)

There are many factors that have affect on the mechanical properties of rigid polyurethane foams. The mechanical properties of struts and walls which are the solid part of the cells,the properties of the fluid in the cells which is the gaseous part and the structure of the cell have affect on the mechanical properties of rigid polyurethane foams.

Mechanical properties of solids:

Stifness, strength and viscoelasticity of the rigid polyurethane foam can be given as examples of the mechanical properties. Mechanical properties of solids in the structure strongly effect on the mechanical properties of the foam. The more strength cell struts and cell walls are, the more strength rigid polyurethane foam is.

Cell structure:

Besides mechanical properties of cell struts and cell walls, cell structure effects the mechanical properties of rigid polyurethane foam. Deformation mechanism of cell structure and cell walls determine the general mechanical properties of the foam. When rigid polyurethane foam exposes compressive or tension, struts and walls of the cells deform. The primary deformation mechanism is bending and stiffness of the rigid polyurethane foam is effected by that bending deformation of struts and cells. Generally, the cells of the rigid polyurethane foams are anisotropic which means one dimension of the cell is bigger than other dimensions. This situation causes different mechanical properties on different dimensions. Commonly, stiffness of the foam on elongation direction is bigger than other dimensions. In addittion, cell sturcture effects Poisson’s ratio of the rigid polyurethane foam.

Fluid in the cells:

There are two types of cell structure in rigid polyurethane foams: Open cells and close cells. When the rigid polyurethane foam exposes a mechanical force, behaviour of the foam changes related to its cell type. There is a gas phase into close cells and the properties of that gas effects the mechanical properties of the foam. If the compressibility of the gas is low, it can be provide stifness. (Ridha, 2007 p. 9–11)

1.7. Nanofillers/Nanoclays

In recent years, polymer nanocomposite applications have been developing rapidly. Polymer nanocomposites are widely used in different industries. Automotive, aerospace and packaging sectors are examples of these sectors. The reason for the use of nano fillers in the polymer composite is that the precise properties of the desired end product can be achieved with these nano fillers. The definition of polymer nanocomposite is that material which includes multiphases with dispersed nano fillers in polymer matrix. Toyota Central Research Laboratory first used “nanocomposite” phenomenon in 1985. They manufactured a belt cover by using nylone- montmorillonite (MMT) polymer-nano clay composite.After that development, studies on nanocomposites were accelerated in worldwide. Because, even if small amounts were used in the matrix, the properties of the polymer could be adjusted on the direction of desired properties.

When the particle size of the material is decreased the nanoscale, surface area of the material increases, and it effects the mobility of the polymer chains in the polymer matrix. Changes of the mobility of the polymer chains influences the properties of the polymer matrix (Valapa et. al., 2017, p.30.).

Energy consumption is the main consideration for most of the electrical devices especially refrigerators. The main insulator material is rigid polyurethane foam in the refrigerators. There are many studies are conducted to decrease energy consumption. With the development in nanocomposite materials, it is started to work on polymer matrix nanocomposite studies with polyurethane and nano fillers. Different types of nanofillers which have different aspect ratios and surface properties have affects on the mechanical, properties such as strength, chemical properties such as biodegrability and thermal properties such as heat resistance and thermal conductivity of the rigid polyurethane foam.

There are many types of nano fillers such as carbon nanotubes, graphenes, nano cellulose etc. It has to be taken into consideration that the nano filler should be compatible with the polymer and provide a good reinforcement to improve the properties of the rigid polyurethane foam. (Valapa et. al., 2017, p.32.).Clays are drawn attention as the nano fillers for rigid polyurethane foams because of their high aspect ratios and easier chemical modification processes. In addition, it is easy to find and cheap and no harmful for nature.

Clay is a material that is used in many areas such as construction, sanitarywares, kitchenwares and addition material for paints, rubber, cosmetic or medicine industry. The definition of clay is “naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried.” acording to Association Internationale pour l’Etude des Argiles and the Clay Minerals Society.

There are many minerals on the earth, but silicates have the largest pie among them. Silicon and oxygen are the most common elements that forms earth’s crust. The chemical representation of silicates is SiO_4. There is one silica atom which has +4 charge that is surrounded by 4 oxygen atoms which are -2 charges in the structure of silicate. Silicate has an anionic atomic structure and charge is -4. Figure 1.27. shows atomic structure of silicates schematically.

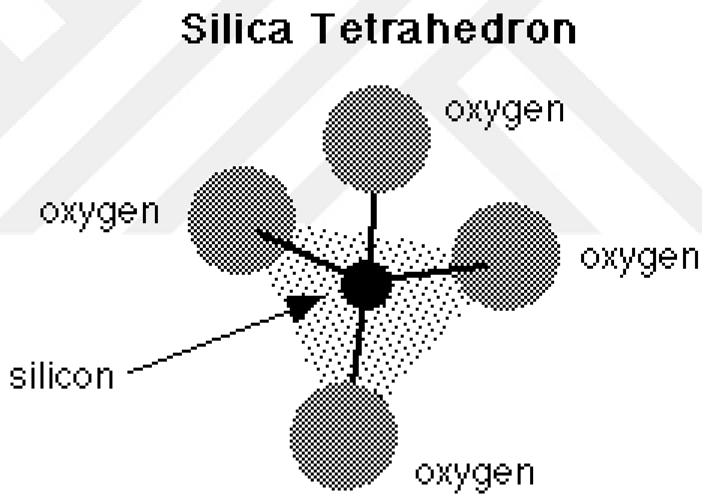


Figure 1.31. *The atomic structure of SiO4 (http-6)*

Silicates include mainly three categories, and with these main three categories, they have many subcategories. Figure 1.31. shows groups and subgroups of the silicates.

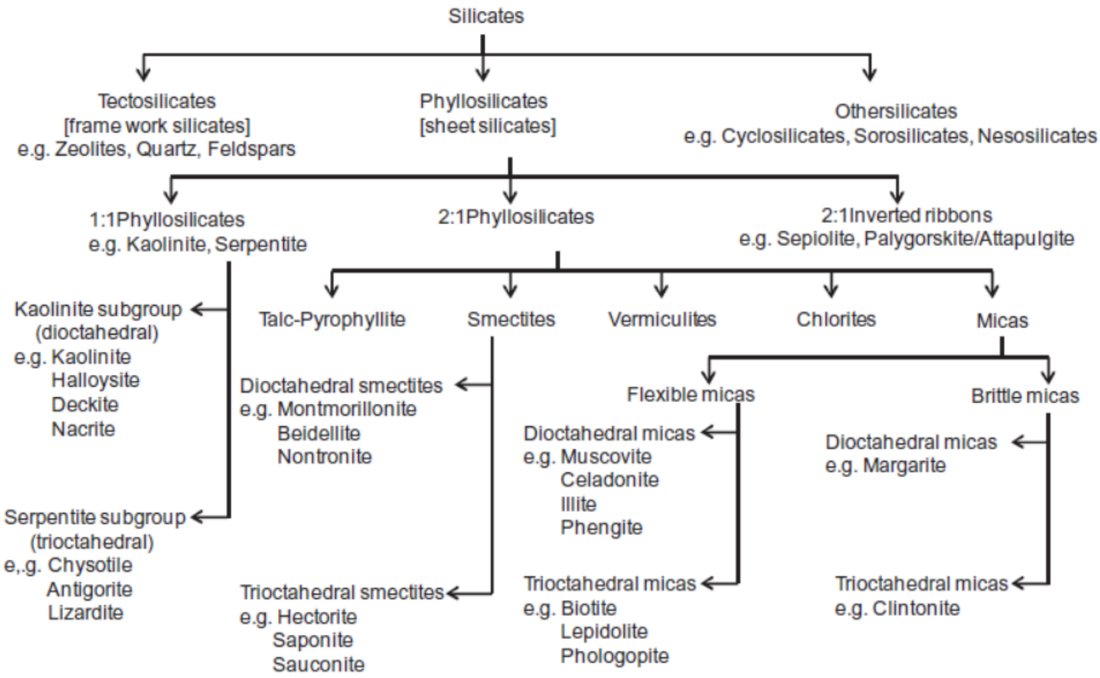


Figure 1.32. *Groups and subgroups of the silicates. (Ray, 2013, p. 2)*

Silicates can be in many forms. Nesosilicates form in single units, sorosilicates form in double units, inosilicates form in chains, phyllosilicates form in sheets, cyclosilicates form in rings and tectosilicates form in framework.Thanks to these different forms, silicates can be used in many different area in many different industry.

Generally, to prepare polymer matrix nanocomposites, phllyosilicate type clays are chosen. Phyllylosilicate type silicates are in sheet form and they are commonly called layered silicates (LSs). Tetrahedron rings are bonded with oxygen atoms to other tetrahedron rings. These bonded tetrahedron rings forms a two dimensional plane and it forms layers/sheetlike structure. This structure is shown in Figure 1.33.

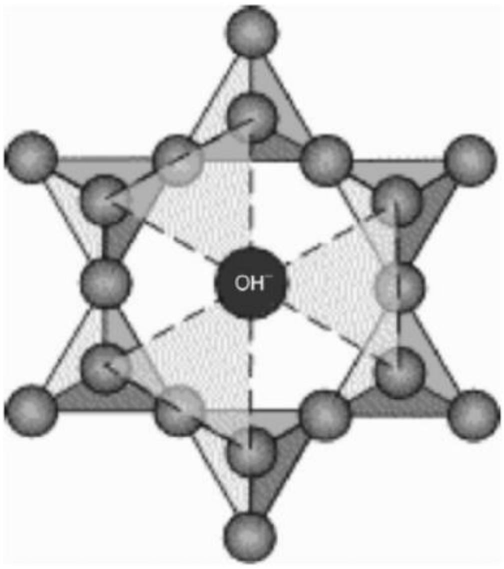


Figure 1.33. *Structure of phyllosilicates (Ray, 2013, p. 3)*

In that structure, one oxygen atom is bonded directly to the silicon atom and half of the other three oxygen atoms are shared with other silicon atoms. Because of that reason, silicon to oxygen ratio is (1:2.5) The symmetry of rings conducts to the symmetry of the structure. However, other layers decreases the symmetry and provides platelet/sheetlike structure. Figure 1.34 shows montmorillonite type silicate structure and Table 1.3. shows some of the subgroups of phyllosilicate type clays.

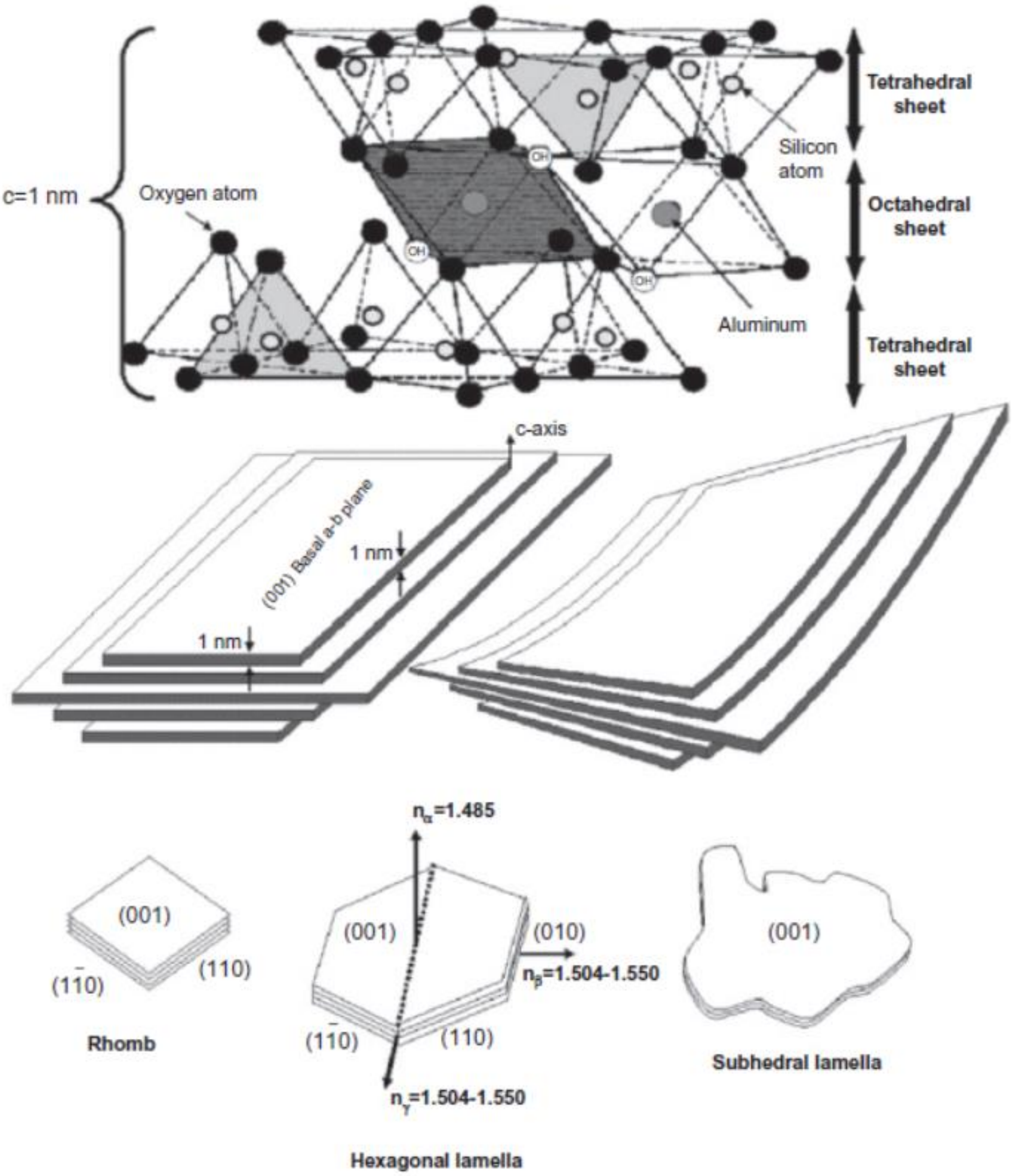


Figure 1.34. *Montmorillonite type clay structure(Ray, 2013, p. 4)*

Table 1.3. *Some of the subgroups of phyllosilicate type clays(Ray, 2013, p. 5)*

Clay group	Chlorite, glaoconite, illite, kaolinite, montmorillonite, palygorskite, pyrophyllite, saoconite, talc, vermiculite
Mica group	Biotite, lepidolite, muscovite, paragonite, phlogopite, zinnwaldite
Sepentine group	Antigorite, clinochrysotile, lizardite, orthochrysotile, serpentine
Others	Allophane, apophyllite, bannisterite, cavansite, chrysocolla, delhayelite, elpidite, fedorite, etc.

It can be seen on Figure 34., the thickness of the layers are commonly around 1nm. The lateral dimensions can be 30 nm to micron levels related to properties of the clay. The layers of the clay are bonded with Van der Waals and there are gaps between them. These gaps are called interlayers. There are -0.25 to -0.9 charges on these layers' surfaces in every unit cell and exchangable cations between these interlayers. If cations replaces with each other between layers, negative charges can be created. For example, if Al^{+3} replaces Mg^{+2}, there is one negative charge. That propertiy of platelet silicates is Cation Exchange Capacity (CEC). The unit of the CEC is mequiv/100gm. Every layer may have different cation exchange capacity, so avarage CEC is taken into consideration for all structure.

Inside the interlayers of phyllosilicates, water molecules are kept. These molecules provides more substitution of the cations. Clay minerals can be categorized as kaolinite, smectite and illite-mica clay.

Kaolinite:

Kaolinite, dickite and nacrite minerals are under the kaolinite group. The general formula can be expressed as $Al_2Si_2O_5(OH)_4$. The general formula is the same for all of three minerals but their structures are different from each others. That phenomena is named as polymorphism.

Smectite:

Vermiculite, saponite, hectorite, montmorillonite, talc, sauconite and nontronite are some of the silicate minerals that are under the smectite group. The general formula can be expressed as $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2$-$xH_2O$. The amount of water molecules can be change from one structure to another and x is for different amount of water molecules.

Illite-Mica Clay:

Hydrated microscopic muscovites are under that category. The general formula is $(K,H)Al_2(Si,Al)_4O_{10}(OH)_2$-$xH_2O$.

To prepare polymer matrix nanocomposites, generally smectite type of clay minerals are chosen. Among them, montmorillonite, saponite and hectorite subgroups are chosen commonly. Table 1.4. shows general formulas and some properties of these clay minerals

Table 1.4. *General formulasi, cation exchange capacities and particle lengths of montmorillonite, saponite and hectorite. (Ray, 2013, p. 6)*

Clays	Chemical Formula	CEC/mequiv.100 g^{-1}	Particle Length/nm
Montmorillonite	$Mx(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100–150
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	87	50–60
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200–300

M, monovalent cation; x, degree of isomorphous substitution (between 0.5 and 1.3).

Vermiculite is a phyllosilicate type clay that takes place in smectite mineral groups. It is a hydrated Mg-Al Silicate mineral. There are many studies with phllosilicate type clays in nanocomposite area and vermiculite is one of the phyllosilicate type clay. Vermiculite is a 2:1 type clay. It is formed by two sheetlike layer of silica and alumina tetrahedra that is linked octahedral layer which is composed oxygen, magnesium, iron atoms and hydroxyl molecules.T-O-T is the expression of octahedral later between two tethrahedral layers. The properties of vermiculite are listed in Table 1.5. Also, the T-O-T structure of the vermiculite is shown in Figure 1.35.

Table 1.5. *The properties of vermiculite (http-7)*

Formula:	$Mg_{0.7}(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4 \cdot 8H_2O$ Formula previously given as $(Mg,Fe,Al)_3((Al,Si)_4O_{10})(OH)_2.4H_2O$.
As a Commodity:	Vermiculite
Colour:	Brown, bronze-yellow
Hardness:	1½ - 2
Crystal System:	Monoclinic
Member of:	Smectite Group
Name:	From Latin "vermiculare", to breed worms, in allusion to its peculiar exfoliation on intense heating.

Forms as an alteration product of biotite or phlogopite, by weathering or hydrothermal action. Vermiculite is mined as a natural insulation material.

Colour:	Brown, bronze-yellow
Hardness:	1½ - 2 on Mohs scale

Formula:	$Mg_{0.7}(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4 \cdot 8H_2O$ Formula previously given as $(Mg,Fe,Al)_3((Al,Si)_4O_{10})(OH)_2.4H_2O$.
IMA Formula:	$Mg_{0.7}(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4 \cdot 8H_2O$
Elements listed:	Al, Fe, H, Mg, O, Si - search for minerals with similar chemistry
Common Impurities:	Ca,Na,K

Crystal System:	Monoclinic
Class (H-M):	2/*m* - Prismatic
Cell Parameters:	a = 5.24 Å, b = 9.17 Å, c = 28.6 Å β = 94.6°
Ratio:	a:b:c = 0.571 : 1 : 3.119
Unit Cell V:	1,369.83 Å³ (Calculated from Unit Cell)
Z:	4
Comment:	Space Group C2/m (a = 5.24(2), b = 9.17(2), c = 28.60(5) A, beta = 94°36'(24'), Z = 4, or space group C2/c (a = 5.349(6), b = 9.255(10), c = 28.89(2) A, beta = 97°7'(6'), Z = 4.

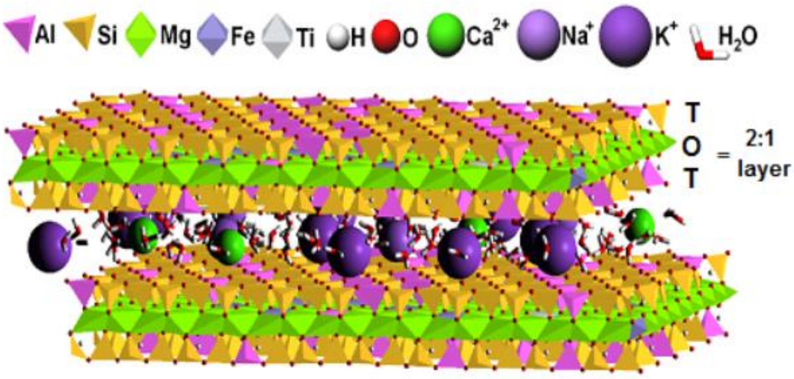


Figure 1.35. *The T-O-T structure of vermiculite (Valášková et. al., 2012, p. 210.)*

Generally, there are three methods to prepare polymer matrix nanocomposites:

Solution blending:

An solvent is used to dissolve polymer and clay is dispersed into the same solvent. Then, dipsersed clay is blended with polymer-solvent solution. When the final solution is homogenized, it is casted and solvent is evaporated. Figure 1.36. shows polymer-modified organoclay nanocomposites prepared by solution blending.

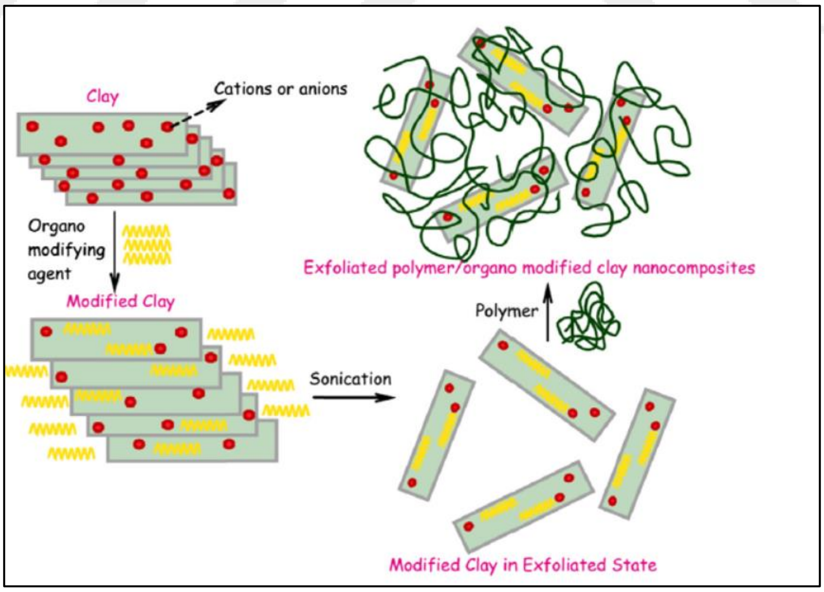


Figure 1.36. *Polymer matrix composite preparation by solution blending (Valapa et. al, 2017, p. 32)*

Melt Blending:

It provides better mixing then solution blending. At the temperature that is higher than melting point of the polymer, polymer and clay mixture is annealed and processed to obtain final product.

In-situ Polymerization:

Compatibility of the component of polymer matrix nanocomposite is achieved better with that method. Clay particles are dispersed in the matrix better because of dispersion the solution that includes monomers.

Figure 1.37. shows the processes of these three methods to prepare polymer matrix nanocomposites. (Valapa et. al.,2012, p. 32-34)

The compatibility and uniform dispersion of clay particles have directly affect on the thermal and mechanical properties of the polymer matrix composite. At that point, to provide good dispersion and compatibility, interaction between clay and polymer chemically or physically and method to obtain polymer organoclay nanocomposite should be taken into consideration. Interaction between the matrix and organoclay can be examined under three categories: Flocculated, intercalated and exfoliated nanocomposites.

Flocculated-Phase Separeted Nanocomposites:

There is a weak interaction between clay and polymer matrix in that situation. Intercalation of polymer in the layer of clay structure is no achieved and it causes phase seperation. There may be modarate improvement for the properties of polymer matrix composites or it is normal to expect no enhance in properties.

Intercalated Nanocomposites:

This type of structure is obtained when polymer chains enters partially into the layers of clay. Interlayer gallery of clay is extends because of the polymer chain intercalation into the layers.Generally, clay is dispersed into polymer matrix at the last step of the polymerization process and it is commonly used in polyurethane-clay nanocomposites.

Exfoliated Nanocomposites:

In this type of interaction, there are completely seperated clay laters into the polymer matrix. That provides higher surface area and higher enhacement of the properties. It can be obtained with in situ polymerization or nanoclay must be dispersed in the early steps of the polymerization. Figure 1.38. shows three interaction types while preparing polymer matrix nanocomposites. (Valapa et. al., 2012, p.34-35) (Patel et. al., 2017, p.175)

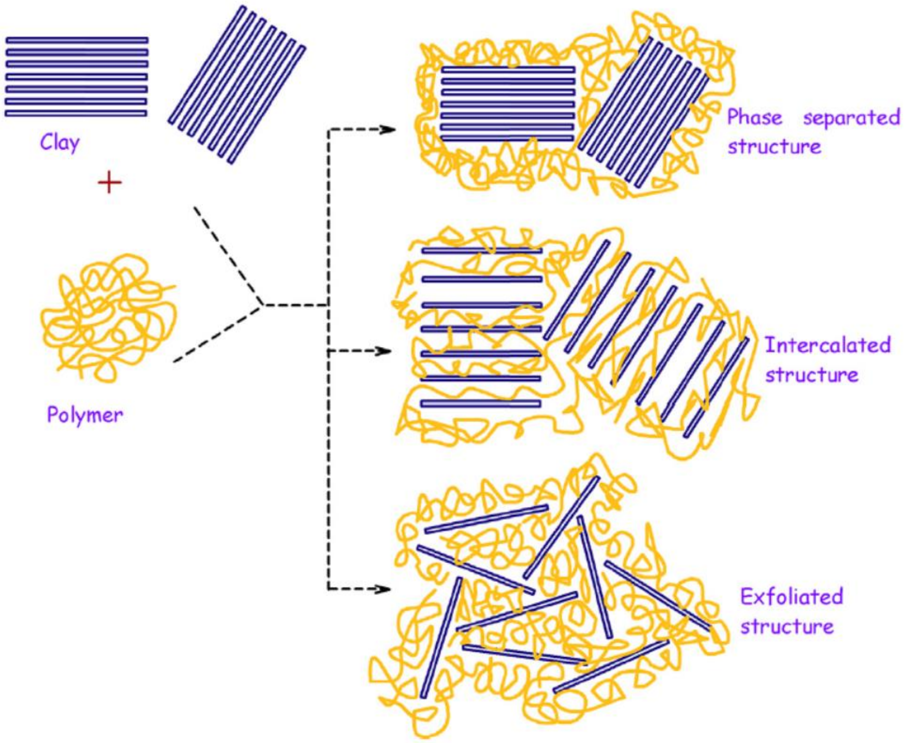


Figure 1.37. *Three types of interactions between nanoclay and polymer matrix*

(Valapa et. al, 2017, p. 35)

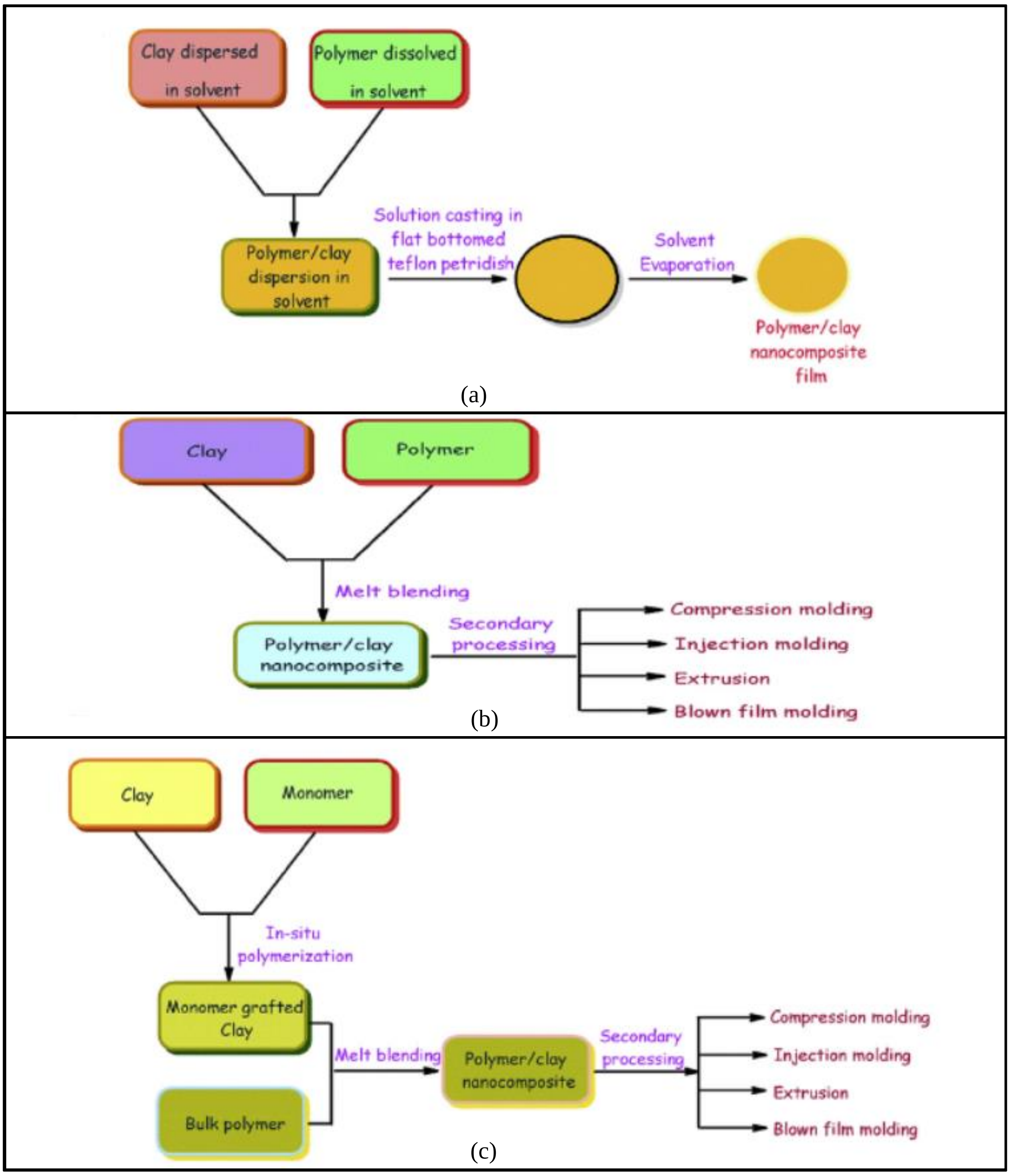


Figure 1.38. *Methods to prepare polymer matrix nanocomposites. (a) Solution blending (b) Melt blending (c) In situ polymerization (Valapa et. al, 2017, p. 32)*

2. LITERATURE REVIEW

Energy efficiency is one of the most important issue in worldwide, because of that reason the number of studies that focus on increasing energy efficiency is increasing day by day. The subjects of these studies are widespread and decreasing in thermal conductivity of rigid polyurethane foams are one of them. Enhancement of thermal insulation property of the rigid polyurethane foam provides decreasing in electrical consumption. Besides, it may help to limit the blowing agents that could be hazardous for environment. General techniques are based on improvement the cells by obtaining fine cell structure and increasing the surface area of struts. That provides to increase infrared extinction coefficient of the rigid polyurethane foam. Using nanoclays as additives into rigid polyurethane foams is a technique to get finer cells. In this chapter, studies that about the improvement thermal insulation property of rigid polyurethane foam and nanoclay-rigid polyurethane foam polymer matrix nanocomposites are examined.

Estravís et. al. (2016, p. 1-15) studied on the cell structure and thermal conductivity relationship by using nanoclays in rigid polyurethane foams. In that study, they have been used a low shear mixing technique to disperse nanoclay and they examined the effects of nanoclay particles on the reaction kinetics, cell structure and thermal conductivity change depends on cell structure.The main raw materials in that study were MDI and polyether polyol, and they preferred chemical blowing agent which is CO_2 from the reaction of water. Other materials were catalysts, additives and surfactants.To modify the nanoclay, Cloisite 30B was used. Nanoclay was a natural montmorillonite. The percentages of using montmorillonite as an additive are 0.5, 1, 3 and 5 wt%.In that study, nanoclays were dispersed with low shear mixing. First, nanoclays were dried to vaporize moisture and premixed with polyol. Then, polyol-nanoclay dispersion was mixed MDI and poured into the mold. The characterization methods were cell size measurement with scanning electrom microscopy (SEM), cell size distribution, open cell measurements, the fraction of mass measurement, interplanar distance measurement with XRD, reaction kineticts with FTIR. According to that study, density of the foam increased by addition of nanoclays and the reason for that was increasing viscosity. It was seen that the cell size distribution spread over wider area with increasing nanoclay addition Also, while increasing in clay content, the avarage cell size decreased.

To sum up, addition of montmorillonite type nanoclay into rigid polyurethane foam provided reduction in thermal conductivity of foam. The best result was obtained with 1% addition of nanoclay. 3 and 5 wt% nanoclay addition did not provide a significant reduction in thermal conductivity.

Another study about rigid polyurethane foam composites was conducted by Li et. al. (2015, p.691-698). In that study, vermiculite and perlite were used to prerpare rigid polyurethane foam-nanoparticle composites and investigated effects on insulating properties of foam. The main raw materials were polyol and MDI, and the additives were vermiculite and perlite. First, vermiculite or perlite were dispersed in polyol and that dispersion mixed with MDI. After reaction started, the mixture was poured into the mold. The percentages of vermiculite and perlite as additives were 5, 10, 15, and 20% by weight. In that study, perlite provided more reducing in thermal conductiviy than vermiculite.The best result was obtained with 10 wt% perlite addition.

Saha et. al. studied on the effect of nanoparticles on the mechanical and thermal properties of the rigid polyurethane foam. (2008, p. 213-222) In this study, in situ polymerization technique was used to infuse nanoparticles. The effects of different nanoparticles with this polymerization on tension, compressive, flextural stress and thermal properties were investigated. The main materials were polyol and MDI, and three types of nanoparticles were used: TiO2, montmorillonite type nanoclay and CNFs. Nanoclay was mixed with MDI different from other studies above, and the percentage of addition was 1 wt%. To provide dispersion of nanoparticles homogeneously, ultrasonic cavitation method was used. Then, nanoclay-MDI dispersion and polyol were strirred and poured into the aluminum mold. To characterize microstructure of nanoparticles and foam, SEM was used. To determine chemical bonding between nanoclay and polymer chains of the foam, Fourier Transform Infrared Spectometer (FT-IR) was used. Thermo-gravimetric analysis (TGA) was used to measure thermal stability of the rigid polyurethane foam.Tension, compressive and flexure tests were conducted to measure the mechanical properties of the foam. To conclude, it was expressed that addition of nanoparticles enchanced the thermal and mechanical properties of the rigid polyurethane foam. CNFs addition into rigid polyurethane foam provided the highest enhancement both thermal and mechanical properties.

Another study was conducted by Pikhurov et. al.(2018, p. 403-414) about the effects of nanoparticles on structure and properties of rigid polyurethane foams. In this study, rigid polyurethane composites were prepared with differend hydrophilic and hydrophobic nanoparticles. The concentration of nanoparticles changed in 0.1-0.6 wt%. The average cell diameter of cells, thermal conductivity and mechanical strength were charecterized related to nanofillers. The main materials were oligomeric aromatic isocyanate MDI, polyether polyol, and as additives the hydrophilic fullerene and Cr_2O_3 nanoparticles were used. Prepolymer technique was used in this work. Bulk density measurement, optical microscopy, FT-IR, mechanical tests, thermal conductivity measurement were conducted to characterize the rigid polyurethane foam. The results of this study shows fullurene soot and Cr2O3 nanoparticle addition increased the diameter of bubbles of RPUF and that caused increasing in thermal conductivit of RPUF. However, mechanical strength of the foam increased with the addition of these nanoparticles.

Qian et. al. (2012, p. 5060-5068) studied on in situ polymerization of polyurethane with the addition of vermiculite that modified with tertiary amine catalysts.In this work, clay was modified with quaternary ammonium salts with tertiary amine groups. Thermal, mechanical and barrier properties of the rigip polyurethane was investigated. The main materials were MDI and polyol. Catalytic modifier was synthesized, and it was CTAB. Additive was nanosized vermiculite. To synthesize vermiculite-polyurethane nanocomposite, first vermiculite was modified with CTAB. Modified vermiculite were dispersed in polyol and the blend was mixed with MDI. Then, this mixture was poured into the mold. With the in situ polymerization and modifying with CTAB, high degrees of intercalation/exfoliation of vermiculite was provied. According to this study, separate micro phases in the structure of the polyurethane matrix did not change by addition of nano clay. Also, nanoclay-polyurethane composite was more sitff and less permeable to CO_2 then neat polyurethane.The best result is obtianed with 5.3 wt% Q50 vermiculite addition; increasing in tensile strength was 390% and decreasing in CO_2 permeability was 40%.

3. EXPERIMENTAL PROCEDURE

3.1. Raw Materials

In this study, the main raw materials to produce polyurethane nanocomposite were polymeric 4,4’-diphenylmethane diisocyanate (pMDI) and polyether polyol with blowing agents, surfactants and catalysts. The functional group NCO content of isocyanate was 31% and the hydroxyl value of polyol is 386 mg KOH/g. Physical blowing agents were cyclopentane and isopentane blend. Polyol involved these blowing agents. To provide finer foam cells,vermiculite that was smectite type clay was used. Vermiculite was provided from Agrekal Company in Turkey. Chemical analysis and physical properties that were provided from supplier are shown in Table 3.1. and Table 3.2.

Table 3.1. *Chemical analysis of vermiculite*

Typical Chemical Analysis	
Element	**Percent by Weight**
SiO_2	34.0 - 38.0
TiO_2	0.4 - 0.7
Al_2O_3	8.0 - 12.0
$Fe2_2O_3$	5.0 - 7.0
MgO	24.0 - 30.0
CaO	0.2 - 0.8
K_2O	< 0.2
Other	0.1 - 1.0

Table 3.2. *Physical properties of vermiculite*

Typical Physical Properties	
Color	Light to dark yellow
Shape	Accordion - shaped granule
Bulk destiny (a)	80 - 115 kg/cu m 4-10 lb/ cu ft
Ph(in water)	7 - 9
Combustibility	Non - combustible
Sintering temperature	1150 - 1250°C 2100 - 2280°F
Fusion point	1200 - 1320°C 2200 - 2400°F
Cation exchange capacity (b)	60 - 100 me/ 100g
Waterholding capacity (a)	260 – 380 %by wt 20 – 50% by vol
Water absorbtion	580 ml per liter

As mentioned above, clays have layered strucuture. The layers consist of tetrahedral layers in which the silicon atom is surrounded by four oxygen and octahedral layers in which metals such as aluminum and magnesium are surrounded by eight oxygen atoms. Tetrahedral (T) and octahedral (O) layers are connected to each other by sharing oxygen atoms. Vermiculite is a smectite type clay and has 2:1 structure. Smectite structure forms when aluminum cations replace by magnesium or iron cations. The negative charge that occurs by that replacement is balanced with sodium or calcium ions. The charge created on the sheets is not locally fixed and may vary from layer to layer. An average charge value for the layers can be calculated by cation exchange capacity (CEC) measurement. According to literature, CEC of raw vermiculite is 40.6 mmol/100 g (Wu et. al.) The size of cations that enters to interlayer are not equal and that causes interlayer distance. The distance is called d spacing (d001).

The basal plane distance of the clays can be calculated by X-Ray Diffraction Technique. The spacing of the interlayer also depends on the nature of the clay and the degree of swelling and hydration of the interlayer cations. The electrostatic and Van der waals forces that hold the layers together are relatively weak, and the distance depends on the charge density, the interlayer cation, and the degree of hydration. Because of the wide spacing of the interlayer and the weak interlayer forces, the cations between the layers can be hydrated in aqueous solutions. This is called swelling of the clay. Due to the interlayer spacing and the weak interlayer forces, other molecules, especially in the hydrated structure, can be intercalated between the layers and this may lead to expansion of the layered structure and even separation of the layers. This is due to the intercalation / exfoliation property of smectite clay minerals, which makes it a strong additive for polymers. (Olad,2011)

Smectites are hydrophilic materials and they are not compatible with polyurethane matrix. It is hard to disperse nanoclay into polymer matrix and can cause agglomeration because of this incompatibility. In this condition, desired enchanced properties of rigid polyurethane-nanoclay composite cannot be achieved. Clay that is used to produce polyurethane nanoclay composite should be hydrophobic because of that reason. Modification techniques are used to obtain compatibility between clay and polymer matrix.Figure 3.1. shows different modification techniques. Cation exchange is one of the most used technique between them. Ammonium salts are used to modify clay. In this study, to modify vermiculite, cetyl trimethyl ammonium bromide (CTAB),an quaternary ammonium compound, was used as the modifier. The chemical formula of CTAB is

$C_{19}H_{42}NBr$ and the molecular weight is 364.46 g/mol CTAB was provided from Vtolo company, China.

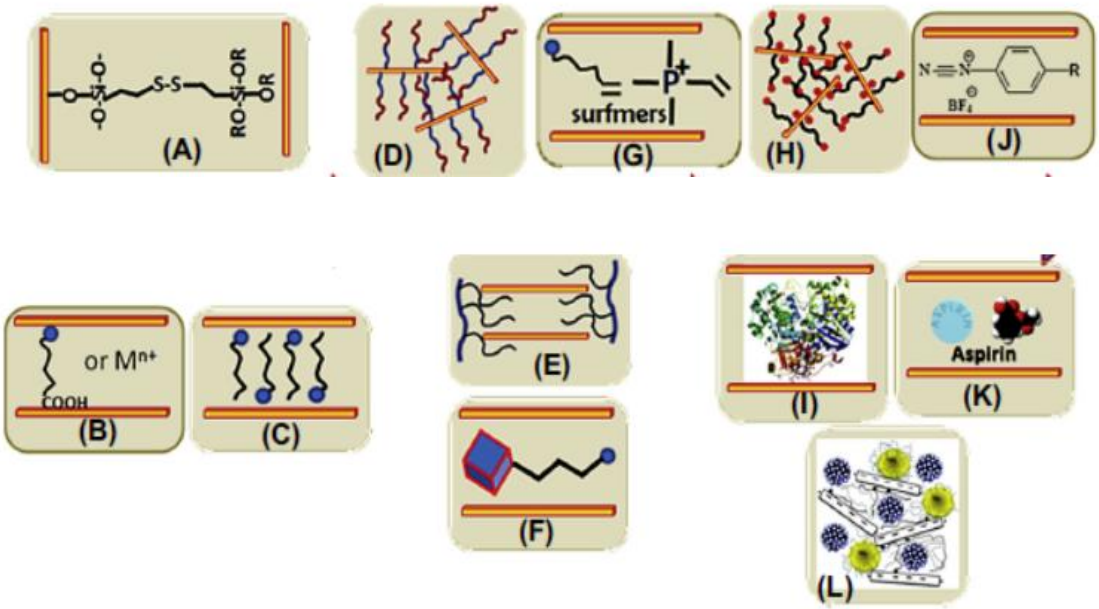


Figure 3.1. *Intercalation strategies. (a) bifunctional bifunctional silane (b) carboxylic acid-functionalized alkylammonium or metal ions (c) alkyl ammonium (d) block copolymers (e) comb copolymers (f) polyhedral oligomeric silsesquioxane (POSS)-functionalized alkyl ammonium (g) ammonium and phosphonium surfmers (h) in-situ-generated carbon nanotubes (i) enzymes (j) diazonium salts (k) drug (l) dendrimer/TiO2 nanoparticle mixtures (Jlassi et. al., 2017, p.23)*

3.2. Preparation of the Rigid Polyurethane Foam

In this study, the effect of 1, 3, 5, 7, 10 wt % of vermiculite that was modified with 1 CEC, 2 CEC, 3 CEC on thermal conductivity of rigid polyurethane foam was investigated. To prepare polyurethane nanoclay composite, the first step was surface modification of the vermiculite.

The physical mixing clay and polyol is not sufficient in the preparation of polymer / clay nanocomposites by the good dispersion of clay layers in the polymer matrix. The distribution of hydrophilic clays in hydrophobic polymers such as polyurethane cannot be easily achieved. The modification of clay layers with hydrophobic agents increases the compatibility of the clay with the polymer chain.

With this modification, the surface energies of the clay layers are increased and the clay layers have a polarity close to the polarity of the polymer.

It is more compatible with organoclay polymers with low surface energy and the dispersion of the organoclay layers within the polymer matrix is easier. Smectite type clays, are not neutral in terms of electrical charge. In this structures, the charge balance is achieved by cations such as sodium (Na^{+}), potassium (K^{+}) and calcium (Ca^{+2}), which can be easily displaced in solution medium and which enter the layers. Surface modification of the clay layers is carried out by ion exchange with organic cations. This process replaces the displaceable cations, such as sodium, calcium, between the clay layers with alkyl ammonium or alkylphosphonium cations.

Before the modification of vermiculite, it was grinded and sieved under 125 micron. Figure 3.2 shows sieve equipment that was used to obtain particle size under 125 micron. After sieving, 50 g vermiculite was weighted for each CEC experiment Then, 800 ml distilled water was mixed with 50 g vermiculite at 60°C. The model of the stirrer was IKA RW16 Mixer and it was mixed with level 4, 4400 rpm for 10 minutes. Figure 3.3. shows the mixer that was used to mix vermiculite and distilled water.

Figure 3.2. *Sieve equipment*

Figure 3.3. *Dispersion process of vermiculite in distilled water.*

In this study, CTAB was used as a modifier. First, to calculate amount of CTAB to use modify the vermicule, CEC of vermiculite was calculated with methylene blue technique. Also, CEC value that found with that technique was compared with CEC value in literature.

Methylene blue method is one of the most common used method to calculate cation exchange capacity of clays. In this method, methylene blue solution is adsorbed onto clay. Then, adsorbed value is determined with UV spectroscopy by reading the value at 663.5 nm wavelength. This wavelength is maximum absorbance of methylene blue on UV spectroscopy. CEC is calculated as the meq or mmol value of the amount adsorbed on 100 g clay.(Erdem, 2010, p.60)

To calculate CEC of vermiculite, 0.5 g vermiculite was weighted and 60 ml, 0.01 M methylene blue solution was added onto clay. Then, this mixture was stirred for 24 h. After stirring, mixture was filtered and CEC was determined as 40.6 mmol/100g Also, it was compared with literature.

In this study, it was investigated that the effect of modifying the clay with 1 CEC, 2 CEC and 3 CEC CTAB on interlayer distance. Molecular weight of CTAB is 364.45 g/mol and cation exchange capacity of vermiculite is 40,6 mmol/100 g.The amount of CTAB for 1 CEC was calculated 7.4 g.

Concurrently, 7.4 g, 14,8 and 22.2 g CTAB was mixed with 300 ml distilled water for each CEC value respectively on magnetic stirrer with 600 rpm for 10 minutes. Figure 3.4 shows the magnetic stirrer that was used to mix CTAB and distilled water.

Figure 3.4. *Dispersion process of CTAB in distilled water*

After vermiculite-distilled water dispersion and CTAB-distilled water dispersion were mixed for 10 minutes, 150 ml CTAB-distilled water dispersion was poured into vermiculite-distilled water dispersion. That mixture was stirred for 10 minutes with 400 rpm. After 10 minutes, remained 150 ml CTAB-distilled water dispersion was poured. Vermiculite and CTAB was mixed for 2 hours with 400 rpm. After 2 hours, the CTAB-vermiculite-distelled water mixture was filtered and washed with distilled water. Agglomeration was controlled with $AgNO_3$ solution, washing process was contiuned till no agglomeration observed. Figure 3.4. shows filtering process of that mixture.

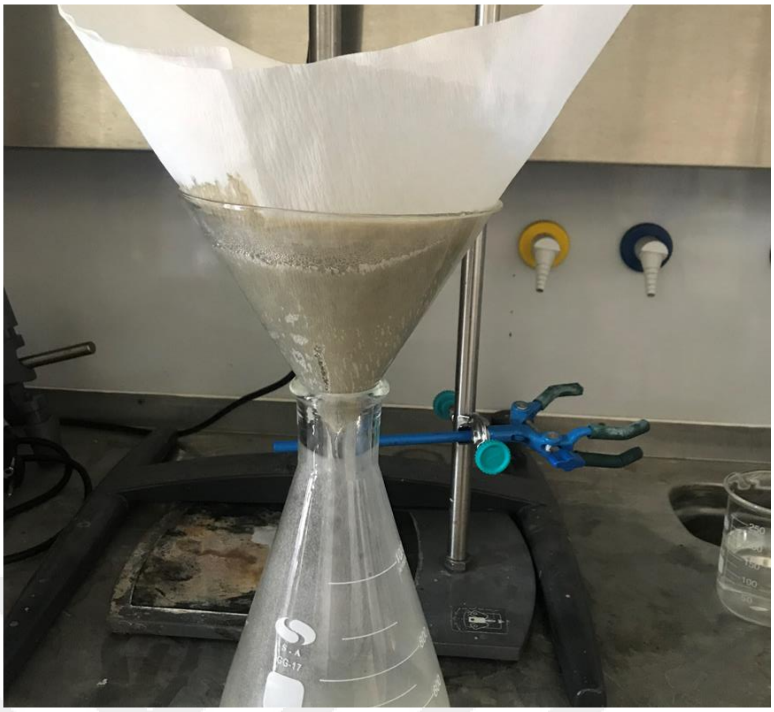


Figure 3.5. *Filtering and washing process of modified vermiculite with CTAB*

After washing and agglomeration controlling, modified vermiculite was dried at drying oven at 110°C. After drying, modified vermiculite was grind and sieved under 125 micron, again. Figure 3.5. shows flowchart of the modifying process.

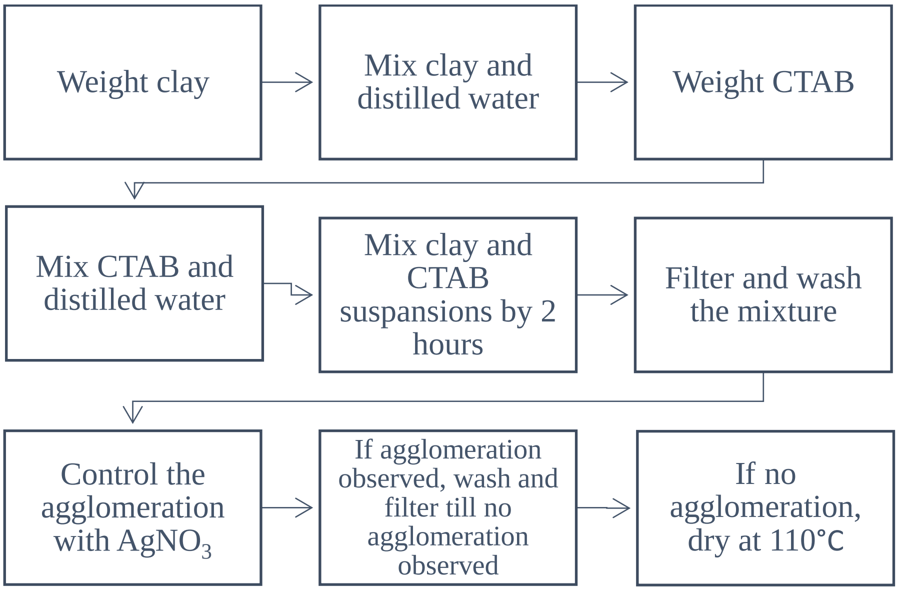


Figure 3.6. *Flowchart of the modifying process of vermiculite*

The next step was preparation of neat polyurethane foam. One-shot process and hand-mixing method was chosen to produce RPUF. In the first stage, 113 g polyol - pentane mixture was put into 1 liter polypropylene cups. The ratio of polyol to pentane in the mixture of polyol to pentane was 100:13. While the polyol pentane mixture was being mixed with a mechanical stirrer, 150 grams of MDI (methylenediphenyldiisocyanate) were added into the polyol pentane mixture. Polyol which includes pentane and isocyanate was mixed 10 seconds with a high-speed mechanical stirrer by using 2000 rpm. After that, this mixture was poured into the mold. Mold was heated before the pouring of mixture. Average mold temperature was 34±2°C. Curing time for RPUF was 5 minutes. The laboratory scale mold was used to produce rigid polyurethane foam. The dimensions of the foam was 300x300x100 mm.

After producing neat rigid polyurethane foam, next step was to produce nanoclay-rigid polyurethane foam composite. Similar methods was used to produce composite. Modified nanoclay was poured into polyol and mixed for 2 minutes with high speed mechanical stirrer. Then, isocyanate was poured into polyol and nanoclay dispersion. After, that mixture was poured onto the mold and cured 5 minutes.

Neat polyurethane foam and nanoclay-polyurethane composite foams were cut to required length to characterization methods. Figure 3.7 shows production method for nanoclay-rigid polyurethane composite.

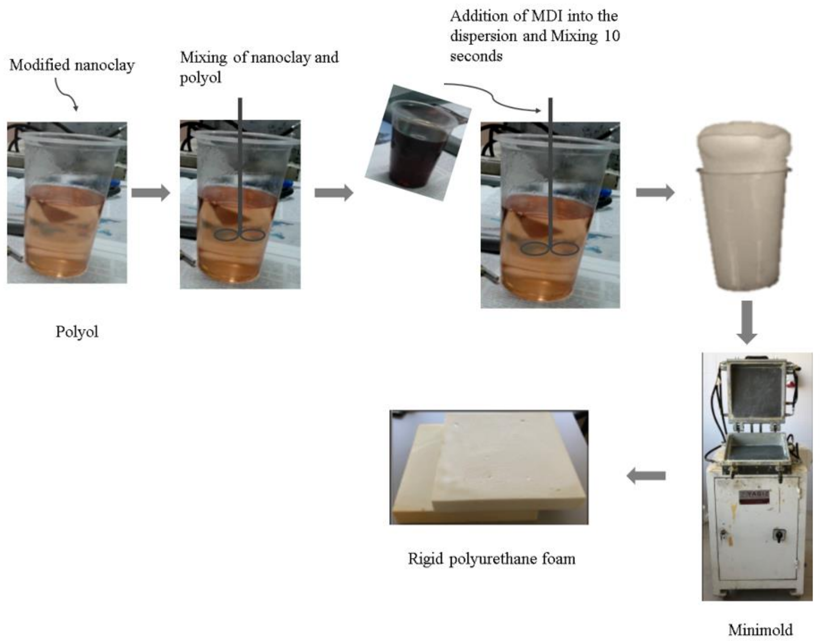


Figure 3.7. *Nanoclay-polyurethane foam production process*

3.3. Characterization Methods

3.3.1. Characterization of Vermiculite

In this study, first characterization of vermiculite was done. TGA, FT-IR, XRD and contact angle measurement analysis was conducted to characterize vermiculite.

TGA anaylysis of raw vermiculite was done at Eskisehir Technical University, Department of Chemistry. The model of device was SETARAM Labsys TG. Thermogravimetric Analysis (TGA) is a technique that shows weight changes with the increasing temperature of the sample. It is possible to observe changes in weight during dehydration or decomposition of a substance depending on time or temperature with TG analysis. Weight change occurs as a result of breaking of physical or chemical bonds at high temperatures. Figure 3.8 shows TGA device.

Figure 3.8. *TGA Device (Karakeçili A., 2018) (http-8)*

To determine plane distance of vermiculite and modified vermiculite with 1, 2, 3 CEC, X Ray Difractometer was used. Analysis was conducted with Rigaku-Rint 220r0 device at Eskisehir Technical University, Department of Materials Science and Engineerig. The X-Ray Diffraction method (XRD) is based on the fact that each crystalline phase diffraction with X-rays in a characteristic order, depending on the specific atomic sequences of the phase. For each crystalline phase, these diffraction profiles define that crystal as a kind of fingerprint.Figure 3.9 shows X Ray Diffraction device.

Figure 3.9. *X Ray Diffraction Analysis device (http-10)*

To analyze th clay modified or not, FT-IR anaylsis was done at Eskisehir Technical University, Department of Chemistry. CTAB was used to modify the vermiculite. The main principle of the FT IR spectroscopy is to evaluate absorption that resulted from vibration, bending or rotating of chemical bonds of molecules which exposed to IR rays. Figure 3.10 shows FTIR device.

Figure 3.10. *FTIR Device (http-9)*

Another characterization method to analyze degree of hydrophobic property of vermiculite was contact angle measurement. This measurement was conducted with Krüss DSA 100 drop shape analyze device, at Eskisehir Technical University, BİBAM.

The nano-layer structures are very difficult to disperse into hydrophobic polymers, because of their tendency to form agglomerates and their hydrophilic structures. Due to the inherent compatibility problem of hydrophilic clay layers with hydrophobic polymer chains, poor interaction may occur between them. This poor interaction and incompatibility will prevent the dispersing of the clay and make it difficult to obtain improved nanocomposite properties. For these reasons, clay must be hydrophobic and the measurement of this property is necessary in this sense. Clays are expected to be hydrophobic as a result of surface modification applications. Whether the clays are hydrophilic or hydrophobic is measured by the contact angle of the clay pellet with the water droplet. For a solid to be called hydrophobic, the theta angle between the solid surface and the water drop must be greater than 90 °. Figure 3.11 shows contact angle measurement device.

Figure 3.11. *Contact angle measurement device. (http-11)*

3.3.2. Characterization of rigid polyurethane foam

First, thermal conductivity of rigid polyurethane foam was measured. To measure thermal conductivity, LASERCOMP FOX 314 device was used. This device had heat flow meter and could measure thermal conductivity coefficient between 0,05-10W/mK. Figure 3.12 shows thermal conductivty coefficient measurement device.

Figure 3.12. *Thermal conductivty coefficent measurement device (http-12)*

Thermal conductivity (k) is defined;

$$k = \frac{q\Delta L}{\Delta T} \tag{3.1}$$

q: Heat flow through section A

$\Delta\ L$: Thickness

ΔT: Temperature difference

Schematically representation of heat flow that belongs measurement of thermal conductivity of a sample is shown in Figure 3.13.

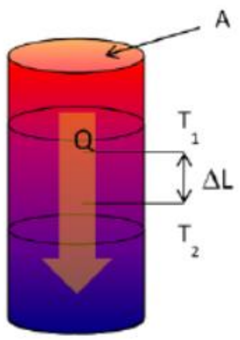


Figure 3.13. *Schematically representation of heat flow (Sözbir, 2014)*

Another characterization method for rigid polyurethane foam was open cell measurement.Gas pycnometer device was used to calculate open cell ratio with Micromeritics AccuPyc 1330 helium pycnometer. Figure 3.14 shows gas pycnometer.

Figure 3.14. *Gas pycnometer (http-13)*

Gas pycnometer is a commonly used device to determine the actual volume of solids. This device operates in accordance with the principle of displacement of a volume of gas equal to its volume of a solid (including closed cells). The open cell content of the foam can be determined with this device. A known geometric volume foam sample (rectangular or cylindrical) is used. The difference between the geometric volume of the foam and the actual volume measured shows the presence of open cells. For example, The solid sample is cut in rectangular geometry and edge lengths are measured with a ruler. Sample is put into the sample chamber of the device. The measured edge length values of the sample are entered from the device program. The pycnometer calculates the actual volume of the sample together with the closed cells. The difference between the actual volume and the geometric volume of the solid sample gives the open cell volume. The device gives this amount in percentage. (Howson et al., 2005)

After open cell measurement, cell size measurement of cells was done with Olympus SZ-PT stereo microscope. Figure 3.15 shows stereomicroscope.

Figure 3.15. *Stereomicroscope (http-14)*

Light microscopes are types of microscopes in which the visible wavelength (4000-7000 Å) of light is used as light source and glass lens systems are used as magnification elements. In light microscopes other than stereo microscopes, the light source is under the object to be examined. Light passes through the object and reaches the eye. So it examines the cross-sectional properties of the object. Stereo microscopes are reflected on the object and sent to the lens. As such, it reveals the surface properties of the object to be examined, the image is three-dimensional (Kabaçı, 2015, p.55).

Compressive strength of rigid polyurethane foam samples was measured with Zwick Roell Proline device.whic is shown in Figure 3.16.

Figure 3.16. *Compressive strength measurement device. (http-15)*

The external forces acting from the surface of the materials through inner side of it are called compressive forces and generate pressure stresses. It is considered to be the opposite of the tensile test. The strength of the brittle materials are generally determined by the compressive test. In the compressive test, cylindrical or cubic samples are placed between two parallel tables and measured with the help of deformations caused by the applied force.

Finally, cell structure was investigated with ZEISS EVO 50 Scanning Electron Microscope which is shown in Figure 3.17.

Figure 3.17. *Scanning Electron Microscope (http-16)*

Scanning electron microscope (SEM) is a type of electron microscope that receives images from the sample by scanning the sample with the focused electron beam. In scanning electron microscopy, the image is obtained by focusing the high-voltage accelerated electrons on the sample, collecting the effects of various interferences between the electron and the sample atoms during scanning of this electron beam on the sample surface and passing it to the screen of a cathode ray tube after passing through the signal amplifiers. The signals from these sensors are converted to digital signals and given to the computer monitor. Scanning electron microscope consists of three basic parts: optical column, sample cell and imaging system. Figure 3.18 shows the parts of the scanning electron microscope. (Kabaçı, 2015, p.56)

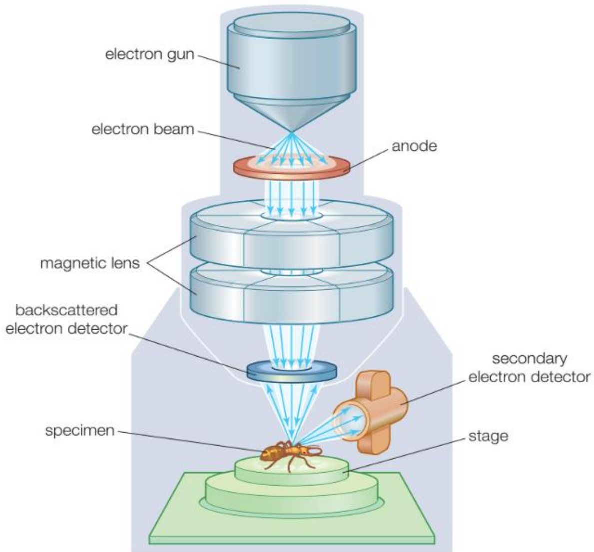


Figure 3.18. *Parts of SEM (http-17)*

4. RESULTS AND DISCUSSIONS

Rigid polyurethane foam is one of the crucial material that used in home appliances technology, especially refrigreators. The importance of energy efficiency is getting increasing day by day and there are many works to increase efficiency in both industry and universities. In this study, it was focused on improvement properties especially energy efficiency of rigid polyurethane foam by using modified vermiculite. Both vermiculite and nanoclay-rigid polyurethane foam characterization were characterized and evaluated in the frame of structure-property relationship

4.1. Evaluation of Vermiculite Characterizations

4.1.1. Thermogravimetric analysis of vermiculite

Thermogravimetric analysis is the technique that measures reduction in mass while temperature of sample is increasing. Change in mass (m) according to the its initial value (m0) (Δm = m-m0) is given by a function of time or temperature. Mass loss is caused by removal of volatile compounds, reaction as a result of the desorption of the resulting products and decomposition of sample.

According to literature, TGA curve of vermiculite shows 3-4 different steps. Causes of these separate steps are removal of water that occurs different forms in the vermiculite structure. Water loses from vermiculite causes by losing of adsorbed water, free and bound water and dehydroxylation which means losing of OH groups from the structure. The factors that effects these water loses are interlayer cations, dipole monent and dielectric interlayer constant of interlayer water. Figure 4.1. shows TGA graphics of vermiculite from literature and Figure 4.2. shows TGA graphics of vermiculite that was used in this study.

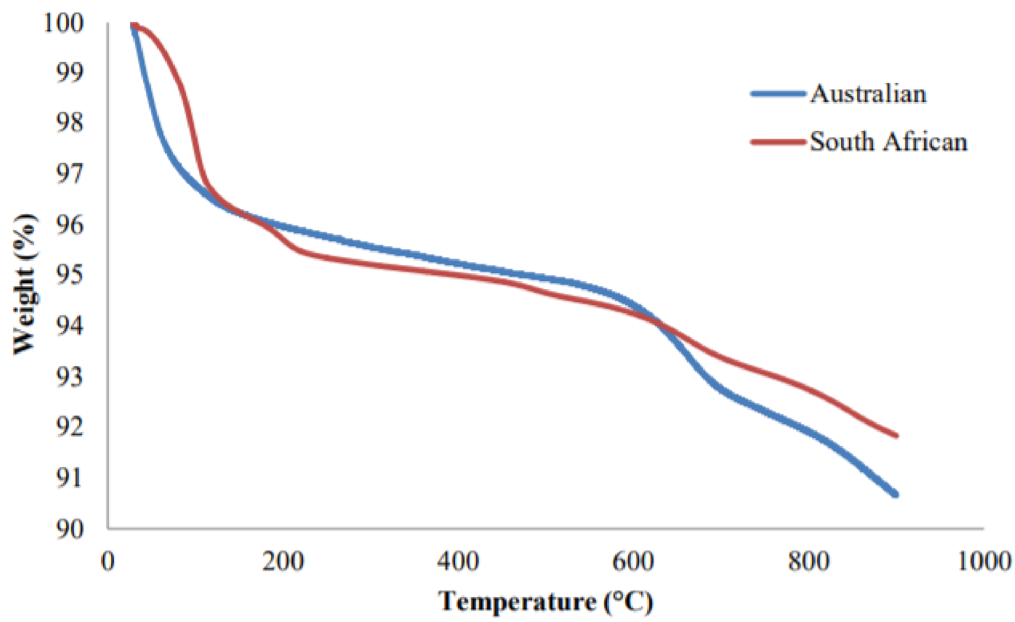


Figure 4.1. *TGA curves of two different vermiculite on the literature (Folorunso, 2015)*

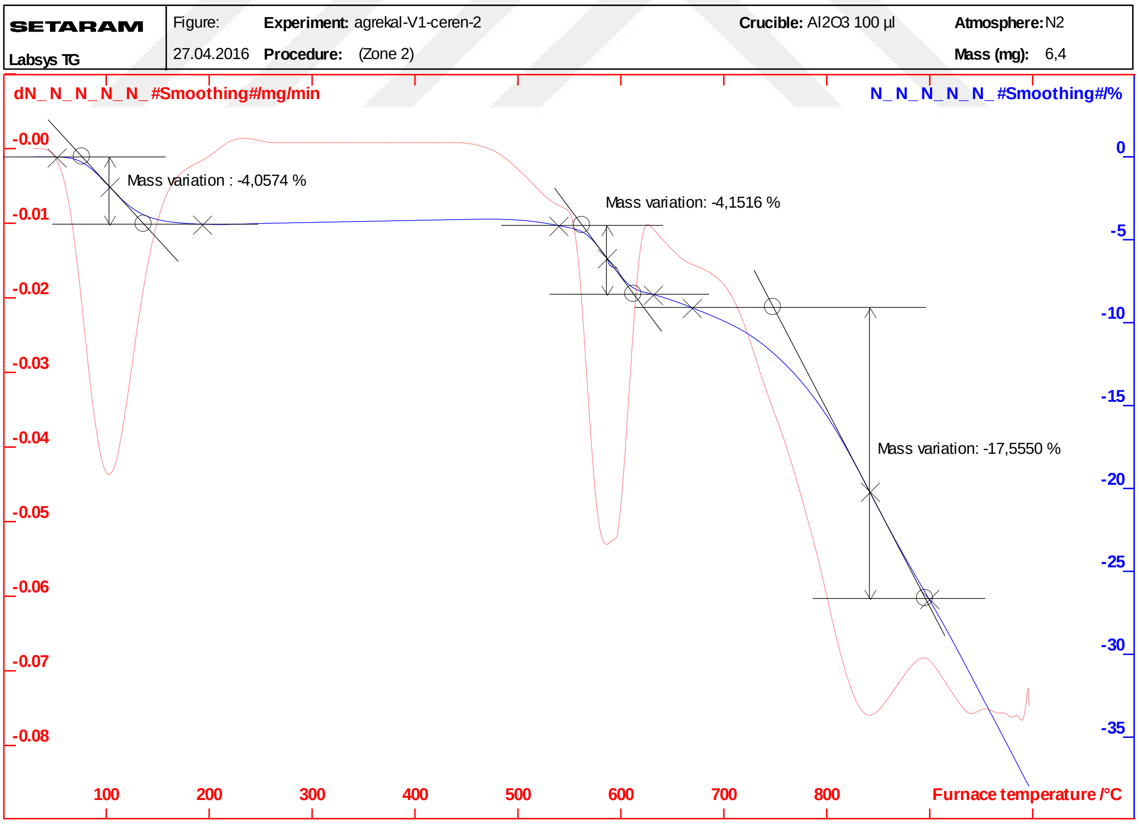


Figure 4.2. *TGA and DTG curve of vermiculite that was used in this study*

Water removal of vermiculite was achieved at three steps. First step was at about 100°C with the ratio of 4.1%. That was the removal of water that places in interlayer without chemical bonding. About 600°C, there was a second step of water loss with the 4.15%. That was the removal of water that is chemically bonded in interlayers of vermiculite. And the last water removal was after 800°C and the reason of that step was decompostion and gradual loss of OH groups in the structure. TGA curve that was obtained in this study was similar to TGA curve on the literature. That proved vermiculite that was used to obtain rigid polyurethane foam had similar properties to previous literature.

4.1.2. XRD analysis of vermiculite

X Ray Diffraction is a non-destructive analysis method to characterize crystallography and phases of materials. Each material which has crystalline structre have its own atomic structure. These atomic structure scatters X rays beams with a certain angle. Figure 4.3 shows X Ray Diffraction schematically.

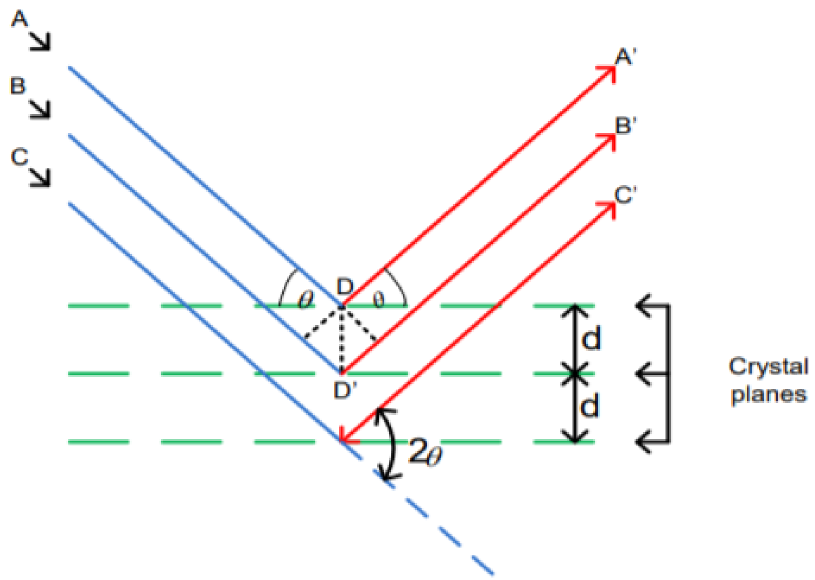


Figure 4.3. *X Ray Diffraction on the planes according to Bragg's Law. (Folorunso, 2015)*

The distance between planes is called basal distance (d-spacing), and it can be calculated with Bragg's Law.

$$n\lambda = 2d \sin \theta \qquad (4.1)$$

n:Integer

λ: Wavelength (Å)

d: Basal plane distance

θ: Angle which is between incident ray and the plane that ray scatters

As mentioned previous sections, the plane distance of vermiculite was expected to change with modification with CTAB. To determine change in plane distance of vermiculite, X Ray analysis raw vermiculite and modified vermiculite with 1, 2, 3 CEC. The comparison of d spacing of vermiculite that modifies with 1 CEC, 2 CEC and 3 CEC is shown in Figure 4.4.

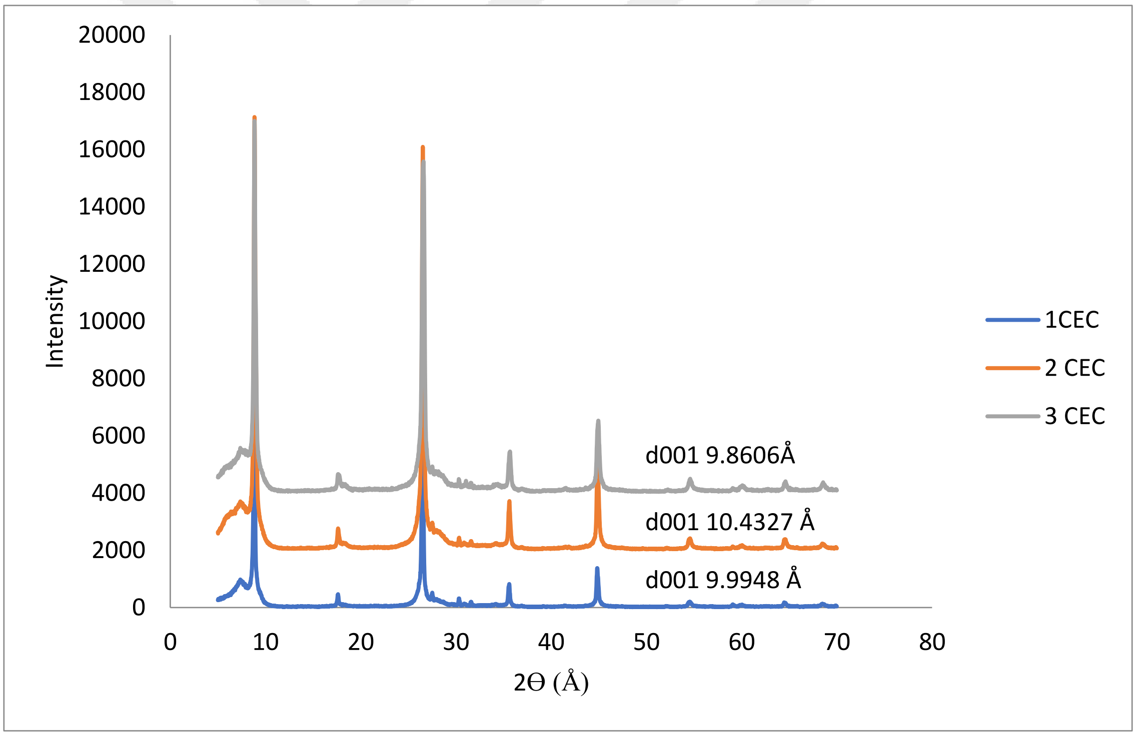


Figure 4.4. *The d-spacings of vermiculites that modifed with 1 CEC, 2 CEC and 3 CEC*

During the modification process, CTAB molecules enters the interlayer distance of vermiculite and that causes increasing in interlayer distance. d spacing was 9.86 Å for 1 CEC modification, 10.43 Å for 2 CEC modification and 9.99 Å for 3 CEC modification. The trend was increased from 1 CEC to 2 CEC modification but it can be seen that there was no significant increasing with 3 CEC modification.

4.1.3. FT-IR analysis of vermiculite

Physical mixing is not enough to disperse clay particles into polymer matrix while preparing polymer-matrix nanocomposites. It is not easy to provide dispersion of hydrophilic clay particles into hydrophobic polyurethane matrix. Modification of clay with hydrophobic agents increase the compatibility of clay particles with polymer chain. Schematically representation of entering CTAB molecules to the interlayer distance of vermiculite is shown in Figure 4.5.

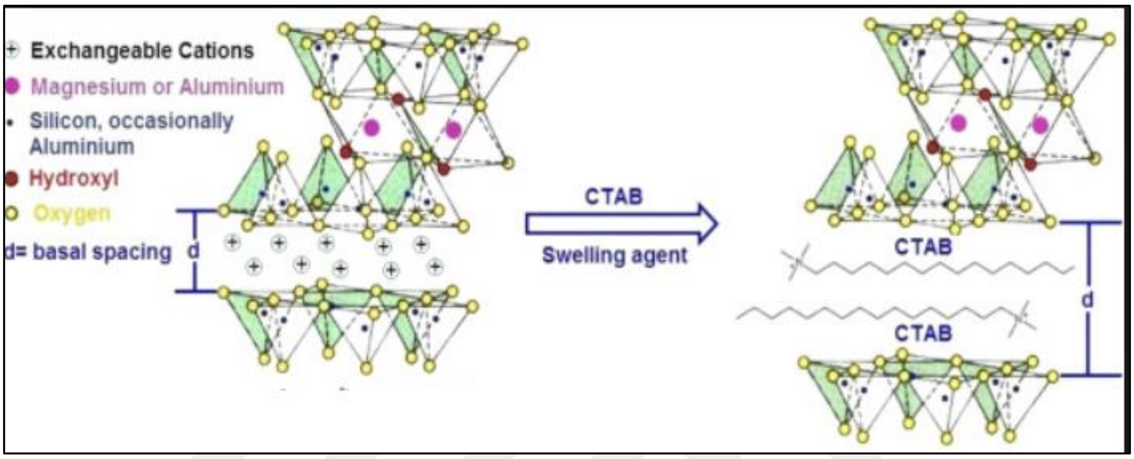


Figure 4.5. *.Interaction of CTAB with clay particles (Kıranşan et. al. 2014)*

Modification with CTAB increases surface energy of the vermiculite clay layers and the polarity of the layers of clay becomes close to the polarity of the polyurethane. Organoclays with lower surface energy are more compatible with polyurethane matrix. Modification of clay layers are achieved with replacement of ammonium cations to Calcium or Potasium ions that place in layers of the clay. That provides both intreaction between clay -polyurethane matrix and inreacing in interlayer spacing.

The chain length of CTAB causes vibration or rotation of CH2 molecules. The molecular structure of CTAB is shown in Figure 4.6.

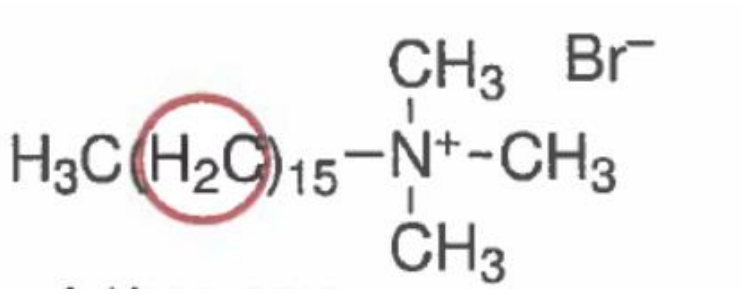


Figure 4.6. *Molecular structure of CTAB*

These vibrations provide to observe absorption bands on 2850 $cm^{-1}$and 2981 cm^{-1} on FT-IR spectrum. That helps to understand whether clay is modified or not. Figure 4.7. shows FT-IR spectrums of vermiculite that was non-modified , modified with 1 CEC, 2 CEC and 3 CEC.

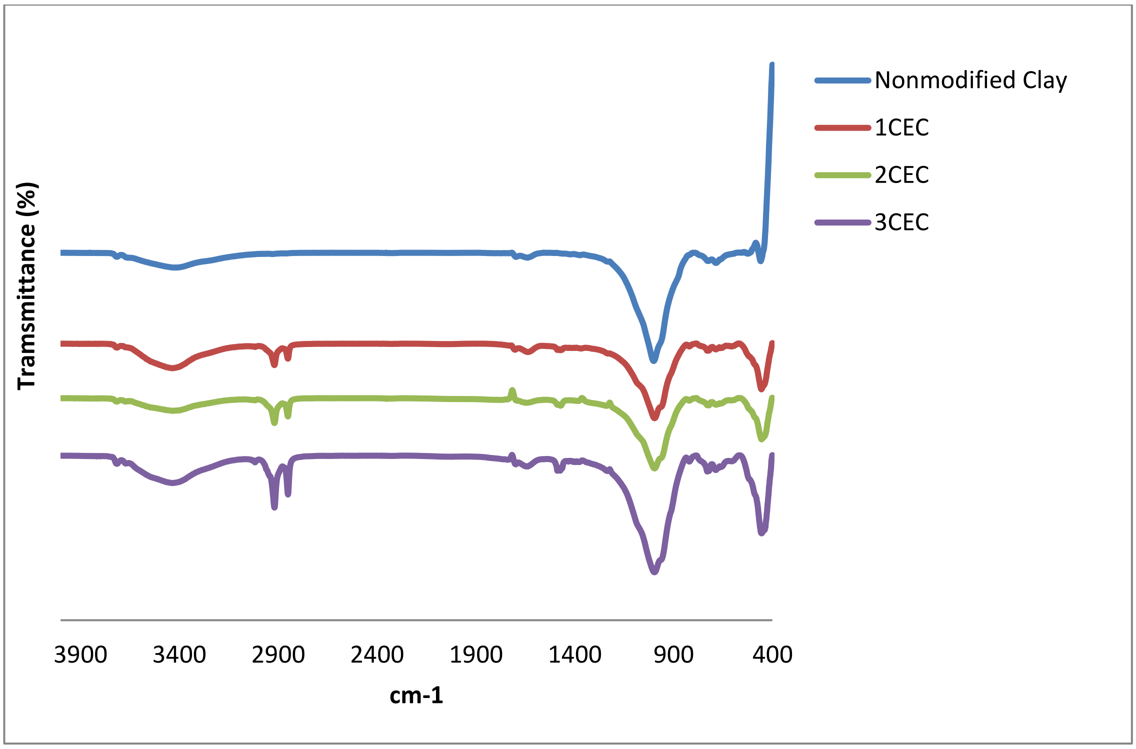


Figure 4.7. *FT-IR spectrum of vermiculets that non-modified, modified with 1 CEC, 2 CEC and 3 CEC*

Table 4.1 shows wavelength of different chemical bond vibrations with the changing CTAB ratios.

Table 4.1. *The wave numbers on FT IR spectrum of different chemical bondings in the structure of vermiculite with the changing CTAB ratios.*

Assgn.	Wave Number (cm^{-1}) (3)			
	Nonmodified Clay	1CEC	2CEC	3CEC
ν(O-H)	3429	3435	3435	3435
ν(CH_2)	-	2918	2918	2918
ν(CH_2)	-	2850	2850	2850
ν(Si-O)	1000	996	995	996
ν(Al-O-Si)	685	728	721	729
ν(Si-O)	459	455	454	455

The peaks can be seen at 2850 $cm^{-1}$and 2981 $cm^{-1}$and that means modifying process was achieved.

4.1.4. Contact angle measurement

Clays are commonly hydrophilic materials and it is hard to disperse into polymer matrix, as mention above. Modificiation processes are conducted to obtain hydrophobic clay layer surface and at the end of the modification processs whether layer surfaces are hydrophilic or hydrophobic is measured by the contact angle of the clay pellet with the water droplet. Drop shape measurement device helps to get a image of while water drops onto the clay surface and measure the angle of that droplet. Surface and droplet have the theta angle between the solid surface and the water drop must be greater than 90 °. Figure 4.8. shows contact angle measurement of non modified vermiculite and modified vermiculite with 1 CEC, 2 CEC and 3 CEC and Figure 4.8 shows change results in contact angle with modification.

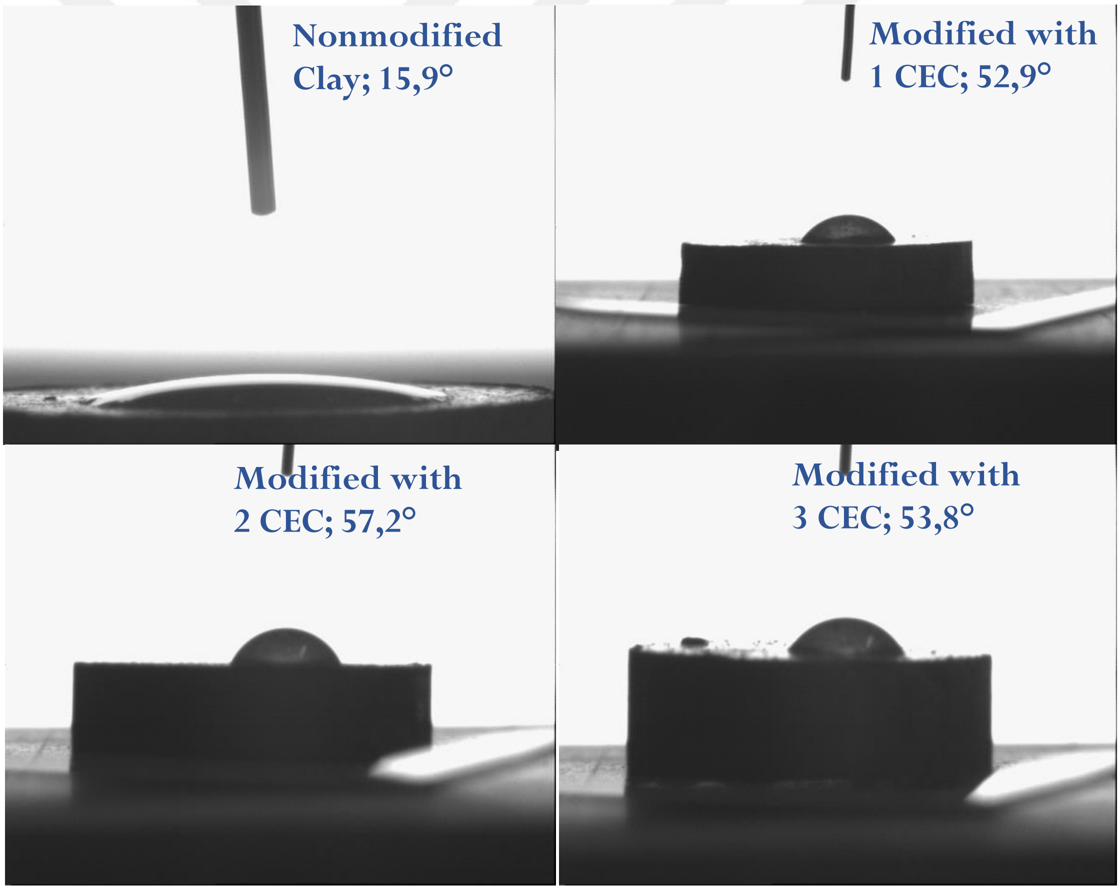


Figure 4.8. *Contact angle measurement of non modified vermiculite and modified vermiculite with 1 CEC, 2 CEC and 3 CEC.*

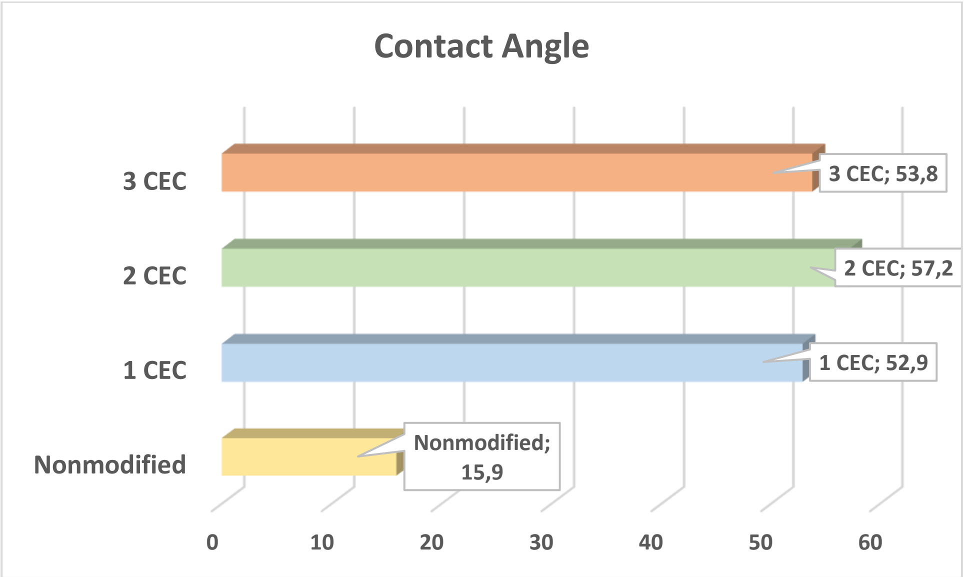


Figure 4.9. *Change in contact angle values with modification*

According to contact angle measurement, none of modified vermiculite was hydrophobic but the contact angle was increasing that means hydrophobicity of clay was increasing. That made easier dispersion of clay into polymer matrix. The optimal result was obtained with 2 CEC modification of clay.

4.1.5. Evaluation of rigid polyurethane foam characterization

After modifying vermiculite, the next step was preparation of rigid polyurethane foam-nanoclay composite. The main properties of raw materials that are used to prepare rigid polyurethane foam is given in Table 4.2.

Table 4.2. *Properties of main raw materials*

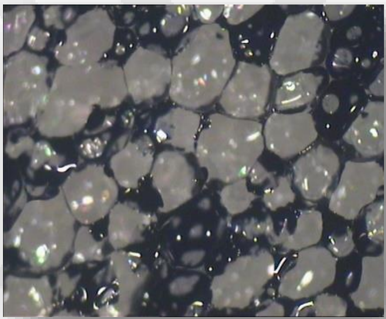
Properties	Unit	Polyol	Isocyanate
Hydroxyl Number	Mg KOH/g	386	-
NCO	%	-	31
Water	%	2,5	-
Viscosity (25°C)	mPa.s	5900	200
Density (25°C)	g/ml	1,08	1,23

In this study, modifyin vermiculie was added into polyol. There are some studies that conducted addition of clay into MDI because of its lower viscosity, but MDI can crystallize when it contact with air for a while. Because of that reasons, addition into polyol was chosen.

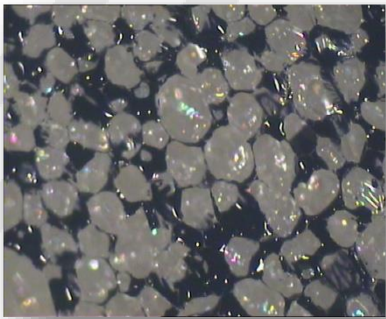
Cell size measurement with stereomicroscope, thermal conductivity measurement, compressive strength measurement and cell structure investigation with scanning electron microscope analaysis were achieved to characterize rigid polyurethane foam-nanoclay composite.

4.1.6. Evaluation of mean cell size characterization

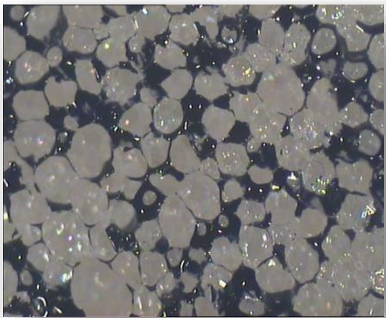
Cell size measurement was done with stereo microscope. After the surface was flattened with a blade, the surface was painted by pressing on the ink tray. The reason of the surface was painted under the light microscope to get a clear image. After these operations, cell images were taken at 2.5 magnification setting. Images were taken with the help of a computer software and cell size measurements were made by a program again. Images that are getting from stereomicroscope are given Figure 4.10.



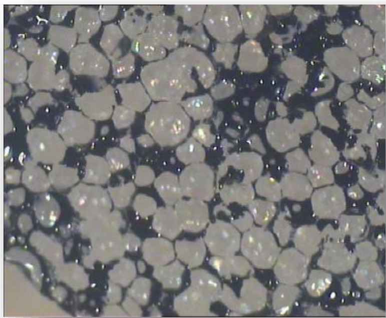
Standart PU Foam



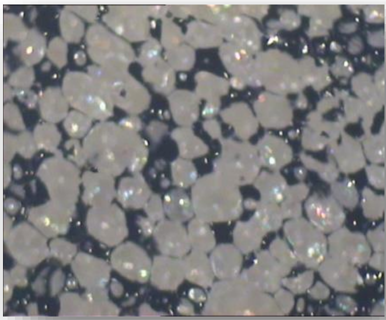
Modified with 1CEC, 3 wt% vermiculite



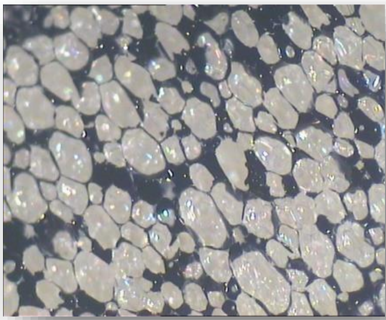
Modified with 1CEC, 5 wt% vermiculite



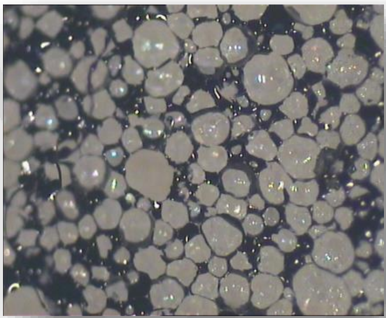
Modified with 1CEC, 7 wt% vermiculite



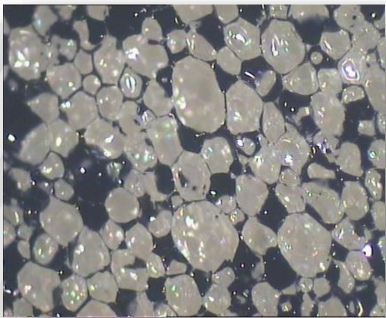
Modified with 1CEC, 10 wt% vermiculite



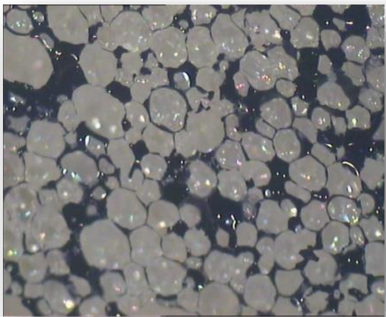
Modified with 2 CEC, 1 wt% vermiculite



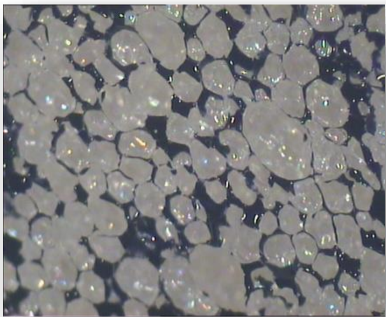
Modified with 2 CEC, 3 wt% vermiculite



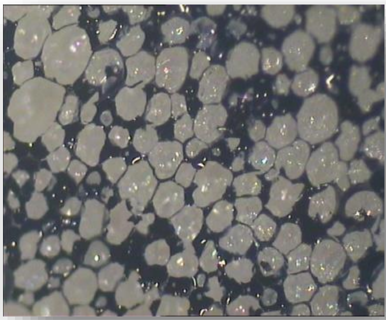
Modified with 2 CEC, 5 wt% vermiculite

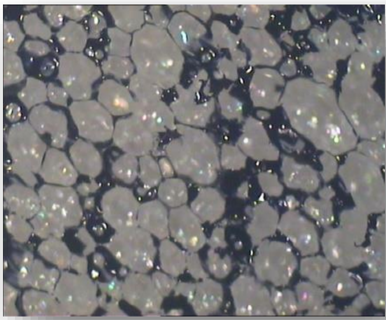


Modified with 2 CEC, 7 wt% vermiculite

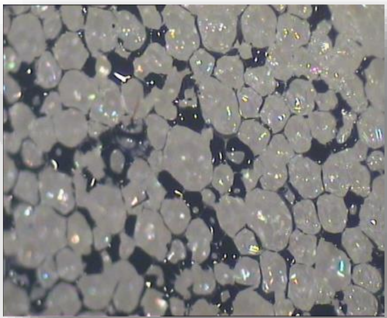


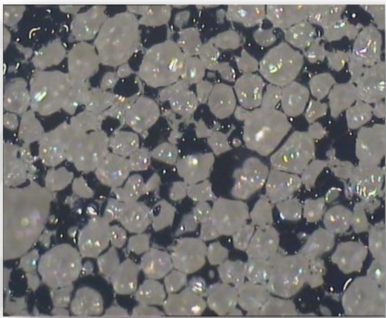
Modified with 2 CEC, 10 wt% vermiculite



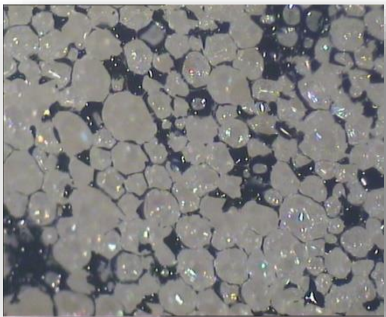


Modified with 3 CEC, 1 wt% vermiculite Modified with 3 CEC, 3 wt% vermiculite





Modified with 3 CEC, 5 wt% vermiculite Modified with 3 CEC, 7 wt% vermiculite



Modified with 3 CEC, 10 wt% vermiculite

Figure 4.10. *Stereo microscope images of rigid polyurethane foam-vermiculite nanocomposite with different additve and CEC ratios.*

Cell size measurement was done with IMAGEJ program by using images that get from stereo microscope. Sample codes are giving in Table 4.3 and cell size measurement results are giving in Table 4.4.

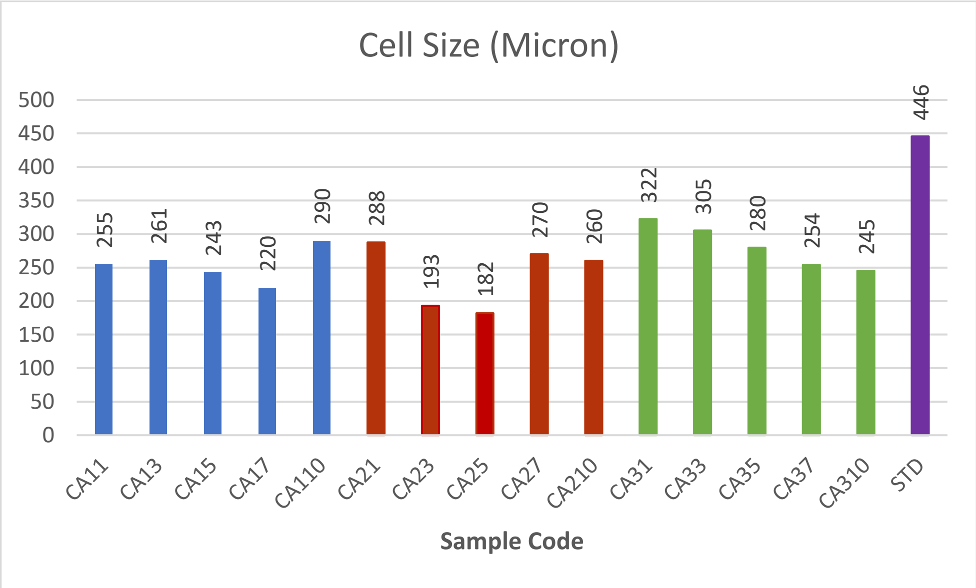
Table 4.3. *Sample codes that were used in this study*

Sample Code	Sample	CEC Ratio	Clay Content
CA11	1 CEC, 1wt% vermiculite	1	A
CA13	1 CEC, 3wt% vermiculite	1	B
CA15	1 CEC, 5wt% vermiculite	1	C
CA17	1 CEC, 7wt% vermiculite	1	D
CA110	1 CEC, 10wt% vermiculite	1	E
CA21	2 CEC, 1wt% vermiculite	2	A
CA23	2 CEC, 3wt% vermiculite	2	B
CA25	2 CEC, 5wt% vermiculite	2	C
CA27	2 CEC, 7wt% vermiculite	2	D
CA210	2 CEC, 10wt% vermiculite	2	E
CA31	3 CEC, 1wt% vermiculite	3	A
CA33	3 CEC, 3wt% vermiculite	3	B
CA35	3 CEC, 5wt% vermiculite	3	C
CA37	3 CEC, 7wt% vermiculite	3	D
CA310	3 CEC, 10wt% vermiculite	3	E
STD	Standard	-	-

Table 4.4. *Mean Cell size regarding to CEC content and amount of vermiculite*

Sample Code	Mean Cell Size (Micron)
CA11	255,28
CA13	261,39
CA15	243,37
CA17	219,93
CA110	290,06
CA21	287,50
CA23	193,13
CA25	181,88
CA27	269,96
CA210	260,17
CA31	322,36
CA33	305,30
CA35	279,66
CA37	254,07
CA310	245,25
STD	445,60

The graphic that shows cell size-clay content and CEC ratio relation and cell size distribution graphic are shown in Figure 4.11.



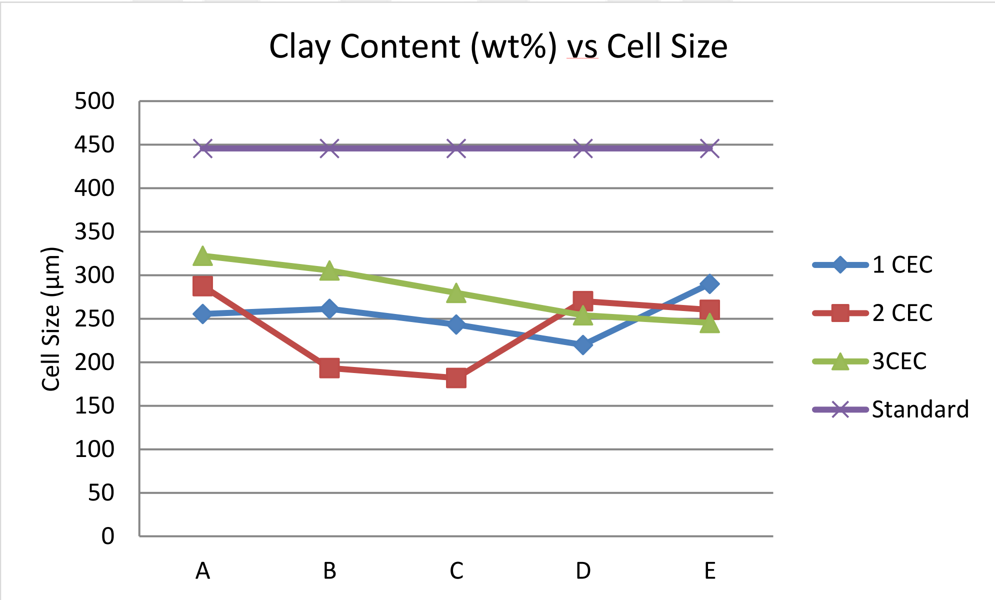


Figure 4.11. *Cell size change with clay content and CEC ratio*

The results of cell size measurements show that addition of vermiculite with nanoscale particle size provides reducing in cell size of rigid polyurethane foam.The cell size of the standard rigid polyurethane foam which had no additive was 445.6 micron. It can be seen that from graphics and images, optimal cell size was obtained with 2 CEC ratio and 5 wt% vermiculite. The cell size with 5 wt% vermiculite with modified 2 CEC ratio decreased the cell size from 445.6 micron to 181.9 micron.

When the literature is reviewed, there are many studies showing that clay additive in nanoscale decreases cell size. According to Widya et. al., smaller cell sizes could improve insulation property of RPUFS. For that purpose nanosize clays were appropriate materials because of they acted as bubble nucleating agents and they could prevent bubble growth because of their rheology. In their study that was about nanoclay composite polyurethane foam, adding nanoclay provides reducing in cell size. (Widya et. al., 2005)

According to another study in literature that achieved by Mondal et. al, it was observed that the average cell size of rigid polyurethane foam decreased with the addition of nanoclay.The reason for reducing cell size was that clay particles were nucleation sites for bubbles. Also, the viscosity of the medium could be increased with the addition of clay. Increasing viscosity provided to reduce coalesence of bubbles and number of cells increased. (Mondal P. et. al., 2005)

Further, Han et. al. was conducted a study about nanoclay polymer nanocomposites. According to their study, addition of intercalated clay that had nanosize particles provided to reduce cell size. For instance, 5 wt% intercalated nanoclay addition to polystyrene provided to reduce cell size near 56%. In this study, it was asserted that additives which were organic, inorganic or metal powders took a role as nucleation agents to provide decreasing in nucleation energy, and that provided to obtain controlled cell structure. Nucleation mechanisms of cells and growth mechanisms could be hightly affected by fine dimensions and larger surface area of nanosize clay particles. Nanosize particles enchanced contact between clay and polymer matrix.

Also, it was mentioned that in Han et. al.'s study, while clay concentration was being increased, cell density increased. Cell density was related with number of cell nucleation sites.

$$void\ fraction = \frac{volume\ of\ cells}{volume\ of\ foam} \tag{4.1}$$

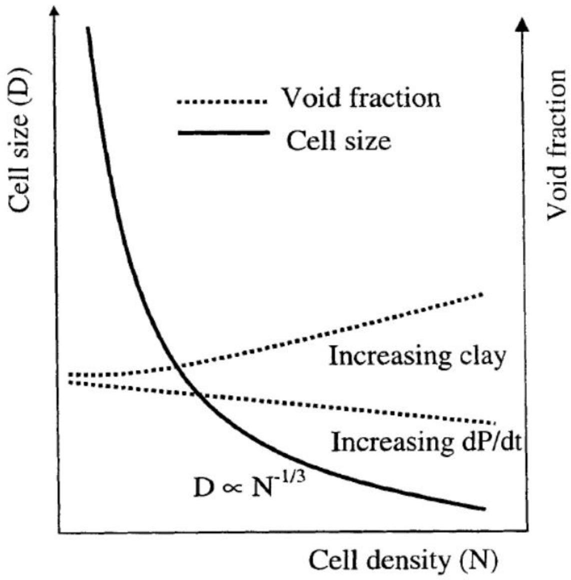
$$= N\left(\frac{cells}{m^3}\right)\frac{4}{3}\pi\left(\frac{D(cm)}{2}\right)^3$$

where;

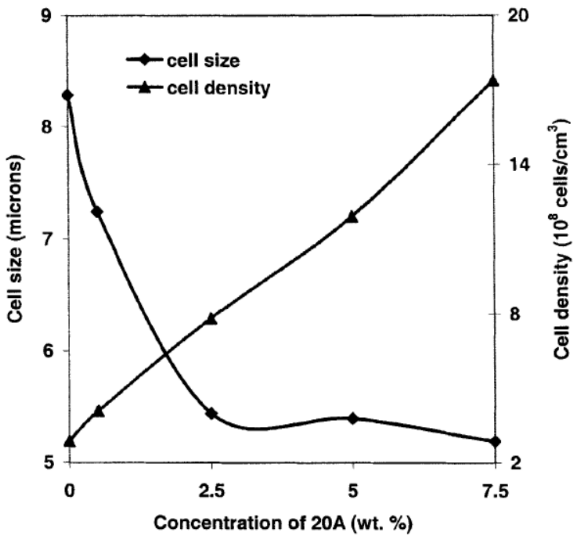
D: Cell diameter/size

N: Cell density-Number of cells per unit (volume)

According to their study, there was a proportional relationship between cell size and $cell\ density^{1/3}$ for a same void fraction.They explained that phenomena with an example: For a constant void fraction 0.6; if it was wanted to reduce cell size from 10 micron to 0.1 micron, cell density had to increase from the degree of 10^9 to 10^{15}. Figure 4.12 shows cell size, number of cells per unite and void fraction trend with the increasing amount of clay.



(a)



(b)

Figure 4.12. *(a) Graphically representation of cell diameter, cell density and void fraction with increasing amount of clay.(b) Cell size-cell density-clay content relationship. (Han et. al., 2005)*

When the cell size trend is investigated in this study, it can be seen that the cell size was decreasing up to certain amount of vermiculite for 1 CEC and 2 CEC modified vermiculite addition. Also, there was a decreasing trend with all additive amount for 3 CEC modified vermiculite. The results for this study was parallel to studies in literature.

First, vermiculite has a platelet structure with high aspect ratio and surface area. Modification with CTAB provides intercalation of plates of vermiculite, and increases compatibility with the medium by increasing level of hydrophobic structure. Intercalation of plates increases surface area that contact with polymer matrix. As mentioned above, every particule in the medium is a site for the heterogeneous nucleation. With the intercalation of layers of vermiculite, hetergeneous nucleation sites increases. Increasing in nucleation sites increases the cell density. It means number of cells in the unit increases. Decreasing cell size with the addition of nanosize vermiculite in this study is compatible with Figure 4.12.

Also, with the intercalation of layers by modify the vermiculite, the viscosity of the medium increases. With the increasing viscosity, the probability of coalescence of the bubbles decreases. (Mondal et. al., 2007) In this study, decreasing in cell size up to certain amount of clay content for 1 CEC and 2 CEC was observed. For 1 CEC, cell size decreased up to 7 wt% vermiculite addition and for 2 CEC up to 5 wt% vermiculite addition. The optimal result was obtained with 5 wt% addition of 2 CEC modified vermiculite. The average decreasing was near 59 %. For 3 CEC modified vermiculite, cell size decreased for all amount of addition. That decreasing in cell size with increasing of clay content, also can be explained with increasing in viscosity and decreasing in mobility of molecules.

Increasing in cell size after 7wt% addition for 1 CEC vermiculite and 5 wt% addition for 2 CEC vermiculite can be explained with non-uniform dispersion of clay in the medium. Also, aggregation might be the reason for increasing in cell size.

4.1.7. Evaluation of close cell content

Open cell size ratio measurements was done with gas picnometer device. Results are given in Table 4.5 and close cell-clay content; CEC ratio graphic is given in Figure 4.13.

Table 4.5. Close cell content results

Sample Code	Close Cell Content (%)
STD PU	90,42
CA11	88,41
CA13	88,64
CA15	90,39
CA17	90,58
CA110	91,23
CA21	90,77
CA23	90,59
CA25	90,99
CA27	92,80
CA210	91,09
CA31	92,49
CA33	91,92
CA35	93,05
CA37	93,12
CA310	90,36

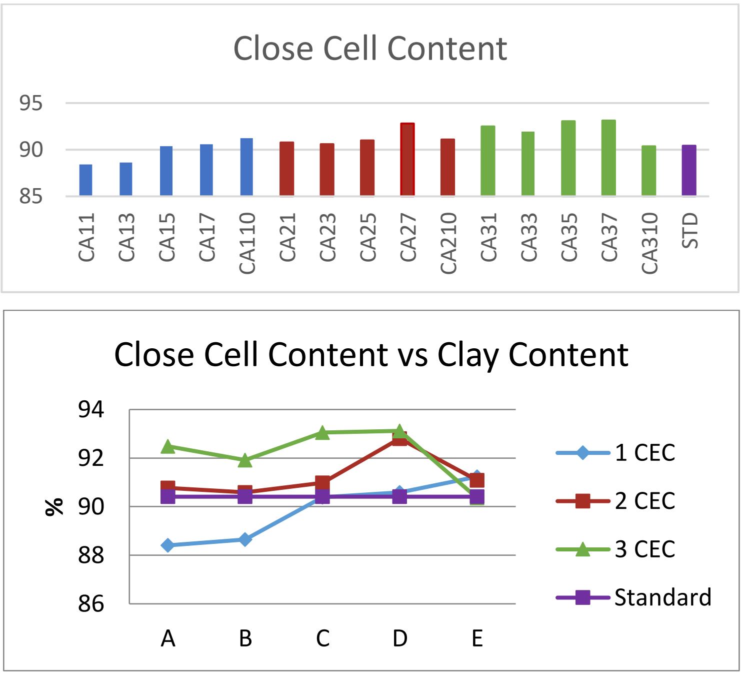


Figure 4.13. *Close cell vs clay content with changin CEC ratios*

Open cell structure is not the desired structure for rigid polyurethane foams that are used for their insulation properties. Becase the gas in the cells diffuse out by time, and diffusion of air into the cells is achieved. This behaviour effects thermal property of rigid polyurethane foams directly. Close cell structure has same importance as cell size of the rigid polyurethane foam.

Kang et. al. investigated three different additives on the closed cell content. According to their study, addition of clay caused reducing in the closed cell content of the rigid polyurethane foam. They asserted the reason for that, fillers (Closite 30B) that was not dispersed uniformly in the medium caused microfillers and these particules interfered the foam morphology while bubble growth. They ruptured the cells and caused negative effect on cell structure. (Kang et. al., 2009, p.860)

However, Patro et. al. conducted a study about vermiculite-nanoclay composites. According to their studies, ratio of close cells increased with the addition of vermiculite. They referred to studies that showed decreasing in close cell content and they explained they mentioned about vermiculite did not rupture the cells in contrast MMT type clays and addition of it did not caused increasing in open cell structure. (Patro et. al., 2008, p.2)

In this study, it was observed that close cell content was increased up to certain addition of vermiculite for 2 CEC and 3 CEC modified vermiculite. For 1 CEC modified vermiculite, close cell content increased with all amount of vermiculite addition.

In rigid polyurethane foams, the closed cell ratios depend on the equivalent weight of the polyol, the surfactant used in the foam formation process and the degree of crosslinking. (Szycher M., 2003)

During the experiments, polyol and surfactants were same for all experiment sets, because of that reason significant increasing in close cell content did not expected. However, addition of 7 wt% of 3 CEC modified vermiculite provided highest close cell content. In the light of that information, it is more accurate to evaluate the decrease in cell size and increasing in close cell content together.

4.1.8. Evaluation of thermal conductivity

The main indicator to determine energy efficiency of rigid polyurethane foam is thermal conductivity coefficient. In this study, effect of different amount of vermiculite addition that modifying with different ratio of CTAB was invastigated.

As mentioned Chapter 1.5., Heat transfer within RPUF dominates three heat transfer mechanism:

(a) Heat transfer in solid phase: Struts and cell walls
(b) Heat transfer in gas phase within the cells: Blowing agent
(c) Radiation

$$\lambda_f = \lambda_m + \lambda_g + \lambda_r \tag{4.1}$$

λ_f= Total thermal conductivity of rigid polyurethane foam

λ_m=Thermal conductivity of the matrix

λ_g=Thermal conductivity of the gas within the foam cells

λ_r=Thermal conductivity with radiation

Thermal conductivity of the matrix was calculated theoretically with the formula below:

$$\lambda_m = \lambda_s \frac{(1-\Pi)}{3}[f_s(\frac{a}{b})^{1/2} + 2(1-f_s)(\frac{a}{b})^{1/4}] \tag{4.2}$$

a and b are the cell diameters that are perpendicular and parallel to the direction of the heat transfer, Π is the porosity, λ_s=205×10-3 W/(mK) (Kabakçı, 2015, p.18)

t is the thickness of the cell wall, d is the cell diameter, $p_s = 1200\ kgm^{-3}$ which is polymer density andρ_f is the density of the foam. According to study of Glicksmann et. al.,it can be assumed that $f_s = 0{,}8$. (Glicksman, 1987, 189).

Pentane was used as blowing agent to prerpare all of the samples. Thermal conductivity coefficient of pentane (λ_g)was 14.60 mW/mK.

And the expression for radiation heat transfer in total heat transfer mechanism:

$$\lambda_r = -\frac{16}{3K^*}\sigma T^3 \tag{4.3}$$

where;

σ = The Stefan-Boltzmann Coefficient (5,667x10-8 W/m^{2}K^4)

K*= The Extinction Coefficient of the Foam (m^{-1})

T = Temperature in Kelvin

The Glicksman Extinction Coefficient (K_G) is as a function of cell diameter, foam density and solid polymer density for an isotropic foam with pentagonal dodecahedral cells:

$$K_G = K_{struts} + K_H K_W \quad (4.4.)$$

$$K_G = 4.10 \frac{\sqrt{f_s \frac{\rho_f}{\rho_s}}}{\emptyset} + (1 - f_s) \frac{\rho_f}{\rho_s} K_W \quad (4.5)$$

where;

∅=Diameter of the cell

ρ_f=Foam Density (kg/m^3)

ρ_s=Solid Density(kg/m^3)

Kw = 60000 m^{-1} is calculated by Glicksman. (Doermann et al.,1996, p. 2)

Theoretical calculations were achieved for thermal conductivity in solid phase and thermal conductivity with radiation by using formulas above. Table 4.5 shows the results of theoretical calculations and experimental results for all samples.

Table 4.6. *Theoretical λm, λg, λr, λf, experimental λf and % difference between theoretical calculations and experimental measurements*

Sample Code	Theoretical λ_m mW/mK	Theoretical λ_g mW/mK	Theoretical λ_r mW/mK	Theoretical λ_f mW/mK	Experimental λ_f mW/mK	Δ (%)
STD PU	3,71	14,60	4,64	22,94	22,5	2,0%
CA11	3,62	14,60	2,94	21,17	21,35	-0,9%
CA13	3,61	14,60	2,96	21,17	21,17	0,0%
CA15	3,63	14,60	2,61	20,84	21,21	-1,7%
CA17	3,55	14,60	2,49	20,64	21,05	-2,0%
CA110	3,61	14,60	3,30	21,51	21,33	0,9%
CA21	3,62	14,60	3,17	21,39	21,34	0,2%
CA23	3,47	14,60	2,22	20,29	20,77	-2,3%
CA25	3,44	14,60	2,15	20,18	20,68	-2,4%
CA27	3,48	14,60	3,06	21,14	20,87	1,3%
CA210	3,47	14,60	2,97	21,04	21	0,2%
CA31	3,62	14,60	3,55	21,77	21,18	2,8%
CA33	3,47	14,60	3,44	21,51	21	2,4%
CA35	3,47	14,60	2,82	20,88	21,01	-0,6%
CA37	3,47	14,60	2,78	20,86	21,07	-1,0%
CA310	3,67	14,60	2,59	20,86	21,7	-3,9%

Also, the graph that shows clay content-CEC ratio and thermal conductivty coefficient is given in Figure 4.14.

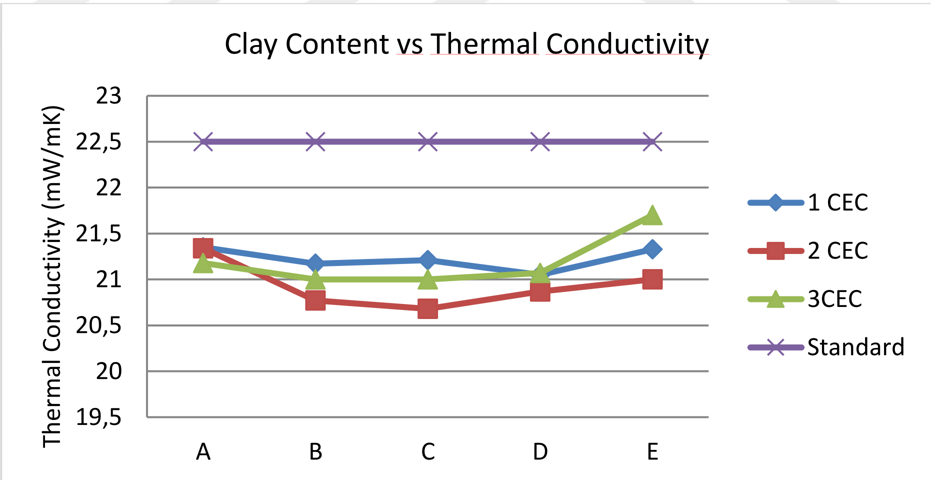


Figure 4.14. *Clay content-CEC Ratio and Thermal .conductivity coefficient change*

The main usage area of rigid polyurethane foams is insulation. The thermal properties of RPUFs are better than thermoplastic foams, generally. Mainly, properties of blowing agent, cell diameter and open/close cell morphology of the RPUFs determine the insulation property of the RPUFs. Because of that reason, decreasing in cell size and increasing in close cell content of the foam are the important subjects to enhance thermal insulation properties of RPUFs.

According to Widya et. al., smaller cell size provided to decrease in thermal conductivity of rigid polyurethane foam and to enhance insulation property. Figure 4.15. shows cell size/thermal conductivity graphs in that study. As mentioned in Section 4.2.1., nanoclays acts nucleation sites in the medium and prevents bubble growth and it provides decreasing in cell size. Smaller cell size provides longer diffusion path. (Widya et. al., 2005, p. 898)

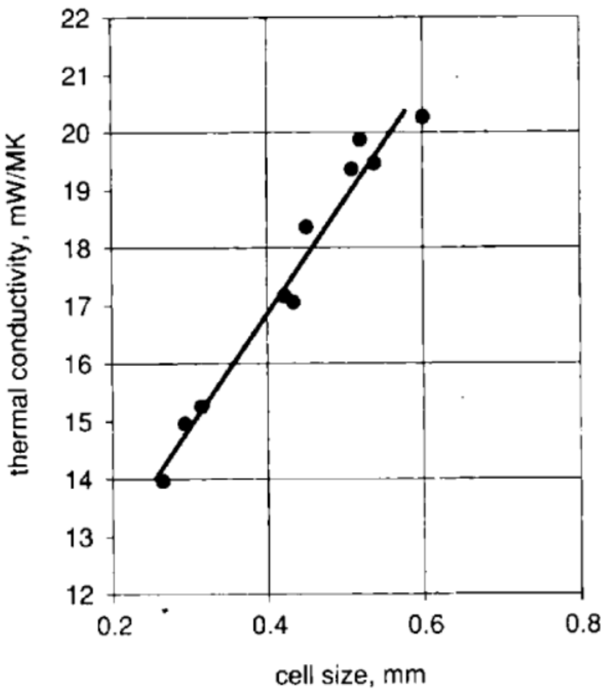


Figure 4.16. *Cell size-thermal conductivity relationship for rigid polyurethane foam.*

(Widya et. al., 2005, p. 898)

Also, Widya et. al. mentioned about that nanofillers acted as diffusion barriers in the medium. Because of their high aspect ratio, they were expected to decrease permeability of the cells. In that study, it was explained with theoretical Nielsen model for gas diffusion for a polymer film that includes dispersed high aspect ratio disks. It was assumed that clay platelets were perpendiuclar to the diffusion direction. The reason for perpendicular direction was cell window drainage while bubble growing step. Because of perpendiuclar orientation of platelets to the diffusion direction, there occurs a tortuosity in the diffiusion path and platelets became diffusion barriers. Figure 4.15 shows theroretical Nielsen Model. (Widya et. al., 2005, p. 906)

As mentioned before in Section 1.5., according to Ball et.al study, heat transfer with radiation is proved with linear variation of cell size and heat transfer with conduction and convection in solid and gas phase should not be depend on cell size of the polyurethane foam. In this study, theoretical calculations showed that improvement of thermal conductivity in solid phase was 7% while improvement in thermal conductivity with radiation was 54% for optimal results that was obtained with 2 CEC modified vermiculite addition by 5% wt. Also, difference between theoretical calculation for thermal conductivity and experimental thermal conductivity measurement for the smallest thermal conductivity of foam was 2.4%. It can be said that addition of modified vermiculite provided decreasing in cell size and it provided reducing in heat transfer with radiation with this study.

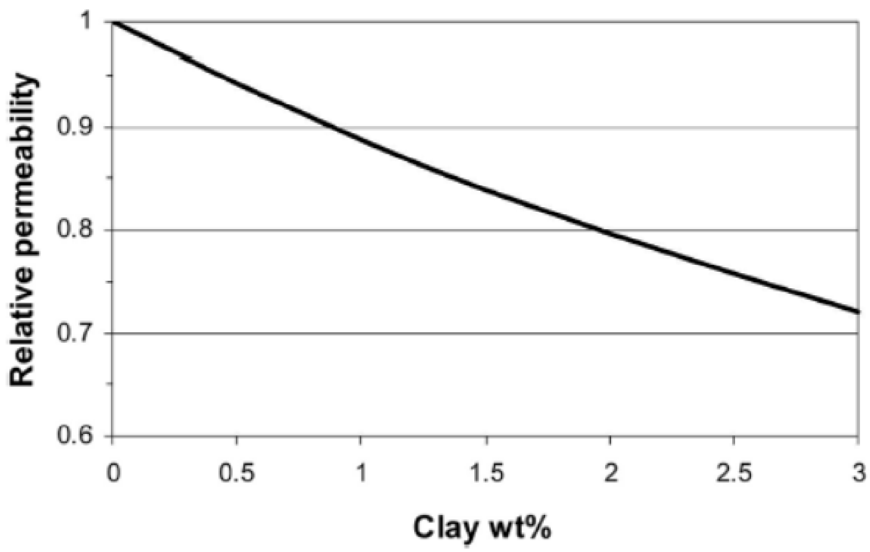


Figure 4.15. *Theoretical Nielsen Model for gas diffusion-clay content relationship. (Widya et. al., 2005, p. 906)*

Patro et al. studied the changes in reaction kinetics and. rheology changes by adding vermiculite into the polyol. Figure 4.16 shows viscosity change of polyol by adding vermiculite.

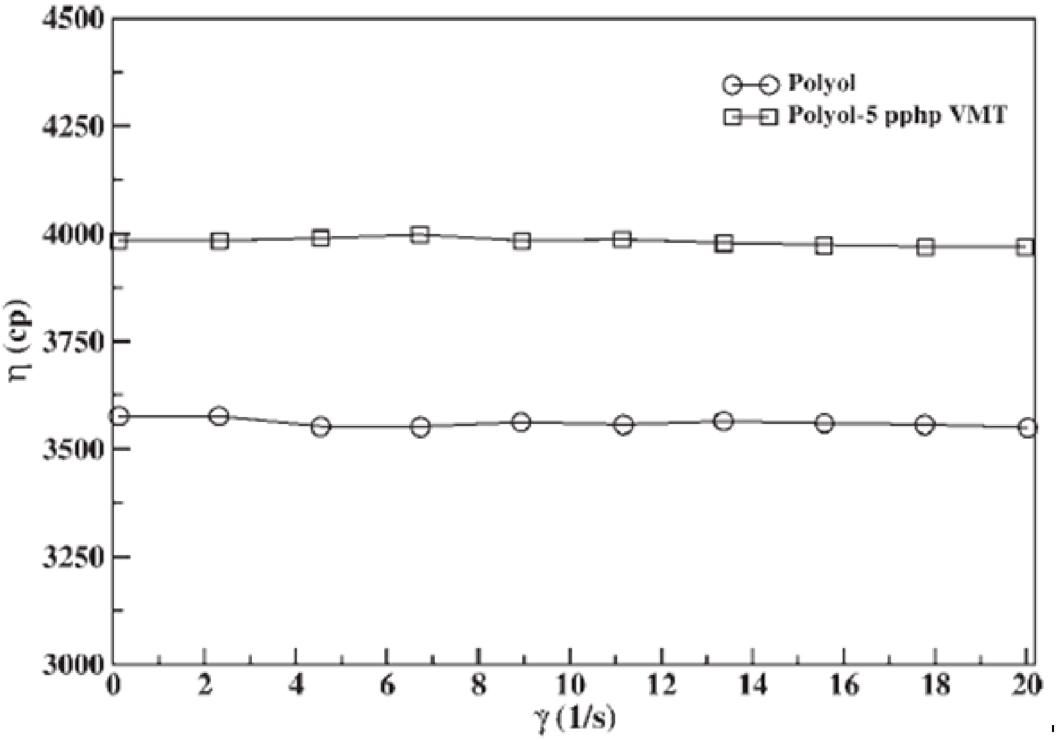


Figure 4.16. *Viscosity change in polyol with the addition of 5 wt% vermiculite (Patro et. al., 2008, p.1780)*

The addition of vermiculite resulted in an increase in the viscosity of the polyol. The increase was about 10%. Despite the increase in viscosity with vermiculite addition, the structure continued to behave in a Newtonian way when evaluated as the behavior with shear stress. However, when montmorillonite clays are used, the structure passes from the Newtonian Shear Thinning behavior. That viscosity behaviour had directly affects on the cell morphology of rigid polyurethane foam. In that study, it was observed that thermal conductivity decreased, cell size decreased and closed cell ratio increased with nanosize vermiculite addition. The decrease in thermal conductivity was evaluated to result from decrease in cell sizes. *(Patro et. al., 2008)*

In this study, thermal conductivity of standard rigid polyurethane foam that had no nano additive was 22.5 mW/mK. Addition of 1 CEC modified vemiculite provived to reduce thermal conductivity till 7 w% addition, up to that point it was observed increasing in thermal conductivity coefficient. Addition of 2 CEC modified vermiculite provided to reduce thermal conductivity till 5 wt% percent and up to that point thermal conductivity of rigid polyurethane foam started to increase. For 3 CEC modified vermiculite addition, the optimal result was obtained with 1 wt% addition of vermiculite.

Overall, the lowest thermal conductivity was obtained with 2 CEC modified vermiculite with 5 wt% addition. To evaluate effect of CEC ratio and addition of vermiculite content, it is better to investigate both cell size and close cell structure. Figure 4.17 shows the graphics of thermal conductivity, cell size and close cell ratio that are function of clay content-CEC ratio.

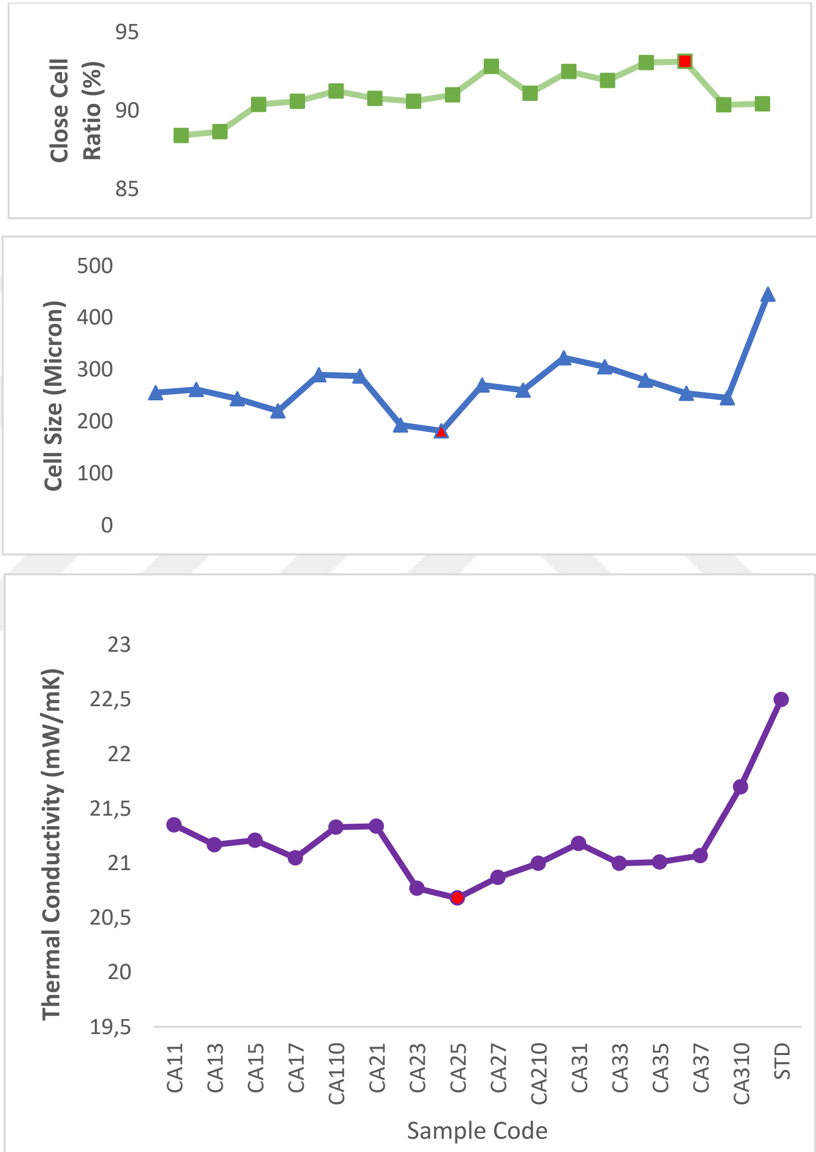


Figure 4.17. *Thermal Conductivity, Cell Size and Close Cell Content by a function of clay content with different modification ratios.*

According to Figure 4.17, optimal result obtained with preparation of rigid polyurethane-nanoclay composite by 5 wt% addition of 2 CEC modified vermiculite into polyol. The smallest cell size obtained with 5 wt% addition. That results are paralell to the studies in the literature.

4.1.9. Evaluation of compressive strength

Rigid polyurethane foams are like skeleton systems for refrigerators. They provides rigidity. Because of that reason, it is not to be desired situtaion that decreasing in compressive strength of the polyurethane foam. Compressive strength measurement results are given in Table 4.7.

Table 4.7. *Compressive strength measurement results*

Sample Code	Compressive Strength (kPa)
STD PU	175,00
CA11	137,50
CA13	135,00
CA15	165,00
CA17	140,00
CA110	132,00
CA21	125,67
CA23	126,00
CA25	116,00
CA27	125,33
CA210	121,00
CA31	117,67
CA33	134,00
CA35	153,00
CA37	198,00
CA310	132,67

Also, the graphic that shows clay content-CEC ratio and compressive strength is given in Figure 4.18.

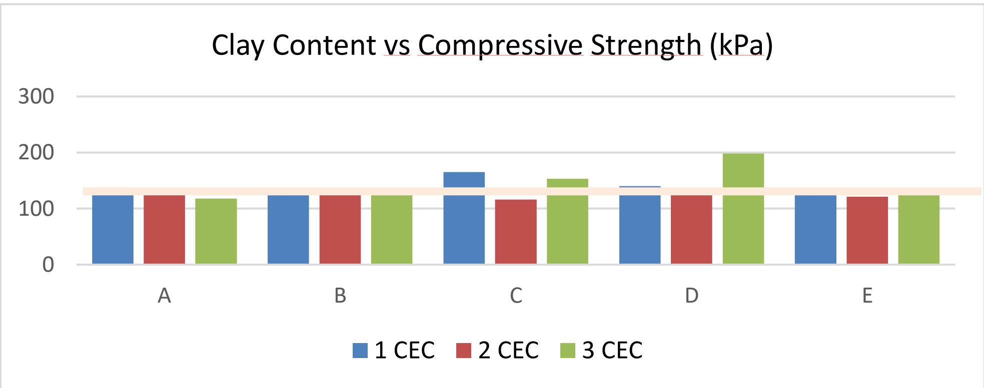


Figure 4.18. *Clay content-CEC Ratio-Thermal Conductivity*

The increase in viscosity by dispersing the nanoclay additive in the polyol during the foam formation process leads to the formation of higher density foams. On the other hand, it is known that one of the most important parameters affecting the mechanical properties of the foams is the foam density. An increase in compressive strength with clay additive is generally expected. However, it is also known that the presence of clays prevents the formation of hydrogen bonds between the urethane groups which contribute positively to the mechanical properties of the polyurethane. Consequently, it can be said that the mechanical performance of the polyurethane foams is determined by the competition between the positive effect of increasing density with the clay additive and the negative effect caused by the inhibition of hydrogen bond formation.

In the study that belongs Kang et. al., additive content and compressive strength relationship was investigated by considering density of the foam. According to that study, when the clay content increased, compressive strength of the polyurethane foam increased. Figure 4.20. shows compressive strength and additive content relationship in Kang et. al.'s study.

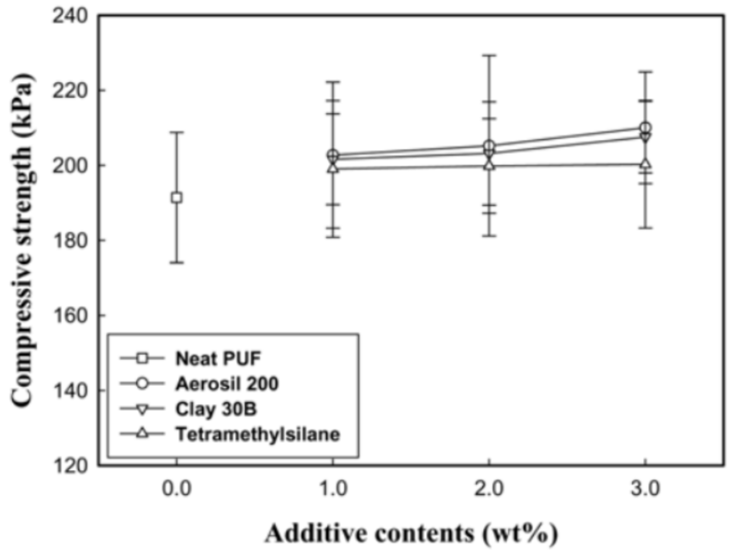


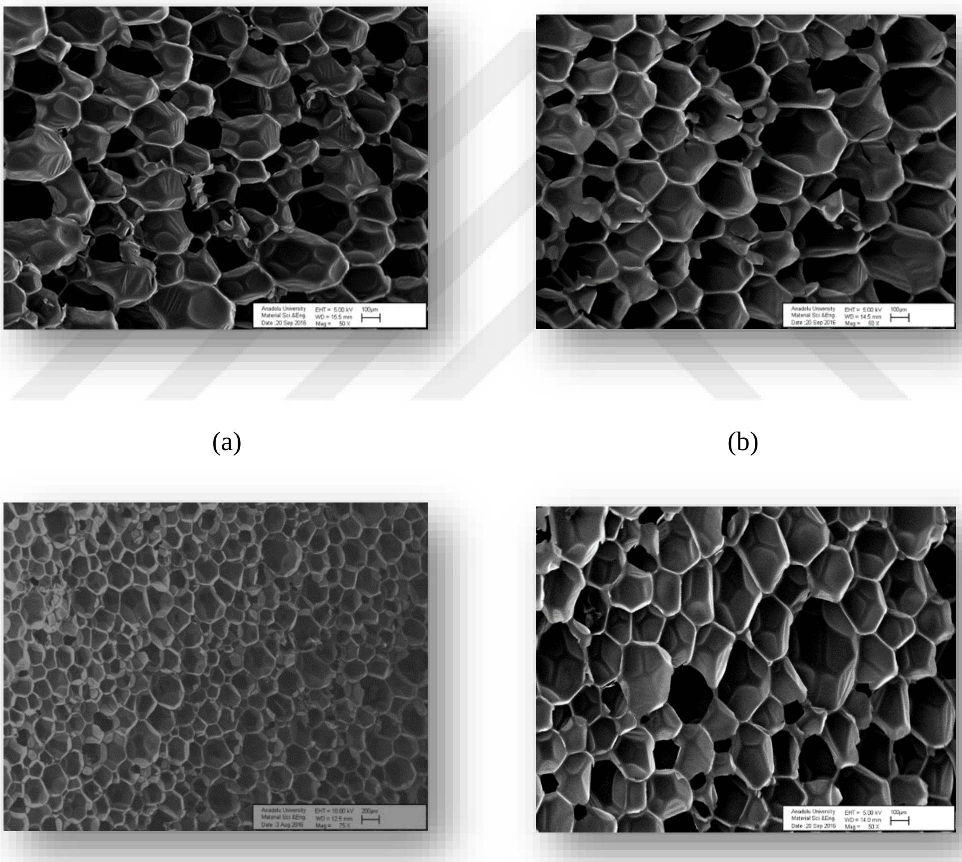
Figure 4.19. *Compressive strength of RPUF related to different additives. (Kang et. al., 2009, p.860)*

Another study that mentioned about mechanical properties of rigid polyurethane foam nanoclay composites was conducted Patro et. al. According to their study, compressive strength increased with the increasing clay content. Nanosize vermiculite provide reinforcement to struts of the rigid polyurethane foam. The reason of small decreasing with the higher additive amounts was explained agglomeration of clay layers.

In this study, the highest compressive strength was obtained with 3 CEC modified 7 wt% vermiculite additive. The highest value for compressive strength was 198 kPa. The limit in the industry for copmression strength is 120 kPa. In this study, none of samples were not under that value. Figure 4.19. shows graphics of compressive strength with vermiculite content.

4.1.10. Evaluation of cell structure

To investigate cell morphology, scanning electron microscope was used. With SEM, the structure of cell walls, struts, damaged cells were investigated. The SEM images that shows standard PU, CA15, CA25 and CA35 samples are given in Figure 4.14.



(a) (b)

(c) (d)

Figure 4.20. *SEM images of 5wt% vermiculite added rigid polyurethane foam (a) Neat (b) 1CEC (c) 2 CEC (d) 3 CEC*

In this study, average cell size measurement was conducted by stereo microscope (Section 4.2.1.) SEM images also shows cell size of the foams. It can be see that the smallest cell size among them was 5 wt% addition of 2 CEC vermiculite.

Also, the cell size distirubition of 2 CEC modified vermiculite added rigid polyurethane foam was more uniform then others. As mentioned before open cell structure is highly depends on polyol and surfactant. The main raw materials are the same for all foam samples, because of that reason there is no significant difference between them.

5. CONCLUSION

The objective of this research was to develop rigid polyurethane foams with lower thermal conductivity wit desired mechanical properties. For this purpose, first vermiculite was modified CTAB to intercalate the interlayers. 1 CEC, 2 CEC and 3 CEC ratios were used to investigate effect of modification ratio. And to producre nanoclay polyurethane composite, different amount of vermiculites that had nanosize particles which modified 1, 2, and 3 CEC were added into polyol. To characterize clay and its modification, TGA, XRD, FT IR and contact angle measurement methods were used. To characterize nanoclay rigid polyurethane foam composite, cell size measurement, open-close cell measurement, thermal conductivity measurement and cell morphology investigation was conducted.

The summarize for the results are given below:

- To intercalation of vermiculite interlayers, three different ratios of CTAB were used; 1 CEC, 2 CEC and 3 CEC. The highest interlayer distance was obtained with 2 CEC, 10,4Å.
- The optimal results for cell size was obtained with 5 wt% addition of 2 CEC vermiculite. The cell size reduced from 445 micron to 182 micron. The average cell size reduction was near 59 %.
- The highest close cell content was obtained with 7 wt% addition of 3 CEC modified vermiculite. Close cell content increased from 90,4% to 93,1%. The average increasing in close cell structure was near 2,9%
- All amount of vermiculite which modified with different CTAB ratio provided to decrease in thermal conductivity of rigid polyurethane foam.
- The lowest thermal conductivity was obtained with the addition of 5 wt%, 2 CEC modified vermiculite. Thermal conductivity decreased from 22,5 mW/mK to 20,68 mW/mK. The average reduction in thermal conductivity was 8,08%.
- With the decreasing in cell size, theoretical heat transfer with radiation was improved. Thermal conductivity with radiation decreased from 4.64 mW/mK to 2.15 mW/mK.
- None of the samples were under the limit of 120 kPa for compressive strength.
- The highest compressive strength was obtained with the addition of 7 wt% 3 CEC modified vermiculite. Compressive strength increased from 175 kPa to 198 kPa. The average increasing in compressive strength was 13%

With this study, it was explained that preparing rigid polyurethane foam-nanoclay composite with vermiculite that had nanosize particles provided to enchance both thermal and mechanical properties of the rigid polyurethane foam.

For future works;

- Different modifying agents can be used to intercalate/exfoliate the layers of vermiculite.
- Experiments can be achieved with reaction injection molding instead of lab.scale production.
- Reaction kinetics can be investigate with the addition of vermiculite by producing in reaction injection molding.

REFERENCES

Aneja A. (2002). *Structure-Property Relationships of Flexible Polyurethane Foams,* Published Doctoral Disertation, Virginia: Virginia Polytechnic Institute and State University

Ashida K., (2007), *Polyurethane and Related Foams*, New York: Taylor &Francis

Austin A., Hicks D., (2017). A review of the global PU industry in 2016 and outlook for 2017, *PU Magazine,* 3-4

Avalle, M., Belingardi, G. ve Ibba, A.,(2007). Mechanical models of cellular solids, parameters identification from experimental tests, *International Journal of Impact Engineering*, 34, p. 4

Bora A.V., (1998). Recent Developments in Polyurethanes. Published Master of Science Dissertation, Massachusetts: University of Massachusetts Lowell, Department of Plastics Engineering

Doermann D., Sacadura J.F., (1996). Heat Transfer in Open Cell Foam Insulation, Int. J. Heat Mass Transfer,118, p.88-93

Ebert, H.P. (2015). Functional materials for energy-efficient buildings, *EDP Sciences*, 2

Erdem B., (2010). Heterohalkalı Aromatik Bileşiklerin Doğal Killere Adsorpsiyonun İncelenmesi. Doctoral Disertation, Anadolu University, Graduated School of Science.

Estravís S., Mediavilla J. T., Santiago-Calvo M., Herrero J.L.R., Villafañe F., Pérez M.A.R.,(2016). Rigid polyurethane foams with infused nanoclays: Relationshi between cellular structure and thermal conductivity. European Polymer Journal, 80(2016), 1-15

Estravís S., Mediavilla J. T., Calvo M.S., Herrero J.L.R., Villafañe F., Pérez M.A.R., (2016). Rigid polyurethane foams with infused nanoclays: Relationship between cellular structure and thermal conductivity, Eurpean Polymer Journal, 2

Folorunso O.,(2015). Microwave Processing of Vermiculite. Doctoral Disertation, University of Nottingham, Energy and Sustainability Research Division, Faculty of Engineering

Grünbauer H.J.M., Bicerano J, Clavel P., Daussin R.D., de Vos H.A.,Elwell M.J., Kawabata H, Kramer H., Latham D.D.,. Martin C.A, Moore S.E., Obi B.C, Parenti V., Schrock A.K., and van den Bosch R., (2004) Rigid Polyurethane Foams. S.T. Lee, N.S. Ramesh (Eds), Polymeric Foams (p. 275), CRC Press LLC: USA, Washington D.C.

Gama N.V., Ferreira A., Timmons A.B., (2018). Polyurethane Foams: Past, Present, and Future, Materials, 3

Glicksman, L.R., Methods to enhance the insulating values of closed-cell foam, Massachusetts Institute of Technology.

http-1:https://www.iea.org/weo2018/ (Date: 21.06.2019)

http-2:https://www.iea.org/tcep/buildings/appliances/ (Date: 21.06.2019)

http-3:http://www.polyurethanes.org/en/what-is-it/timeline (Date: 21.06.2019)

http-4:http://www.plasticsinsight.com/resin-intelligence/resin-prices/polyurethane/

(Date: 21.06.2019)

http-5: http://soft-matter.seas.harvard.edu/index.php/Nucleation (Date: 10.07.2019)

http-6: http://www.columbia.edu/~vjd1/minerals.htm (Date: 27.07.2019)

http-7: https://www.mindat.org/min-4170.html (Date: 29.07.2019)

http-8:https://www.setaram.com (Date: 02.08.2019)

http-9:https://www.hutton.ac.uk/research/groups/environmental-andbiochemical-sciences/analysis-equipment/chemical (Date: 02.08.2019)

http-10:https://www.rigaku.com/ (Date: 02.08.2019)

http-11:https://www.kruss-scientific.com (Date: 02.08.2019)

http-12:https://www.tainstruments.com/fox-314/ (Date: 02.08.2019)

http-13:https://hitechtrader.com/micromeritics-accupyc-1330

(Date: 02.08.2019)

http-14:https://www.olympus-ims.com/en/microscope/szx/

(Date: 02.08.2019)

http-15:http://www.directindustry.com/prod/zwickroell-gmbh-co-kg/product-15660-2089889.html (Date: 02.08.2019)

http-16:http://www.speciation.net/Database/Instruments/Carl-Zeiss-AG/EVO-50-Series-;i663 (Date: 02.08.2019)

http-17:https://www.britannica.com/technology/scanning-electron-microscope

(Date: 02.08.2019)

Hoogendoorn C.J., (1994). Thermal Aging. A. Cunningham, Hilyard N.C., (Ed), Low Density Cellular Plastics-Physical Basis of Behaviour (p. 154), Springer: Netherlands

Howson, A. ve Tucker, M., (2005). Automatic gas pycnometer for the characterisation of rigid foams, Urethanes Technology

Ionescu M., (2016), Chemistry and Technology of Polyols for Polyurethanes (2nd Edition), United Kingdom: Smithers

Jlassi K., Chehimi M.M., Thomas S., (2017). Overview: Clay Preparation, Properties,Modification. Clay-Polymer Nanocomposites, Elsevier, 23

Karakeçili A.,(2018). Termal Analizler-1 Lecture Notes, Ankara University

Kang W.J. Kim J.M., Kim. M.S., Kim Y. H., Kim W.N., (2009). Effects of Nucleating Agents on the Morphological, Mechanical and Thermal Insulating Properties of Rigid Polyurethane Foams. Macromolecular Research, 17(11), 856-862

Kıranşan M., Soltani R.D.C., Hassani A., Karaca S., Khataee A., (2014). Preparation of cetyltrimethylammonium bromide modified montmorillonite nanomaterial for adsorption of a textile dye, Journal of the Taiwan Institute of Chemical Engineers, 45

Landrock, A. H. (1995). Handbook of plastic foams: Types, properties, manufacture and applications. Elsevier.

Lee, S. T. and Ramesh, N. S. (2004). Polymeric foams: Mechanisms and materials. CRC press.

Li T.T., Chuang Y.C., Lou C.W., Lin J. H., (2015). Applying Vermiculite and Perlite Fillers to Sound Absorbing/Thermal-Insulating Resilient PU Foam Composites. Fibers and Polymers, 16(3), 691-698

Mondal P., Khakhar D.V., (2005). Rigid Polyurethane–Clay Nanocomposite Foams:Preparation and Properties. Journal of Applied Polymer Science, 103, 2802–2809

Patel D.K., Mahanta A.K., Maiti P., (2017) Polyurethane Nanocomposites of Layered Silicates, Polyurethane Polymers: Composites and Nanocomposites. Elsevier. p.175

Patro U.T., Harikrishnan G., Misra A., Khakhrar D.V., (2008). Formation and Characterization of Polyurethane—Vermiculite Clay Nanocomposite Foams, Polymer Engineering and Science

Qian Y., Liu W., Park Y.T., Lindsay C.I., Camargo R., Macosko C.W., Stein A., (2012). Modification with tertiary amine catalysts improves vermiculite dispersion in polyurethane via in situ intercalative polymerization. Polymer, 53(2012), 5060-5068.

Ray S.S. (2013). Clay-Containing Polymer Nanocomposites: From Fundamentals to Real Applications. Elsevier:Netherlands

Ridha, M. (2007). Mechanical and failure properties of rigid polyurethane foam undertension, Doctoral Dissertation, National University of Singapore, Mechanical Engineering.

Saha M.C., Kabir M.E., Jeelani S.,(2008). Enhancement in thermal and mechanical properties of polyurethane foam infused with nanoparticles. Materials Science & Engineering, 479(2008), 213-222

Sonnenschein, M. F. (2014). Polyurethanes: Science, technology, markets, and trends (Vol. 11). John Wiley&Sons.

Sözbir, N., (2014). Isı iletim katsayısının belirlenmesi deneyi, Makina Mühendisliği Laboratuarı II Dersi, Sakarya

Szycher M., (2013) Szycher's Handbook of Polyurethanes Second Edition, New York: CRC Press

Valapa R.B., Loganathan S., Pugazhenthi G., Thomas S., Varghese S.O., (2017). An Overview of Polymer- Clay Nanocomposites, Clay-Polymer Nanocomposites. p.31-32. Elsevier:Netherlands

Valášková M., Martynková G. S., (2012). Vermiculite: Structural Properties and Examples of the Use, Clay Minerals in Nature – Their Characterization, Modification and Application, InTech.Open. p. 210

Verdolotti L., Di Caprio M.R., Lavorgna M., Buonocore G. G., (2017). Polyurethane Nanocomposite Foams: Correlation Between Nanofillers, Porous Morphology, and Structural and Functional Properties S.Thomas, J. Datta, J. Haponiuk, A. Reghunadhan (Editors). Polyurethane Polymers: Composites and Nanocomposites First Edition, USA: Elsevier

Widya T., Macosko C.W., (2005). Nanoclay-Modified Rigid Polyurethane Foam. Journal of Macromolecular Science, 44, 897-908

Wu N., Wu L., Liao L., Lv G., (2015). Organic intercalation of structure modified vermiculite. Journal of Colloid and Interface Science, 457(2015), 257-271

Zafar F., Sharmin E., (2012), Polyurethane, Crotia: Intech

Zang X., (1998). Role of Silicone Surfactant in Polyurethane Foaming Process, Published Doctoral Disertation, Minnesota: University of Minnesota

Zimmermann, J.P., Evans, M., ,Griggs, J., King, N., Harding, L., Roberts, P., Evans, C. (2012).IntertekreportR66141—Household Electricity Survey A Study of Domestic Electrical Productusage, Intertek, 242

CIRRICULUM VITAE

Name Surname : Ceren IRMAK KARAMEŞE

Foreign Language : English

Birth Date and Place : Çankırı/1991

E-Mail : cerenirmakk@gmail.com

Education and Professional Background:

- 2015, Anadolu University, Faculty of Engineering, Materials Science and Engineering
- 2015, Anadolu University, Faculty of Engineering, Industrial Engineering
- 2015, Process Speacilist, Eskisehir Arcelik Refrigerator Plant, Department of Prodcuting Engineering

National / International Presentations / Posters:

- Irmak, C., Suvacı, E., Erdem, M., Uysal, O., Sayer, G., Kaya, M. and *Akdoğan, E.* "Effect of Phyllosilicate Type Organoclay Addition on The Properties of RigidPolyurethane Foam" Polyurethane Technical Conference, Baltimore, Maryland USA, September 2016