ESKİŞEHİR TECHNICAL UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY
A- APPLIED SCIENCES AND ENGINEERING

19th National Clay Symposium (Clay'2023) Special Issue 2023

2023, Vol.24, pp. 1-8, DOI: 10.18038/estubtda.1367889

EFFECT OF BENTONITE AND DOLOMITE ADDITIVES ON RIGID POLYURETHANE FOAM

Sinem TÜMÜK [1,*], Bilgehan GÜZEL [2], Erdem DELİL [3]

[1,3] Teknopanel Roof and Wall Panels Production Inc., Mersin, Turkey.
[2] Department of Chemistry, Faculty of Arts and Sciences, Çukurova University, Adana, Turkey

ABSTRACT

In this study, clay minerals such as bentonite and dolomite were included in the rigid polyurethane foam against the reference foam in order to increase the compressive tensile strength and reduce the thermal conductivity. The effect of different combinations and amounts of clay minerals on the test parameters of the foam was investigated. The surface morphology of the doped foams was investigated by scanning electron microscopy (SEM). Polyurethane foams were subjected to compressive-tensile strength and thermal conductivity tests. Improvement was observed in the thermal conductivity of polyurethane foams containing 1% bentonite and in the compressive and tensile strengths of polyurethane foams containing 2% dolomite. When clay minerals were added to polyurethane foam in combination, both thermal conductivity and compressive and tensile strengths were improved.

Keywords: Polyurethane, Bentonite, Dolomite, Strength, Thermal conductivity

1. INTRODUCTION

As the demand for energy increases with the increase in the world population, the issue of energy efficiency is becoming increasingly important. One of the most important issues in energy efficiency is thermal insulation. Polyurethane foam is a versatile material that can be rigid, flexible or semi-rigid, resulting from the chemical reaction between the functional group of isocyanate and the hydroxyl groups of polyol. Rigid polyurethane foams are closed-cell thermoset plastics that contain gas with low thermal conductivity inside the foam cells and provide high thermal insulation [1]. Due to their superior mechanical properties, excellent thermal insulation properties, low apparent density and high resistance to weathering, they are widely used in various industries, such as automobile, marine, construction, packaging, and furniture industries. The main application purposes are thermal insulation, acoustic, shock absorption, and sound absorption applications [2]. Rigid polyurethane foam materials are widely used as thermal insulation materials in different sectors, especially due to their low thermal conductivity coefficients. In general, the heat conduction coefficient of rigid polyurethane foams depends on the foam density, cell size, cell orientation, open/closed cell ratio, the type of gas contained in the cell, and the heat conduction coefficient of fillers, if any [3]. Since polyols and isocyanate used in polyurethane synthesis are petroleum-derived materials, constantly increasing oil prices, and the exhaustibility of petroleum resources, it is increasingly important to reduce the petroleum-derived input by researching inorganic additives and incorporating them into the composite material as fillers. In many studies, nanoclays have been successfully used in thermoplastic foams to reduce cell size and increase strength [4]. Clay is a naturally occurring, naturally occurring, fine-grained, crystalline material present in rocks and soils that exhibits plastic properties when water is added. Clay minerals find almost innumerable applications, and the diversity of uses is still increasing [5]. Clay minerals are hydrated aluminosilicates containing certain amounts of Mg, K, Ca, Na and Fe and contain two-dimensional repeating tetrahedral layers in their composition [6]. Bentonite is formed by the chemical weathering and decomposition of volcanic ash, tuff and lava, predominantly in colloidal silica structure, rich in aluminium and

*Corresponding Author: sinemtumuk@teknopanel.com.tr
Received: 01.10.2023 Published: 29.11.2023

magnesium. It consists mainly of montmorillonite minerals and is defined as a light-coloured rock composed of very small crystals, soft, porous and easily shaped. The specific gravity of bentonite, which can be observed in various colours such as white, grey, brown and cream, varies between 2.7–2.8 g/cm^3. The theoretical formula of bentonite is $Si_8Al_4O_4(OH)_4.nH_2O$ and its chemical composition theoretically includes 65.4% SiO_2, 23.2% Al_2O_3 and 3.6% MgO [7]. Dolomite mineral, whose general composition is $CaMg(CO_3)_2$, is a mineral with different properties from calcite. Unlike calcite minerals, CaO is partially or completely replaced by MgO components. It has different usage areas such as ceramics, chemical industry, water filtration, and filler in the paint industry [8].

In these polymer composites, inorganic materials were used to reinforce polymers with the idea of taking advantage of the high heat durability the high mechanical strength of inorganic and the ease of processing polymers [9].

This study aimed to reduce the thermal conductivity coefficient while increasing the compressive tensile strength of polyurethane foams. Bentonite was added to rigid polyurethane foam material at 1, 5 and 10% by mass. Thermal conductivity and compressive tensile strength values of the reference foam and bentonite-added foam materials were measured. Then, dolomite was added to the rigid polyurethane foam material at 2, 10 and 15% by mass. The thermal conductivity and compressive tensile strength values of the reference foam and dolomite-added foam materials were measured.

2. MATERIALS AND METHODS

Polyol, polymeric MDI ([4,4′–Methylenebis (phenyl isocyanate)], additives and catalyst chemicals were obtained from Flokser Textile Company. CR1120 is provided as an additive to regulate the polyurethane cell size. N,N-Dimethylcyclohexylamine (DMCHA) was used as the catalyst and pentane was used as the blowing agent. Dolomite was obtained from Şişecam and bentonite was obtained from KarBen Bentonite Company. The chemical content of dolomite used in the study (wt.%) is as follows: 0.26%±0.05 SiO_2, 0.08%±0.03 Al_2O_3, 0.015%±0.05 Fe_2O_3, 31.90%±0.30 CaO and 20.25%±0.25 MgO. Its chemical composition data were obtained from the company where the dolomite was supplied.

The chemical content (wt.%) of bentonite is 61.28% SiO2, 17.79% Al2O3, 3.01% Fe_2O_3, 4.54% CaO, 2.70% Na2O, 2.10% MgO and 1.24% K_2O. The company from which the bentonite was supplied also provided this chemical composition data. A carbon-coated polished thin section of a polyurethane cell was examined using an FEI Quanta 650 field-emission gun scanning electron microscope, at 20 kV. Tensile strength (kPa) and compression strength (kPa) tests of the obtained polyurethane were performed using Devotrans DVT FU50 D NN. Additionally, thermal conductivity (W/mK) was measured using a Heat Flow Meter by Netzsch HFM 436 Lambda.

The bentonite and dolomite to be added to the rigid polyurethane foam material were kept in an oven at 100^{o}C for 24 hours before use, and the moisture in these materials was removed. Bentonite, whose moisture is removed, is added to 100 grams of polyether polyurethane foam at a ratio of 1, 5 and 10%. It is mixed with a high-speed mechanical mixer. After obtaining a homogeneous mixture, 3.9 grams of catalyst, 3.7 grams of cell organizer, and 8.5 grams of blowing agent are added and mixed. One hundred sixty grams of polymeric MDI are reacted and poured into a mold with dimensions of 35×35×7 cm and left to cure. The dehumidified dolomite is added to 100 grams of polyether polyolefin at a ratio of 2, 10 and 15%. It is mixed in a high-speed mechanical mixer. After obtaining a homogeneous mixture, 3.9 grams of catalyst, 3.7 grams of cell organizer, and 8.5 grams of blowing agent are added and mixed. 160 grams of polymeric MDI is reacted and poured into a mold measuring 35×35×7 cm and left to cure. When the thermal conductivity and compression-tensile values were analyzed, 1% bentonite and 2% dolomite combination foam were made in the same process as the clays with the best results.

3. RESULTS AND DISCUSSION

3.1. Foam Formulation

The amounts of polyol, additive, catalyst, blowing, MDI, bentonite and dolomite in polyurethane foams are given in Table 1.

Table 1. Polyurethane foam formulations

Sample Name	Polyol (g)	Additive (g)	Catalyzer (g)	Blowing Agent (g)	MDI (g)	% Bentonite	% Dolomite
Sample 1	99	3.7	3.9	8.5	160	1.0	–
Sample 2	95	3.7	3.9	8.5	160	5.0	–
Sample 3	90	3.7	3.9	8.5	160	10.0	–
Sample 4	98	3.7	3.9	8.5	160	–	2.0
Sample 5	90	3.7	3.9	8.5	160	–	10.0
Sample 6	85	3.7	3.9	8.5	160	–	15.0
Sample 7	97	3.7	3.9	8.5	160	1.0	2.0
Reference	100	3.7	3.9	8.5	160	–	–

3.2.SEM Analysis

SEM images of polyurethane foams synthesized by adding 1, 5, and 10 wt.% bentonite and 2, 10, and 15 wt.% dolomite to the polyol chemical were examined. The reference polyurethane foam synthesized without adding bentonite and dolomite is shown in Figure 1. The polyurethane cell sizes are similar and the pore structure is quite regular. In Figure 2, SEM images of the polyurethane foam with 1, 5, and 10% by mass of bentonite were given. It was seen that the pore structure of the foams with 1% added bentonite was similar to the reference foam. It was observed that the pore sizes of the polyurethane foams with 5% added bentonite started to become irregular. In comparison, the pore sizes of the polyurethane foams with 10% added bentonite became completely irregular and the cells were broken. In Figure 3, SEM images of polyurethane foams with 2, 10, and 15% dolomite added by mass were given and it was seen that the pore structure of 2% dolomite-doped foams was similar to the reference foam. It was observed that the pore sizes of 10% dolomite doped polyurethane foams started to become irregular, the pore sizes of 15% dolomite doped polyurethane foams became completely irregular and the cells were ruptured. When examined against the reference, it was observed that the polyurethane foam cell structure obtained with the combination of 1% bentonite and 2% dolomite was suitable.

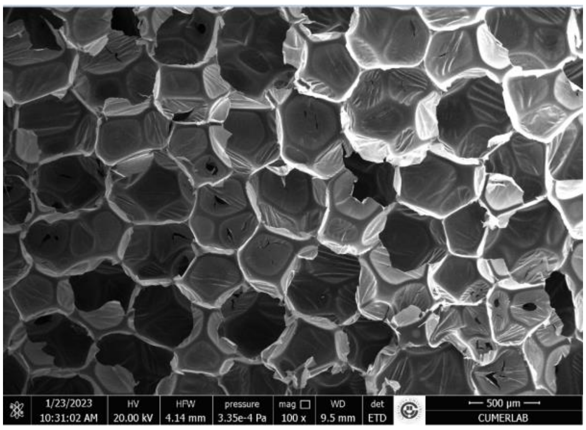
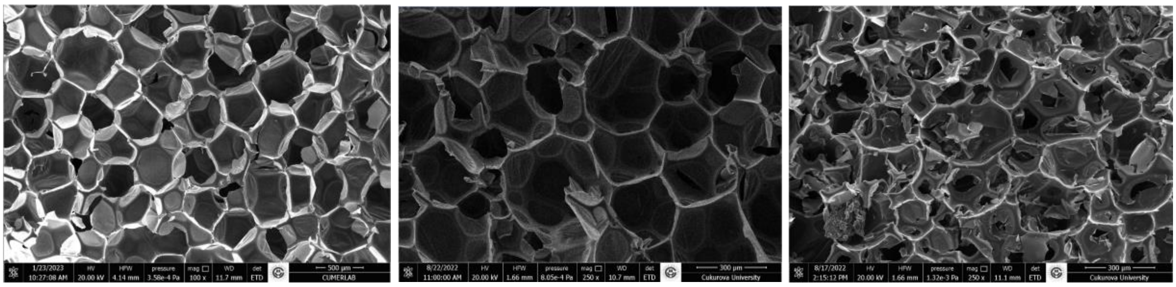
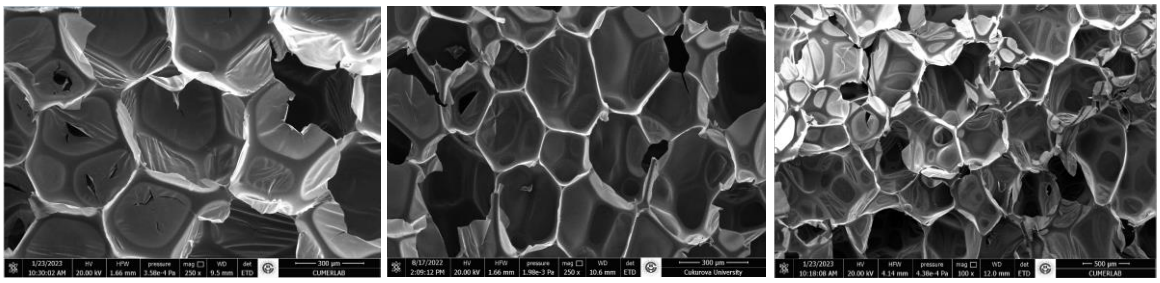


Figure 1. SEM image of reference foam without bentonite and dolomite additives



(a) **(b)** **(c)**

Figure 2. SEM image of polyurethane foam with 1% **(a)**, 5% **(b)** and 10% **(c)** bentonite additives



(d) **(e)** **(f)**

Figure 3. SEM image of polyurethane foam with 2% **(d)** 10% **(e)** and 15% **(f)** dolomite additives

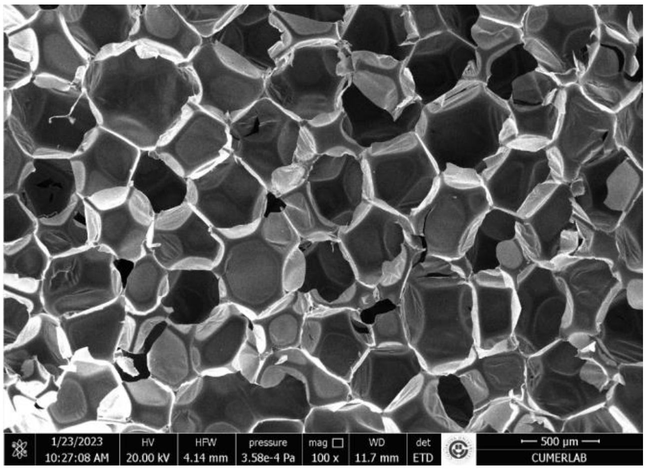


Figure 4. SEM image of polyurethane foam with 1% bentonite and 2% dolomite additives

3.3. Compression/Tensile and Thermal Conductivity Tests

Compression/Tensile strength and thermal conductivity values of the reference foam and synthesised polyurethane foams are given in Table 2.

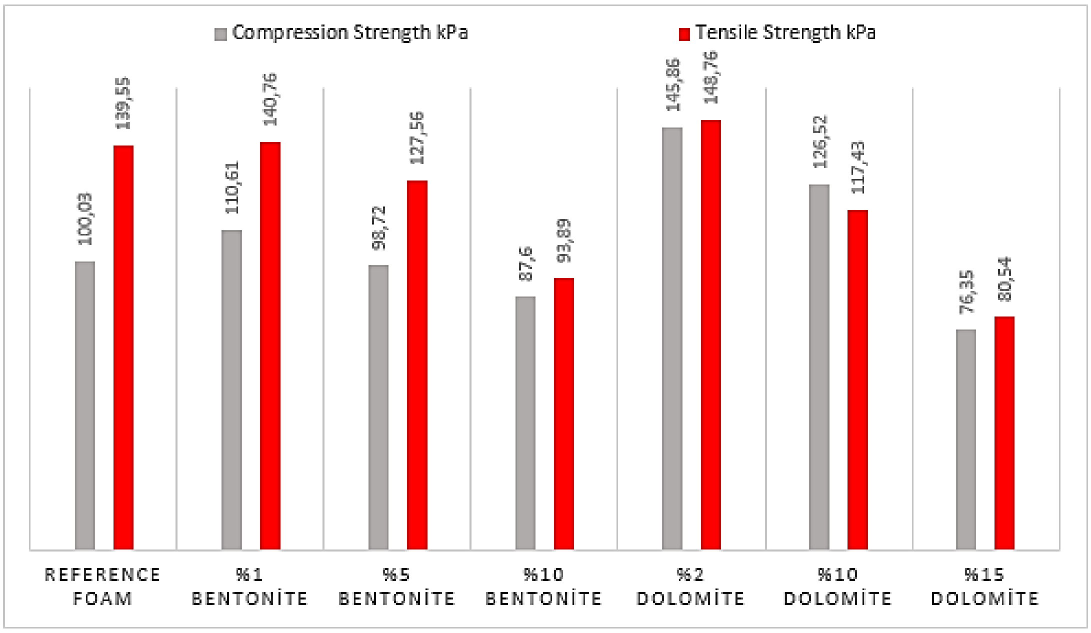


Figure 5. Compression/Tensile Strenght results of polyurethane foams with bentonite and dolomite

When the foam doped with 1% bentonite is analysed against the reference foam, it is seen that the compression tensile strength values increase. As the bentonite ratio increased, it was observed that the compression polyurethane foam cells ruptured, and the compression tensile strength values decreased. When the foam doped with 2% dolomite was analysed against the reference foam, it was observed that the compression tensile strength values increased. As the dolomite content increased, it was observed that the polyurethane foam cells ruptured and the compression tensile values decreased. While both bentonite and dolomite minerals show improvement in compressive and tensile strength values against the reference, it is clearly seen that 2% dolomite doped polyurethane foam shows a better result than 1% bentonite doped polyurethane foam.

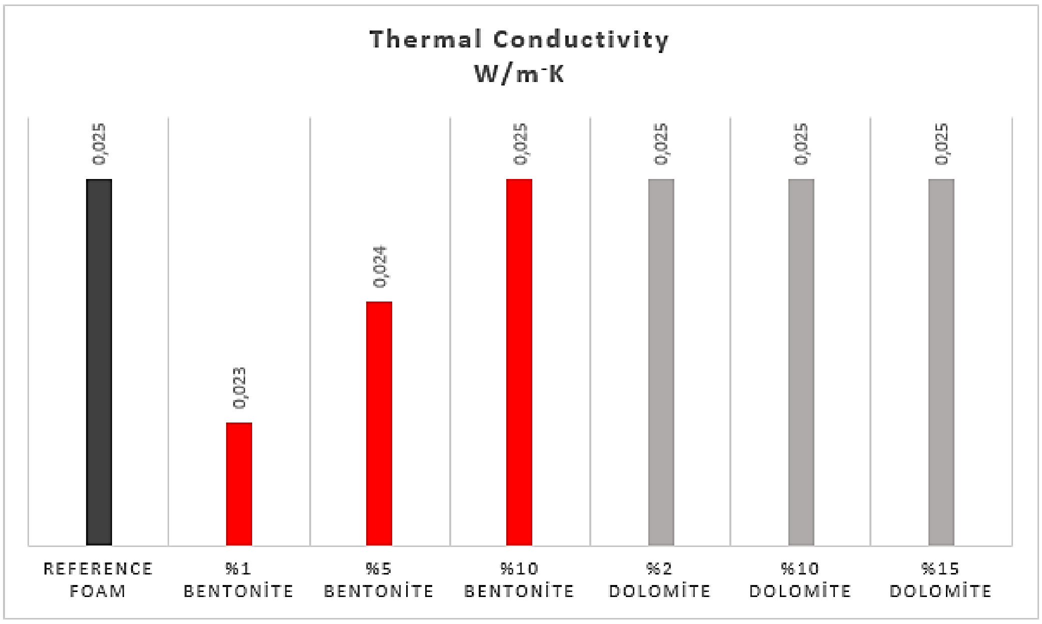


Figure 6. Thermal conductivity results of polyurethane foams with bentonite and dolomite

When the thermal conductivities of bentonite and dolomite doped polyurethane foams against the reference foam were analysed, it was seen that the thermal conductivity coefficient decreased from 0.025 to 0.023 with the addition of 1% bentonite to the polyurethane foam. The decrease in the thermal conductivity coefficient means the thermal insulation performance will improve. Although the thermal conductivity coefficient increased by increasing the amount of bentonite, it showed a better result than the reference. No improvement or decrease in thermal conductivity coefficients was observed in polyurethane foams to which dolomite was added.

Table 2. Combined recipe compressive tensile strength and thermal conductivity results

Sample Name	Compression Strengths (kPa)	Tensile Strenghts (kPa)	Thermal Conductivity (W/mK)
Sample 8	145.72	149.53	0.023
Reference	100.03	139.55	0.025

A combination recipe of polyurethane foams with 1% bentonite additive and 2% dolomite additive was made with the best results in thermal conductivity and compressive tensile strength and the highest compressive tensile and lowest thermal conductivity coefficient values were obtained as shown in Table 2.

4. CONCLUSIONS

In this study 1, 5 and 10% bentonite and 2, 10 and 15% dolomite were added to rigid polyurethane foams. When the SEM images were examined, the SEM images that resembled the reference foam were Sample 1 and Sample 4. Cell sizes and arrangements are very similar to the reference foam. It was observed that as the amount of dolomite and bentonite in the foam increased, the size of the polyurethane foam cells became irregular and broke. Irregular size of the foam cells and rupture of the foam cells cause the compressive and tensile strengths to decrease. When the bentonite added to Sample 2 and Sample 3 is examined against the reference, the decrease in compressive and tensile strength is due to the excessive amount of bentonite tearing the polyurethane foam cells and as a result, the number of carrier cells decreases. When the dolomite added to Sample 6 is examined against the reference, the decrease in compressive and tensile strength is due to the excessive amount of dolomite tearing the polyurethane foam cells. As a result, the number of carrier cells decreases. When the compressive and tensile strengths were examined, it was seen that the values of Sample 1, Sample 4 and Sample 5 were higher than the reference. When Sample 1, Sample 4 and Sample 5 were compared, it was seen that Sample 4 gave the best result. The reason is that the determined amounts of dolomite and bentonite increase the number of carrier cells. With the 1% bentonite additive amount in the foam cells, the average cell size decreased. Thus, the thermal conductivity also decreased. Thermal conductivity values are lower in Sample 1 and Sample 2 when examined against the reference. Sample 3 did not provide an improvement in the thermal conductivity value because the excess amount of bentonite ruptured the foam cells. It has been observed that depending on the amount of bentonite added to the polyurethane foam, it causes a decrease in the average cell size and a decrease in its thermal conductivity. It has been observed that dolomite used as a filling material increases the compressive and tensile strength of rigid polyurethane foam up to specific amounts. To simultaneously increase thermal conductivity and compressive tensile strength, the combination recipe Sample 8 containing 1% bentonite and 2% dolomite, which achieved the best results, was synthesized. When the combination recipe was compared with the reference foam, it was observed that there was an improvement in both compressive tensile strength and thermal conductivity values.

CONFLICT OF INTEREST

We state that there are no conflicts of interest of any type as regards the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Sinem Tümük: Literature survey, data collection and analysis, writting, supervising and reviewing.
Bilgehan Güzel: Literature survey, supervising and reviewing.
Erdem Delil: Literature survey, data collection.
All authors stated that there are no conflicts of interest regarding the publication of this article.

REFERENCE

[1] Chuayjuljit S, Maungchareon A & Saravari O. Preparation and Properties of Palm Oil-Based Rigid Polyurethane Nanocomposite Foams. J. Reinf. Plast. Compos 2010; 29(2): 218-225.

[2] Omotoyinbo JA, Oladele IO, Jabar JM, Borode JO, Alaneme KK, Akinwekomi, AD, Samuel RO, Omotosho TF, Saliu LO. Comparative investigation of the influence of Kaolin and Dolomite on the Properties of Polyurethane Foam. Manufacturing Rev 2021; 8: 27-32.

[3] Aydoğan B, Nazım USTA. Experimental Investigation of Thermal Conductivity, Thermal Degradation and Burning Resistance of Rigid Polyurethane Foams with Nanocalcite and Swelling Flame Retardant Addition. Isı Bilimi ve Tekniği Dergisi 2015; 35(2): 63–74.

[4] Widya T & Macosko CW. Nanoclay-Modified Rigid Polyurethane Foam. J Macromol Sci B: Phys J 2005; 44(6): 897–908.

[5] Alan N & İşçi S. Surface Modification of Sepiolite Particles with Polyurethane and Polyvinyl Alcohol. Prog. Org. Coat 2014; 77(2): 444–448.

[6] Erdem M, Ortaç K, Erdem B, Türk H. Effect of Reactive Organobentonite Additives on Some Performance Properties of Rigid Polyurethane Foam. Gazi Üniversitesi Mühendislik Mimarlık Fakültesi Dergisi 2017; 32(4): 1209–1220.

[7] Baysal B. The Effect of Phosphonium Salt on Thermal Stability and Mechanical Properties in Montmorillonite/Polymer Nanocomposites Master Thesis, İstanbul University, İstanbul, Turkey, 2012.

[8] Aydoğan B. Investigation of Thermal Decomposition and Combustion Behaviors of Polyurethane Based Composite Materials Containing Natural Minerals, Doctoral Thesis, Pamukkale University, Denizli, Türkiye, 2015.

[9] Rehab A & Salahuddin N. Nanocomposite Materials Based on Polyurethane Intercalated into Montmorillonite Clay. Mater. Sci. Eng. A, 2005; 399(1-2): 368–376.