DEVELOPMENT OF POLYURETHANE–SILICA AEROGEL COMPOSITE AS THERMAL INSULATION MATERIAL FOR CRYOGENIC INSULATION APPLICATION

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Polyurethane (PU) has demonstrated effectiveness in insulation applications across a broad temperature range due to its adaptability to modifications. Its specific properties can be improved by incorporating reinforcements into its matrix.

Abstract. Polyurethane (PU) has demonstrated effectiveness in insulation applications across a broad temperature range due to its adaptability to modifications. Its specific properties can be improved by incorporating reinforcements into its matrix. This study synthesized polyurethane-silica aerogel (PU-SA) composites for use in thermal insulation applications. Using a typical sol-gel process and ambient pressure drying, silica aerogel (SA) was synthesized from sodium silicate solution. According to earlier research, combining PU and SA in a composite lead to brittle fracture at lower temperatures. This study improves the PU mechanical properties, by reformulation with ethylene glycol acting as an antifreeze and chain extender. Various composites were then produced by adding varying percentages of SA (0.5, 1.0, 1.5 and 2.0 wt.%), differential scanning calorimetry (DSC) between 0 and -80 °C, shows that the inclusion of SA shifts the Tg by 12 % and stabilizes heat flow exhibited by the material. The impact of SA particles on altering the morphology of the material matrix is visible in SEM Micrographs. 1 wt.% of SA content was found optimal and introducing the particle at a greater content resulted in cell degeneration and disruption, smaller-sized cells were generated with the help of lower particle content between 1-2 wt.%, which improved the material's compressive strength and thermal insulation properties. The developed material is a promising option for application in a cargo containment system (CCS) that demands material with strong compressive strength to withstand loads caused by sloshing.

Keywords: Polyurethane, silica aerogel, composite, material morphology, scanning electron microscopy

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1. INTRODUCTION

Polymeric materials are known for their promising insulation performance, for low and high-temperature applications. Polyisocyanurate and polyurethane (PU) have exhibited remarkable performance in insulating piping that transports cryogenic substances like LNG, safeguarding them against heat exchange with ambient temperatures. Materials are typically modified with reinforcements to enhance their thermal insulation properties and compressive strength. Particles such as glass fiber introduced into polyisocyanurate [1] and Kevlar fiber introduced into PU [2] have been found to improve their compressive strength, with minimum compressive strength of 0.196 MPa attained through such reinforcement [3]. Sture et al. [4] reported a minimum compressive strength of 0.11 MPa achieved through the utilization of various renewable fillers in the production of polyurethane composites designed for cryogenic insulation applications. Similarly, thermal conductivity one of the fundamental properties is enhanced through the introduction of a super insulating material. Park et al. [5] reported the incorporation of silica aerogel (SA) which was found to enhance compressive strength a term that quantifies material capacity to withstand size reduction without fracturing and thermal insulation properties at 1 wt.% loading. However, polymeric material suffers instability with a decrease in temperature, the material glass transition temperature (Tg) is far above the cryogenic temperature, and as a result, the material becomes brittle as the temperature difference widens [6].

Material thermal insulation property as well as its compressive strength are directly related to cellular matrix morphology where the presence of smaller cell sizes facilitated by low particle loading supports compressive loads, and high particle loading causes cell disruption with distorted morphology that diminishes thermal insulation performance. SA particle as a superinsulation material was found to enhance thermal insulation properties at 1 wt.% loading the particles promotes the generation of uniform cells at lower loading [7]

In the current study effort was made to determine the influence of SA particles on material stability, the SA particles were incorporated into polyurethane between 0.5-2 wt.%. Using PU reformulated with the optimal amount of antifreeze and blowing agent as reported by [8]. The research intends to determine the influence of SA inclusion in PU-SA compressive strength and heat flow within its matrix at the temperature range of -80 0C to 0C. PU reformulation was aimed to shift the material Tg towards a lower temperature. The inclusion of hydrophobic SA into the PU aimed to stabilize material heat flow and influence the generation of PU cells capable of improving material compressive strength.

2. MATERIALS AND METHODS

2.1 Materials

The PU used in this study was Semi-Rigid Hydrophobic PU PUF301, which has a density of 1 gcm^{-3} and a viscosity of 2800±200 cps at 25 °C. It has a hydroxyl value ranging from 510 to 537 mg $KOHg^{-1}$. Ethylene Glycol (EG), supplied from Sigma Aldrich Chemical Company, Inc., served as a chain extender and anti-freezing agent. Supelco Merck Darmstadt, Germany, supplied acetic acid and a sodium silicate solution with a density of 1.35 gcm^{-3}. Trimethylchlorosilane (TMCS), a silylating compound having a density of 0.86 gcm^{-3}, was obtained from Sigma-Aldrich Co., Merck, Germany. Merck Co., Germany, supplied N-Hexane (C_6H_{14}, 99%) with a density of 0.66 gcm^{-3}, while V-Chem Laboratories

Pvt. Ltd., Malaysia, supplied ethanol. Deionized water was used as the blowing agent. All the reagents used were of analytical grade.

2.2 Methodology

Figure 1 shows process of silica aerogel synthesis from sodium silicate via ambient pressure drying and process flow of PU-SA composite casting. As shown in Figure 1, sodium silicate was used as a precursor to make SA. In a volume ratio of 1:3, the precursor was diluted with deionized water. The solution was then acidified dropwise with acetic acid, resulting in a sol-gel transition at pH 5-5.5. According to Abdul Halim et al. [9]. The resultant sol-gel was aged in distilled water for 48 hours at a temperature of 60-70 °C. Following that, the aged gels were washed to remove soluble salts before being subjected to solvent exchange. The solvent exchange was completed within 72 hours using soxchlet utilizing ethanol as the exchange medium.

The surface of the solvent-exchanged alcogel was modified from hydrophilic to hydrophobic. The alcogel was modified by immersing it in a silylating mixture containing TMCS and N-Hexane, in a 2:8 volume ratio. Specifically, 100 ml of alcogel was immersed in 100 ml of the mixture and gently stirred for 2 hours, as described by Abdul Halim et al. [9] The resulting gel was rinsed with fresh N-Hexane to remove the HCl by-product and any unreacted TMCS. After being exposed to ambient air in a fume cupboard and allowing N-Hexane to evaporate, the hydrophobic alcogel was heated at 100 °C at ambient conditions. Figure 1(b) depicts the composite casting process, the synthesized aerogel powder was loaded into the reformulated PU. Based on Nuhu et al. [8], a composition of 15 mL PUF 301, 1 mL EG, and 1 mL deionized water was used to achieve material optimal compressive strength.

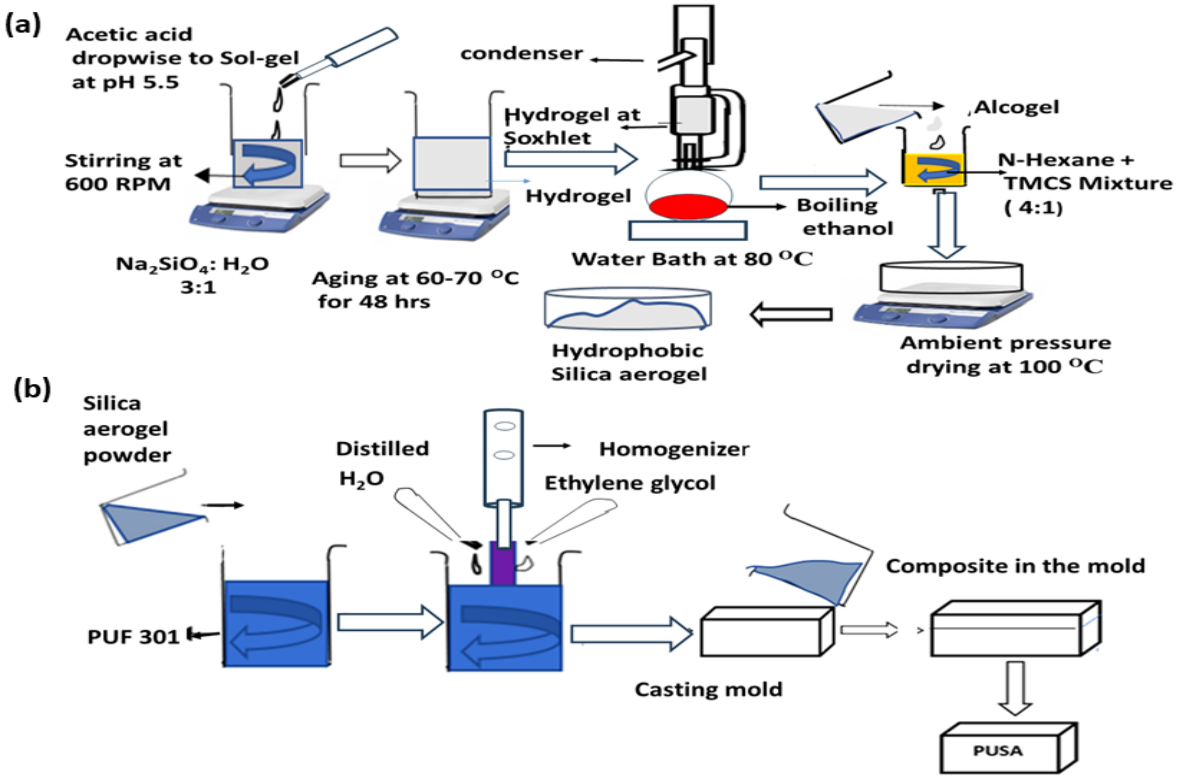

Figure 1: (a) Process of silica aerogel synthesis from sodium silicate via ambient pressure drying and (b) Process flow of PU-SA composite casting

3. RESULTS AND DISCUSSION

Figure 2 shows the SEM micrographs and EDX mapping of the PUSA composite samples fabricated in this study. In Figures 2(b) and (c) containing 0.5 and 1.0 wt.% SA the composites exhibit more circular cells with distinct geometry compared to those in Figures 2(d) and (e) with 1.5 and 2.0 wt.% SA. The materials also exhibit more homogeneous particle dispersion with circular cells at 0.5 wt.% loading.

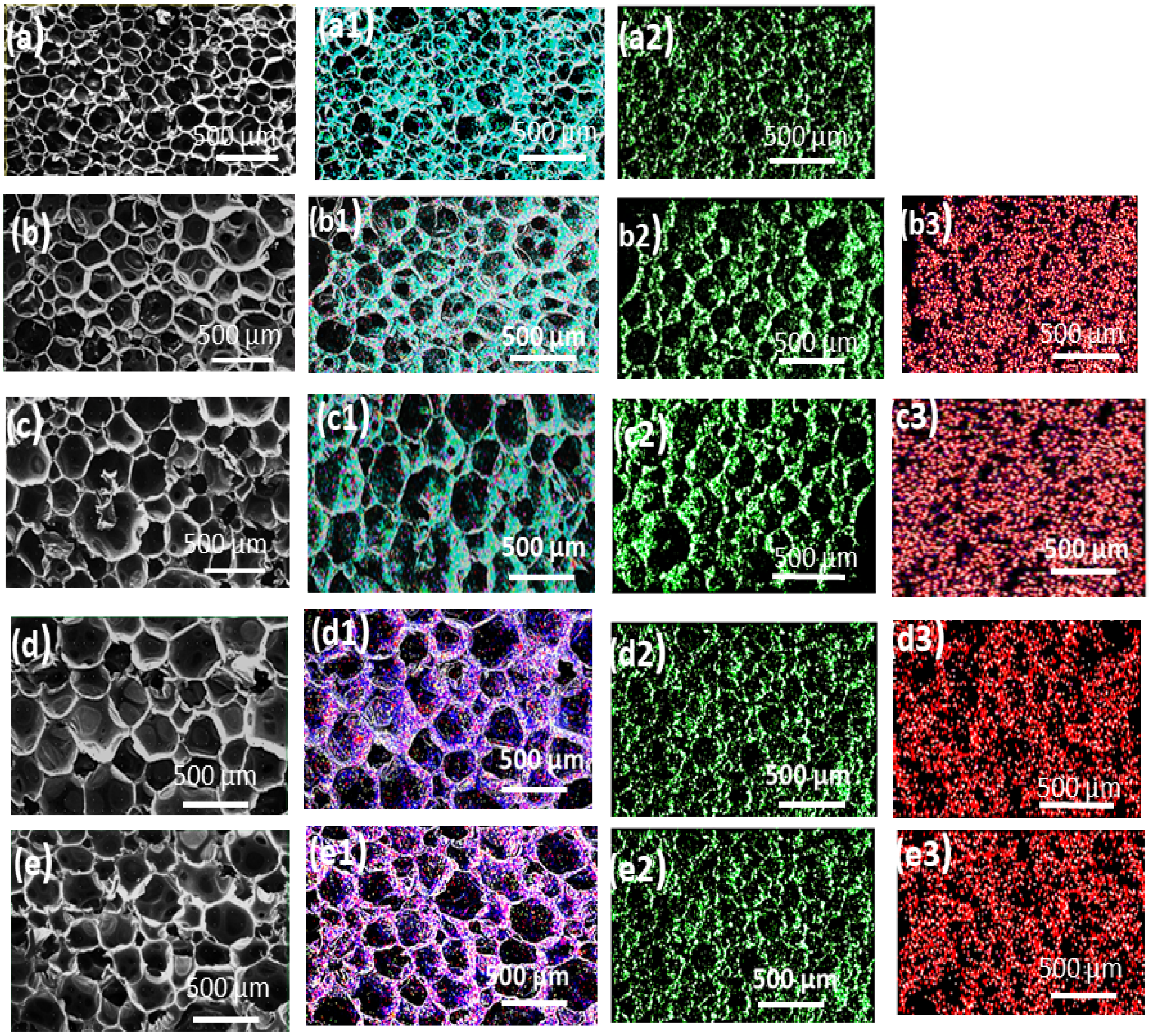

Figure 2: SEM micrograph and EDX Mapping of (a) PUSA0 with 0 wt.% of SA, (b) PUSA1 with 0.5 wt.% of SA (c) PUSA2 with 1 wt.% of SA (d) PUSA3 with 1.5 wt.% of SA and (e) PUSA4 with 2.0 wt. % of SA. Label (a1) to (e1) correspond to their respective EDX mapping, and elemental dispersion of Carbon in (a2) to (e2) and Silicon in (b3) to (e3), respectively

Similarly, as the loading increased to 1 wt.%, the matrix remained homogeneous which referred to even distribution of particles within the mixed constituents and with an increased cell size compared to 0.5 wt.%. However, as the loading increased, the cell walls ruptured and the cell geometry distorted, changing to elliptical and disfigured with non-uniform particle dispersion, as shown in Figures 2(d) and (e). The more air that is included during the forming process, the greater the nucleation effect [10]. Similarly, the introduction of nanoparticles alters the matrix morphology in the cell formation process. Cell morphology is altered at optimal loading without significant distortion and ruptures, which could result in the loss of desired composite properties. Cell struts rupture above the critical loading (PUSA2), could results in a loss of mechanical strength and increased porosity, The material loses mechanical properties as more particles are added above the critical value, according to the studies of [11] and [12].

Figure 3 shows a BET pore size distribution of the study samples, the samples have a pore range dimeter up to 50 nm confirming a mesoporous matrix [13]. It could be seen that the pore volume distribution increases with the aerogel contents at almost same pore diameter, the demonstrated behavior translates the effect of particle dispersion within the PU matrix with respect to different particle loading. Increase of pore size distribution indicates increases in matrix non homogeneity and cells disruptions.

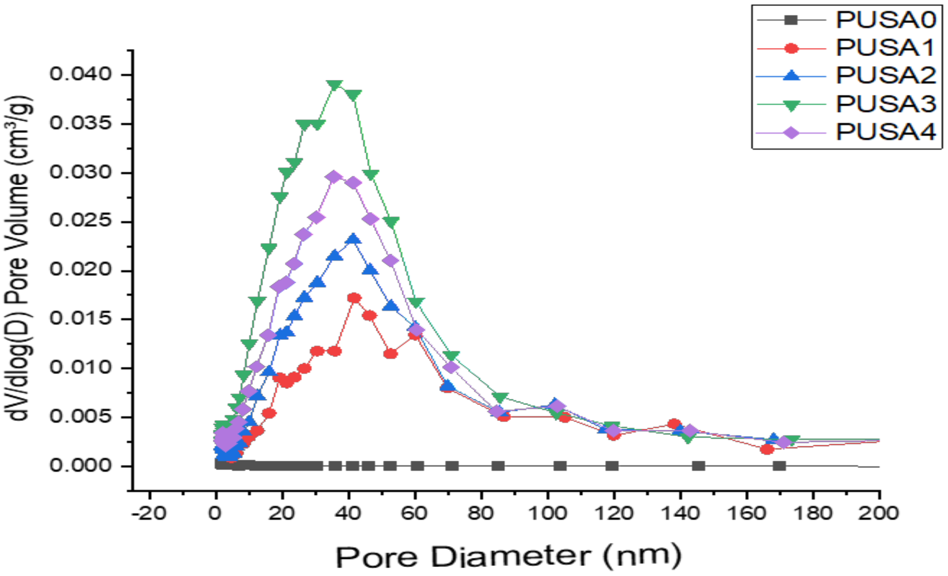

Figure 3: Variation of PU-SA material pore sizes with different loading of SA

3.1 Composite Stability with Temperature

The DSC Thermogram of the composites samples as seen in Figure 4 reveals EG influence on the material Tg. The addition of EG improved the material Tg by approximately 12%, increasing from -51.34 °C in the pristine PU to -57.46 °C. However, due to the amorphous nature of SA, the transition temperature shifts slightly in a positive direction when silica aerogel is added. Furthermore, with Aerogel concentrations ranging from 0.5 to 2.0 wt.%. The matrix Tg shift is negligible, the exhibited behavior could be attributed to the anti-freezing activity of EG, which was less effective with the addition of SA at the tested concentrations. Surprisingly, the addition of SA to PU results in a stable heat flow.

Figure 4 shows the DSC thermogram of a reformulated sample with a lower Tg than the pristine PU without EG (PUH2). It demonstrates the effect of SA particles on the composite's stable heat flow over the test temperature range [14]. As the material Tg was shifted toward a lower temperature, the material stability was improved by reducing the wide gap that exists between the material Tg and cryogenic temperature.

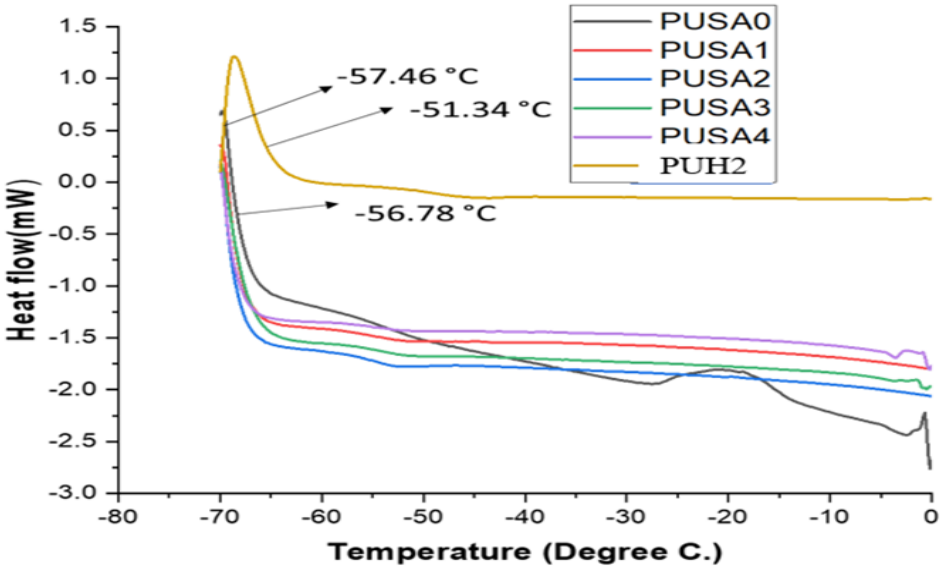

Figure 4: DSC Thermogram of PUSA composites reformulated with EG and Pristine PUH2 (without EG)

3.2 Compressive Strength

Figure 5 shows the stress-strain curve of the study composites. It could be seen that due to the lower particle concentration and uniform particle dispersion, the cells in the 1% composite are relatively smaller, closed, and regular. This resulted in uniform cells that can effectively support compressive loads due to the air pressure enclosed in the pores [15]. The 1.5 wt.% composite, on the other hand, demonstrated lower compressive strength due to cell degeneration and the presence of more open cells. The higher the particle content, the more cell deterioration occurs, resulting in larger pores and particle agglomeration in the struts. This has a negative impact on the mechanical properties of the composite because larger cells weaken its strength. The presence of the study found that an optimal loading of 1 wt.% SA provided the highest compressive strength.

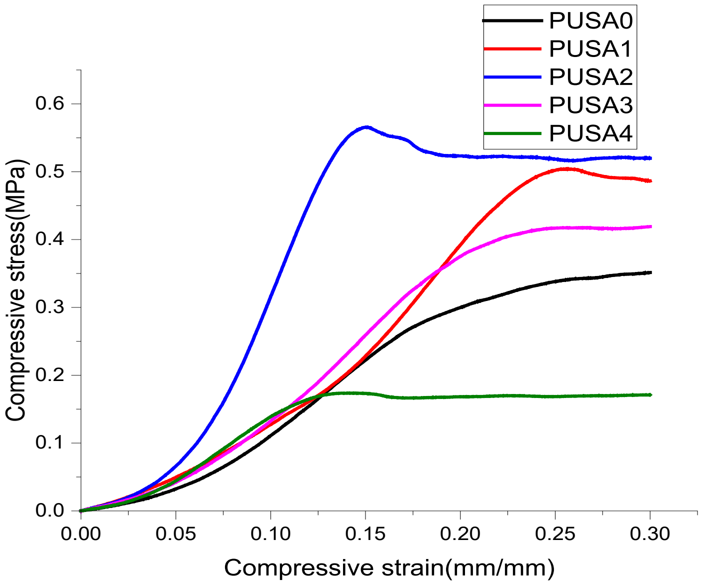

Figure 5: Stress-Strain curves of PU-SA composites with different SA loading.

3. CONCLUSIONS

The impact of SA particles on matrix morphology and stability at low temperatures was investigated. In this study SA was introduced into the PU that had been reformulated with optimal amount of EG as antifreeze and blowing agent. SA was discovered to influence a stable heat flow at temperatures ranging from 0 to -80 ^{0}C at lower loading. PU-SA with 1% SA was found optimal in matrix homogeneity and compressive strength. The develop composite with enhanced stability will decrease the material's susceptibility to becoming brittle in cold conditions, thus lowering the likelihood of cracking and preventing moisture from penetrating the insulation mass. This, in turn, helps prevent insulation failure and corrosion under insulation (CUI)). For further study a reformulated polyisocyanurate could be used to serve as a base composite for enhance compressive strength and material stability.

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Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of conflict of interest

The authors have no disclosures to declare.

Compliance with ethical standards

The work is compliant with ethical standards.

References

[1] Yoo, J. K.,Wagle, R., Lee, C. W. & Lee, E. Y. (2019). Synthesis of silica aerogel thin sheets and evaluation of its thermal, electrical and mechanical properties. *International Journal of Applied Ceramic Technolology*, 16(2), 832–842.

[2] Oh, J. H., Bae, J., Kim, J., Lee, C. S. & Jae-Myung, L. (2019). Effects of Kevlar pulp on the enhancement of cryogenic mechanical properties of polyurethane foam. *Polymer Testing*, 80, 106093.

[3] Wang, Z., Wang, C. & Gao, Y. (2023). Porous thermal insulation polyurethane foam materials. *Polymers (Basel)*, 15(18), 3818.

[4] Sture, B.,Vevere, L., Kirpluks, M., Godina, D., Fridrihsone, A. & Cabulis, U. (2021). Polyurethane foam composites reinforced with renewable fillers for cryogenic insulation. *Polymers (Basel)*, 13(23), 4089.

[5] Park, S, B., Lee, C., Choi, S. W., Kim, J. H., Bang, C. H. & Lee, J. M. (2016). Polymeric foams for cryogenic temperature application: Temperature range for non-recovery and brittle-fracture of microstructure. *Composite Structures*, 136, 258-269.

[6] Kim, J. H., Ahn, J., Kim, K. D., Lee, D. H., Kim, S. K. & Lee, J. M. (2021). Influence of silica-aerogel on mechanical characteristics of polyurethane-based composites: Thermal conductivity and strength. *Materials (Basel)*, 14(7), 1790.

[7] Cimavilla-Román, P., Tamarit, S. P., Santiago-Calvo, M. & Rodríguez-Pérez, M. (2020). Influence of silica aerogel particles on the foaming process and cellular structure of rigid polyurethane foams. *European Polymer Journal*, 135, 109884.

[8] Nuhu, I., Awang, N., Wan Ali, W. F. F. & Mat Yajid, M. A. (2023). Enhancement of polyurethane mechanical properties through optimization of its pristine microstructure. Proceedings of the Sustainable and Integrated Engineering Conference (SIE 2022) Langkawi Kedah,Malaysia 12-14 Nov. (2023).

[9] Abdul Halim, Z. A., Mat Yajid, M. A. & Hamdan, H. (2021). Effects of solvent exchange period and heat treatment on physical and chemical properties of rice husk derived silica eerogels. *Silicon*, 13(1), 251–257.

[10] Merillas, B., Villafañe, F. & Rodríguez-Pérez, M. A. (2021). Nanoparticles addition in pu foams: The dramatic effect of trapped-air on nucleation. *Polymers (Basel),* 13(17), 1–11.

[11] Nazeran, N. & Moghaddas, J. (2017). Synthesis and characterization of silica aerogel reinforced rigid polyurethane foam for thermal insulation application. *Journal of Non-Crystalline Solids*, 461, 1–11.

[12] Kausar, A. (2018). Polyurethane composite foams in high-performance applications: A Review. *Polymer - Plastics Technology and Engineering*, 57(4), 346-369.

[13] Horvat, G., Pantić, M., Knez, Z. & Novak, N. (2022). A brief evaluation of pore structure determination for bioaerogels. *Gels*, 8(7), 1–18.

[14] Jang, D., Yoon, H. N., Seo, J., Lee, H. K. & Kim, G. M. (2021). Effects of silica aerogel inclusion on the stability of heat generation and heat-dependent electrical characteristics of cementitious composites with CNT. *Cement and Concrete Composites*, 115, 103861.

[15] Linul, E. (2017). Experimental determination of mixed-mode fracture toughness for rigid polyurethane foams. In Fracture at all Scales proceedings, (SpringerLink), pp 221–237.