Chemically Bonded Thermally Expandable Microsphere-silica Composite Aerogel with Thermal Insulation Property for Industrial Use

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Abstract: Thermally expandable microsphere and aerogel composite was prepared by chemical compositization. Microsphere can produce synergies with aerogel, especially an enhancement of mechanical property. Through condensation between sulfonated microsphere and hydrolyzed silica sol, chemically-connected composite aerogel could be prepared. The presence of hydroxyl group on the sulfonated microsphere was observed, which was the prime functional group of reaction with hydrolyzed silica sol. Silica aerogel-coated microsphere was confirmed through microstructure analysis. The presence of silicon-carbon absorption band and peaks from composite aerogel was observed, which proved the chemical bonding between them. A relatively low thermal conductivity value of 0.063 W/m·K was obtained.

Keywords: Thermally expandable microsphere, aerogel, organic-inorganic, composites, insulator

1. Introduction

Due to the increase in industrial power generation and use of coal fuels, environmental problems such as global warming have become a big issue all over the world.[1] Especially, with the development of heavy chemical industry, energy consumption has increased greatly. For these reasons, reducing energy use in heavy chemical industry has an important meaning in the energy saving of the whole country.[2] The easiest way to reduce energy use in the heavy chemical industry is to reduce heat energy losses, and designing the effective insulation system is very important to reduce these losses.[1-2] Therefore, it is required to save energy by improving thermal insulation properties of industrial materials.[3] Industrial thermal insulation coatings, which are used to enhance the insulation properties of various equipment in the industrial field, have a function to prevent heat exchange with the outside air, which is very important in energy saving and economical and industrial aspects.[4-5]

Industrial insulation technology that preserves the heat energy generated in the industrial field is a very important area of research for energy conservation technology. Based on this trend, effective thermally expandable microsphere is considered as a good insulation material.[5-9] Thermally expandable microsphere is a type of insulation material in which an impermeable copolymer shell surrounds a liquid hydrocarbon (isobutane or isopentane) coated with a blowing agent.[6] The copolymer shell of thermally expandable microsphere is polymerized with various kinds of polymer such as vinylidene chloride, acrylonitrile, methacrylonitrile and methyl methacrylate, polyurethane and polyepoxy.[6,10] When microsphere is heated, gaseous blowing agent can compress the copolymer shell and expand up to 60 times as spherical form.[11] Therefore, the expansion range of thermally expandable microsphere are mainly determined by the content of blowing agent and copolymer shell.[12] Thermally expandable microsphere maintains its shape at room temperature and cool condition due to plastic deformation of the copolymer shell, and the expansion is generally not reversible.[11-13] The copolymer shell is very dense and can block external gases. Also, it has good chemical resistance.[14] Spherical-formed thermally expandable microsphere is the prime materials which has wide vacancy inside for high insulation properties, because the heat cannot be conducted well.[15] It can be used at the temperature

in the range of 85-230ºC. So, thermally expandable microspheres can be used as good insulator in industrial field.[16]

Aerogel is an outstanding solid material due to high surface area, extremely low thermal conductivity and low density based on nanoporous structure.[17-20] Aerogel is also very applicable because it can be synthesized using various silica precursor such as tetraethyl orthosilicate (TEOS), methyltrimethoxysilane (MTMS), waterglass, and so on.[21-24] Because of these good characteristics, aerogel can be used in various industrial field example like oil filter, drug agent, absorbent, thermal insulator, and so on.[25-27]

In this study, microsphere and silica aerogel composite was prepared through chemical compositization. Thermally expandable microsphere can form hydroxyl (-OH) groups on the surface through sulfonation.[15] The aerogel can also be chemically connected to other material having a hydroxyl group. Therefore, it is possible that the two materials are chemically connected through a condensation reaction.[28] Aerogel can occupy empty spaces between thermally expandable microspheres and can be hybridized on the surface of thermally expandable microspheres. For these reasons, spherical form microsphere can make synergy effect with aerogel.[29] Based on this principle, aerogels can complement the properties of thermally expandable microsphere composed of organic materials that are weak in high temperature or heat.[30-31] Through this conducted experiment, we have investigated the possibility of compositization between thermally expandable microsphere and silica aerogel, and the verification of microstructure. Finally, we observed the formation and thermal properties of a board-like insulation material which can be used in the insulation industry.

2. Experimental

2.1. Materials

Thermally expandable microsphere (Expancel 920 DET 40 d25, AkzoNobel) and tetraethyl orthosilicate (TEOS, Sigma-Aldrich) were used as the organic and inorganic precursor, respectively. For sulfonation of thermally expandable microsphere, sulfuric acid (H_2SO_4, Duksan) was used. Distilled water was used for neutralization of pH. The acid treated microspheres were filtered through the Whatmann filter paper (125Ø). Methanol solvent was used during sol-gel process. As the acid and base catalyst for aerogel synthesis, oxalic acid (Sigma-Aldrich), ammonium hydroxide (NH_4OH, Daejung) was used, respectively. To verify the applicability, curable silicone resin was used to make board-like insulator material.

2.2. Sulfonation of thermally expandable microsphere

The principle mechanism of compositization is the sulfonation of thermally expandable microsphere by using sulfuric acid. By sulfonation, thermally expandable microsphere can get the hydroxyl group,[15] which is the prime reaction site of chemical bonding between thermally expandable microsphere and hydrolyzed silica sol. This sequence is shown in Fig. 1. Sulfonation was occurred when the thermally expandable microsphere was immersed in a certain concentration of sulfuric acid for several hours with stirring. This acid treated thermally expandable microsphere was needed to be neutralized, so filter paper and distilled water were used for neutralization of pH. After drying in oven for 2 hours, sulfonated thermally expandable microsphere was prepared. By this sulfonation process, hydroxyl group can be attached to surface of thermally expandable microspheres.

2.3. Synthesis of thermally expandable microsphere-TEOS silica composite aerogel

Through chemical compositization, silica aerogel can be hybridized with sulfonated thermally expandable microsphere which has hydroxyl group. TEOS, methanol and oxalic acid were introduced in one container to make hydrolyzed silica sol. Hydrolyzed silica sol has lots of hydroxyl group from a substitution of ethoxy group of TEOS. So, silica sol and thermally expandable microsphere can be connected through condensation reaction between them. Through this process, sulfonated microsphere-silica composite aerogel can be synthesized.[28, 30]
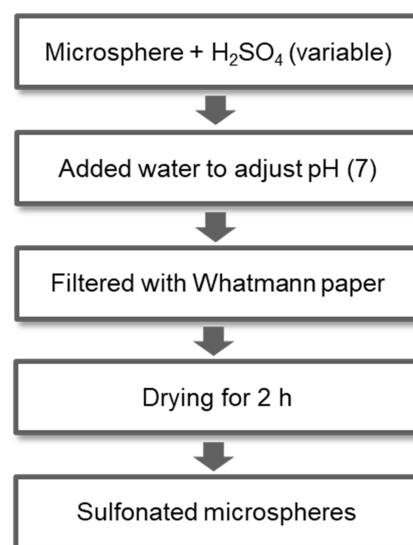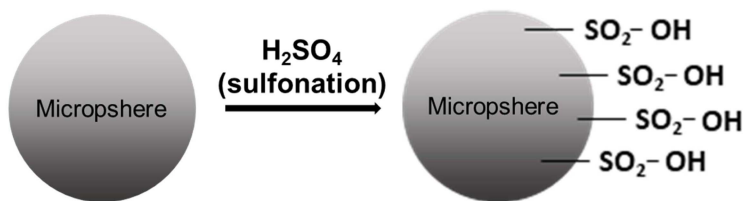

Fig. 1. Synthesis process of sulfonation of thermally expandable microsphere.

1) Formation of hydroxyl group by sulfonation of microsphere

2) Sulfonated microsphere-silica composite aerogel

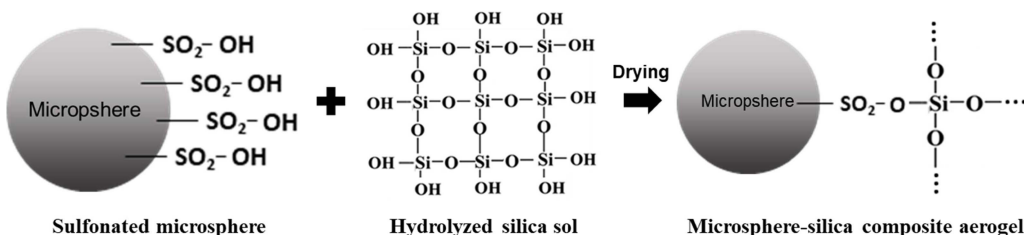Sulfonated microsphere   Hydrolyzed silica sol   Microsphere-silica composite aerogel

Fig. 2. Synthesis process of sulfonation of microsphere and thermally expandable microsphere-silica composite aerogel.

After mixing of the sulfonated thermally expandable microsphere and silica sol followed by hydrolysis and condensation, aging and solvent exchange were conducted. On the surface of the wet-composite gel, methanol solvent for aging was introduced softly, and the wet-composite gel was kept around 48 hours to finish the aging process. Solvent exchange using methanol solvent was also performed for 2-3 days. After that, through CO_2 supercritical drying, the aged wet-composite gel was changed to a porous aerogel structure. Finally, the sulfonated thermally expandable microsphere and TEOS silica composite aerogel was synthesized. The schematic of overall synthesis process is shown in Fig. 2.

2.4. Sample analysis methods

For chemical bonding structure analysis, sulfonation of the thermally expandable microsphere was proven by Fourier-transform infrared (FT-IR) using a Perkin Elmer (Model no. 760) IR spectrophotometer. To verify the presence of additives in the samples, FT-IR spectroscopic study was also conducted in the 380-4,000 cm^{-1} range. The surface morphology and composition of samples were observed using scanning electron microscopy (SEM; JEOL, JSM-7001F). To analyze the thermal properties, Thermal Gravimetric Analysis (TGA) analyzer (TA Instruments, Q50) was used. Also, thermal conductivity was measured by heat flowmeter (ASTM C518-15).

3. Results and Discussion

Fig. 3 shows the FT-IR spectra of pristine thermally expandable microsphere and sulfuric acid-treated micro-
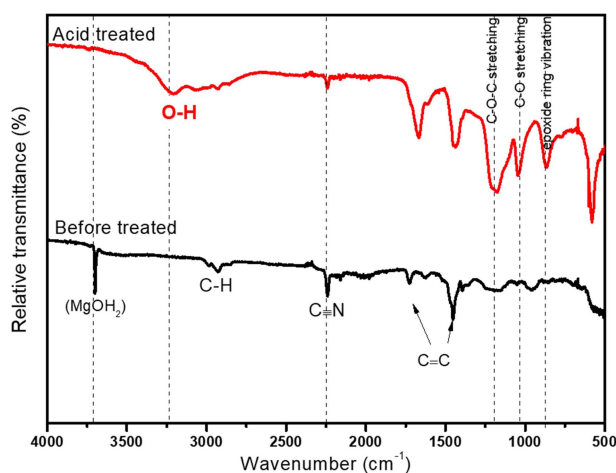

Fig. 3. FT-IR spectra of pristine microsphere (black line) and functionalized microspheres (red line).

spheres. As the chemical mechanism of sulfonation, there were some differences between pristine and sulfonated thermally expandable microsphere. The absorption band in the pristine microspheres at 3700 cm^{-1} is from $MgOH_2$, the fire-retardant component. Before sulfonation (before treated), wide peak of hydroxyl group was not detected. After sulfonation (acid treated) of microsphere, wide peak of hydroxyl group was observed in the range of 3,500-3,000 cm^{-1}. Equally, the peaks of other component of microsphere such as C-H (2,860 cm^{-1}), C≡N (2,250 cm^{-1}) and C=C (1,460 cm^{-1}) bonding were shown in the range of 2,500-500 cm^{-1}. The presence of hydroxyl group on the sulfonated microsphere was observed, which is the prime functional group of reaction with hydrolyzed silica sol to form coating layer. The increased absorption of the band at

3,300 cm^{-1} was due to the enhanced hydroxyl groups in the acid treated microspheres.

To further confirm the presence of silica on the thermally expandable microspheres, FT-IR spectra were recorded. Fig. 4 shows the FT-IR spectra of pristine silica aerogel and thermally expandable microsphere-silica composite aerogel. Typical absorption bands from Si-O, Si-O-Si, Si-O chemical bonds of TEOS were observed in pristine silica aerogel in the range of 1,500-500 cm^{-1}. In the thermally expandable microsphere-silica composite aerogel, the peaks from both the thermally expandable microsphere and silica aerogel were all observed. Also, composite structure of Si-C was also shown at 750 cm^{-1}, so it proves they are chemically connected. Carbon is the component of thermally expandable microsphere, and silicon is the component of silica aerogel. The presence of Si-C absorption band and peaks from microspheres and silica aerogel confirms the formation of composites.

Fig. 5 shows the morphology of the pristine thermally expandable microsphere, pristine silica aerogel and microsphere-silica composite aerogel, observed by SEM. Spherical particle of pristine expanded microspheres was observed as shown in Fig. 5(a). It is due to the expansion by heat, but size ordinally depends on the amount of treated heat.[16] The surface of expanded microsphere looks clear, nothing is coated on the surface in apparent character. Also, typical nanoscale sized particle of pristine silica aerogel was observed in Fig. 5(b). It shows typical porous structure of aerogel, so it can show good thermal stability and low thermal conductivity.[17-24] Spherical shape of the microsphere and chemically coated silica aerogel onto the microsphere were shown in thermally expandable microsphere-silica composite aerogel. On the surface of microsphere, aerogel-coated structure was observed as shown in Fig. 5(c). The microspheres were coated well with aerogel on the outer

surface, which confirms the composite formation. The silica aerogel coating on the outer surface of microsphere was observed in the image, which confirms the composite formation. Additionally, elemental analysis confirmed the presence of a silica coating around the microspheres. As observed in Fig. 5(c), the silica aerogel coating is present on the outer surface of microsphere is non-uniform. The EDS conclude that the silica aerogel coating present on both the areas. At one point the silica content is less compared to the other area, this suggest the non-uniform distribution of silica onto the microspheres. But all the outer surface of microsphere is covered with silica aerogel. Fig. 5(d) shows EDS at two different points of microsphere.

The TGA results of pristine thermally expandable microspheres and microsphere-silica composite aerogel are shown in Fig. 6. Before 200ºC, decomposition of hydrocarbon blowing agent was observed. After 200ºC, decomposition of copolymer contents in thermally expandable microsphere was observed. The outer shell of thermally expandable microsphere is made up of copolymers, so it displayed large amount of weight loss of due to decomposition of copolymers. In other words, it is decomposition of prime component of pristine microspheres. The remaining weight loss fraction was expected to be the loss of the remaining methyl group component. In conclusion, pristine thermally expandable microsphere and thermally expandable microsphere-silica composite aerogel showed similar trend of decomposition because prime decomposed component is organic microsphere, which has lower thermal stability than silica aerogel component.

In order to confirm the industrial applicability of composite aerogels, the specimens were fabricated in 30×30×4 (cm^3) size and the thermal conductivity was measured. As the matrix material for composite aerogel, curable silicone resin was prepared. Curable silicone resin consists of the
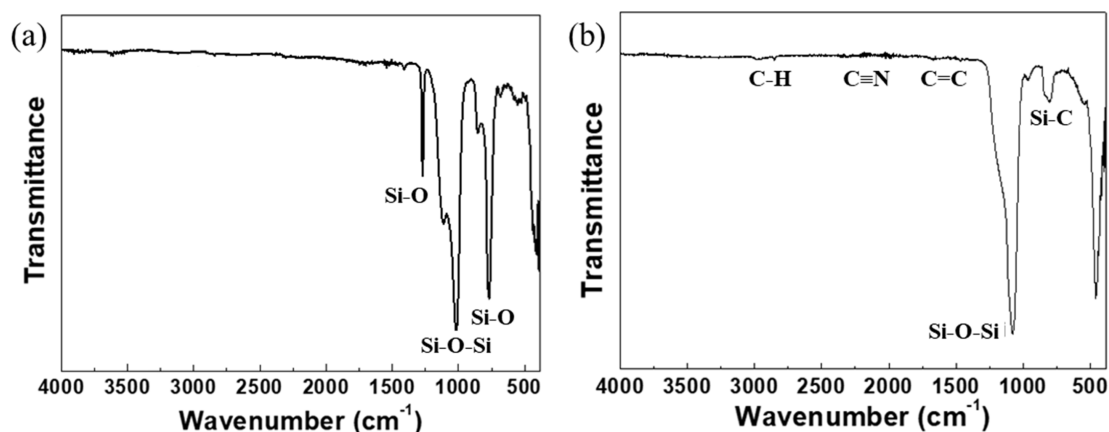

Fig. 4. FT-IR spectra of (a) pristine silica aerogel and (b) thermally expandable microsphere-silica composite aerogel.

Element	Weight %	Atomic %
C K	63.23	72.77
O K	24.56	21.22
Si K	12.21	6.01

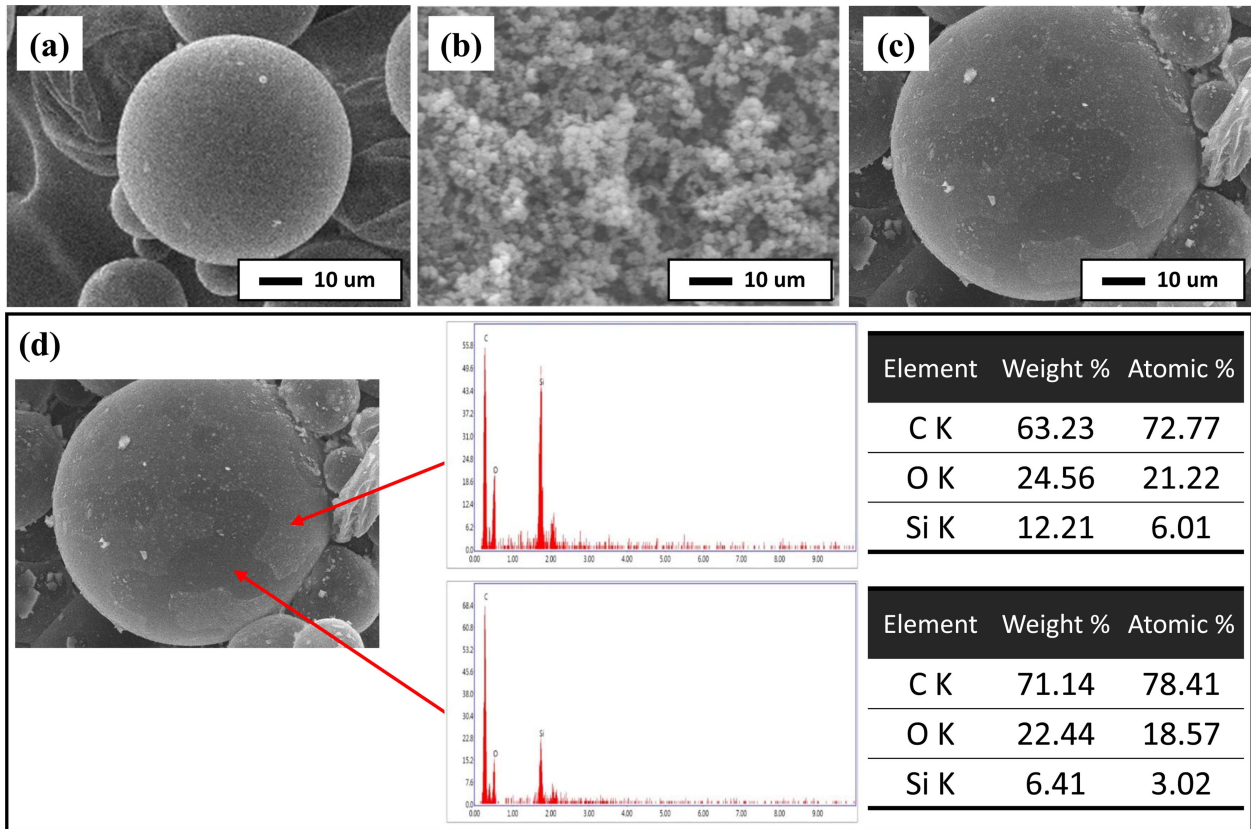| Element	Weight %	Atomic %
C K	71.14	78.41
O K	22.44	18.57
Si K	6.41	3.02

Fig. 5. SEM images of (a) thermally expandable microsphere, (b) pristine silica aerogel, (c) thermally expandable microsphere-silica composite aerogel and (d) the EDS result of thermally expandable microsphere-silica composite aerogel.
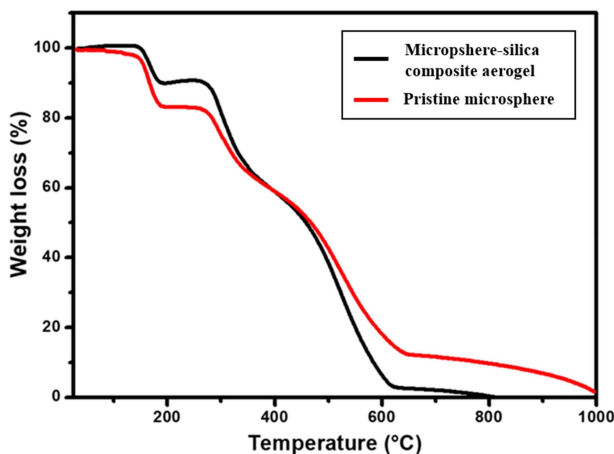

Fig. 6. TGA result of pristine thermally expandable microsphere and thermally expandable microsphere-silica composite aerogel.

base and curing agent, and it can be cured by mixing the base and curing agent.[32] So, it is possible to produce board-type composite insulator by mixing composite aerogel with the base of silicone resin and adding curing agent.[33] The result of thermal conductivity measurement is shown in Table 1 with the molar ratio (M) of silicone resin and microsphere-silica composite aerogel. Pristine silicone

Table 1. Thermal conductivity of pristine silicone resin and mixture of silicone resin and thermally expandable microsphere-silica composite aerogel

Sample composition (M=molar ratio of silicone resin:composite aerogel)	Thermal conductivity (W/m·K)
Pristine silicone resin	0.200
Silicone resin:composite aerogel (M=1:8.25)	0.063
Silicone resin:composite aerogel (M =1:9.25)	0.071

resin showed relatively high thermal conductivity as 0.200 W/m·K. However, the optimized composition of silicone resin and composite aerogel mixture (M=1:8.25) showed good thermal insulation property as 0.063 W/m·K. However, when the amount of composite aerogel larger than the optimized amount was introduced as the sample of silicone resin and composite aerogel mixture (M=1:9.25), the thermal conductivity rather increased as 0.071 W/m·K.

This phenomenon is due to the open pore structure of the aerogel. As mentioned before, aerogel can occupy empty spaces between thermally expandable microspheres and can be hybridized on the surface of thermally expandable microspheres. But, when higher amounts of aerogel than optimized amount was introduced, components of the cur-

able silicone resin can be adsorbed in the aerogel pores.[30] It caused not only the loss of some porosity of aerogel, but also the loss of insulation property of composite material as silicone resin and composite aerogel mixture (M=1:9.25). In addition, when more than certain amount of aerogel was mixed, there may be particles which cannot be combined with the microspheres. In this case, due to external influences, aerogel can easily be broken and scattered.[34] For these reasons, the nature of the aerogel may not be uniformly exhibited in composite material. So, if the appropriate mixing ratio of aerogel is found and applied as the composition of silicone resin and composite aerogel mixture (M=1:8.25), the thermal conductivity is expected to be further improved.

4. Conclusion

Silica aerogels hybridized with sulfonated thermally expandable microsphere were synthesized by chemical compositization between thermally expandable microsphere and TEOS silica aerogel through sol-gel process to get good thermal properties. The presence of spectra peaks about silicon, oxygen, nitrogen and Si-C bonding showed the evidence of hybridization between thermally expandable microspheres and silica aerogels. The structure of silica aerogel coated microspheres was observed through SEM images. Pristine thermally expandable microsphere and thermally expandable microsphere-silica composite aerogel showed similar trend of decomposition because prime decomposed component is organic microsphere. Relatively low thermal conductivity value of 0.063 W/m·K and applicability were observed by using the curable silicone resin matrix and composite aerogel mixture. If the optimum mixing ratio is found and applied, the thermal conductivity is expected to be further improved.

Acknowledgement

References

1. Z.-L. Yu, N. Yang, V. Apostolopoulou-Kalkavoura, B. Qin, Z.-Y. Ma, W.-Y. Xing, C. Qiao, L. Bergstrom, M. Antonietti, and S.-H. Yu, "Fire-retardant and thermally insulating phenolic-silica aerogels", Angew. Chem. Int. Ed., 57(17), 4538 (2018).

2. Y. Lei, X. Chen, H. Song, Z. Hu, and B. Cao, "Improvement of thermal insulation performance of silica aerogels by Al_2O_3 powders doping", Ceram. Int., 43(14), 10799 (2017).

3. T. Feczkó, L. Trif, and D. Horák, "Latent heat storage by silica-coated polymer beads containing organic phase change materials", Sol. Energy, 132, 405 (2016).

4. L. M. Sanz-Moral, A. Aho, N. Kumar, K. Eranen, M. Peurla, J. Peltonen, D. Y. Murzin, and T. Salmi, "Synthesis and characterization Ru–C/SiO_2 aerogel catalysts for sugar hydrogenation reactions", Catal. Lett., 148, 3514 (2018).

5. G. Vamvounis, M. Jonsson, E. Malmström, A. Hult, "Synthesis and properties of poly(3-n-dodecylthiophene) modified thermally expandable microspheres", Eur. Polym. J., 49, 1503 (2013).

6. S. Ries, A. Spoerrer, and V. Altstaedt, "Foam injection molding of thermoplastic elastomers: Blowing agents, foaming process and characterization of structural foams", Proc. AIP Conf., 1593(1), 401 (2014).

7. S.-Y. Chen, Z.-C. Sun, L.-H. Li, Y.-H. Xiao, and Y.-M. Yu, "Preparation and characterization of conducting polymer-coated thermally expandable microspheres", Chin. Chem. Lett., 28, 658 (2017).

8. M. Jonsson, D. Nyström, O. Nordin, and E. Malmström, "Surface modification of thermally expandable microspheres by grafting poly(glycidyl methacrylate) using ARGET ATRP", Eur. Polym. J., 45, 2374 (2009).

9. A. Schmid, L. R. Sutton, S. P. Armes, P. S. Bain, and G. Manfre, "Synthesis and evaluation of polypyrrole-coated thermally-expandable microspheres: an improved approach to reversible adhesion", Soft Matter, 5(2), 407 (2009).

10. J. F. Illescas, and M. J. Mosquera, "Producing surfactant-synthesized nanomaterials in situ on a building substrate, without volatile organic compounds", ACS Appl. Mater. Interfaces., 4(8), 4259 (2012).

11. C. Zhang, C. Zhang, R. Huang, and X. Gu, "Effects of hollow microspheres on the thermal insulation of polysiloxane foam", J. Appl. Polym. Sci., 134(18), 44778 (2017).

12. H. E. Cingil, J. A. Balmer, S. P. Armes, and P. S. Bain, "Conducting polymer-coated thermally expandable microspheres", Polym. Chem., 1(8), 1323 (2010).

13. S. Grama, Z. Plichta, M. Trchová, J. Kovářová, M. Beneš, and D. Horák, "Monodisperse macroporous poly(glycidyl methacrylate) microspheres coated with silica: design, preparation and characterization", React. Funct. Polym., 77, 11 (2014).

14. H. Aglan, S. Shebl, M. Morsy, M. Calhoun, H. Harding, and M. Ahmad, "Strength and toughness improvement of cement binders using expandable thermoplastic microspheres", Constr. Build. Mater., 23(8), 2856 (2009).

15. Y. Lu, J. Broughton, and P. Winfield, "Surface modification of thermally expandable microspheres for enhanced performance of disbondable adhesive", Int. J. Adhes. Adhes., 66, 33 (2016).

16. M. Jonsson, O. Nordin, A. L. Kron, and E. Malmström,

"Thermally expandable microspheres with excellent expansion characteristics at high temperature", Journal of applied polymer science, 117(1), 384 (2010).

17. S. Mulik, C. Sotiriou-Leventis, G. Churu, H. Lu, and N. Leventis, "Cross-linking 3D assemblies of nanoparticles into mechanically strong aerogels by surface-initiated free-radical polymerization", Chem. Mater., 20, 5035 (2008).

18. X. Hu, K. Littrel, S. Ji, D. G. Pickles, and W. M. Risen, "Characterization of silica-polymer aerogel composites by small-angle neutron scattering and transmission electron microscopy", J. Non-Cryst. Solids., 288, 184 (2001).

19. Z. Li, X. Cheng, S. He, D. Huang, H. Bi, and H. Yang, "Preparation of ambient pressure dried MTMS/TEOS co-precursor silica aerogel by adjusting NH$_4$OH concentration", Mater. Lett., 129, 12 (2014).

20. N. Hüsing, and U. Schubert, "Aerogels – airy materials: chemistry, structure, and properties", Angew. Chem., Int. Ed., 37, 22 (1998).

21. D. B. Mahadik, H.-N.-R. Jung, Y. K. Lee, K.-Y. Lee, and H.-H. Park, "Elastic and Superhydrophobic Monolithic Methyltrimethoxysilane-based Silica Aerogels by Two-step Sol-gel Process", J. Microelectron. Packag. Soc., 23(1), 35 (2016).

22. K.-Y. Lee, H.-N.-R. Jung, D. B. Mahadik, and H.-H. Park, "Characterization of mechanical property change in polymer aerogels depending on the ligand structure of acrylate monomer", J. Microelectron. Packag. Soc., 23(3), 1 (2016).

23. H.-Y. Nah, H.-N.-R. Jung, K.-Y. Lee, Y. S. Ku, and H.-H. Park, "Effect of acid catalyst kinds on the pore structural characteristics of water glass based silica aerogel", J. Microelectron. Packag. Soc., 24(3), 13 (2017).

24. Y. Kim, T. Kim, J. G. Shim, and H.-H. Park, "The effect of acetonitrile on the texture properties of sodium silicate based silica aerogels", J. Microelectron. Packag. Soc., 25(4), 143 (2018).

25. D. Ge, L. Yang, Y. Li, and J. Zhao, "Hydrophobic and thermal insulation properties of silica aerogel/epoxy composite", J. Non-Cryst. Solids., 355, 2610 (2009).

26. N. Kuthirummal, A. Dean, C. Yao, and W. Risen, "Photo-formation of gold nanoparticles: photoacoustic studies on solid monoliths of Au(III)–chitosan–silica aerogels", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 70(3), 700 (2008).

27. J. T. Seo, S. M. Ma, Q. Yang, L. Creekmore, H. Brown, R. Battle, K. Lee, A. Jackson, T. Skyles, B. Tabibi, K. P. Yoo, S. Y. Kim, S. S. Jung, and M. Namkung, "Large optical nonlinearity of highly porous silica nanoaerogels in the nanosecond time domain", J. Korean Phys. Soc., 48, 1395 (2006).

28. H. M. Kim, Y. J. Noh, J. Yu, S. Y. Kim, and J .R. Youn, "Silica aerogel/polyvinyl alcohol (PVA) insulation composites with preserved aerogel pores using interfaces between the superhydrophobic aerogel and hydrophilic PVA solution", Compos. Pt. A-Appl. Sci. Manuf., 75, 39 (2015).

29. A. Stojanovic, S. Zhao, E. Angelica, W. J. Malfait, and M. M. Koebel, "Three routes to superinsulating silica aerogel powder", J. Sol-Gel Sci. Technol., 90(1), 57 (2019).

30. H. M. Kim, H. S. Kim, S. Y. Kim, and J. R. Youn, "Silica aerogel/epoxy composites with preserved aerogel pores and low thermal conductivity", e-Polymers, 15(2), 111 (2015).

31. P. Alves, J. F. J. Coelho, J. Haack, A. Rota, A. Bruinink, and M. H. Gil, "Surface modification and characterization of thermoplastic polyurethane", Eur. Polym. J., 45, 1412 (2009).

32. M. Ochoa, A. Lamy-Mendes, A. Maia, A. Portugal, and L. Durães, "Influence of structure-directing additives on the properties of poly(methylsilsesquioxane) aerogel-like materials", Gels, 5(1), 6 (2019).

33. H. Lee, D. Lee, J. Cho, Y.-O. Kim, S. Lim, S. Youn, Y.-C. Jung, S.-Y. Kim, and D.-G. Seong, "Super-insulating, flame-retardant, and flexible poly(dimethylsiloxane) composites based on silica aerogel", Compos. Pt. A-Appl. Sci. Manuf., 123, 108 (2019).

34. K.-Y. Lee, H,-Y, Nah, H, Choi, V, G. Parale, and H.-H. Park, "Methyltrimethoxysilane silica aerogel composite with carboxyl-functionalised multi-wall carbon nanotubes", Int. J. Nanotechnol., 15(6-7), 587 (2018).