T.R.
ONDOKUZ MAYIS UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF NANOSCIENCE AND NANOTECHNOLOGY

THE EFFECTS OF SILVER-MODIFIED NANOCLAYS ON THERMAL, MECHANICAL AND ANTIBACTERIAL PROPERTIES OF POLYURETHANE RIGID FOAMS

Master Thesis

Nsaem Abdulmajood Ahmed ALBOBADRAN

Supervisor

Prof. Dr. Engin BURGAZ

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ACCEPTANCE AND APPROVAL OF THE THESIS

The study entitled **"THE EFFECTS OF SILVER-MODIFIED NANOCLAYS ON THERMAL, MECHANICAL AND ANTIBACTERIAL PROPERTIES OF POLYURETHANE RIGID FOAMS"** prepared by **Nsaem ALBOBADRAN** and supervised by. **Prof Dr. Engin BURGAZ** was found successful and unanimously accepted by committee members as a Master's Thesis of the Department of Nanoscience and Nanotechnology, following the examination on the date 04 /07/ 2022.

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Chairman	Assoc. Prof. Dr. Bekir DIZMAN Sabancı University İntegrated Manufacturing Technologies Research and Application Center		☒Accept ☐ Reject
Member	Prof. Dr. Ömer ANDAÇ Ondokuz Mayıs University Department of Chemistry		☒Accept ☐ Reject
Member	Prof. Dr. Engin BURGAZ Ondokuz Mayıs University Department of Metallurgical and Materials Engineering		☒Accept ☐ Reject

This thesis has been approved by the committee members that already stated above and determined by the Institute Executive Board.

APPROVAL
… / … / …
Prof. Dr. Ali BOLAT
Head of Institute of Graduate Studies

DECLARATION OF COMPLIANCE WITH SCIENTIFIC ETHIC

I hereby declare and undertake that I complied with scientific ethics and academic rules in all stages of my master thesis, that I have referred to each quotation that I use directly or indirectly in the study and that the works I have used consist of those shown in the sources, that it was written in accordance with the institute writing guide and that the situations stated in the article 3, section 9 of the Regulation for TÜBİTAK Research and Publication Ethics Board were not violated.

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DECLARATION OF THE THESIS STUDY ORIGINALITY REPORT

Thesis Title: THE EFFECTS OF SILVER-MODIFIED NANOCLAYS ON THERMAL, MECHANICAL AND ANTIBACTERIAL PROPERTIES OF POLYURETHANE RIGID FOAMS.

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ÖZET

GÜMÜŞ İLE MODİFİYE EDİLMİŞ NANOKİLLERİN POLİÜRETAN SERT KÖPÜKLERDEKİ ISISAL, MEKANİK VE ANTİBAKTERİYEL ÖZELLİKLERE ETKİLERİ

Nsaem ALBOBADRAN
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Nanobilim ve Nanoteknoloji Anabilim Dalı
Yüksek Lisans, Haziran /2022
Danışman: Prof. Dr. Engin BURGAZ

Bu çalışmada, rijit Poliüretan köpükler (PURF'ler) (Cloisite 30B, sodyum montmorillonite Na MMT) modifiye edilmemiş nanokil ve (Gümüş modifiye montmorillonit kil Ag MMT, Gümüş modifiye kloisit-30B kil Ag 30B) nanokil ile sentezlenmiştir.

Önce ağırlıkça %1 kil izosiyanat (PMDI) içinde ultrasonik olarak dağıtıldı, ardından izosiyanat karışımı polyol, katalizör ve şişirme maddesi ile mekanik olarak karıştırılarak RPUF köpük numuneleri elde edildi. Hazırlanan PURF numuneleri, Yoğunluk Ölçümü testi, X-ışını kırınımı (XRD), Fourier transfer kızılötesi spektroskopisi (FTIR) analizi, mekanik test, Taramalı Elektron Mikroskobu (SEM), termal iletkenlik testi gibi farklı özelliklerle test edilmiştir, termogravimetrik analiz (TGA) karakterizasyon yöntemleri ve antibakteriyel özellik testleri disk difüzyon yöntemi kullanılarak yapılmıştır.

Poliüretan köpüklerin fonksiyonel grupları FTIR ile belirlendi. FT-IR'deki üretan zincirinde bulunan karbonil (C=O) ve amin (N-H) gruplarının pikleri poliüretan oluşumunu teyit eder. Poliüretan sert köpük RPUF numunelerinin mekanik özellikleri basma testi ile incelenmiştir. Ağırlıkça % 1 kil içeren numunede basınç dayanımı ve basınç modülünde hiçbir gelişme görülmemiştir. Köpük numunelerinin termal özellikleri, termal iletkenlik katsayısı k-faktörü ile incelenmiştir. Köpük örneklerinin SEM görüntüleri, modifiye edilmemiş ve modifiye edilmiş nanokil ilavesinin ortalama hücre boyutunu sırasıyla % 6 ve % 22 oranında azalttığını ve köpüklerin hücre yoğunluğunu arttırdığını göstermiştir. köpük numunelerin çevresinde hiçbir inhibisyon bölgesi oluşmadığı için seçilen patojenik mikroorganizmalara karşı herhangi bir antibakteriyel özellik gözlenmemiştir.

Anahtar Kelimeler: poliüretan sert köpük, nanokil, termal iletkenlik, antibakteriyel, mekanik özellikler.

ABSTRACT

THE EFFECTS OF SILVER-MODIFIED NANOCLAYS ON THERMAL, MECHANICAL AND ANTIBACTERIAL PROPERTIES OF POLYURETHANE RIGID FOAMS

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Master, June /2022
Supervisor: Prof. Dr. Engin BURGAZ

In this study, rigid Polyurethane foams (PURFs) were synthesized with (Cloisite 30B, sodium montmorillonite Na MMT) unmodified nanoclay and (Silver modified montmorillonites clay Ag MMT, Silver modified cloisite-30B clay Ag 30B) nanoclay.

Firstly 1wt.% clay was dispersed in the isocyanate (PMDI) ultrasonically, then mixed with a polyol, catalyst, and blowing agent mixture by mechanically stirred to produce foams samples. Prepared samples of PURFs were tested with different characterization such as Density Measuring test, X-ray diffraction (XRD), Fourier transfer infrared spectroscopy (FTIR) analysis, mechanical test, Scanning Electron Microscopy (SEM), thermal conductivity test, thermogravimetric analysis (TGA) characterization methods, and antibacterial properties tests were performed by using the disc diffusion method.

Functional groups of polyurethane foams were determined by FTIR. Peaks of carbonyl (C=O) and amine (N-H) groups of urethane chain in FT-IR confirm the formation of polyurethane. The mechanical properties of rigid polyurethane foam RPUFs samples were tested by compression test. At 1 wt. % clay, there are no compressive strength and compressive modulus improvements. Thermal properties of foam samples were investigated by thermal conductivity coefficient k-factor. The SEM images of the foam samples showed that the addition of unmodified and modified nanoclay reduced the average cell size by 6 % and 22 %, respectively, and increased the cell density of foams. Results show no antibacterial effect against the selected pathogenic microorganisms, as there was no inhibition zone around the foam samples.

Keywords: rigid polyurethane foam, nanoclay, thermal conductivity, antibacterial, mechanical properties.

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Nsaem ALBOBADRAN

CONTENTS

SYMBOLS AND ABBREVIATION

PMDI : Polymeric 4, 4-di-phenylmethane diisocyanate

PU : polyurethane

RPUFs : Rigid polyurethane foams

SEM : Scanning Electron Microscopy

XRD : X-ray diffraction

T_d : Decomposition Temperature

FTIR : Fourier Transform Infrared Spectroscopy

TGA : Thermogravimetric Analysis

FIGURES LEGENDS

TABLES LEGENDS

1. INTRODUCTION

1.1. Polyurethanes

Polyurethanes are one of the important groups of polymeric materials. These super properties make them suitable for a different range of applications. Also, they have excellent mechanical properties, resilience, and chemical resistance. The presence of reactive functions in the main chain of polyurethane increases its compatibility with some polymers, so it is suitable for forming networked structures. The chemical bond contained in the polymer is referred to as urethane [-NH-CO-O-] and is the most reactive part of polyurethane. Depending on the starting material, the final product differs in its nature, applications, and properties. The first synthesis was in 1937 by the brilliant German chemist Professor Otto Bayer through a multi-antibody reaction. (Engels et al. 2013; Kraitape and Thongpin 2016; Sharmin and Zafar 2012).

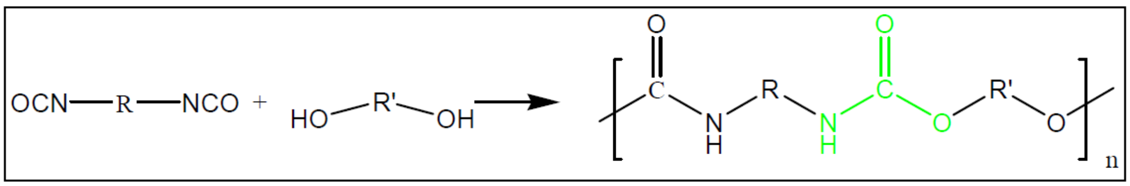

Figure 1.1. Chemical structure of polyurethane (Sharmin and Zafar 2012).

Polyurethane has urethane linkages and can be prepared by the reaction between polyols and isocyanates.(Kraitape and Thongpin 2016).

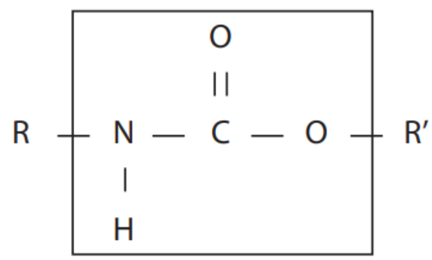

Figure 1.2. Urethane linkage (Szycher et al. 2012).

1.2. Polyurethane foams

Polyurethane foams are widely used in applications primarily in the fields of insulation and packaging. We can find polymeric foams everywhere with their useful properties. Polyurethane foams are an important classification of polymeric foams. Polyurethane foam (PUF) can be classified as flexible polyurethane foam (open-cell) and rigid polyurethane foam (RPUFs) (closed-cell) (Madaleno et al., 2013; Verdolotti et al.,2007).

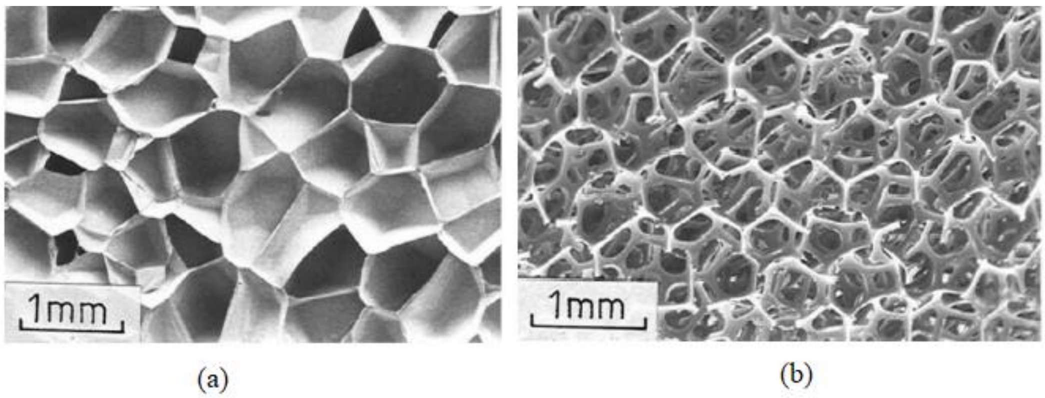

Figure 1.3. Cellular structures (a) closed-cell foam and (b) open-cell foam (Gibson and Editor 2003)

1.2.1. Flexible Polyurethane Foams

Polyurethane flexible foams are the most used in our life due to their multiple advantages in terms of ease of production, durability, longevity, and versatility (Engels et al. 2013).

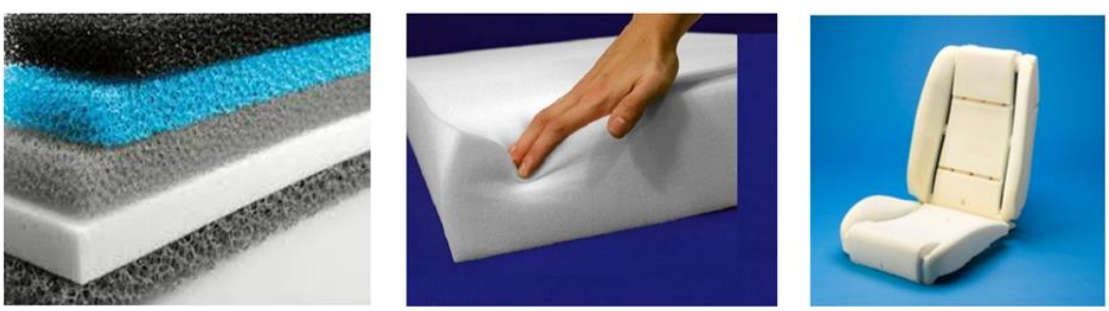

Figure 1.4. Flexible polyurethane foam applications are used in our daily life (Anonymous, 2021a).

In the global polyurethane market, flexible polyurethane foam is the largest market among all polyurethane foam products. They are used in a variety of commercial applications like car seating, comfort cushioning, and sound-absorbing material, in the automotive industry, and in many other important materials used in our daily life (Lefebvre et al. 2005).

1.2.2. Rigid Polyurethane Foams

Rigid polyurethane foams (RPUFs) are one of the most polymeric materials used to a great extent, due to their outstanding performance in thermal insulation, low density, shock, and sound-absorbing properties despite their lightweight. These properties make it desirable in various engineering applications (Nasirzadeh and Sabet 2014; Tan et al. 2011).

Rigid polyurethane foam is an excellent insulating material with properties for its lowest thermal conductivity over other cellular materials. Insulation has an essential role in reducing energy consumption, and it also creates a comfortable and healthy living space, RPUFs are used in several applications from refrigerators to large industrial buildings (Akdogan et al. 2020; Tan et al. 2011).

Figure 1.5. Rigid polyurethane foam applications are used in our daily life (Anonymous, 2022b).

However, the rigid polyurethane foam RPUFs also have disadvantages, like low thermal stability, low mechanical strength, etc. To overcome these disadvantages nanocomposite polyurethane foams have been developed in recent years (Chen, Tien, and Wei 2000; Wang and Pinnavaia 1998).

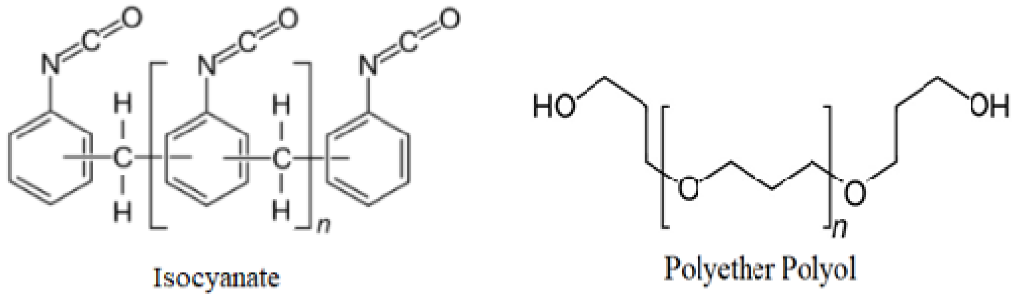

Figure 1.6. Chemical structure of isocyanate and polyether polyol (Gaidukov et al. 2013).

RPUFs are formed by a chemical reaction between a polyester or polyether polyol and isocyanate in the presence of blowing agents and catalyst forming repeating urethane groups. The porous form of rigid polyurethane foam consists of the reaction of polymerization and the expansion process in the presence of surfactants and catalysts. The surfactants and the catalysts are important in the synthesis of RPUFs because they play a key role in the foaming process, controlling the formation of the bubble during synthesis, and balancing between the reactions (Chattopadhyay and Raju 2007; Rahman, Rabbani, and Saha 2019; Verdolotti et al. 2017).

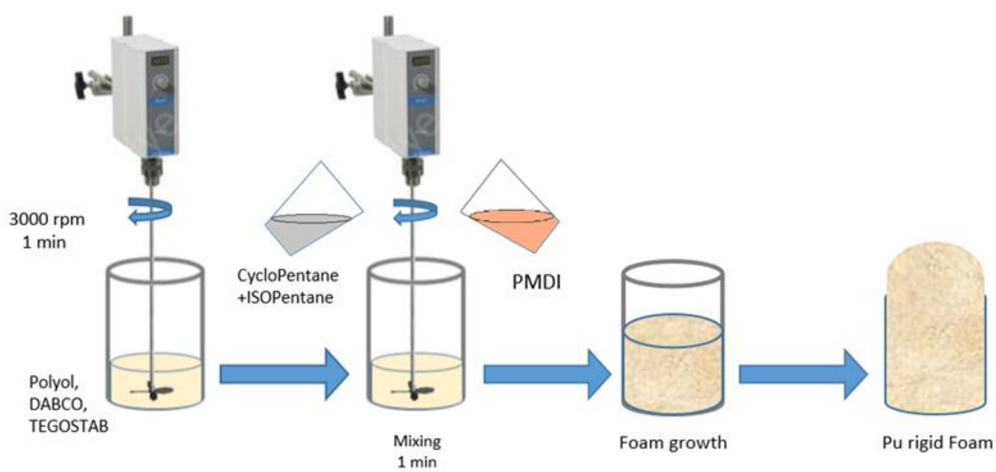

Figure 1.7. Schematic drawing of phases of rigid polyurethane foam production.

After the material mixing process is completed, the mixture will start to rise and the rate of foam formation has been evaluated from the characteristic formation times, cream, gel, rise, and tack-free time of RPUFs. The cream time is starting after isocyanate and polyol are mixed until the reaction started between the material, the color of the mixture becomes brightened and the mixture appears creamy due to the introduction of bubbles. When the mixture reaches the gel time a long chain of polymer is formed. The Rise time is when the foam stops expanding but is still viscoelastic. The tack-free time is when the surface became free of stickiness and can remove the foam from the mold. (Kim, Kim, and Lim 2008; Kraitape and Thongpin 2016).

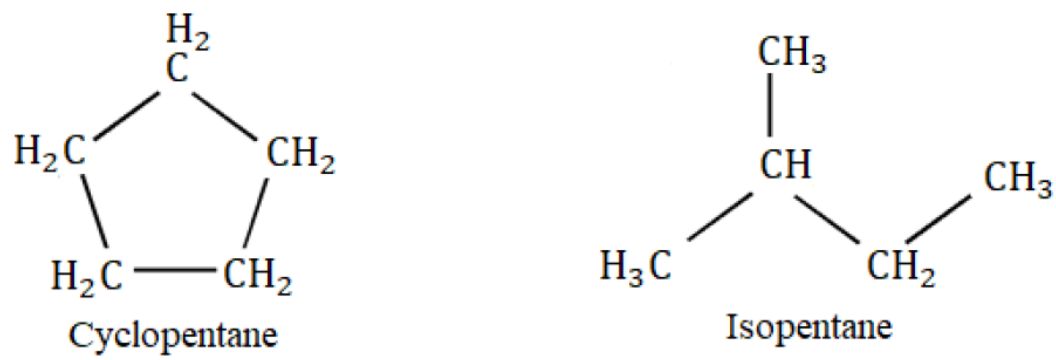

Figure 1.8. Chemical structure of blowing agents; Cyclopentane and Isopentane.

The essential advantage of RPUFs is that the cells of the foam are closed and blowing agents are entrapped within the cells (Szycher et al. 2012). Polyurethane foams PUF have a gaseous phase consisting of chemical blowing agents or physical blowing agents. for physical blowing agents like Cyclopentane, reactions between polyol and isocyanate produce polyurethane linkages as the blowing agent vaporizes, trapping the gas in the closed cells of the foam. Because the closed cell is filled with blowing agents, the PUFs provide a great thermal insulating and low moisture permeability properties which make them preferred in many applications (Choe et al. 2004; Kim et al. 2008)

Polyurethane PU has been developed and it was found that the nanomaterials significantly increased the properties of polyurethanes in many applications. Mixing foams with other components or materials provide low thermal conductivity and mechanical strength. A review of the related literature indicates that applying nanoclay to the foams contributes a better improvement to heat resistance and mechanical properties(Uthaman, Majeed, and Pandurangan 2006; Yan et al. 2012).

(Cao et al. 2005) used modified montmorillonite to improve several properties of RPUFs. The presence of nanoclay leads to a decrease in compressive strength and a decrease in cell size compared to pure RPUF samples.

(Widya and Macosko et al. 2005) found the addition of 1w. % nanoclay into RPUFs reduces the average cell size, decreases the diffusion of the blowing agent, and decreases the compressive strength.

1.3. Nanoclay

Nanoclays are nanoparticles has layered mineral silicates that depend on morphology and the chemical structure of nanoparticles. The mechanical and thermal properties are improved by using nanoparticles in polyurethane foam. Nanoclays have higher thermal and higher mechanical properties than the polymer matrix. The most widely used nanoclay material is montmorillonite (Madkour 2019; Valizadeh, Rezaei, and Eyvazzadeh 2011; Widya and Macosko 2005).

(Kim et al., 2010) reported that nanoclay acts as a heterogeneous nucleating agent produced in a nanocomposite foam with a uniform cell structure and small cell size.

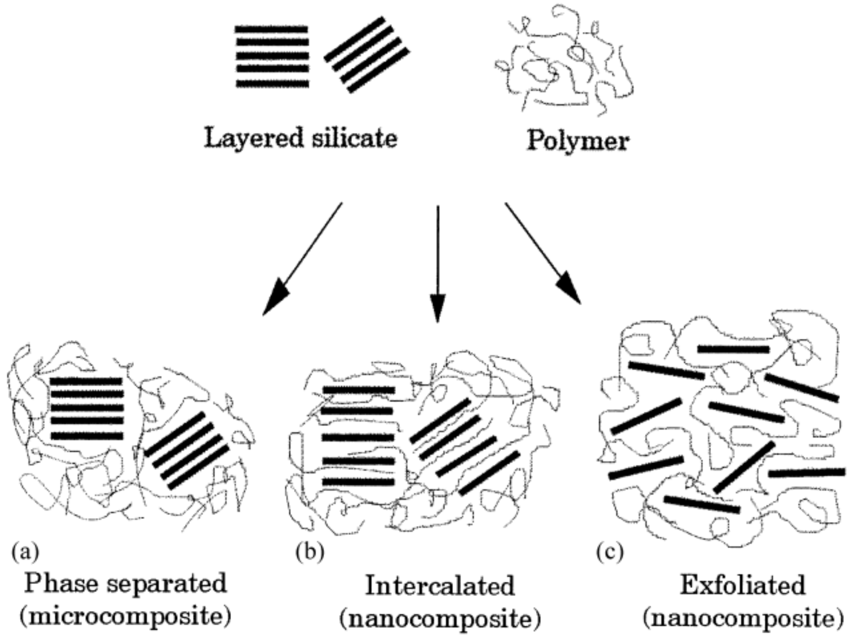

Figure 1.9. polymer nanocomposite structures using layered Nanoclays: a.microcomposite, b. intercalated nanocomposite and c. exfoliated nanocomposite (Alexandre and Dubois 2000).

The clay can increase the barrier properties, which makes a tortuous path and delaying the polymer matrix gas molecules progress (Nayani, Gunashekar, and Abu-zahra 2013). However, dispersing the particles homogeneously and increasing the reinforcing efficiency in the matrix is an important problem so many methods are used such as ultrasonication to distribute the nanoclay within the RPUFs matrix (Gaidukov et al. 2013).

1.3.1. Unmodified nanoclay Sodium Montmorillonite clay (Na MMT) and, Cloisite 30B

Montmorillonite MMT clay consists of the central octahedral alumina sheet and two external sheets of tetrahedral silica. Clay structure is important to improving thermal and mechanical of the polymer layered silicate nanocomposites (Valizadeh et al. 2011).

The Sodium Montmorillonite clay (Na MMT) and Cloisite 30B have been the widest reinforcement agents used in polymer to obtain nanocomposites with unique properties such as a liquid and gas barrier, and mechanical improvement. Which is used to improve the physical properties like the strength and, stiffness in the polymers. (Kotal and Bhowmick 2015; Sin et al. 2013).

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Cloisite 30B is one of the most widely used clays for many nanocomposites due to the hydroxyl functional groups in the clay are reactive and suitable for many chemical modifications. (Sin al. et 2013).

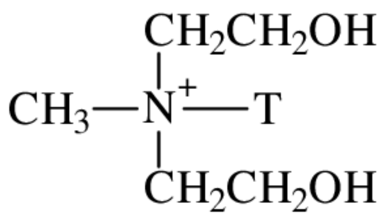

Figure 1.10. Chemical structure of Cloisite ® 30B nanoclay (Sin et al. 2013).

(Cao et al. 2005) studied the processing, structure, and properties of PU nanocomposite foams, for the flexible and rigid, observed that the density increased and the cell size reduced for nanocomposites compared with pure polyurethane foam. Also, they found that the mechanical properties of the nanocomposite foams, such as compression strength, and compression modulus were reduced with the addition of nanoclay.

(Harikrishnan, Patro, and Khakhar 2006) also studied the effect of add nanoclays to the RPUFs on the thermal properties, the presence of clay is able to decrease the cell size, and there was no affected on the thermal conductivity of the RPUFs by clay addition.

1.3.2. Modified nanoclay: Silver modified montmorillonites clay (Ag MMT) and Silver modified cloisite-30B clay (Ag 30B).

Silver nanoparticles have obtained attention as an antibacterial activity because of the higher reactivity of nanoparticles compared to their bulk counterparts, making these materials used in various fields including antibacterial activity, in the industrial, and healthcare products, coatings, and the food industry, due to their unique chemical and physical properties (Morena et al. 2020; Tashi, Vishal Gupta, and Mbuya 2016).

The antibacterial activity and stability of the nanoparticles are dependent on the surface chemistry of silver nanoclay. The silver nanoparticles showed antibacterial activity against yeast and E. coli, their inhibitory effect on S. aureus growth was mild. This indicates that the antibacterial effects of silver nanoparticles are specific against Gram-negative bacteria (Madkour et al. 2016).

(Sun et al.,2020) found that the silver nanoparticles can improve polyurethane thermal stability. In addition, it can provide the nanocomposite surface with a good antibacterial activity.

2. EXPERIMENTAL

2.1. Raw Materials:

- PMDI (polymeric 4, 4-di-phenylmethane diisocyanate) - Supplied from Ravago Chemicals. Its density is 1.23 g /cm^3, viscosity 230 MPa.s and NCO index %31, 5.
- Polyol (polyether polyol) - Supplied from Ravago Chemicals. Its density is 1.10 g /cm^3 and viscosity 5500-8500 MPa.s.
- Cloisite 30B unmodified clay (30B).
- Sodium Montmorillonite unmodified clay (Na MMT).
- Silver modified montmorillonites clay (Ag MMT).
- Silver modified cloisite-30B clay (Ag 30B).
- TEGOSTAB as silicone surfactant.
- DABCO as a catalyst.
- Cyclopentane (C_5H_{10}).
- Isopentane (C_5H_{12}).

2.2. Preparation of Rigid Foam Samples

- Firstly, all of the clays that were used dried at 60°C for 48 hours in a vacuum oven before dispersion in the isocyanate (PMDI) components. The nanoparticle size of the clays is 2 nm.

Figure 2.1. Vacuum oven.

- A 1w. % of clay was added to isocyanate (PMDI) in a closed container and stirred for 30 min with a magnetic stirrer until they are dispersed. Then put into sonication for 10 minutes. Ultrasonication treatments were used to help dispersion.

Figure 2.2. Magnetic stirrer.

Figure 2.3. Ultrasonic Bath Device.

- 15 gr Polyol, 1.35 gr of DABCO as a catalyst, and 1.35 gr of TEGOSTAB as silicone surfactant are mixed by hand via a spatula in another cup before adding to the mold.

Figure 2.4. Cyclopentane and Isopentane.

Figure 2.5. TEGOSTAB and DABCO.

- For blowing agents, 2.25 gr of Isopentane and 4.5 gr of Cyclopentane are mixed in a different cup.

Figure 2.6. Modified nanoclay Ag MMT, Ag 30B and unmodified nanoclay Na MMT, 30B.

Table 2.1: Sample composition of rigid polyurethane foams

Sample code	Polyol	PMDI	TEGO	DABCO	Cyclopentane	Isopentane	30B	Na MMT	Ag 30B	Ag MMT
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Pure Pu	15	18.5	1.35	1.35	4.5	2.25	0	0	0	0
30 B	15	18.5	1.35	1.35	4.5	2.25	0.365	0	0	0
Na MMT	15	18.5	1.35	1.35	4.5	2.25	0	0.365	0	0
Ag 30B	15	18.5	1.35	1.35	4.5	2.25	0	0	0.365	0
Ag MMT	15	18.5	1.35	1.35	4.5	2.25	0	0	0	0.365

Figure 2.7. Preparation of raw materials prior to mixing.

- The cup that has Polyol, DABCO, TEGOSTAB was poured into a PET bottle and mixed by a mechanical stirrer at 3000 rpm.

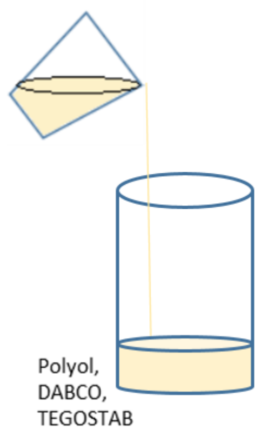

Figure 2.8. Pouring down polyol, DABCO, TEGOSTAB into the PET bottle.

Figure 2.9. Mixing the polyol, DABCO and TEGOSTAB.

- After that, the mixture of PMDI/clay and the mixture of cyclopentane and isopentane were simultaneously added to the PET bottle

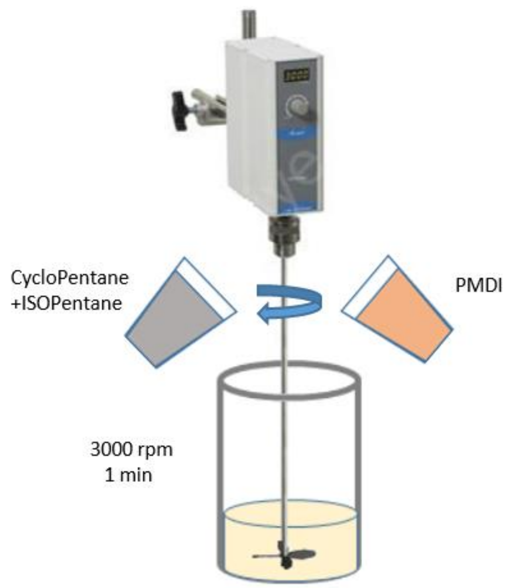

Figure 2.10. Pouring down blowing agents (Cyclopentane/Isopentane) and PMDI mixture to the PET bottle.

- After all the components are added in, the mixture mechanically stirred for 1 min at 3000 rpm.

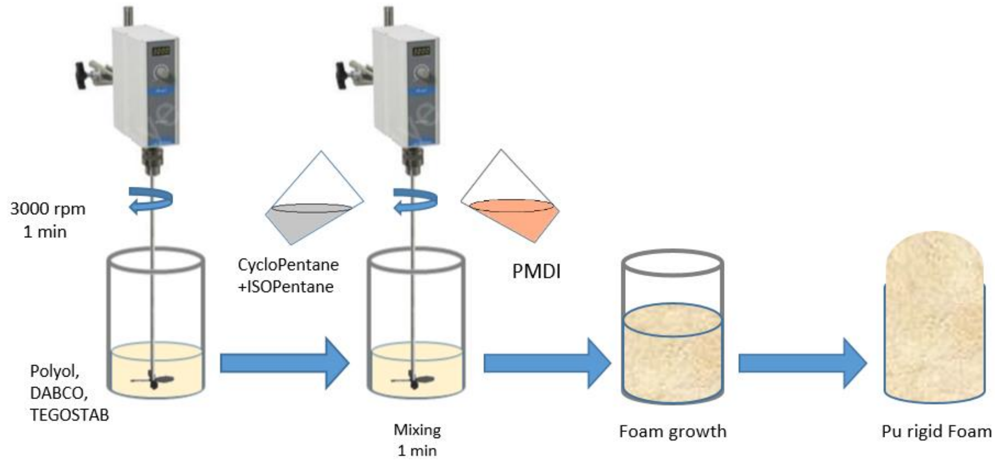

Figure 2.11. Mixing all the ingredients until rising phase starts.

- For 1 min of mixing at 3000 rpm, the mixture starts to raise and reach the viscoelastic stage.
- When the viscoelastic stage has passed, polyurethane foam reaches its final form.

Figure 2.12. Final form of rigid polyurethane foam produced in PET bottle.

Figure 2.13. Image of samples produced in O.M.U laboratories for this study

2.3. Characterization Methods

2.3.1. Fourier Transform Infraed (FTIR)

The Fourier transform infrared spectroscopy (FTIR) tests of samples were recorded by a Bruker Tensor 27 type instrument with a range of 4000 cm⁻1 and 400 cm⁻1 in the room temperature.

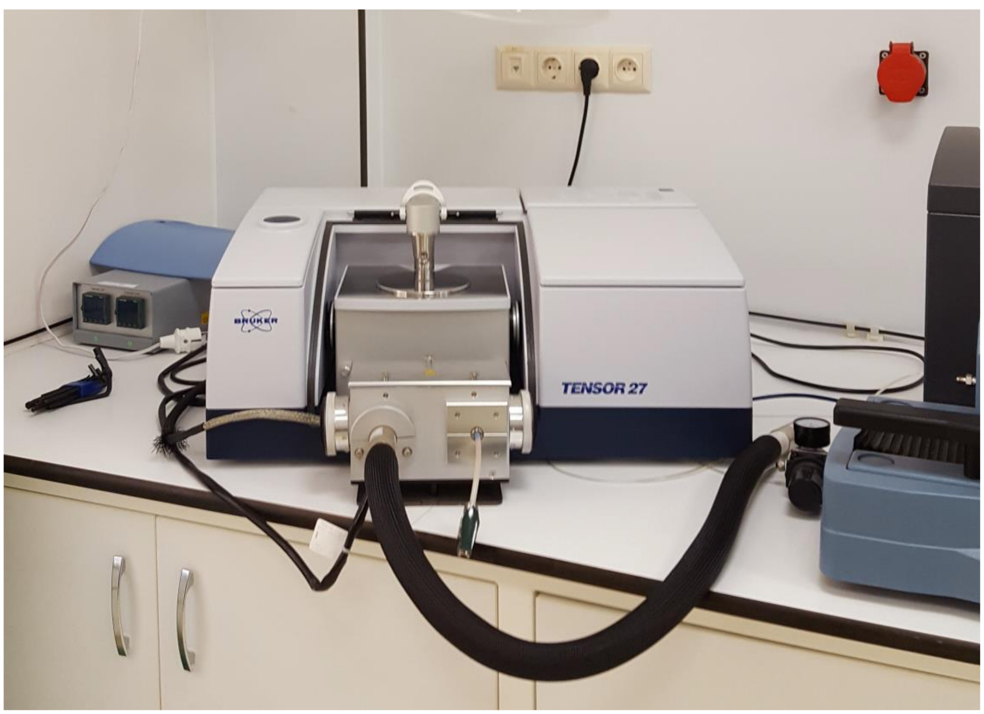

Figure 2.14. FTIR test device

2.3.2. Mechanical Compression Test

The mechanical properties of samples were done by using Instron (100 KN) Universal Testing Instrument. Dimensions of samples are (2.5x5x5) cm (length × width × thickness). Samples were cut from different heights and minimum 4 samples were tested to get an average value. In all tests, compressive strain of 0.4 was achieved.

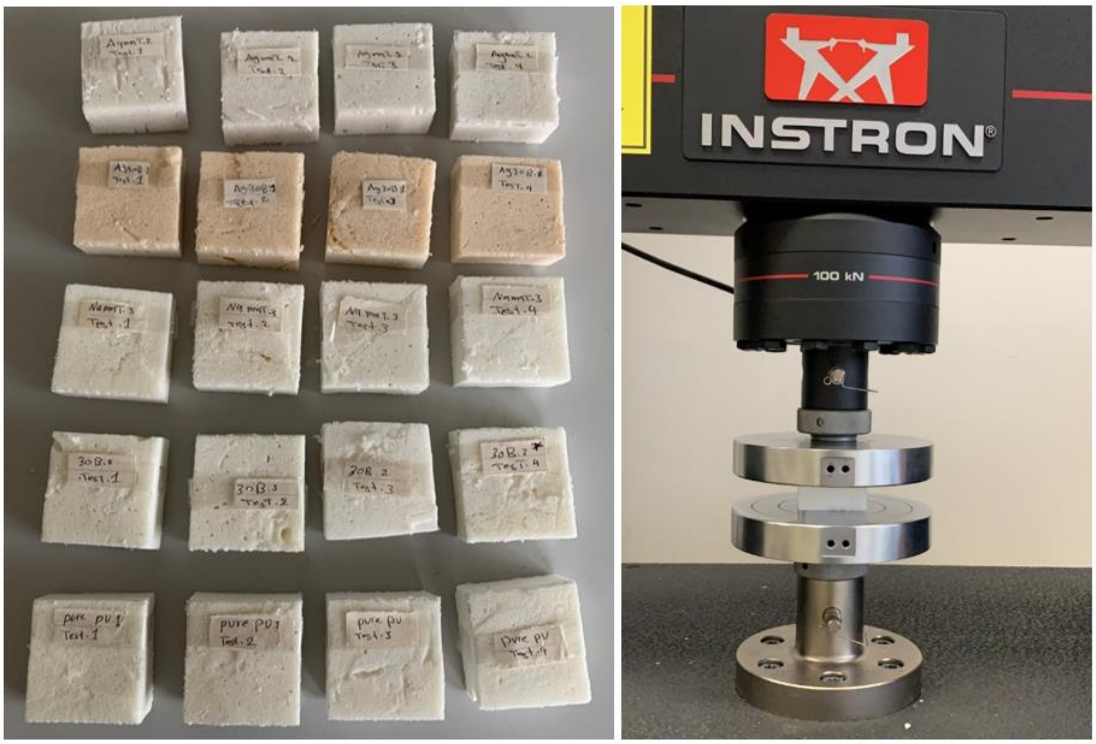

Figure 2.15. The test samples and universal testing machine for compression test.

2.3.3. Thermal Conductivity Test

Thermal conductivity tests were done using a KD2 Pro Thermal Properties Instrument (Decagon Devices). The instrument has a needle sensor inserted into the foam samples to obtain the average value for each sample.

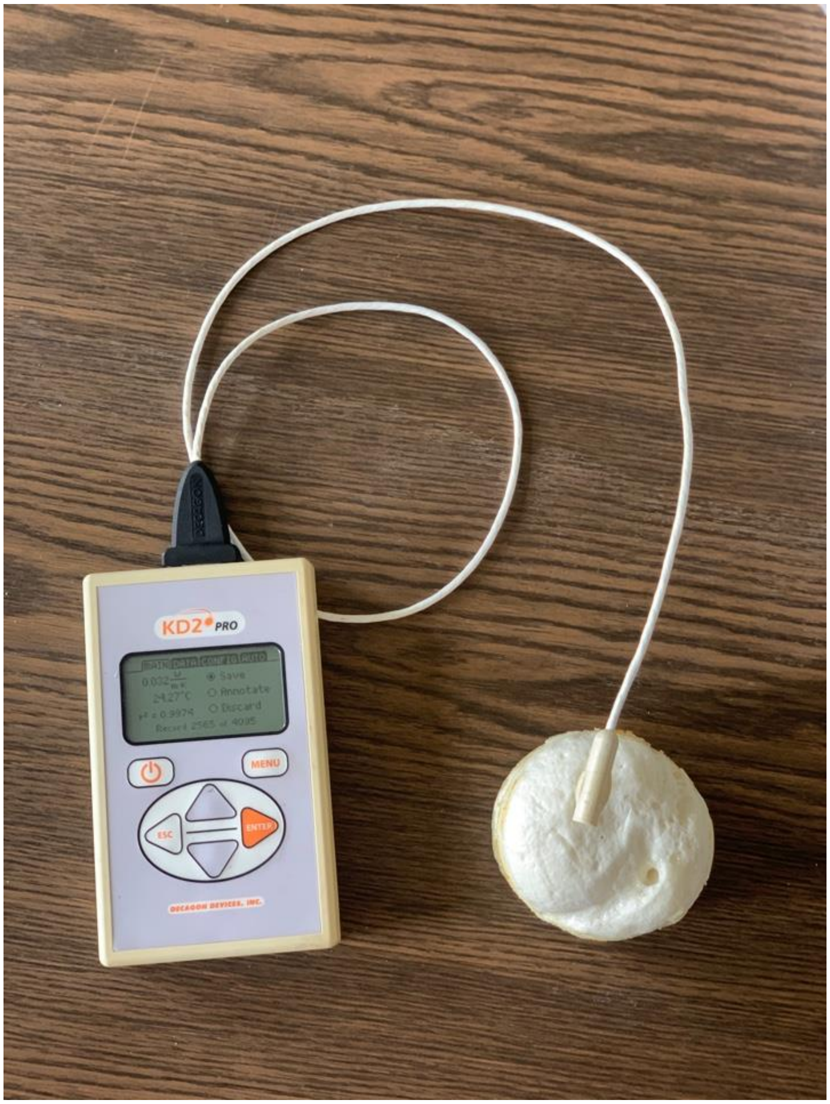

Figure 2.16. Thermal conductivity test device.

2.3.4. Scanning Electron Microscopy (SEM)

SEM Scanning electron microscopy experiments were done by using a JEOL-JSM device, with an acceleration voltage of 10 kV. SEM image analysis by using ImageJ software computer program to get average cell sizes for the foam samples.

Figure 2.17. Scanning Electron Microscopy.

2.3.5. X-ray diffraction (XRD)

X-ray diffraction (XRD) experiments were done by using a Rigaku diffractometer. The instrument has a (λ = 1.542 Å) radiation. XRD was operated at 30 mA and 40 k, with scanning speed was 0.02°/min. During XRD tests, 2-Theta(2θ) range of 5°–70° was used. The d-spacing of the nanoclay was analyzed by using Bragg's equation ($n\lambda = 2d \sin \theta$).

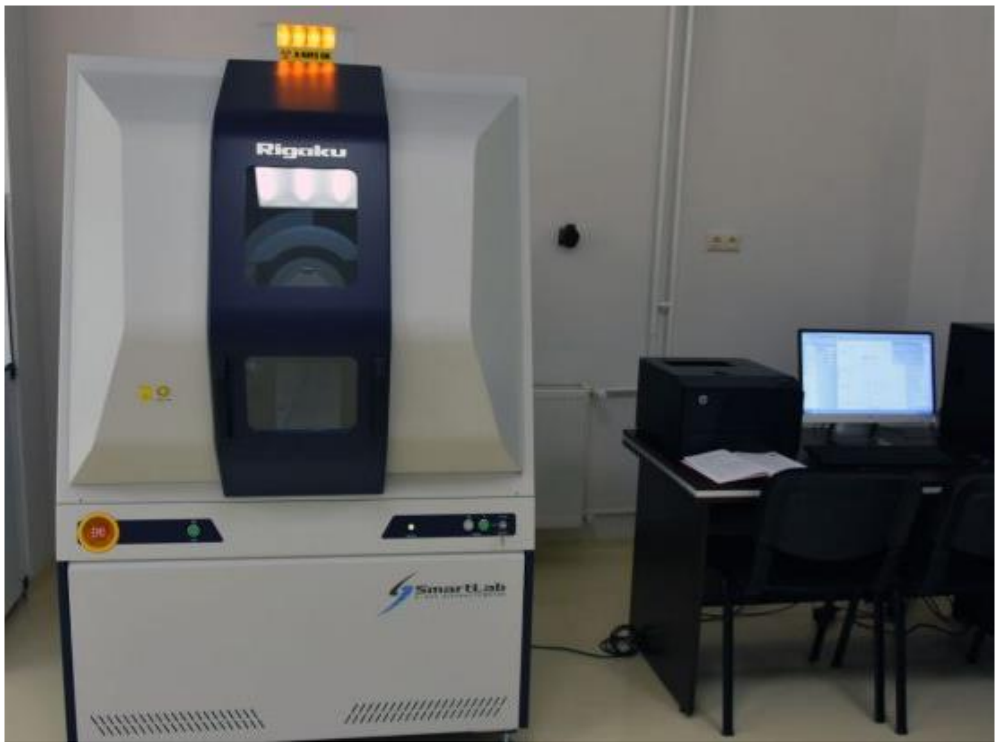

Figure 2.18. The X-ray diffraction (XRD) device.

2.3.6. Density Measuring Test

The density of the foam samples were measured by RADWAG AS.220.R2 device at room temperature. Three different specimens were selected from different parts of each foam sample with a size of 1cm^3 and were tested to get an average value.

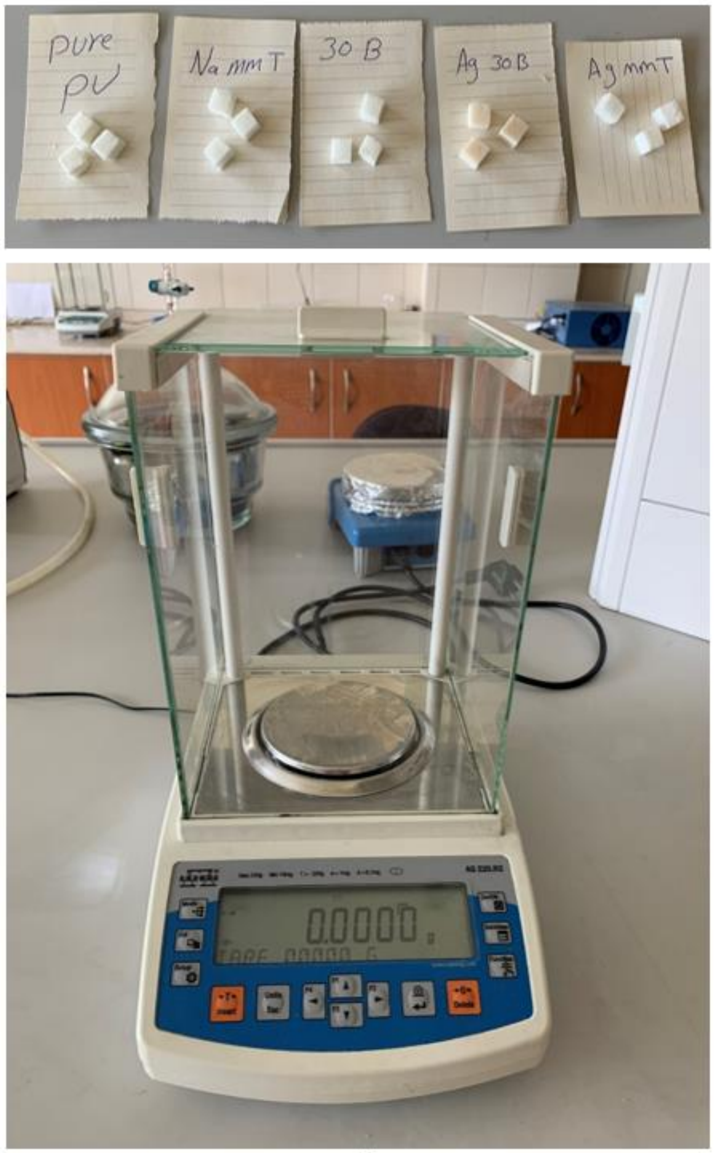

Figure 2.19. The test samples and density measuring device.

2.3.7. Thermogravimetric Analyses

Thermogravimetric analysis (TGA) of foam samples was performed to examine the degradation profile of the foam samples by calculating the weight loss of the foam samples, using TA Instruments SDT Q600 instrument. Foam samples were heated to 600 °C/min under N2 flow with a 20 °C/min heating rate.

Figure 2.20. Thermogravimetric analysis device.

2.3.8. Antibacterial test

The antibacterial activity properties of the foam samples against selected pathogenic microorganisms including two Gram-positive are (Bacillus cereus NRRLB-3711 and Staphylococcus aureus ATCC-33862) and two Gram-negative are (Listeria monocytogenes ATCC-7644 and Escherichia coli ATCC-25922) bacteria, one (Candida albicans ATCC-10131) yeast using Mueller Hilton agar medium for the bacterial strains and RPMI 1640 agar medium for the yeast strain as growth media, according to disc diffusion method.

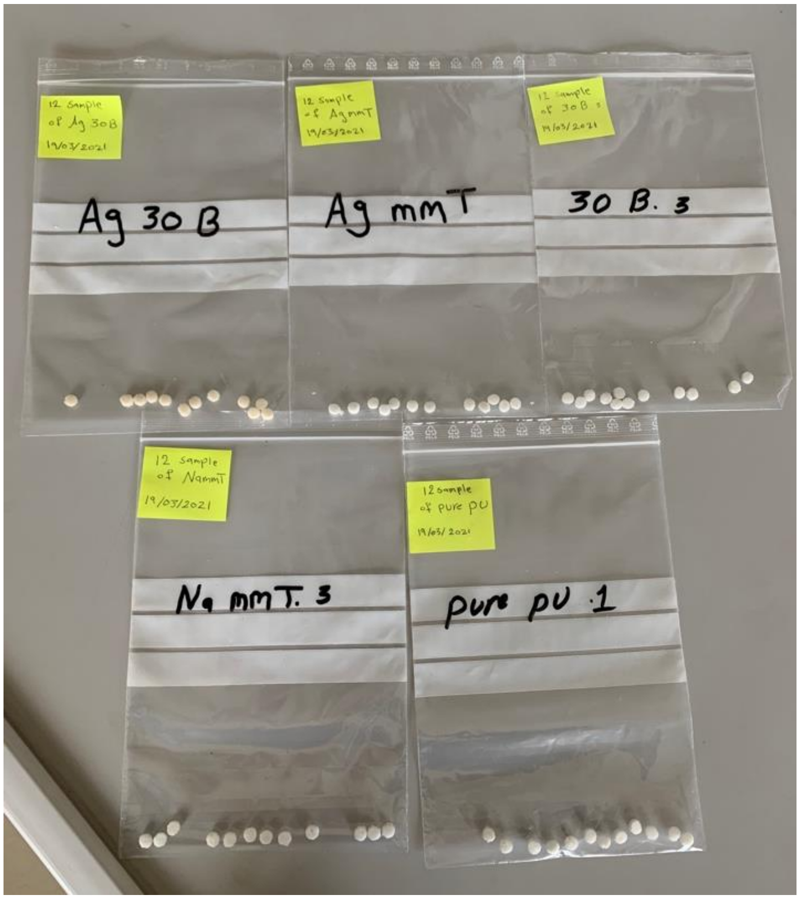

Figure 2.21. Antibacterial test samples (discs diameter 6.4 mm).

The foam samples were set in the form of a disc (the disc diameter was 6.4 mm). It was used active cultures of the pathogenic microorganisms (24 h culture of yeast strains and 18 h broth culture of each bacteria), with density equivalent to a final concentration of 108 CFU/mL, with an additional twofold dilution for yeast strain adjusted to a concentration of 105 CFU/mL. Then, the sterile plates containing the aforementioned media were homogeneously inoculated using impregnated sterile cotton swabs with these inoculums. Immediately afterward, the prepared films were placed on the inoculated Petri dishes. And the plates were incubated for 20 h at 35 ^{o}C for the bacteria and 48 h at at 25^{o}C for yeast cultures. After the incubations, the inhibition zone diameters surrounding film discs (colony free perimeter) were measured and expressed in millimeters.

3. RESULTS AND DISCUSSION

3.1. Fourier Transform Infrared (FTIR) analysis

Fourier Transform Infrared technique (FTIR) is widely used to study the analysis of the isocyanate reaction, urethane bonds formation in the polymeric matrix, and the (-NCO-) group within the polyurethane foams (Panda et al. 2018).

The (FTIR) spectra of pure polyurethane rigid foam and RPUFs nanocomposites foams between 4000 cm^{-1}-400 cm^{-1} are shown in figure 3.1. The small peak show at 2275 cm^{-1} is assigned to the N=C=O group. Two Peaks shown at 1720 cm^{-1} and 1530 cm^{-1} matched carbonyl C=O stretching vibration and N–H bending vibration of urethane structure. N-H and C=O vibration are the most important zones to study the hydrogen bonding and confirmed the formation of polyurethane (Chattopadhyay and Raju 2007; Panda et al. 2018).

The asymmetric and symmetric C-H stretching vibrations peaks show at 2977cm^{-1} and 2900 cm^{-1} respectively (Francés and Bañón 2014). The N-H stretching vibration band at 3324 cm^{-1} of urethane groups (Burgaz and Kendirlioglu 2019).

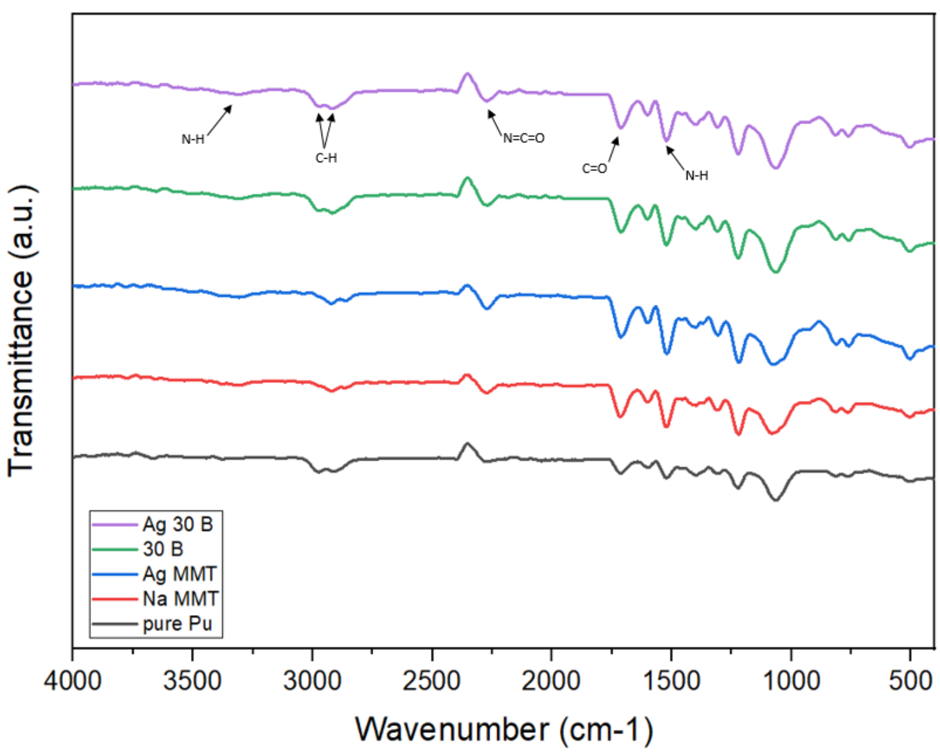

Figure 3.1. FTIR of samples between wavelengths of (4000 cm^{-1} -400 cm^{-1}).

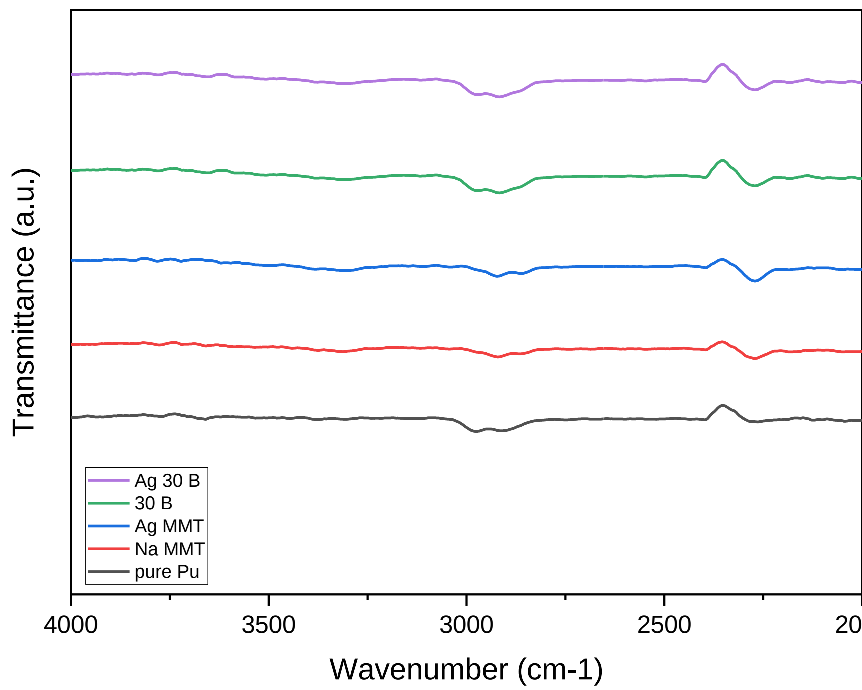

Figure 3.2. FTIR of samples between wavelengths of (4000 cm^{-1} -2000 cm^{-1}).

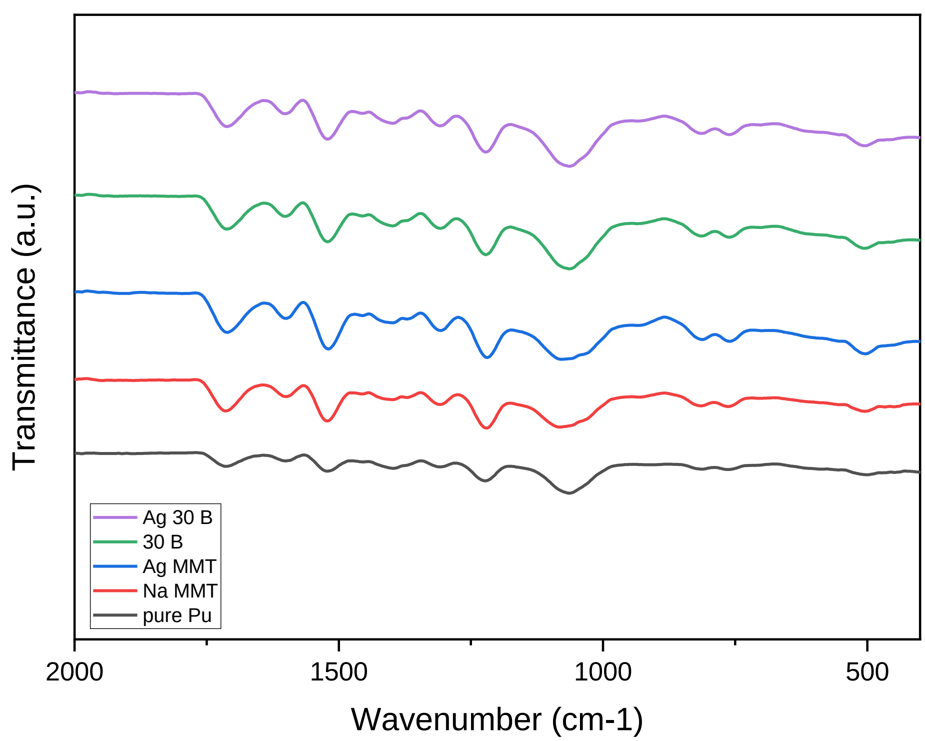

Figure 3.3. FTIR of samples between wavelengths of (2000 cm^{-1} - 400 cm^{-1}).

3.2. Compression Test

The mechanical performances of the samples were measured by the compression test. Figure 3.4 shows the compressive stress-strain curves for the five samples of pure and nanocomposite RPUFs.

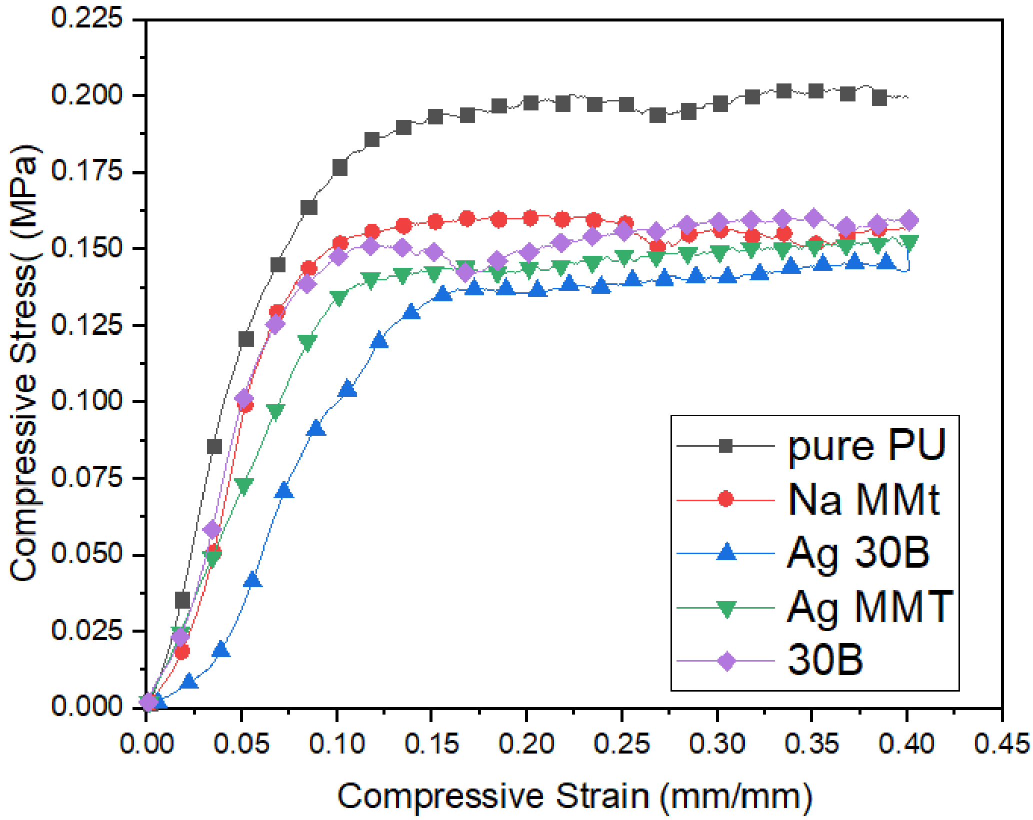

Figure 3.4. Compression test results of samples

Results of the compression strength for the foam samples show a decrease with nanoclay addition as shown in Figure 3.4. Maybe the decrease in the compression strength due to the lower density of the foam.

It can be seen from Figure 3.5, compressive strength of pure RPUF has 0.202 MPa and 1.95 MPa compressive modulus. 30B sample has 0.158 MPa compressive strength and 1.65 MPa compressive modulus. Na MMT sample has 0.161 MPa compressive strength and 1.86 MPa compressive modulus. Ag 30B sample has 0.146 MPa compressive strength and 1.05 MPa compressive modulus. Ag MMT sample has 0.153 MPa compressive strength and 1.31 MPa compressive modulus.

Table 3.1: Results of the compression test.

Sample Code	Density	Compressive Strength	Compressive Modulus	Specific Compressive Strength	Specific Compressive Modulus
	g/cm^3	MPa	MPa	MPa.cm3/g	MPa.cm3/g
Pure Pu	0.0360±0.0015	0.202±0.002	1.95±0.005	5.61±0.0017	54.16±0.42
30B	0.0291±0.003	0.158±0.003	1.65±0.003	5.49±0.003	56.70±0.61
Na MMT	0.0300±0.001	0.161±0.002	1.86±0.001	5.36±0.0015	62.03±0.1
Ag 30 B	0.0363±0.008	0.146±0.005	1.05±0.009	4.02±0.006	28.92±0.52
Ag MMT	0.0335±0.0015	0.153±0.002	1.31±0.003	4.59±0.002	39.10±0.9

According to these results, the nanoclay additive significantly reduced the compressive strength of the RPUFs. One of the biggest reasons for this may be that the clay is not dispersed homogeneously in the mixture during the reaction, and accordingly, the formation of rigid foams with extremely large pores. In a study by (Widya and Macosko 2005), it was found that adding nanoclay to the rigid polyurethane foam reduces the compression strength and compression modulus due to the reduction in cell size. This also coincides with our results on mechanical strength.

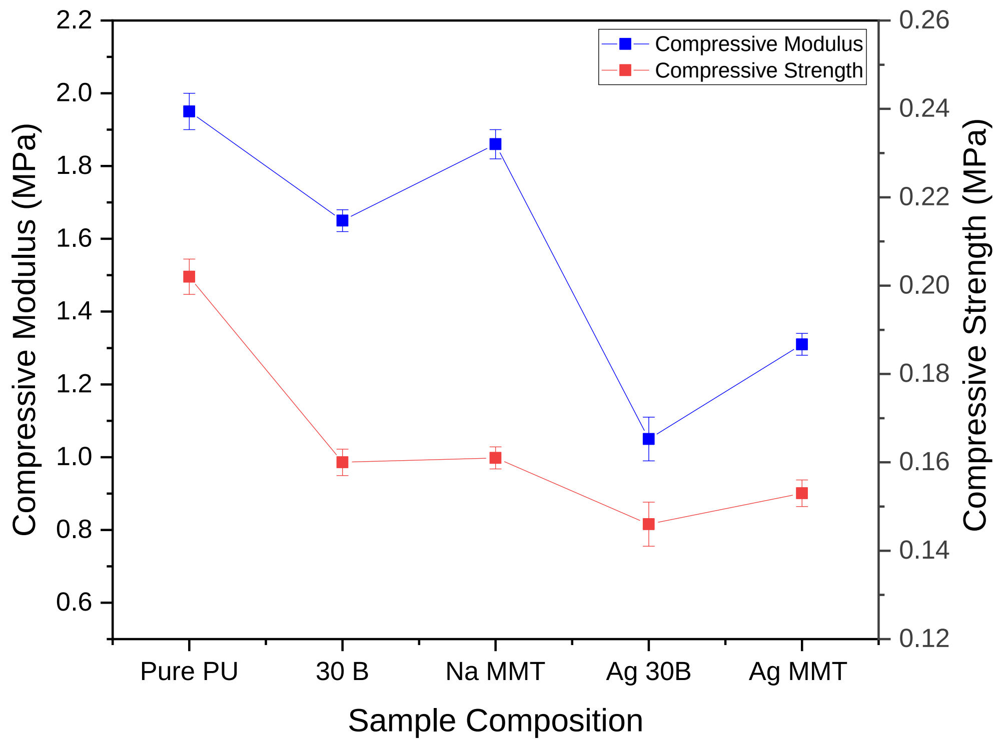

Figure 3.5. Compressive modulus and compressive strength results for the samples.

The 30B addition provided around 50 % loss on compressive strength and around 30 % loss on compressive modulus. The addition of Na MMT caused a 40 % loss on compressive strength and 10 % loss on compressive modulus. Ag 30B lost 60 % of its compressive strength and loses 90 % on compressive modulus. Ag MMT lost 50 % on compressive strength and loses 60 % on compressive modulus.

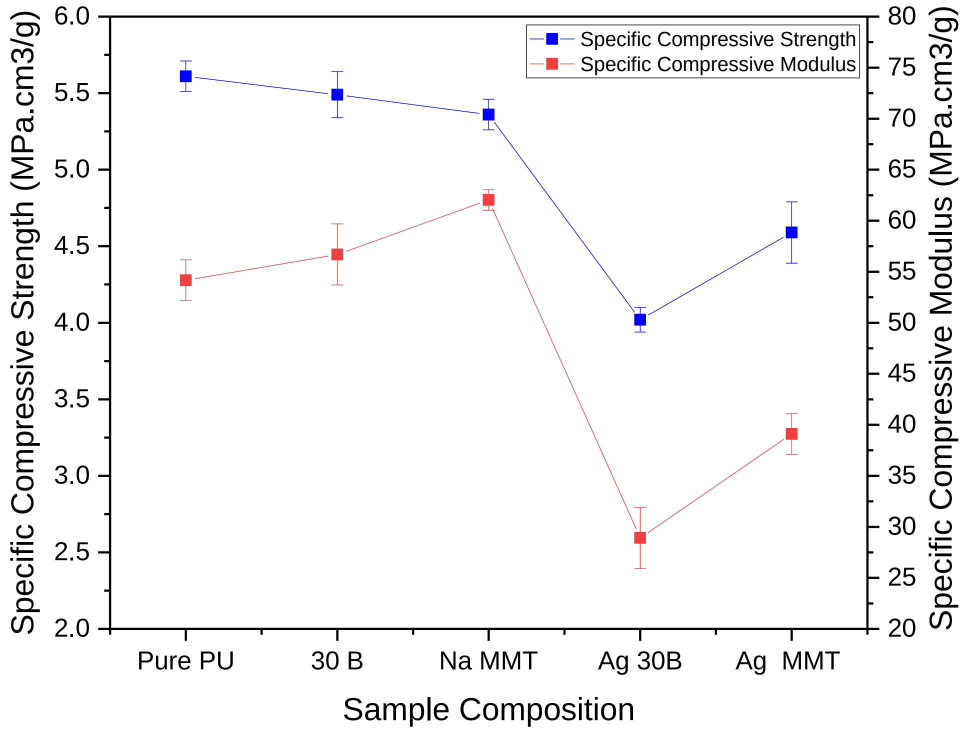

Figure 3.6. Specific compressive modulus and Specific compressive strength results for the samples.

In Figure 3.6 we can compare the results of specific compressive modulus and specific compressive strength. 30B has 5% more specific compressive modulus and 2 % less specific compressive strength. Na MMT has 14% more specific compressive modulus and 4% less specific compressive strength. Ag 30B 45 % less specific compressive modulus and 28 % less specific compressive strength. Ag MMT has 27% less specific compressive modulus and 18 % less specific compressive strength than pure PU.

3.3. Cellular morphology (SEM)

The physical properties of foam depending on the foam cellular structures and polymer matrix rigidity. SEM image of the cellular structure of the pure PU is shown in Figure 3.7 and for nanocomposite RPUFs in figures 3.8, and 3.9, respectively. For each sample, two SEM images were taken one perpendicular to foam rise and the other in parallel to foam rise.

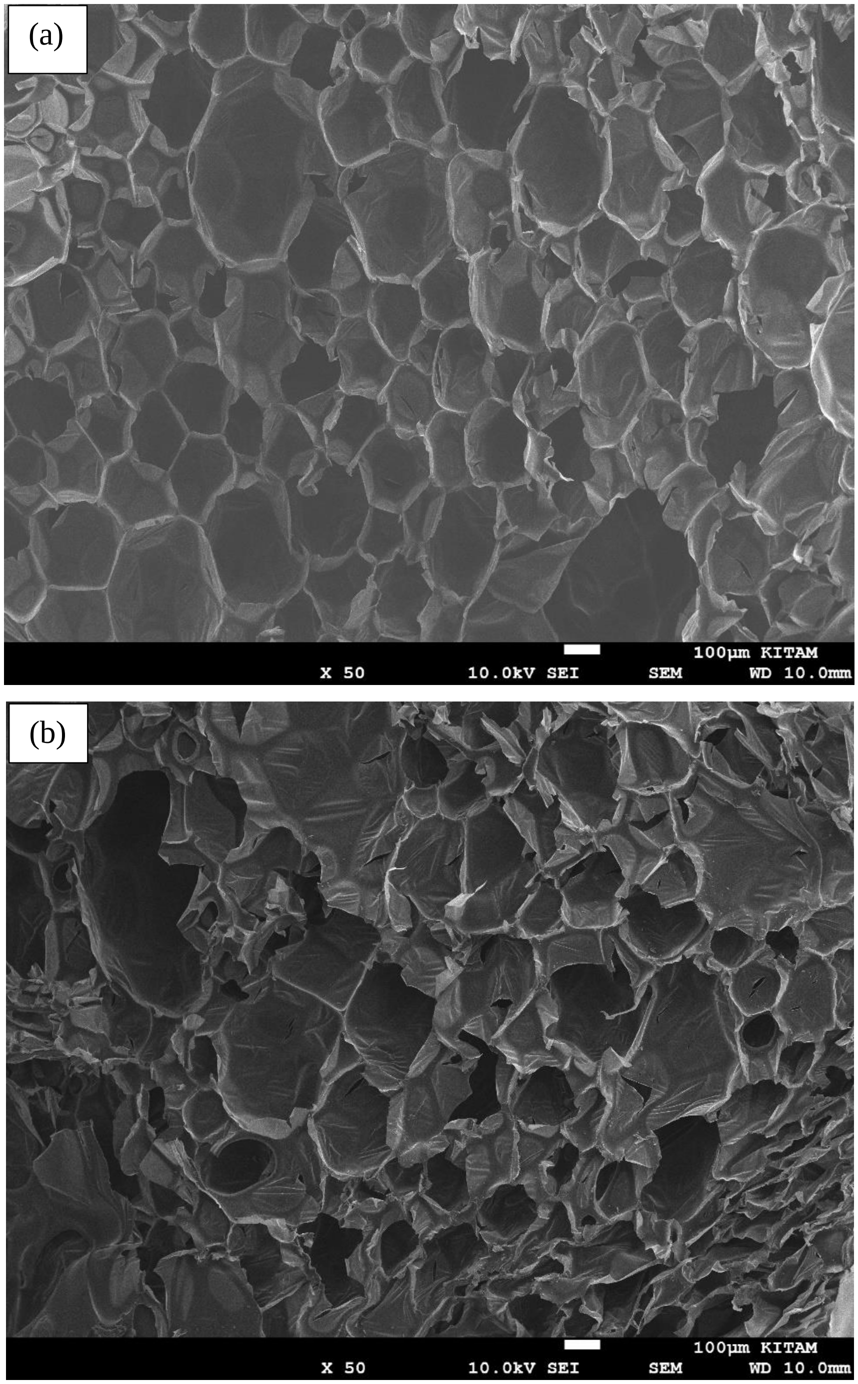

Figure 3.7. SEM images for pure PU sample ;(a) perpendicular to foam rise, (b) parallel to foam rise.

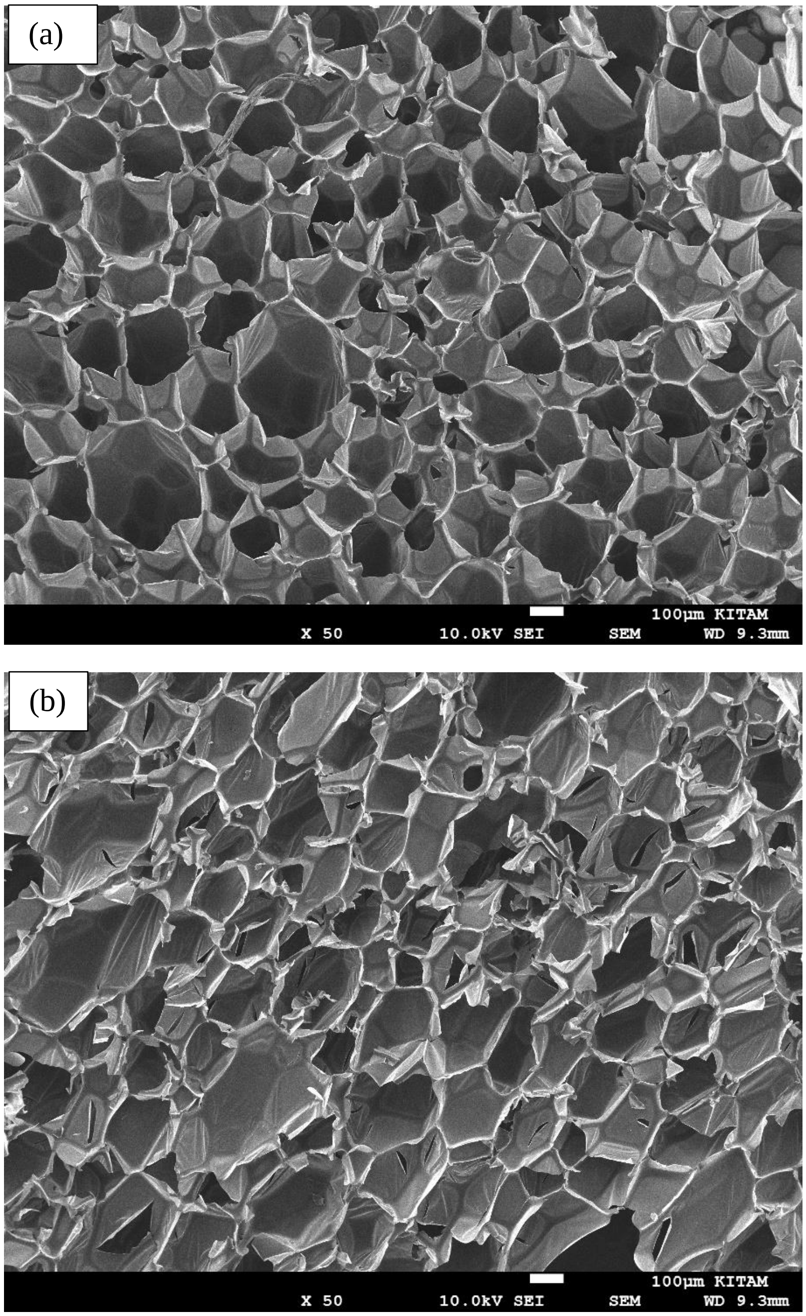

Figure 3.8. SEM images of Na MMT unmodified nanoclay sample ;(a) perpendicular to foam rise, (b) parallel to foam rise.

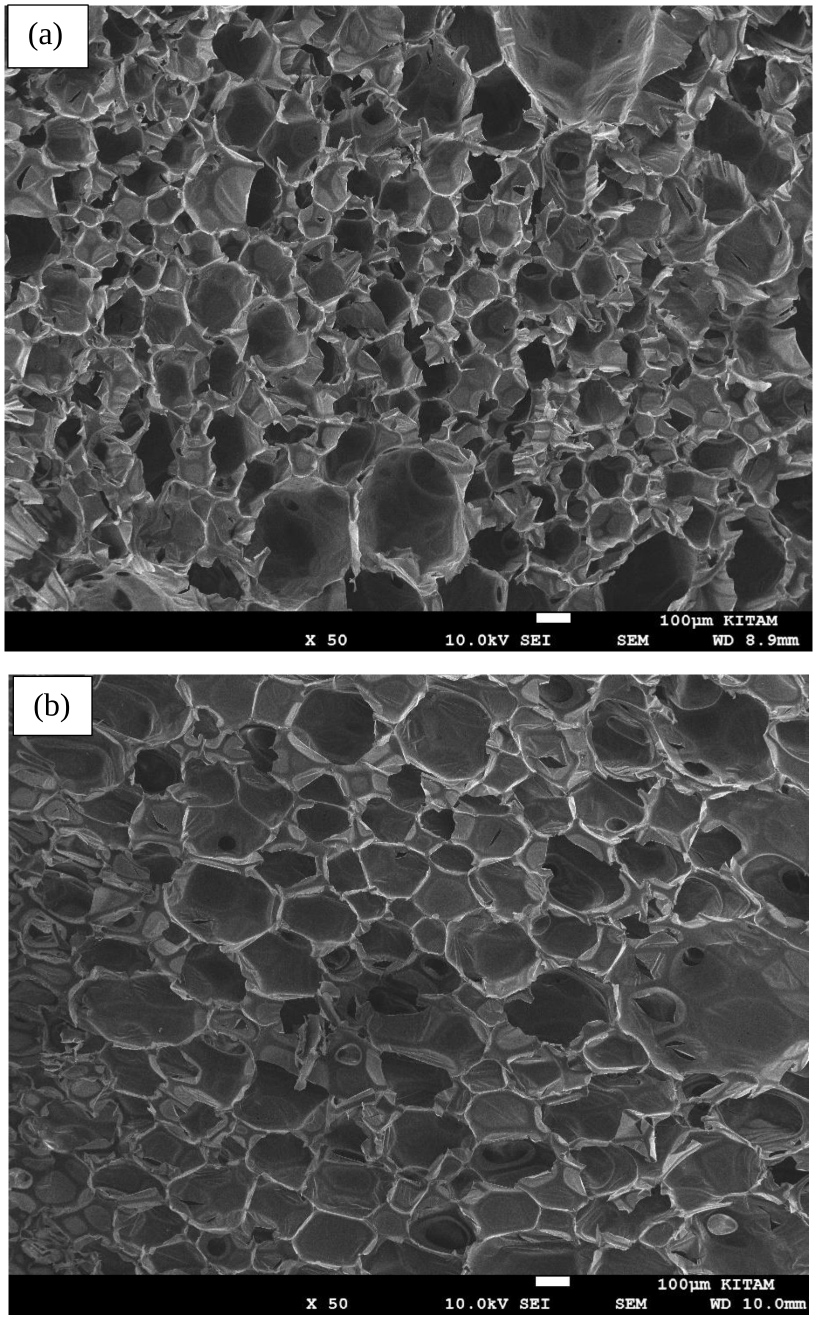

Figure 3.9. SEM images of Ag MMT modified nanoclay sample ;(a) perpendicular to foam rise, (b) parallel to foam rise.

The SEM images of the foam samples that were taken parallel to the foam rise show slight elongation cells. Due to the free foaming process, where the cells are grown in the foam rise direction. And for the perpendicular to the foam rise SEM images the cells show almost circular in shape.

SEM of the nanocomposite RPUF for modified Ag MMT and unmodified Na MMT is shown in figures 3.8 and 3.9, respectively. With the addition of nanoclay, the cell size decrease compared with the PU pure foam. alterations can be observed in the morphology of the cell as the cell wall becomes thinner and there are some broken cells because the addition of the nanoparticles affects in the cell nucleation process. (Dolomanova et al. 2011).

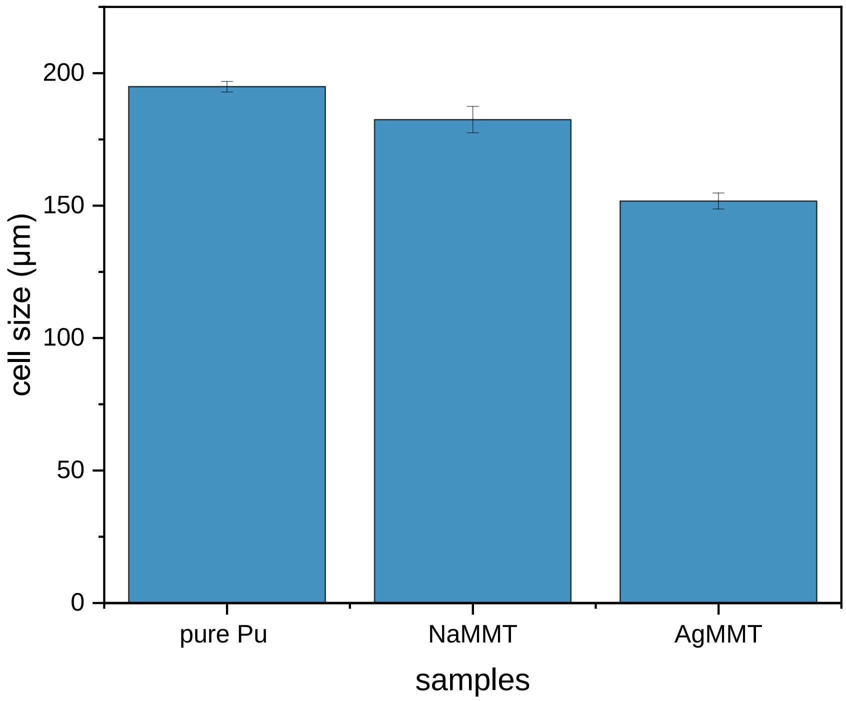

Figure 3.10. The average cell size for the samples.

The values of the average cell sizes of the foams were analyzed by ImageJ software from SEM images as shown in figure 3.10, results show the average cell size of the nanocomposite RPUFs decreases compare with PU pure foam.

The addition of Na MMT caused 6% decrease in average cell size and for Ag MMT addition, average cell size decreased by 22 %. The reduced foam cell size is due to the effect of nanoclay addition which leads to the formation of a larger number of cells and thus a smaller cell size.

The Figure 3.11 and Figure 3.12 show the cell density and, cell size values obtained from the SEM images perpendicular and parallel to foam rise direction.

Based on the result, it was shown that the addition of Na MMT unmodified and Ag MMT modified nanoclay to rigid polyurethane foam reduced cell size of the foam and increased cell density compared to the PU pure foam, due to the dispersed nanoparticles of clay that act as heterogeneous nucleation sites during the reactive foaming process and, make a homogenous cell structure with increase in cell number, small cell size and increase in cell density (Burgaz and Kendirlioglu 2019; Cao et al. 2005).

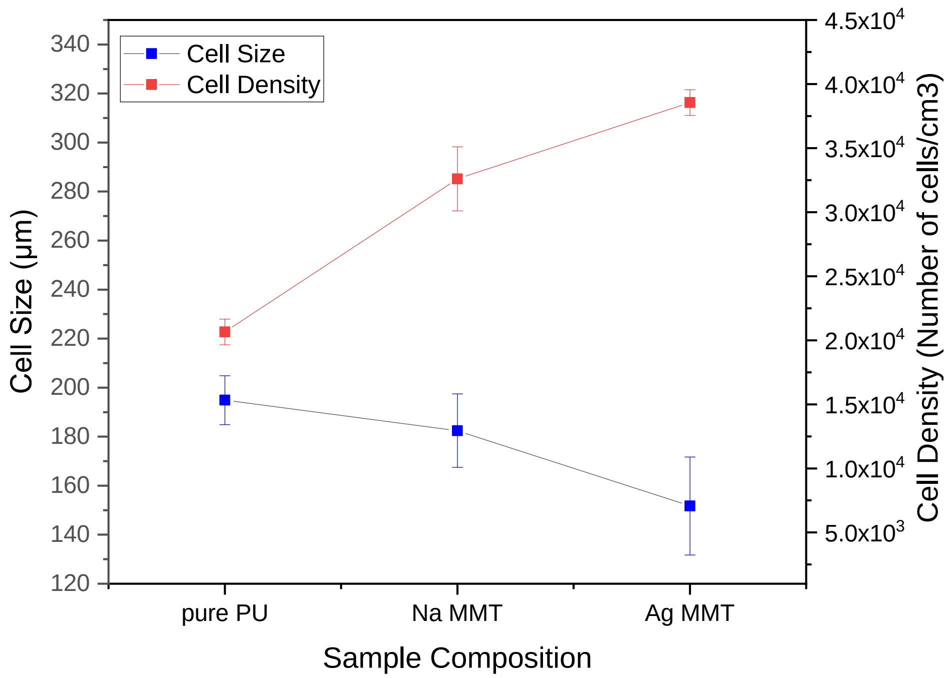

Figure 3.11. Cell size and cell density in perpendicular to foam rise SEM images

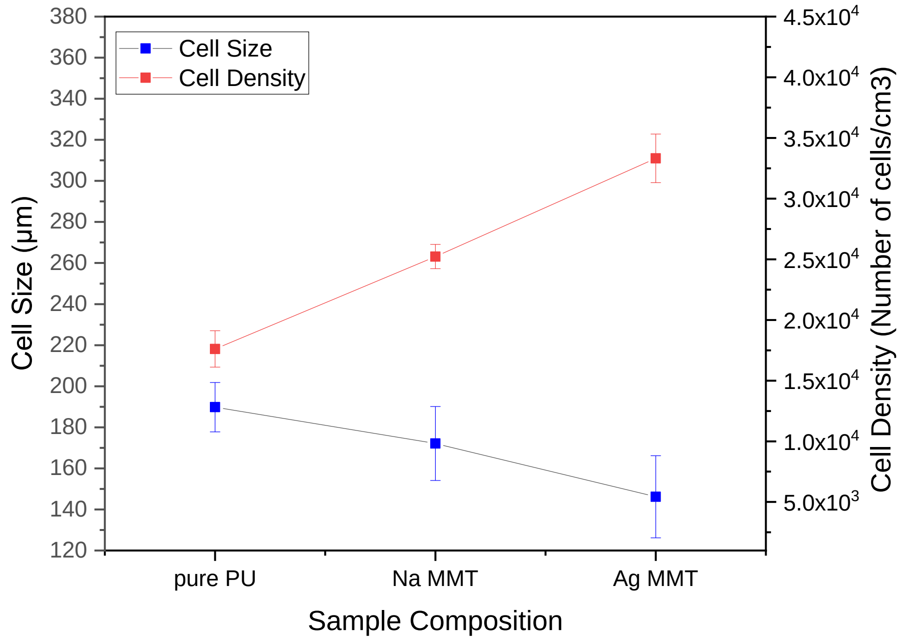

Figure 3.12. Cell size and cell density in parallel to foam rise SEM images.

3.4. (XRD) diffraction Analysis

Figure 3.13. shows the XRD patterns of Na MMT and Ag MMT nanoclay powder. According to the XRD graph, Montmorillonite MMT is the main component of this clay due to the d001 spacing of 1.21 nm (at $2\theta = 7.31°$) These results are similar to previous research data about XRD montmorillonite nanoclay (Ayat, Belbachir, and Rahmouni et al. 2016). The d-spacing of Ag MMT, 1.21 nm, and Na MMT, is 0.98 nm when the $2\theta = 7.31°$ for Ag MMT and, $2\theta = 9.04°$ for Na MMT. For the Ag MMT, the intensity of the reflections was lower, whereby the increase of the interlayer space.

It can be seen that Na MMT shows peaks at 20.05°, 21.05°, 26.86°,35.11°, 54.31°, and 62.35° 64.54° which matches the Na MMT diffraction peaks. Ag MMT shows diffraction peaks at 38.12°, 44.38°, and 64.54° which is referred to as crystalline silver (Ru and Wang et al. 2018).

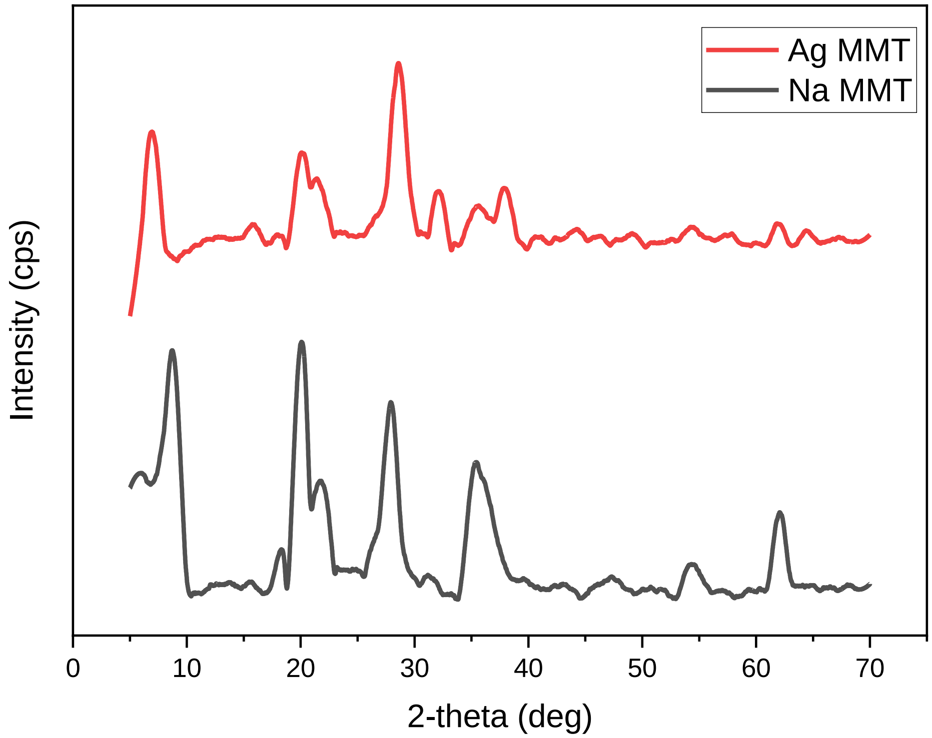

Figure 3.13. (XRD) Diffraction patterns of Na MMT and Ag MMT nanoclay.

3.5. The Analysis of Density Measurements

The density of the pure PU foam and nanocomposite RPUFs foam samples show the figure 3.14. it shows the foam density decreased, at the unmodified nanoclay 30B addition about 19 %. While Na MMT decreased about 16 %. And, it was observed that the density of the silver-modified nanoclay Ag MMT decreased about 7 %. While there is a slight difference for Ag30B density compared to pure polyurethane foam density.

Nevertheless, the polyurethane foam density is sensitive to small changes in environmental conditions, like moisture and temperature (Thirumal et al. 2008).

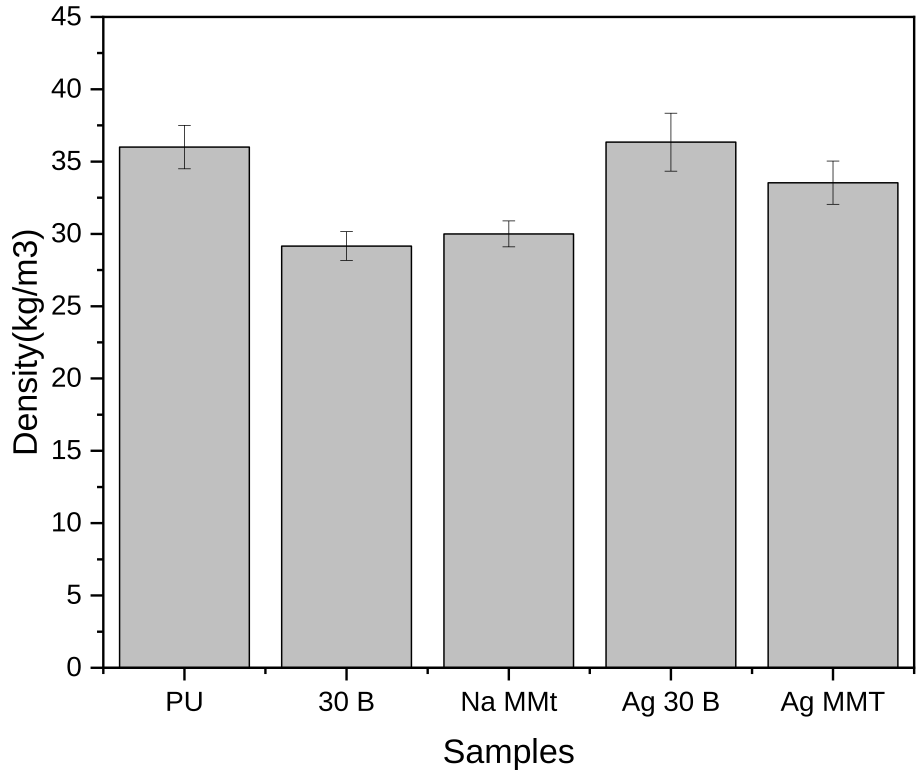

Figure 3.14. Measured density of samples.

3.6. Thermal conductivity

Thermal conductivity of RPUFs depends on foam density and foam cell size, the ratio of the open to close cell content, and also thermal conductivity of blowing agents and additives (Modesti et al, 2007).

Thermal conductivity tests are done in two different methods. Samples were probed perpendicular to the foam rise direction and also parallel to the foam rise direction.

According to the results shown in the Figure 3.15. It was seen that Na MMT and Ag 30B nanoclay added to the rigid polyurethane foam did not affect the thermal conductivity values. While the thermal conductivity values increased with 30B and Ag MMT addition, maybe the clays are not dispersed homogeneously in the foam mixture.

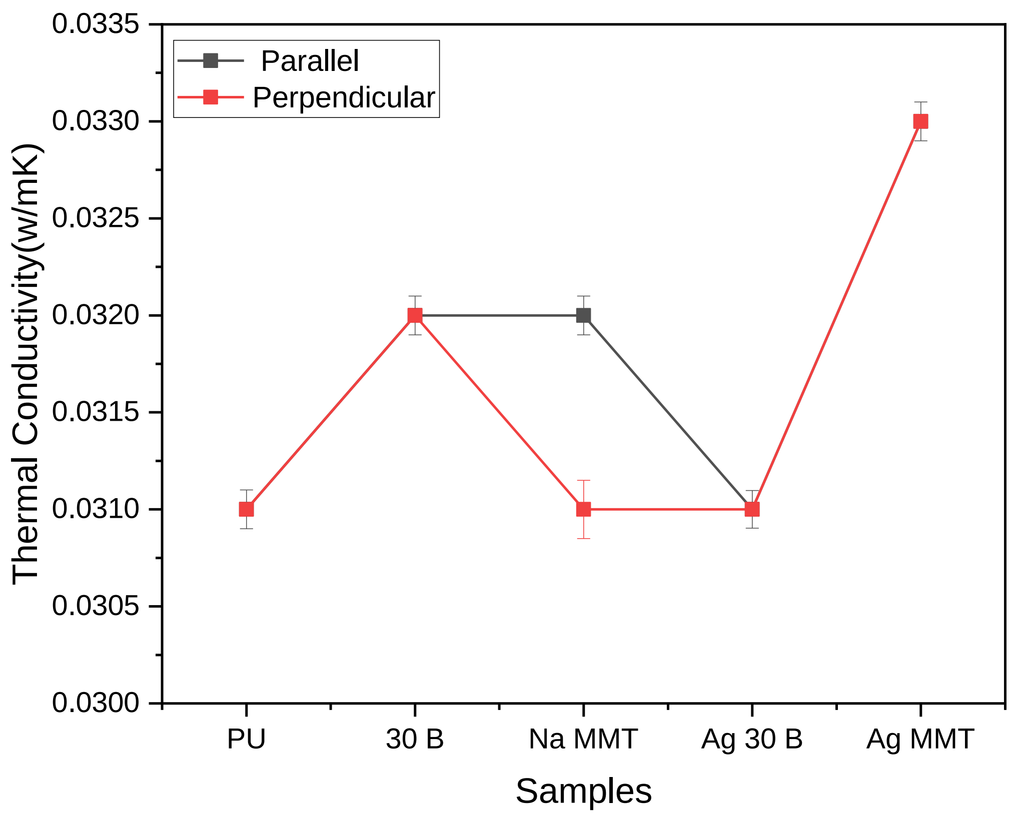

Figure 3.15. Thermal conductivity result of the foam samples.

3.7. Thermogravimetric Analysis (TGA)

By using thermogravimetric analysis (TGA), the thermal stability of rigid polyurethane foam samples was examined.

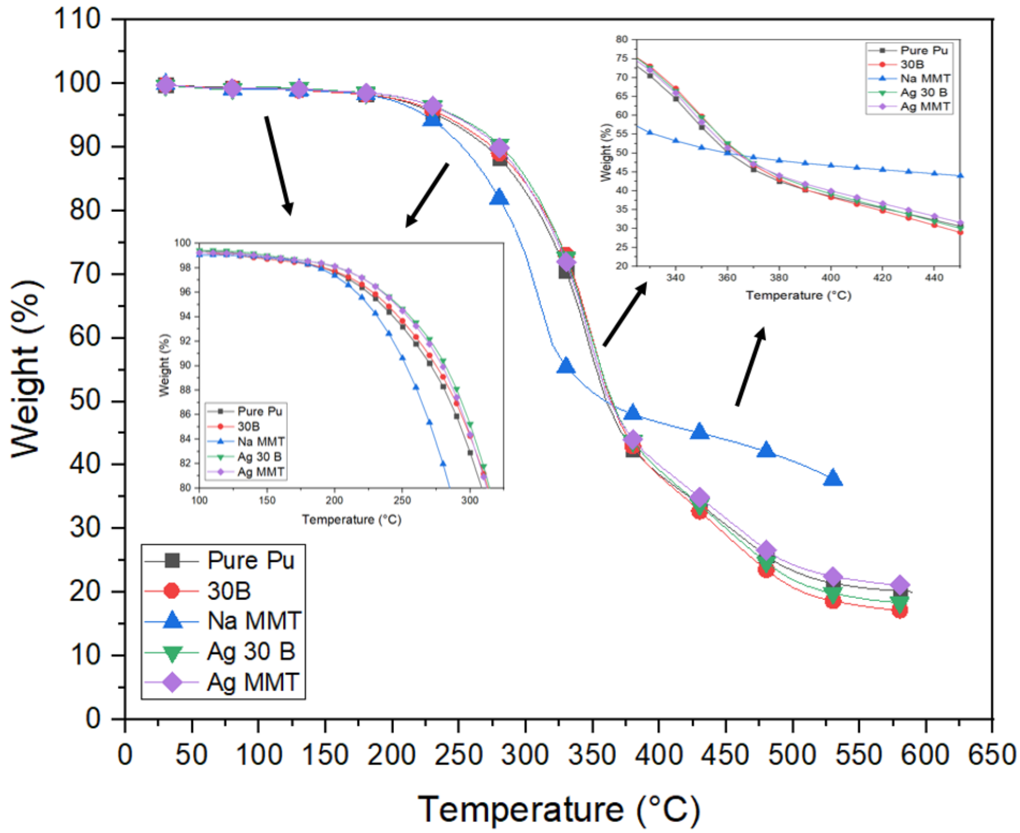

Figure 3.16. Thermogravimetric analysis of foam samples.

TGA results of RPUFs are shown in Figure 3.16. The decomposition temperature of RPUFs increased with the addition of modified nanoclay Ag 30B and Ag MMT. And also the decomposition temperature increased for unmodified 30B in comparison to the pure polyurethane foam.

Until 350 °C best performing sample was Ag 30B. At 600°C Na MMT has 40 % of the mass remained unburned while other samples had 20 % of their total masses unburned. The lower rate of burning of nanocomposites is due to the increased rigidity and the nanoclay also acts as a barrier for the volatile components (Kalita et al. 2018)

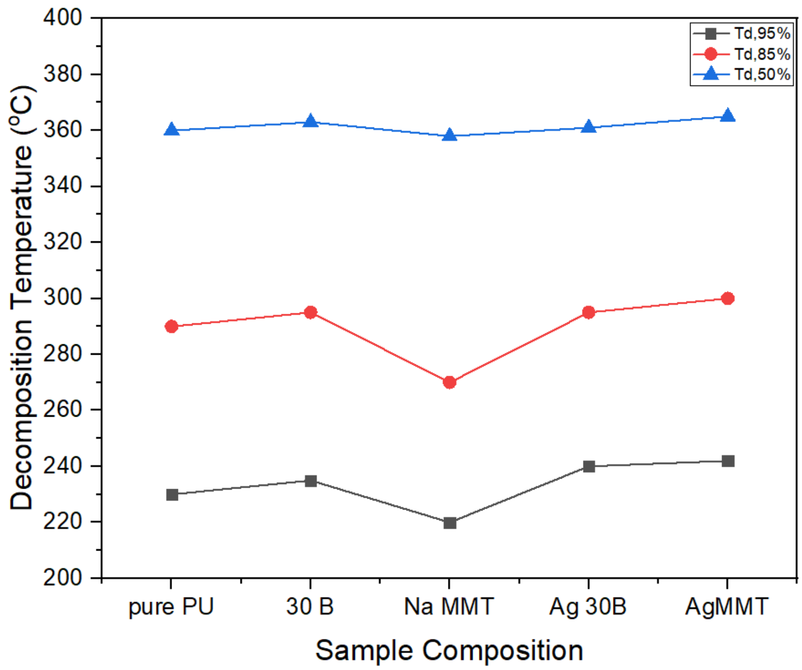

Figure 3.17. Decomposition temperature of the samples

It reveals that the thermal degradation process of RPUFs proceeds in three stages. In the first degradation stage, in the temperature of 200°C the degradation of hard segments into starting raw materials, such as isocyanate and polyol. In the second stage at the 200–350 °C temperature range, the decomposition of soft segments of RPUFs. The third degradation stage in the temperature above 500°C the isocyanates start to the decomposition (Jiao et al. 2013).

Table 3.2: Results of the Decomposition temperature of the samples

Sample Code	Td,%95 (°C)	Td,%85 (°C)	Td,%50 (°C)
Pure Pu	230	290	360
30 B	235	295	363
Na MMT	220	270	358
Ag 30 B	240	295	360
Ag MMT	242	300	365

Figure 3.17. shows us the exact temperatures where samples lost a specific part of their masses during thermogravimetric analysis. 5%, 15%, and 50% represent mass losses from the starting mass of the samples. The thermal decomposition temperatures Ag MMT has the best performance in terms of thermal stability compared to the other foam samples.

(Chattopadhyay and Webster et al. 2009) investigated the higher thermal stability of modified clays due to the crosslink structure between the urethane groups and the modified montmorillonite (MMT).

3.8. Antibacterial result

The Antibacterial test were performed on all the foam samples using disc diffusion method as shown in the figure 3.18.

As seen in the results pictures for bacteria species that show no inhibition zone around the foam samples. The results reveal that silver modified nanoclay addition does not exhibit any antibacterial effect. Due to the low concentration of silver modified nanoclay. The antibacterial activity of the RPUFs foams is related to the concentration of silver nanoparticles on the foam surface (Jain and Pradeep 2005).

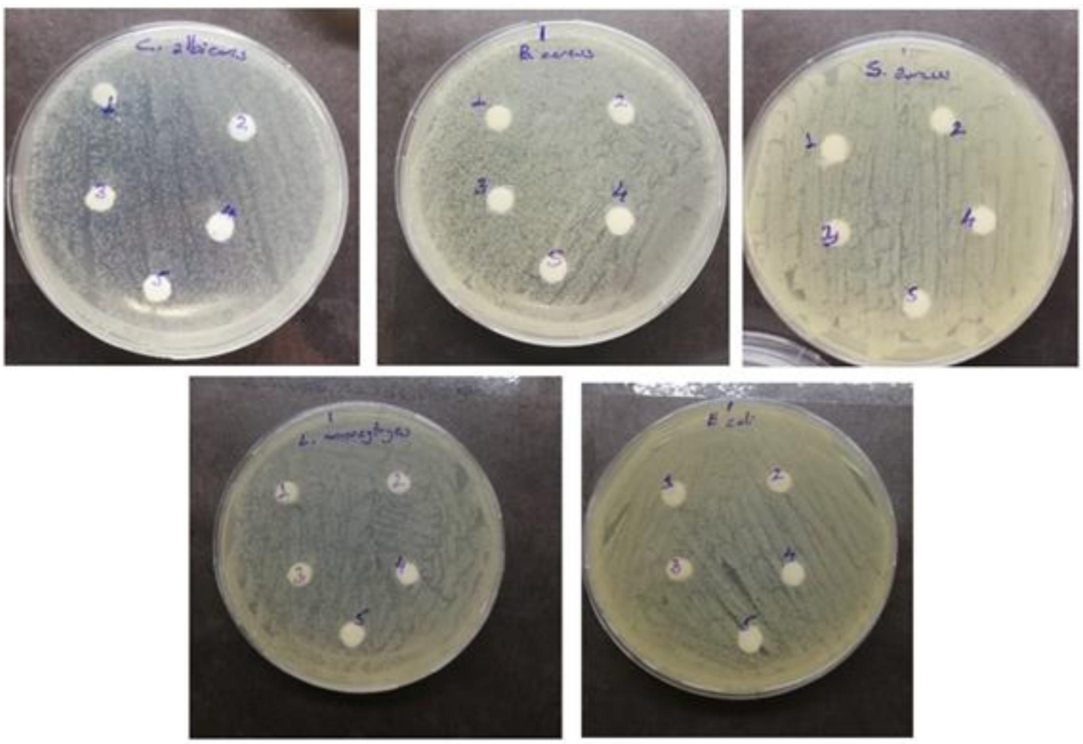

Figure 3.18. The Antibacterial test result for the samples, which include the discs 1. Ag MMT, 2. 30B, 3. Ag 30B, 4. Pure PU, and 5. Na MMT.

4. CONCLUSIONS

Pure and nanocomposite rigid polyurethane foams were produced in this study by mixing the isocyanate and polyol with a catalyst and blowing agent. 1wt.% of Na MMT, Cloisite 30 B unmodified and Ag MMT, Ag 30 B silver modified nanoclay disperse in isocyanate to produce nanocomposites rigid foams. Thermal, mechanical, and antibacterial properties were analyzed for all the foam samples.

The characterization of rigid polyurethane foams RPUFs was also described in this study. Clay dispersion is affected by the foaming process. The addition of 1% (Na MMT, and 30 B) unmodified, and (Ag MMT, and Ag 30 B) silver modified nanoclay resulted in increased cell density and reduced cell size of nanocomposite RPUFs.

FTIR of pure rigid polyurethane and nanocomposite rigid polyurethane foams shows no change in the chemical structure of PURFs with the addition of nanoclay. The best performance in the thermogravimetric (TGA) was Ag 30B foam sample until 350 °C. At 600°C Na MMT has 40 % of the mass remained unburned while other hybrid samples had 20 % of their total masses unburned. The compression strength and compressive modulus of the nanocomposites foams samples generally decrease with nanoclay addition. The antibacterial activity of the RPUFs foams with the silver modified nanoclay addition does not exhibit any antibacterial effect, due to the low concentration of silver modified nanoclay.

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