

Composite Aerogel for Heat Insulation

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Silica aerogels are often brittle and MTMS is rather expensive. Therefore, it is necessary to strengthen MTMS silica aerogels and lower their cost. In this research, hydrophobic composite monolithic methyltrimethoxysilane (MTMS) based aerogels were investigated. The aerogels were synthesized by an acid base sol-gel process with solvent exchange and freeze drying. Silica extracted from rice husk ash, poly vinyl alcohol (PVA) and glass wool were combined with MTMS to form the composite aerogels, whose microstructure, thermal property and hydrophobicity were evaluated. The aerogels were found to have thermal conductivity as low as 0.032 W/m.K and water contact angle as high as 152.2°.

1. Introduction

Silica aerogels are highly porous materials with extremely low density, making them potential candidates for heat insulation applications (Becker et al., 2019). They are made from two primary sources, organic (silicon alkoxides) and inorganic (water glass).

Various successful attempts have been made to fabricate silica aerogel from silicon alkoxides with interesting properties. Tamon et al. used tetraorthosilicate (TEOS) to make transparent aerogels with mesoporous structure (Tamon et al., 1998). Rao et al. studied the flexibility of hydrophobic methyltrimethoxysilane (MTMS) aerogels (Venkateswara Rao et al., 2006). However, these chemicals tend to be costly and pose possible health risks, thus, making them less applicable. This has driven researchers away to seek for more plausible silica sources (Cui et al., 2015). Water glass, or sodium silicate solution, was one of the 'jellies' from which Kistler made the first aerogels (Kistler, 1931). It is commercially common, and can be extracted from inexpensive biomass sources such as bamboo (Kow et al., 2014) and rice husk (Balasundram et al., 2017). Yet, it produces brittle aerogels.

One way to approach both problems is to combine water glass with organic silicon compounds, including TEOS (Hwang et al., 2007), trimethylethoxysilane/trimethylchlorosilane (TMES/TMCS) (Nah et al., 2018) and MTMS (Pan et al., 2017). Other methods of improvement involve addition of binders like poly vinyl alcohol (PVA) (Luo et al., 2019), poly ethylene glycol (PEG) (Kim et al., 2017); and glass fibers (Zhou et al., 2018).

This work was an attempt to embrace all mentioned solutions in order to reduce cost and strengthen the structure of the aerogel, but still manage to retain its heat insulating nature. Here, MTMS was combined with silica from rice husk ash, PVA and glass wool.

2. Experimental

2.1 Chemicals

MTMS (95 %) from Sigma Aldrich, ethanol absolute (98 %), hydrochloric acid (36.5 %), ammonia solution (25 %) and sodium hydroxide were purchased from China. PVA $M_w=160,000$ was originated from India and rice husk ash was supplied by Biomass Laboratory of Ho Chi Minh University of Technology.

2.2 Preparation

First, to the beaker were added 8 mL of ethanol, 2 ml of MTMS, 1 mL of HCl 0.01 M and 0.5 mL of PVA aqueous solution (0 % - no PVA, 5 %, 10 % and 15 % w/v), in that order. The mixture was stirred constantly for 2 h to create Solution 1.

On the other hand, silica from rice husk ash was obtained by dispersing 40 g of ash into 250 mL of NaOH 1 M. The mixture was heated to 100 °C and stirred vigorously for 2 h before it was allowed to cool down to room temperature and filtered under vacuum. The solid residue was disposed of whilst the liquid passed through an ion exchange column to bring the pH value down to circa 3 to form Solution 2.

Afterwards, 2 mL of Solution 2 was mixed together with Solution 1 and NH_3 was added drop by drop until the mixture turned opaque, at which it was poured into molds containing glass wool and gelation occurred within 1 h. The gels were aged for 48 h before undergoing solvent exchange with deionised water and freeze drying (Toption TPV-50F, China).

2.3 Characterisation

Water contact angle was captured by a **SEO Phoenix 300 Touch** (Korea). Specific surface area was calculated by BET nitrogen adsorption analysis (TriStar II 3020, Micromeritics Instruments Corporation, USA). Physical characteristic and thermal conductivity were studied using an Instron 5500 microtester (USA) and thermal conductivity analyzer (TCi thermal conductivity analyzer, C-Therm Technologies, Canada), respectively. The structure of the aerogel was determined by X-ray diffraction (XRD) operating at $\text{CuK}\alpha$, 40kV, 20 mA, 2θ scanning from 2° to 50° with a rate of 0.042°/s (D8, Bruker AXS, Germany). Field emission scanning electron microscopy (FE-SEM) was performed at 2kV to study the morphology of the aerogel (S-4800, Hitachi, Japan).

3. Results and discussion

3.1 Effect of pH to the gelation time of composite aerogel prepared from MTMS, rice husk ash extract and PVA

From Figure 1, it is obvious that the gelation time becomes shorter when the pH value of the mixture of MTMS, rice husk ash extract and PVA rises from 7.5 to 13.5. However, when the gelation time is too fast, the final composite aerogel is easily broken after freeze drying.

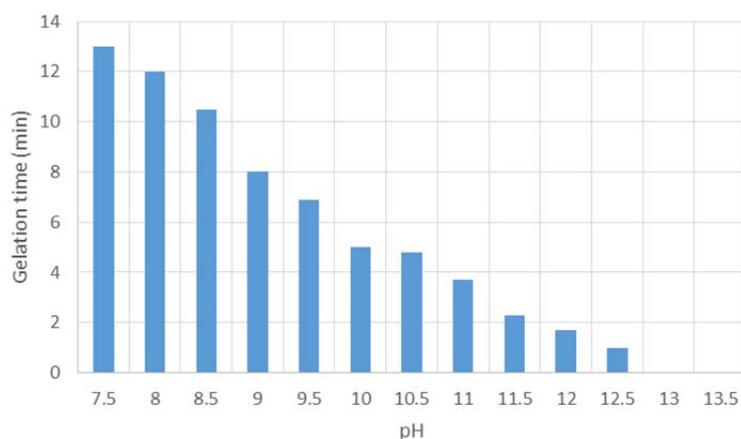


Figure 1: Effect of pH to gelation time of silica aerogel prepared from MTMS, rice husk ash extract and PVA

3.2 Mechanical property and thermal conductivity

Table 1 shows Young's moduli and thermal conductivities of MTMS aerogels, prepared with the same mixing time (1.5 h) and aging time (48 h) but different MTMS/water molar ratios. It can be seen that MTMS/water molar ratio has a strong effect on the Young's moduli of MTMS aerogels. When raising the ratio from 1:7 to 1:6 and 1:5, the Young's modulus rises from 0.88 to 1.22 and 1.96 MPa and the thermal conductivity increases from 0.032 to 0.037 and 0.040 W/m.K. Ratios smaller than 1:7 were not studied as gelation takes a long time to occur or does not happen at all because large concentration of water promotes hydrolysis and slows down the condensation rate. The MTMS aerogel sample with the MTMS/water molar ratio of 1:7 is used for further investigation for its lowest thermal conductivity.

Table 1: Young's moduli and thermal conductivities of pure MTMS aerogels

	MTMS/water ratio		
	1:5	1:6	1:7
Young's modulus (MPa)	1.96	1.22	0.88
Thermal conductivity (W/m.K)	0.040	0.037	0.032

Table 2 displays the effect of PVA content on the physical and thermal properties of the aerogels. Young's modulus increases once PVA is added, from 3 to 19 MPa due to the fact that the binding of PVA strengthened the aerogel. The thermal conductivity of the composite aerogel increases, not significantly, up to 0.037 W/m.K when increasing PVA concentration from 0 to 15 %.

These results imply that the composite aerogels possess similar heat proofing capability to their precursor aerogel, but are structurally stiffer. For more context, the composite aerogel's insulating property is impressively comparable to various conventional insulators such as polystyrene (0.038 - 0.040 W/m.K), glass wool (0.037 W/m.K), cellulose (0.04 W/m.K), and is better than sheep wool (0.052 W/m.K) and hemp fiber (0.06 W/m.K) (Hittini et al., 2019).

Table 2: Young's moduli and thermal conductivities of composite aerogels

	% PVA			
	0	5	10	15
Young's modulus (MPa)	3	7	13	19
Thermal conductivity (W/m.K)	0.032	0.033	0.035	0.037

3.3 Thermal stability of composite aerogels

Figure 2 presents TG-DTA curves of the composite aerogel synthesized from MTMS + rice husk ash extract + 15 % PVA + glass wool. There is an endothermic peak at 110 °C accompanied by a massive gravimetric drop of 27.9 % the initial mass due to moisture and residual solvent vaporization. The aerogel is thermally resistant up until 258 °C, at which appears an exothermic peak assigned to the removal of structural OH groups. This means the composite aerogel is stable in normal working conditions and fit for insulation application.

When it is furtherly heated, another exothermic peak spikes up at 411 °C due to the degradation of methyl groups (Durães et al., 2015). A sharp peak at 525 °C is from the destruction of PVA binder (Zeytuncu et al., 2014). At the end, at approximately 600 °C, only less than 60 % of the initial sample, attributed to fiber glass, remains, signifying total decomposition of both silica and PVA in the aerogel. While there is no change in mass, there is a glass transition peak at 725 °C.

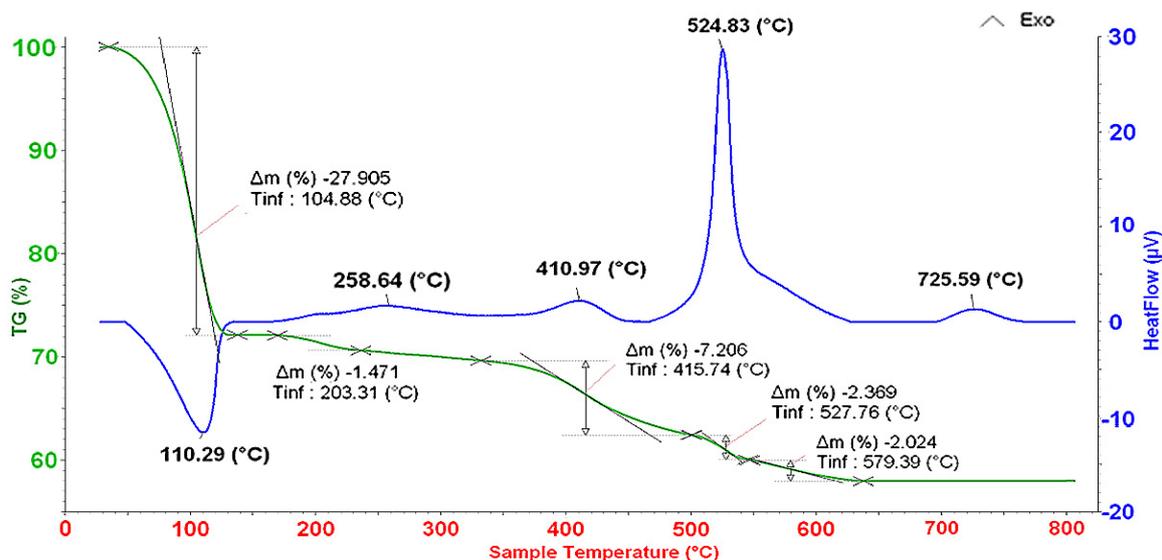


Figure 2: TG-DTA result for composite aerogel synthesized from MTMS + rice husk ash extract + 15 % PVA + glass wool

3.4 Water contact angle

It can be seen that the addition of PVA to the composite aerogel improves the hydrophobicity of the material. As shown in Figure 3, water contact angle increases from 124.6° to 152.2°, correspondingly to the increasing of PVA from 0 to 15 %. It is suggested that OH groups of PVA reacted with the uncondensed silanol (Si-OH) groups of the precursors, thus, decreasing the hydrophilicity of the material. The good water repellency of the material prevents the adsorption of humidity and thus, facilitates its potential thermal insulation application.

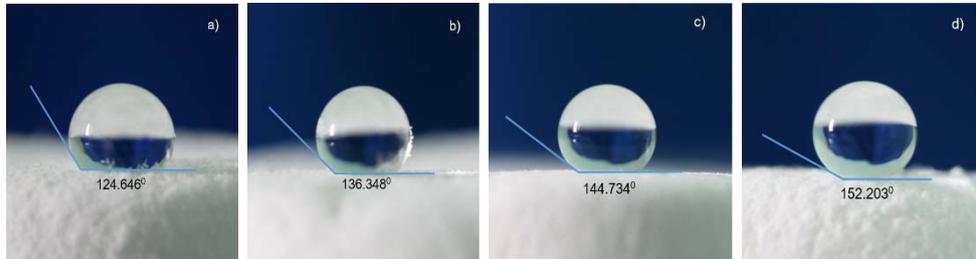


Figure 3: Water contact angles of composite aerogels with (a) 0 % PVA, (b) 5 % PVA, (c) 10 % PVA and (d) 15 % PVA

3.5 Density, porosity and specific surface area

The density, porosity and specific surface area of aerogel samples are summarized in Table 3. Porosity is determined using Eq(1):

$$\varepsilon = \left(1 - \frac{\rho_{aerogel}}{\rho_{silica}}\right) \times 100\% \quad (1)$$

in which, ε is porosity (%), $\rho_{aerogel}$ is density of aerogel, defined as mass of aerogel per unit bulk volume (gcm^{-3}), and ρ_{silica} is density of silica (2.56 gcm^{-3}).

Table 3: Effect of PVA concentration on density, porosity and specific surface area of composite aerogel samples

% PVA	Density ($\frac{\text{g}}{\text{cm}^3}$)	Porosity (%)	Specific surface area ($\frac{\text{m}^2}{\text{g}}$)
0	0.076	97.2	365
5	0.084	96.0	337
10	0.089	93.3	311
15	0.098	89.3	117

While the presence of PVA improves the hydrophobic nature and does not affect the thermal conductivity of the composite aerogels, the porous structure is sacrificed. Table 3 shows a clear tendency that increasing PVA content yields less desirable results. Specifically, density increases from 0.076 to 0.098 g/cm^3 whilst porosity drops from 97.2 to 89.3%, which explains the specified Young's moduli's large escalation. This is due to PVA clogging up pores, obstructing nitrogen from going inside and adsorbing onto pore walls. As proposed by Pirzada and Shah, because of the smaller amount of PVA compared to silica and their strong interaction towards each other (between Si-OH and OH), most of the PVA will be confined within the silica framework during gelation (Pirzada and Shah, 2011).

It is also worth noting that the specific area of 15 % PVA declines dramatically, from over 300 m^2/g (0 % PVA) down to 117 m^2/g . This is probably because the polymer chains in 15% PVA solution are much sterically longer and larger, hence, not only filling up the void inside but also blocking the pores on the surface of the gels.

3.6 Structure and morphology

3.6.1 XRD result

As shown in Figure 4, XRD pattern of the composite aerogel presents only low and broad peaks, one of which is the distinctive broad peak at 25° of amorphous silica, indicating the non-crystalline nature of the sample. There are, notably, no sharp diffraction peaks of PVA, which is an indication of PVA losing its crystalline structure owing to the strong silanol-OH group interaction (Pirzada and Shah, 2011).

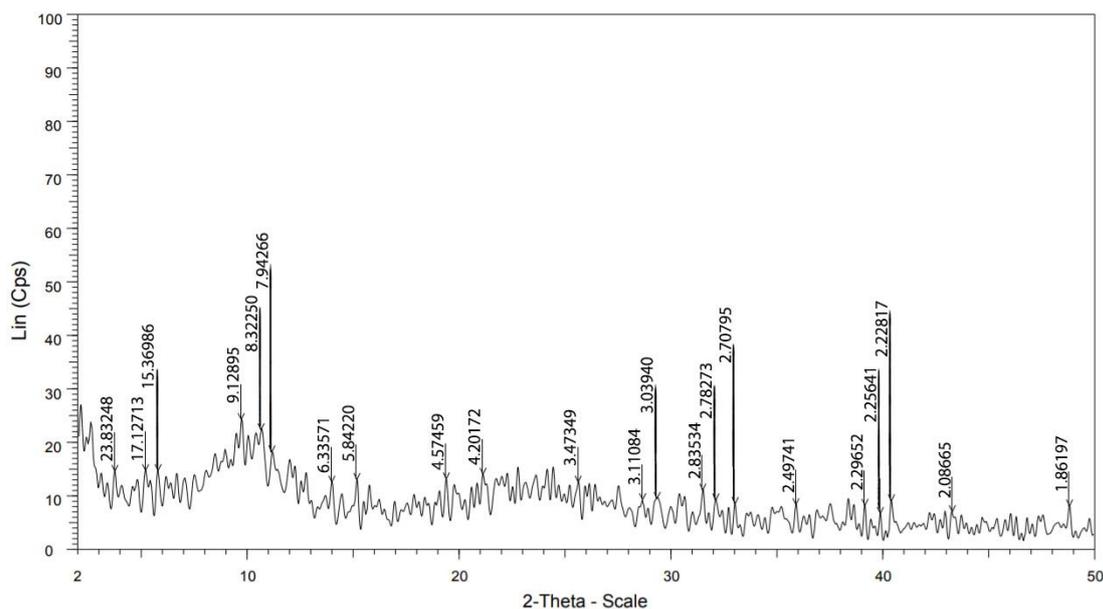


Figure 4: XRD pattern of composite aerogel sample with 10 % PVA

3.6.2 SEM result

Figure 5a and 5b show the morphology of silica aerogels prepared from MTMS and MTMS + rice husk ash extract. It can be seen that silica particles are connected together to form porous structures. However, silica particles of the aerogel from MTMS + rice husk ash have smaller size than silica particles from MTMS. As MTMS has one silanol group less than orthosilicic acid $\text{Si}(\text{OH})_4$, the probability of two silanol groups from two MTMS molecules coming together is smaller, hence, creating large clusters and pores. The additional silica from rice husk bonds with uncondensed silanol groups and forms smaller clusters of particles (Pan et al., 2017).

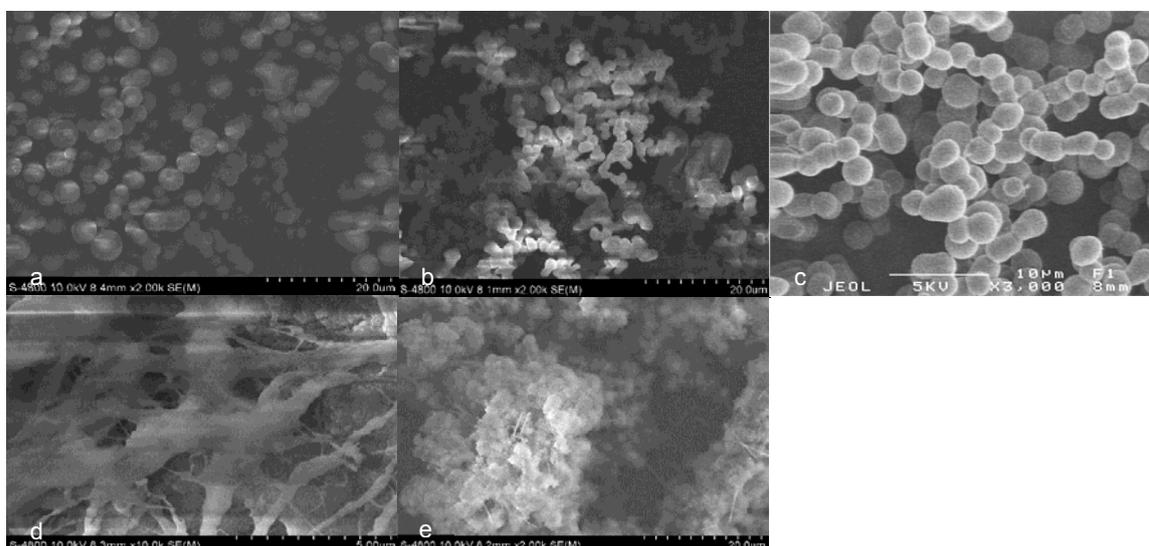


Figure 5: SEM images of aerogels prepared from a) MTMS, b) MTMS + rice husk ash extract, c) MTMS + rice husk ash extract + 5 % PVA, d) MTMS + rice husk ash extract + 15 % PVA, e) MTMS + rice husk ash extract + 15 % PVA + glass wool

When PVA is added, more connection is formed in the porous structure (Figure 5c) owing to Si-OH and OH interactions. Figure 5d indicates that when a higher amount of PVA is added, it covers pores of the aerogel, resulting in aforementioned smaller porosity and specific surface area. Figure 5e shows that when glass wool is added into the composite aerogel, a more rigid and less porous structure is formed.

4. Conclusion

The synthesis of MTMS/sodium silicate/PVA/glass wool aerogels was successful. pH plays a strong effect on the gelation time of the hydrogel. The addition of PVA and glass wool not only considerably improves the aerogel's hydrophobicity up to 152.2° and Young's modulus as high as 19 MPa, but also reduce the dependency on the costly MTMS. More importantly, composite aerogels possess low thermal conductivity, capable of heat proofing better than glass wool, cellulose, sheep wool and hemp, making them promising for thermal insulation application.

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References

- Balasundram V., Ibrahim N., Kasmani R. M., Hamid M. K. A., Isha R., Hasbullah H., 2017, Thermogravimetric catalytic pyrolysis and kinetic studies of coconut copra and rice husk for possible maximum production of pyrolysis oil. *Journal of Cleaner Production*, 167, 218-228.
- Becker T., Pico D., Lipin J., Lehmann T., Lüking A., Hitz M., Gries T., 2019, Novel Insulation Material Based on Basalt Fibres and Silica Aerogels, *Chemical Engineering Transactions*, 73, 49-54.
- Cui S., Yu S.-w., Lin B.-l., Shen X.-d., Gu D., 2015, Preparation of SiO₂ aerogel from rice husk ash. *RSC Advances*, 5, 65818-65826.
- De Marco I., Miranda S., Riemma S., Iannone R., 2016, LCA of Starch Aerogels for Biomedical Applications. *Chemical Engineering Transactions*, 49, 319-324.
- Durães L., Maia A., Portugal A., 2015, Effect of additives on the properties of silica based aerogels synthesized from methyltrimethoxysilane (MTMS). *The Journal of Supercritical Fluids*, 106, 85-92.
- Hittini W., Mourad A.-H., Abu-Jdayil B., 2019, Cleaner production of thermal insulation boards utilizing buffing dust waste. *Journal of Cleaner Production*, 236, 117603.
- Hwang H. J., Kim C. E., & Cha Y. C., 2007, Strengthening of Water Glass Based Aerogel by TEOS. *Materials Science Forum*, 544-545, 1053-1056.
- Kim K. H., Lee D., & Oh Y.-J., 2017, Ambient drying silica aerogel coatings modified with polyethylene glycol. *Journal of Ceramic Processing Research*, 18, 55-58.
- Kistler S. S., 1931, Coherent Expanded Aerogels and Jellies. *Nature*, 127, 741-741.
- Kow K.W., Yusoff R., Aziz A. R.A., Abdullah E.C., 2014, From bamboo leaf to aerogel: Preparation of water glass as a precursor. *Journal of Non-Crystalline Solids*, 386, 76-84.
- Luo X., Akram M.Y., Yuan Y., Nie J., Zhu X., 2019, Silicon dioxide/poly(vinyl alcohol) composite hydrogels with high mechanical properties and low swellability. *Journal of Applied Polymer Science*, 136, 46895.
- Nah H.Y., Parale V.G., Lee K.Y., Choi H., Kim T., Lim C.H., 2018, Silylation of sodium silicate-based silica aerogel using trimethylethoxysilane as alternative surface modification agent. *Journal of Sol-Gel Science and Technology*, 87, 319-330.
- Pirzada, T., Shah, S.S., 2011, Potential of PVA templated Silica Xerogels as Adsorbents for Rhodamine 6G. *Journal of Korean Chemical Society*, 55, 1024–1029.
- Pan Y., He S., Gong L., Cheng X., Li C., Li Z., 2017, Low thermal-conductivity and high thermal stable silica aerogel based on MTMS/Water-glass co-precursor prepared by freeze drying. *Materials & Design*, 113, 246-253.
- Tamon H., Kitamura T., Okazaki M., 1998, Preparation of Silica Aerogel from TEOS. *Journal of Colloid and Interface Science*, 197, 353-359.
- Venkateswara Rao A., Bhagat S.D., Hirashima H., Pajonk G.M., 2006, Synthesis of flexible silica aerogels using methyltrimethoxysilane (MTMS) precursor. *Journal of Colloid and Interface Science*, 300, 279-285.
- Zeytuncu B., Akman S., Yucel O., Kahraman M., 2014, Preparation and characterization of UV-cured hybrid polyvinyl alcohol nanofiber membranes by electrospinning. *Materials Research*, 17, 565-569.
- Zhou T., Cheng X., Pan Y., Li C., Gong L., Zhang H., 2018, Mechanical performance and thermal stability of glass fiber reinforced silica aerogel composites based on co-precursor method by freeze drying. *Applied Surface Science*, 437, 321-328.