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Influences of Halloysite Nanoparticles on the Mechanical Properties of Polyurethane Foam

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Abstract

This research aims to scatter halloysite nanotubes to test the mechanical properties of foamed polyurethane nanocomposites. The modified nanotubes were incorporated into a polyurethane matrix to create a range of polyurethane/halloysite nanocomposites. The halloysite nanoparticles were mixed with the polyol, surfactant, fire retardant, and catalyst in the B-side components. To make the polyurethane nanocomposite, polymeric isocyanate was added. The results of this investigation established that "halloysite nanotubes" were an excellent reinforcing filler for waterborne polyurethane without impairing the product's toughness significantly. The polyurethane nanocomposites were subjected to tensile strength, stress, hysteresis loss, compressive force deflection, ball rebound, and tear strength tests. The results demonstrate significant enhancement in nanocomposites with varying nanotube loadings. The halloysite nanoparticles increases the tensile strength and and increases the stress of the poluurethane by twice; however, it has minor change to the elongation.Commercialization of these findings remains a hurdle, owing to the scarcity of efficient dispersion pathways for large-scale applications and the activity's cost-effectiveness.

Keywords: Polyurethane; halloysite; nanotubes; nanocomposites; foam; reinforcement.

1. Introduction

Typically, polyurethane (PU) foams are formed by reacting the isocyanate and alcohol groups in polyols with selected flame retardants, physical and/or chemical blowing agents, surfactants, and catalysts[1-3]. Polyurethane foams come in a range of forms, from hard and crosslinked resins to lightweight foams and flexible and durable elastomers. A diverse range of additives, natural intermediates, fillers, and petrochemical enables the manufacture of foams with specific properties such as apparent density, tensile and flexural strength, cost, abrasion resistance, and biodegradability[4, 5]. Polyurethane foam is gaining a more popular alternative in the modern engineering and industrial sector because of the progressively strict quality criteria for building materials, such as durability, high "strength-to-weight" ratio, and corrosion resistance[6].

In terms of the polyurethane market, the electronics sector accounted for 15 percent in 2019. Because of the widespread use of PU foam in furniture to achieve a cushioning effect, the furniture industry is expected to dominate in the approaching years. It has a high level of durability and stability. In the furniture sector,

polyurethane is mostly utilized for bedding and cushions. This is due to the fact that it can provide comfort, durability, and flexibility. Furthermore, people's lives are continuously changing, and the world's population is growing, creating demand for furniture worldwide[7, 8].

Asia Pacific had USD 26.23 billion in revenue in 2019.[9] The region is poised to capture a sizable market share, backed by rising demand from the building and furniture industries. Because of the huge need for automotive applications in the United States, North America would experience significant growth. The majority of the market's leading players are headquartered in the Asia Pacific. The majority of them are concentrating on expanding their product portfolios by developing new PU applications[3, 10-12]. Others are attempting to meet increased consumption from a variety of industries. Based to Global Industry Marketing, Inc., the global polyurethane market will continue to exceed USD 93 billion in sales by 2026. To reduce environmental effects, there is a growing shift toward the usage of lightweight and eco-friendly polymers in application industries ranging as automotive and construction,

which has boosted consumption for sustainable plastic solutions[9, 13-15].

Polyurethane (PU) foam, on the other hand, has poor mechanical characteristics and thermal stability[16, 17]. It must be improved to address these issues. The insertion of nanoparticles into the polymeric matrix is the most extensively utilized method for improving the characteristics of polymeric materials. Inorganic nanomaterials such as carbon nanotubes[18], nano SiO_2, graphene, and nanoclay[19] were utilized to modify PU.

Nanoparticles are very small particles with diameters ranging from 1 to 100 nanometers. Nanoparticles, which are imperceptible to the human eye, may have vastly different physical and chemical properties than its larger counterparts. Nanoparticles get a comparatively large surface area to volume ratio as compared to bulk materials such as powders, plates, and sheets owing to their extremely small size. Nanoparticles might have unexpected optical, physical, and chemical capabilities since they are small enough to confine their electrons and create quantum impact.[20-23].

Halloysite (HS) nanotubes are a novel form of important nanomaterial composed of crystalline nanotubular structures with multiple walls. Every halloysite nanotube has an external surface made of siloxane "Si-O-Si" groups and an inside surface composed of a "gibbsite-like" array of aluminol "Al-OH" groups[24]. Halloysitenanotubes "HTs" have been used as catalyst loader, medication delivery systems, and filler renforcements due to its distinctive structure, surface characteristics, chemical synthesis, and ease of affordability[25, 26]. Furthermore, halloysite nanotubes have a shape similar to carbon nanotubes, making them a feasible substitute for more expensive carbon nanotubes[27].

WPU/AgHNT nanocomposites were developed by in situ polymerization by Fu et al.[28] By lowering silver ions withNaBH$_4$, silver nanoparticles were loaded onto HNTs. Various characterization techniques were applied onWPU/AgHNT nanocomposites films. WPU/AgHNTnanocomposites have improved thermal and mechanical properties. The nanocomposites were very effective against Staphylococcus aureus. It may be used in antimicrobial coatings.

Mohammadzadeh et al.[29] studied polyurethane nanocomposites. Two different step polymerization methods were used: hexamethylene diisocyanate and 1,4-butanediol. It has between 1% and 2% nanoparticles by weight. These techniques investigated phase separation and shape memory. Higher molecular weight polyols demonstrated greater phase separation. Due to the halloysite nanotubes' tendency to harden, introducing nanoparticles

improves phase separation. More nanoparticles increased shape fixity and shape recovery. Nanocomposite materials' shape memory behavior was also examined.

The present work synthesized polyurethane foam via the exothermic polymerization process and reinforced it with the halloysite nanoparticles. Tensile, stress, elongation, compression force deflection, ball rebound, and hysteresis tests were used to determine the influence of the HS on the mechanical cahracteristics of the PU foam nano composites.

2. Experimental method

2.1. Materials

The polyurethane foam formulas included "JEFFOL® G31-35" Tipped Triol and polymeric "Methylene diphenyl diisocyanate (PMDI)" from "Huntsman Company". For all experiments, an isocyanate index of 1.1 had been used. Distilled water was utilized as a chemical blowingagent. The characteristics of the polyol and PMDI are featured in Table 1. "Polyethermodified polysiloxane" copolymer was utilized as a surfactant. As catalysts, 1% "Triethylene diamine" in "dipropylene glycol" and "Bis(2-dimethylaminoethyl) ether" were used. All studies used the same quantity of surfactants and catalysts.

Table 1.
Specifecations of JEFFOL® G31-35 and PMDI.

Property	JEFFOL® G31-35	PMDI
Specific gravity (@25°C)	1.02	1.223
Average M.Wt	4500	339
Functionality	3.0	2.80
Hydroxyl number (mgKOH/g)	35	-
VaporPressure (mmHg@25°C)	-	<9
Water content	0.1%	-
Equivalent weight	1600	135
NCO content (wt %)	-	31.2
Viscosity (mPa.s @ 25°C)	860	156-216
Specificheat (g.cal/g.@25°C)	-	0.38

Sigma-Aldrich Ltd. provided the halloysite (HS) nanoclay "Al2Si2O5(OH)4.2H2O / molecular weight of 294.19 g/mol." The halloysite nanoclay was natural and had an adhesion promoter applied to the surface. The average dimensions were 700 nm in length and 30 to 70 nm in diameter. To further improve the dispersion of the HS nanoparticles, the surface of the nanotubes was modified using a silane coupling agent.

The polyol and the HS nanoparticles were dried overnight in a vacuum oven at 100°C and then mixed for 20 min. The blend was mixed during a sonication for one hour to obtain good nanoparticles dispersion.

2.2. Foaming process

The B-side materials (polyol, catalysts, surfactant, and nanoparticles) were mixed in a plastic cup and then mixed with the PMDI for 10 seconds using a 2000 rpm mixer blade attached to a floor-model drill press. The mixture was quickly poured into an 11 x 11 cm^2 base wooden box with "aluminium foil" lining, and the foam was able to expand. The foaming temperature was increased due to the exothermic polymerization reaction of the polyurethane, and the foam was allowed to grow until the temperature started decreasing, indicating the end of the reactions.

2.3. Mechanical testing

Dynamic frequency sweeps were performed using an "Anton Paar Ltd MCR 302" rotational strain-controlled rheometer with angular frequencies ranging from 0.05 to 300 rad per second. The experiment was conducted at ambient temperature with 50 mm parallel plates. ADMET's eXpert 7601 single-column testing machine performed the tensile and elongation tests, according to the ASTM D-412 standard.

The compression force deflection test "CFD" determines the force necessary to compress a foam sample to 50% thickness. This test was carried out using ADMET's eXpert 5600F equipment, according to ASTM D3574 C. The sample is sandwiched between two compression platens that are larger than the sample. The Compression Force Deflection test typically consists of a preflex sequence followed by a testing sequence. The thickness of the foam is set prior to the preflex and testing sequences. The thickness of the testing sequence is indicated at the end of the test. The same instrument was used to measure the hysteresis, according to ASTM D3574 X6.

The polyurethane foam samples were tested for resilience using the Bareiss Ball Rebound Tester instrument (BR500M). The fundamentals are completely following DIN EN ISO 8307 and ASTM D3574. A 16-mm magnetic steel ball is dropped freely onto the specimen from a height of 500mm during the test. This instrument's electronic device would present the computed values and percentage of the average value. FPT-H1, a fully-featured test system controlled by software running on a personal computer, was utilized for measuring the split trouser tear of the polyurethane samples, according to ASTM D-1938.

Figure 1 depicts the frequency sweep curves of the dispersions. At low HS nanoparticle concentrations of 4wt.%, the loss modulus values (G") are still greater than the storage modulus values (G'), indicating a liquid-like nature. A crossover over influence is detected at concentrations of 12 wt percent and beyond, and this is regarded as the percolation threshold of these particles. Thus, the reported

percolation threshold coincides well with predictions of a homogenous dispersion of the nanoparticles in the polyol. The existence of functional groups, such as OH moieties, on the surface of the HS nanoparticles makes them efficient to disperse in the polyol.
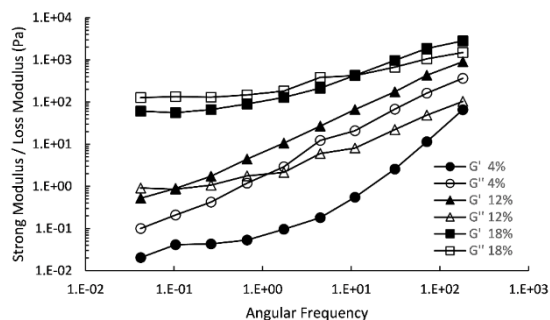

Figure 1. Frequency sweep curves of the HS nanoparticles in the polyol.

Figure 2 depicts the tensile strength values. Before introducing the HS nanoparticles, the polyurethane foam's tensile strength was 80.8 psi. The material's tensile strength grows gradually with the addition of HS nanoparticles at concentrations below 10%, eventually reaching around 30%. The growth is substantially rapid at greater HS concentrations, nearly four times at HS nanoparticle concentrations of 18%. This increase in tensile strength is attributable to adequate reinforcement and appropriate nanoparticle dispersion in the polyurethane matrix.

The stress at 100 percent elongation follows a similar pattern, as seen in Figure 3. When HS nanoparticles concentrations of 18 weight percent are compared to the polyurethane foam before adding the nanoparticles, the stress value is more than twice as high. The HS nanoparticles have a percolation threshold of around 15 weight percent. As a result, it's acceptable to assume that the network produced by the HS nanoparticles is responsible for the higher increase in characteristics.
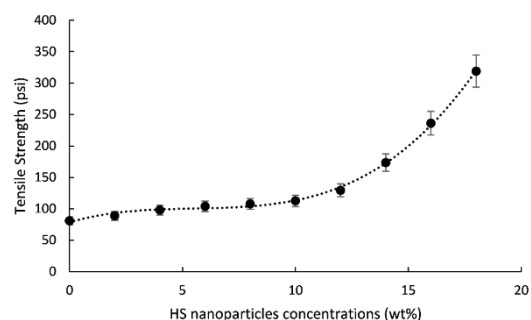

Figure 2. The tensile strength of polyurethane foam has varying amounts of HS nanocomposites. Dot line refers to the increasing trend.
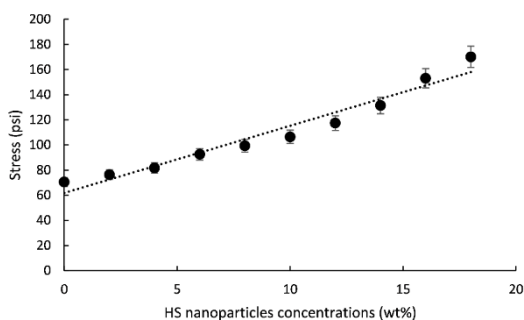
Figure 3. The stress at 100% elongation of polyurethane foam has varying amounts of HS nanocomposites. Dot line refers to the increasing trend.

Figure 4 shows that even when the concentration of HS nanoparticles is significant, the eventual elongation maintains somewhat constant. As a result, the elastomer's toughness is not affected whenever the tensile strength and modulus are raised.
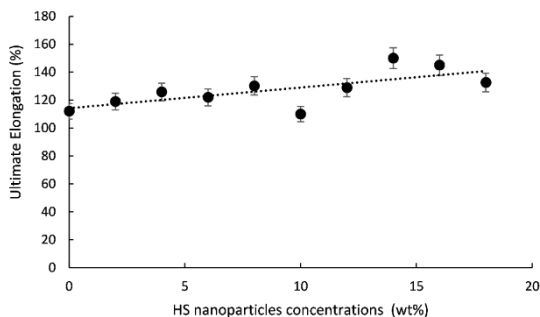

Figure 4. The ultimate elongation of polyurethane foam has amounts of HS nanocomposites. Dot line refers to the increasing trend.

Figure 5 demonstrates a consistent hysteresis loss for the polyurethane foam up to a 10% HS content. When the concentration of HS nanoparticles was greater than 10% by weight near the percolation threshold, an increase was seen. As a result, the breakdown of the nanotube network in the polymers throughout the experiment is most likely to be responsible.

Figure 6 summarizes the output of the compression force deflection. Since all of the nanocomposites had a larger compression force deflection than the reference elastomer, unlike tear strength, the compression force deflection does not demonstrate a rising pattern with concentration.
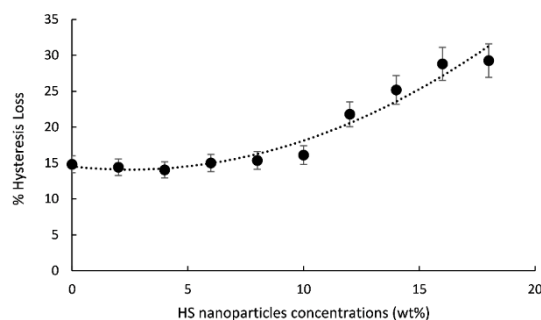

Figure 5. Hysteresis loss of polyurethane foam has varying amounts of HS nanocomposites. Dot line refers to the increasing trend.
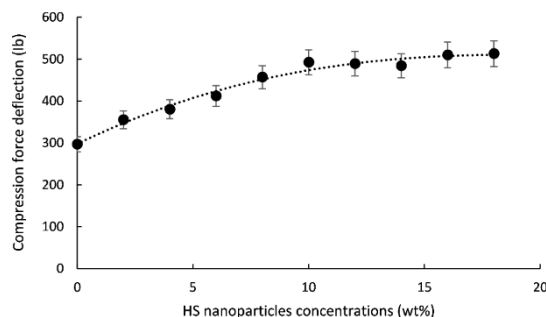

Figure 6. compressive force deflection of polyurethane foam has varying amounts of HS nanocomposites. Dot line refers to the increasing trend.

Polyurethane resilience is often assessed in various techniques, the most common of which is the Bashore Rebound Test. Resilience is graded on a scale of 0 to 100%. Upon recovery, a material that is 100 percent robust would restore all of the input energy. Figure 7 illustrates the findings of the ball rebound. As the concentration of HS nanoparticles is raised, the ball rebound stays nearly unchanged, demonstrating that the nanoparticles' presence does not impair the elasticity of the polyurethane foam.
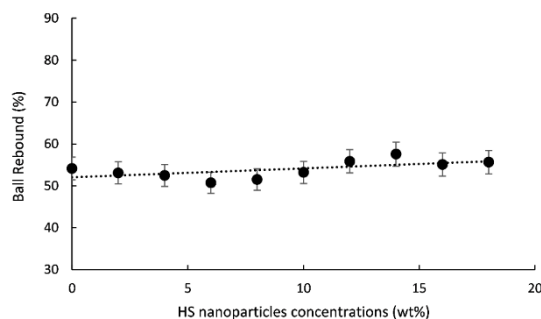

Figure 7. Ball rebound of polyurethane foam having varying amounts of HS *nanocomposites. Dot line refers to the varying trend.

The tear strength of polyurethane is a crucial attribute to evaluate while working in abrasive or destructive conditions. It is especially crucial if the polyurethane will be under tension and there is a risk of cuts or nicks. The tear strength of urethane is determined by a variety of basic characteristics such as modulus and tensile strength. Figure 8 shows the tear strength values. Tear strength improvement follows the same trend as modulus and tensile strength improvements. The tear strength gradually grows until it reaches a concentration of 10% HS, which rapidly increases. When the HS concentration is 18%, the tear strength is five times that of the polyurethane foam prior to the nanoparticles being added.
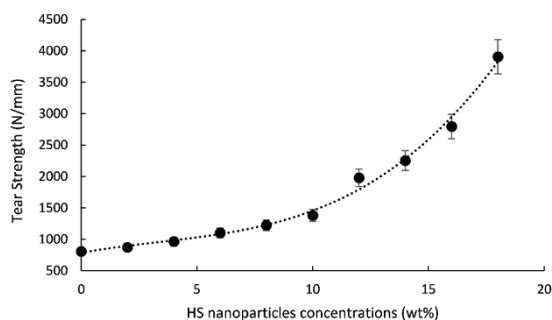

Figure 8. The tear strength of polyurethane foam has varying amounts of HS nanocomposites. Dot line refers to the increasing trend.

3. Conclusions

The accelerated innovation of many nanoparticles over the last two centuries has sparked considerable interest in integrating these materials with traditional polyurethanes, either full density or cellular, in order to improve efficiency or introduce new functions. Halloysite nanoparticles were mixed with polyurethane to form a variety of polyurethane/halloysite nanocomposites. Because of the surface functional groups that interact with the PU components, halloysite nanotubes scatter more easily in the PU precursors. Tensile strength, stress, hysteresis loss, compressive force deflection, ball rebound, and tear strength tests were performed on the polyurethane nanocomposites. The results indicate that nanocomposites with different nanotube loadings exhibit considerable enhancement. The halloysite particles increases the stress and the stress; however, it has minor change in elongation and compression force deflection. The ultimate elongation remains relatively consistent. Commercialization of these discoveries remains a challenge, owing to the scarcity of efficient dispersion channels for large-scale applications and the cost-effectiveness of the work.

4. Acknowledgement

5. Conflict of interest

There are no conflicts to declare.

6. References

[1]. Ashida K., Polyurethane and Related Foams: Chemistry and Technology. 2006: Taylor & Francis.

[2]. Al-Moameri H., Zhao Y., Ghoreishi R., and Suppes G., Simulation Silicon Surfactant Rule on Polyurethane Foaming Reactions. *Iranian Journal of Chemistry and Chemical Engineering (IJCCE).* **40**(4): p. 1256-1268(2021)

[3]. Al-Moameri H. H., Jaf L. A., and Suppes G. J., Simulation Approach to Learning Polymer Science. *Journal of Chemical Education.* **95**(9): p. 1554-1561(2018)

[4]. Cavaco L. I. and Melo J. A., Polyurethane: Properties, structure and applications. Polyurethane: Properties, Structure and Applications. 2012: Nova Science Publishers, Inc. 1-162.

[5]. Al-Moameri H. H., Nabhan B. J., Tawfeeq Wasmi M., and Abdulrehman M. A. Impact of blowing agent-blends on polyurethane foams thermal and mechanical properties. in *2nd International Conference on Materials Engineering and Science, IConMEAS 2019.* 2020. American Institute of Physics Inc.

[6]. Avar G., Polyurethanes 2008: Kunststoffe international

[7]. Rohan. Polyurethane Foam Market worth 74.24 Billion USD by 2021. 2009; Available from: http://www.marketsandmarkets.com/PressReleases/polyurethane-foams.asp.

[8]. Al-Moameri H., Zhao Y., Ghoreishi R., and Suppes G. J., Simulation of liquid physical blowing agents for forming rigid urethane foams. *Journal of Applied Polymer Science.* **132**(34)(2015)

[9]. Polyurethane Market Demand, Booming Business Ways with Strong Growth Prospects by 2026 | Fortune Business Insights. 2020 [cited 2021 November, 12]; Available from: https://www.globenewswire.com/news-release/2021/10/08/2311239/0/en/Polyurethane-Market-Demand-Booming-Business-Ways-with-Strong-Growth-Prospects-by-2026-Fortune-Business-Insights.html.

[10]. Gama N. V., Ferreira A., and Barros-Timmons A., Polyurethane foams: Past, present, and future. *Materials.* **11**(10): p. 1841(2018)

[11]. Al-Moameri H., Jaf L., and Suppes G. J., Viscosity-dependent frequency factor for modeling polymerization kinetics. *RSC Advances.* **7**(43): p. 26583-26592(2017)

[12]. Al-Moameri H., Ghoreishi R., and Suppes G., Impact of inter- and intra-molecular movements on thermoset polymerization reactions. *Chemical Engineering Science.* **161**: p. 14-23(2017)

[13]. Al-Moameri H., Jaf L., and Suppes G. J., Simulation approaches for the mechanisms of thermoset polymerization reactions. *Molecular Catalysis*. **504**(2021)

[14]. Al-Moameri H., Ghoreishi R., Zhao Y., and Suppes G. J., Impact of the maximum foam reaction temperature on reducing foam shrinkage. *RSC Advances*. **5**(22): p. 17171-17178(2015)

[15]. Al-Moameri H., Zhao Y., Ghoreishi R., and Suppes G. J., Simulation Blowing Agent Performance, Cell Morphology, and Cell Pressure in Rigid Polyurethane Foams. *Industrial and Engineering Chemistry Research*. **55**(8): p. 2336-2344(2016)

[16]. Szycher M., Szycher's handbook of Polyurethane, ed. 2. 2013: CRC Press

[17]. Zhang L., Zhang H., and Guo J., Synthesis and Properties of UV-Curable Polyester-Based Waterborne Polyurethane/Functionalized Silica Composites and Morphology of Their Nanostructured Films. *Industrial & Engineering Chemistry Research*. **51**(25): p. 8434-8441(2012)

[18]. Kim Y. J. and Kim B. K., Synthesis and properties of silanized waterborne polyurethane/graphene nanocomposites. *Colloid and Polymer Science*. **292**(1): p. 51-58(2014)

[19]. Deng S., Zhang J., and Ye L., Halloysite–epoxy nanocomposites with improved particle dispersion through ball mill homogenisation and chemical treatments. *Composites Science and Technology*. **69**(14): p. 2497-2505(2009)

[20]. Mohanraj V. and Chen Y., Nanoparticles-a review. *Tropical journal of pharmaceutical research*. **5**(1): p. 561-573(2006)

[21]. Alminshid A. H., Abbas M. N., Alalwan H. A., Sultan A. J., and Kadhom M. A., Aldol condensation reaction of acetone on MgO nanoparticles surface: An in-situ drift investigation. *Molecular Catalysis*. **501**: p. 111333(2021)

[22]. Mohammed Ali N. S., Alalwan H. A., Alminshid A. H., and Mohammed M. M., Synthesis and Characterization of Fe3O4-SiO2 Nanoparticles as Adsorbent Material for Methyl Blue Dye Removal from Aqueous Solutions. *Pollution*. **8**(1): p. 295-302(2022)

[23]. Mohammed M. M., Mohammed Ali N. S., Alalwan H. A., Alminshid A. H., and Aljaafari H. A. S., Synthesis of ZnO-CoO/Al2O3 nanoparticles and its application as a catalyst in ethanol conversion to acetone. *Results in Chemistry*. **3**: p. 100249(2021)

[24]. Yuan P., Southon P. D., Liu Z., Green M. E. R., Hook J. M., Antill S. J., and Kepert C. J., Functionalization of Halloysite Clay Nanotubes by Grafting with γ-Aminopropyltriethoxysilane. *The Journal of Physical Chemistry C*. **112**(40): p. 15742-15751(2008)

[25]. Barczewski M., Wojciechowska P., and Szostak M. Mechanical properties and structure of reactive rotationally molded polyurethane-basalt powder composites. in *International Scientific-Technical Conference MANUFACTURING*. 2019. Springer.

[26]. Hood M. A., Wang B., Sands J. M., La Scala J. J., Beyer F. L., and Li C. Y., Morphology control of segmented polyurethanes by crystallization of hard and soft segments. *Polymer*. **51**(10): p. 2191-2198(2010)

[27]. Al-Moameri H. H., Al-Sharify N. T., Abdulrehman M. A., and Al-Sharify Z. T., Impact of nanoparticles on polyurethane resin's final properties. *Journal of Green Engineering*. **10**(6): p. 3114-3126(2020)

[28]. Fu H., Wang Y., Li X., and Chen W., Synthesis of vegetable oil-based waterborne polyurethane/silver-halloysite antibacterial nanocomposites. *Composites Science and Technology*. **126**: p. 86-93(2016)

[29]. Mohammadzadeh F., Haddadi-Asl V., Balzade Z., and Sahebi Jouibari I., Switch segment and halloysite nanotube role in the phase separation behavior of shape-memory thermoplastic polyurethane. *Polymer Composites*. **41**(7): p. 2625-2633(2020)