Thermal Conductivity of Silica-aerogel (SA) and Autoclave Aerated Concrete (AAC) Composites

Qu Mingliang¹, Tian Shuaiqi¹, Fan Liwu^{1*}, Yu Zitao¹, Ge Jian²

¹Institute of Thermal Science and Power Systems, School of Energy Engineering, Zhejiang University, Hangzhou 310027, China

²Institute of Building Technology, School of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310058, China

Abstract. Improving the thermal insulating performance of porous building materials is of great practical significance for building energy conservation. In this work, silica aerogels (SA) with ultralow thermal conductivity were proposed as an appropriate candidate to be integrated with autoclaved aerated concrete (AAC) to produce novel SA-AAC composites with higher thermal insulating performance by physical solution impregnation method. The pore-structures, mechanical and thermal properties of the SA-AAC composites were probed by various experimental tests. According to the microscopy and porosimetry results, SA were observed to adhere to the surface walls of the AAC holes, thus reducing the amount of macro-sized pores. In addition, the improved thermal insulating performance of AAC was successfully achieved with the relative improvement depending on the porosity of the pristine AAC. At the mass fraction of SA of ~7%, the highest relative improvement was found to be ~30%. The results of this work exhibited a great potential of this novel SA-AAC composite in engineering applications.

1 Introduction

With growth of energy crises and global warming, energy conservation and emission reduction have become more and more critical in the building field. The heating ventilation and air conditioning (HVAC) systems are utilized frequently to ensure the indoor comfort, thereby increasing the building energy consumption, especially with poor thermal insulation building envelope [1][2]. There are some novel thermal insulation materials such as binderless cotton stalk fiberboard (BCSF) [3], vacuum insulation panels (VIP) and aerogels[4], indicating better thermal insulation performance, which is likely to reduce the overall building energy consumption[5][6]. Even though, these novel materials have excellent thermal insulation performance, the high cost and complex process limited the using large scale. In recent years, many attentions have been paid on the modification of typical building materials such as concrete [7], wood [8] and xonotlite-type calcium silicate [9] to reduce their thermal conductivity and increase thermal insulating performance [10][11]. Especially, autoclave aerated concrete (AAC) is a typical green building material with lightweight and high porosity, and has been extensively used in building envelopes[12]. Therefore, it is necessary to further decrease the thermal conductivity of AAC by introducing materials with lower thermal conductivity, for extending the application fields of AAC with cheap. Although there have been many attempts on the modification of AAC on improving some essential performances such as adding carbon, fibers and other

nano-particles [13][15], there are still lacks in the knowledge on reducing the thermal conductivity, namely enhancing the thermal insulation performance. Silica-aerogel (SA) is a possible candidate to be introduced to further decrease the thermal conductivity of AAC due to its low density, high porosity, and even lower thermal conductivity than AAC. However, it is impossible to employ SA individually in the building envelope because of its poor mechanical strength. Currently, some scholars have attempted to combine SA with some typical porous materials such as fiber and xonotlite-type calcium silicate [16]-[18] and found that the thermal insulation performance of these composite materials was indeed increased. Meanwhile, the mechanical performances of the composites were also increased, which expands the application of SA. Furthermore, the physical doping method recently exerts a tremendous fascination on researchers, for it is not needed supercritical drying technique, which was utilized in this work [19][20].

In this study, SA-AAC composites with various SA loadings were fabricating through physical doping method for decreasing the thermal conductivity of AAC. The pore structure and thermal conductivity were measured to evaluate the overall performance of the composites, which could guide the development of a novel thermal-insulating building materials.

* Corresponding author: Liwufan@zju.edu.cn

2 Experimental

2.1. Specimen preparation

The nanoscale SA used in this paper was supplied by Jinwei Chemical Co., Ltd., China. The porosity of this kind of SA is higher than 90%, while the density is around 40 kg/m³. Polyacrylamide (PMA>95%) was purchased from Tianjin Zhiyuan Reagent Co., Ltd., China. 3-aminopropyltrimethoxysilane (KH550) was supplied by Nanjinchuangshi Chemical Co., Ltd., China. The AACs studied in this work were provided by Zhejiang Kaiyuan New Material Co., Ltd., whose density, porosity and mean pore diameters are shown in Table 1 [21]. Obviously, the AAC-300 sample has the highest porosity and the lowest density, while the AAC-500 is the opposite.

Table 1. Measured density and porosity of the various pristine AAC samples.[21]

Product No.	ρ (kg/m ³)	ρ_m (kg/m ³)	ϕ_o (%)	$d(nm)$
AAC-300	341.8±6.3	2245.0±4.5	85.50±0.05	215±14.0
AAC-400	438.5±6.7	2360.4±9.5	79.25±0.05	90.6±4.6
AAC-500	524.9±8.5	2295.1±8.8	74.32±0.05	78.2±3.0

Fig. 1 Process of specimens preparation.

As shown in Fig.1, the modified solution was synthesized by mixing ethanol, deionized water and analytical pure PMA. The SA powders were added into the solution with KH550 after the solution had been stirred for 2 min. The SA powders were completely dispersed in solution by ultrasonic dispersion (59 kHz, 90 W) for 10 min [22]. The mass fractions of each components in the solution are shown in Table 2.

Table 2. The mass fractions of each contents of the solution

Ethanol (wt.%)	Deionized Water (wt.%)	PMA (wt.%)	KH550 (wt.%)	SA (wt.%)
60.00	34.00	0.10	5.90	0.0
58.80	33.32	0.10	5.78	2.0
57.60	32.64	0.10	5.66	4.0
56.40	31.96	0.10	5.55	6.0
55.20	31.28	0.10	5.43	8.0

The modified solution has a lower fluidity than water, thus it is somewhat difficult to directly impregnate solution into the interconnected capillary pores of AAC under the normal atmospheric pressure. As a consequence, we set the 8 wt.% as the maximum mass fraction of SA in modified solution. The process for preparing composite samples is shown in Fig.1. The pristine AAC specimens (50 × 50 × 20 mm³) were first dried in a thermostat with 60.0 ± 1.0 °C which was stated to be relatively mild to the pore structure of cement-based materials [23]. The dry samples were then immersed in the modified solution for 3 hours, and which were afterwards placed in a ventilation room at 23.0 ± 1.0 °C for 5 hours. The residual SA clinging on the surface of specimens was scraped after ventilation. We can see from the fabrication process that as compared with sol-gel method, the physical doping method is easier to manufacture [18]-[19]. The fabricated composites were finally dried for 48h in a thermostat at 60.0 ± 1.0 °C. The realistic mass fractions of SA were also measured by an electronic balance (0.01g) based on the following equation, and the results are shown in Table.3.

$$\theta = \frac{m_{SA}}{m_{dry}} \quad (1)$$

Where m_{dry} is the mass of raw specimens, m_{SA} is the mass of SA,

Table 3. The realistic mass fraction (wt.%) of SA in composites with various porosity and intended mass fraction of impregnation (ϵ)

	AAC-300	AAC-400	AAC-500
2	1.80±0.66	1.75±0.10	1.56±0.49
4	3.65±0.11	3.43±0.05	3.01±0.42
6	4.95±0.14	4.66±0.15	4.52±0.07
8	6.72±0.39	6.45±0.31	5.86±0.03

2.2 Measurement methods

The pore structures of the composite samples were photographed by scanning electron microscope (SEM) SU70. In addition, pore size distributions were tested by Auto Pore IV 9510 while the pressure range of mercury intrusion porosimetry (MIP) was from 0.1 to 60000 psia and surface tension was 485 dynes/cm. The thermal conductivities were measured by the transient plane source (TPS) technique via Hot Disk TPS 3500, whose thermal conductivity range is 0.005-500 (W/m·K) while the measurement accuracy is 3%, which was subjected to considerable research [24]. In order to eliminate the effect of moisture, all specimens were dried again in a thermostat with a temperature at 60.0 ± 1.0 °C until the relative mass variations were less than 0.1% over a 24 h duration [25]. In order to ensure a proper contact between the TPS sensor and the samples, the surfaces of all specimens were polished and the experimental temperature was controlled at 23.0 ± 1.0 °C via another thermostat. Additionally, in order to ensure repeatability, the TPS sensor was placed at different locations on each

test and three parallel measurements were taken for each specimen. The main sources of the thermal conductivity uncertainty are connected to measurement of the temperature and the satisfaction of the experimental condition as they are supposed in the analytical model. The main source of non-measurement errors cause difference between the real condition and assumptions of the analytical model. All of uncertainties are considered to be independent here, and the thermal conductivity is less than 4%. The thermal conductivity of SA is 0.0311 ± 0.0001 (W/m·K), which was measured by stacking SA powder and TPS sensor into a professional container that was supplied by Hot Disk Co., Ltd., to measure powder [26].

3 Results and discussion

3.1 Pore structure features

The pore structure is expected to have significant effect on the thermal properties of the composite materials. Fig.2(a) illustrates the SEM image of pristine AAC with a magnification of $30\times$, from which the smooth pore surfaces could be observed. By contrast, Fig.2 (b) shows the SEM image of SA-AAC composites at the magnification of $70\times$. Obviously, many SA lamellas are found to be randomly clinging on the surfaces of the pore. With increasing the magnification to $350\times$, as shown in Fig. 2(c), the average size of a sheet-shaped SA is found to be approximately $100\ \mu\text{m}$, and the SA lamellas cling tightly on the surface of AAC. In Fig.2(d) showing the pristine AAC with a much higher of magnification of $10000\times$, a large amount of sheet-like capillary pores can be observed from the figure. The SEM image of SA-AAC composites under $7000\times$ magnification is shown in Fig.2 (e), some irregular groups with size of $2\text{--}5\ \mu\text{m}$ are clinging on the sheet-shaped tobermorite pore surface. With further increasing the magnification to $20000\times$, these irregular groups in the capillary pores are found to consist of porous and continuous nanoparticles as shown in Fig.2(f). From Fig.2, we can conclude that the SA cling to the pore surface of AAC well with the lamella shape.

Fig. 2 SEM images of (a) pristine AAC at $30\times$ magnification (b) SA-AAC composites at $70\times$ magnification (c) SA-AAC composite at $350\times$ magnification (d) pristine AAC at $10000\times$ magnification (e) SA-AAC composite at $7000\times$ magnification (f) SA-AAC composite at $20000\times$ magnification.

The pore size distributions of pristine AAC samples as determined by MIP are shown in Fig.3(a). The internal

pores of the AACs could be divided into two main types: one is capillary pores with the diameters ranging from 0.01 to $1\ \mu\text{m}$, another is macroscopic pores with diameters around $100\ \mu\text{m}$. In addition, taking the case of SA-AAC-300 composite samples which have a large amount of macroscopic pore as an example, the various pore size percentages are shown in Fig.3(b). The proportion of pore size of $1\sim 100\ \mu\text{m}$ decline mildly with increasing the SA content, while the proportions of other pore sizes generally keep unchanged.

Fig. 3 (a) Pore size distributions for various AAC samples as determined by MIP; (b) Relative volume percentage of total pores in different pore size.

As mentioned above, when SA is added into the raw material, there are some SA lamellas clinging on the pore surfaces. This may be due to the process of fabrication: SA was actually introduced into the pores through the modified solution, the solvent of the solution was then volatilized away from the sample, and the SA lamellas were left. Impregnating SA does not affect the pore size distribution of AAC as well. Although there is some SA cling to the capillary pore, the effect of the change by the addition of SA is not of great significance, this may attribute to the thickness of SA lamella is thin.

3.2 Thermal conductivity

The thermal conductivity of SA-AAC composites were tested by Hot Disk Thermal Analyzer TPS3500 at $23.0 \pm 1.0\ ^\circ\text{C}$, and the result are plotted in Fig.4. The error bars

of each data point in y-direction represent the uncertainties associated with thermal conductivity measurements, also the error bars of x-direction represent the uncertainties associated with realistic content of SA in AACs. The thermal conductivities of AACs have a downward trend with the increase of SA mass fraction. The thermal conductivities of the pristine AAC were measured to be 0.1149, 0.1375 and 0.1527 (W/m·K) for AAC-300, AAC-400 and AAC-500 samples, respectively. When the mass fraction of SA in the specimens increases from 0 to near 7%, the thermal conductivities decrease to 0.08139, 0.1084 and 0.1407 (W/m·K), respectively. Apparently, the SA lamellas clinging on the pore surface would provide additional contact thermal resistances due to the ultralow thermal conductivity of SA [27]. In addition the thermal conductivity of AAC-300 decreases by 29.1% while AAC-500 just decrease by 7.9%. It means that with increasing the porosity, the decrement of the thermal conductivity as increasing the same content of SA increases with increasing the porosity. Generally, higher porosity means the more pore space and large pore size for impregnating SA. Therefore, more SA lamellas cling in on the surface of the inner pores, which increases the contact thermal resistance. However, some SA lamella would accumulate and fabricate a new thermal transfer path in the specimens with small pore size, then whose thermal conductivity decrease mildly. Fig. 4(b) compares the thermal conductivity of some typical types of foamed concrete, which actually have low thermal conductivity as well [28][33]. The SA-AAC composites are found to have even lower thermal conductivity than that of most materials with similar density.

Fig. 4 (a) Measured thermal conductivity for the AACs based composite samples as a function of SA content; (b) Comparison of the thermal conductivity and density of SA-AAC and conventional foamed concrete.

The excellent thermal insulation performance of SA-AAC composites presents a promising application prospect. It is hence possible to introduce SA into AAC through the modified solution, which will certainly enhance the thermal insulation performance of pristine AAC due to the ultralow thermal conductivity of SA and the contact thermal resistance between the SA and AACs.

4 Conclusions

In this paper, the SA was impregnated into AAC through a physical doping method to fabricate a novel SA-AAC composite which has lower thermal conductivity than that of AAC. The composites could be used as material of building envelope for building energy saved.

Through the SEM images of SA-AAC composite, SA lamellas were found to adhere to inner pore surface and even appear on the sheet-shaped tobermorite pore surface, which indicates that SA combines with material tightly. The thermal conductivities of composite materials decrease with increasing the content of SA. The composite with the highest porosity (SA-AAC-300) was found to have the fastest trend of thermal conductivity decrease. With the maximum load of SA (~7 wt.%), the decrement was 29.1% compared to the pristine AAC-300 sample.

There are several advantages of SA-AAC composites. Firstly, the SA-AAC composites are fabricated by a novel physical doping method, whose process is easier than the normal sol-gel method, the raw materials are less toxicity and readily available as well. Additionally, the thermal insulation performance can be increased significantly by adding SA even a low mass fraction.

Admittedly, there are also some restrictions of this method. The content of SA in the composite is subjected to the mass fraction of SA in the modified solution. The effect of modifying is also restricted by the open porosity of material, which provides space to accommodate SA lamellas. Further research on this topic is hence encouraged, such as optimum modified solution formula to increase the mass fraction of SA.

This material is based upon work supported by the China National Key R&D Program under Grant No. 2016YFC0700302, the Zhejiang Provincial Natural Science Foundation of China under Grant No. LR17E060001 and the National Natural Science Foundation of China under Grant No. 51979246. L.-W. Fan would like to thank a start-up fund granted by the “100 Talents Program” of Zhejiang University.

References

- [1] S. Mirrahimi, M. F. Mohamed, L. C. Haw, N. L. N. Ibrahim, W. F. M. Yusoff & A. Aflaki, *The effect of building envelope on the thermal comfort and energy saving for high-rise buildings in hot-humid climate*, *Renew. Sustain. Energy Rev.*, vol. **53**, pp. 1508–1519, (2016).
- [2] R. Diao, L. Sun & F. Yang, *Thermal performance of building wall materials in villages and towns in hot summer and cold winter zone in China*, *Appl. Therm. Eng.*, vol. **128**, pp. 517–530, (2018).

- [3] X. Zhou, F. Zheng, H. Li & C. Lu, *An environment-friendly thermal insulation material from cotton stalk fibers*, *Energy Build.*, vol. **42**, no. 7, pp. 1070–1074, (2010).
- [4] B. P. Jelle, *Traditional, state-of-the-art and future thermal building insulation materials and solutions—Properties, requirements and possibilities*, *Energy Build.*, vol. **43**, no. 10, pp. 2549–2563, (2011).
- [5] H. Binici, O. Aksogan, M. N. Bodur, E. Akca & S. Kapur, *Thermal isolation and mechanical properties of fibre reinforced mud bricks as wall materials*, *Constr. Build. Mater.*, vol. **21**, no. 4, pp. 901–906, (2007).
- [6] T. M. I. Mahlia, B. N. Taufiq & H. H. Masjuki, *Correlation between thermal conductivity and the thickness of selected insulation materials for building wall*, *Energy Build.*, vol. **39**, no. 2, pp. 182–187, (2007).
- [7] M. R. Hall, K. B. Najim & C. J. Hopfe, *Transient thermal behaviour of crumb rubber-modified concrete and implications for thermal response and energy efficiency in buildings*, *Appl. Therm. Eng.*, vol. **33**, pp. 77–85, (2012).
- [8] T. Li, M. Zhu, Z. Yang, J. Song, J. Dai, Y. Yao, W. Luo, G. Pastel, B. Yang & L. Hu, *Wood composite as an energy efficient building material : Guided sunlight transmittance and effective thermal insulation*, *Adv. Energy Mater.*, vol. **6**, no. 22, p. 1601122, (2016).
- [9] G. Wei, Y. Liu, X. Zhang, F. Yu & X. Du, *Thermal conductivities study on silica aerogel and its composite insulation materials*, *Int. J. Heat Mass Transf.*, vol. **54**, no. 11–12, pp. 2355–2366, (2011).
- [10] B. Abu-Jdayil, A.-H. Mourad, W. Hittini, M. Hassan & S. Hameedi, *Traditional, state-of-the-art and renewable thermal building insulation materials: An overview*, *Constr. Build. Mater.*, vol. **214**, pp. 709–735, (2019).
- [11] Z. O. Pehlivanlı, İ. Uzun, Z. P. Yücel & İ. Demir, *The effect of different fiber reinforcement on the thermal and mechanical properties of autoclaved aerated concrete*, *Constr. Build. Mater.*, vol. **112**, pp. 325–330, (2016).
- [12] N. Narayanan, K. Ramamurthy, *Structure and properties of aerated concrete: a review*, *Cem. Concr. Compos.*, vol. **22**, no. 5, pp. 321–329, (2000).
- [13] M. Deyazada, B. Vandoren, D. Dragan & H. Degée, *Experimental investigations on the resistance of masonry walls with AAC thermal break layer*, *Constr. Build. Mater.*, vol. **224**, pp. 474–492, (2019).
- [14] N. Uddin, M. A. Mousa & F. H. Fouad, *Impact behavior of hybrid fiber-reinforced polymer (FRP)/autoclave aerated concrete (AAC) panels for structural applications*, in *Developments in Fiber-Reinforced Polymer (FRP) Composites for Civil Engineering*, Elsevier, 2013, pp. 247–271.
- [15] Z. O. Pehlivanlı, İ. Uzun & İ. Demir, *Mechanical and microstructural features of autoclaved aerated concrete reinforced with autoclaved polypropylene, carbon, basalt and glass fiber*, *Constr. Build. Mater.*, vol. **96**, pp. 428–433, (2015).
- [16] X. Yang, Y. Sun, D. Shi & J. Liu, *Experimental investigation on mechanical properties of a fiber-reinforced silica aerogel composite*, *Mater. Sci. Eng. A*, vol. **528**, no. 13–14, pp. 4830–4836, (2011).
- [17] P. Zhai, X. F. Duan, Q. L. Zhang, H. S. Wang, H. H. Cheng & X. H. Zhang, *Characterization of SiO₂ Aerogel/SiO₂ Fiber Composites Prepared by Sol-Gel Method*, in *Key Engineering Materials*, 2016, vol. **697**, pp. 409–413.
- [18] B. Yuan, S. Ding, D. Wang, G. Wang & H. Li, *Heat insulation properties of silica aerogel/glass fiber composites fabricated by press forming*, *Mater. Lett.*, vol. **75**, pp. 204–206, (2012).
- [19] Y. Wang, J. Huang, D. Wang, Y. Liu, Z. Zhao & J. Liu, *Experimental investigation on thermal conductivity of aerogel-incorporated concrete under various hygrothermal environment*, *Energy*, vol. **188**, p. 115999, (2019).
- [20] S. Ng, B. P. Jelle, L. I. C. Sandberg, T. Gao & Ó. H. Wallevik, *Experimental investigations of aerogel-incorporated ultra-high performance concrete*, *Constr. Build. Mater.*, vol. **77**, pp. 307–316, (2015).
- [21] S.-Q. Tian *et al.*, *Experimental determination and fractal modeling of the effective thermal conductivity of autoclave aerated concrete (AAC) impregnated with paraffin for improved thermal storage performance*, *Appl. Therm. Eng.*, vol. **163**, p. 114387, (2019).
- [22] D. Hua, J. Tang, J. Jiang, Z. Gu, L. Dai & X. Zhu, *Controlled grafting modification of silica gel via RAFT polymerization under ultrasonic irradiation*, *Mater. Chem. Phys.*, vol. **114**, no. 1, pp. 402–406, (2009).
- [23] Q. Zhang, Q. Zeng, D. C. Zheng, J. Wang & S. L. Xu, *Oven drying kinetics and status of cement-based porous materials for in-lab microstructure investigation*, *Adv. Cem. Res.*, vol. **30**, no. 5, pp. 204–215, (2018).
- [24] B. Adl-Zarrabi, L. Boström & U. Wickström, *Using the TPS method for determining the thermal properties of concrete and wood at elevated temperature*, *Fire Mater. An Int. J.*, vol. **30**, no. 5, pp. 359–369, (2006).
- [25] H.-Q. Jin, X.-L. Yao, L.-W. Fan, X. Xu & Z.-T. Yu, *Experimental determination and fractal modeling of the effective thermal conductivity of autoclaved aerated concrete: Effects of moisture content*, *Int. J. Heat Mass Transf.*, vol. **92**, pp. 589–602, (2016).
- [26] E. T. Afriyie, P. Karami, P. Norberg & K. Gudmundsson, *Textural and thermal conductivity properties of a low density mesoporous silica material*, *Energy Build.*, vol. **75**, pp. 210–215, (2014).
- [27] E. Cuce, P. M. Cuce, C. J. Wood & S. B. Riffat, *Toward aerogel based thermal superinsulation in buildings: a comprehensive review*, *Renew. Sustain. Energy Rev.*, vol. **34**, pp. 273–299, (2014).
- [28] Z. Zhang, J. L. Provis, A. Reid & H. Wang, *Mechanical, thermal insulation, thermal resistance and acoustic absorption properties of geopolymer foam concrete*, *Cem. Concr. Compos.*, vol. **62**, pp. 97–105, (2015).
- [29] D. Bouvard *et al.*, *Characterization and simulation of microstructure and properties of EPS lightweight concrete*, *Cem. Concr. Res.*, vol. **37**, no. 12, pp. 1666–1673, (2007).
- [30] K.-H. Yang, K.-H. Lee, J.-K. Song & M.-H. Gong, *Properties and sustainability of alkali-activated slag foamed concrete*, *J. Clean. Prod.*, vol. **68**, pp. 226–233, (2014).
- [31] A. A. Sayadi, J. V. Tapia, T. R. Neitzert & G. C. Clifton, *Effects of expanded polystyrene (EPS) particles on fire resistance, thermal conductivity and compressive strength of foamed concrete*, *Constr. Build. Mater.*, vol. **112**, pp. 716–724, (2016).
- [32] M. Albayrak, A. Yörükoğlu, S. Karahan, S. Atlıhan, H. Y. Aruntaş & İ. Girgin, *Influence of zeolite additive on properties of autoclaved aerated concrete*, *Build. Environ.*, vol. **42**, no. 9, pp. 3161–3165, (2007).
- [33] P. Li, H. Wu, Y. Liu, J. Yang, Z. Fang & B. Lin, *Preparation and optimization of ultra-light and thermal insulative aerogel foam concrete*, *Constr. Build. Mater.*, vol. **205**, pp. 529–542, (2019).